Clarifying the role of inorganic carbon in Blue Carbon policy and practice

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Background – Blue Carbon in Marine Policy

Since the term “blue carbon” was coined by the report of Nellerman et al. (2009) the marine carbon cycle has firmly entered the realm of marine policy alongside its terrestrial neighbour, “green carbon” (Crooks et al., 2018). Many marine policy decisions rely on accurate information concerning the stocks of blue carbon in a region, the annual sequestration rates associated with those stocks and the threats posed to those stocks by human activities, and especially recently by bottom-trawling (e.g. Sala et al., 2021). Hence policy officials are reliant on accurate blue carbon scientific advice. However, at the present moment there is one topic that is contributing confusion to policy-science understanding, and that is the topic of organic vs. inorganic carbon. This is true of both tropical and temperate marine environments where a diverse range of potential blue carbon habitats are being currently considered for protection and restoration. The aim of this short note is to clarify the differences between organic and inorganic blue carbon and to recommend how they are treated in policy formulation and the provision of scientific advice.

Blue vs. Green Carbon

“Green carbon” is associated with sources of terrestrial photosynthesis such as trees and forests. We can see these, and directly visualise and understand how they remove carbon dioxide (CO_2) from the atmosphere that surrounds them and converts the carbon derived from atmospheric CO_2 into organic molecules locked into the structure of the plant material, and hence into soil if the plant material is buried.

However, the carbon cycle in the sea is much more complex (Tanhua et al., 2013). It involves different forms of carbon (organic and inorganic) in different physical states (dissolved and particulate) passing through different media (e.g., the water column, living organisms in the sea, seabed sediment, biogenic material, sediment pore water) (Ciais et al., 2013). In the sea, carbon is flowing through a complex system, and the flows are controlled by many different biological, physical and geological processes which we cannot see, struggle to measure and certainly do not fully understand (Bauer et al., 2013). Each of these processes act at different rates on different components of the carbon, and the rates the carbon flows through the different components of the marine carbon cycle depend on many other factors such as temperature, salinity, light, water depth, and the biological species present. All of these themselves vary with time and spatially across the oceans (Yamamoto et al., 2018).

A source of confusion

Despite the uncertainties, increasingly the carbon locked into this complex web of processes has been termed a “nature-based solution” (NbS) for climate change mitigation and falls under the umbrella term of blue carbon (Macreadie et al., 2021). We now believe we understand blue carbon and its management enough to place monetary value on its protection, restoration and enhancement in the form of carbon credits (Freiss et al., 2022).

However, some confusion still exists surrounding carbon sequestration and storage in the sea, especially concerning the significant difference between the organic carbon and the inorganic carbon components of blue carbon. Although authors have noted this difference before (e.g., Macreadie et al., 2017; Fodrie et al., 2017; Lee et al., 2020), there still remain distracting ambiguities in blue carbon policy discussions and in policy-supporting documents. Recently, however, in a policy relevant review of blue carbon ecosystems, the role of heavily calcifying organisms has been highlighted as non-actionable within climate change policy (Howard et al., 2023).

Background – The Science

Carbon which is locked into molecules of CO_2 in the atmosphere can enter the sea in two ways, directly and indirectly. The direct way involves CO_2 dissolving into surface seawater when the surface seawater is not saturated with this gas. The indirect way is through the action of marine plants and algae which remove the CO_2 dissolved in seawater and fix it into organic carbon within their tissues during the process of photosynthesis. Photosynthesis requires the energy from the sun and so these algae and plants inhabit surface or shallow waters. During photosynthesis, CO_2 is removed from seawater and the shortfall, or undersaturation, can be made up by more CO_2 being directly dissolved into the sea from the atmosphere (Falkowski, 1994).

