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Research Article

Identification and quantification of naphthalene in water samples of Buriganga River in Bangladesh by gas chromatography-mass spectrometry

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Abstract

A new GC-MS method has been developed for the determination of the polycyclic aromatic hydrocarbon (PAH), naphthalene, in water samples of Buriganga River in Bangladesh. The water samples were extracted with liquid phase extraction using dichloromethane (DCM) solvent. A silica clean-up column followed by gel permeation chromatography (GPC) was used to eliminate the interfering organic compounds, as well as the lipids. The extracts were quantified with GC-MS. The method was successfully applied to determine the concentration of naphthalene present in river water samples collected from three different sampling stations in the Buriganga River. The method also showed good recovery values, 79 to 89%. A high concentration of naphthalene was found, 1.015 µg/L, in the surface water sample which was collected from Postagolla middle sampling station.

Keywords: organic pollutants**,** toxic polycyclic aromatic hydrocarbon, PAH, DCM, GPC, liquid-phase extraction, GC-MS.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are the products of incomplete combustion, and in urban and industrial atmospheres, are almost entirely anthropogenic in origin. Most carcinogenic PAHs have been found to associate with particulate, predominately with fine particulate [1]. Some PAHs are strong carcinogens and can cause pulmonary inflammation and allergic asthma in human airway cells [2, 3]. A study of the bioactivity of particulate matter both *in vivo* and *in vitro* indicates that the size of particulate may play a role in the effect on pulmonary inflammation and allergic asthma [4]. Particulates in the low-micrometre range traverse deep into lungs and inflict more death damage than that of larger particles that are arrested in the upper respiratory tract and removed by

mucociliary action. Thus, it is important to analyze particulate size distributions when assessing the possible influence of PAHs on human health.

Motor vehicles have proven to be a significant source of PAH emissions [5, 6]. Particulate emissions from motor vehicles are among the major contributors to fine particle concentrations in the urban atmosphere [7, 8, 9]. Furthermore, particulate PAHs measured in roadway tunnels and in dynamometer measurements have been found in the respirable size range. In order to assess health risk, it is necessary to specify both the size distribution and the chemical composition of particulate emissions as they occur at their sources. Size distributions of PAHs emitted from diesel and gasoline vehicles have been studied based on samples collected in roadway tunnels [10, 11] and using a dynamometer facility [9, 12]. All these studies utilized a cascade impactor as the sampling device. To the best of our knowledge, there are no data on the particulate and PAH size distribution pertaining to emissions from motor vehicles in the current literature.

In many countries, motor vehicles are one of the most important modes of transportation. In Dhaka City, for example, there are over one million different vehicles, which account for 67% of all motor vehicles. The health risk from scooter, bus, car and microbus in these countries would be high. One PAH, naphthalene, was selected as the target compound in this study for carcinogenicity.

The aim of this study is to quantify the level of toxic polycyclic aromatic hydrocarbon, naphthalene, in the water of the Buriganga River of Bangladesh by using GC-MS.

Materials and Methods

General experimental procedures

Chemicals

Dichloromethane (BDH, UK) was of HPLC grade. Anhydrous sodium sulphate (Merck, Germany) was cleaned by heating at 200^{o}C before use. Silica gel (60-120 mesh, Loba, India) activated at 400^{o}C for 12 hr. prior to use. Naphthalene of (Sigma-Aldrich) was used as standard in the present study. The pH of water samples was adjusted with o-phosphoric acid (Merck). Other reagents were purchased from Merck.

