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Addressing calcium carbonate cycling in blue carbon accounting

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The white elephant in the blue carbon room

The capacity of the world’s ecosystems to sequester carbon dioxide (CO2) is a major focus of research guiding conservation and restoration of these natural sinks to help mitigate climate change. Seven years ago the term “blue carbon” was coined to describe the disproportionately large organic carbon storage potential of coastal vegetated ecosystems (Nellemann et al. 2009). Efforts are now underway to include blue carbon in global carbon offset schemes by managing these ecosystems to enhance carbon sequestration by focusing on their effect on organic carbon processing. However, it is unclear what role inorganic carbon processing in blue carbon ecosystems plays in their overall carbon sequestration. Here, we argue that there are key uncertainties that will need to be addressed before we can account for this important process to more accurately estimate carbon offsets in blue carbon ecosystems.

Scientific Significance Statement

There is considerable interest in measuring the capacity of the world’s ecosystems to trap and store excess atmospheric carbon dioxide to mitigate human-induced climate change. Blue carbon describes the carbon storage potential of vegetated coastal ecosystems including tidal marshes, mangroves, and seagrasses. Efforts are now underway to include blue carbon in global carbon offset schemes by managing these ecosystems to enhance carbon sequestration by focusing on their effect on organic carbon processing. However, it is unclear what role inorganic carbon processing in blue carbon ecosystems plays in their overall carbon sequestration. Here, we argue that there are key uncertainties that will need to be addressed before we can account for this important process to more accurately estimate carbon offsets in blue carbon ecosystems.

production and dissolution unaccounted for, despite calcium carbonate cycling having been key drivers of changes in climate over Earth’s history (Falkowski et al. 2000). Calcium carbonate production runs counter (i.e., an atmospheric CO2 source) to the effects of organic carbon production (CO2 sink through photosynthesis), because in the oceans calcification increases pCO2 (by depleting CO2 3 and therefore reducing total alkalinity, “TA”), which facilitates the return of CO2 to the atmosphere (Frankignoulle et al. 1994; Zeebe and Wolf-Gladrow 2001). Specifically, for every mole of CaCO3 precipitated, two moles of TA and one mole of DIC are consumed, resulting in increased pCO2 and potential flux to the atmosphere (Fig. 1).

Hence, calcium carbonate production could represent a process that—depending on the timescale (Archer et al. 1998)—exacerbates climate change and/or fuels ocean acidification, whereas calcium carbonate dissolution would act as a CO2 sink. Timescales are important to bear in mind; overall climate impacts resulting from such changes are predicted to be minor over the new few centuries, especially when compared to the influence of anthropogenic CO2 emissions; however, the effects are expected to be significant in the long-term (Tyrrell 2008). Of immediate relevance, however, is how calcium carbonate cycling (i.e., precipitation and dissolution) is treated in national and global blue carbon
accounting, and in quantifying the importance blue carbon ecosystems in climate change mitigation.

Current blue carbon offset schemes focus solely on organic carbon, ignoring calcium carbonate cycling. Further, there has been a rapid expansion of scientific literature on blue carbon, with minimal attention paid to the importance of calcium carbonate precipitation and burial. Yet some blue carbon ecosystems, particularly tropical seagrass meadows, are hotspots for calcium carbonate production owing to their provision of 3D habitat for calcifying organisms (Mazarrasa et al. 2015) (Fig. 2). Indeed, coastal sediments can hold enormous quantities of calcium carbonate accumulated over geological time scales (e.g., the White Cliffs of Dover). The burning question is how accounting for the balance between calcium carbonate production and dissolution, i.e., net calcium carbonate production, in blue carbon ecosystems affects estimates of their CO2 sink capacity based on organic carbon sequestration? And, importantly, how will the balance of calcium carbonate production and dissolution and its effects on blue carbon budgets change in the future as oceans warm and absorb anthropogenic CO2 emissions? It has been demonstrated already that shallow-water oceans are

Table 1. “Back-of-the-envelope” estimates of C fluxes in seagrass ecosystems based on the balance between their organic carbon accumulation (CO2 sink) and inorganic carbon accumulation (CO2 source) rates.

