Modelling seawater carbonate chemistry in shellfish aquaculture regions: insights into CO_2 release associated with shell formation and growth

JP Morris [1, ¥, *], MP Humphreys [2, 3, ¥, *]

[1] Royal Belgian Institute of Natural Sciences, Rue Vautier 29, 1000 Brussels, Belgium

[2] Centre for Ocean and Atmospheric Sciences, School of Environmental Sciences, University of East Anglia, Norwich NR4 7TJ, UK

[3] Ocean and Earth Science, University of Southampton, European Way, Southampton SO14 3ZH, UK

[¥] Authors contributed equally

* Corresponding authors

Abstract

Mollusc aquaculture is a high-value industry that is increasing production rapidly in Europe and across the globe. In recent years, there has been discussion of the potential wide-ranging environmental benefits of this form of food production. One aspect of mollusc aquaculture that has received scrutiny is the production of calcareous shells ($CaCO_3$). Mollusc shell growth has sometimes been described as a sink for atmospheric CO_2, as it locks away carbon in solid mineral form. However, more rigorous carbonate chemistry modelling, including concurrent changes in seawater pCO_2, pH, dissolved inorganic carbon, and total alkalinity, shows that calcification is a net CO_2 source to the atmosphere. Combined with discussions about whether mollusc respiration should be included in carbon footprint modelling, this suggests that greater in-depth understanding is required before shellfish aquaculture can be included in carbon trading schemes and footprint calculations. Here, we show that regional differences in the marine carbonate system can alter the amount of CO_2 released per unit $CaCO_3$ formation. Our carbonate chemistry modelling shows that a coastal mussel farm in southern Portugal releases up to ~0.290 g of CO_2 per g of $CaCO_3$ shell formed. In comparison, an identical farm in the coastal Baltic Sea would produce up to 33 % more CO_2 per g of $CaCO_3$ (~0.385 g-CO_2·(g-$CaCO_3$)$^{-1}$). This spatial

variability should therefore also be considered if mollusc aquaculture is to be included in future carbon trading schemes, and in planning future expansion of production across the industry.

1. Introduction

Aquaculture continues to expand its share of global marine food production by mass (FAO, 2016). Considering that marine fisheries production has stalled since the 1990s, the importance of aquaculture in future global food security is now well recognised (FAO, 2016; Godfray et al., 2010; Subasinghe et al., 2009). Molluscs represent a significant portion of our current aquaculture production, accounting for ~22% of the total global harvest, or 16.1 million tonnes by live weight in 2014 (FAO, 2016). Although global aquaculture production is currently dominated by East Asia, the EU also hosts a high value industry: in 2012, first sale value from aquaculture totalled €4.76 billion (thousand-million). Of this, molluscs made up 28 % of the total value (Bostock et al., 2016). Beyond production volume, when practiced sustainably, mollusc aquaculture is important because: 1) it does not require additional feed or freshwater input; 2) it provides a highly nutritious and proteinaceous food source; 3) simple culture techniques can negate the need for energy-intensive processes; and 4) in many respects (nutrient cycling, for instance), mollusc culture can be benign or even ecologically beneficial to the surrounding environment (Bostock et al., 2016; Klinger and Naylor, 2012; Shumway et al., 2003). Such considerations are necessary in light of energy and food security concerns, impending freshwater shortages, and an increasing human population (Bogardi et al., 2012; Ozturk et al., 2013). Shelled-mollusc aquaculture is part of a group of potentially sustainable and low-impact “food sources of the future” currently being advocated (Jacquet et al., 2017). Recent scientific and technological advances, such as the development of offshore farming (Buck et al., 2010), farming as part of an integrated multi-trophic aquaculture approach (Chopin et al., 2012; Granada et al., 2015), and land-based recirculating systems (Kuhn et al., 2013) hold potential for the further expansion of the sector. However, many aspects of mollusc aquaculture remain understudied. Our understanding of the potential environmental effects, both positive and negative, must keep pace with this rapidly growing sector in order to maintain its sustainability.

One aspect of shelled-mollusc aquaculture that is regularly overlooked is the effect of intensive cultivation on the local seawater carbonate system. Carbon dioxide (CO_2), the marine carbon cycle, and ocean acidification (OA) have been intensely scrutinized by climate change researchers (IPCC, 2014), and their implications for the growth of calcareous-shell-producing organisms is now taken into account both by researchers and the aquaculture industry alike (Ellis et al., 2016; Scanes et al., 2017). However, biogenic calcium carbonate ($CaCO_3$) formation, the energetics of the calcification process, and heterotrophic consumption/respiration all influence localised carbonate chemistry as well, and their complex coupled interactions are not well understood in the context of aquaculture.

