Determination of Normal Saturated- and Polycyclic Aromatic Hydrocarbons in the River Water of Bangladesh by Liquid-Liquid Extraction and Gas Chromatography

M. A. Mottaleb,[*] D. K. Sarma, S. Sultana,[†] M. M. Husain,[‡] S. M. M. Alam, and S. M. Salehuddin[†]

Department of Chemistry, University of Rajshahi, Rajshahi 6205, Bangladesh
[†]Chemistry Division, Atomic Energy Center, Ramna, Dhaka 1000, Bangladesh
[‡]Council for Science and Industrial Research, Dhanmondi, Dhaka 1205, Bangladesh
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A liquid-liquid extraction followed by evaporative concentration method was used to determine the concentration of normal, or straight chain, saturated hydrocarbons (NSH) (C_{10} to C_{24}) and polycyclic aromatic hydrocarbons (PAH) here defined as: fluorene, anthracene, pyrene, chrysene and perylene, in the Buriganga River water of Bangladesh. Samples were collected from 5 and 25 cm depth of water at the southern, middle and northern parts of the river at Postogolla, Sadarghat and Sowarighat stations. Hydrocarbons were extracted from 450 mL of water into 75 mL *n*-hexane and then concentrated into 1 or 2 mL solution by evaporation. These solutions were analyzed by gas chromatography. The highest and lowest concentrations were determined as 257 μg L^{-1} for C_{13} and 0.24 μg L^{-1} for C_{22} at 5 cm depth of water, at the northern part of the Sowarighat and southern part of the Postogolla, respectively. This method could allow the analysis of water for C_{22} as low as 0.24 μg L^{-1}.

Key Words : Saturated hydrocarbons, PAH, Gas chromatography, River water, Extraction and preconcentration

Introduction

Gas chromatography (GC) is one of the most popular analytical tools for the quantification of hydrocarbons from environmental matrices. Gupta and Kurieisy[1] found the mean concentration of dissolved and dispersed hydrocarbons in the Arabian Sea between 0.20°N and 20-24°E. The average concentrations of hydrocarbons were 32.5 ± 1.1 μg kg^{-1} in the surface waters and 24.1 ± 1.3 μg kg^{-1} in the waters collected from 20 m depth. Fondekar and Gupta[2] determined the concentration of dissolved hydrocarbons in some parts of the Northern Indian Ocean to be in the range of 0.6 to 26.5 μg L^{-1}. Higher values were reported along the oil tanker route compared with the coastal region, from surface to about 10 m depth. Bernard *et al.*[3] investigated the non-aromatic hydrocarbon (NAH) and PAH in surface water from the Lagoons of Grand Cul-de-Sac and Petit Cul-de-Sac Marine in the Caribbean Island of Guad Eloup (61°30'W 16°N). Hydrocarbons were extracted from water and fractionated by adsorption chromatography. The NAH and PAH components were detected as 28-4100 μg g^{-1} and 103-1660 μg g^{-1}, respectively. They concluded that the naturally occurring NAH hydrocarbons predominated along the coastline and the PAH correlated with a pyrolytic origin. Esteves *et al.*[4] measured the total aromatic hydrocarbons in water and sediments in costal zones of Patagonia, Argentina. Water samples were extracted twice with 50 mL CCl_4 by a UNESCO method for the years 1982-1984. The concentrations of hydrocarbons were reported as 0.4-126 μg g^{-1} in sediment and 0.6-41 μg L^{-1} in water.

Stranes *et al.*[5] determined the concentration range of total hydrocarbons in lake water and found this to be 1.6 to 26.5 μg L^{-1}. A 4.5 m long GC column packed with 2% SE-30 on chromosorb G was used. The temperature program employed was 60 to 275 °C at a rate of 8 °C min^{-1} with a helium gas flow rate of 50 mL min^{-1}. The *n*-alkanes over the carbon range C_{15}-C_{31} were predominant and the lower hydrocarbons (C_9-C_{11}) were absent. Al-Sadd and Khatun[6] reported the distribution and seasonal variations of *n*-alkanes in the dissolved water of marshes. Variables including temperature, evaporation, bacterial degradation, adsorption, and photochemical oxidation are postulated to produce pronounced seasonal variations of *n*-alkanes in water. The *n*-alkanes showed a regular distribution pattern of the odd and even carbon number compounds between C_{13} to C_{34} with the following additional characteristics associated with biological phenomena: greater abundance of C_{17} and C_{19} due to algal origin and greater abundance of C_{25}, C_{27}, C_{29} resulting from plant inputs. The concentrations of PAH were determined in sediments of a coastal area, Oaxaca, Mexico[7] using the Caripol-IOCARIBE extraction and purification method.[8] An open tubular capillary column, 25 m × 0.25 mm i.d. containing 5% phenyl-methyl silicone, with a column temperature program of 40 to 300 °C at 6 °C min^{-1} was employed. The detection limit for individual PAH was recorded as 0.01 μg g^{-1} dry weight. Zinjarde and Pant[9] investigated the degradation of hydrocarbons in tropical marine environment and demonstrated that more than 10%