However, there is another form of carbon that is produced by marine plants and animals, and that is inorganic carbon in the form of calcium carbonate ($CaCO_3$), most commonly as the minerals calcite and aragonite. Certain phytoplankton (e.g., coccolithophores), zooplankton (e.g., foraminifera), molluscs and corals produce abundant $CaCO_3$ skeletons, which over time build up a store of carbon. When $CaCO_3$ forms, despite the fact that carbon is removed from seawater to make the mineral, the calcification process results in a change to the seawater chemistry which in turn results in an increase in dissolved CO_2, and this excess or supersaturation of CO_2 can lead to a release of CO_2 to the atmosphere (Frankignoulle et al., 1994).

Plants that calcify (e.g., coralline algae such as maerl) will also inhabit surface or shallow waters as they also need to photosynthesise. Thus, the excess CO_2 (or supersaturation) will drive CO_2 out of the seawater into the atmosphere quite quickly. Animals that calcify (e.g. corals, molluscs) may or may not inhabit shallow waters. If they live away from the surface the excess CO_2 may remain in seawater for a long time before it is able to exchange with the atmosphere.

Transport of carbon to the sedimentary environment

Carbon in both organic matter and as $CaCO_3$ can eventually be transported to a sedimentary environment in a number of ways. Phytoplankton debris can sink to the seafloor, sometimes being accelerated by zooplankton packaging and faecal pellet deposition (DeVries, 2022). Debris from macroalgae, such as kelp, can also be added as organic matter to the seafloor through transport by ocean currents and deposition (Ortega et al., 2019; Krause-Jensen and Duarte, 2016). Finally, some plants grow in the sediments and the organic matter from their belowground tissues (roots and rhizomes) can be directly buried within the sediments and their aboveground biomass (stalks and leaves) deposited onto the sediment surface and subsequently buried (e.g., saltmarshes, seagrasses and mangroves) (Hilmi et al, 2021).

In most seas, sedimentary organic carbon is derived from both terrestrial (transported by rivers) and marine (plant and algae debris) sources (Legge et al., 2020), while inorganic carbon in $CaCO_3$ is largely made up of broken marine shells (Fig. 1). Inorganic carbon is also stored in the shells of live shellfish and skeletons of cold-water corals.