Some in the aquaculture industry have suggested that shelled-mollusc growth may be a CO_2 sink process (i.e. driving net removal of carbon from the atmosphere and storing it in $CaCO_3$ shells) (e.g. Hickey, 2009; Pi-hai et al., 2014; Tang et al., 2011). However, it is well established that $CaCO_3$ formation is actually a CO_2 source (e.g. Frankignoulle *et al.* 1994; Gattuso *et al.* 1995; Humphreys *et al.* 2018), which is exacerbated from a whole-organism perspective by respiration. Mollusc cultivation is therefore a net CO_2 source process, as highlighted by recent aquaculture-specific research (Mistri and Munari, 2013, 2012; Munari et al., 2013; Wang et al., 2016). The effects of intensive mollusc aquaculture on carbon cycling have also been considered at an integrated ecosystem level by Filgueira *et al.* (2015). Filgueira and colleagues suggest separating tissue and shell production when considering the CO_2 fluxes of mollusc cultivation, thus allow for the potential inclusion of shell production in carbon trading schemes. In this case, CO_2 sources arising from tissue production are considered a function of food production, whilst $CaCO_3$ shell production is considered a by-product.

Here, we apply a marine carbonate system model to further our understanding of the carbonate chemistry changes associated specifically with calcification during mollusc aquaculture. Where previous studies have targeted individual sites, we consider the generalised effects of mussel cultivation, focussing on four major *Mytilus* sp. aquaculture regions in Western Europe. We use blue mussels as our focus species because of the prevalence of their cultivation across latitudinal gradients in Western Europe. However, our model is relevant to all commercial bivalve molluscs, and our results are generically applicable to all calcification. We aim to determine whether abiotic marine carbonate system variables significantly affect the carbon footprint of the mussel shell growth process. A better understanding of the spatial variation in CO_2 dynamics associated with mollusc calcification can be used to determine sites that are likely to have a greater or lesser environmental impact, from a CO_2 perspective. Furthermore, with a growing interest in seawater alkalinisation methods as a potential mitigation strategy for on-going OA (Hartmann et al., 2013; Rau, 2014; Royal-Society, 2009; Vaughan and Lenton, 2011; Renworth and Henderson, 2017) and the concurrent increasing understanding of the importance of circular economy thinking, we comment on the seeding of powdered shell-waste as a pH buffering mechanism. We discuss whether this could ameliorate the effects of CO_2 released by mollusc cultivation, thus providing a sustainable solution to the industry's shell waste problem (Morris et al., 2018).

2. Materials and methods

2.1 Calcification, respiration, and CO_2

In seawater, dissolved inorganic carbon (DIC) is the sum of the concentrations of aqueous CO_2 and the bicarbonate and carbonate ions that it reacts to form (Zeebe and Wolf-Gladrow, 2001). Total alkalinity (TA) quantifies the capacity for seawater to store DIC in equilibrium with a given atmospheric partial pressure of CO_2 (pCO_2). The seawater pCO_2 can be calculated from DIC and TA, and is equal to the atmospheric pCO_2 that would be in equilibrium with a given seawater sample. The difference between the seawater and atmospheric pCO_2 values is rarely equal to zero, and it drives the net direction of air-sea CO_2 exchange, with higher seawater values leading to net sea-to-air CO_2 transfer

(Takahashi et al., 2009). A process that takes up DIC, and/or increases seawater TA, therefore decreases the seawater pCO_2 and drives a compensatory CO_2 flux from the atmosphere into the ocean. Such a process is considered a CO_2 'sink'. On the other hand, a process that increases DIC, and/or decreases TA, increases the seawater pCO_2. This promotes sea-to-air CO_2 transfer and can thus be described as a CO_2 'source'. Calcification (i.e. $CaCO_3$ formation) takes up both TA and DIC from seawater, in a 2:1 stoichiometric ratio (Wolf-Gladrow et al., 2007). The CO_2 source effect from TA loss is greater than the CO_2 sink effect from DIC loss, leading to an overall increase in seawater pCO_2 and thus a net CO_2 source. The source's magnitude can be quantified as a function of the underlying seawater chemistry (Frankignoulle et al., 1994; Humphreys et al., 2018). Conversely, $CaCO_3$ dissolution increases the capacity for seawater to store CO_2 by increasing TA, but the associated DIC increase only partially fills this additional capacity, leaving a deficit that can drive CO_2 uptake from the atmosphere.