[*]Corresponding author and present address: EPA/NRC Postdoctoral Research Associate, Environmental Sciences Division, National Exposure Research Laboratory, U.S. Environmental Protection Agency, P.O. Box 93478, Las Vegas, NV 89193-3478, USA. Fax: +1-702-798-2142, e-mail: mottaleb.mohammad@epamail.epa.gov

supplied crude oil could be degraded by yeast and bacteria except aromatic or asphaltene fractions.

In this study, the water of Buriganga River was investigated. The river runs through the capital of Bangladesh and has an enormous impact over socio-economic development of the country through industrial and shipping/marine activities. The sewage from tanker washing, shipping of scrap particles, oil spillage, etc. are common features on the river in different ghats (marine terminals). As a result, the water of the Buriganga River is continually polluted by different organic pollutants, such as hydrocarbons, through influx of marine and land-based sources. In addition, aromatic solvents are being increasingly used in industry and wastes are sometimes disposed into the aquatic environment. Consequently, the river has become more contaminated with pollutants and the public has become alarmed by the pollution of water. The use of polluted water can create problems for human and aquatic life, so there has been a general demand that the pollution be controlled and the concentration levels of different pollutants in the river are determined. Previously, we reported a method for extraction and quantitative determination of pesticides from environmental matrices.[10] The pesticides were extracted from samples with different solvents followed by a clean-up method using a C_{18} cartridge and average recoveries exceeding 89% were reported.[10] Recently, we investigated the concentration of volatile organic compounds (VOCs) in the Buriganga River water using a solid phase extraction (SPE) method.[11] The VOCs were extracted with *n*-hexane from water samples and adsorbed onto a C_{18} SPE cartridge. Finally, VOCs were eluted with CH_2Cl_2 and the constituents were obtained in the range of 0.1 to 0.37 μg mL^{-1}. The present paper describes the preliminary concentration levels of NSH and PAH constituents in water of the Buriganga River. A liquid-liquid extraction method followed by gas chromatography has been applied to the determination of NSH and PAH constituents in the water sample.

Experimental Section

Apparatus. A Shimadzu gas chromatograph, Model GC-14B (Japan) equipped with a flame ionization detector (FID) and a capillary column: length 25 m, i.d. 0.33 mm, o.d. 0.43 mm, DB-5 type bonded phase, film thickness 0.52 μm, was employed. A column oven temperature 80 to 250 °C at 4 °C min^{-1} and holding at 250 °C for 6 min, injector temperature 250 °C, detector temperature 260 °C and flow rate of N_2 gas 20 ± 1 mL min^{-1} were used. The concentration used for each NSH standard component was 100 μg mL^{-1}. The standard concentrations of PAH for fluorene, anthracene, pyrene, chrysene and perylene were 77, 223, 370, 137 and 117 μg mL^{-1}, respectively. A volume of 0.4 μL standard solution and 1 μL for the sample solution was injected into the GC for the analysis. Blank experiments were performed prior to inject the standard and sample solutions into the GC under the same conditions. Replicate analyses were done for confirming the each measured constituent. An LQ-300 Epson printer was used to record the detector signal.

Collection points and sampling of water samples. About 18 liters of water sample were collected on July 9, 2000 in 18 glass bottles from the Buriganga River from three different stations: Postogolla, Sadarghat, and Sowarighat that were at least 1 km in distance from each other. The locations of the sampling points are shown in Figure 1. Six samples were collected from each of the sampling stations and each station consisted of three sampling points: southern, middle and northern parts. A sample was collected from each sampling point at 5 and 25 cm depths of the water. Each sample was collected in a 1.1 L capacity volume, clean, dark glass bottle. At first, the bottle was lowered slowly into the water and its cork opened by hand. When the bottle was filled with water, it was closed, drawn up carefully and marked with the desired depth in cm. Then, 100 mL of water was discharged from the glass bottle, and 10 mL of *n*-hexane was added and the bottle was shaken for 10 min. Care was taken against contamination and loss of integrity of the sample constituents. The sample was stored in the dark glass bottle, inside a cupboard, to avoid accidental losses and to await further analysis.

