Biogeochemistry of the dissolved organic matter (DOM) in the estuarine rivers of Bangladesh–Sundarbans under different anthropogenic influences

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ABSTRACT
The Bangladesh-Sundarbans is the Outstanding Universal Value (OUV) articulated by UNESCO, is under different anthropogenic stress. The present study focused on the status of estuarine biogeochemistry of the dissolved organic matter (DOM) of the Bangladesh-Sundarbans using different optical methods. Four fluorophores: Peak A (230-265/408-488 nm), Peak M (290/414 nm), Peak C (365/488 nm), and Peak W (320/410 nm), and three fluorescent dissolved organic matter (fDOM) components (two humic-like, one detergent-like) were identified in the Sundarban mangrove Rivers by Excitation-Emission Matrix (EEM) and Parallel Factor (PARAFAC) analyses. Among the three components, the terrestrial-derived humic-like Component had a high intensity in five samples among six in the Bangladesh-Sundarbans. The total fluorescent intensity and calculated dissolved organic carbon (DOC) concentration were maximum in Harbaria and minimum in Kotka and Dublar char, respectively. Synchronous fluorescence spectroscopy (SFS) identified protein-like component besides humic-like DOM. The optical indices described that natural fDOM components were from terrestrial sources, were matured, and autochthonous fDOM production was low. The DOM components were relatively lower in molecular size and aromaticity in Harbaria. However, water samples in Harbaria contained organometallic compounds that had much absorbance at 254 nm wavelength. DOM components had low energy and more π-conjugated molecules in structure in the Dublar char and Kotka. Components in Dublar char had comparatively higher molecular size and weight than other sampling stations. The Harbaria and Mongla port contained more hydrophobic and less polar substances than other stations. This study will firmly add diversified notions to future research regarding mangrove forest.

1. Introduction

Sundarbans mangrove forest (SMF) is the largest mangrove forest globally, comprising both Bangladesh and West Bengal of India. The SMF-Bangladesh is listed as a UNESCO World Heritage Site in 1997 and articulated as the Outstanding Universal Value (OUV) (UNESCO, 1997). It is a reserve forest and also a Ramsar-declared wetland of global importance (Aziz and Paul, 2015; Khan et al., 2020). The total land area of SMF is 601,700 ha which covers 38.12% of the whole forest and 4.3% of Bangladesh (Bangladesh Forest Department, 2021a). The Sundarbans mangrove ecosystem is accepted as a worldwide concern for its rich biodiversity and its essential role in ecosystem-service-providing, including abundant goods and safeguarding against cyclones and storm surges (Payo et al., 2016). Bangladesh Forest Department (BFD) manages the entire Bangladesh Sundarbans and operates development activities through the annual development programme each year (Khan et al., 2020).

Mangrove forests are highly productive coastal ecosystems that significantly influence the global biogeochemical cycle (Ray et al., 2018). Mangroves are the most carbon-rich biomes, accounting for 14% of carbon sequestration by the global ocean as coastal habitats (Alongi 2012). Dissolved organic matter (DOM) performs an essential role in maintaining the mangrove ecosystems throughout the ecological function (Kida et al., 2019). DOM is the most significant portion of organic carbon in the coastal, estuarine, and riverine waters, led by anthropogenic inputs and leached from soil (Das and Hazra, 2018). The distribution of dissolved organic carbon (DOC), particulate organic carbon (POC), and dissolved inorganic carbon (DIC) significantly influences the estuarine mangrove ecosystem (Ray et al., 2018). Globally, >10% of the refractory DOC is transported to the sea by terrestrial-related mangroves (Dittmar et al., 2006). Furthermore, microbial activities in the sediments

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and water columns also regenerate organic matter. The nature of DOC and colored dissolved organic matter (CDOM) for the SMF-Bangladesh, and SMF-India has been studied previously (Prasad et al., 2014; Ray et al., 2018; Sanyal et al., 2020). Prasad et al. (2014) also identified autochthonous marine humic-like substances, humic-like substances, tryptophan-like substances, and humic substances with recent materials.

A considerable number of development activities are going on in the Bangladesh Sundarbans side. The increased industrialization, as well as rapid but unplanned urbanization, are going on in Khulna, Bagerhat, and Satkhira districts (Bangladesh Forest Department, 2021b). Heavy structural developments are occurring in and around the ecological critical area (ECA) and port activities are one of them. Mongla seaport is the second-largest seaport in Bangladesh, which locates at the convergence of the Poshur River and the Mongla River. Mongla port is very close to the ecologically critical area of SMF-Bangladesh, which has trade links worldwide. All kinds of ships and cargo boats carry goods through the rivers of SMF to the port (Islam et al., 2017). According to the Mongla port authority (MPA, 2021), in the fiscal year 2014–15, traffic was compared to the ships in 2019–2020.

