Seasonal shifts in diurnal variations of $pCO_2$ and $O_2$ in the lower Ganges River

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Scientific Significance Statement
Impoundment and pollution can affect monsoon-driven seasonality in water and carbon flows through the Ganges, an understudied river despite contributions to the global river discharge and carbon fluxes. Little is known about the mechanisms underlying temporal variations in CO2 dynamics of the lower Ganges integrating upstream influences of damming and pollution. High-frequency CO2 and O2 measurements were combined with dissolved organic matter characterization to show concurrent increases in CO2 and terrestrial organic matter during monsoon floods contrasting with phytoplankton-driven diurnal variations in $CO_2$ uptake and O2 production during dry months. Despite large temporal variations, the lower Ganges acted as a source of CO2 throughout the year. Increasing hydrologic variability and nutrient input can amplify the large seasonal variations in CO2 emissions from the Ganges.

Abstract
High-frequency, paired measurements of the partial pressure of CO2 ($pCO_2$) and dissolved O2 were combined with dissolved organic matter (DOM) characterization to investigate diurnal (7:00–19:00) and seasonal variations in CO2 dynamics in the lower Ganges River. Diurnal variations in $pCO_2$ shifted seasonally, concurring with changes in DOM optical properties, biodegradable DOM, and O2 departures from atmospheric equilibrium ($\Delta O_2$). Increased $pCO_2$ and CO2 flux ($FCO_2$) in August–September corresponded to monsoonal floods carrying more terrestrial materials. Lower dry-season $pCO_2$ and $FCO_2$ concurred with higher $\Delta O_2$, and exhibited strong relationships with DO and pH, indicating a dominant influence of phytoplankton production. Despite large variations in $pCO_2$, the year-long positive $FCO_2$ implied that the lower Ganges acted as a CO2 source, reaching 122 mmol m$^{-2}$ d$^{-1}$. Increasing hydrologic variability and pollution in the Ganges Basin can amplify $pCO_2$ variations linked to seasonal shifts in terrestrial inputs and phytoplankton production.

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Additional Supporting Information may be found in the online version of this article.

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Active transformations of terrestrial carbon (C) occur during riverine transport and exchange with the floodplains, sediments, and atmosphere (Cole et al. 2007; Battin et al. 2009). The global estimate for CO$_2$ emission from inland waters has been wide-ranging and increasing from 0.75 to 3.88 Pg C yr$^{-1}$ (Drake et al. 2018), comparable to the net terrestrial (3.2 Pg C yr$^{-1}$) and oceanic (2.5 Pg C yr$^{-1}$) sinks of anthropogenic CO$_2$ (Friedlingstein et al. 2019). Inland waters in the Indian subcontinent have been estimated to account for only 0.3–1.8% of the global CO$_2$ emissions (Panneer Selvam et al. 2014; Li and Bush 2015). However, scarce field measurements in large rivers such as the Ganges under increasing influences of water pollution and impoundment can result in inaccurate estimation of global riverine CO$_2$ emissions (Friedlingstein et al. 2019).

When combined with the discharge from the Brahmaputra (510 km$^3$ yr$^{-1}$) and the Meghna (150 km$^3$ yr$^{-1}$), the Ganges (493 km$^3$ yr$^{-1}$) represents the third-largest river after the Amazon (6590 km$^3$ yr$^{-1}$) and the Congo (1325 km$^3$ yr$^{-1}$) (Parua 2009; Table 1). About 411 million people depend on the river water for drinking, irrigation, and hydropower, causing anthropogenic perturbations to riverine metabolic processes and CO$_2$ emissions (Parua 2009; Park et al. 2018). Over 140 large dams and barrages have been constructed on the main stem and tributaries of the Ganges (Dutta et al. 2020). Approximately 15,435 and 2500 million liters of sewage and industrial wastewater, respectively, are daily discharged into the Ganges, with only 22% being treated (Dwivedi et al. 2018). The scarcity of pCO$_2$ measurements, available only for the lower reaches (Manaka et al. 2015) and the Hooghly estuary (Mukhopadhyay et al. 2002; Samanta et al. 2015), hinders our understanding of CO$_2$ emissions from the Ganges under increasing anthropogenic stress (Li and Bush 2015; Park et al. 2018).