Extraction and removal of residual water. Extraction by solvent[12-14] was carried out within 72 h after collection of the samples. This method required two 1-L capacity separatory

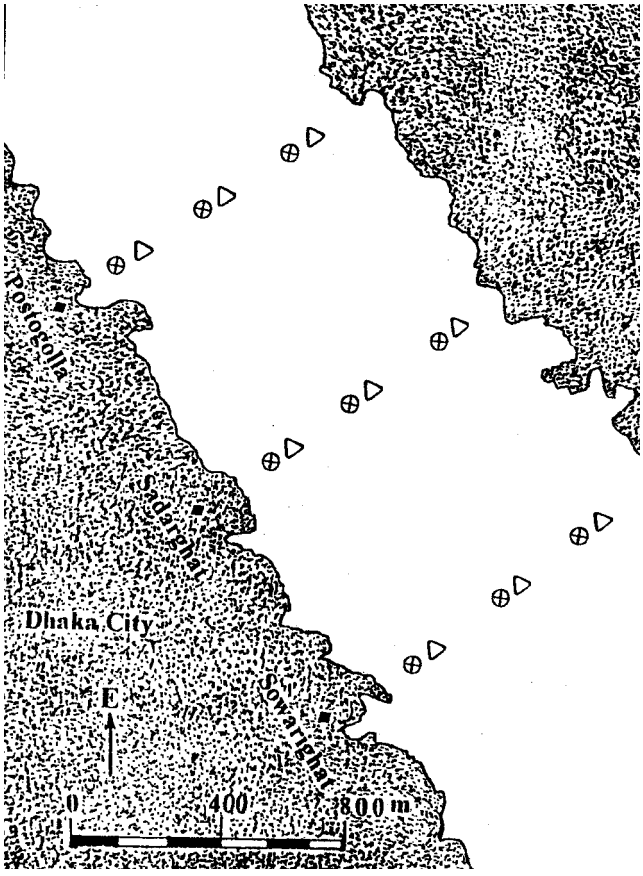

Figure 1. Map of the Buriganga River showing the location of sampling stations and collection points of water samples: ◆ sampling stations; ⊗ sample collection points, 5 cm depth; △ sample collection points, 25 cm depth.

funnels with Teflon stopcocks and stoppers. Four-hundred and fifty mL of each water sample were poured into the separatory funnel and 45 mL *n*-hexane was added to it. The mixture was then shaken vigorously for 30 min and then allowed to stand for 30 min. The separatory funnel was vented to reduce the pressure inside. Following this operation, the organic and aqueous layers were separated. The aqueous layer was drained off leaving the organic (hexane/ extract) layer in the funnel. The extract was then transferred into a volumetric flask. The aqueous layer was extracted again by shaking with 25 mL *n*-hexane and the extract was collected and stored. An aliquot amount of *n*-hexane extract was obtained from the sample collection bottle where 10 mL of *n*-hexane was added. All extracts were combined into a volumetric flask and additional pure hexane was added to make the final volume 75 mL. The flask was kept in a cool environment. All 18 samples were extracted in similar ways. Residual water was removed from the extract by treating with the anhydrous sodium sulphate. Sodium sulphate (50 g) was placed in the separatory funnel and watered slightly to make a layer of solid. The extract was then passed through the funnel and collected in another clean volumetric flask. The treated extract was stored in a refrigerator for further examination.

Preconcentration and analysis of the extract. The extracts were reduced to a volume of 1 or 2 mL by evaporative concentration using Kuderna-Danish techniques, *i.e.*, the hexane was evaporated slowly using a evaporation procedure similar to that reported earlier.[12-14] Special attention was given to avoid loss of extract and the 75 mL volume of extract was reduced to 1 or 2 mL of solution. The preconcentrated solutions were injected into the GC and peaks of NSH and PAH constituents were found in the chromatograms. Each constituent was identified and quantified by comparing its retention time and peak area with that of a known concentration of standard solution that was injected into GC under the same experimental condition. The concentrations of each NSH/PAH components were calculated by using equation (1):

Conc. of component

$$x = \frac{\mathrm{A}x}{\mathrm{A}std} \times \frac{\mathrm{V}std}{\mathrm{V}x} \times \mathrm{C}std \times 2.22 \times 1000\ \mu\mathrm{g\ L^{-1}} \qquad (1)$$

Where, Ax = Peak area of desired constituent x in sample solution, Astd = Peak area of the constituent in the standard solution, Vx = Injected volume of sample solution, Vstd = Injected volume of standard solution, Cstd = Concentration of the constituent in the standard solutions. The 2.22 represent a concentration factor: a ratio of the amount of each sample collected from the river (1-L) to the amount of sample taken from the collected sample for extraction (0.45 L).

