

# Global Biogeochemical Cycles

## COMMENTARY

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### Key Points:

- Asymmetric changes in pCO<sub>2</sub> and pH seasonal cycles are expected until RCP8.5
- Summer biased observing network creates challenge for observing these asymmetries

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## Complexity of Marine CO<sub>2</sub> System Highlighted by Seasonal Asymmetries

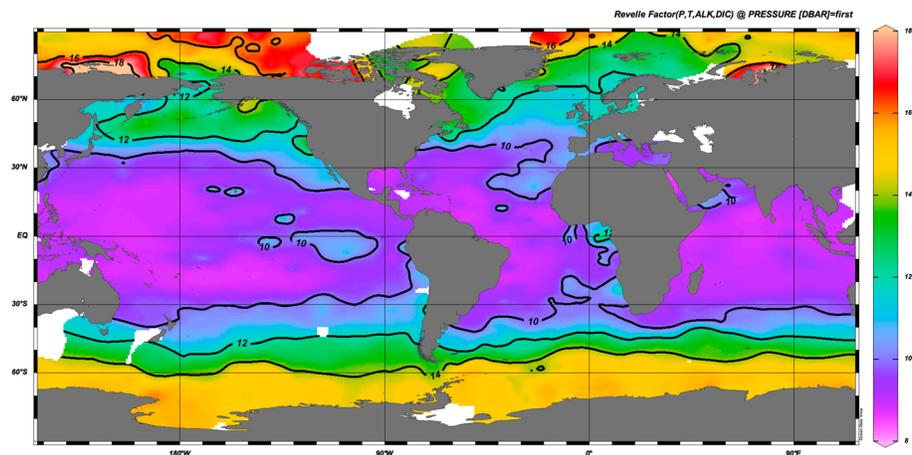
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**Abstract** The complexities of the marine carbon cycle continue to be uncovered. In this issue, Fassbender et al. (2018, <https://doi.org/10.1029/2017GB005855>) combined measured surface ocean partial pressure of carbon dioxide (pCO<sub>2</sub>) with model predictions of increases in dissolved inorganic carbon to explore seasonal pCO<sub>2</sub> changes. They find that when seasonal cycles of other variables (temperature, salinity, total alkalinity, and dissolved inorganic carbon) are maintained to climatological means, seasonal amplitudes of pCO<sub>2</sub> are affected asymmetrically. Thus, even ignoring other natural or climate change factors, the assumption that the seasonal cycle of pCO<sub>2</sub> will be preserved may not be valid. Fassbender et al. (2018) intentionally ignore the influence of other variables such as a global warming signal in order to hone in explicitly on carbon system dynamics. The results show that when studying CO<sub>2</sub> fluxes, especially into the future, the full seasonal cycle must be investigated, as what happens at one time of year may not translate to the rest of the year. Practically, this means that in order to fully understand the marine carbon cycle and its control over atmospheric CO<sub>2</sub> levels, there is an urgent need for more surface pCO<sub>2</sub> data covering more months of the year particularly in the polar oceans that are highly seasonally biased.

The marine carbon cycle is an area of intense research interest due to perturbations caused by the uptake of anthropogenic CO<sub>2</sub> from the atmosphere. The flux of CO<sub>2</sub> from the atmosphere to the ocean acts to slow the rate of CO<sub>2</sub> increase in the atmosphere and its climate change impacts but is not without its own consequences to the ocean. Increases in dissolved inorganic carbon (DIC) result in decreases in pH (Caldeira & Wickett, 2003), which have a plethora of consequences to nearly every marine organism (Barton et al., 2015; Koch et al., 2013; Kroeker et al., 2010). Although increases of CO<sub>2</sub> in the atmosphere leading to increases of CO<sub>2</sub> in the ocean seems simple, it is in fact rather complicated. The complexities result in many nonlinearities and counterintuitive effects. For example, as total DIC increases the concentration of carbonate ions, [CO<sub>3</sub><sup>2-</sup>] actually decreases (Millero, 2007). This lowering of [CO<sub>3</sub><sup>2-</sup>] makes it harder for calcifying organisms to make their calcium carbonate shell, despite an increase in the total amount of carbon available. There is still much of this dynamic system that is not understood.

Many of the intricacies in the CO<sub>2</sub> system arise from CO<sub>2</sub> being a weak acid in water. As a result, once CO<sub>2</sub> gas dissolves in seawater it reacts to form several carbon and non-carbon aqueous species (CO<sub>3(aq)</sub><sup>2-</sup>, HCO<sub>3(aq)</sub><sup>-</sup>, CO<sub>2(aq)</sub>, H<sub>2</sub>CO<sub>3(aq)</sub>, and H<sub>(aq)</sub><sup>+</sup>). The relative proportions of the various species are related to the equilibrium constants (*K<sub>i</sub>*), which themselves are a function of temperature, salinity, and pressure. The subscript *i* refers to the different equilibrium reactions (not shown but can be found in Millero, 2007). Combining these physical chemical properties with other biological and physical factors, some parts of the ocean are sinks for atmospheric CO<sub>2</sub>, others are sources, and yet others can be sinks during part of the year and sources at other times. Understanding the regional and seasonal variability in the oceanic exchange of CO<sub>2</sub> with the atmosphere is of utmost importance for analyzing and predicting changes in the global carbon cycle.