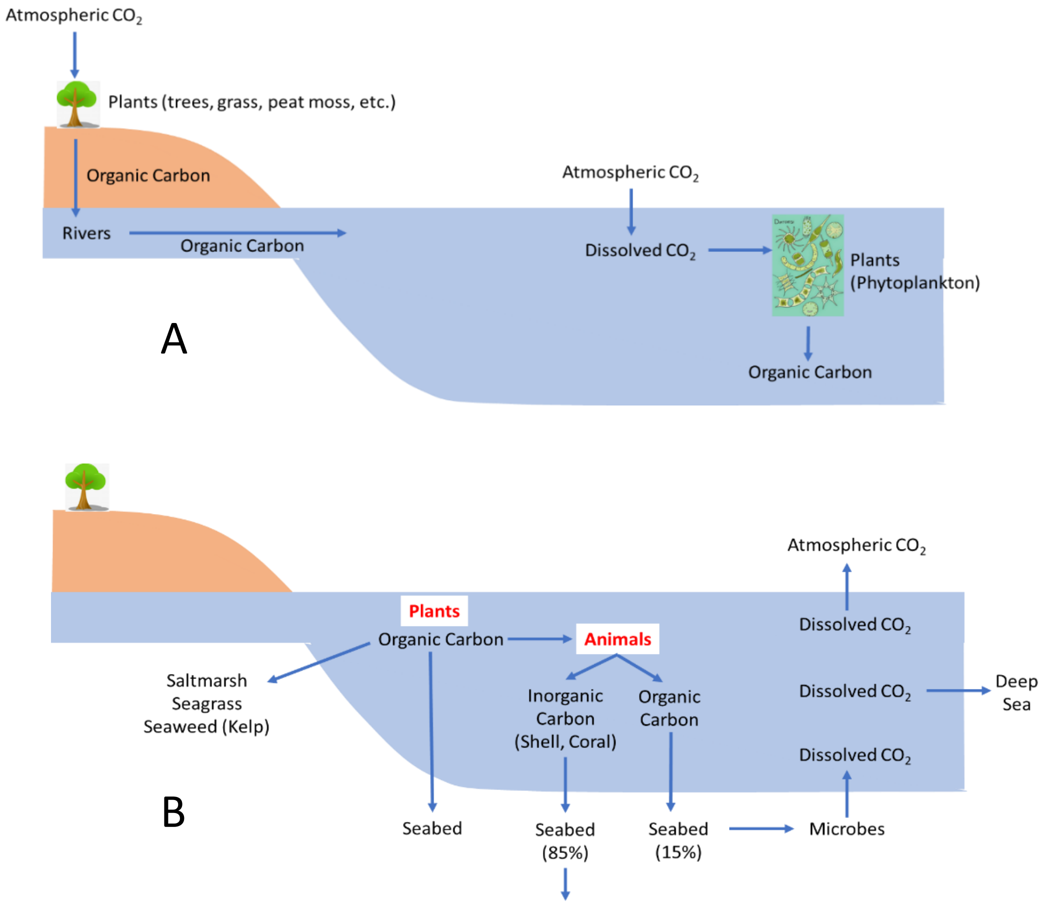

Figure 1. a) Summary of how organic carbon can enter the sea. b) Summary of how organic carbon and inorganic carbon can reach the seabed, and how marine carbon can re-enter the atmosphere.

Inorganic carbon v. Organic carbon – Difference in formation

It can be seen from the above that carbon within the sea can take two principal forms, organic carbon and inorganic carbon, and that these are very different. In simple terms, the formation of inorganic carbon can result in CO_2 being released to the atmosphere from the sea, while the formation of organic carbon results in the absorption of CO_2 from the atmosphere into the sea. In some ways inorganic carbon (such as shell material and corals) could be thought of as “negative blue carbon”, and organic carbon as “positive blue carbon”, when the sequestration of carbon away from the atmosphere is being considered (Gattuso et al., 1995).

Hence it can be seen that when we assess the stocks of “blue carbon” we have in our seas and in our marine habitats we must be very careful to distinguish organic carbon from inorganic carbon. We must also not sum these together as “total carbon” unless we fully understand what we are using the resulting numbers for.

Estimating Seabed Carbon Stocks

For seabed sediment, the different proportions of organic and inorganic carbon can be directly estimated by heating a sample of sediment and measuring the emitted CO_2 gas as the organic carbon and the $CaCO_3$ are broken down at different temperatures (Heiri et al., 2001). For example, if one takes a sample of seabed sediment, dry it and then heat it up, as it heats to about 400°C CO_2 is emitted from the sample due to labile (easily broken down) organic carbon stored within it. If the sample is then heated to 600°C, more CO_2 is emitted due to refractory (resistant to being broken down) organic carbon stored in the sediment sample. If it is even further heated to 900°C more CO_2 is emitted due to the inorganic carbon stored in the shell material ($CaCO_3$) within the sample breaking down (Smeaton et al., 2021). In a recent “stock take” of Scottish seabed carbon, using this method to determine the carbon content of seabed samples, it was estimated that approximately 14% (357 ± 72 Mt) of seabed carbon was organic carbon, while the remaining 86% (2,265 ± 156 Mt) was inorganic carbon made up from predominantly shell material (Smeaton et al., 2021). Hence, for this region, it is vital to explicitly quantify organic and inorganic stocks separately as they differ in overall magnitude, differ in spatial distribution and differ in their relevance to possible protection policies.

Inorganic carbon v. Organic carbon – Difference in burial

Once on the seabed, the pathways of organic and inorganic carbon leading to their eventual burial in the sediment are different (Middelburg, 2019; LaRowe et al. 2020). The fate of buried carbon depends strongly on the type and rate of organic matter or $CaCO_3$ deposited, the activity of animals living in the sediment, the strength of local water currents, the amount of oxygen in the sediment, and the interaction between different particle types. Eventually though, carbon will become buried by further material being added from the water column above.