While monsoonal floods have been implicated as carriers of soil-derived CO$_2$ (Manaka et al. 2015) and organic matter (OM; Ittekot et al. 1985) to the Ganges waters, little is known about dry-season variability in riverine metabolic processes and CO$_2$ dynamics. Our objectives were to (1) explore temporal variations in pCO$_2$ in the lower Ganges using high-frequency sensor measurements, and (2) examine the controlling mechanisms for CO$_2$ dynamics by relating pCO$_2$ to other measurements including concentrations of dissolved organic C (DOC) and biodegradable DOC (BDOC), optical properties of dissolved organic matter (DOM), $\delta^{13}$C–CO$_2$, pH, and dissolved oxygen (DO). Specifically, we tested the hypothesis that degradation of OM flushed from soils during monsoon floods can elevate riverine pCO$_2$ levels, while the balance between phytoplankton consumption and microbial production of CO$_2$ controls pCO$_2$ and its relationships with DO during dry months.

**Materials and methods**

**Study site and field measurements**

The Ganges originates in the Himalayas and drains an area of 1050 $\times$ 10$^3$ km$^2$ across northern India and Bangladesh, discharging 1153 km$^3$ yr$^{-1}$ into the Bay of Bengal after converging with the Brahmaputra and Meghna (Table 1). The main stem and tributaries drain a variety of geological formations, including Precambrian metamorphic and felsic intrusive rocks (Kuehl et al. 2005). Fertile soils and abundant water allow extensive agriculture in basin (Parua 2009).

High-frequency sensor measurements of pCO$_2$ and O$_2$, combined with water sampling, were conducted at a site near the Hardinge Bridge (24°03’57.04”N, 89°01’42.85”E) in Kushita, Bangladesh (Fig. S1). The monitoring station, where long-term hydrological (water temperature, discharge, and rainfall) and water quality (pH and total alkalinity) data are available, is located ~ 160 km downstream of the Farakka Barrage. The surface water pCO$_2$ was measured 20 cm below the water surface using a diffusion-type CO$_2$ sensor (CARBOCAP, GMT222, Vaisala) enclosed in a water-impermeable membrane, as described by Yoon et al. (2016). The CO$_2$ sensor was deployed for 12–13 h (7:00–19:00) once every month from May 2018 to April 2019 to examine the diurnal (day-time) variability in pCO$_2$ including some nightly measurements during early morning or early night hours. CO$_2$ concentrations were measured at 10-s intervals and averaged for data presentation at intervals of 1 min, 10 min, or 1 h. To examine whether the limited sensor deployment due to safety concern could cover the full diel cycle of pCO$_2$, an extended sensor deployment was conducted for 48 h on 19–21 March 2019. Sunshine hours with solar radiation exceeding 0.8 kW m$^{-2}$ were used to distinguish measurements during sunlight hours from those taken when the sun was set (https://www.pveducation.org). The level of pCO$_2$ in the ambient air was simultaneously measured using another sensor placed ~ 1 m above the water surface.

The sensors were calibrated with standard gases of known concentrations (Supporting Information, Text S1). The sensor outputs were corrected for temperature and pressure, following Johnson et al. (2010). In order to validate the sensor measurements, dissolved gas samples were collected using manual headspace equilibration (Yoon et al. 2016), together with ambient air samples (Fig. S2). CO$_2$ concentrations and stable C isotope ratios in the manual equilibration and air samples were measured using a gas chromatograph (7890A; Agilent) and an isotopic analyzer (ThermoScientific, Bremen, Germany), respectively (Supporting Information, Text S2).