Instruments and operating conditions

GC-MS was carried out using total ion monitoring mode on a Varian 3800 gas chromatograph interfaced to a Varian Saturn ion trap 2200 GC-MS mass spectrometer. The temperatures of transfer line and ion source were 280°C and 275°C respectively. Ions were obtained by electron ionization mode. The VF-5 capillary column (30 m length, 0.25 mm I.D., 0.25 μm film thickness) was used. A 20% split injection mode was selected with a solvent delay time of 3 min. with injection volume 1μl. The initial column temperature was started at 40°C for 1 min, programmed at 8°C min^{-1} to 200°C and heated until 300^{o}C at 10^{o}C min^{-1}. Injection port was set at 250°C. Helium was used as carrier gas with a flow-rate of 1 ml min^{-1}. Molecular ions were monitored for identification. Mass range: 40-500 m/z. Identification of the crude dichloromethane extract was based on GC retention time on VF-5 capillary column, computerized matching of mass spectra with standards (Mainlab, Replib and Tutorial data of GC-MS

systems). The reference compound, naphthalene was used as marker. The marker was accurately weighed and dissolved in dichloromethane to produce a series of concentrations. Standard calibration curves were established by plotting the peak areas against different concentrations of the reference compound (varying from 0.5 to 10µg/ml). The external standard method was used for quantification of the marker in the Buriganga River water extract.

River water samples

On 9 April 2009, 18 water samples were collected into the cleaned amber-colour glass bottles from three different stations, namely; Postagulla, Sadarghat and Sowarighat of the Buriganga River. Sampling stations were at least 1 Km from each other. The locations of the sampling points of the river are shown in Figs. 1a and 1b. Six samples were collected from each of the sampling stations and two samples from each sampling point, at surface and 30 cm depth of water. Each sample was collected in a 1.1-1 capacity volume, well washed amber-colour glass bottle. At first, the bottle was lowered slowly into the water and its cork was opened by hand, marked accordingly in cm at the desired depth. When the bottle was filled with water, it was closed and drawn up carefully. 100 ml of water was then discharged from the glass bottle. At the same time 10% $CuSO_4$ was added as a stabilizing agent into the water samples and shaken vigorously by hand and finally closed by the cork.

