https://doi.org/10.5194/egusphere-2023-2528
Preprint. Discussion started: 8 November 2023

Distribution of nutrients and dissolved organic matter in a eutrophic equatorial estuary, the Johor River and East Johor Strait

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Abstract. Estuaries have strong physicochemical gradients that lead to complex variability and often high rates of biogeochemical processes. The biogeochemistry of many estuaries is also increasingly impacted by human activities. Yet our understanding of estuarine biogeochemistry remains skewed towards temperate systems in the northern hemisphere, with far less research from tropical estuaries. This study examined seasonal and spatial variability in dissolved organic matter (DOM) and nutrient biogeochemistry along a partly eutrophic, mixed agricultural/urban estuary system in Southeast Asia, the Johor River and the East Johor Strait. Dissolved organic carbon (DOC) and chromophoric DOM (CDOM) properties showed non-conservative mixing, indicating significant DOM inputs along the estuary. The CDOM spectral slopes and CDOM:DOC ratios suggest that these inputs are dominated by terrigenous, soil-derived DOM along the Johor River, but that phytoplankton production and microbial recycling are more important DOM sources in the Johor Strait. Nitrate consistently showed conservative mixing, while nitrite concentrations peaked at intermediate salinities of 10–25. Ammonia decreased with salinity in the Johor River. In the Johor Strait, however, ammonia increased up to 50 µmol l^{-1}, often dominating the dissolved inorganic nitrogen (DIN) pool. Phosphate was low (<0.5 µmol l^{-1}) throughout the Johor River, but increased in the Johor Strait, where DIN:phosphate ratios were typically at or above 16:1. This suggests that phytoplankton in the Johor Strait may sometimes experience phosphorus limitation. Moreover, internal recycling is likely important for maintaining high nutrient concentrations in the Johor Strait.

1 Introduction

The biogeochemical functioning of estuaries and coastal waters is greatly influenced by terrestrial inputs as well as by biogeochemical transformations taking place along the land–ocean aquatic continuum (Bianchi and Morrison, 2023; Martin and Bianchi, 2023; Voss et al. 2011). These fluxes and biogeochemical processes can be greatly affected by increasing coastal development, changing land-use practices, and climatic changes. Because of the ecological and economic importance of estuaries and coastal waters, it is important to better understand these fluxes and processes and how they are changing. Southeast Asia is experiencing amongst the highest rates of coastal urbanisation (Neumann et al., 2015), land-use change (Hansen et al., 2013; Stibig et al., 2014), and increased nutrient pollution (Sinha et al., 2019). However, our understanding of estuarine and coastal biogeochemistry remains skewed towards temperate latitudes (Lønborg et al., 2021b; Vieillard et al.,

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2020). Thus, although tropical estuaries receive a large fraction of the global land–ocean fluxes of carbon, nutrients, and sediments (Jennerjahn, 2012), many tropical estuaries remain comparatively poorly studied.

Eutrophication of estuaries and coastal waters due to anthropogenic nutrient input remains a globally significant problem, resulting in phytoplankton blooms, oxygen depletion and dead zones (Altieri et al., 2017; Le Moal et al., 2019). Globally, agriculture is the main source of anthropogenic N and P input, but many other point and non-point sources may be important in a given location (Beusen et al., 2016; Le Moal et al., 2019). Anoxic conditions in eutrophic systems can promote nutrient recycling, especially release of phosphorus from sediments (Sulu-Gambari et al., 2018; Ballagh et al., 2020). Although nitrogen is usually lost by denitrification and anammox under anoxic conditions (Voss et al., 2011; Zhu et al., 2013; Teixeira et al., 2016), dissimilatory nitrate reduction to ammonia (DNRA) can also take place and recycle nitrogen (Dong et al., 2011; Bernard et al., 2015). Importantly, the relative rates of these biogeochemical processes may differ in tropical compared to temperate systems (Dong et al., 2011; Li et al., 2019).

Estuaries also receive large fluxes of terrestrial organic carbon, partly as a result of human activities (Regnier et al., 2022; Martin and Bianchi, 2023). Tropical rivers are particularly significant sources of dissolved organic carbon (DOC) to the ocean (Dai et al., 2012), with mangroves thought to be a disproportionally large source of terrigenous DOC (Dittmar et al., 2006). Terrigenous DOC is typically rich in coloured dissolved organic matter, CDOM (Coble, 2007; Massicotte et al., 2017), and terrigenous CDOM typically has distinct optical properties compared to CDOM in the open ocean and coastal seas (Stedmon and Nelson, 2015). Specifically, CDOM spectral slopes at ultraviolet wavelengths (Helms et al., 2008) and specific UV absorbance at 254 nm, $SUVA_{254}$ (Traina et al., 1990; Weishaar et al., 2003) have become widely used metrics to distinguish terrigenous dissolved organic matter (DOM) from autochthonous DOM produced in aquatic environments (Asmala et al., 2016; Fichot and Benner, 2011; Lønborg et al., 2021a; Zhou et al., 2021).

Tropical peatlands are the largest source of terrigenous DOC to the coastal ocean in Southeast Asia. Most research on land–ocean DOC fluxes in this region has therefore focused on peatland-draining rivers (Baum et al., 2007; Martin et al., 2018; Sanwlani et al., 2022; Wit et al., 2015), leaving us with a more limited understanding of the concentrations and optical properties of DOM in non-peat-draining estuaries. Moreover, there have been few studies of the distributions of DOM and nutrients across more urbanised and eutrophic estuaries in Southeast Asia.

Here, we examined the seasonal dynamics and mixing behaviour of DOC, CDOM, and dissolved inorganic nutrients across salinity gradients in the Johor River estuary and the eutrophic East Johor Strait, at the southern tip of the Malay Peninsula. The objectives of our study were to identify the sources (terrigenous versus marine) and cycling behaviour of these substances, determine whether there is seasonal variation, and examine how the optical properties of CDOM delivered by the Johor River compare to those in the eutrophic Johor Strait.

2 Methods

2.1 Study Area

The Johor River (Fig. 1) is around 123 km long and provides a crucial freshwater source for Johor State and for Singapore (Kang and Kanniah, 2022). The Johor River drains into a large estuary to which several other rivers also contribute, with a

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total drainage basin area of around 2640 km^2, before flowing southwards past the East Johor Strait into the Singapore Strait (Fig. 1). The main land cover in the catchment is agricultural, especially rubber and oil palm plantation, with some urban and industrial land use (Kang and Kanniah, 2022; Fig. 1a). The Johor River estuary has fringing mangroves along most of its length, providing a narrow buffer zone to the mostly agricultural areas. Sand extraction takes place in the river, and in the lower parts of the estuary, small-scale aquaculture is practiced. Along the Johor River and its estuary, inputs from wastewater treatment plants and fertiliser run-off are likely significant sources of ammonia, with point-source inputs via wastewater being more important during drier periods and non-point-source inputs from fertiliser use more important during wetter periods (Pak et al., 2021; Samsudin et al., 2017).

