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Distribution of Polycyclic Aromatic Hydrocarbons in Gomti River System, India

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Polycyclic aromatic hydrocarbons (PAHs) are a group of compounds consisting of two or more fused aromatic rings. Most of these are formed during incomplete combustion of organic material such as wood and fossil fuels, petroleum products, coal and the composition of PAHs mixture varies with the source(s) and also due to selective weathering effects in the environment (Neff 1979). The PAHs are ubiquitous pollutants frequently found in different environments, such as freshwater and marine sediments, atmosphere and ice (Fernandez et al. 2000). Due to their wide distribution, the environmental pollution by PAHs has aroused global concern. Combination of their physico-chemical properties such as low aqueous solubility, moderate vapour pressure, high octanol-water partition coefficient (Kow) and persistence in environment make them capable of long range transport. Once in the atmosphere, they can travel long distances and deposited in remote areas such as mountain, lakes and even the Arctic and Antarctic (Fernandez et al. 1999). Atmospheric transport is a major pathway for the loading of these contaminants to the systems in remote regions with no history of their use. Wet and dry depositions are the common removal modes for PAHs. The bioconcentration factors (BCFs) of PAHs in aquatic organisms frequently range between 100-2000 and it increases with increasing molecular size. The critical effect of many PAHs in mammals is their carcinogenic potential. The metabolic action of these substances produces intermediates that bind covalently with cellular DNA. Benzo(a) anthracene, benzo(a)pyrene, dibenzo(a,h)anthracene, benzo(b)fluoranthene and indeno (1,2,3-cd)pyrene have been classified as probable/possible carcinogens to humans (IARC 1987). Due to tendency of PAHs to accumulate in the food-chain, their release during dredging operations, episodes of high scouring, or leaching from confined disposal facilities poses a threat to aquatic ecosystems and consequently a potential threat to human health (Tabak et al. 2003). Although, several studies on behaviour of PAHs in various aquatic systems (Fernandez et al. 1999; Watanabe et al. 2003; Dodder et al. 2003) have been conducted, data on distribution and level of PAHs in the Indian water resources are rare. A recent report (UNEP 2003) has identified the PAHs as the priority persistent toxic substances (PTS) for the Indian Ocean Region and emphasises for a need to generate data on their distribution pattern. This study was undertaken with a view to generate data on distribution of PAHs in river system in India and presents preliminary information on the concentration and distribution of different PAHs in the water and bed sediments of the Gomti river, Uttar Pradesh (India) at different locations.

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MATERIALS AND METHODS

The Gomti river, one of the major tributaries of the river Ganga originates from a natural reservoir in the swampy and densely forested area (Miankot, elevation of about 200m; North latitude 28°34' and East longitude 80°07') in Pilibhit district of Uttar Pradesh, India. The soil sediments here are silty sands. The river flowing through the districts of Pilibhit, Shajahnpur, Sitapur, Lucknow, Barabanki, Sultanpur, Jaunpur and Ghazipur in Uttar Pradesh traverses a total distance of about 730 km before finally merging with the Ganga river in Ghazipur district about 30 km north of Varanasi (Fig 1).