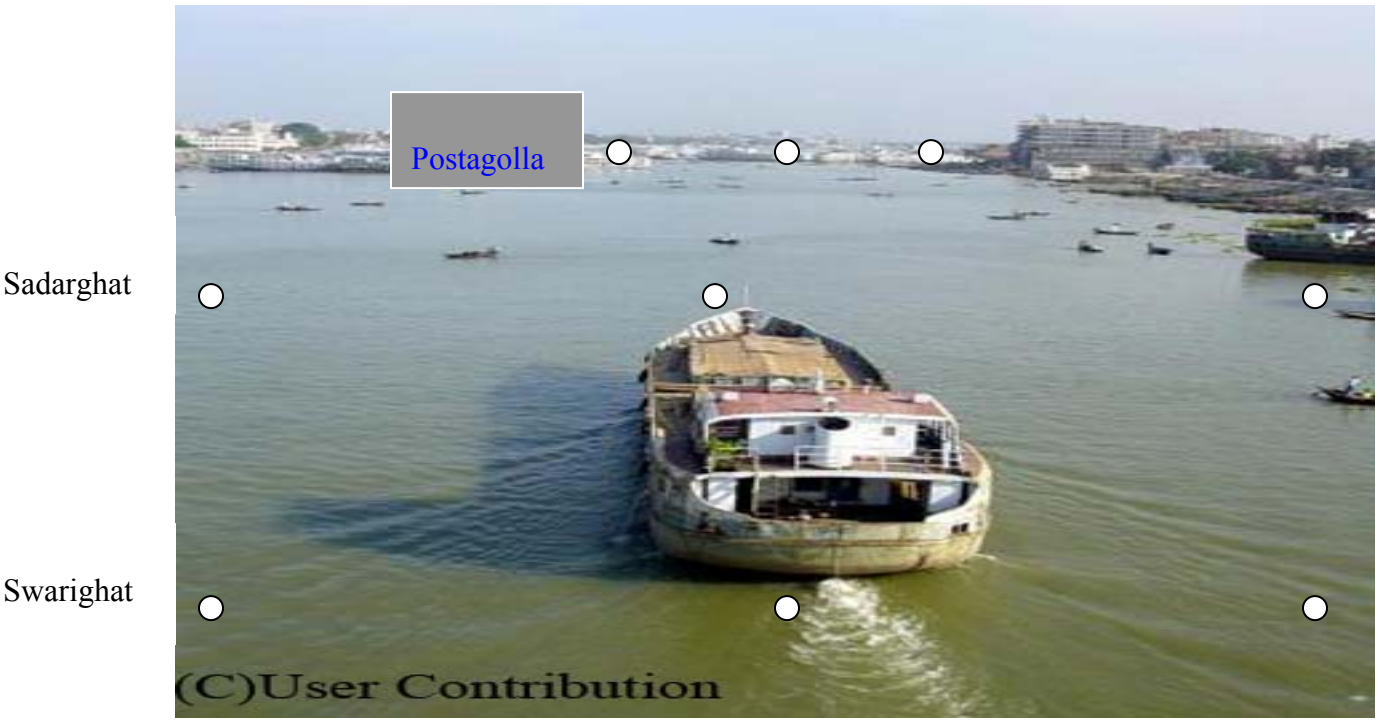

Figure 1a. Buriganga River showing the locations of the sampling stations and collection points of water samples: ○ Sampling collection points.