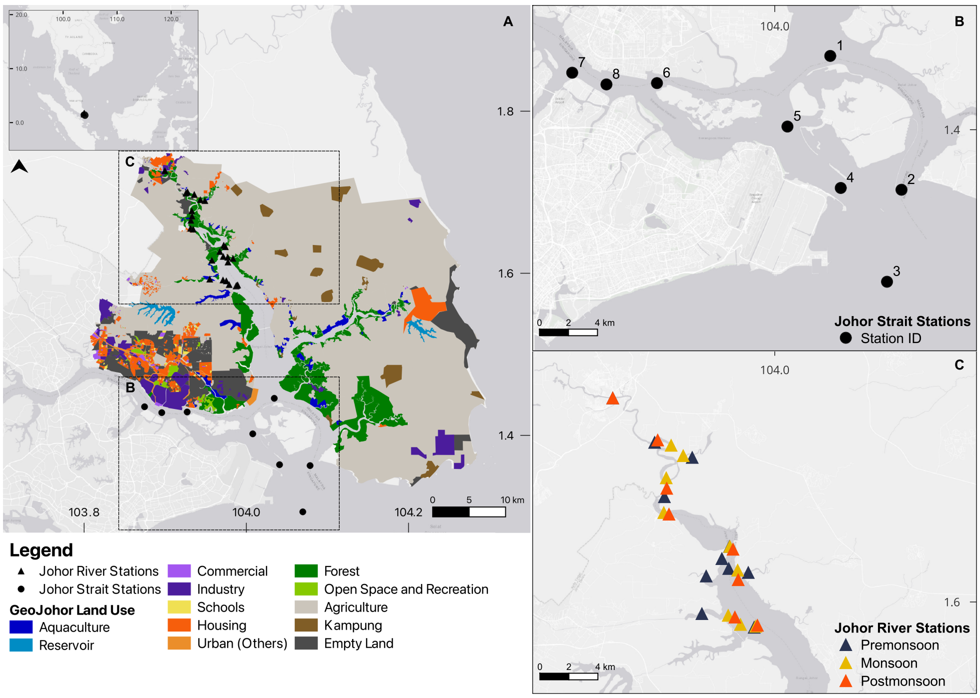

Figure 1. Map of the study region. Triangles show stations in the Johor River estuary, points show stations in the Johor Strait. (A) Land-use in the area around the Johor River estuary, taken from GeoJohor Johor land-use portal (http://geoportal.johor.gov.my/en/, accessed 11 December 2022). Dashed boxes show locations for panels (B,C). (B) Station locations sampled in the Johor Strait. (C) Station locations sampled in the Johor River estuary.

The Johor Strait is the narrow (1–2 km wide) channel that separates Singapore from Malaysia (Figs. 1a,b). It is divided by a causeway into the East and West Johor Strait, with limited water exchange between the two. The East Johor Strait receives run-off from both Malaysia and Singapore, with both sides of the Strait dominated by urban and industrial land use; fringing mangroves are also found especially in the eastern part of the Strait (Fig. 1a). Aquaculture is practiced especially around the island of Pulau Ubin. Both the East and West Johor Strait are eutrophic water bodies, and occasional harmful algal blooms by diatoms and dinoflagellates have been reported (Chénard et al., 2019; Gin et al., 2000; Kok and Leong, 2019; Wijaya et al., 2023).

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Singapore and Malaysia experience two monsoon seasons: the northeast monsoon from November to March and the southwest monsoon from mid-May to mid-September. Rain falls year-round, but there is a distinct increase in precipitation during the early northeast monsoon (November to early January), followed immediately by the driest time of year in the late northeast and intermonsoon period (February to March/April). Average monthly rainfall for 2000–2020 and monthly rainfall during our study period was calculated over the area 1.2°N 103.6°E to 1.8°N 104.4°E, using data from the GPM IMERG Final Precipitation L3 0.1°-resolution product processed by the Royal Netherlands Meteorological Institute (Huffman et al., 2014). Discharge from the Johor River at the gauging station in Rantau Panjang (1.781°N 103.746°E) was obtained from the Department of Irrigation and Drainage, Malaysia. We designated data collected prior to December 2017 as pre-monsoon, data collected during December and January as monsoon, and data collected after January 2018 as post-monsoon, and distinguish between these three periods in our plotting and analysis.

2.2 Sampling

We collected surface water samples in the East Johor Strait at eight stations approximately monthly from August 2017 to June 2018 (Fig. 1b). Samples were collected in the Johor River in November 2017 (pre-monsoon), January 2018 (monsoon) and March 2018 (post-monsoon) at 8–10 stations (Fig. 1c). Water samples were collected either using a hand-held polyethylene jug (Johor River) or a Niskin bottle (Johor Strait, at 1 m depth). At each station, a conductivity-temperature-depth (CTD) and chlorophyll-a (chl-a) fluorescence profile was taken using a Valeport FastCTD, and we use the average values over the upper 1 m in our analysis. Salinity is reported on the practical salinity scale. Due to a CTD malfunction on 09 March 2018, CTD profiles could not be taken in the Johor Strait on this date, and salinity was instead measured using an optical refractometer

Samples for dissolved inorganic nutrients were syringe-filtered (0.22 µm, Pall Acrodisc) in the field into acid-rinsed 15-mL polypropylene centrifuge tubes, immediately frozen in a dry shipper, then stored at -20°C until analysis. For DOC and CDOM, unfiltered water was stored in pre-combusted (450°C, 4 h) amber borosilicate bottles at ambient temperature in the dark and then filtered back on land on the same day through Whatman Anodiscs (0.2 µm, 45 mm diameter) in an all-glass filtration system. The filtration system was rinsed with 1 M HCl and ultrapure deionised water (Elga 18.2 MΩ cm^{-1}; referred to as DI water below) prior to every sample. DOC and CDOM samples were then stored in amber borosilicate vials at +4°C until analysis; DOC samples were acidified with 50% H_2SO_4 immediately after filtration.

2.3 Sample analyses

2.3.1 Dissolved organic carbon (DOC) analysis

Samples were analysed within three months of collection as non-purgeable organic carbon on a Shimadzu TOC-L system with the Shimadzu high-salt kit, using potassium hydrogen phthalate for calibration. Deep-sea water certified reference material from the University of Miami (42–45 µmol l^{-1}) was analysed with every run, and returned a long-term mean ± SD of 48 ± 3.5 µmol l^{-1}.

