

- Miller and co-workers present an observational study on diel and seasonal cycling of $p\text{CO}_2$ and air-sea CO_2 flux in a mesohaline reach of the Chesapeake Bay. Based on three years of high-resolution observational data, the authors calculated a set of indicators including gas transfer velocity, gas solubility and air-sea CO_2 fluxes. This study paid particular attention on the daily and seasonal cycles of $p\text{CO}_2$ and CO_2 fluxes, as well as their controlling mechanisms in this mesohaline reach. Their results highlight that $p\text{CO}_2$ changes rapidly and across a wide range in a 24-hour cycle, and $p\text{CO}_2$ and CO_2 fluxes are primarily regulated by temperature effects on biological activity. In my opinion, this is a very well-written paper with useful information regarding the carbonate chemistry dynamics of Rhode River, a shallow mesohaline reach of the Chesapeake Bay. Given the quality of the manuscript, it should be published with a minor revision.

I only have some minor comments, outlined as follows.

Line 93-98: This paragraph outlines your findings and conclusions. It would be best placed in the results section.

We agree and will make that edit.

Line 101: study location – Although the authors emphasized that Muddy Creek contributes little freshwater to the study area, I guess it would be better to provide brief information regarding the riverine inputs, such as the saturation condition of $p\text{CO}_2$, pH etc.

In the absence of measurements of the pH, $p\text{CO}_2$ of the freshwater entering the Rhode River from Muddy Creek or other lesser freshwater inputs to the estuary, we are unable to report these $p\text{CO}_2$ or pH values. However, given the exceedingly small overall volume of freshwater input to the Rhode River from its surrounding watershed (see lines 115-120), it is not considered a river-dominated estuary so is not expected to be substantially influenced by the chemical characteristics of this input. This is not to say there is no freshwater influence, only that such influences are likely quite local when mixing with far larger volumes of water from the Chesapeake Bay and therefore beyond resolution of this study.

Line 323: better to pinpoint the average surface water temperature in June-November and Dec-May.

(We agree with this suggestion and will include mean water temperatures for these two seasons. Water temperatures (mean +/- 1 sd) Cold months: 10.9 +/-5.66 deg C. Warm months: 23.2 +/- 6.90 deg C.

Line 358: it's hard to tell the difference between day and night $p\text{CO}_2$ in Fig. 3. Maybe average the day/night $p\text{CO}_2$ in a month scale?

(Yes, we agree and struggled to make this figure as descriptive as possible. The primary issue is that the directionality of $p\text{CO}_2$ tends to be opposite during the day (when CO_2 is assimilated and drawn down due to the net primary productivity) to what it is during the night (CO_2 is generated via respiration with no compensation from photosynthetic activity, especially during warm months). However, the extent of photosynthetically active radiation varies with solar angle and cloudiness during the day, so $p\text{CO}_2$ can rise during parts of those days when respiration rates are higher than photosynthetic rates. At dusk, $p\text{CO}_{2\text{day}}$ and $p\text{CO}_{2\text{night}}$ are equal (as they are at dawn) rising throughout the night and falling during the day, generating strong overlap and visual occlusion. One solution could be to call out a typical week during the warm and cold seasons, to illustrate direction of $p\text{CO}_2$ movement, as below.)