Results and Discussion

Mixtures of components, which have similar or nearly the same boiling points are difficult to separate into individual components by GC. For separating such types of components, careful column temperature programming is most essential. The GC column temperature program employed was 80 to 250 °C at 4 °C min^{-1} and holding for 6 min at 250 °C. The injector and detector temperatures were 250° and 260 °C, respectively.

NSH and PAH in river water samples. The water samples obtained from 5 and 25 cm depths of water of the Buriganga River were investigated to determine NSH containing 10 to 24 carbon atoms and fluorene, anthracene, pyrene, chrysene and perylene PAH. The samples collected from the southern, middle and northern parts of Postogolla, Sadarghat and Sowarighat stations of the river were extracted, preconcentrated, and analyzed by GC-FID. A series of GC chromatograms were obtained. Figure 2 depicts a typical GC-FID chromatogram for (A) a standard solution of NSH, (B) a standard solution of PAH and (C) a water sample collected from 5 cm depth of water at middle point of the Sadarghat. This shows a good comparison of retention time of NSH and PAH components detected in standard and sample solutions. Many of the NSH and PAH constituents

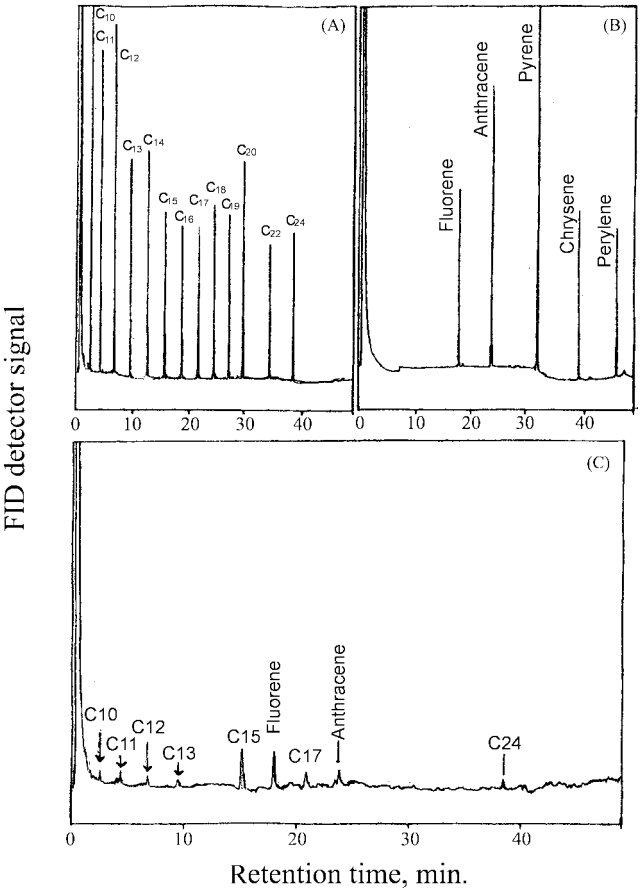

Figure 2. Comparison of GC-FID chromatograms of retention times of different NSH and PAH constituents for (A) standard solutions of NSH, (B) standard solutions of PAH and (C) water samples which were collected from 5 cm depth of water at the middle point of Sadarghat. Conditions: injector temperature 250 °C, column oven temperature 80 to 250 °C at 4 °C min^{-1} and held at 250 °C for 6 min, detector temperature 260 °C, flow rate of carrier gas (nitrogen) 20 ± 1 mL min^{-1}.