Over time SMF ecosystem has been significantly affected naturally and anthropogenically. The natural factors include the shifting river channels, diminished freshwater flow, sedimentation, rising salinity intrusion, and climate change effects (Khan et al., 2020). On the contrary, anthropogenic activities include over-exploitation of resources within the SMF, shrimp cultivation, increased shipping operation, tourism, oil pollution, sewage pollution, and many development activities. During the 2020–21 COVID-19 pandemic, domestic tourism activities in the Sundarbans increased manifold and threatened the Sundarbans ECA.

According to the latest report on “Strategic Environmental Assessment of the South West Region of Bangladesh for Conserving the Outstanding Universal Value of the Sundarbans Project” led by Bangladesh Forest Department (2021b), the wet season phosphate level has a significant concern. Although the nitrate level is within the limit of inland surface water quality standards (ECR 1997 and Draft ECR 2017), phosphate levels exceeded the standard limit of 0.5 mg/L in many parts of the Sundarbans region (Table 1).

At least 40 types of industries/mills were found to release nitrates and phosphates into the Passur-Shibsa river system, including agro-food processing (11), jute mill (private) (5), power plant (12), steel and metal (10), sugar mill (2), battery manufacturing (2), beverage production (1), food production and processing (10), leather processing (5), plastic processing (9), seafood processing (19), tobacco processing (6), cable manufacturing (1), oil refineries (4), plywood and wood processing (5), and textile (6). In addition, one export processing zone and two types of manufacturing (1), oil refinery (1), fish processing (11), leather processing (5), plastic processing (1), jute mill (private) (5), power plant (12), steel and metal (10), and textile (6). The climate is humid to subtropical, with a mean air temperature of 18–23 °C for the winter and 27–31 °C for the summer (Hossain and Bhiyani, 2015; Aziz and Paul, 2015). The mean yearly precipitation is 1980 mm; summer (May to September) provides about 81% of the yearly precipitation, while winter precipitation is about 19%.

### Table 1. Nitrate and phosphate levels in three different locations of the Sundarbans (Bangladesh Forest Department, 2021b).

| Location  | Season | Nitrate (mg/L) | Phosphate (mg/L) |
|-----------|--------|----------------|-----------------|
| Mongla    | Dry    | 3.3–4.0        | 0.2–0.3         |
|           | Wet    | 2.0–2.5        | 0.5–0.7         |
| Harbaria  | Dry    | 3.2–3.5        | 0.2–0.3         |
|           | Wet    | 2.1–2.5        | 0.5–0.6         |
| Hiron point | Dry  | 2.6            | 0.1             |
|           | Wet    | 1.3            | 0.5             |

2. Materials and methods

2.1. Study area

The Sundarbans mangrove forest (SMF) is a deltaic swamp developed by sediment deposition through the Ganges River from the Himalayas (Aziz and Paul, 2015). Geographically it is situated in the southwest region of Bangladesh (Islam et al., 2017). The forest meets the Bay of Bengal in the south. The SMF-Bangladesh locates between 21°18’N and 22°30’N latitudes and 89°01’E and 90°18’E longitudes (Hossain and Bhiyani, 2015; Aziz and Paul, 2015). The area of SMF-Bangladesh is about 6,017 km², of which the land area is 4,143 km² and water bodies 1874 km² comprising a complicated ecosystem of rivers, canals, and tidal creeks (Aziz and Paul, 2015).

The climate is humid to subtropical, with a mean air temperature of 18–23 °C for the winter and 27–31 °C for the summer (Hossain et al., 2013). The mean yearly precipitation is 1980 mm; summer (May to September) provides about 81% of the yearly precipitation, while winter precipitation is about 19%.

2.2. Sampling

Seasonally, we have collected only winter season samples in January as it is the accessible month in the Sundarbans mangrove forest with the permission of the Bangladesh Forest Department. We have collected 12 river water samples from 6 different river points from January 4–6, 2020, using the tourist vessel MV Vessperd. The sampling locations and local river names are given in Figure 1. pH, total dissolved solids (TDS), electrical conductivity (EC), turbidity, and water temperature data were collected in situ by using YSI EXO2 multiparameter water quality sonde. Water samples were collected using PET bottles rinsed with HNO3 acid, Milli-Q water, and sample water wash. All collected water samples were transported to the Hydrobiogeochemistry and Pollution Control Laboratory at the Department of Environmental Sciences, Jahangirnagar University. The water samples were filtered through a 0.45 μm GF/F filter paper and stored in the laboratory at 4 °C for further analysis.