The size of the potential CO_2 source driven by calcification can be quantified from the seawater temperature, salinity, and carbonate chemistry using the parameter Φ (Humphreys et al., 2018). Numerically, Φ is equal to the additional reduction in DIC required, relative to the amount of DIC converted into $CaCO_3$, such that there would be no net change in seawater pCO_2. We can therefore consider Φ to represent the potential amount of CO_2 released by mollusc calcification. We use the word 'potential' because while the uptake of DIC and TA instantaneously sets up the pCO_2 gradient required to drive air-sea CO_2 exchange, the actual CO_2 exchange process takes on the order of months to a year to re-equilibrate the surface ocean mixed layer following a perturbation (Jones et al., 2014). The absolute size of the CO_2 sink driven by $CaCO_3$ dissolution is also equal to Φ.

More intuitively than calcification, respiration acts as a CO_2 source. This process releases CO_2 into seawater, thus increasing DIC. Conversely, autotrophic production is a CO_2 sink. The relatively small TA changes associated with these processes (Wolf-Gladrow et al.,

2007) are synergistic with the DIC change in terms of their effect on the seawater acting as a CO_2 source or sink.

2.2 Data

We merged DIC, TA and auxiliary measurements from the Global Ocean Data Analysis Project version 2 (GLODAPv2) dataset (Olsen et al., 2016), results from the UK Shelf Sea Biogeochemistry research programme (UK-SSB) (Humphreys et al., *in press.*; Hartman et al., *in press.*), and measurements from the Boknis Eck coastal time series site (KBE) near Kiel, Germany (Lennartz *et al.* 2014; Steinhoff and Bange *unpublished data*: available from https://www.bokniseck.de/database-access). We selected only the data falling within 150 km of the continental coastline and shallower than 20 m (Fig. 1) for our analysis.

We focussed our analysis on four regions across Western Europe where molluscs are cultivated (Table 1, Fig. 1). “West Scotland” is near the Isle of Mull in the Inner Hebrides of the UK. The “Baltic” site is in the western Baltic Sea near Kiel (Germany), and lies within 5 km of the coast. “Galicia” and “Algarve” fall in the eastern North Atlantic, off the coast of Spain (near Vigo) and Portugal (near Faro) respectively.

2.3 Calculations

We used version 1.1 of CO_2SYS for MATLAB (van Heuven et al., 2011) to calculate the seawater partial pressure of CO_2 (pCO_2) from the TA and DIC measurements, using the carbonic acid and bisulfate equilibrium constants of Lueker et al. (2000) and Dickson (1990) respectively, and the boron:chlorinity of Lee et al. (2010). We then adjusted these seawater pCO_2 values to the year 2020, assuming a constant anthropogenic increase at a rate of 1.61 $\mu atm \cdot yr^{-1}$ (Tjiputra et al., 2014), and used CO_2SYS to recalculate DIC and all other marine carbonate system variables from the original TA and adjusted seawater pCO_2. This adjusted dataset was used for all subsequent analysis.

We calculated Φ following Humphreys *et al.* (2018) using code freely available online at https://github.com/mvdh7/biogeochem-phi. The default units of Φ are moles of CO_2 released per mole of $CaCO_3$ formed. We thus converted into units of ‘grams per gram’ by multiplying Φ by a factor of 0.440, which is the ratio of the relative molecular masses of CO_2 and $CaCO_3$ (i.e. 44.01 $g \cdot mol^{-1}$ / 100.0869 $g \cdot mol^{-1}$). The value of Φ shows CO_2 release for calcification only; the total CO_2 released by mussels will be greater still due to respiration, but this is not included in the calculation of Φ.

3. Results

To first order, the amount of CO_2 generated by calcification (i.e. Φ) around the European Atlantic coast is positively correlated with latitude, in the range from about 0.27 to 0.42 g-CO_2·(g-$CaCO_3$)$^{-1}$ (Fig. 2). This Φ distribution is dominantly controlled by the seawater temperature and its pCO_2, with the amount of CO_2 released by calcification being greater in colder waters and/or where seawater pCO_2 greater (Humphreys et al., 2018). Formation of $CaCO_3$ therefore generally releases more CO_2 as the calcification site moves polewards into colder waters. The first-order carbonate chemistry and Φ distributions are further modulated by smaller-scale processes, particularly in hydrographically and biogeochemically complex continental shelf sea, near-coastal and estuarine environments. For example, riverine and sedimentary inputs have been shown to elevate TA in continental shelf seas (e.g. Thomas *et al.* 2009; McGrath *et al.* 2016), thus decreasing Φ. Similar effects are particularly noticeable at Kiel, driving high variability in Φ there.

