DETERMINATION OF THE TOTAL HYDROCARBON CONCENTRATIONS IN THE SHIPPING CHANNEL IN THE SUNDARBANS MANGROVE FOREST OF BANGLADESH BY MODIFIED PARTITION GRAVIMETRIC TECHNIQUE

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Abstract: To determine the level of total hydrocarbon concentrations (THCs) along the shipping channel in the Sundarbans Mangrove Forest of Bangladesh, surface water samples were collected in December 2004. Water samples were analyzed for THCs by modified Partition-Gravimetric Technique developed in this study. In this method, the detection limit for THCs was 3 mgL⁻¹ at room temperature with a relative error of 33.3%. At ~15ºC, 93% of hydrocarbons could be recovered. The THCs along the shipping channel in the Sundarbans varies between <3 mgL⁻¹ to 8.3 mgL⁻¹; the latter being observed only at Mongla Port. THCs recorded in this study were significantly lower than the maximum permissible level (10 mgL⁻¹). This indicates that the Sundarbans is still safe free from oil pollution.

Key words: total hydrocarbon concentration; sundarbans mangrove forest; partition-gravimetric technique

Introduction

The extensive shipping of crude oil over the world’s oceans has increased concern about accidental spillage of petroleum in the marine environment. Petroleum products enter into the marine environment through natural seepage, offshore drilling and production, and transportation losses. However, major spills are associated with ocean transport of crude and refined petroleum products. Oil spills in the coastal water affecting mangrove ecosystems is of great concern in Bangladesh.

In Bangladesh, accidental damage from heavy oil spills in the mangrove forests does not appear to be frequent, but there is every possibility of accidental damage anytime. Bangladesh boasts of two international ports namely Chittagong and Mongla, with potential oil spill risks. Mongla, the second largest seaport of Bangladesh, is on the northeastern border of the Sundarbans and reached by 60km long channel through the mangrove forest (Fig.1). According to the port authority, in 1998-99, 381 ships moored at the port and in the decade (1987-97) the number of ships anchoring in the port were 4,117. 2.95 million metric ton of cargo was imported and 0.37 million metric ton exported through the port in 1998-99 and 2.70 million metric ton of cargo was imported and 0.31 million metric ton exported through the port in 1999-2000. The port is capable of handling 30 to 40 ships at a time. About 500 sea-going vessels are handled at Mongla port yearly. Moreover, numerous mechanized boats ply inside the mangrove area regularly for different purposes. So there is potential risk for the mangroves to be affected by oil pollution (Siddiqi, 2001). In 1990, a
big oil spill from an unknown origin was reported near the Jongra forest camp in Chandpai Range. In 1994 a cargo vessel capsized near Dangmari forest station. Oil from the fuel tank spread about 15 km downstream from the ship and affected a considerable part of the Sundarbans. Instant mortality of Heritiera fomes and Excoecaria agallocha seedlings, grasses, fishes, shrimps and other aquatic animals was reported as a result of the incidence (Karim, 1994). In 1999 and 2001 bunker oil and diesel oil were also recorded at offshore of Hiron point and Khulna respectively (Anon, 2002). So, monitoring of oil pollution in Sundarbans is essential due to its ecological significance.

The impact of a given oil discharge is determined by the nature of the hydrocarbons weather conditions and the distance of the discharge from shore (Kerr, 1977). Mielke (1990) observed that low molecular weight hydrocarbons, which are highly toxic, is quickly removed through evaporation and dissolution of these compounds.

One of the major problems frequently associated with oil spills onto surface waters is the identification of the oils involved in the spill. Methods for the determination of total petroleum hydrocarbons (TPH) in environmental samples are based on extraction of the TPH from the samples and their determination in the extract by (i) a partition-gravimetric method, (ii) gas chromatography (GC-FID or GC-MSD) and (iii) infrared (IR) spectrometry. In partition-gravimetry, the detection limit of total hydrocarbon is 10 mg/L (Anon, 1992). Although the maximum allowable concentration of oil in natural waters is 10 mgL⁻¹, individual aromatics such as benzene, toluene, and naphthalene may be toxic even in lower concentrations. For this reason, determination of total hydrocarbon in low concentration is important. Thus effort was made to develop partition gravimetric method for measuring oil spill at low concentration.

This study was undertaken in an attempt to provide some base line data on the level of total hydrocarbon in the shipping channel of the Sundarbans. An effective method has

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**Fig.1. Locations of sampling sites.**

been developed in order to determine the low concentrations of total hydrocarbon in natural water. This method could in oil spill identification and monitoring which is essential for sustainable management of the Sundarbans mangrove forest.