DO, water temperature, and pH were measured at the same intervals (10 s) using a multiparameter probe (6920V2; YSI Inc.) after calibration prior to each deployment. Air temperature and atmospheric pressure were recorded using a HOBO data logger (H21; Onset). Daily weather data at Paksey and the daily mean discharge at the Hardinge Bridge were obtained from World Weather Online (https://www.worldweatheronline.com) and the Bangladesh Water Development Board, respectively.

**Water analysis and BDOC measurement**

Water samples were collected using acid-cleaned polycarbonate (PC) bottles between 15:00 and 17:00 during monthly
Table 1. Comparison of basin area, discharge, $pCO_2$, and $FCO_2$ among 10 global rivers ranked by discharge (excluding the fifth river Yenisey due to limited data availability).

| River          | Reach            | Study period | Basin area (km$^2$)$^a$ | Discharge (km$^3$ yr$^{-1}$)$^a$ | $pCO_2$ (μatm) | $FCO_2$ (mmol m$^{-2}$ d$^{-1}$) | References                          |
|---------------|------------------|--------------|-------------------------|-----------------------------------|----------------|-------------------------------|--------------------------------------|
| Amazon        | Basin            | 2007–2010    | 6,112,000               | 6590                              | 70–16,880$^b$ | -                            | Borges et al. (2015)                 |
|               | Lower            | 2014–2016    |                         |                                    |                 |                               |                                      |
| Congo         | Eastern          | 2010–2015    | 3,698,000               | 1325                              | 3218 ± 1656    | 596.2 ± 501.1                | Sawakuchi et al. (2017)              |
|               | Lower (Barrancas, Colombia) | 1982–1985 | 1,100,000               | 1135                              | 446$^c$–$^a$   | 0.3$^c$                      | Araujo et al. (2014)                 |
| Yangtze       | Basin            | 2013–2014    | 1,808,000               | 928                               | 528–1908$^c$   | -                            | Liu et al. (2016)                    |
| Lena          | Basin            | 2016         | 2,460,000               | 588                               | 400–1400       | 78.8–140.8$^d$              | Vorobyev et al. (2021)               |
| Mississippi   | Basin            | 2000–2001    | 2,980,000               | 580                               | 1095–1916$^e$  | 73.6                         | Dubois et al. (2010)                 |
| Parana        | Lower (Santa Fe, Argentina) | 1981–1984 | 2,783,000               | 568                               | 2600–3700$^*$$^f$ | -                            | Depetris and Kempre (1993)          |
| Brahmaputra   | Basin            | 2011–2012    | 580,000                 | 510                               | 28–6706$^*$$^f$ | -                            | Park et al. (2018)                   |
| Ganges        | Basin            | 2011–2012    | 1,050,000               | 493                               | 65–2620$^*$$^f$ | -                            | Park et al. (2018)                   |
|               | Lower (Bangladesh) | 2011–2012 |                |                                    | 377–1763$^*$$^f$ | 51.0$^f$                  | Manaka et al. (2015)                 |
|               | Lower (Bangladesh) | 2018–2019 |                |                                    | 376–1709       | –5.0–122.0$^g$            | This study                           |
| Ayeyarwady    | Middle to lower  | 2013         | 410,000                 | 486                               | 1222–3157$^*$$^f$ | -                            | Park et al. (2018)                   |

Values are either the mean ± standard deviation and/or range depending on data availability in the cited references. $pCO_2$ values calculated from pH and alkalinity are indicated by asterisks.

$^a$Basin area and discharge data from Raymond and Spencer (2015).

$^b$Data shown in ppm.

$^c$Values measured in the estuary.

$^d$Range of the means for five reaches.

$^e$pCO$_2$ measured at the Hardinge Bridge.

$^f$FCO$_2$ calculated from Manaka et al. (2015).