2.3.2 Coloured dissolved organic matter (CDOM) analysis

CDOM absorption spectra (230-900 nm) were measured with a Thermo Evolution300 dual-beam spectrophotometer against a DI water reference using 10-cm quartz cuvettes. The absorbance spectra were corrected for instrument baseline drift following

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Green and Blough (1994), smoothed using a loess function, and converted to Napierian absorption coefficients using Equation (1):

$$a_\lambda = 2.303 \times \frac{A_\lambda}{l} \quad (1)$$

where a_λ is the absorption coefficient (m^{-1}), A_λ is the absorbance, l is the cuvette path length (in m), and subscript λ indicates wavelength. We then calculated the spectral slopes between 275–295 nm ($S_{275–295}$), between 350–400 nm ($S_{350–400}$), and the slope ratio S_R (ratio of $S_{275–295}$ to $S_{350–400}$) using linear regressions of the natural log-transformed absorption against wavelength following Helms et al. (2008). The specific UV absorbance at 254 nm ($SUVA_{254}$) was determined by dividing the decadic absorption at 254 nm (i.e., the absorbance per metre) by the DOC concentration (in mg l^{-1}). CDOM data processing was carried out in MATLAB. We report CDOM absorption at 350 nm (a_{350}) as a measure of CDOM concentration.

2.3.3 Nutrient analysis

Samples for NO_x (i.e., NO_3^- + NO_2^-), NO_2^-, PO_4^{3-}, $Si(OH)_4$, and NH_4^+ were thawed and analysed on a SEAL AA3 segmented-flow autoanalyzer following SEAL methods G172, G173, G297, and G177. NH_4^+ was measured fluorometrically (Kérouel and Aminot, 1997). Detection limits were 0.05 µmol l^{-1} (NO_x), 0.01 µmol l^{-1} (NO_2^-), 0.03 µmol l^{-1} (PO_4^{3-}), 0.10 µmol l^{-1} ($Si(OH)_4$), and 0.25 µmol l^{-1} (NH_4^+). Dissolved inorganic nitrogen (DIN) was calculated as $NO_x + NH_4^+$. Where measurements were below the detection limit (1 sample for PO_4^{3-}, and 25 samples for NH_4^+), the concentration was assumed to be 0.5 x the detection limit. The nutrient data for the Johor River samples were previously published by Liang et al. (2020).

2.4 Conservative mixing models

For DOC and CDOM, we used a two-endmember mixing model to calculate concentrations expected under conservative mixing across the salinity gradient. The freshwater endmember values were taken from the station furthest upriver (Kota Tinggi, 1.6973°N 103.9358°E), while the marine endmember values were taken from the southernmost station (Station 3 in Fig. 1b, where the Johor Strait opens into the Singapore Strait). The mixing models were calculated for DOC and for CDOM absorption spectra using Equation 2:

$$X_{mix} = f_{riv}X_{riv} + (1 - f_{riv})X_{mar} \quad (2)$$

Where X_{mix} is the predicted DOC concentration or CDOM absorption at each intermediate salinity, f_{riv} is the fraction of freshwater at that salinity, and X_{riv} and X_{mar} are the riverine and marine endmember values for DOC or CDOM absorption. The mixing models were calculated at salinity increments of 1. Because CDOM spectral slopes change non-linearly during conservative mixing, we calculated the predicted absorption spectrum at every wavelength using Eq. 2 and then calculated the predicted spectral slope parameters from the predicted spectra, following Stedmon and Markager (2003).

3 Results

3.1 Rainfall pattern and river discharge at Kota Tinggi, Johor

Rainfall across the study region (Fig. 2a) is relatively high year-round, but with a distinctly wetter period during the early part of the northeast monsoon (Nov–Jan) and a drier period during the late northeast monsoon (Feb–Mar). During our study period, November 2017 was the wettest month with 407 mm of rain, while February 2018 was the driest month with 106 mm of rainfall. The overall monthly rainfall distribution during our study period was similar to the long-term average from 2001 to 2020.

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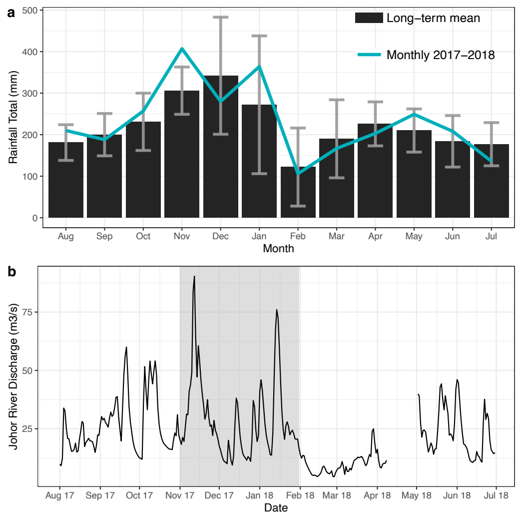

Figure 2. (a) Monthly rainfall (mm) data for the study region extracted from KNMI climate explorer (see text). Line shows monthly rainfall during the study period from August 2017 to July 2018. Bars show the long-term mean rainfall from 2001–2020, with error bars indicating 1 standard deviation. (b) Daily river discharge for the Johor River measured at Rantau Panjang hydrological station (1.781°N , 103.746°E).

Discharge of the Johor River measured at Rantau Panjang showed a distinct minimum during the dry period in the late northeast monsoon (February–March 2018; Fig. 2b). Discharge during the early northeast monsoon showed two distinct peaks, on 12 November 2017 (90.38 m^3/s) and 14 January 2018 (76.04 m^3/s), but discharge was otherwise not notably elevated during November–January relative to other periods, except compared to the late northeast monsoon (February–March; Fig. 2b).

3.2 Temperature and Salinity

In the Johor River, surface salinity ranged from 0.5–26.8 (November, pre-monsoon), 0–16.1 (January, monsoon), and 4–28.3 (March, post-monsoon), with lowest salinity always furthest upstream at Kota Tinggi town. Salinity ranged from 21.6–32.4 for all stations in the Johor Strait, with lowest salinity (mean 25.9, range 21.6–29.0) typically found at Station 1, where the Johor River estuary meets the Johor Strait, while Station 3, located at the entrance to the Singapore Strait, had the highest salinity (mean 30.9, range 30.0–32.4).

Surface temperature varied little and spanned nearly identical ranges in the Johor River (26.7–30.2°C) and the Johor Strait (26.5–31.6°C), with the lower values found during the northeast monsoon, but otherwise no distinct seasonal variation.