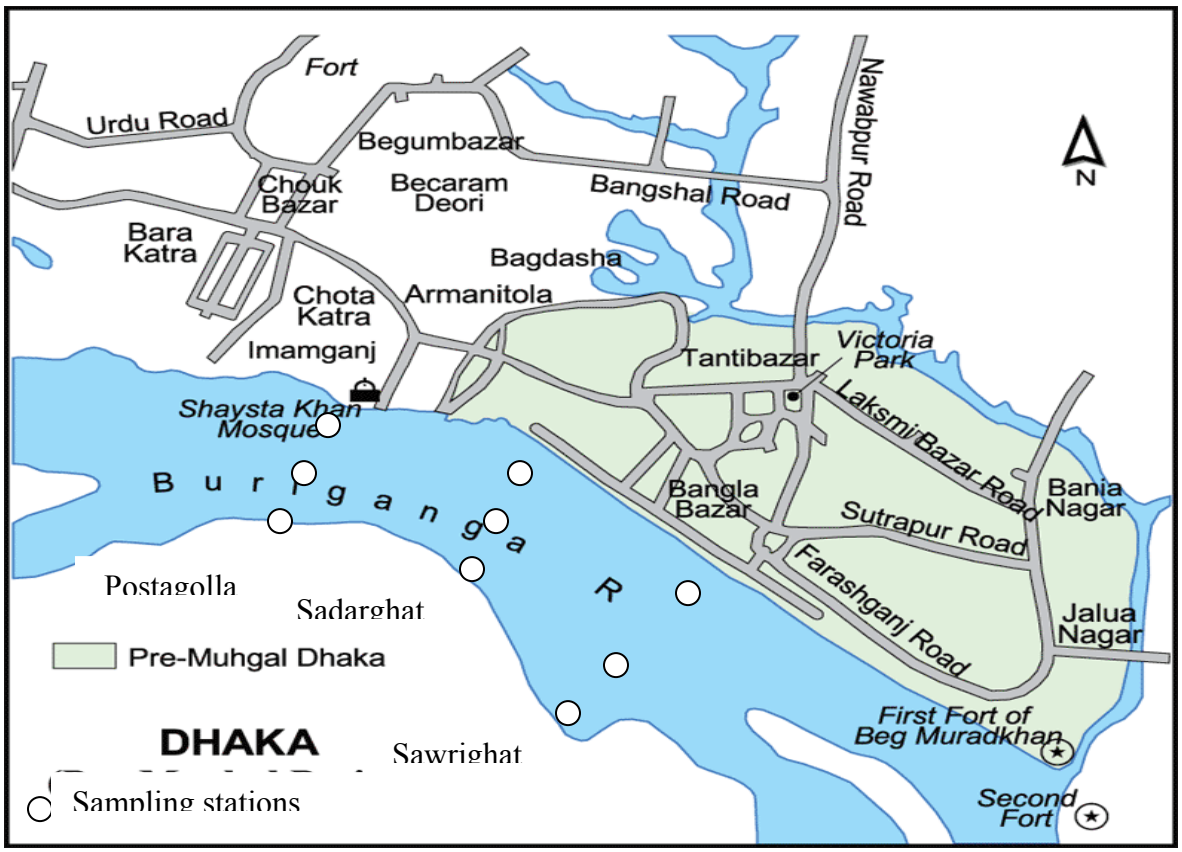

Figure 1b. Map of the Buriganga River showing the locations of the sampling stations and collection points of water samples: ○ Sampling collection points.

Extraction

The extraction was carried out for 72 hrs after collection of the samples by solvent extraction method. This method required two 50-50 capacity conical flasks with Teflon stop corks. Each water sample with a volume of 20 ml was poured into the conical flask; then 20 ml of dichloromethane was added and the mixture shaken vigorously for 1 hr by Lab Tech shaker (Manufacture of Lab. Ind. and Vac. Instrument). The water-solvent was transferred to the separating funnel and it was then allowed to stand in a rack for 10 min. The aqueous layer was drained into a jar by means of a Teflon stop cork, leaving the dichloromethane layer (extract) in the separating funnel. The extract was transferred into a volumetric flask. The aqueous layer was extracted again with 10 ml of dichloromethane and the extract was collected and stored. Both extracts were combined into a volumetric flask and kept under cool atmosphere. All samples (18) were extracted in similar ways.

Removal of residual water from sample extract

In order to remove the residual water from the extract, the extract was treated with anhydrous sodium sulphate. Sodium sulphate (50 gm) was placed in a funnel and slightly

watered to make a layer of solid form that does not mix with the extract. The extract was then passed through the funnel and collected in a pre-cleaned volumetric flask. The treated water was restored. The operation was done quickly to avoid possible losses of any volatile compounds in the extract. A column (60 cm long x 1 cm i.d.) was used for this operation as well. Fifteen centimeters of the column were packed slowly with silica gel/solid silver nitrate mixture. Before the column was packed, the silica gel was activated at 120^{o}C for 10 hr. and deactivated with 3% distilled water by weight. The 10 ml of dichloromethane was introduced into the column to rinse the gel; here 5 ml of dichloromethane was discarded and the remaining 5 ml was retained in the column. Under this condition, the sample extract was passed slowly and carefully through the column. Finally the extract was collected in a suitable container for analysis. All the samples were treated in the same manner.

Pre-concentration and analysis of the extract

The extracts were reduced to a volume of 2 ml by evaporation using Kuderna-Danish techniques. By the techniques, dichloromethane was slowly evaporated; a similar evaporation procedure was reported earlier. Special attention was given to avoid extra evaporation and the volume of extract (30 ml) was reduced to 2 ml solution. The concentrated solution was preserved in a refrigerator for further analysis. The pre-concentrated solutions were injected into the GC-MS instrument and different peaks of naphthalene obtained in the chromatogram. The naphthalene was identified and quantified by comparing its retention time and peak area with that of known concentration of standard solution which was also injected into the GC-MS system under the same conditions. The concentration of naphthalene was calculated by using the equation:

Concentration of naphthalene = ($_{s}$/A_{std}) x (I_{std}/I_{s})x (C_{std})x2 (Conc. Factor)x1000ppb

Here A_s and A_{std} represent the peak area of component of sample and standard solutions, I_s and I_{std} indicate the injected volume of sample and standards and C_{std} is the concentration of standard solution.