Inorganic carbon v. Organic carbon – Difference in breakdown

<u>Remineralisation of Organic Carbon</u>: Organic carbon can be broken down by microbes (Figure 1b) which derive energy from the process of respiration, converting the organic carbon back into CO_2, which is dissolved back into the seawater. This is called remineralisation of organic carbon, and this process increases the amount of dissolved CO_2 in the water trapped between sediment grains, termed pore water (Martin et al., 2003). The excess of dissolved CO_2 in the pore waters leads to its transport (flux) into the overlying seawater. If the overlying seawater becomes supersaturated and the water column, with some degree of turbulent mixing of the water column, the dissolved CO_2 can

reach the sea surface and potentially re-enter the atmosphere as CO_2 gas, hence increasing the greenhouse gas content of the atmosphere. If the sediment-water interface is a long way from the surface of the ocean, the excess CO_2 may remain in deeper seawater for a long time before it is brought to the surface and is able to exchange with the atmosphere. In tropical ecosystems such as mangrove and in temperate saltmarsh, CO_2 can be exported to local seawater via outwelling and this must be considered as an additional source of CO_2 (Santos et al., 2019; Sippo et al., 2019).

Dissolution of Inorganic Carbon: However, $CaCO_3$ cannot be digested by microbes, but can be dissolved back into the seawater chemically (dissolution) if conditions (mainly the temperature and the acidity or *pH*) of the pore waters are right for $CaCO_3$ dissolution (Martin et al., 2003). This mainly occurs near the interface between the sediment surface and the overlying seawater (sediment-water interface) where microbes are using dissolved oxygen to break down organic matter resulting in suitable chemical conditions for enhanced $CaCO_3$ dissolution. The dissolution of $CaCO_3$ has the opposite effect to that of $CaCO_3$ formation. When $CaCO_3$ dissolves, it changes the chemistry of the pore waters and the net effect is that there is a deficit of CO_2. The deficit of dissolved CO_2 in sediment pore waters leads to its transport (flux) from the overlying seawater. In shallow waters with some degree of turbulent mixing of the water column, there can be a deficit (undersaturation) of CO_2 in the overlying seawater so that more CO_2 can potentially enter the sea from the atmosphere, resulting in a reduction of atmospheric greenhouse gasses (Figure 2). If the sediment-water interface is a long way from the surface of the ocean, the deficit in CO_2 may remain in deeper seawater for a long time before it can exchange with the atmosphere.

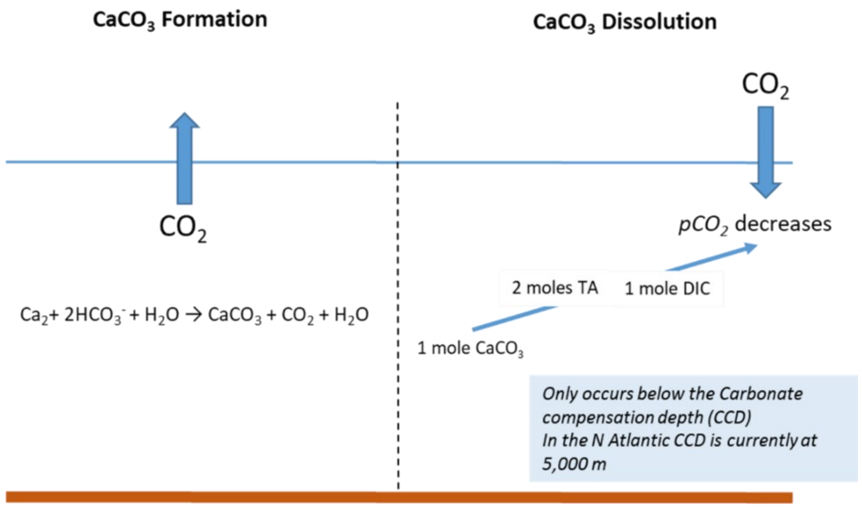

Figure 2. Summary of the chemistry involved in the creation and dissolution of inorganic seabed carbon ($CaCO_3$).