On the Algarve, our southernmost study site, 0.290 ± 0.009 g of CO_2 is released per g of $CaCO_3$ formed. Relative to the Algarve, Φ increases by 3% at Galicia to 0.298 ± 0.007 g-CO_2· (g-$CaCO_3$) $^{-1}$, and by 10% in West Scotland to 0.317 ± 0.023 g-CO_2· (g-$CaCO_3$) $^{-1}$. Lower still TA at the Baltic site, driven by riverine and brackish Baltic Sea influences (Hjalmarsson et al., 2008), increases Φ there by 33% relative to the Algarve, to 0.385 ± 0.042 g-CO_2·(g-$CaCO_3$)$^{-1}$. The ± values for Φ are the standard deviation at each site, and they indicate real variability in Φ due to variability in its drivers, rather than being an estimate of measurement uncertainty. It is important to note that although mussel aquaculture installations in the Algarve sit up to 4 km off the adjacent coastline (DGRM, 2016), and some aquaculture installations in the Baltic float 1 km off the coast (e.g. Lyngsgaard et al., 2017), sites in Galicia and Scotland are typically closer to the coastline and estuaries than the carbonate system dataset that we used. Consequently, it is likely that CO_2 release by shellfish in this region has greater variability than modelled and indicated in Fig. 2, in particular due to freshwater inputs. However, with a growing interest in the movement of aquaculture offshore, and projects underway to expand aquaculture offshore from Portugal (DGRM, 2016) to the North Sea (Buck et al., 2017), all of our chosen sites provide insights for potential future zones of exploitation by the aquaculture industry despite localised limitations in carbonate system data coverage for some current culturing activities.

An important component of the variability in Φ is seasonal (Fig. 3). All of this variability is captured at the Baltic site, where the dataset covers the entire seasonal range. Data are more sparse at the West Scotland site, but still there are samples there representing the full seasonal range. At Galicia and Algarve, the data are more biased towards the summer months, so there could be greater variability in Φ at these sites than indicated in Fig. 2. However, this is not expected to be significant, as follows. Galicia and Algarve are in a part of the Atlantic Ocean where the seasonal cycle of seawater $p\text{CO}_2$ is dominantly controlled by temperature (Takahashi et al., 2009). This causes these variables to have opposing effects on Φ that roughly cancel each other out, leading to a relatively small amplitude seasonal cycle for Φ itself (Humphreys et al., 2018).

Tissue-to-shell ratios in mussels vary widely according to phenotype as well as other biotic and abiotic factors. Meat yield (MY) is an established market index for mussels, expressed as the percentage wet meat yield of total live weight. It has been shown to be seasonally variable, but averaged 25% in Scottish mussels (Okumuş & Stirling, 1998), and 31% in Galician mussels (Fuentes et al., 2009). So, assuming a 1:3 ratio by mass when harvested, then ~870 to 1200 g of CO_2 could be released by calcification from seawater to the atmosphere for each kilogram of meat produced. This is additional to the net CO_2 that the mussels release through respiration. This CO_2 release could increase slightly in the future, as Φ is expected to increase with $p\text{CO}_2$ (Humphreys et al., 2018). Indeed, calcification is known to act as a positive feedback on atmospheric $p\text{CO}_2$ (Frankignoulle et al., 1994), with the magnitude of the feedback modulated by simultaneous seawater warming (Humphreys, 2017).

4. Discussion

While many in the aquaculture industry had previously considered mollusc cultivation to be a CO_2 sink process due to the sequestration of carbon as mineral $CaCO_3$, Munari and colleagues (2013) highlighted the importance of considering CO_2 fluxes associated with mollusc cultivation as a balance between the abiotic formation of $CaCO_3$ and the energetic processes of respiration and calcification. Munari and colleagues calculated that a mussel farm in Italy acts as a CO_2 source, and therefore could not be considered as a carbon credit-producing process in carbon trading schemes. In contrast, Filgueira *et al.* (2015) suggested that mollusc aquaculture should be considered at an integrated ecosystem level, and that benthic-pelagic interactions and phytoplankton dynamics should be included in carbon budget estimates. In this way, secondary effects of mollusc cultivation such as enhanced primary productivity and nutrient cycling could ameliorate the carbon source processes of mollusc growth. Further, Filgueira and colleagues (2015) discussed the concept of separating the process of proteinaceous food production, and the generation of shells as a by-product, focussing on the key ecosystem service that mollusc culture provides. Indeed, it is common practice in industry life cycle analysis (LCA) protocols not to include respiration in calculations of the carbon footprint of bio-derived materials if they are a secondary product of a process (Aubin et al., 2018). Both approaches offer insight into the environmental effects of mollusc aquaculture at a time when the practice is undergoing rapid expansion. A whole-ecosystem approach provides a broader picture but is inherently more difficult to study and likely to be non-comparable between different locations. A whole-organism approach provides a well-constrained understanding of the carbon dynamics of a single species within a system, but might provide ambiguous conclusions for broader decision making in the industry.