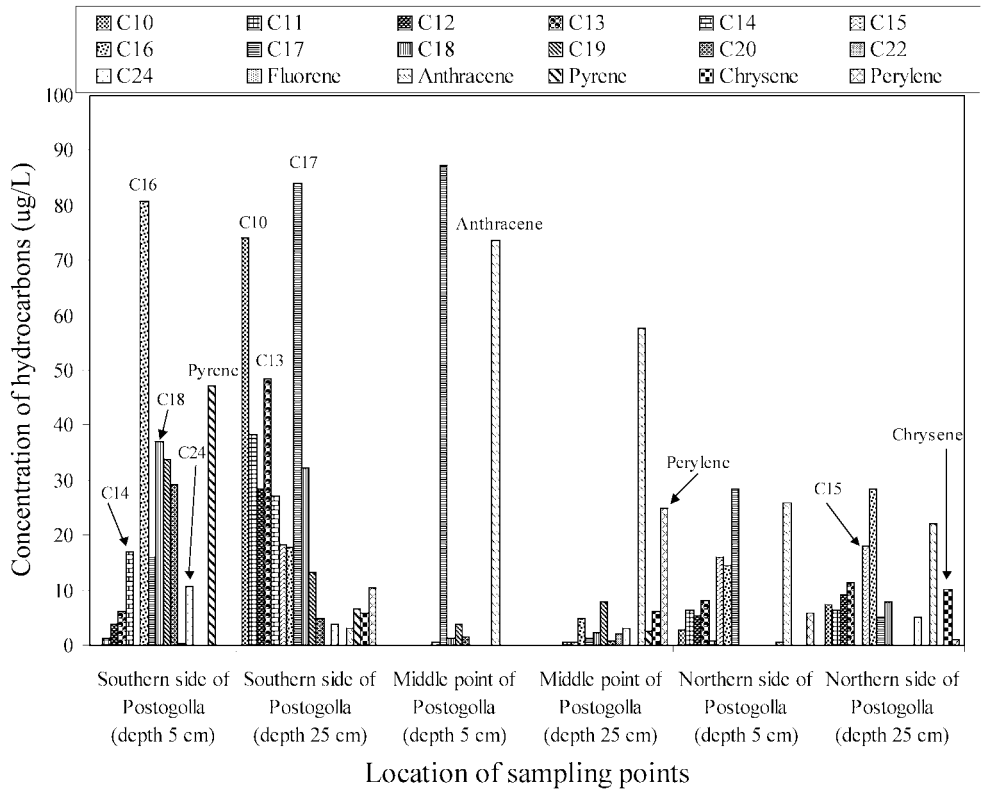

Figure 3. Concentrations of individual NSH and PAH constituents in 5 and 25 cm depth of water at southern, middle and northern sides of Postogolla station of the Buriganga River. Major concentrations of individual NSH and PAH have been indicated.

were not observed in the water samples. This is probably due to the very low concentrations, which cannot be detected by GC-FID. Chromatograms with different peaks of hydrocarbons were obtained for 5 and 25 cm depths of the water collected from Postogolla and Sowarighat stations. These are not shown.

Postagolla Station. The concentrations of NSH and PAH obtained from the water samples from 5 and 25 cm depths at southern, middle and northern sides of the Postogolla station are shown in Figure 3. This compares the concentration of NSH and PAH individual constituents at various locations of the station. Irrespective of the depth and locations, the water samples contained the maximum number of hydrocarbons at 25 cm depth compared to that of the 5 cm. It can also be observed that the higher concentration of C_{16}, C_{18}, C_{19}, C_{20} and pyrene (southern side), and C_{17} and anthracene (middle point) were obtained at 5 cm depth compared to the sample, collected from 25 cm. The predominance of C_{16}, C_{17}, C_{18}, C_{19}, C_{20} could suggest that the presence of aliphatic hydrocarbons, may not only be due to the human or shipping activities, but also may be a result of phytoplankton, terrestrial vegetation and bacterial activity.[15] The dominance of pyrene and anthracene indicates the presence of aromatic hydrocarbons, which are mainly attributed to oil spillages, municipal and waste discharges, and atmospheric transport[16] and the activity of some organisms, such as bacteria, algae and fungi.[17] The obtained concentrations of C_{10}, C_{11}, C_{12}, C_{13}, C_{14}, C_{15} and perylene in the southern side at 25 cm depth are higher than at 5 cm depth. Increased concentrations of hydrocarbons at 25 cm depth are likely to be a result of the removal of oil from the water surface. Fast evaporation of light fractions and photochemical condensation reactions increase the weight of hydrocarbon residues, thus causing the hydrocarbons to aggregate and sink.[18]

Sadarghat Station. Figure 4 compares NSH and PAH concentrations in the water, collected from 5 and 25 cm depth at southern, middle and northern parts of the Sadarghat. Regardless of the depth, it can be seen that the maximum concentrations of the components were obtained in the northern part at 5 cm depth water compared to those of the middle and southern parts. The northern part is a launch terminal where the launches, tankers, sea-/speed boats often stop for loading and unloading goods, and passengers or fuels etc. As a result, petroleum products may float on the surface of the water. The concentration of NSH at the middle part of Sadardghat of 25 cm depth is higher than at 5 cm. The increased concentrations of NSH in 25 cm depth water at the middle point are likely to be a result of the removal of oil from the water surface. A similar explanation can also be given that the fast evaporation of light fractions and photochemical condensation reactions increase the density of the hydrocarbon residues, thus causing aggregation and sinking.[18] The abundance of C_{16} and C17 obtained at the southern part at 5 and 25 cm depths, respectively, are generally attributed to input from the terrestrial higher plants.[15] The greater numbers of PAH and their higher concentrations were obtained at 5 cm depth compared to 25 cm. This was accounted for as oil spillages, municipal and