$^g$Estimates based on Raymond et al. (2013) (Table S2).
monitoring. Samples were immediately frozen and shipped to Korea for laboratory incubation and chemical analysis. Thawed water samples were filtered through a glass fiber filter (GF/F; 0.7 μm) followed by a PC membrane filter (0.2 μm; Whatman). Filtered samples were incubated at 25°C in the dark for 5 days following the widely used methods for BDOC measurements (Servais et al. 1987; Begum et al. 2019). A 60 mL sample in a 120 mL glass bottle was amended with an inoculum (0.6 mL) of native microbiota of an additional river water sample, collected from the monitoring site in September 2019 and filtered through a 2 μm PC filter. Given logistical constraints, a single inoculum was used to compare DOM biodegradability among 12 monthly samples under the same controlled conditions including the inoculum, although this approach cannot simulate the seasonal variability in microbial communities.

The filtered samples were analyzed for DOC concentration (TOC-VCPH; Shimadzu), ultraviolet–visible (UV–Vis) absorbance (Agilent 8453), and fluorescence excitation-emission matrices (EEMs; F7000; Hitachi). Specific UV absorption at
254 nm (SUVA254; Weishaar et al. 2003), humification index (HIX; Zsolnay et al. 1999), fluorescence index (FI; McKnight et al. 2001), and biological index (BIX; Huguet et al. 2009) were calculated from the corrected fluorescence EEMs and UV absorbance. The relative intensities of the three fluorescent DOM components, obtained from a previous study on Asian rivers (Begum et al. 2021), were calculated from the corrected EEMs: C1 (humic; ex/em 350/460 nm), C2 (microbial-humic; 305/400 nm), and C3 (protein; 275/345 nm; Figure S3). More analytical details are provided in Supporting Information (Text S3).

Calculation of CO2 and O2 departures and CO2 fluxes

Departures of O2 (ΔO2) and CO2 (also known as water-atmosphere CO2 gradient; ΔCO2) from atmospheric equilibrium were calculated from in situ measurements of DO and pCO2 using Eqs. 1 and 2, as described by Vachon et al. (2020) and modified from Weiss (1974).

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\begin{align*}
\Delta O_2 &= [O_2] - [O_2]_{eq} \\
\Delta CO_2 &= [CO_2] - [CO_2]_{eq}
\end{align*}
\]

where [O2]eq was calculated as the DO concentration at atmospheric equilibrium following the equations of Needoba et al. (2012) modified from Benson and Krause (1984) and Garcia and Gordon (1992), and [O2] was taken from the in situ DO concentration. [CO2] and [CO2]eq are the CO2 concentrations in water and at atmospheric equilibrium, respectively. Water-air CO2 flux (FCO2) was calculated by multiplying ΔCO2 with gas transfer velocity (k) which was calculated by following different methods (Alin et al. 2011; Raymond et al. 2012, 2013; Lauerwald et al. 2015), as described in Supporting Information (Text S4). All data are accessible in a public data repository (Haque et al. 2021).

Results

Diurnal and seasonal variations in pCO2 and FCO2

The pCO2 measured during each of 12 sensor deployments spanned 448 ± 56 to 1588 ± 50 μatm (mean ± standard deviation), indicating a year-long supersaturation of CO2 in the lower Ganges with respect to atmospheric equilibrium (422 μatm) (Figs. 1 and S4; Table S1). The 48-h continuous monitoring in March 2019 exhibited the highest pCO2 and FCO2 values at dawn (~06:00) and the lowest values in the afternoon (~16:00) (Fig. S4; Tables S1 and S2). Therefore, the 12-h sensor deployment may have covered most of the diel variations in pCO2. The pCO2 levels during the monsoon displayed a wider range of variations (804–1588 μatm) with no clear diurnal pattern, compared to the smaller dry-season
values (448–864 μatm) revealing distinct diurnal variability (Figs. 1b and S4; Table S1).