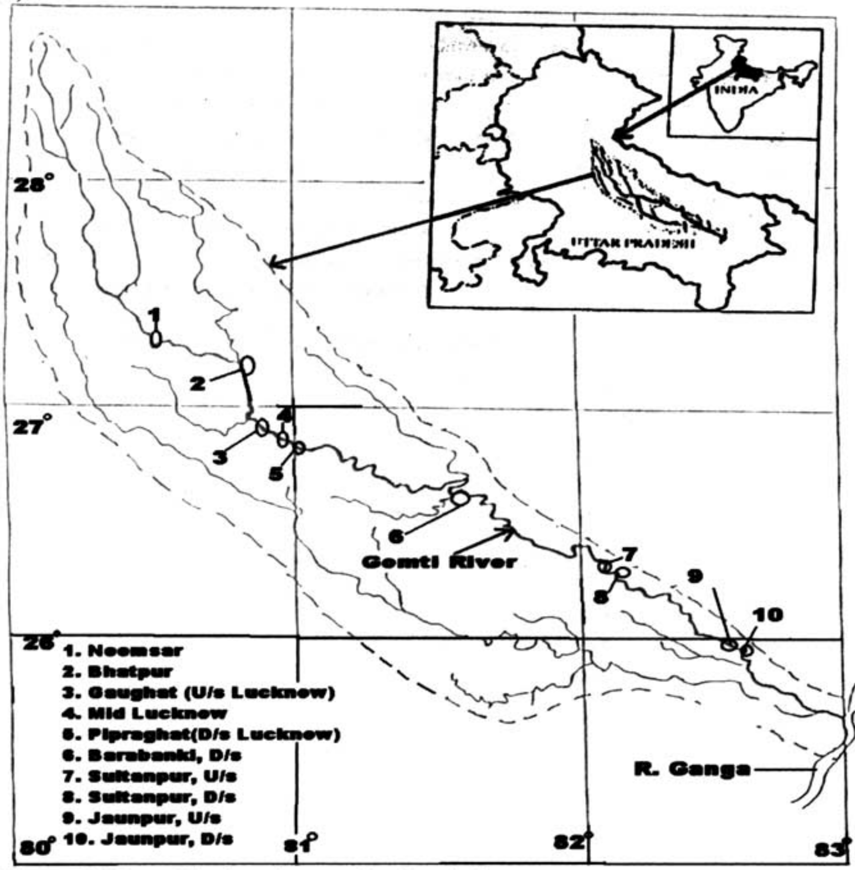

Figure 1. Map of the locations on the Gomti river

Throughout its stretch, there are a few small tributaries (Kathna, Sarayan, Reth, Kalyani and Sai) originating within short distances and carrying the wastewater and industrial effluents from different towns and industrial units in the basin. Lucknow, Sultanpur and Jaunpur are the three major urban settlements on the banks of the river, and there are several industrial units in the catchments of the river in this region. Further, the river serves as one of the major source of drinking water for the Lucknow City, the State capital of Uttar Pradesh with a population of about 3.5 million. The river subsequently receives the untreated wastewater and effluents from Lucknow, Jagdishpur, Sultanpur and Jaunpur directly in its course through more than 40 drains. The study area covers 10 different locations namely Neemsar, Bhatpur, Gaughat, Mid-Lucknow, Pipraghat, downstream of Barabanki, upstream and downstream of Sultanpur and Jaunpur (Fig 1) on the river spread over about 500 km stretch of the river.

Grab samples of water and bed sediments were collected from each of the locations in the month of December 2002. The sediments samples were collected from three points (1/4,1/2 and 3/4) across the river width at each of the ten locations using Ekman sediment sampler. The samples collected in the polyethylene bags were transported to the laboratory in icebox under low temperature conditions. In the laboratory, pebbles, shells and vegetable matter were removed and the samples were air-dried. The air dried samples then ground with pestle-mortar and sieved to 200 BSS mesh size. The organic carbon content of the sediment was determined using back titration method (Walkely and Black 1934). For PAHs analysis 5.0 ± 0.05 g sediment sample from each location were soxhlet extracted with 50 mL of dichloromethane for 6 hr. The extracts were demoisturised using anhydrous granular sodium sulphate and concentrated in a rotary evaporator. The working solvent was exchanged to acetonitrile making up final volume to 2 mL. The samples were stored in dark at 4°C till the analysis was performed. The river water samples collected from midstream of the river (30 cm below the surface) in brown glass bottles were transported to the laboratory under ice conditions. For PAHs analysis, 1L of the water sample from each location was triply extracted by liquid-liquid extraction in a separatory funnel using 50, 30 and 30 mL of dichloromethane solvent. The combined solvent extracts were demoisturised using anhydrous granular sodium sulphate and concentrated in a rotary evaporator and the solvent was exchanged to acetonitrile with a final volume of 2 mL. All the sediment and water samples were analysed for 16 PAHs viz. naphthalene, acenaphthylene, fluorine, acenaphthene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a) anthracene, chrysene, benzo(k)fluoranthene, benzo(b)fluoranthene, benzo(a)pyrene, dibenzo(a,h) anthracene, indeno(1,2,3-cd)pyrene, and benzo(g,h,i) perylene using the high purity grade water-acetonitrile solvent system on HPLC (Waters, USA) equipped with UV-VIS detector (Model 2486). The PAHs standards (99.9% purity) were supplied by Sigma-Aldrich, USA. All the analysis were carried out in duplicate and the recoveries of individual PAHs were determined through spiked sample method, which were found between 93-98 percent. Recovery correction factors were applied to the final results.

RESULTS AND DISCUSSION

The levels of different individual and total PAHs contents in water and sediments of Gomti river at all the selected locations are presented in table-1&2 respectively. Total PAHs in water at all the nine locations studied ranged between 0.65-75.57µg/L. In the river water the most abundant hydrocarbon was acenaphthylene followed by naphthalene. A highest concentration of the ΣPAHs (75.57µg/L) in river water was observed at the location in the mid of the Lucknow city. Further, it is notable that the concentrations of ΣPAHs in the river water at all the locations were higher than the Bureau of Indian Standards (BIS) guideline value of 0.2µg/L (BIS 1982). The ΣPAHs contents in the river sediments at different locations ranged between 207.57-3365.13

Table 1. Concentration (μg/L) of individual PAH in Gomti river water at different locations.

