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Distribution, Sources and Characterization of Polycyclic Aromatic Hydrocarbons in the Sediment of the River Gomti, Lucknow, India

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Abstract Sediment samples were collected for PAHs analysis (upstream, midstream and downstream) from the bank of the river Gomti in Lucknow city, India during 2005–2007. Total concentration of the PAHs ranged from 0.068 to 3.153 μg/g dry weight. A correlation existed between the sediment organic carbon content (f_{OC}) and the total PAHs concentration with a correlation coefficient (r^2) of 0.788, suggesting that sediment organic carbon content played an important role in controlling the PAHs levels in the sediments. According to observed molecular indices, PAHs contamination in the river Gomti seems to be originated both from the high temperature pyrolytic process as well as from the petrogenic source, indicating a mixed PAH input pattern.

Keywords Polycyclic aromatic hydrocarbons · Sediment · Gomti River

Polycyclic aromatic hydrocarbons (PAHs) includes a class of several hundreds of individual compounds containing at least two condensed benzene rings and 16 of them have been identified as “Priority Pollutants” by the United States Environment Protection Agency (US EPA) (Zhang et al. 2006). They are ubiquitous constituents of urban airborne particulates and are of major health concern mainly due to their well-known carcinogenic and mutagenic properties (Zhou et al. 2005). PAHs are adsorbed strongly to the organic fraction of sediments and soil. Sediments and soils are therefore usually considered as the main sinks for PAHs in the environment and PAHs with four or more aromatic rings are persistent in the environment (Chen et al. 2004).

The sources of PAHs in the urban atmosphere of industrialized countries included automobiles, re-suspended soils, refineries and power plants. In addition in the Indian urban environment, cooking fuel combustion is a likely source of PAHs. High concentration of PAHs have been observed in smoke from solid fuel, burning wood, coal and dried cattle excreta and kerosene stoves all of which are used as the primary cooking source by urban slum dwellers (Kulkarni and Venkataraman 2000). Because of their hydrophobic character (water solubility between 10^{-10} and 10^{-13} mol L^{-1}), they are easily sorbed onto suspended particulate matter (Chiou et al. 1998). In this form they are more persistent to biodegradation (Soclo et al. 2000) in comparison to dissolved PAHs. The most important anthropogenic sources of PAHs are petrogenic and pyrolytic origin, the latter type being usually largely prevalent in aquatic environments (Zakaria et al. 2002; Stout et al. 2004).

The river Gomti, also known as the Gumti or Gomati is a tributary of the river Ganges. It originates near Pilibhit, Uttar Pradesh, India (Miankot, elevation of about 200 m North Latitude 28° 34′ and East Longitude 80° 07′) from underground water springs. It extends 900 km (560 miles) through Uttar Pradesh in India. Lucknow, Sultanpur, Jaunpur are some other major cities located on the banks of the river Gomti. The river is getting polluted owing to the factories and tanneries in the state of Uttar Pradesh, which has affected aquatic life particularly fish population. The objective of the present study was to investigate PAH contamination, identify possible PAH sources, and assess

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potential toxicological impact of the sediment in the river Gomti. In 2002, there was a study on PAHs in sediment of Gomti (Malik et al. 2004). During 2003–2004 there was removal of silt from the river by the municipal authorities to make it clean. In view of this, it was thought to conduct another PAHs level assessment during 2005–2007.