The FCO2 for each sensor deployment ranged from 2 ± 3 to 108 ± 7 mmol m⁻² d⁻¹ (mean ± standard deviation), with the monsoonal average (73 mmol m⁻² d⁻¹) four times higher than the dry-season counterpart (17 mmol m⁻² d⁻¹), corresponding to the large monsoonal increases in pCO2 and discharge (Fig. 1a,c; Table S2). The average FCO2 estimated for each sensor deployment based on flow velocity (Raymond et al. 2012) ranged from 2 to 108 mmol m⁻² d⁻¹, falling in the lowest range of other estimates obtained using higher k values (Fig. 1c; Table S2). Monsoonal increases in pCO2 and FCO2 concurred with a large decrease in δ¹³C–CO₂ during the initial monsoon month (Fig. 1d). Although the observed pCO₂ levels were lower than those measured in some tropical rivers such as the Amazon and Congo (Table 1), CO₂ in the lower Ganges was supersaturated with respect to atmospheric equilibrium throughout the year, with FCO₂ generally increasing during monsoon months (Fig. 1c).

O₂ supersaturation (positive ΔO₂) in the dry season contrasted with the monsoonal undersaturation (negative ΔO₂), resulting in a unique seasonal shift along the 1 : −1 relationship between ΔCO₂ and ΔO₂ (Fig. 2). While the relationships between ΔCO₂ and ΔO₂ found during the monsoon were clustered slightly below the 1 : −1 line, those of the dry season displayed large deviations from the 1 : −1 line, with upward day-time departures across the season. The relationships between pCO₂ and DO or pH (Fig. S6) were strongly linear and differentiated between day and night during the dry season, but weaker without any clear day-night distinction during the monsoon. Regression analyses established significant relationships between pCO₂ and DO or pH, except during a few monsoon months (Figs. S5 and S6).

**Biodegradability and optical properties of DOM**

DOC concentrations exhibited large seasonal variations similar to those for pCO₂ (Fig. 3; Table S3), being generally higher during the monsoon (1.1–2.3 mg L⁻¹) than during the dry season (0.9–1.7 mg L⁻¹). Water temperature, DOC concentrations, and DOM indices of terrestrial origin (HIX and C1) were higher during the monsoon, whereas DO, pH, FI, BIX, and C3 exhibited the opposite trends (Fig. 3; Table S1).

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**Fig. 3.** Monthly measurements of DOC (a), BDOC (b), FI (c), BIX (d), SUVA254 (e), HIX (f), C1 (g), C2 (h), and C3 (i) at a downstream location of the Ganges from May 2018 to April 2019. The shaded region represents monsoonal data. Error bars indicate standard deviations of the triplicate measurements.
and S3). The proportion of BDOC in DOC averaged 25.9%, peaking in September (47.2%) (Table S4). The second BDOC peak occurred in January (43.7%) when both DOC concentration and \( pCO_2 \) were much lower than the first peaks (Table S1 and S4).

**Relationships between \( pCO_2 \) and water quality measurements**

The means of \( pCO_2 \) measured during the 12 sensor deployments showed significant positive relationships with those of discharge and water temperature (Fig. 4). In contrast, the values of \( pCO_2 \) were negatively correlated with those of pH, DO, and \( \Delta O_2 \). While \( pCO_2 \) exhibited significant positive relationships with HIX, C1, and C2, the opposite was observed for BIX and C3. BDOC concentrations showed a significant positive relationship only with discharge. Multiple linear regression models (Table S5) revealed that DOM optical properties (SUVA254 and C1) and hydroclimatic variables (discharge and water temperature) can explain 80% and 94% of the variability in \( pCO_2 \), respectively (Fig. S7).