In this study, we explored the extent to which natural geographical gradients in the chemical and physical properties of seawater can alter the net CO_2 released by calcification at four different aquaculture production regions in Western Europe, to highlight how the geographical location of farms influences their impact on the carbon cycle. The novelty of this study is the consideration of the CO_2 source dynamics of a mollusc aquaculture site as a function of its location and that locale's specific water chemistry. We found a significant difference (up to 33 %) in the amount of CO_2 produced per g of $CaCO_3$ formed between the four sites selected in this study. The trend follows generalised latitudinal and temperature patterns and shows that for an identical mussel farm in each of the four locations, the colder, more northerly Baltic site, as an example, acts as a stronger CO_2 source than the warmer, more southerly Algarve site. Although this study focusses on mussel aquaculture, our results are equally applicable to other commercial bivalve mollusc species such as scallops, oysters, clams, and indeed any calcifying species. We have thus highlighted how the state of the seawater carbonate system controls the CO_2 release associated with $CaCO_3$ formation (i.e. shell formation and growth), and we have shown for the first time how the geographical location of shellfish aquaculture sites can influence the calcification-driven CO_2 source magnitude. This variability is driven primarily by surface ocean patterns of seawater temperature and $p\text{CO}_2$, with colder, higher latitude farms exhibiting greater potential CO_2 release.

It is important to emphasise that we consider only the effect of calcification itself. CO_2 release is additionally influenced by respiration, feeding dynamics, and growth rate of mussels, which are not expected to be identical in different locations. Rather, these processes are also partly dependent on temperature, as well as other biotic and abiotic factors. Furthermore, the blue mussel complex (*Mytilus sp.*) contains three closely related "sub"-species that readily hybridise with each other where population ranges overlap (Michalek et al., 2016). At the Baltic and West Scotland sites, *Mytilus edulis* dominates, but the southern range of *Mytilus trossulus* overlaps, and hybridisation has been noted in the Baltic Sea (Stuckas *et al.* 2017) and the Norwegian North Sea coastline (Śmietanka and Burzyński, 2017). At the Galicia and Algarve sites, *Mytilus galloprovincialis* is the principal species; however, the southern range of *Mytilus edulis* extends over both areas and hybridisation is a possibility in local natural and farmed populations (Daguin et al., 2001). Again, growth, feeding, and respiration rates can be partly a function of the particular *Mytilus* species or hybrid considered. These factors highlight the complexity of comparing biological variance over the large geographic range considered in this study. Combined with the chemical variability in the effect of calcification on air-sea CO_2 exchange, this illustrates the complexity of evaluating (for carbon trading purposes) the key potential ecosystem service of carbon sequestration that has been cited in relation to mollusc aquaculture.

The primary function of shellfish aquaculture installations is food provision. In recent years, as discussions of global food security issues have gained volume, shellfish aquaculture has been branded as a sustainable food source of the future by many because it does not rely on feed or freshwater input, and can act in other environmentally positive ways (e.g. nutrient and water clarity control). Carbon and nutrient dynamics have also been discussed in relation to shellfish aquaculture and its potential inclusion in carbon and nutrient trading schemes. Our results illustrate how the location of mussel farms could influence their potential value in carbon trading schemes. In addition, shelled molluscs are known, in general, to be particularly sensitive to lowering seawater pH (Parker et al., 2013). Ocean acidification is of increasing concern globally, and its impacts on current and future shellfish cultivation will require co-ordinated national and international action (Ekstrom et al., 2015). In view of OA vulnerability, and the results presented here, planning of shellfish aquaculture sites must incorporate area-specific carbonate chemistry considerations. If aquaculture, and its mollusc component, are to continue market expansion as predicted and advocated for (European Commission, 2012), then international collaboration and broad-scale location planning will play an increasingly important role. Our results show that marine carbonate system variables should be included in the list of parameters for consideration in this context.