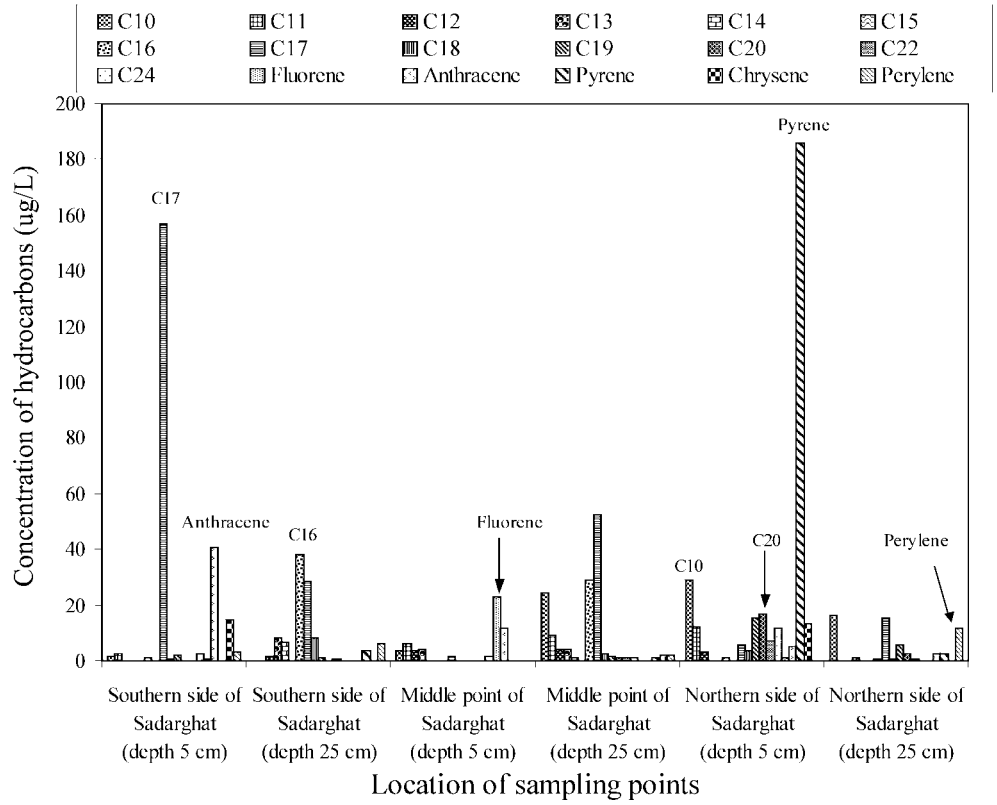

Figure 4. Concentrations of individual NSH and PAH constituents in 5 and 25 cm depth of water at southern, middle and northern sides of Sadarghat station of the Buriganga River. Major concentrations of individual NSH and PAH have been indicated.