<table>
<thead>
<tr>
<th></th>
<th>Mean</th>
<th>SD</th>
<th>Max</th>
<th>Min</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>PIC accumulation (g C m^{-2} yr^{-1})</td>
<td>126.3</td>
<td>31.5</td>
<td>157.8</td>
<td>94.8</td>
<td>Mazarrasa et al. (2015)</td>
</tr>
<tr>
<td>POC accumulation (g C m^{-2} yr^{-1})</td>
<td>138.0</td>
<td>38.0</td>
<td>176.0</td>
<td>100</td>
<td>McLeod et al. (2011)</td>
</tr>
<tr>
<td>Net CO2 sequestration (g C m^{-2} yr^{-1})</td>
<td>58.4</td>
<td>116.3</td>
<td>0.59</td>
<td></td>
<td>This study*</td>
</tr>
<tr>
<td>Global seagrass area (m²)</td>
<td>3.9E+11</td>
<td>6.0E+11</td>
<td>1.8E+11</td>
<td></td>
<td>McLeod et al. (2011)</td>
</tr>
<tr>
<td>Global net CO2 sequestration (Tg C yr^{-1})</td>
<td>22.6</td>
<td>69.8</td>
<td>0.1</td>
<td></td>
<td>This study†</td>
</tr>
</tbody>
</table>

* Calculated by multiplying the PIC accumulation rate by 0.63 to meet the assumption that 0.63 moles of CO2 is released per mole of CaCO3 precipitated, then deducting this adjusted PIC value from the POC accumulation rates to get net CO2 sequestration.
† Calculated by multiplying net CO2 sequestration by global seagrass area.

Table 2. Uncertainties in the dynamics of calcium carbonate and organic carbon cycling within blue carbon ecosystems and research questions that will need to be addressed in order to account for those uncertainties.

<table>
<thead>
<tr>
<th>Uncertainties</th>
<th>Research questions</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Stoichiometry and fate of CO2 fluxes during calcium carbonate cycling are</td>
<td>Is CO2 release during calcification buffered by metabolic processes (i.e.,</td>
<td>Frankignoulle et al. (1994),</td>
</tr>
<tr>
<td>unknown for blue carbon ecosystems</td>
<td>photosynthesis) and physical processes (e.g., tides, waves)?</td>
<td>Russell et al. (2013),</td>
</tr>
<tr>
<td>2. Varying temporal scales for preservation of organic carbon and calcium</td>
<td>What are the decay rates of calcium carbonate and organic carbon pools, and at</td>
<td>Mazarrasa, et al. (2015),</td>
</tr>
<tr>
<td>carbonate</td>
<td>what depth/age should organic carbon accumulation be considered a long-term sink?</td>
<td>Burdige (2007), Maher et al. (2017)</td>
</tr>
<tr>
<td>3. The presence of geogenic calcium carbonates could lead to an overestimation</td>
<td>What proportions of the calcium carbonate pool are made up of geogenic calcium</td>
<td>Zamanian et al. (2016)</td>
</tr>
<tr>
<td>of calcification rates</td>
<td>carbonate (fossil) and biogenic calcium carbonate (recent)?</td>
<td></td>
</tr>
<tr>
<td>4. Calcium carbonate production may enhance sediment accumulation, organic</td>
<td>Are there positive feedbacks between the accumulation of calcium carbonates and</td>
<td>McLeod et al. (2011), Le Quere, et</td>
</tr>
<tr>
<td>carbon deposition, and preservation</td>
<td>organic carbon?</td>
<td>al. (2016), Gattuso et al. (1998)</td>
</tr>
<tr>
<td>5. The net impacts of climate change on calcium carbonate precipitation/</td>
<td>How will future climate change scenarios (ocean acidification, rising temperatures,</td>
<td>Gattuso et al. (1998)</td>
</tr>
<tr>
<td>dissolution are not known</td>
<td>and sea level rise) affect organic carbon and calcium carbonate cycling?</td>
<td></td>
</tr>
</tbody>
</table>

Macreadie et al. Addressing CaCO3 cycling in blue CO2 accounting
particularly dynamic and can switch between acting as an atmospheric CO₂ source or sink depending on human activities (Andersson and Mackenzie 2004). Biogenic production of calcium carbonate is expected to decrease by 42% by 2100 due to declining carbonate saturation states of surface ocean waters (Andersson et al. 2003, 2005). The overall influence of the latter on climate will be relatively minor compared to anthropogenic emissions, but nevertheless should be taken into account in carbon budgets now, and into the future.