An understanding of regionally variable seawater carbonate chemistry changes associated with mollusc farming can provide information relevant to potential CO_2 sequestration techniques. For instance, calcification-driven CO_2 release during mollusc growth could be reversed if the $CaCO_3$ shells were dissolved back into the seawater following harvesting. This process may begin to occur naturally if low-alkalinity terrestrial inputs and/or ocean acidification render $CaCO_3$ minerals undersaturated in coastal regions. Any in situ $CaCO_3$ dissolution at a mussel site due to low $CaCO_3$ saturation states (for example resulting from low-alkalinity riverine inputs) would reduce the net amount of $CaCO_3$ formed per mussel and thus the total amount of CO_2 released. Dissolution would not alter the amount of CO_2 released per net unit $CaCO_3$ formed. Indeed, on timescales of whole-ocean mixing or longer (i.e. hundreds to thousands of years), dissolution of deep-sea $CaCO_3$ sediments may naturally buffer the anthropogenic increase in atmospheric CO_2 (Archer, 2005). The main insight added by our results is that CO_2 taken up by this dissolution would vary between the different sites, and would be equal and opposite to the amount of CO_2 released by calcification at the same site. Artificial acceleration of the dissolution process to mitigate CO_2-driven climate change has been investigated, by supplying ground-up minerals that increase TA (e.g. $CaCO_3$) to the surface ocean (Feng et al., 2017; Köhler et al., 2010). However, the forms of $CaCO_3$ produced by mussels (calcite outer-layer and aragonite inner-layer) are relatively insoluble, and $CaCO_3$ is oversaturated throughout much of the global surface ocean (Takahashi et al., 2014). There is no reason to expect even powdered $CaCO_3$ to dissolve in oversaturated seawater (Morse et al., 2007). Indeed, added particles could even act as nuclei promoting abiotic precipitation of $CaCO_3$ and thus further CO_2 release. Possible workarounds have been suggested in which mussel shell $CaCO_3$ dissolution could be enhanced in a collected volume of seawater, for example through acidification by addition of CO_2, or using electrochemical techniques (Rau, 2008; Rau and Caldeira, 1999; Renworth and Henderson, 2017). Once dissolved, the mussel shells would have increased the seawater's TA, thus enabling it to retain higher DIC at atmospheric equilibrium after being released back into the ocean. Of course, a panoply of associated technical challenges would need to be carefully studied before any large-scale application. The "real-world" efficacy of these approaches remain uncertain, and their application controversial.

5. Conclusions

The process of calcification, for example as carried out by mussels to form their $CaCO_3$ shells, acts as a net source of CO_2 to the atmosphere. Natural spatial variability in seawater temperature and in the marine carbonate system causes $CaCO_3$ formation to release different amounts of CO_2 in different geographical locations. To first order, more CO_2 is released from calcification in colder waters; for our four study sites in western Europe, the CO_2 released per unit calcification increases by 33 % from the southernmost site (Algarve, Portugal) to the northernmost (Baltic, Germany). Additional CO_2 is released by mussel respiration. The amount of CO_2 release by actual mussel farms may vary further still, as different species – and even the same species in different environments – may form different amounts of $CaCO_3$ in producing the same amount of harvestable food. We discussed our results primarily in the context of mussels because of the prevalence of their cultivation in Western Europe. However, our findings are equally relevant to the wider bivalve mollusc aquaculture industry, and they hold true for all calcifying molluscs including oysters, scallops, and clams. Our results have important implications for determining the potential value of shellfish aquaculture in carbon trading schemes, and should be considered when planning locations for new mussel farms.

Acknowledgements

JPM was funded by the European Union Seventh Framework Programme through grant No.605051 - Marie Skłodowska-Curie actions CACHE-ITN “Calcium in a Changing Environment” http://www.cache-itn.eu/. MPH was funded by the Natural Environment Research Council (UK) through “A Thermodynamic Chemical Speciation Model for the Oceans, Seas, and Estuaries” (NE/P012361/1) and “CaNDyFloSS: Carbon and Nutrient Dynamics and Fluxes over Shelf Systems” (NE/K00185X/1).

We thank Hermann Bange for assistance accessing the Boknis Eck time series dataset.

Contributions

JPM devised the concept with advice from MPH. MPH performed the data analysis and modelling. JPM and MPH wrote the article together.

Figures

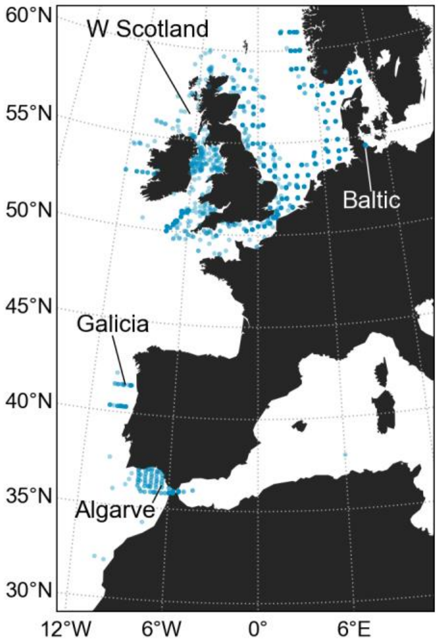

Figure 1. Distribution of the merged GLODAPv2 + UK-SSB + KBE dataset within 150 km of the continental coastline and shallower than 20 m, and locations of our four case study sites. Individual data points are semi-transparent, so darker colours indicate multiple measurements at the same location.