To give more precise details of inorganic carbon dissolution, when one mole of calcium carbonate is dissolved, two moles of total alkalinity (TA) and one mole of dissolved inorganic carbon (DIC) are released into the seawater. This decreases the partial pressure of dissolved carbon dioxide (pCO_2) in the surrounding seawater, which can then potentially draw CO_2 gas from the atmosphere into the sea (Macreadie et al., 2017). Conversely, because of the equilibrium that exists in the sea for dissolved CO_2, any removal of dissolved carbonate (or bicarbonate) from the seawater during the formation of $CaCO_3$ leads to an increase in the dissolved CO_2 level (Frankignoulle et al., 1994). This in turn can result in CO_2 escaping from the sea back into the atmosphere. In fact the “coral reef hypothesis” proposes that the dramatic increase in atmospheric CO_2 during the last glacial-interglacial period was caused by increased $CaCO_3$ creation by corals when the sea level rose (Vecsei and Berger, 2004).

Inorganic carbon v. Organic carbon – Effect of Disturbance

It has recently been suggested that a large potential loss of organic carbon from the seabed may be being caused by bottom trawling (e.g. Sala et al. (2021). It is also suggested that this loss may result in a release of CO_2 back into the atmosphere which might result in a negative climate impact (i.e., an increase in atmospheric CO_2) due to the disturbance (Figure 3). In essence, following disturbance by this type of fishing, the enhancement of the remineralisation of seabed organic carbon by microbial activity is being proposed. However, thus far there has been no similar assessment of how seabed disturbance may affect the other component of seabed carbon, $CaCO_3$. If the disturbance was found to enhance the dissolution of $CaCO_3$, it could potentially produce a positive climatic impact (i.e. reduce atmospheric CO_2). If disturbance by bottom trawling had no effect on the dissolution of $CaCO_3$, then stocks of this form of carbon are irrelevant to a discussion of fishing impact.

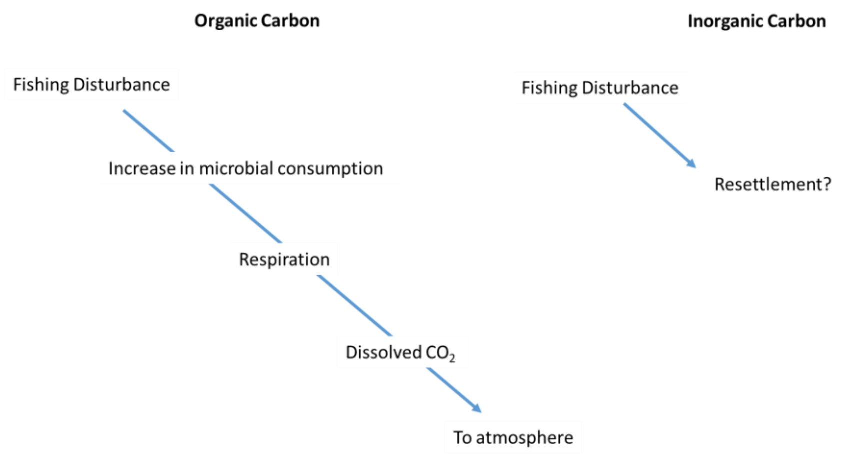

Figure 3. Summary of the different effects of seabed disturbance on organic and inorganic forms of blue carbon.