PAH	Bhatpur	Gaughat	Mid Lko	Pipraghat	Barabanki D/s	Sultanpur U/s	Sultanpur D/s	Jaunpur U/s	Jaunpur D/s
Naphthalene	0.42	1.47	1.32	0.36	0.66	5.37	0.39	0.20	ND
Acenaphthylene	3.41	7.03	65.85	9.68	3.26	0.38	0.37	3.68	ND
Fluorene+Acenaphthalene	0.04	0.37	0.06	2.67	ND	2.36	0.08	ND	ND
Phenanthrene	0.01	1.04	0.36	0.06	0.46	0.05	0.29	0.01	0.39
Anthracene	0.02	ND	0.86	0.07	ND	ND	ND	0.02	ND
Fluoranthene	0.03	3.19	0.45	0.07	0.23	0.03	0.02	0.03	0.02
Pyrene	0.03	ND	0.42	0.14	ND	0.08	0.09	ND	0.13
Benzo(a)anthracene+chrysene	0.04	5.76	1.16	0.06	0.04	0.04	ND	0.02	ND
Benzo(k)fluoranthene	ND	2.22	0.14	ND	0.01	ND	ND	ND	0.03
Benzo(b)fluoranthene	ND	ND	0.09	0.53	ND	ND	ND	ND	ND
Benzo(a)pyrene	ND	3.41	0.12	ND	0.23	0.02	ND	0.06	ND
Dibenzo(ah)anthracene	ND	ND	4.70	ND	1.02	ND	ND	ND	0.08
Indeno(123cd)pyrene	ND	0.53	0.04	ND	0.03	0.01	1.04	ND	ND
ΣPAHs	4.01	25.01	75.57	13.65	5.92	8.34	2.28	4.02	0.65

Table 2. Concentration (ng/g dry wt.) of individual PAH and organic carbon (%) in Gomti river sediments at different locations.

PAH	Neemsar	Bhatpur	Gaughat	Mid Lko	Pipraghat	Barabanki	SultanpurU/s	SultanpurD/s	JaunpurU/s	JaunpurD/s
Naphthalene	5.90	10.58	8.12	415.19	128.13	90.85	52.29	81.72	41.18	70.73
Acenaphthylene	553.80	776.44	199.80	726.29	838.21	629.28	82.16	126.98	135.79	113.85
Fluorene+Acenaphthalene	116.94	81.72	30.30	10.32	37.17	63.53	23.03	28.9	44.73	68.72
Phenanthrene	4.57	2.79	2.59	54.16	28.84	5.41	1.47	1.53	1.58	12.51
Anthracene	12.98	31.14	3.46	76.32	51.42	35.71	2.50	3.23	3.76	9.78
Fluoranthene	16.40	14.70	10.37	190.78	180.15	12.92	5.15	9.36	3.77	6.32
Pyrene	28.80	21.55	6.86	55.92	23.74	9.78	1.40	2.01	1.41	4.35
Benzo(a)anthracene+chrysene	8.60	11.81	6.42	1569.94	153.32	12.07	4.63	7.56	6.52	12.87
Benzo(k)fluoranthene	5.74	2.13	2.52	43.28	9.73	5.35	2.87	6.49	3.46	3.86
Benzo(b)fluoranthene	6.71	70.35	ND	21.43	92.12	3.97	1.35	0.92	0.49	3.75
Benzo(a)pyrene	3.65	ND	0.65	149.57	53.15	231.35	3.48	3.11	3.23	4.90
Dibenzo(ah)anthracene	640.79	223.15	376.12	12.77	124.26	26.69	16.84	3.10	ND	69.48
Indeno(123cd)pyrene	3.37	0.25	2.86	39.17	12.40	350.73	5.43	3.61	3.93	11.73
ΣPAHs	1408.24	1246.60	650.10	3365.13	1732.65	1477.66	207.57	278.58	249.84	392.84
% OC	0.04	0.10	0.29	2.27	0.51	0.22	0.07	0.06	0.04	0.04

Table 3. Comparison of ΣPAHs content (ng/g dry wt) in the sediments of the Gomti river and other aquatic systems.