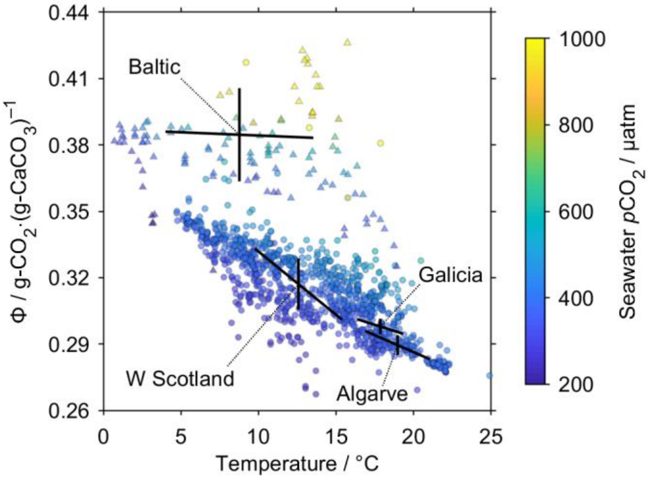

Figure 2. Potential CO_2 released per gram of DIC converted to $CaCO_3$ (i.e. Φ) for our entire combined dataset (Fig. 1), as a function of seawater temperature and seawater pCO_2. Triangles show data from the Baltic site, while all other data points are circles. Black crosses are centred on the mean values for each study site, and show one standard deviation of the principal components of all data at each site. The Algarve and Galicia have low Φ with small variability, due to their high temperature and relatively constant pCO_2. High pCO_2 and low temperature at the Baltic site drive a high mean Φ there, and high variability in both input variable drives a wide range in Φ. West Scotland occupies an intermediate Φ state with intermediate variability.

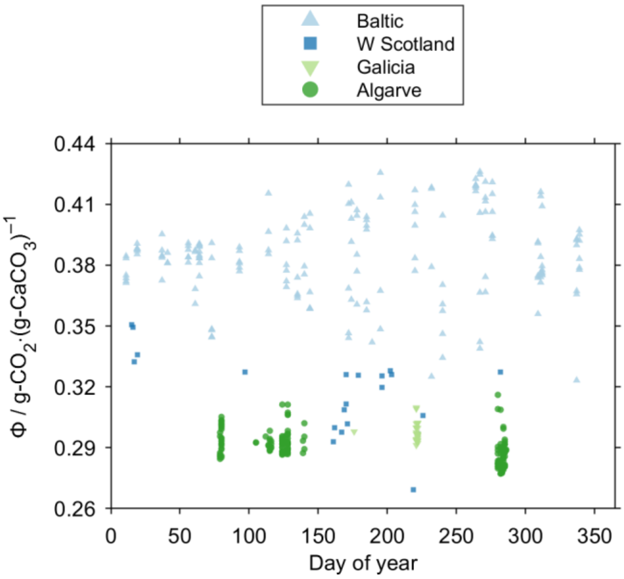

Figure 3. Potential CO_2 released per gram of DIC converted to $CaCO_3$ (i.e. Φ) for our entire combined dataset (Figs. 1 and 2), as a function of the day of the year. High-resolution sampling at the Baltic site reveals the full seasonal cycle there. West Scotland was sampled at lower resolution, but still the full range of seasons is represented. Galicia and Algarve are biased to the summer months, but little seasonal Φ variability is expected at these sites (see main text; also discussion by Humphreys et al., 2018).

Tables

Table 1. Locations and summary statistics for our four study sites.

Site	Location	SST* / °C	Φ* / g-CO_2·(g-$CaCO_3$)$^{-1}$
West Scotland	56.45°N, 6.71°W	12.6 ± 5.6	0.317 ± 0.023
Baltic	54.52°N, 10.04°E	8.8 ± 9.5	0.385 ± 0.042
Galicia	41.52°N, 9.65°W	17.8 ± 3.0	0.298 ± 0.007
Algarve	36.21°N, 6.51°W	19.0 ± 4.2	0.290 ± 0.009

*Mean ± 2 standard deviations, indicating natural variability rather than measurement uncertainty.