Taking sinks of seagrass soil organic carbon burial into account (ranging between 100 and 176 g C organic m⁻² yr⁻¹; McLeod et al. 2011) and sources of non-organic carbon (net calcium carbonate deposition; ranging between 95 and 158 Tg C inorganic yr⁻¹; Mazarrasa et al. 2015), seagrass meadows seem to constitute a net sink of CO₂ (ranging from 0.59 g C m⁻² yr⁻¹ to 116 g C m⁻² yr⁻¹) (Table 1). After accounting for release of CO₂ after calcification, our estimates suggest that seagrass meadows worldwide accumulate CO₂ at a mean rate of 22.6 Tg C yr⁻¹, which is about half of the accumulation potential accounting for organic carbon alone. It is important to note that the net drawdown of CO₂ by seagrasses and other blue carbon ecosystems will only offset a small fraction of anthropogenic CO₂ emissions (~0.23% based on ~10 Pg C emitted per year; Le Quere et al. 2016), regardless of whether calcium carbonate cycling is taken into account. This is not to say that blue carbon should be ignored in climate change mitigation efforts, but that it should be considered as one of many strategies necessary to limit temperature increase, which must involve an important reduction of emissions. This includes avoided emissions from destruction of blue carbon ecosystems, which is estimated to release about 0.04–0.28 Pg C per year (0.42–2.83% of global emissions) (Pendleton et al. 2012).

The wide range of values reported above and in Table 1 highlight the large uncertainty associated with current estimates of organic carbon burial, calcium carbonate burial, and even seagrass area. Therefore, caution should be exercised when interpreting these results. For example, the values reported by Mazarrasa et al. (2015) assumed that all calcium carbonate present in seagrass soils was biogenic, thereby ignoring the presence of calcium carbonate within the mineral matrix. Indeed, whereas organic carbon density drops substantially in sediments outside seagrass meadows, calcium carbonate density remains elevated, suggesting that calcium carbonate loads in sediments are not the sole result of calcification processes in seagrass meadows (Mazarrasa et al. 2015). Currently, these estimates can be useful to highlight the potential importance of calcium carbonate cycling within blue carbon ecosystems for carbon accounting and crediting, but are susceptible to large changes as the uncertainties pointed out are yet to be clarified. Determining calcification rates for a given blue carbon ecosystems using DIC and TA measurements, as well as actual rates of net community calcification, will help to determine the relative importance of the organic to inorganic carbon cycle, while also avoiding erroneous calcification estimates based on geogenic...
carbonates. On the other hand, however, translating short- 
term calcification rates into long-term calcium carbonate 
burial would be prone to error due to the potential for disso- 
lution and temporal variability in calcification.

How should we deal with calcium carbonates  
in blue carbon science?

We maintain that calcium carbonate production should be  
accounted when estimating carbon sequestration potential of  
blue carbon ecosystems. But how? If calcium carbonate pro- 
duction is a net source of CO₂, then the release of CO₂ from  
calcium carbonate production should be subtracted from  
organic matter sequestration. For example, simply accounting  
for the ratio of OC : IC burial, the stoichiometry associated  
with the buffering of the CO₂ released during calcification  
(i.e., the assumption that 0.63 moles of CO₂ are released per  
mole of CaCO₃ precipitated) and the decay of buried OC over  
time is a good starting point (Fig. 3). While seemingly simple,  
this accounting approach relies on complex assumptions that  
need be resolved.

In Table 2, we summarize five key uncertainties and ques- 
tions that need be resolved in order to properly account for  
calcium carbonate cycling in blue carbon ecosystems. These  
range from equilibrium assumptions about CO₂ exchange  
between the land and sea (Smith 2013), to the extent to  
which blue carbon ecosystems utilize the higher CO₂  
concentrations as a result of calcium carbonate production  
offsetting atmospheric CO₂ release (McConnaughey and  
Whelan 1997; Invers et al. 2001; Schneider and Erez 2006;  
Semesi et al. 2009).

The stoichiometry of the calcification reaction (Fig. 1) in  
coastal environments is complicated due to the buffering  

Fig. 2. (A) The calcifying green alga Halimeda showing various stages of thallus deterioration, from a healthy algae (left), through dead and partially disintegrated thalli (center) to the calcium carbonated tissues giving rise to gravel and sand in some tropical ecosystems (right); and (B) coupling of the biological carbon-carbonate pump. Here, carbonate-forming algae growing on seagrass Thalassodendron pachyrhizum, increase pCO₂ through calcification which may then enhance seagrass photosynthesis resulting in a positive feedback that could potentially avoid an atmospheric fate of the CO₂ released during calcification. Photos by Sven Beer (top row) and John Huisman (bottom row).
the fate of CO₂ released after calcification, which could deter-
diurnal metabolic processes. Moreover, there is uncertainty in
in blue carbon systems is largely driven by tidal, seasonal, and
concentrations. Indeed, the natural variability in calcium car-
bonate dynamics (i.e., CO₂ emissions related to calcification)
in blue carbon systems is largely driven by tidal, seasonal, and
diurnal metabolic processes. Moreover, there is uncertainty in
the fate of CO₂ released after calcification, which could deter-
mine whether calcification in blue carbon ecosystems consti-
tutes a CO₂ source (e.g., in the form of atmospheric CO₂
release) or sink (e.g., through enhancement of organic matter
production and burial rates).