3.2 Dissolved organic matter distribution

DOC concentrations ranged from 101 µmol l^{-1} to 186 µmol l^{-1} in the Johor River (average 136 µmol l^{-1}) and between 71 µmol l^{-1} to 208 µmol l^{-1} in the Johor Strait (average 113 µmol l^{-1}; Fig. 3a). DOC concentrations in the Johor River estuary showed a clear non-conservative mixing pattern indicative of additional DOC sources to the estuary; DOC concentrations in the Johor River only showed a decrease after salinity exceeded about 22. In the Johor Strait, DOC mostly showed a relatively linear decrease with salinity, with lowest values consistently found at Johor Strait Station 3 (average of 79 µmol l^{-1}), closest to the

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open sea in the Singapore Strait (Figs. 1,3). Seasonal variability was not pronounced, although at salinities between 5 and 25, DOC concentrations were lower during the northeast monsoon. Moreover, five stations in the Johor Strait showed elevated DOC concentrations relative to their salinity (four stations in February, one station in June), which were associated with a phytoplankton bloom (see Section 3.3). Overall, the distribution of DOC did not follow simple 2-endmember conservative mixing between the Johor River and the Singapore Strait, with essentially all stations within the salinity gradient having higher than predicted DOC concentrations (Fig. 3a).

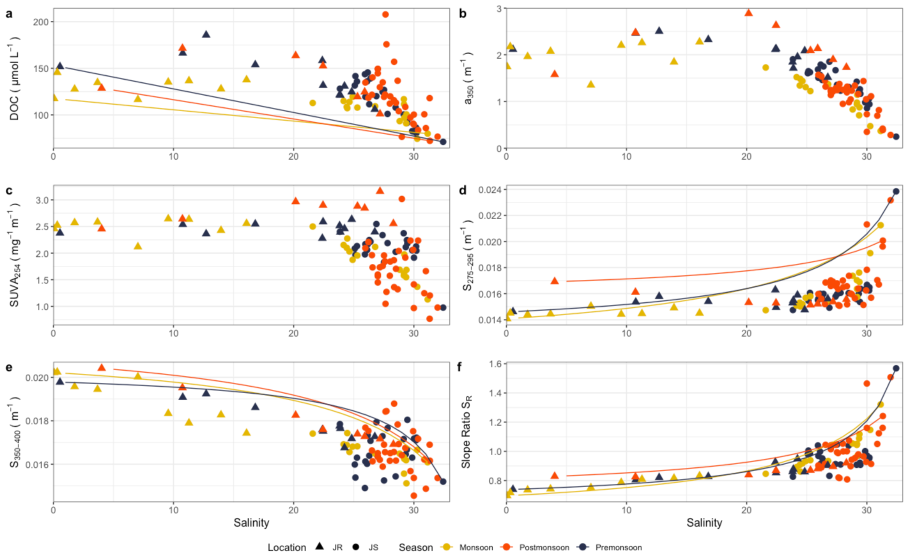

Figure 3. Distribution against salinity of (a) DOC concentration, (b) CDOM a_{350}, (c) SUVA$_{254}$, (d) CDOM spectral slope $S_{275\text{-}295}$, (e) CDOM spectral slope $S_{350\text{-}400}$, (f) CDOM spectral slope ratio S_R. The solid triangles represent data from the Johor River, circles represent data from the Johor Strait, and symbol colours indicate sampling season. Solid lines indicate theoretical conservative mixing lines calculated for each sampling season.

CDOM a_{350} and SUVA$_{254}$ showed a very similar distribution to DOC, with relatively stable values up to salinity 25 in the Johor River and then a linear decrease with salinity above 25. CDOM a_{350} ranged from 1.35–2.88 m^{-1} in the Johor River, and from 0.25 – 1.90 m^{-1} in the Johor Strait (Fig. 3b), while SUVA$_{254}$ ranged from 2.1–3.2 mg^{-1} m^{-1} throughout the Johor River and from 0.8–3.0 mg^{-1} m^{-1} in the Johor Strait (Fig. 3c). The CDOM spectral slope $S_{275–295}$ showed low values (0.0141 – 0.0176 nm^{-1}) up to salinity of 30 but increased to 0.0196–0.0239 nm^{-1} at the highest salinities (Fig. 3d). The spectral slope $S_{350–400}$ showed a steadily decreasing trend over the salinity gradient, from ≥0.0194 nm^{-1} at salinities below 7 to values ranging between 0.0146–0.0188 nm^{-1} in the Johor Strait (Fig. 3e). The slope ratio, S_R, consequently mirrored the pattern in $S_{275–295}$, with values consistently below 1.0 up to salinity of 25, and then increasing to values between 1.0 – 1.6 at the higher salinities (Fig. 3f). There was only limited seasonal variability in the CDOM parameters, values of a_{350}, $S_{275–295}$, and $S_{350–400}$ showing slightly lower values during the northeast monsoon at salinities between 5–25; this was not seen in S_R or in SUVA$_{254}$. Especially $S_{275–295}$ clearly departed from the conservative mixing models, while $S_{350–400}$ and S_R showed somewhat closer agreement (Fig. 3). The five stations with high DOC concentrations due to phytoplankton blooms did not stand out clearly in the CDOM parameters.

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3.3 Chlorophyll-a concentration

The chl-a concentration, as measured with the CTD fluorometer, ranged mostly between 0–7 µg l^{-1} in both the Johor River and the Johor Strait, with the exception of five stations in the Johor Strait, where chl-a ranged from 10.1–50.3 µg l^{-1} (Fig. 4a). These were stations 5, 6, 7 and 8 in February, and station 7 in June, indicating that two phytoplankton blooms took place in the inner part of the Johor Strait. Leaving aside these five stations, chl-a overall showed no seasonal pattern in the Johor River or the Johor Strait.

Overall, chl-a showed no clear relationship to DOC concentration, except for the five stations affected by the phytoplankton bloom in the Johor Strait, which followed a roughly linear relationship between DOC and chl-a (Fig. 4b). This pattern was not seen with a_{350} or with $S_{275–295}$, and the five bloom stations had a_{350} values that were close to the overall average for the Johor Strait (1.19 ± 0.39 m^{-1}), but had consistently low $S_{275–295}$ (Fig. 4c,d). However, the bloom stations showed a decreasing trend of $SUVA_{254}$ with chl-a, and had overall relatively low $SUVA_{254}$ (Fig. 4e).