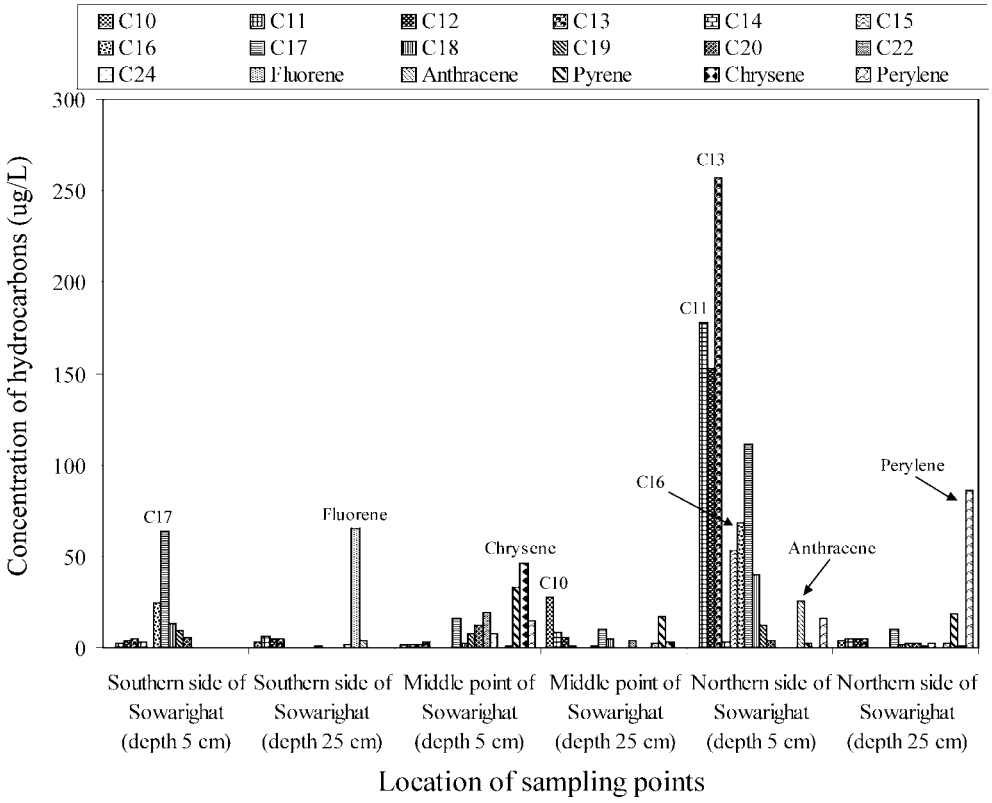

Figure 5. Concentrations of individual NSH and PAH constituents in 5 and 25 cm depth of water at southern, middle and northern sides of Sowarighat station of the Buriganga River. Major concentrations of individual NSH and PAH have been indicated.

industrial waste discharges and atmospheric transport, or incomplete combustion of fossil hydrocarbons, and discharges from the oil refinery.[16] The abundance of perylene at the northern part at 25 cm depth is attributed to synthesis by some organisms, such as bacteria, algae, and fungi.[17] The lower concentration or absence of NSH and PAH constituents may be due to their high volatility, biological degradation, photo-oxidation and rapid photolysis[19] or they may not be present at any detectable at all in the water of Sadarghat.

Sowarighat Station. The concentrations of NSH and PAH in the river water are shown in Figure 5. The samples were obtained from 5 and 25 cm depths of water from the southern, middle and northern sides of the Sowarighat station. It has been observed that the maximum number of hydrocarbons with increased concentration was found to occur at the northern side at 5 cm compared to middle and southern parts of the station. It was discussed earlier that some petroleum products fall on the water surface due to shipping activities. As a result, C_{11}, C_{12}, and C_{13} components are more abundant at 5 cm depth water than those at 25 cm. The presence of higher concentrations of *n*-alkanes at 5 cm depth also is indicative of terrestrial vegetation, phytoplankton, and bacterial activities.[15] The abundance of pyrene and chrysene at the middle point of 5 cm depth is generally attributed to oil spillages, municipal and industrial waste discharges, and atmospheric transport.[16] The abundance of fluorene at the southern and perylene at the northern sides at 25 cm is believed due to removal of oil from the water surface. The majority of PAH are thought to derive from fossil fuels[20] or combustion products.[21] The absence of other PAH components is probably due to their presence of very low amounts, not detectable by GC. Alternatively, these PAH may be degraded, or biodegraded to other constituents, so reducing the concentration of PAH.[22] Depletion may continue over weeks and months through dissolution, biodegradation and photo-oxidation, which further reduce the concentration of the resolved components.[23]

Comparison of hydrocarbon concentrations at different stations and depths. The concentrations of NSH and PAH constituents at different locations and stations, and their relative abundances, with probable causes, have been discussed in earlier sections. From these discussions, it has been observed that the predominance of individual NSH or PAH concentrations in all the different locations and stations are not similar. The concentrations of C_{16}, C_{17}, and anthracene at 5 cm, C_{10} to C_{18} at 25 cm depth of water at Postogolla; C_{10}, C_{16}, C_{17}, and pyrene at 5 cm depth of water at Sadarghat, and C_{11}, C_{12}, C_{13}, C_{16}, and C_{17} at 5 cm, and perylene at 25 cm of water at Sowarighat were found to be higher than the other hydrocarbon constituents. As the concentrations of the constituents obtained were between the nano- and sub-milligram ranges in the water sample, so it was difficult to identify the components in the bar diagram (Figures 3 to 5) detected at the lower concentration levels. The concentration of individual NSH and PAH constituents at 5 and 25 cm depths of water collected from various locations, depths, and stations of the river has been summarized in Tables 1 and 2. The concentrations of most NSH constituents at 5 cm depth of water at the northern side of the Sowarighat are relatively higher than the other two stations, Postogolla and Sadarghat. The water collected at 25