2.3. EEM-PARAFAC analysis

The excitation-emission matrix and parallel factor analysis (EEM-PARAFAC) are three-way multivariate analyses, extensively applied to fluorescence signals obtained from EEM spectra (Stedmon et al., 2003; Yamashita et al., 2008) to distinguish fluorescent components in DOM (Yamashita and Tanoue, 2003). They are applied extensively in freshwater and marine samples to isolate and quantify the individual fluorescence component signals in terms of fluorescence intensity. Fluorescent components of the water samples were analyzed by parallel factor analysis (PARAFAC) from the EEMs using the DOMfluor Toolbox (v1.7) (Stedmon and Bro, 2008). The EEM fluorescence spectra of the water samples solution were recorded with a fluorescence spectrophotometer (F-4600, HITACHI, Japan) in 3-D scan mode with a
700–voltage xenon lamp at room temperature. The EEM spectra were collected at 5 nm increments over an excitation (Ex) range of 225–400 nm, with an emission (Em) range of 250–500 nm by every 1 nm. The excitation and emission slits were set to 5 nm of band-pass, respectively. The scan speed was 1200 nm min$^{-1}$. All the cuvettes before analysis were rinsed with Milli-Q water. The Milli-Q water blank solution was subtracted from the sample’s EEM spectra to remove Raman scattering, and Rayleigh spectral lines entirely to calculate the correct component numbers. Samples were also corrected to remove the inner filter effects following the equation:

$F_{\text{corr}} = F_{\text{obs}} \times \frac{10^{(A_{\lambda_{\text{ex}}} + A_{\lambda_{\text{em}}})/2}}$

described in Panigrahi and Mishra (2019), where $A_{\lambda_{\text{ex}}}$ and $A_{\lambda_{\text{em}}}$ are the optical density of samples at excitation and emission wavelength, respectively. Dilution was not performed during EEM sampling. Arbitrary units were transformed into Raman fluorescence units (RU) (Stedmon

| Location         | pH    | EC (mS/cm) | TDS (mg/L) | Turbidity (FTU) | Temperature (°C) |
|------------------|-------|------------|------------|-----------------|-----------------|
| Harbaria         | 7.9 ± 0.03 | 3.8 ± 0.03 | 1944.5 ± 12.0 | 39.4 ± 3.5 | 21.3 ± 0.4 |
| Kotka            | 7.8 ± 0.2 | 19.0 ± 0.1 | 12420.0 ± 820.2 | 8.8 ± 3.2 | 21.0 ± 0.0 |
| Betmore Gang     | 8.2 ± 0.1 | 25.4 ± 0.5 | 11845.0 ± 63.6 | 9.3 ± 0.4 | 20.1 ± 0.1 |
| Hiron point      | 8.2 ± 0.1 | 35.8 ± 4.8 | 16800.0 ± 28.3 | 12.7 ± 2.3 | 21.2 ± 0.4 |
| Dublar char      | 7.6 ± 0.1 | 36.1 ± 0.4 | 18025.0 ± 35.3 | 8.0 ± 0.1 | 19.1 ± 0.1 |
| Mongla           | 7.7 ± 0.03 | 3.5 ± 0.03 | 1805.5 ± 7.8 | 92.5 ± 3.5 | 21.2 ± 0.2 |
2009). 12 water samples were used for a single PARAFAC analysis. Approximately 97% variation was covered by PARAFAC three-component analysis.

Samples were also measured for synchronous fluorescence spectroscopy (SFS) between 225 and 550 nm excitation wavelength keeping excitation and emission interval at 15 nm. Sample data in SFS were read at the arbitrary unit (AU). We ran synchronous fluorescence spectra in wavelength scanning mode at a fluorescence spectrophotometer (<F-4600, HITACHI, Japan>) to identify DOM compounds (Barker et al., 2009; Lu et al., 2021).