Over long time-scales it is assumed that CO₂ in the form
of dissolved inorganic carbon (DIC) will remain in the
oceans until CO₂ concentrations in the water body exceed
those in the atmosphere. However, this equilibrium assump-
tion, which applies for the global ocean (Smith 2013; Smith
and Mackenzie 2016), may not apply in blue carbon ecosys-
tems and over short time scales where fluxes can be influ-
enced by weather (e.g., wind speeds, temperature) and
metabolic processes (e.g., calcification, primary productivity,
and respiration). For example, in the case of seagrasses, CO₂
produced through calcium carbonate formation can be rap-
idly utilized (through photosynthesis) by epiphytes and
nearby plants, potentially offsetting rises in CO₂ (McCon-
naughey and Whelan 1997; Invers et al. 2001; Schneider and
Erez 2006; Semesi et al. 2009), leading to greater productivity
and higher rates of blue carbon sequestration (Russell et al.
2013). Conversely, photosynthetic activity within blue
carbon ecosystems could increase pH and enhance calcifica-
tion of nearby calcareous organisms (De Beer and Larkum
2001).

Another key uncertainty relies on the fact that the
organic carbon pool (i.e., organic matter) is more labile com-
pared to the inorganic carbon pool (i.e., calcium carbonates),
and it is therefore important to consider the temporal scale
when accounting for the CO₂ sequestration capacity of blue
carbon ecosystems. Indeed, the presence of geogenic calcium
carbonates in blue carbon ecosystems could lead to an over-
estimation of calcification rates. Therefore, there is a need to
differentiate between geogenic and biogenic calcium car-
bonates within blue carbon soils in order to properly assess the
role of carbon cycling in blue carbon accounting. Moreover,
simple calculations also assume that calcium carbonate and
organic carbon cycling in blue carbon ecosystems are inde-
pendent processes. However, available evidence suggests that
calcium carbonate and organic carbon cycling in blue carbon
ecosystems are unlikely to be independent processes. For
example, primary production is conducive to conditions that
facilitate calcification, whereas respiration favors carbonate
dissolution. In addition, calcium carbonate production can
increase the burial efficiency of organic carbon, by interfer-
ating with microbial access to organic carbon in close physical
association with calcium carbonate minerals (Mayer 1994;
Ingalls et al. 2004). Calcium carbonates also support much
of the sediment accretion rate in many seagrass meadows
(Mazarrasa et al. 2015), a major component of the capacity
of vegetated coastal ecosystems to preserve organic carbon
and help adapt to sea level rise (Duarte et al. 2013). Further,
respiration of organic matter produced in blue carbon eco-
systems can fuel calcium carbonate dissolution, thereby
resulting in no net effect of calcification on atmospheric
CO₂ (Burdige et al. 2008). Addressing the key uncertainties
arising from complexities of calcium carbonate cycling in
blue carbon ecosystems, and resolving the key questions that
currently preclude proper accounting for net calcium car-
bonate production in blue carbon ecosystems requires a con-
certed research effort.

In summary, calcium carbonate cycling makes an impor-
tant contribution to global carbon budgets over geological
timescales, yet the magnitude and direction of its influence
on CO₂ sinks within blue carbon is unclear and currently
unaccounted for. Considering the rapid rise of interest in
blue carbon as a climate change mitigation and adaptation
strategies, we argue that calcium carbonate cycling needs to
be included when assessing the importance of these globally
significant carbon stores as CO₂ sinks. Addressing calcium
carbonate cycling in blue carbon accounting is timely given
that anthropogenic activities and climate change may alter
calcium carbonate cycling within coastal ecosystems with
unknown feedbacks for climate change. For example, with
increasing atmospheric CO₂ and ocean acidification, the
ratio of released CO₂ to precipitated calcium carbonate is

![Fig. 3. Model of net atmospheric CO₂ sink associated with different ratios of organic carbon : inorganic carbon (OC : IC) burial. The model assumes a decay rate for OC of 0.0056 yr⁻¹ (Serrano et al., 2016), no dissolution of calcium carbonates, and assumption of 0.63 moles of CO₂ released per mole of calcium carbonate precipitated.](image-url)
expected to rise (Frankignoulle et al. 1995). Yet increased calcium carbonate dissolution (Fig. 1), and decreased calcification rates are also coupled to higher atmospheric CO₂, with both processes lowering the rate of CO₂ fluxed to the atmosphere. Moreover, partial dissolution of the large calcium carbonate stock deposited in blue carbon ecosystems may provide a buffer to ocean acidification while acting as a CO₂ sink. Clearly accounting for calcium carbones in blue carbon systems is a tricky business.

References


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