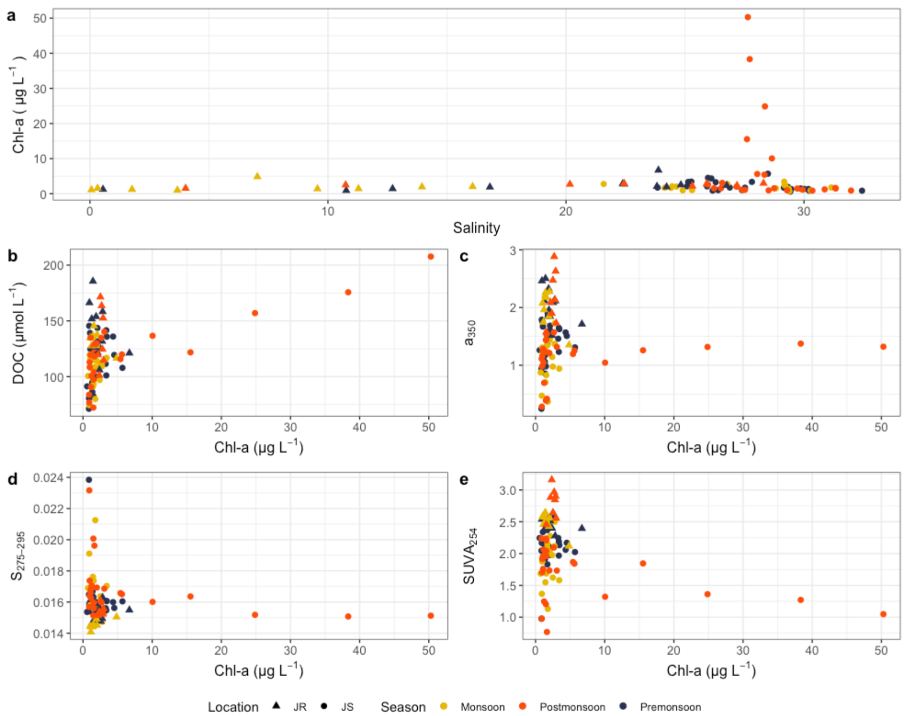

Figure 4. (a) Distribution of chlorophyll-a concentration against salinity. Scatter plots against chlorophyll concentration of (b) DOC concentration, (c) CDOM a_{350}, (d) CDOM spectral slope $S_{275-295}$, (e) $SUVA_{254}$. Triangles represent data from the Johor River, circles represent data from the Johor Strait, and symbol colours indicate sampling season.

3.4. Relationships between dissolved organic matter parameters

There was a significant correlation between a_{350} and DOC across all sampling seasons and stations (Spearman's rank correlation, rho = 0.691, $p < 0.0001$, Fig. 5a), although the Johor River stations typically had higher a_{350} at a given DOC

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concentration than the Johor Strait stations. The CDOM spectral slope $S_{275-295}$ and the slope ratio S_R both showed negative correlations with DOC, with the highest DOC samples from the Johor Strait falling in the same range as the Johor River samples (Figs. 5b,c). A strong inverse correlation was observed between $S_{275-295}$ and $SUVA_{254}$ (Spearman's rank correlation, rho = -0.714, $p < 0.0001$, Fig. 5d), with the five Johor Strait bloom stations clearly separating from the other data points.

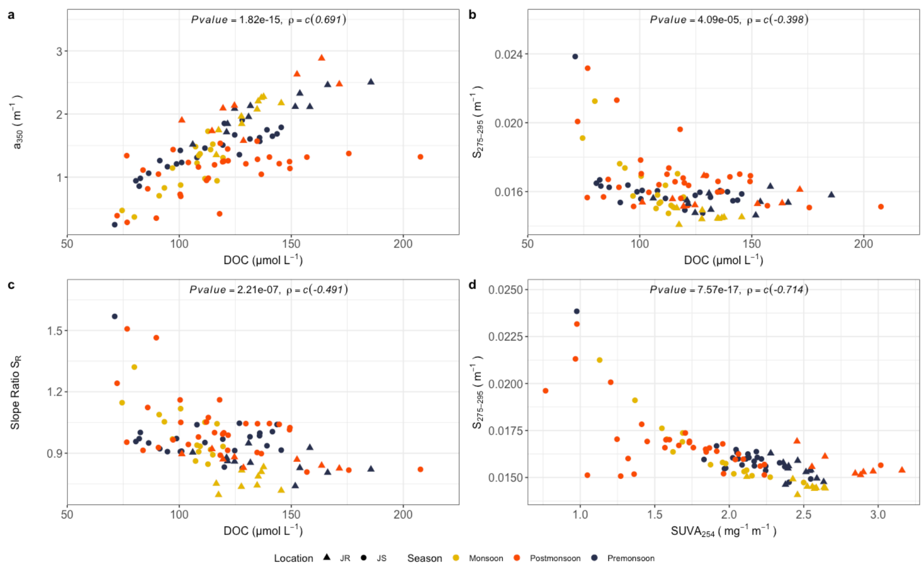

Figure 5. Scatter plots to show correlations between (a) CDOM a_{350} and DOC concentration, (b) CDOM spectral slope $S_{275-295}$ and DOC concentration, (c) CDOM spectral slope ratio and DOC concentration, and (d) CDOM spectral slope $S_{275-295}$ and $SUVA_{254}$. Triangles represent data from the Johor River, circles represent data from the Johor Strait, and symbol colour indicates sampling season.

3.5 Dissolved inorganic nutrients

NO_3^- showed a strong and linear decrease with salinity, ranging from 3.1–59.7 µmol l^{-1} in the Johor River and from 0.3–15.2 µmol l^{-1} in the Johor Strait (Fig. 6a). There was no clear seasonal variation in the NO_3^-–salinity relationship, although some pre- and post-monsoon samples in the Johor River estuary had lower NO_3^- concentrations than the monsoon samples.

In contrast, NO_2^- showed a clear enrichment at salinities between 10–27 in both the Johor River and Johor Strait, reaching concentrations of 5–10 µmol l^{-1} (Fig. 6b). At all stations with salinities >31, NO_2^- was <0.53 µmol l^{-1}, reaching as low as 0.014 µmol l^{-1}, but was always detectable. The highest NO_2^- concentrations were found in the pre- and post-monsoon samples in the Johor River, suggesting that there might be a seasonal pattern (Fig. 6b). Moreover, there was a significant correlation between NO_2^- and water temperature (rho = 0.278, n=94, p=0.008) (Fig. 6c).

The concentration of NH_4^+ generally decreased with salinity in the Johor River, with values ranging from undetectable to 39 µmol l^{-1} (Fig. 6d). In the Johor Strait, NH_4^+ was low at salinities ≥30 (undetected to 2.8 µmol l^{-1}), but very variable at salinities of 20–30 (undetected to 51.5 µmol l^{-1}; Fig. 6d). NH_4^+ did not show a seasonal pattern.