2.4. DOM indices

We have done parallel determination of DOC and DOM-UV of the river water samples. Water samples were measured for UV absorption at Specord 210 Plus, Analytikjena instrument within the wavelength between 190 and 1100 nm keeping scan speed 60 nm/min. Milli-Q (18MΩ·cm) water was taken for the reference solution in the UV analysis. Due to laboratory limitations for instrumental analysis by total organic carbon (TOC) analyser, DOC was calculated from UV data using a two-wavelength model reported in Cook et al. (2017). Specific ultraviolet absorbance (SUVA2, SUVA280, SUVA350, SUVA370) was computed using calculated DOC values (Gao et al., 2016; Hansen et al., 2016). The absorption ratio (E280/E350) and spectral slope ratio (Sβ) were also calculated from the UV data (Helms et al., 2008). Hydrophobicity and Polarity describing two indices were calculated from the data ratio at wavelengths 254/204 nm and 220/254 nm (Al-Juboori et al., 2015; Erlandsson et al., 2012).

Indices such as fluorescence index (FI), humification index (HIX), biological index (BIX), and freshness index (fβα) were computed using fluorescent data to specify identical sources of organic matter, and their production and decomposition state. FI was computed from the emission ratio of 470 nm and 540 nm at 370 nm excitation wavelength (Cory and McKnight, 2005). HIX was determined from the emission ratio between 435–480 nm and 300–345 nm at excitation wavelength 254 nm (Ohno, 2002). BIX was calculated from the emission wavelength ratio between 380 nm and 410 nm at 310 nm excitation wavelength (Huguet et al., 2009). fβ was quantified from the emission wavelength ratio between 380 nm and 420–435 nm at 310 nm excitation wavelength (Wilson and Xenopoulos, 2009). Humification and absorbance characteristics describing the other two indices, RF and a log K, were also calculated besides HIX (Santín et al., 2009). Moreover, the EEM model was divided into five spectral regions (regions: I for tyrosine, II for tryptophan, III for fulvic acids, IV for microbial byproducts, and V for humic acids) visualized in Fig. S1. Stokes shift parameter (SSP) and wavelength parameter (WP) were calculated to describe the fluorescence energy of DOM components using intensities in spectral regions (Li et al., 2021; Marhuenda-Egea et al., 2007; Yu et al., 2015).

3. Results and discussions

3.1. Physicochemical parameters

Water quality parameters showed spatial heterogeneity in the SMF-Bangladesh. The winter water temperature varied from 19.1 to 21.3 °C (mean = 20.6 °C, σ = 0.9), showing maximum and minimum temperatures at Harbaria and Dublar char, respectively (Table 2). The study by Rahman et al. (2013) also found water temperature in the winter season between 21.4 and 23.5 °C. However, there might be the effect of a cold wave passing over the country, including the Sundarbans. However, the estuarine stretch did not demonstrate a substantial change in water temperature with the tidal cycles (Rahaman et al., 2013). pH ranged from 7.6 to 8.2 (mean = 7.9, σ = 0.3) at different locations in the Sundarban mangrove (Table 2). Starting from the Mongla port, the pH of the river water (7.7) was increasing until Hiron Point (8.2), and at Dublar Char, it was 7.6 (Table 2). Previously Rahman et al. (2013) also recorded the pH of Sundarban between 7.1 and 7.9. High pH values were usually found during the high tide and winter season (Rahaman et al., 2013). Electrical conductivity (EC) ranged from 3.5 mS/cm at Mongla Port to 36.1 mS/cm at Dublar Char (mean = 20.6 mS/cm, σ = 14.0) (Table 2). EC in this study was higher than the Sibuti mangrove forest (0.8–96.1 µS/cm) at Mīrī Sarawak of Malaysia (Gandaseca et al., 2015), but comparable to the mangrove region (32.8–51.6 mS/cm) in the Krishnapatnam Coast of India (Dattatreya et al., 2018). TDS varied from 1805.5 mg/L at starting point Mongla Port to 18025.0 mg/L at the Dublar Char (mean = 10473.3, σ = 7079.5) (Table 2). TDS in this study was largely higher than in the mangrove swamps of Lagos, Nigeria (88–2560 mg/L) (Lawson, 2011). The SMF water would be considered unhealthy for human consumption according to the standards set by the environmental protection agency (EPA) as the TDS values exceeded 1000 mg/L in this study (Lawson, 2011). Turbidity varied from 8.0 FTU at Dublar Char to 92.5 FTU at Mongla Port (mean = 28.5, σ = 33.6) (Table 2). Turbidity values in the Harbaria, Hiron point and Mongla port regions of the SMF-Bangladesh were higher than the Sibuti mangrove forest (10.2–15.3 FTU) at the Mīrī Sarawak of Malaysia (Gandaseca et al., 2015). The maximum turbidity value at Mongla port was related to the marine vehicle movement, different types of industrial and sewage pollution, oil spillage, and continuous dredging for channel navigation. The salinity in the SMF-Bangladesh varied from 1 to 20 g/L (mean = 8.2 g/L) throughout the year (Rahaman et al., 2013).