**Materials and Methods**

The study area is the Sundarbans mangrove forest located in the estuary of the river Ganges and lies between latitudes 21°31' and 22°30' N and longitudes 89° and 90°E. The locations of the
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Sampling sites are shown in Fig. 1. Sampling took place in December 2004. Water samples were collected in wide mouth glass bottle that was washed with soap, rinsed with water and finally rinsed with solvent mixture (80% n-hexane and 20% methyl-tert-butyl ether). The samples were acidified to pH 2 with 1:1 HCl and transported from field to laboratory in ice box and refrigerated. The standard solution was prepared by taking 1 ml of diesel oil, (density 0.8331 gm/cc) in a 100 ml volumetric flask and filled with solvent mixture (n-Hexane/ Methyl-tert-butyl ether). The concentration was 8331 mgL⁻¹. From this stock solution 100, 50, 10, 5, 4, 3, 2 and 1 mgL⁻¹ concentrations were prepared. Standard solution samples were transferred from the bottles to a separatory funnel and hydrocarbons were extracted with the solvent (80% n-hexane and 20% methyl-tert-butyl ether) at approximately 10°C, 15°C, 20°C and room temperatures (28°C). Extracted solvents were distilled in distilled recovery flask at 85°C in water bath. To maximize solvent recovery with speed, a vacuum adapter was fitted with distillation flask. When visible condensation stopped, flask was removed from water bath and the samples were weighed as in simple gravimetry. The same procedure was applied for unknown samples collected from sampling sites.

### Results

**Table 1:** Different standard solution of oil (Diesel) measured by modified Partition-Gravimetric method at ~28°C

| Concentration in mgL⁻¹ | 100 | 50 | 10 | 5  | 4  | 3  | 2  | 1  |
|------------------------|-----|----|----|----|----|----|----|----|
| True value in mg (100 ml solution) | 10.00 | 5.00 | 1.00 | 0.50 | 0.40 | 0.30 | 0.20 | 0.10 |
| Measured value (constant weight) in mg | 9.20 | 4.60 | 0.90 | 0.39 | 0.31 | 0.20 | -   | -   |

**Table 2:** Standard solution (100 mgL⁻¹) of oil (Diesel) measured by Partition-Gravimetric at different temperatures.

| Temperatures in °C | at ~10°C | at ~15°C | At ~20°C | at ~28°C |
|--------------------|----------|----------|----------|----------|
| Measured Value in mg | 89.20    | 92.60    | 85.60    | 84.50    |

**Table 3:** Oil contents in different locations of Sundarbans mangrove forest

| Location | Oil Content in mg/L | Standard Deviation |
|----------|--------------------|--------------------|
| Chalna   | 3.7                | ±0.9               |
| Mongla Port | 8.3              | ±1.3               |
| Dhangmari | 6.8                | ±1.2               |
| Tambulbonia | <3              | -                  |
| Dudmukhi  | <3                | -                  |
| Katka     | 4.3                | ±1.0               |
| Dublarchar | 5.1              | ±1.2               |
| Nikomol   | <3                | -                  |
| Tinkona   | <3                | -                  |
| Pasakhali | <3                | -                  |
| Bhadra    | <3                | -                  |
| Harbaria  | <3                | -                  |

**Discussion**

Partition gravimetry is a widely accepted simple analytical procedure for determining total hydrocarbon concentrations (Kirschman and Pomeroy, 1949). At low concentrations quantitative analysis based on partition-infrared method is possible but required expensive instrumentation with calibration (Gruenfeld 1973). Partition-gravimetry is cost-effective than the partition-infrared method because in partition–gravimetry only some glass-wires and solvents are required. In partition-gravimetry total hydrocarbons present in water are extracted with solvent mixture (hexane and methyl-tert-butyl ether). Trichlorotrifluoroethane is also the prescribed solvent for better extraction but could not be used for environmental problem associated with chloroflourocarbons. Groups of substances with similar solubility in an organic extracting solvent are determined quantitatively by gravimetry. There is no need to calibrate this method. In order to determine the THCs at lower concentration, the preserved samples are extracted for THC at room temperature and determined by gravimetry (Table 1). One Sample (100 mgL⁻¹) was extracted at
different temperatures and determined for THCs (Table 2) in this study. The identified lower concentration was 3 mgL\(^{-1}\) for THCs with a relative error 33.3% (Fig. 2) but the maximum recovery of hydrocarbon was 93% (Fig. 3) through extraction at \(\sim\)15°C. So the extraction of the sample at 15°C was best for the recovery of oil. This was the modification of the existing partition-gravimetric method in which samples are extracted at room temperature (~28°C) (Anon, 1992). The relative error of the analysis was lowest (8.0%) at 50ppm concentration analysis (Fig. 2). This method is less applicable for accurate determination at low concentration but helpful for monitoring and to take decision for further analysis with by GC-FID.

![Fig.2 Relative error (%) of oil content determination by partition-gravimetric method.](image1)

![Fig.3 Maximum recovery of oil at different temperature by partition-gravimetric method.](image2)

Samples were not collected from western part of SMF because the movement of merchant vessel in that part of SMF is insignificant. The range of THCs in the shipping channel in the SMF varying between <3 mgL\(^{-1}\) and 8.3 mgL\(^{-1}\) (Table 3). The highest value was observed in at Mongla port in which vehicle movement and residence time is maximum. But this value is less than the maximum allowable concentration (10 mgL\(^{-1}\)). This could be attributed to an insignificant input of hydrocarbon sources or due to efficient mixing during tide.

**Conclusion**

The study reveals that the Sundarbans is still safe from the oil pollution. However, as the SMF is a sensitive ecosystem and harbors the Mongla port, potential threat from oil pollution cannot be over-ruled. Partition-gravimetric method developed in this study would be important for Continuous monitoring and surveillance program for oil spill management.

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