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PO_4^{3-} concentrations were consistently very low in the Johor River, always <0.4 µmol l^{-1} and in numerous cases <0.05 µmol l^{-1}. In the Johor Strait, PO_4^{3-} concentration showed a pattern similar to NH_4^+, with low concentrations (<0.34 µmol l^{-1}) at salinities ≥30, and variable concentrations (<0.05 to 2.7 µmol l^{-1}) at salinities between 20–30 (Fig. 6e). This contrasts with the much stronger NO_3^-–salinity relationship (Fig. 6a). PO_4^{3-} did not show any seasonal variation.

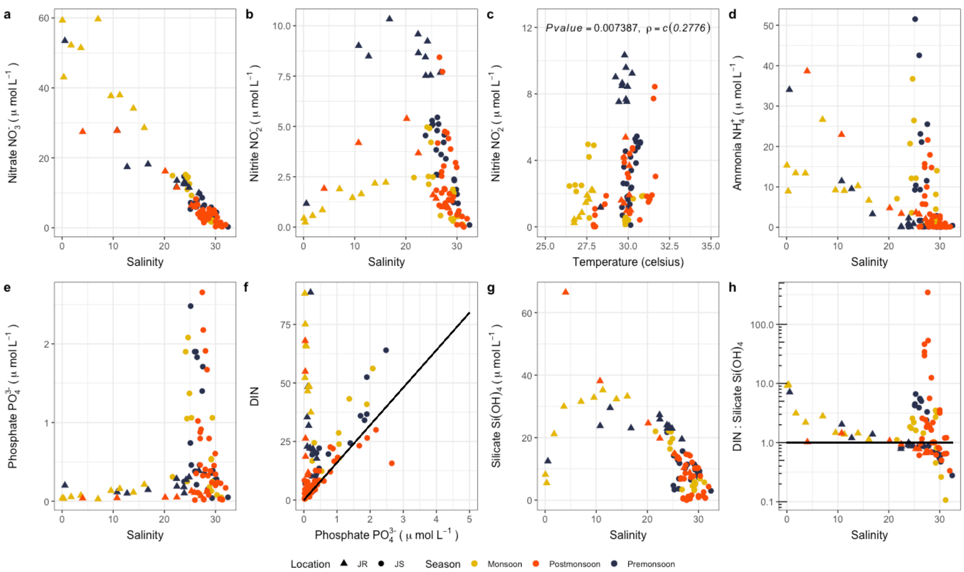

Figure 6. Concentrations of (a) nitrate and (b) nitrite against salinity. (c) Nitrite concentration showed a significant correlation with temperature (Spearman's rank correlation). Concentrations of (d) ammonia and (e) phosphate against salinity. (f) Dissolved inorganic nitrogen was generally correlated with phosphate concentration in the Johor Strait, but not in the Johor River where phosphate concentrations were very low. Solid line indicates 16:1 Redfield ratio. (g) Concentration of silicate against salinity. The very low silicate concentration for low-salinity Johor River samples are likely an artefact of sample freezing; see discussion in Section 4.2. (h) Ratio of dissolved inorganic nitrogen to silicate against salinity. Solid line indicates 1:1 ratio. In all panels, triangles represent data from the Johor River, circles represent data from the Johor Strait, and symbol colour indicates sampling season.

In the Johor River, there was consequently no clear DIN–PO_4^{3-} relationship and the DIN:PO_4^{3-} ratio was much greater than the Redfield ratio of 16:1, while the Johor Strait data did show a correlation between DIN and PO_4^{3-}, with most data either close to or slightly greater than a 16:1 ratio (Fig. 6f), suggesting an environment that is slightly enriched in N as compared to P. This relationship was mainly driven by the relationship between NH_4^+ and PO_4^{3-}, which followed the Redfield ratio of 16:1 fairly closely (Figs. 6d,e,f).

The $Si(OH)_4$ concentration appeared to follow a unimodal relationship, with low concentrations of <10–15 µmol l^{-1} at the lowest salinity in the Johor River (except for one high measurement of 66.5 µmol l^{-1}), rising to 23–38 µmol l^{-1} at salinities of 10–20, and then decreasing linearly with salinity to values <1 µmol l^{-1} (Fig. 6g). The DIN:Si ratios in the Johor River were mostly between 0.7–3.1, with the lowest-salinity stations reaching 7.1–10, while the Johor Strait samples ranged mostly between 0.2–6.0, but with stations 6–8 in February (i.e., the phytoplankton bloom stations with chl-a concentration >25µmol L^{-1}) reaching values between 13–347 (Fig. 6h). Overall, most stations exhibited an excess of DIN relative to the canonical

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Redfield DIN:Si ratio of 1:1. Within the Johor Strait, stations 6–8 typically had higher concentrations of NO_2^-, NH_4^+, and PO_4^{3-} than the other stations.

4 Discussion

4.1 Sources and mixing pattern of dissolved organic matter

DOC concentrations observed in the Johor River (115–150 µmol l^{-1}) are at the lower end of values reported from river systems in Malaysia and Indonesia (Huang et al. 2017), where rivers draining tropical peatlands can carry 1000–5000 µmol l^{-1} (Alkhatib et al., 2007; Wit et al., 2015; Martin et al., 2018). Our values are closer to those reported upstream of peatlands in the Rajang River (~120 µmol l^{-1}; Martin et al., 2018) and to the wet season value of 214 µmol l^{-1} reported from the Johor River by Huang et al. (2017). Our comparatively low values of CDOM absorption, with a_{350} <2.5 m^{-1} at the lowest salinities in the Johor River, are also a contrast to the extremely CDOM-rich blackwater rivers found in peatland-draining catchments in Southeast Asia (Martin et al., 2018; Siegel et al., 2019). Neither DOC nor a_{350} followed a conservative mixing pattern, with significant DOM addition happening both within the Johor River estuary and in the Johor Strait.

The low values of $S_{275–295}$, S_R, and elevated $SUVA_{254}$ (Figs. 3c,e,f) are consistent with a predominantly terrestrial DOM source within the Johor River estuary. These CDOM parameters are used widely to trace terrigenous DOM in estuaries and river-influenced coastal seas (Clark and Mannino, 2021; Fichot and Benner, 2011; Lu et al., 2016). $SUVA_{254}$ is proportional to the DOM aromaticity (Weishaar et al., 2003) and terrigenous DOM typically has high $SUVA_{254}$ (Massicotte et al., 2017). $SUVA_{254}$ was also found to be relatively robust at distinguishing terrigenous from aquatic DOM in decomposition experiments (Lee et al., 2018). $S_{275-295}$ is inversely proportional to the apparent molecular weight of DOM (Helms et al., 2008). S_R also correlates with DOM apparent molecular weight, and has been described as a suitable proxy to distinguish terrestrial and marine CDOM, with marine-like CDOM having S_R >1 (Helms et al., 2008; Helms et al., 2014). However, Han et al. (2021) found that in a temperate estuary system in Korea, S_R was actually elevated (~1.3) in samples richer in terrigenous DOM, which they attributed to prior decomposition. While this indicates that caution is needed when interpreting DOM optical properties as source indicators, we also note that the relatively low concentrations of chl-a in the Johor River suggest that autochthonous production is probably not a major source of DOM. Moreover, the high turbidity in the Johor River (total suspended matter concentrations at our stations were typically 10–30 mg l^{-1}; Liang et al., 2020) make it unlikely that submerged vegetation or macroalgae contribute substantially to the DOM pool. However, fringing mangroves are found along much of the Johor River estuary, and might provide a significant input of terrigenous DOM (Jennerjahn and Ittekkot, 2002; Dittmar et al., 2006), which would help to explain the observed non-conservative mixing pattern. A terrigenous source of DOM in the estuary is also consistent with the non-conservative mixing pattern of $S_{275–295}$ (Fig. 3d).