3.2. DOC and EEM analysis

DOC concentration were ranged between 0.8 and 1.1 mg/L (mean = 0.9 mg/L, σ = 0.1) in the SMF-Bangladesh (Table 3). DOC concentrations were maximum in Harbaria and minimum in Dublar char. DOC had weak

| Table 3. DOM indices in the SMF-Bangladesh. |
|--------------------------------------------|
| Indices | Harbaria | Kotka | Betmore Gang | Hiron point | Dublar char | Mongla |
| FI | 1.5 | 1.4 | 1.3 | 1.3 | 1.4 | 1.4 |
| HIX | 5.8 | 9.3 | 5.9 | 6.0 | 7.6 | 8.3 |
| BIX | 0.7 | 0.6 | 0.8 | 0.8 | 0.8 | 0.8 |
| fβα | 0.1 | 0.04 | 0.1 | 0.1 | 0.1 | 0.1 |
| E280/E350 | 6.1 | 4.3 | 4.9 | 5.5 | 3.9 | 3.9 |
| Sβ | 1.1 | 1.8 | 2.0 | 2.1 | 0.1 | 0.9 |
| DOC | 1.1 | 0.9 | 0.9 | 0.9 | 0.8 | 0.9 |
| SUVA254 | 10 | 3.9 | 2.4 | 3.1 | 1.9 | 4.5 |
| SSP | 2.4 | 3.9 | 2.0 | 2.1 | 3.3 | 3.0 |
| WP | 1.1 | 2.1 | 0.7 | 1.0 | 3.7 | 1.5 |
| Hydrophobicity | 0.1 | 0.02 | 0.01 | 0.02 | 0.01 | 0.1 |
| Polarity | 5.2 | 6.0 | 6.6 | 5.9 | 7.5 | 4.7 |
and insignificant heterogeneity (p > 0.05) in the Sundarban estuarine rivers.

The 3D-EEM analysis identified four fluorophores from the 6 river water samples in the Sundarbans. Fluorophores showed their positions at $\text{Ex/Em} = 230-265/408-488$ nm (Peak A), $290/414$ nm (Peak M), $365/488$ nm (Peak C), and $320/410$ nm (Peak W) (Figure 2). Fluorophore intensity of all 6 locations is given in RU in Figure 3. Fluorophores such as Peak A, Peak M, Peak C, and Peak W showed fluorescence intensities between 0.25-1.28 RU (mean = 0.76 RU, $\sigma$ = 0.42), 0.06–0.33 RU (mean = 0.21 RU, $\sigma$ = 0.12), 0.03–0.14 RU (mean = 0.08 RU, $\sigma$ = 0.05), and 0.05–0.29 RU (mean = 0.18 RU, $\sigma$ = 0.1), respectively. Among the four fluorophores, Peak A had maximum intensity at all six samples in the Sundarban (Figure 3). Fluorophore intensity in descending order at six samples was: Peak A > Peak M > Peak W > Peak C (Figure 3). Fluorophores showed maximum intensity at Harbaria and minimum in Kotka (Figure 3). The presence of detergent-like fluorophore peak W in the present study indicates the presence of fluorescence whitening agents (FWA) in the river waters of Sundarbans-Bangladesh (Mostofa et al., 2010; Niloy et al., 2021b). The source might come from industrial activities and sewage pollution. Unlike Prasad et al. (2014), the present study did not find any tryptophan-like protein peak T related to the microbiological production of surface water.