**Discussion**

Combined results of CO2 and DOM suggest monsoonal floods and phytoplankton production as the primary drivers of the seasonal shifts in diurnal variability of \( pCO_2 \) in the lower Ganges. The distinct day-time decline in \( pCO_2 \) during the dry season indicates CO2 uptake by aquatic plants and phytoplankton, whereas respiration by aquatic plants and microbes increases \( pCO_2 \) at night (Gómez-Gener et al. 2021). Higher day-time temperatures decrease CO2 solubility but can accelerate OM decomposition processes (Peter et al. 2014); however, the observed small diurnal variations in temperature may not have a dominant effect on OM biodegradation (Table S1; Fig. S4). The strong linear relationships between \( pCO_2 \) and DO or pH displaying a distinct day-night separation weakened during the monsoon (Figs. S5 and S6). This, together with the seasonal separation of the relationship between \( \Delta CO_2 \) and \( \Delta O_2 \) (Fig. 2), implies an overriding influence of terrestrial OM and CO2 inputs carried by monsoonal floods over the photosynthesis-controlled coupling of CO2 and O2 dynamics.

The hydrologic regime of the lower Ganges is governed by monsoon rainfalls and the Farakka Barrage. Large concurrent increases in discharge, \( pCO_2 \), and \( FCOD \) from August to September (Fig. 1; Table S1) imply hydrologically mediated responses of riverine CO2 dynamics to the inputs of soil-derived OM and CO2 flushed during storm events (Hope et al. 2004; Samanta et al. 2015). Higher temperatures during the monsoon can also enhance the biodegradation of labile OM in soils and streams (Figs. 1 and 3; Hope et al. 2004). The observed \( \delta^{13}C-CO_2 \) values (−22.2‰ to −15.5‰; Fig. 1d) were within the usual range of \( \delta^{13}C-DIC \) or \( \delta^{13}C-CO_2 \) in streams and rivers (Yoon et al. 2017; Deirmendjian and Abril 2018). The large decrease in \( \delta^{13}C-CO_2 \) (−22.2 ‰) during the early
monsoon (Fig. 1d) indicates a significant contribution of soil-derived OM from the initial inundation of floodplains. In contrast, the higher dry-season values of δ13C–CO2 (−18.9 ‰ to –15.5 ‰; Fig. 1d) imply the selective removal of lighter isotopes from the riverine CO2 pool by primary production and CO2 evasion (Finlay and Kendall 2007; Jin et al. 2018).

The relationships between ΔCO2 and ΔO2 (Fig. 2) also support the role of monsoonal floods rich in CO2 and DOM in producing excess CO2 relative to O2. The centroid shape and offset magnitude of the monsoonal data suggest respiration and photodegradation as the dominant drivers of both gases (Fig. 2a; Vachon et al. 2020). While excess O2 across dry months led to a photosynthetic quotient (PQ) > 1 (Fig. 2b), the monsoonal downward deviation of ΔCO2 and ΔO2 from the 1 : 1 line resulted in a respiratory quotient (RQ) < 1, indicating greater O2 consumption relative to CO2 production (Fig. 2c; Vachon et al. 2020). The low RQ indicates a potential contribution of photodegradation that consumes more O2 than biodegradation (Cory et al. 2014), while photodegradation may be contingent on intermittent sunlit conditions during the monsoon. Metabolic quotients have been shown to vary with the type and magnitude of photochemical and biological reactions at play (Rocher-Ros et al. 2020; Vachon et al. 2020). However, these results should be interpreted with care, because the water-air exchange tends to be faster with O2 than that of CO2 buffered by HCO3− (Stets et al. 2017).

The highest pCO2 levels observed in August and September are consistent with the monsoonal increase in labile DOM, as indicated by the highest concentration of BDOC in September (Fig. 3). Wetlands represent a major source of labile DOM given the large wetland areas and oxbow lakes along the lower Ganges. For example, the wetlands in northwestern Bangladesh cover 771 km2 (Islam et al. 2021), while the wetlands in India amount to 28,575 km2 (Indian Institutes of Technology 2012). The increasing contribution of labile OM from inundated oxbow lakes and depressions along the lower Ganges during the monsoon was reported by Ittekkot et al. (1985). While sewage drains in India and Bangladesh can also release large amounts labile OM to the Ganges, CO2 depleted in 13C (Fig. 1) compared to the 13C–CO2 measured in sewage drains in the Ganges Basin during the monsoon (−18.3‰ to −14.6‰) indicate a rather minor contribution or slower transformation of the sewage-derived OM than the natural OM flushed from soils (Begum et al. 2021). Monsoonal increases in indices associated with terrestrial DOM, such as HIX, C1, and C2 (Fig. 3), support the role of humic-like materials derived from soils in fueling OM degradation and CO2 production (Samanta et al. 2015).