Table 1. Concentrations of NSH and PAH constituents at 5 cm depth of water at different stations and sampling sides of the Buriganga River

Types of hydrocarbons	Constituents	Concentration of constituent (μg/L)								
		Postogolla station with following sampling sides			Sadarghat station with following sampling sides			Sowarighat station with following sampling sides		
		Southern	Middle	Northern	Southern	Middle	Northern	Southern	Middle	Northern
NSH	C10	–	–	2.8	1.7	3.4	29	–	1.3	–
	C11	1.3	–	6.3	2.5	6.2	12	2.3	1.5	178
	C12	3.9	–	5.4	–	3.6	2.8	3.6	1.8	153
	C13	6.1	–	8.1	–	4.3	–	4.5	3.2	257
	C14	17	–	0.8	–	–	–	2.9	–	2.9
	C15	–	–	16	1.3	–	1	–	–	53.3
	C16	81	0.6	14	–	–	–	24	–	68.6
	C17	16	87	28	157	1.6	5.4	64	16	111
	C18	37	1.3	–	0.8	–	3.4	13	2.2	39.6
	C19	34	3.8	–	1.9	–	15	9.2	7.3	12
	C20	29	1.6	–	–	–	17	5.7	12	3.9
	C22	0.2	–	–	–	–	7.3	–	19	–
	C24	11	–	–	2.4	1.6	12	–	7.4	–
PAH	Fluorene	–	–	0.4	0.4	23	1	–	–	–
	Anthracene	–	74	26	41	12	5	–	1	25
	Pyrene	47	–	–	–	–	186	–	33	2.6
	Chrysene	–	–	-	14.5	–	13	–	46	–
	Perylene	–	–	5.9	3.2	–	–	–	15	16

The sign '–' represents not detected.

Table 2. Concentrations of NSH and PAH constituents at 25 cm depth of water at different stations and sampling sides of the Buriganga River

Types of hydrocarbons	Constituents	Concentration of constituent (μg/L)								
		Postogolla station with following sampling sides			Sadarghat station with following sampling sides			Sowarighat station with following sampling sides		
		Southern	Middle	Northern	Southern	Middle	Northern	Southern	Middle	Northern
NSH	C10	74	–	7.4	–	24	16	2.8	28	4
	C11	38	–	6.2	–	9	–	6	8.7	4.5
	C12	28	–	9.1	1.6	4.2	–	5	5.6	4.9
	C13	48	–	12	8	4.2	1.2	5	0.6	4.8
	C14	27	0.6	–	6.7	1	–	0.2	–	–
	C15	18	0.4	18	–	–	–	–	–	–
	C16	18	4.8	28	38	29	0.5	–	1.1	–
	C17	84	1.3	5.1	29	52	15	–	10	10
	C18	32	2.4	8	7.9	2.3	0.7	1	4.4	1.4
	C19	13	7.9	–	1.1	1.4	5.4	–	–	2.1
	C20	4.8	0.8	–	–	1.2	2.3	–	–	2.6
	C22	–	2.1	–	0.7	1.1	0.6	–	3.8	1.1
	C24	3.7	3.1	5	–	0.9	–	1.3	–	2
PAH	Fluorene	–	–	–	–	–	–	65	–	–
	Anthracene	3	57.5	22	–	–	2.3	3.6	2	2.5
	Pyrene	6.5	2.6	-	3.4	1	2.5	–	17	18
	Chrysene	5.9	6	10	–	2	–	–	3.2	0.5
	Perylene	11	24.9	1.1	6.1	2	12	–	–	86

The sign '–' represents not detected.

cm depth of the southern side of the Postogolla contained relatively increased numbers of NSH components such as C_{10} to C_{24}. The highest concentration of C_{13} was found as 257 μg L^{-1} at 5 cm at the northern side of the Sowarighat and the lowest value found was 0.24 μg L^{-1} for C_{22} and C_{14} components at 5 and 25 cm at the southern side of Postogolla and Sowarighat, respectively. Concentrations of remaining NSH components fell between these values at different depths, locations and stations. Four PAH constituents, anthracene, pyrene, chrysene and perylene were detected. At 5 cm depth, the lowest and the highest amounts of PAH were due to fluorene and pyrene at 0.37 and 186 μg L^{-1}, respectively at the respective northern and southern sides of the Sadarghat.

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