Aquatic System	n*	ΣPAHs (ng/g dry wt.)	PAH/OC (μg/g)	Reference
Gomti River, India	16	207.6-3365.1	148.1-4023.5	Present Study
East River, USA	18	1069910	17831.83	Tabak et al. 2003
NY/NJ Harbor, USA	4	1100	26.44	Tabak et al. 2003
Todos Santos Bay, Mexico	16	7.6-813.1	–	Zamora et al. 2002
Morava river , Czeck Republic	16	636-13205	–	Vondracek et al. 2001
Remote Mt. Lakes	–			Fernandez et al. 1999
Tatra Mts. , East Europe		13000-18000	130	
Iberian Peninsula		180-1100	7.2-7.8	
Passic River, USA	19	0.22-8000	–	Huntley et al.1995

*n= no. of hydrocarbons estimated.

Table 4. Concentration (ng/g dry wt) of possible mutagenic/carcinogenic hydrocarbons in the sediments of Gomti river and other aquatic systems.

Aquatic system	n*	Benzo(a) Anthracene	Benzo(b)flu -oranthene	Benzo(a) pyrene	Dibenzo(ah) anthracene	Indeno(1,2,3 - cd)pyrene	Reference
Gomti river India	10	4.6-1569.9[1]	ND-92.1	ND-231.4	ND-640.8	0.25-350.7[2]	Present Study
NY/NJ harbor, USA		-	-	200	-	-	Tabak et al. 2003
East river, USA		70100	67700	52900	4400	29800	Tabak et al. 2003
Todos Santos Bay	33	0.5-27.2	ND-29.6	ND-740	ND-29.7	ND-115.6	Zamora et al. 2002
Mar piccolo, Italy	10	ND-502	-	ND-163	10-61	-	Storelli & Marcotrigiano 2000

*no. of sampling points;[1]benzo(a)anthracene+chrysene; [2]indeno(123-cd)pyrene+benzo(ghi) perylene ;[3] benzo(b+k)fluoranthene, ND=not detected

ng/g dry wt. Like in water, the most abundant hydrocarbon among all the analysed hydrocarbons in the river sediments was acenaphthylene. Similar to water, the highest concentration of ΣPAHs in the river sediments was found at Mid-Lucknow (3365.13 ng/g dry wt). Between Gaughat and Mid-Lucknow locations, there are some 25 drains carrying about 400 million litres per day (mld) of untreated sewage and industrial wastewater from different parts of the city, discharging directly into the river. Moreover, a little upstream of the Pipraghat, there is a barrage to restrict the river flow to maintain water level in the river for abstraction at Gaughat for urban water supply. The ΣPAHs content in the sediments at Pipraghat was found to be 1732.65ng/g dry wt. At upstream of the Pipraghat (downstream of Lucknow), there is a crematoria on the river bank, where funeral activities are carried out through out the year and may be a major source of the hydrocarbons to the river through surface run-off and atmospheric transport. A comparison of the ΣPAHs burden of Gomti river with other aquatic resources (Table 3) suggests that Gomti river is heavily polluted. There was found a good correlation (r^2 =0.69) between the concentration of ΣPAHs in the water and sediment of the river Gomti (Fig.2a). Further, at each of the locations, ΣPAHs

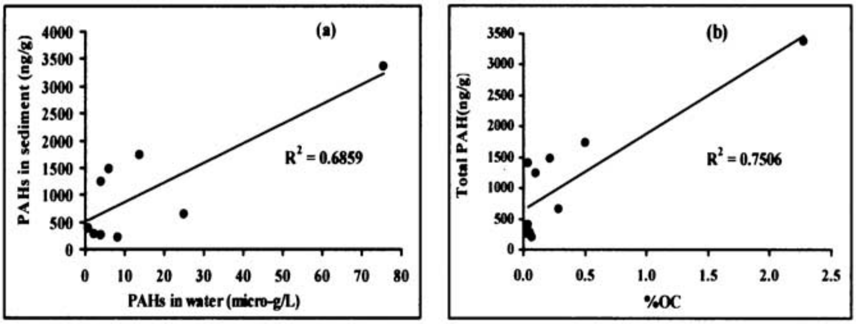

Figure 2. **(a)** correlation between the concentration of PAHs in water and sediments of the river Gomti **(b)** correlation between the total PAHs and organic carbon (%) content in the sediments of the Gomti river.