The upward day-time departures of ΔO2 from the 1 : 1 line across the dry season (Fig. 2b) reflect the prevailing influence of photosynthesis on O2 dynamics, while the relatively large ΔCO2 during several dry months and the exceptional, negative ΔO2 in June (Fig. 2b) may indicate stochastic, secondary contributions from anaerobic respiration in sediments, groundwater inputs, or carbonate precipitation (Rocher-Ros et al. 2020; Vachon et al. 2020). CO2 supersaturation and relatively high %BDOC during dry months (>12%) (Figs. 1 and 3) indicate an alternative source of labile OM such as phytoplankton exudates that can enhance CO2 production (Morana et al. 2014). Enhanced BDOC in the dry season did not elevate pCO2 because of CO2 consumption by phytoplankton, as indicated by high DO and ΔO2 (up to 68 μM) (Figs. 2 and S5). Without dilution effects on the downriver water quality by monsoon rainfalls (Manaka et al. 2015), abundant nutrients released from the Farakka Barrage can enhance the eutrophic level and hence primary production, lowering pCO2 in the lower Ganges during low-flow periods, as reported in other impounded rivers (Liu et al. 2016; Jin et al. 2018).

The year-long supersaturation of CO2 together with the relatively high mean BDOC (26%), illustrated the critical role of active OM biodegradation in controlling temporal variations in pCO2. The relatively high %BDOC in the Ganges compared to BDOC values measured in various inland waters (6–16%; LaBrie et al. 2020) implies that heterotrophy in the Ganges may be fueled by additional labile OM sources including autochthonous DOM. However, enhanced dry-season primary production can simultaneously lower pCO2 by active phytoplankton uptake of CO2 (Gómez-Gener et al. 2021). A recent global compilation of high-frequency CO2 measurements found that nocturnal CO2 emissions are 27% greater than the diurnal counterparts controlled by photosynthesis (Gómez-Gener et al. 2021). Although our measurements could not cover the full span of diel variations, the observed day-night differences in pCO2 were usually within 276 μatm during dry months and 165 μatm during monsoon months (Fig. S4). The rather small diel variations are consistent with the findings from other large rivers such as the Congo (Borges et al. 2019) and the Lena (Vorobyev et al. 2021). While lowered dry-season pCO2 may be common in impounded reaches of the Ganges, untreated wastewater along the urbanized reaches can create local hotspots for CO2 by elevating supersaturation levels even during the dry season with high photosynthetic activity (Jin et al. 2018; Begum et al. 2021). Rising organic pollution in growing metropolitan areas across the basin can also increase monsoonal peaks in pCO2 via discharges of CO2 and labile OM from poorly treated wastewater (Park et al. 2018; Begum et al. 2021).

Despite the limitation of measuring pCO2 and DOM at a single site, this year-long monitoring provided the first field-based evidence of the coupled, seasonal variations in pCO2, O2, and DOM composition in the lower Ganges. In response to the unprecedented population growth and anthropogenic perturbations in the Ganges Basin, C fluxes along the rivers may continue to increase in the coming decades. Given the increasing hydrologic variability associated with impoundments and climate change in the Ganges Basin (Park et al. 2018), increasing seasonal variations in discharge and
trophic state may continue to amplify the observed seasonal variability in pCO2 and DOM composition. The temporal variations in biogeochemical processes observed in the lower Ganges may be common in many understudied river systems worldwide, which also underscores the importance of high-frequency measurements of pCO2 to constrain the global riverine C budget.

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