The data from the Johor Strait showed more variability in the CDOM properties. The low values of $S_{275–295}$ and S_R in most of these samples (below 0.018 and 1.1, respectively), are typically associated with terrigenous DOM in river-influenced coastal margins (Fichot and Benner, 2011; Carr et al., 2019; Lønborg et al., 2021a; Zhou et al., 2021). The low surface salinities in the Johor Strait found in the present study and reported previously (Gin et al., 2000; Kok and Leong, 2019; Mohd-Din et al., 2020) suggest that terrigenous DOM input from runoff probably does contribute to the DOM pool in the strait, while the fringing mangroves along the strait will also supply terrigenous DOM. However, the $SUVA_{254}$ values were mostly lower in the Johor Strait than in the Johor River estuary at a given salinity, which points to an increasing contribution from autochthonous DOM.

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Given the eutrophic status of the Johor Strait (Gin et al., 2000; Chénard et al., 2019; Kok and Leong, 2019), autochthonous DOM production is likely substantial. This is evident from the high DOC concentrations at the five bloom stations (Figs. 3a, 3b), but also demonstrated by the bottom water hypoxia and sedimentary anoxia found in both the West and East Johor Strait (Kok and Leong, 2019; Chai et al., 2021). However, the phytoplankton bloom did not appear to be a very significant source of CDOM, given that the a_{350} showed little change with chl-a (Fig. 4c). This would explain the low $SUVA_{254}$ relative to $S_{275–295}$ of the bloom stations (Fig. 5d), because production of mostly non-coloured DOM by the bloom would lower $SUVA_{254}$ without influencing $S_{275–295}$. Our data therefore suggest that direct production by phytoplankton is probably not a major source of CDOM in the Johor Strait. This leaves production by heterotrophic microbes as a more likely pathway of generating autochthonous CDOM, given that the hypoxia in the inner part of the Johor Strait (Mohd-Din et al., 2020; Chai et al., 2021) clearly indicates that heterotrophic reprocessing of organic matter is substantial. CDOM produced by microbial reprocessing of DOM can have absorbance and fluorescence properties that resemble terrigenous CDOM (Hansen et al., 2016; Osburn et al., 2019).

4.2 Nutrient sources and implications for phytoplankton dynamics

Although NO_3^- showed close to linear mixing behaviour across the Johor River and Johor Strait, the pattern of the other nutrients clearly shows that different patterns of nutrient cycling operate in the two locations. Our data indicate that the Johor River is notably enriched in DIN relative to PO_4^{3-}. While wastewater treatment plants in the Johor River catchment may be significant point sources of NH_4^+ (Pak et al., 2021), the NO_3^- probably originates from soil nitrogen, similar to observations in the Rajang River system on Borneo (Jiang et al., 2019), and possibly from fertiliser use in the largely agricultural catchment. The low PO_4^{3-} concentrations would be consistent with soil nutrient sources, given the predominance of highly weathered acrisol soils in the catchment (Pak et al., 2021) that are likely to be phosphorus-poor. The concentrations of NO_3^- and NH_4^+ are broadly in line with values reported from other river systems in tropical and subtropical Asia with varying degrees of anthropogenic impacts, which can reach from 10s to 100s of µmol l^{-1} (Jennerjahn et al., 2004; Cai et al., 2015; Kuo et al., 2017; Suratman et al., 2018; Jiang et al., 2019). The clear increase in NO_2^- at salinities between 10–25 (Fig. 6b) indicates active nitrogen recycling within the Johor River estuary and in the Johor Strait, likely from nitrification of the NH_4^+ pool. In a subtropical North American estuary, Schaefer and Hollibaugh (2017) reported that NO_2^- oxidation rates slowed relative to NH_4^+ oxidation rates at temperatures of 20–30°C, leading to similar accumulation of NO_2^- as in our data. Whether this temperature-dependent mechanism uncoupling the two steps of nitrification also applies in permanently warm tropical systems is unknown, although the significant correlation between NO_2^- and temperature across our dataset suggests that the temperature-sensitivity of biogeochemical rates in tropical estuaries would be an important topic for future research.

The high accumulation of NH_4^+ and PO_4^{3-} in the Johor Strait in proportions following the Redfield ratio (Figs. 6d,e,f) suggests that substantial internal recycling of nutrients takes place in the strait; the importance of recycling is also evident from the accumulation of NO_2^- at lower salinities (Fig. 6b). Elevated concentrations of NH_4^+, PO_4^{3-}, and NO_2^- were found especially at Stations 6–8, closer to the inner Johor Strait. Given that the NH_4^+:PO_4^{3-} ratios were generally fairly close to 16:1 (Fig. 6f), recycling via aerobic respiration is likely important. However, Chai et al. (2021) showed that sedimentary anammox, denitrification, and dissimilatory nitrate reduction to ammonia (DNRA) occur throughout the East and West Johor Straits at rates ranging from <0.5–11 µmol kg^{-1} h^{-1}, and that the sediments contain a large fraction of iron-bound phosphorus. Although denitrification + anammox usually exceeded DNRA, the rate of DNRA always exceeded that of anammox and was between 50% and >100% of the denitrification rate at all but one station. Chai et al. (2021) therefore concluded that there is net

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sedimentary N loss, but that DNRA also recycles an appreciable fraction of NO_3^- to NH_4^+, and that release of iron-bound P from the sediments might also be important. Our data are consistent with N and P recycling helping to maintain a eutrophic state within the Johor Strait. Further research is therefore warranted to pelagic and sedimentary recycling rates.