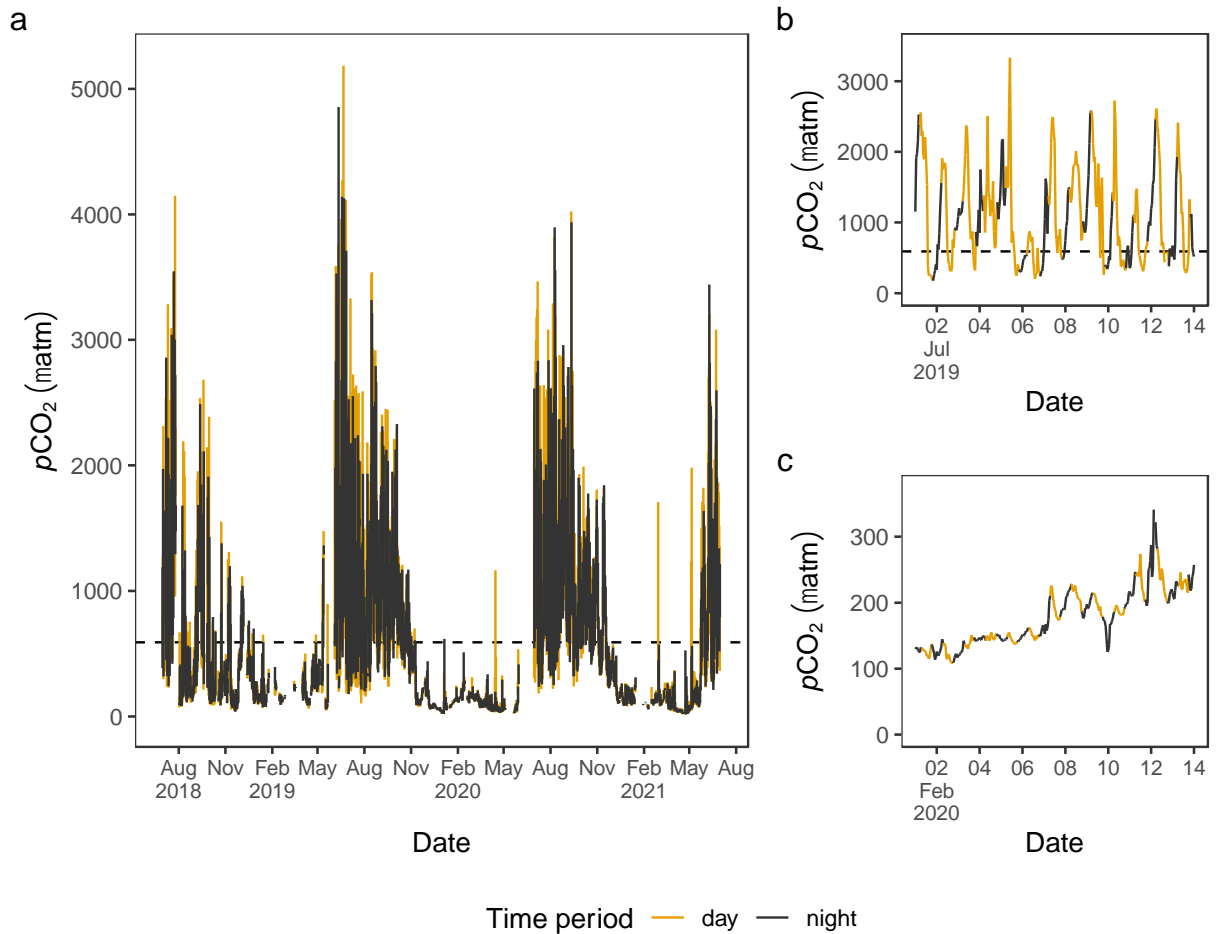


Fig. 3. a. Daily range of $p\text{CO}_2$ measurements categorized by readings taken during the day (yellow) or night (black). Note extensive range overlap among days and nights, illustrating the daily oscillation from high to low values during day and low to high values at night. Horizontal dashed line indicates grand mean of hourly $p\text{CO}_2$ (= 591 µatm) over three years. Panels b. and c. illustrate typical week-long periods during warm and cold months, revealing how CO_2 tends to be drawn down during daylight hours and to accumulate during night-time hrs.

Line 457: the effective size of seasonal and day/night $k600$ is comparable according to Table 2.

(Thank you for pointing out this inconsistency and lack of clarity in our text. We propose clarifying with modified language.)

“The mean overall Rhode River k600 value for CO₂ (mean ± SD, 7.86 ± 2.05 cm · hr⁻¹) was of comparable in magnitude to that of the New River Estuary (9.37 ± 9.47 cm · hr⁻¹). However, wind speed varied far less on the Rhode River than the New River estuary and day/night explained more variability in wind speed than season. Because wind speed directly influenced the formulation of K₆₀₀ (Eq. 2), the effect size of day/night is similarly greater than the seasonal effect on gas transfer velocity (Table 2). Nevertheless, effect sizes (ω^2) indicate that “season” explained at least 10 times more of the observed variance of pCO₂water, pCO₂air, air-water concentration gradient, CO₂ flux, and gas-specific solubility than “day/night” or their interaction (Table 2).”

Line 626: Fig. 7 - very interesting to see CO₂ sources in the daytime, but sinks in the nighttime, which seems contrary to the fact that photosynthesis assimilates DIC in daytime and respiration release DIC in the nighttime. Any comments?

*(In the Rhode River estuary, CO₂ flux depends on the concentration gradient between the atmosphere and water (ΔC), with CO₂ moving across phases from high concentration to low concentration. Because pCO₂water may be either supersaturated, undersaturated, or in equilibrium with respect to the atmosphere, ΔC can be positive or negative, regardless of day/night condition. *It is important to remember that the day/night flux (Fig. 7, 3rd panel from left) represents the overall mean 3-year CO₂ flux, regardless of season. However, when observations are broken up by season, the **net daytime CO₂ flux** is shown to be negative (a sink) during cold months and net positive (a source) during warm months, regardless of time of day (Fig. 7, 1st panel on left). Note: flux conditions are more variable during warm months than cold months, as indicated by error bars (+/- 1 SD) that cross above and below the equilibrium line (zero CO₂ flux) in Fig. 7. Whereas during cold months, error bars remain below the equilibrium line, indicating near continuous sink conditions. Our interpretation is that metabolic respiration (e.g., microbial, phytoplankton) is reduced drastically during cold months and concomitant biogenic CO₂ production essentially stops. Yet, photosynthetic activity appears less susceptible to cold temperatures and continues during cold months, albeit at lower rates than warm water months. The presence of occasional winter phytoplankton blooms that generate lower than normal pCO₂ suggest this to be the case.)**

The authors emphasized that the pCO₂ and CO₂ flux were mainly regulated by temperature effects on biological activity, not the solubility associated with the temperature. I think the authors better to elaborate more about the biological effects. For example, why the study area is more autotrophic during cold months?

With higher algae growth? Why it is more heterotrophic in warm months? With higher oxidation of organic matters?

(Although we did not measure net primary production, community heterotrophic respiration, or lateral export of DIC or DOC directly, strong seasonal patterns across three years emerged. Based on the inverse relationship of pCO₂ and DO across seasons, DO was consistently high during cold months while pCO₂ was consistently low (Fig. S1), we hypothesize that community respiration from phytoplankton and heterotrophic bacteria in the sediments and water column must slow relative to photosynthetic rates when waters are cold. The abrupt onset of elevated pCO₂ at the end of the cold season, typically during May/June when water temperatures rise above ~10 C, suggest that heterotrophic respiration resumes, perhaps in relation to a temperature threshold. Interestingly, despite seasonal rates of warming and cooling being similar to one another (Fig. S1), the reduction of pCO₂ is far more gradual at the end of the warm season/beginning of cold season. We believe this asymmetric pattern may be attributed to organic carbon buildup over the winter when heterotrophic respiration is low which then provides readily accessible fuel for heterotrophs when threshold water temperatures are achieved. No such priming is apparent at the onset of the cold season.)