Clean-up procedure

The cleanup column (i. d. = 1 cm) was filled with cotton at the bottom. An activated silica gel (17 gm) was soaked with dichloromethane, loaded into the cleanup column (5 cm), which was then topped with 1.5 cm of anhydrous sodium sulphate. Five ml of dichloromethane was added to wash the sodium sulphate and the silica gel. The dried 1 ml sample was then transferred into the column, the vessel was rinsed twice with 2 ml dichloromethane, which was also added to the column. Sixty ml of dichloromethane was added to the column and allowed to flow through the column at a rate of 3–5 ml/min, and the eluent was collected. The collected eluent from the cleanup procedure was re-concentrated to 1 ml with K-D concentrator.

Results and Discussion

The capital of Bangladesh, Dhaka, is situated on the banks of the Buriganga River. About 180 million people live in this mega city. Along the banks there is a sprawl of small and large industries such as dyeing, painting, etc. They are discharging effluent into the river. The river is even being affected by the more than one million different kinds of vehicles running in the city every day. They are polluting the environment continuously. Following rain, water washes the roads and other polluted areas and ends up flowing into the river. Naphthalene, a PAH, was selected as the target compound in this study for carcinogenicity [6, 7].

Measurement of naphthalene in river water samples

Identification of naphthalene was carried out by GC-MS analysis, and/or by comparison and combination of their retention times, and mass spectra of the peaks with those of authentic samples. Quantitative data were calculated by GC-MS peak areas compared with those of external standard calibration curves (Fig. 2). The evaluation was performed using three- point linear standard calibration curves (r^2 >0.9820) calculated by GC-MS.