Materials and Methods

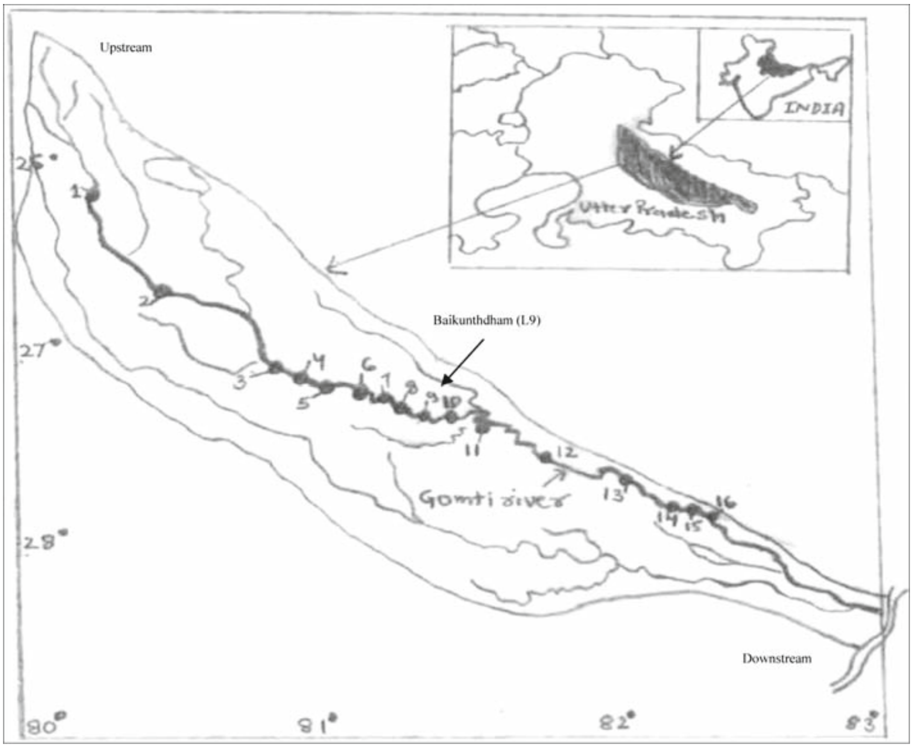
To assess the distribution of PAHs, a total of 80 surface sediments (five from each location) were collected during 2005–2007 as shown in Fig 1. The sampling sites included upstream (Pilibhit), midstream (Lucknow) and downstream (Sultanpur) of the river Gomti from Lucknow. The river also serves as one of the major source of drinking water for the Lucknow city. The river at the end of the city subsequently receives the untreated waste water and effluents from Lucknow. Grab samples of sediments were collected from each location and the details are shown in Table 1. In the laboratory the samples were air-dried then ground with pestle-mortar and sieved to 200 BSS mesh size. About 16 EPA priority PAHs were analyzed in the collected samples (Table 4).

The standards procured from M/S Supelco, Bellefonte (PA, USA) were used for the preparation of mixed external reference standard solution. Purity of all individual PAH standards were in the range of 93.4%–99.7%. All the chemicals and solvents used were of analytical or HPLC grade procured from E Merck, India.

Five grams of the sediment sample blended with 5 g of anhydrous sodium sulfate, in extraction thimble was placed in Soxhlet extractor and extracted with 300 mL dichloromethane for 16–18 h. The final extract was passed through anhydrous sodium sulfate bed and concentrated up to almost dryness under reduced pressure using rotatory evaporator (Buchi). Then the solvent exchange was done by evaporation of the solvent with Cyclohexane. The concentrated extract in the cyclohexane was passed through a silica gel column pre-eluted with the 40 mL n-pentane. The column was then eluted first with 25 mL of n-pentane and eluent was discarded. The final elution was done with 25 mL of dichloromethane/n-pentane (2:3). The collected fraction was concentrated to almost dryness followed by exchange of solvent by acetonitrile and the volume was raised upto 5 mL. The final extracts were analyzed on HPLC (Waters Miliford, MA, USA) for identification and quantification of PAHs and the representative samples were confirmed by GC-MS (Perkin Elmer, USA). The organic carbon content of the sediment was determined using back titration method (Walkely and Black 1934).

The HPLC analysis was performed using a reverse phase C-18 ODS analytical column (75 mm × 4.6 mm id, 3.5 µm particle size). The injection volume was 20 µL. Satisfactory separation was achieved by Isocratic mobile phase (70% acetonitrile: 30% water) with flow rate of

Fig. 1 Map of sediment collection sites in the river Gomti, Lucknow



LI- Gomath Tal, L2- Neem Sar, L3- Gau Ghat, L4- Gulala Ghat, L5- Kuria Ghat, L6-Hanuman Setu, L7- Paper Mill, L8- Kukrail Bandha, L9- Bakunth Dham, L10- Gomti Barage, L11- Pipra Ghat, L12- Jatan Ganj, L13- Gorriya Kala, L14- Hyder Garh, L15- Gola Ghat, L16- Sita Kund

Table 1 Composition and concentration of PAHs from surface sediments in Gomti River

Locations	2 Ring and 3 ring (%)	4 Ring (%)	5 Ring and 6 ring (%)	*t*PAH (µg/g)
L1	85	6	9	1.125
L2	83	3	14	2.274
L3	53	18	29	0.161
L4	89	5	6	0.418
L5	97	2	1	1.071
L6	90	8	2	0.254
L7	74	10	16	2.987
L8	65	28	7	0.098
L9	19	3	78	1.421
L10	50	43	7	0.068
L11	63	7	30	1.646
L12	74	13	13	0.62
L13	41	1	58	3.153
L14	46	21	33	0.348
L15	89	11	0	0.597
L16	56	5	39	2.677

1 mL/min for a run time of 30 min with UV–Vis detector at 254 nm. Further confirmation was done on GC-MS with auto system-XL coupled with a Turbomass detector with a capillary column DB5-MS (30 m × 0.25 mm id, 0.25 µm film thickness). The carrier gas was helium at a flow rate of 1.1 mL/min. The oven was held at 50°C for 1 min then ramped at 25°C/min to 200°C, again ramped at 8°C/min to a final temperature of 280°C (injection volume 2 µL). MS was performed in EI in scan mode.