One concept that is often used to understand the carbon system is the Revelle factor (RF), which is one of many measures for quantifying the buffering capacity of seawater (Eggleston et al., 2010). It is a measure of the sensitivity of pCO<sub>2</sub> to a given perturbation of DIC assuming constant total alkalinity (TA). Areas that have a high RF are highly sensitive to changes in DIC, that is, small changes in DIC result in relatively large changes in pCO<sub>2</sub>. Therefore, two sites with the same DIC and pCO<sub>2</sub> but different RF can exhibit different responses to increasing CO<sub>2</sub> including differences in seasonal pCO<sub>2</sub> amplitudes. In general, equatorial waters have low RF, which then increases with increasing latitude (Figure 1). Therefore, polar waters experience larger changes in pCO<sub>2</sub> for a given increase in DIC than subtropical latitudes. This difference makes polar waters more dynamic



**Figure 1.** RF for the global surface ocean. Values were calculated from total alkalinity and DIC measurements compiled in the GLODAPv2 database (Key et al., 2015; Olsen et al., 2016). Equations for calculating RF can be found in Egleston et al. (2010). Equatorial waters have low RF and have a low sensitivity to changes in DIC, while polar water have a higher RF and are more sensitive to DIC changes. DIC = dissolved inorganic carbon; RF = Revelle factor.

and more susceptible to anthropogenic perturbations. The greater buffering capacity of lower latitude waters makes them capable of absorbing more anthropogenic  $\text{CO}_2$  (Egleston et al., 2010).

How  $\text{pCO}_2$  varies seasonally can be broken down into two competing drivers: temperature and other biophysical factors (e.g., biological activity and mixing). Both drivers occur globally, but their magnitude, timing, and relative importance varies greatly (Takahashi et al., 1993). The idea that these two drivers will change with increasing DIC has been considered before (Gorgues et al., 2010; Hauck & Völker, 2015; Kwiatkowski & Orr, 2018), but what Fassbender et al. (2018) do differently is look at whether such changes are monotonic across seasons or more dynamic, resulting in a seasonal asymmetry. A seasonal  $\text{pCO}_2$  asymmetry results when the amplitude grows differently in one season than another. While their results vary by location, they nearly always observe increasing seasonal amplitudes and seasonal asymmetries.

The reason for these asymmetries is that although the temperature and biophysical drivers counteract each other, changes in one tends to dominate over changes in the other. This can be seen by the change in the ratio of the temperature to biophysical drivers and changes in RF (see their figure 4). Asymmetries also result from out of step phasing. Even when the two drivers have potential to cancel each other out they do not align perfectly in time, allowing asymmetries to build, much like several small waves in the ocean interacting to build larger waves.

The authors expand their results beyond  $\text{pCO}_2$  by also looking at implications for pH. They find some counterintuitive results. The biophysical component increases over time at each site, but the temperature component increases at some sites, while decreasing at others. The reason for the differences in the temperature driver is that the sensitivities of the proton concentration,  $[\text{H}^+]$ , and  $\text{pCO}_2$  are not constant. This means that the temperature component of pH does not grow in constant proportion to the annual mean value, while  $\text{pCO}_2$  does. The result is that when viewed as pH, in some areas the amplitude of pH decreases over time, but when viewed as  $[\text{H}^+]$  the amplitude increases (Fassbender et al., 2018, figure 5). The cause of this apparent discrepancy is that the log scale of pH conceals the magnitude of the change in  $[\text{H}^+]$ , giving the impression that the changes are smaller than they actually are.

There are some important caveats to remember when interpreting and applying the results to the real ocean. Limitations in the data set add some large uncertainties and errors. The Surface Ocean  $\text{CO}_2$  Atlas data set (Bakker et al., 2016), although the largest and most comprehensive  $\text{pCO}_2$  atlas available, includes only  $\text{pCO}_2$ . In order to fully characterize the  $\text{CO}_2$  system another parameter is necessary (DIC, TA, or pH). The locally interpolated alkalinity regression algorithm (Carter, Frölicher, et al., 2016) is employed to estimate TA since measured values are not available. Combining the uncertainties from estimating values with uncertainties inherent in the calculations of the  $\text{CO}_2$  system can be significant. The uncertainty is compounded over

time because errors in CO<sub>2</sub> system calculations increase with increasing pCO<sub>2</sub> (Millero, 2007). For most of the ocean the uncertainties are lower than the signals estimated by Fassbender et al. (2018), indicating they are robust features and the asymmetries are real. However, other locations, such as the Southern Ocean, where errors become much larger underscore the need for more data in these regions, particularly in the winter.

The intent of the study is to isolate impacts of increasing DIC from other physical, biological, and chemical influences. In doing so, they (rightly) ignore changes already occurring or predicted to occur. Their projections do not include a global warming component. They also assume constant alkalinity, a parameter likely to change in the future due to carbon cycle feedbacks (Carter, Williams, et al., 2016). Increased temperature will augment the temperature driver and potentially amplify the signal further, while TA changes could amplify or dampen the signal by altering the buffering capacity. Both of these factors may have their own seasonal asymmetries. There may also be changes in other important parameters not mentioned here. Although these assumptions are for an idealized ocean, it does not negate the importance of their results. The future marine carbon cycle will not operate similarly to the modern cycle just with higher concentrations of DIC and pCO<sub>2</sub>, and lower pH. Rather the carbon cycle is much more dynamic and complex. Feedbacks as well as external factors will alter the cycle in ways yet to be unraveled. Separating and attributing different drivers to carbon system changes will not necessarily be easy, but it will be important. Fassbender et al. (2018) make a great contribution to helping us better understand seasonal changes in the marine carbon cycle.

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