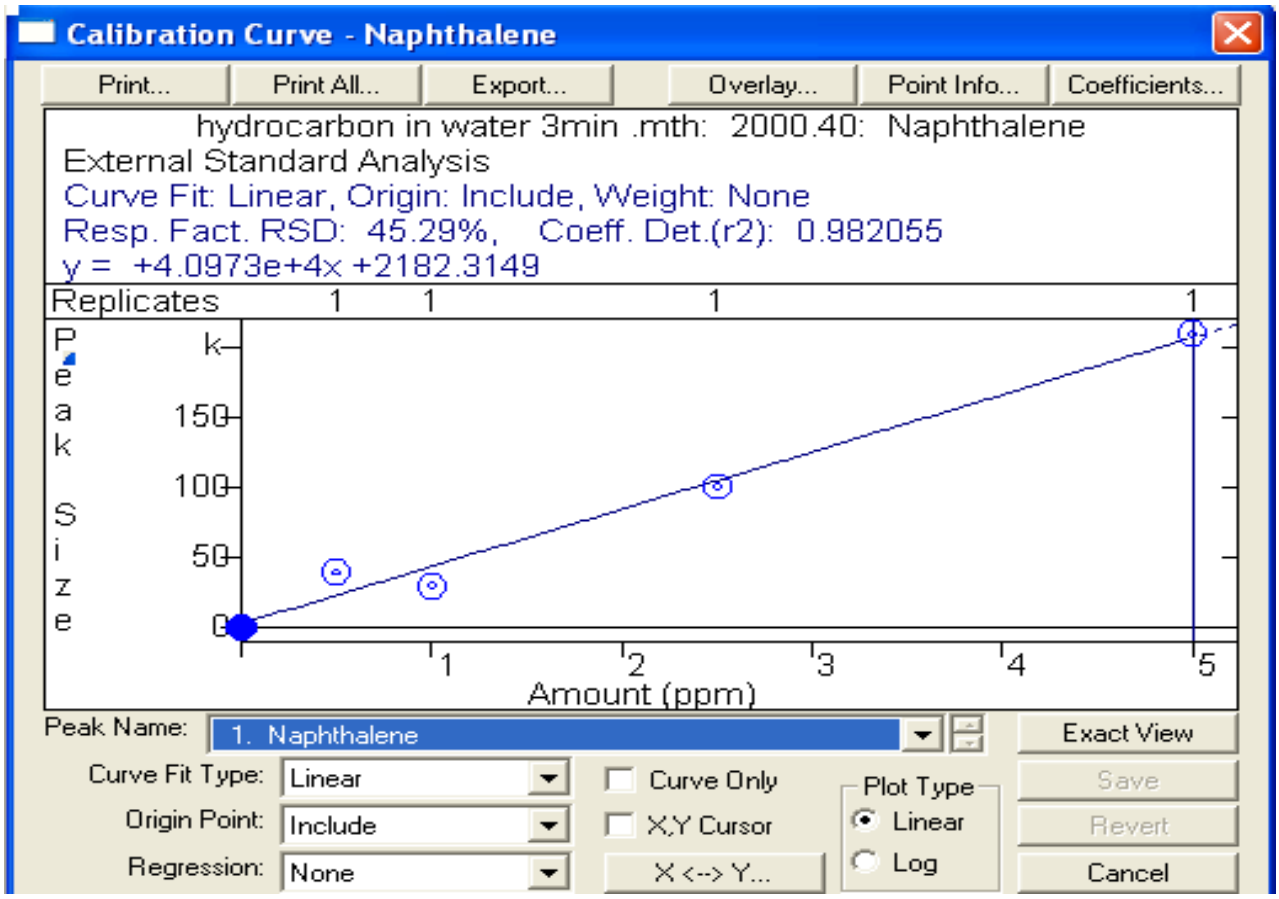

Figure 2. Standard Calibration Curve of Naphthalene.

In order to determine the concentration of naphthalene in surface and 30 cm depth of water at Postagolla, Sadarghat and Sowarighat stations of the Buriganga River, the pre-concentrated samples were injected into the GC-MS instrument. A comparison of mass spectra between the standard solutions of polycyclic aromatic hydrocarbon (PAHs), naphthalene and sample solutions collected from surface water and from 30 cm depth at Postagolla station is shown in Fig. 3.