Quality control samples were processed in a manner identical to actual samples. A minimum of three method blanks were made for every batch of samples (15 no). Before starting the experiment LOD and LOQ for the different PAHs in the sediment were also measured by doing the recovery experiment and values are 3 and 10 ng/g, respectively in all cases except acenaphthylene where LOD and LOQ are 7 and 20 ng/g, respectively. Blank levels were no more than three times the method detection limit. All the analysis was carried out in duplicate. The recovery was found to be in the range of 80%–90% at the level of 2 µg/g each PAHs in sediment. The data was plotted in excel work sheet for appropriate representation of source of PAH.

Results and Discussion

Table 1 depicts the quantitative profile of different PAHs in surface sediments collected from 16 locations (L1–L16) (Fig 1). The total PAH concentrations (sum of the 16 priority pollutants) in sediments of the river Gomti ranged from 0.068 to 3.153 µg/g dry weight with mean value of 1.182 µg/g dry weight. Maximum PAHs level was found at Gorriya Kala, L_{13} (3.153 µg/g) and minimum at Gomti Barrage, L_{10} (0.068 µg/g) (Fig. 2). The total percent of organic carbon of the same locations were measured and a graph of tPAHs versus %TOC is indicated in Fig 3. According to the number of aromatic rings, 16 PAHs were divided into 2-3, 4 and 5-6 ring PAHs.

The sources of PAH concentration in Gomti river are from untreated sewage, industrial waste and presence of crematoria at the upstream of pipraghat (one of the sampling location for this study). In the present study, the effect of sediment organic carbon (f_{oc}) on the PAHs concentrations was also investigated. The percent organic carbon contents of sediments in Gomti River were determined and found to be in the range of 0.15–2.1 and were typical of torrential river environment. A linear regression analysis of the total 16 PAHs concentrations in the sediment to that of %TOC has found to have a correlation coefficient of 0.788 (Fig 3), which indicated that sediment organic carbon content which played an important role in contributing towards the PAHs levels in the sediments (Yang 2000).

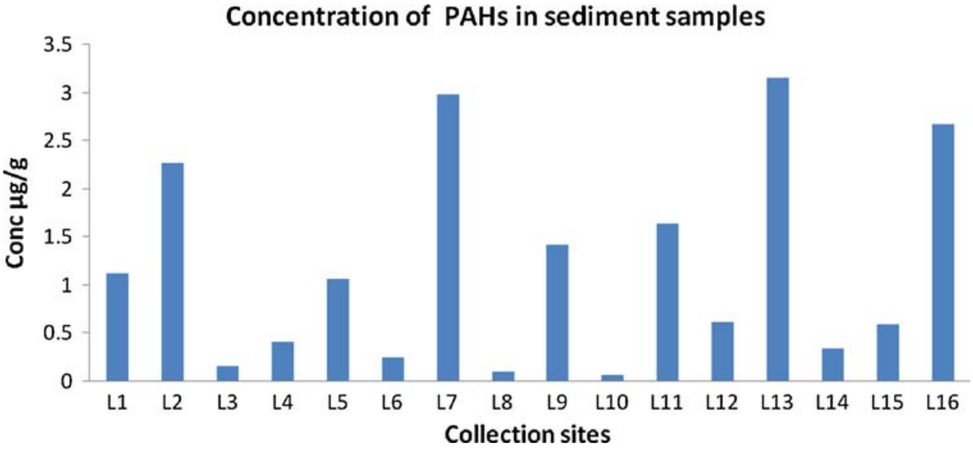


Fig. 2 Average concentration (µg/g) of PAHs at different location in the river Gomti

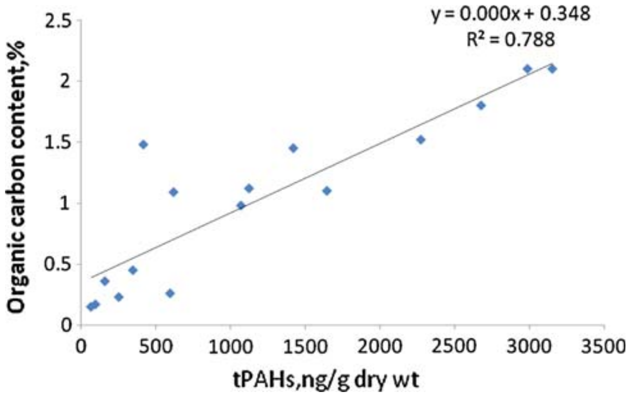


Fig. 3 Correlation between organic carbon content and total PAHs concentration

According to the number of aromatic rings, the 16 PAHs were divided into three groups, representing 2-3, 4, and 5-6 rings PAHs. Table 1 reveals that PAH species with 5-6 rings had the proportion of 0%–78%, 4 rings PAHs contributed 1%–43% and 2-3 rings were 19%–97% in proportion. These proportions suggest that the PAHs contamination in Gomti River comes from varied sources. Apart from these, petrogenic contamination is also one of the causes of PAH contamination.