Tropical rivers typically carry high $Si(OH)_4$ concentrations, averaging close to 200 µmol l^{-1} in Asia (Jennerjahn et al., 2006). Our low-salinity samples mostly returned values below 30 µmol l^{-1}, yielding a distinct unimodal relationship with salinity. Although it is possible for diatom growth to reduce $Si(OH)_4$ in freshwater reaches of an estuary, and for biogenic silica and aluminosilicate mineral dissolution to be enhanced within the saline reaches of an estuary (Eyre and Balls, 1999; Roubeix et al., 2008a; Roubeix et al., 2008b), it is more likely that this was an analytical artefact caused by silicon polymerisation in frozen samples, which affects low-salinity samples and samples with high $Si(OH)_4$ concentrations more strongly (MacDonald and McLaughlin, 1982). This is expected to be less of a problem in the higher-salinity Johor Strait samples where $Si(OH)_4$ concentrations were also lower, and which showed a much more consistent relationship with salinity. Our Johor Strait data indicate a high DIN:Si ratio, typically >1, which is consistent with previous data from the Johor Strait (Chénard et al., 2019; Kok and Leong, 2019). This contrasts with the consistently low DIN:Si ratios, averaging around 0.3, measured in the Singapore Strait and also using frozen samples (Martin et al., 2022). While the Johor Strait does experience diatom blooms (Mohd-Din et al., 2020; Chai et al., 2021), the excess of N and P relative to Si may favour the growth of non-silicifying phytoplankton, including the harmful dinoflagellate blooms that have been observed in the Johor Strait (Kok and Leong, 2019; Chai et al., 2021). Moreover, the fact that DIN:PO_4^{3-} ratios were generally at or above the 16:1 Redfield ratio suggests that phosphorus may play a role in limiting phytoplankton production in the Johor Strait. This is consistent with the data of Kok and Leong (2019) collected in the East Johor Strait between 2015–2017, who found DIN:PO_4^{3-} ratios fairly close to 16:1, and more recent measurements by Wijaya et al. (2023) in 2020, who found DIN:PO_4^{3-} ratios mostly above 16:1.

We do not know the taxonomic composition of the phytoplankton blooms encountered in February (Stations 6–8) and June (Station 7). However, on most sampling dates, chl-a concentrations were not particularly elevated, despite high concentrations of nutrients (DIN 10–50 µmol l^{-1}, PO_4^{3-} 0.5–2.5 µmol l^{-1}). This indicates that factors other than nutrient availability, most likely water column stability, light penetration, and ecological interactions such as grazing or viral lysis, are also important controls over bloom formation in the Johor Strait (Chen et al., 2009; Davidson et al., 2014). The fact that one bloom was observed in February, when rainfall was low and the salinity at the bloom stations was relatively high (27.6–28.7 compared to an overall range of 24.2–29.4 at these three stations across the sampling period) also suggests that direct freshwater run-off was probably not in itself a key trigger for the bloom. Our data are consistent with a recent analysis of microbial community variation over 2 months, which concluded that phytoplankton biomass in the East Johor Strait is likely under a significant degree of top-down control (Wijaya et al., 2023).

4.3 Seasonal biogeochemical variation

Although rainfall and therefore river discharge showed clear seasonal variation, this did not result in strong seasonal variation in the biogeochemical parameters we measured, consistent with previous studies in the Johor Strait (Chénard et al., 2019; Mohd-Din et al., 2020). This is despite the fact that the DOM pool in the Johor River is likely largely of terrigenous origin (based on the optical properties). The somewhat lower DOC concentrations in the Johor River estuary during the northeast monsoon might indicate a dilution effect due to increased rainfall as observed in peatlands (Clark et al., 2007; Rixen et al., 2016). This was not observed for NO_3^-, possibly indicating that NO_3^- originates from shallower in the soil profile than DOC.

The only parameter where some seasonality was apparent was NO_2^-, which we hypothesise might be linked to temperature as discussed above in Section 4.2. The Johor River and Johor Strait are thus different from estuaries in the seasonal wet–dry tropical climates, where large seasonal variation in precipitation causes much more pronounced seasonal variation in biogeochemistry (Eyre and Balls, 1999; Pratihary et al., 2009; Burford et al., 2012). Our data also suggest that dissolved nutrient concentrations in the eutrophic Johor Strait are not primarily controlled by seasonal precipitation and runoff patterns, and that phytoplankton blooms in the strait are not primarily controlled by nutrient availability.

The limited seasonal variability observed in the present study contrast with the Singapore Strait directly to the south, where the monsoonal reversal of the prevailing ocean currents delivers a seasonal input of terrigenous DOM and nutrients during the southwest monsoon (Martin et al., 2022; Zhou et al., 2021). Our data further show that the Johor River carries much lower concentrations of DOC but much higher concentrations of NO_3^- compared to the inferred concentrations of the river input that affects the Singapore Strait (890±150 µmol l^{-1} for tDOC; Zhou et al., 2021; and 23.7±2.2 µmol l^{-1} for NO_3^-; Martin et al., 2022). This further supports the conclusion that input from the Johor River has little impact on the biogeochemistry of the Singapore Strait (Zhou et al., 2021; Martin et al., 2022), as also shown for suspended sediment concentrations by (van Maren et al., 2014). Based on the seasonality and inferred riverine endmember concentrations, the terrigenous input to the Singapore Strait is instead derived from peatland-draining rivers (Zhou et al., 2021; Martin et al., 2022).

5 Conclusion

The Johor River and Johor Strait are clearly biogeochemically distinct and not simply part of the same estuarine mixing continuum. The Johor River appears to carry mostly terrigenous DOM, although with significant non-conservative additions in the estuary, while the eutrophic Johor Strait also sees autochthonous DOM production from phytoplankton blooms. Although $SUVA_{254}$ showed lower values in the Johor Strait than the Johor River, the CDOM spectral slope parameters in the Johor Strait were consistent with typical terrigenous values, demonstrating that CDOM optical properties may be ambiguous source indicators in eutrophic waters where heterotrophic microbes are likely producing CDOM as well. Our data further reveal possible evidence for temperature-dependent NO_2^- accumulation in estuarine waters despite the limited seasonal temperature range. The large contribution of NH_4^+ to the DIN pool, with DIN:PO_4^{3-} ratios generally at or above 16:1, indicate that internal nutrient recycling is likely important in the Johor Strait, and that phosphorus may play a role as limiting nutrient in this system.

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Acknowledgements

We are grateful to Chen Shuang and Ashleen Tan Su Ying for help with sample analysis and field work. This work was funded through the Singapore Ministry of Education Academic Research Fund Tier 2 (grant MOE-MOET2EP10121-0007) and through a Nanyang Technological University Start-Up Grant.

Data availability

All raw data and analysis codes are available via the NTU Data Repository under https://doi.org/10.21979/N9/XJWPHI

Competing Interests

The contact author has declared that none of the authors has any competing interests