The combined role of some organisms in $CaCO_3$ *formation and organic carbon trapping*

As in any description of the processes occurring in marine waters, there are ecosystems where the net effect of organisms growing there may be more complex and the need for policy to protect goes beyond that of climate mitigation. One example is living and dead biogenic reefs (Burrows et al., 2014). These include beds of maerl, as well as beds made up from accumulations of shellfish such as Flame shells (*Limaria hians*), Horse mussels (*Modiolus modiolus*), Blue mussels (*Mytilus edulis*), and Native oysters (*Ostrea edulis*). Biogenic reefs can also be formed by Brittlestars (*Ophiothrix fragilis*), Bryozoans, and cold-water corals. These reefs are often found in shallow waters and the formation of their structures consisting of $CaCO_3$ may lead to an increase in atmospheric carbon. However, biogenic reefs can themselves physically capture and retain organic carbon, thereby enhancing organic carbon deposition, possibly leading to burial, which could mitigate for the release of CO_2 during $CaCO_3$ formation (Lee et al., 2021; Lovelock and Duarte, 2019). In addition, they provide a host of other ecosystem services such as refugia for juvenile fish and can support a wide range of biodiversity. Hence biogenic reefs need separate consideration apart from that based just on their carbon content. The reefs are particularly vulnerable to disturbance by physical contact, including from demersal fishing gear, static seabed gear and vessel anchoring and further research is required to understand the implications with respect to changes in atmospheric CO_2

The potential role of ocean acidification

Some current studies are beginning to suggest that the current decrease in the pH of oceanic and coastal waters, referred to as ocean acidification, may be having an effect on the inorganic carbon chemistry of the sea. Ocean acidification is occurring because of human activities that have increased the CO_2 concentration in the atmosphere and the oceans (Laffoley et al., 2017). Raising CO_2 concentrations lead to more acidic seawater that is under-saturated with respect to $CaCO_3$ minerals, causing them to dissolve. However, the cause of $CaCO_3$ dissolution is not always simply an effect of ocean acidification. For example, Leon et al. (2019) have shown that larval gastropod shells have begun to show signs of dissolution in Scottish coastal waters. Could this be due to ocean acidification? We do not know. Although the shells are made from aragonite, a form of $CaCO_3$, the chemistry of the coastal waters in this region are always supersaturated in relation to aragonite, which means that the seawater chemistry is probably not the cause of their dissolution. Hence other processes must be at work which we do not yet fully understand. This area requires further research (Doo et al., 2020).

Summary

In summary, if organic carbon formed in the sea is eventually buried in seabed sediment it will contribute to reducing CO_2 in the atmosphere. Conversely, the creation of $CaCO_3$ structures by shellfish and corals, with the resulting changes to water chemistry, can potentially increase atmospheric CO_2 content. In the sedimentary environment, the dissolution of $CaCO_3$ structures could potentially decrease atmospheric greenhouse gas CO_2 content, while the microbial remineralisation of organic carbon can increase atmospheric greenhouse gas CO_2 content.

Taking into account these factors, we suggest that the role of inorganic carbon in discussions of blue carbon in relation to climate mitigation should be re-framed and clearly communicated, to avoid a risk that future policy and investment decisions may be taken on the basis of ambiguous interpretations in supporting evidence. Whilst there is clearly a need for further research and evidence to better understand the system dynamics (for example better understanding of the impacts and effects of disturbance and environmental changes on sedimentary inorganic carbon), we propose the following interim position:

- The distinction between organic and inorganic carbon should always be made clear in accounting for all estimates of blue carbon stocks.

- Whilst inorganic carbon locked into marine $CaCO_3$ is clearly a store of carbon, it should not be considered relevant to formal processes for carbon offsetting.

- Any figures for carbon sequestration rates relating to the creation of inorganic carbon (including shell material) should always be shown in context with related CO_2 release to highlight the net effect. In the absence of data quantifying the net effect of inorganic carbon sequestration, only organic carbon sequestration should be cited.

- Notwithstanding these caveats regarding inorganic carbon stores, biogenic habitats play an important role in trapping and storing organic carbon. These habitats also have very a high value for biodiversity, deliver a range of wider ecosystem services and require careful protection and management from various pressures for reasons other than climate mitigation.

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