### 3.3. PARAFAC model analysis

Three fDOM components were identified in the SMF-Bangladesh by PARAFAC analysis. Component 1 had two fluorophores at Peak A ($\text{Ex/Em} = 245/408$ nm), and Peak W ($\text{Ex/Em} = 320/410$ nm) regions (Figure 4a). Such two fluorophores of Component 1 in the Sundarbans mangrove

![Figure 2. EEM model of fDOM samples in the SMF-Bangladesh: (a) Harbaria (b) Kotka (c) Betmore Gang (d) Hiron point (e) Dublar char (f) Mongla port.](image)

![Figure 3. Fluorophores intensity of fDOM samples in the SMF-Bangladesh.](image)
indicated the presence of DSBP (4,4′-bis(2-sulfostyryl) biphenyl disodium salt)-like FWA and according to majority of its origin from the household and commercial detergents, Component 1 was named as detergent-like fDOM fraction in this study (Carstea et al., 2016; Dubler and Gill, 2017; Kramer et al., 1996; Mostofa et al., 2010; Niloy et al., 2021; Poiger et al., 1996; Takahashi and Kawamura, 2007). The presence of detergent-like components indicated household settlement and human activities in the SMF-Bangladesh. Component 2 showed fluorophores at Ex/Em = 265/488 nm (Peak A) and 365/488 nm (Peak C) wavelength regions (Figure 4b). Component 2 could be characterized as terrestrial derived, humic-like, aromatic, and photochemically degradable (Cory and Kaplan, 2012; Cory and McKnight, 2005; Murphy et al., 2006). Component 3 showed fluorophores at Peak A (Ex/Em = 230/416 nm) and Peak M (Ex/Em = 290/414 nm) regions (Figure 4c) and described its characteristics as UV-humic-like, less aromatic, terrestrial originated (Salve et al., 2012).

The fluorescence intensity of DOM components showed spatial variability in the Sundarban mangrove. Component 1, Component 2, and Component 3 showed intensities between 0.08-0.38 RU (mean = 0.25 RU, σ = 0.13), 0.07-0.31 RU (mean = 0.2 RU, σ = 0.1), and 0.09-0.7 RU (mean = 0.3 RU, σ = 0.2), respectively (Figure 5). Among the three components, Component 3 had a high fluorescence intensity in five samples among the six in the Bangladesh-Sundarban (Figure 5). Like fluorophores, fDOM components showed maximum and minimum intensity at the starting point Harbaria and Kotka (Figure 5). The higher intensity ranges of Component 1 at Mongla Port, Hiron point, and Harbaria indicated that various Sundarban mangrove forest traveling transports such as motor launch, speedboats, country boats, and mechanized vessels might dispose more anthropogenic detergent residues at these sampling stations than the rest others. Like intensities of fDOM components and fluorophores, DOC concentration was also higher in Harbaria (Table 3).

### 3.4. Synchronous fluorescence spectroscopy (SFS)

All fDOM samples of the SMF-Bangladesh showed maximum fluorescence intensity at emission wavelength 374 nm in synchronous spectroscopy (Figure 6). The peak wavelength at 374 nm indicates the presence of a fulvic acid-like component in the water of SMF-Bangladesh (Barker et al., 2009; Lu et al., 2021). This fDOM component could be originated from terrestrial plants (Lu et al., 2021). The intensity of this fDOM component followed the descending order: Mongla Port (7937 AU) > Kotka (7024 AU) > Dublar Char (4923 AU) > Hiron Point (4676 AU) > Betmore Gang (4280 AU) > Harbaria (3467 AU) (Figure 6). The rest of the peak positions of fDOM samples were observed at 270 nm, 447 nm, and 510 nm (Figure 6). The emission wavelength at 270 nm in synchronous spectroscopy indicated the presence of tyrosine-like component (Barker et al., 2009; Lu et al., 2021). This component could be predominantly originated from biodegraded or decomposed aquatic plants through biological activities (Lu et al., 2021; Yin et al., 2020). The intensity of this substance was maximum in Kotka (5492 AU) and minimum in Harbaria (2035 AU) (Figure 6). The tyrosine-like component was not identified in the PARAFAC model. The overlapping of a spectral line in the EEM fluorescence spectroscopy could hide this protein-like component. The emission wavelengths at 447 nm and 510 nm described the presence of humic-like components (Barker et al., 2009; Lu et al., 2021). This fDOM component could originate from terrestrial soil and plants (Lu et al., 2021). The intensity variation in sampling stations at 447 nm and 510 nm followed a similar trend of intensities at 374 nm (Figure 6).