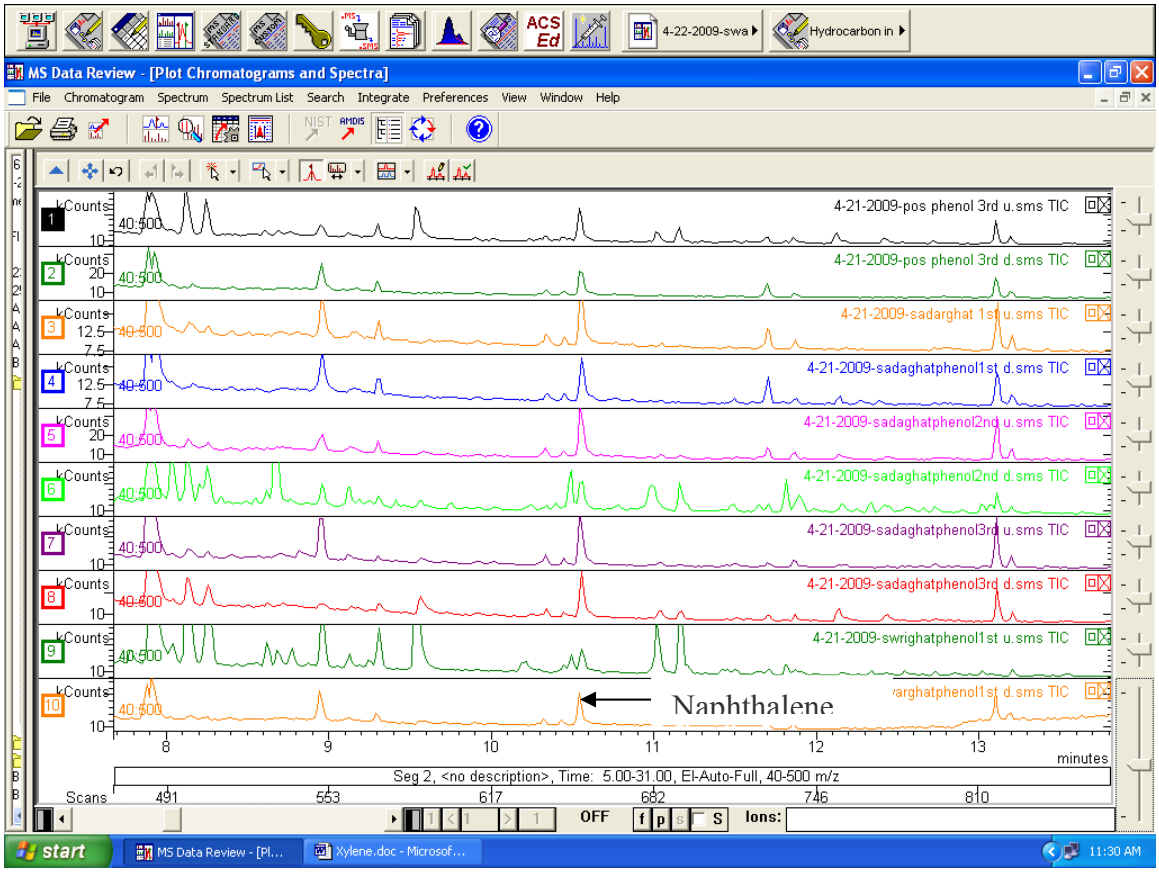

Figure 3. Comparison of the chromatograms of retention time of standard and water samples extract that were collected from different sampling stations.

Column: VF-5 (l. 30 m, i.d. 0.25, film thickness 0.25 µm); delay: 3min; Temperature Program: 40°C(1)—›200°C (8°C)—›300°C (10°C); Injector Temperature: 250°C; Split: 20%; Carrier gas: He; Flow rate: 1ml/min.

This shows an excellent similarity of the retention time (10.549 for standard of naphthalene) of the separated peak of naphthalene between standard and sample solutions. All the surface water samples contain different concentrations of naphthalene, collected from Sawighat, Sadarghat and Postogalla. Very similar types of chromatograms were obtained for surface and 30 cm depth of water samples collected from other stations, such as Postagolla and Sadarghat. These are not shown in the figure. The concentration of naphthalene for surface and 30 cm depth of water collected from the various stations of the Buriganga River is presented in Table 1.

Table1. Concentration of naphthalene in surface and 30 cm depth water at different locations of Buriganga River.

Concentration of naphthalene, ppm									
Naphthalene	**Sowarighat**			**Sadarghat**			**Postagolla**		
	Northern side	Middle	Southern Side	Northern side	Middle	Southern Side	Northern side	Middle	Southern Side
Surface	0.964	0.586	0.503	0.332	0.563	0.863	0.447	1.015	0.530
30 cm depth	0.316	0.357	0.283	0.251	0.157	0.416	0.222	0.458	0.316

Table 1 predominantly shows the high concentration of naphthalene obtained from water samples collected from surface and 30 cm depth of water of all the three stations of the Buriganga River. Relatively lower concentration of naphthalene at different sampling locations is probably due to their volatility, dissolution, biological degradation, photo oxidation and rapid photolysis [13]. It can also be seen that the concentrations of naphthalene in surface water are greater than that of those from 30 cm depth. Industrial discharge of effluent or the vehicle exhausts, eventually washed by the rainfall to the river, is simply the reason for the high concentration of naphthalene in water. The concentration of naphthalene obtained from the samples collected from surface and 30 cm depth of water at Sowarighat, Sadarghat and Postagolla sampling stations at the northern, middle and southern side of the Buriganga River were also investigated. The results are shown as bar diagrams in Fig 4.