Anthropogenic PAHs are formed mainly by two mechanisms: combustion of fossil fuels (pyrogenic) and emission of petroleum related materials (petrogenic). The petroleum derived residues contain relatively higher concentration of 2-3 ring PAH compounds and these are formed by burning of fuels such as wood and coal combustion while high molecular weight PAHs are formed in the high temperature such as vehicle combustion processes. Thus the low molecular weight PAH/high molecular weight PAH (LMW/HMW) ratio may be used to determine the use of petrogenic source and pyrogenic sources. Table 2 indicates the characteristic pattern about pyrogenic and petrogenic origins of PAH. Sample belongs to the locations L9 and L13 has a LMW/HMW value less than 1 which clearly indicates the petrogenic origin of PAH in these locations. The samples analyzed in other locations showed a mixed trend of pyrogenic and petrogenic sources of PAH origin. In Table 3 the current study data is compared with other country data.

The effects range low (ERL) and effects range median (ERM) have been used to assess the aquatic sediment with a ranking of low to high impact values (Long et al. 1995). The observed concentrations of PAHs were compared with the ERL and ERM values. Results in this study showed that the total PAH concentrations at all sites were below the ERL. Also for most of the sites, individual PAH did not exceed ERM, but at some sites there was at least one constituent that may occasionally pose biological impairment (with concentration greater than ERL), as indicated in Table 4 L_1, L_2, L_3, L_5, L_7 and L_{11}, concentrations of naphthalene were 382, 926, 694, 392, 326 ng/g, respectively which exceeded ERL (160 ng/g). At most of the sites the concentration of acenaphthylene was above the ERL and it ranged from 57 to 1,521 ng/g. At site L_7 individual PAH such as naphthalene, acenaphthylene, fluorine, acenaphthene and phenanthrene exceeded their ERLs with

Table 2 Characteristic values of selected molecular ratios for pyrogenic and petrogenic origins of PAHs

	Pyrolytic	Petrogenic	Reference	This study
Flu/Pyr	>1	<1	Baumard et al. (1998)	(0.2–5.28)
Phen/Ant	<10	>15	Baumard et al. (1998)	(0.06–104.44)
Naph/Phen		≪1	Dahle et al. (2003)	(0.04–17.03)
Anth/(Anth + Phen)	>0.1	<0.1	Yunker et al. (2002)	(0.01–0.95)
Flu/(Flu + Pyr)	>0.5	<0.5	Yunker et al. (2002)	(0.16–0.84
LMW/HMW	Low	High	Qiao et al. (2006)	(0.24–97)

Flu Fluoranthene, *Pyr* Pyrene, *Phe* Phenanthrene, *Anth* Anthracene, *Naph* Naphthalene, *LMW* Lower molecular weight, *HMW* Higher molecular weight

Table 3 Comparison of *t*PAHs concentration (ng/g dry wt) in the sediments of the river Gomti and other aquatic system

Location	Range (ng/g)	Reference
Yellow river, China	464–2,621	Jian Xu et al. (2007)
Passic river, USA	0.22–8,000	Huntley et al. (1995)
Morava river, Czeck Republic	636–13,205	Vondracek et al. (2001)
Olbia Harbor, Italy	160–770	Giuseppe et al. (2005)
Gomti river, India	207.57–3,365.13	Malik et al. (2004)
Gomti river, India	68–3,153	Present study

Table 4 Standard pollution criteria of PAH components for sediment matrix (ng/g)

Compound	ERL	ERM	Average (this study)	Maximum (this study)
Naphthalene	160	2,100	178	926
Acenaphthalene	44	640	390	1,521
Fluorene + acenaphthene	35	1,040	68	276
Phenanthrene	240	1,500	57	275
Anthracene	853	1,100	20	122
Fluoranthene	600	5,100	14	38
Pyrene	665	2,600	30	123
Benzo(a)anthracene + chrysene	645	4,400	16	72
Benzo(k)fluoranthene	NA	NA	16	59
Benzo(b)fluoranthene	NA	NA	4	18
Benzo(a)pyrene	430	1,600	10	80
Di benz(a,h)anthracene	63.4	260	56	764
Indino(1,2,3-c,d)pyrene + benzo(g.h.i)perylene	NA	NA	119	923
*t*PAH	4,000	44,792	1,182	3,153

concentrations 392, 1,026, 194, 275 ng/g, respectively which may cause adverse effect to aquatic environment. These findings indicate that in some locations there may be occasional risk due to individual PAH which, however, may be not be from total PAH levels.

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