### 3.5. Optical indices of DOM

The Fluorescence index (FI) is widely used to differentiate the allochthonous and autochthonous sources of natural DOM components (Cory et al., 2007, 2010). Low (1.3–1.4) and high (1.7–1.9) FI values indicate the presence of allochthonous and autochthonous sources of DOM components in surface water (Cory and McKnight, 2005). FI varied between 1.3-1.5 (mean = 1.4, σ= 0.1) in Sundarban mangrove, indicating that DOM components mainly originated from allochthonous sources (Table 3). Nevertheless, of predominant terrestrial inputs into the SMF-Bangladesh, FI > 1.4 described that autochthonous DOM also contributed to a small extent to the DOM resources. Prasad et al. (2014) found FI values between 1.4 and 1.7 in their study and also implied that both prevalent terrestrial DOM and small internal biological cycling contributed to the carbon chemistry of the SMF-Bangladesh.
The Humification index (HIX) is extensively used as a tool to indicate the sorptive capacity, sources, and diagenesis of natural DOM components in the environment (Ohno, 2002; Zsolnay et al., 1999). HIX < 4 indicates the presence of autochthonous, microbial decomposed, and less humic contained DOM in the environment (Parlanti et al., 2000; Salve et al., 2012). The humic character of DOM components starts to increase from HIX > 6. HIX > 10 indicates the presence of strongly humified, high carbon contained terrestrial derived, and aromatic humic substances in the samples (Huguet et al., 2009; Parlanti et al., 2000; Salve et al., 2012). HIX varied between 5.8 and 9.3 (mean = 7.1, σ = 1.5), implying that DOM components were intermediately humified, predominantly terrestrial derived, aromatic, matured, and contained high carbon in their composition (Table 3). HIX values in the SMF-Bangladesh were higher than two major rivers in Bangladesh, the Ganges (2.7–7.8) and the Brahmaputra River (1.5–4.1) (Niloy et al., 2021a, 2022).

The Biological index (BIX) describes the autochthonous or biological production of DOM components (Huguet et al., 2009). BIX values between 0.6–0.7, 0.7–0.8, and >0.8 indicate low, intermediate, and high

Figure 5. fDOM components intensity in the sampling stations of the SMF-Bangladesh. The name of the sampling stations according to the location are mentioned in Figure 1.

Figure 6. Synchronous spectra of water samples in the SMF-Bangladesh Rivers.
amounts of autochthonous DOM production (Huguet et al., 2009). BIX values in the SMF-Bangladesh ranged between 0.6 and 0.8 (mean = 0.7, σ = 0.1) and showed low to intermediate levels of autochthonous DOM production (Table 3). Prasad et al. (2014) also reported BIX values of SMF-Bangladesh low that ranged between 0.6-0.7. Freshness index (RF) varied between 0.04 and 0.1 (mean = 0.05, σ = 0.004), indicating that DOM components were matured and not fresh (Table 3). The presence of matured DOM in the SMF-Bangladesh also described the prevalence of microbial activities.

The E250/E365 describes the relative molecular size of DOM fractions and is inversely correlated with each other (Helms et al., 2008). E250/E365 varied between 3.9-6.1 (mean = 4.9, σ = 0.9) in the SMF-Bangladesh (Table 3). Maximum and minimum E250/E365 values in the Harbaria and Dublar char suggested that these two sampling stations contained the DOM fractions with relatively small and large molecular sizes, respectively (Table 3). Photodegradation plays a vital role in converting large extracellular polymeric substances (EPS) degradation in sunlight irradiation from saline biofilm. Similar activities can initiate from the autochthonous microbes in the estuary. Strong humic signatures from forest cover and absorption by organo-metallic compounds could explain the high aromaticity at Harbaria sampling station in Sundarban, Bangladesh. Aromaticity describing other indices such as SUVA280, SUVA350, and SUVA370 varied between 1.5 and 7.4 L/mg-m (mean = 3.2 L/mg-m, σ = 2.2), 0.6 and 2.2 L/mg-m (mean = 1.1 L/mg-m, σ = 0.6) and 0.5 and 1.6 L/mg-m (mean = 0.9 L/mg-m, σ = 0.4), respectively and showed maximum values in Harbaria sampling station in the SMF-Bangladesh (Table 3). SUVA280 was strongly correlated with SUVA250 (r = 0.998, p < 0.01), SUVA350 (r = 0.958, p < 0.01) and SUVA370 (r = 0.944, p < 0.01). The SUVA values at 254 nm and 280 nm were >6 L/mg-m and <3 L/mg-m at 350 nm and 370 nm in Harbaria indicated that, the suspected organo-metallic compound in this sampling station had higher absorbance in the shorter wavelength than the longer.