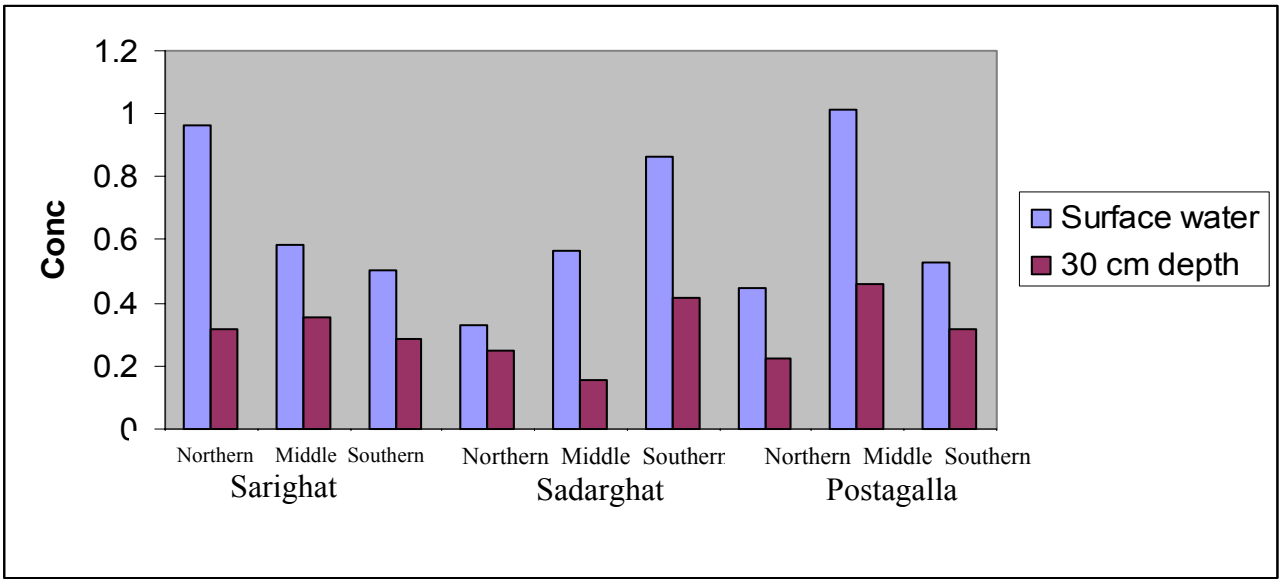

Figure 4. Concentrations of naphthalene in surface and 30 cm depth of water at the northern, middle and southern side of Sowarighat, Sadarghat and Postagolla sampling stations of the Buriganga River.

The higher concentration of naphthalene was found to occur on the northern side of the river, compared to those at middle and southern parts of the stations. The reason is that the river terminals are located on this side. Launches, tankers, speedboats, etc., frequently stop to these terminals for loading and unloading goods, passengers, petroleum fuels, etc., resulting in some raw discharge on the surface water. Furthermore, the northern side is the heart of the city. The human waste, as well as the city washing waste, discharges directly to the northern side of the river causing similar effect. Similar results, as well as a similar explanation, can be drawn for 30 cm depth of water samples. Overall, the concentrations of naphthalene on the northern side of the three sampling stations at Sowarighat, Sadarghat and Postagolla are relatively higher than the middle or southern side. However, the highest concentration of naphthalene was found as 1.015 μg/L in surface water at the middle of Postagolla sampling station.

Conclusion

PAH compounds are important priority pollutants in most countries in the world and many related analytical techniques have been developed for detection of naphthalene. The present work has been undertaken using our previously established method for PAH determination based on without any derivative process. In conclusion, the concentration of naphthalene in water samples at Sowarighat, Sadarghat and Postagolla stations of the Buriganga River were determined. Samples were collected from surface and 30 cm depths of water from each of the sampling stations. The collected samples were extracted, pre-concentrated and analyzed by GC-MS. The highest and the lowest concentrations were obtained in the river water samples at Sowarighat station from surface and 30 cm depth. Similar results were obtained from Postagolla. The experimental results demonstrated that this GC-MS method offers excellent recoveries and could be employed for environmental sample analysis. In view of the rapidity, sensitivity, simplicity and environment-friendly nature, the proposed method will be an excellent alternative detection technology for naphthalene analysis and will be widely employed in environmental and other related fields.

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