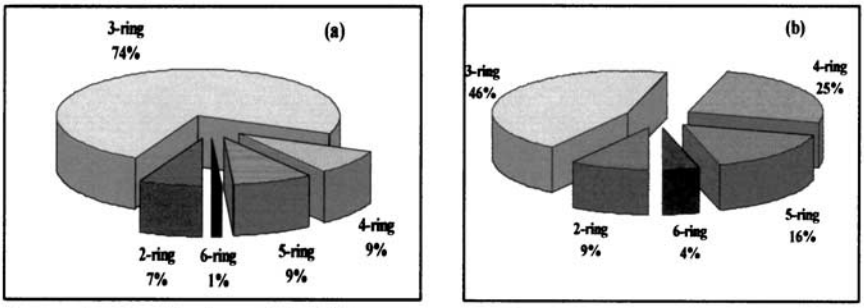

Figure 3. Contribution of the different groups of PAHs to the total PAHs burden in **(a)** water, and **(b)** sediments of Gomti river.

contents of the sediments were found several times higher (ranging 24.9 to 601.6) as compared to the ΣPAHs contents in the water of the Gomti river. The reason for the lower concentrations of PAHs in river water as compared to the sediments may be due to the low aqueous solubility, volatilisation, and affinity of these compounds to the organic matter. The spatial distribution of ΣPAHs generally followed the distribution pattern of organic carbon (%) content as reflected by the observed correlation (r^2=0.75) among the ΣPAHs and the organic carbon (%) contents of the sediments of the Gomti River (Fig.2b). Zamora et al. (2002) have also observed good correlation (r=0.61) for the organic matter content and total PAHs concentration in the sediments of Todos Santos Bay. To assess the carcinogenic potential of the PAHs-contaminated water and sediments of the river, levels of possible carcinogenic hydrocarbons were compared with other published data (Table-4). It was observed that these possible carcinogenic hydrocarbons contributed about 14% and 28% of the total PAHs contents of the river water and sediments, respectively. In terms of the number of fused rings present in the chemical structure of the polycyclic aromatic hydrocarbons, it was observed that the 3-ringed hydrocarbons were the most abundant ones followed by the 4- and 5-ringed hydrocarbons, both in the sediments and in the water of the Gomti river (Fig.3a&b).In the Todos Santos Bay, more than 75% of the total PAHs concentration was represented by three- and four-ringed hydrocarbons (Zamora et al. 2002).The abundance of three- and four-ringed hydrocarbons may be attributed to the

Table 5. Phenanthrene/Anthracene, Fluoranthene/Pyrene and ΣPAHs/OC Ratio in the sediments of the Gomti river.

Location	Phenanthrene/Anthracene	Fluoranthene/Pyrene	ΣPAHs/OC (μg/g)
Neemsar	0.352	0.600	4023.543
Bhatpur	0.090	0.682	1210.287
Gaughat	0.750	1.512	224.161
Mid-Lucknow	0.710	3.412	148.113
Pipraghat	0.561	7.590	343.098
Barabanki D/s	0.151	1.321	687.281
Sultanpur U/s	0.587	3.677	292.349
Sultanpur D/s	0.472	4.649	480.310
Jaunpur U/s	0.421	2.679	624.595
Jaunpur D/s	1.280	1.454	1033.7816

partitioning of these hydrocarbons from the dissolved to organic carbon-rich settling particles, whereas higher molecular weight PAHs exist primarily in the particulate phase in both the atmosphere and water (Bidleman 1988). Some molecular ratio of specific hydrocarbons has been developed to distinguish between the PAHs originating from various sources (pyrolytic, petroleum hydrocarbons and diagenetic). Combustion of organic matter at high temperature generates PAHs characterised by a low Phenanthrene/Anthracene ratio (<10), whereas the slow maturation of organic matter during catagenesis leads to much higher Phenanthrene/ Anthracene ratio (>15) (Soclo 1986). The isomer ratio of fluoranthene and pyrene concentration greater than 1 is characteristic of pyrolytic origin, whereas, values lower than 1 are related to the petroleum hydrocarbons (Sicre et al. 1987). In the Gomti river sediments, ratio of fluoranthene to pyrene concentrations at all the locations was found >1, except at Neemsar and Bhatpur locations, suggesting the chief source of hydrocarbons to be of pyrolytic origin and similarly, ratio of phenanthrene to anthracene concentrations was observed <10 (Table-5) at all the locations which also suggests that majority of the hydrocarbons have originated from combustion processes. Biomass based fuel combustion and open burning of biomass are the common activities in the region and these have been identified as among the major contributors to the PAHs release in the region (UNEP 2003).

Our study shows that the Gomti river is highly contaminated with PAHs and poses high risk to the aquatic life. The findings support that the PAHs present in the river system at most of the locations have their origin from combustion processes in the catchments.

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