The Stokes shift parameter (SSP) and wavelength parameter (WP) varied between 0.2 and 3.9 (mean = 2.8, σ = 0.8) and 0.7–3.7 (mean = 1.7, σ = 1.1), respectively in the SMF-Bangladesh (Table 3). The SSP and WP values were in the higher ranges in Kotka and Dublar char and minimum in Betmore Gang (Table 3). WP values are inversely correlated to the energy level in an excited state, while SSP is proportional to the energy loss of excited fluorophores for molecular relaxation (Li et al., 2021). SSP and WP values in this study indicated that DOM components in Kotka and Dublar char might have low energy and more π-conjugated molecules in structure than the other sampling locations in the SMF-Bangladesh (Table 3). DOM molecules in the Betmore Gang had the highest energy in the excited state in the SMF-Bangladesh.

The RF and Δ log K describes the relative absorbance and absorption characteristics of natural humic components, respectively. The RF and Δ log K values varied between 0.04 and 0.8 (mean = 0.3, σ = 0.3) and 0.3–0.8 (mean = 0.5, σ = 0.2) in the SMF-Bangladesh (Figure 7). RF and Δ log K are inversely correlated with the concentration of coloured DOM fractions and the conjugation system development in the organic molecules, respectively (Santín et al., 2009). The low Δ log K and high RF values describe the high humification of DOM and vice-versa (Santín et al., 2009). The humification type in Figure 7, such as Type A describes the high humification of DOM moieties containing a large amount of aromatic carbon and carboxylic groups. Type C introduces the DOM fractions with low humification, immature, high alkyl carbon content, and end member of Type A components. Type B and Type D describe the transitory level between Type A and Type C (Santín et al., 2009). The samples in the Dublar char and Kotka had comparatively higher aromaticity than other sampling stations (Figure 7). The water sample in Harbaria had the minimum aromaticity. The DOM in the Betmore Gang,
Hiron point, and Mongla contained both aliphatic and aromatic moieties (Figure 7). The minimum aromaticity identified from RF vs Δ log K plot contradicted the maximum SUVA254 value in Harbaria. This contradiction confirmed the presence of organometalloid compounds that had excessive absorbance at 254 nm but rarely had fluorescence properties.

Hydrophobicity and Polarity of organic matters (OM) in the SMF-Bangladesh ranged between 0.01 and 0.08 (mean = 0.03, σ = 0.03) and 4.7–7.5 (mean = 6.0, σ = 1.0), respectively. Hydrophobicity was high in Harbaria and Mongla port similar to SUVA254 value and indicated that aromatic OM in these two sampling stations was poorly degradable. In contrary, Polarity in the SMF-Bangladesh was maximum in Dublar char and minimum in Mongla and Harbaria. Hydrophobicity and Polarity were inversely correlated with each other (r = -0.851, p < 0.05) indicating that water samples in Harbaria and Mongla port contained minimum polar components.

4. Conclusion

Sundarbans mangrove ecosystem is a global interest for its rich biodiversity and essential role in ecosystem services. In addition, as a global carbon sink, the Sundarbans have unique biogeocchemical characteristics that sustain their ecosystem services within it. Our research confirms that anthropogenic activities are threatening the unique biogeocchemical nature of Sundarbans estuarine rivers. EEM and PARAFAC models identified four fluorophores and three DOM components in the Sundarbans estuarine rivers of Bangladesh. The significant intensity of the detergent-like component confirmed the anthropogenic influences in the Sundarban Rivers and creeks. The SPS also identified protein-like component besides humic-like fDOM. In addition, optical properties described that fDOM components were matured, and predominantly originated from terrestrial sources. Autochthonous fDOM production was low in the Sundarban mangrove. DOM components were relatively higher in molecular size and weight in Dublar char and lower in Harbaria, Hiron point, and Mongla. However, water samples in Harbaria contained organometalloid compounds that had much absorbance at 254 nm wavelength. DOM components had low energy and more π-conjugated molecules in structure in the Dublar char and Kotka. The Harbaria and Mongla port contained more hydrophobic and less polar substances than other stations. All these analyses confirmed that the surrounding estuarine ecosystem of Sundarban mangrove forest Bangladesh is in a severe anthropogenic threat and deteriorating day by day. Although this study was conducted in the winter season which is a limitation, we propose that continuous environmental monitoring and management plans should be taken in the mentioned study sites throughout the year for the water quality management of Sundarbans. In addition, the government of Bangladesh should prepare effective strategic environmental management and monitoring plans to protect the estuarine ecosystems of the Sundarbans.

Declarations

Author contribution statement

Nahin Mostofa Niloy: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Mashura Shammi: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Md. Morshedul Haque: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Shafi Mohammad Tareq: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Data availability statement

Data included in article/supplementary material/referenced in article.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

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