References

Archer, D., 2005. Fate of fossil fuel CO_2 in geologic time. J. Geophys. Res. 110, C09S05. https://doi.org/10.1029/2004JC002625

Aubin, J., Fontaine, C., Callier, M., Roque D'Orbcastel, E., 2018. Blue mussel (*Mytilus edulis*) bouchot culture in Mont-St Michel Bay: potential mitigation effects on climate change and eutrophication. Int. J. Life Cycle Assess. 1–12. https://doi.org/10.1007/s11367-017-1403-y

Bogardi, J.J., Dudgeon, D., Lawford, R., Flinkerbusch, E., Meyn, A., Pahl-Wostl, C., Vielhauer, K., Vörösmarty, C., 2012. Water security for a planet under pressure: Interconnected challenges of a changing world call for sustainable solutions. Curr. Opin. Environ. Sustain. 4, 35–43. https://doi.org/10.1016/j.cosust.2011.12.002

Bostock, J., Lane, A., Hough, C., Yamamoto, K., 2016. An assessment of the economic contribution of EU aquaculture production and the influence of policies for its sustainable development. Aquac. Int. 24, 699–733. https://doi.org/10.1007/s10499-016-9992-1

Buck, B.H., Ebeling, M.W., Michler-Cieluch, T., 2010. Mussel cultivation as a co-use in offshore wind farms: potential and economic feasibility. Aquac. Econ. Manag. 14, 255–281. https://doi.org/10.1080/13657305.2010.526018

Buck, B,H., Nevejan, N., Wille, M., Chambers, M.D., Chopin, T., 2017. Offshore and Multi-Use Aquaculture with Extractive Species: Seaweeds and Bivalves. In: Buck, B., Langan, R., (eds) Aquaculture Perspective of Multi-Use Sites in the Open Ocean. 23-69. https://doi.org/10.1007/978-3-319-51159-7_2

Chopin, T., Cooper, J.A., Reid, G., Cross, S., Moore, C., 2012. Open-water integrated multi-trophic aquaculture: Environmental biomitigation and economic diversification of fed aquaculture by extractive aquaculture. Rev. Aquac. 4, 209–220. https://doi.org/10.1111/j.1753-5131.2012.01074.x

Daguin, C., Bonhomme, F., Borsa, P., 2001. The zone of sympatry and hybridization of *Mytilus edulis* and *M. galloprovincialis*, as described by intron length polymorphism at locus mac-1. Heredity. 86, 342–354. https://doi.org/10.1046/j.1365-2540.2001.00832.x

DGRM (Direção-Geral de Recursos Naturais, Segurança e Serviços Marítimos Portugal)., 2016. Interactive map available at: http://eaquicultura.pt/navegue-pelo-mapa-da-aquicultura-em-portugal/ Accessed on: 06/09/2018

Dickson, A.G., 1990. Standard potential of the reaction: $AgCl_{(s)}$ + 0.5 $H_{2(g)}$ = $Ag_{(s)}$ + $HCl_{(aq)}$, and the standard acidity constant of the ion HSO^{4-} in synthetic sea water from 273.15 to 318.15 K. J. Chem. Thermodyn. 22, 113–127. https://doi.org/10.1016/0021-9614(90)90074-Z

Ekstrom, J.A., Suatoni, L., Cooley, S.R., Pendleton, L.H., Waldbusser, G.G., Cinner, J.E., Ritter, J., Langdon, C., van Hooidonk, R., Gledhill, D., Wellman, K., Beck, M.W., Brander, L.M., Rittschof, D., Doherty, C., Edwards, P.E.T., Portela, R., 2015. Vulnerability and adaptation of US shellfisheries to ocean acidification. Nat. Clim. Chang. 5, 207–214. https://doi.org/10.1038/nclimate2508

Ellis, R.P., Urbina, M.A., Wilson, R.W., 2016. Lessons from two high CO_2 worlds - future oceans and intensive aquaculture. Glob. Chang. Biol. 2100, 1–8. https://doi.org/10.1111/gcb.13515

European Commission, 2012. Blue Growth - Opportunities for marine and maritime sustainable growth. https://doi.org/10.2771/43949 Accessed on 06/09/18

FAO, 2016. The state of world fisheries and aquaculture. http://www.fao.org/3/a-i5555e.pdf Accessed on 06/09/18

Feng, E.Y., Koeve, W., Keller, D.P., Oschlies, A., 2017. Model-based assessment of the CO_2 sequestration potential of coastal ocean alkalinization Earth's Future. 5, 1252–1266. https://doi.org/10.1002/2017EF000659

Filgueira, R., Byron, C.J., Comeau, L.A., Costa-Pierce, B., Cranford, P.J., Ferreira, J.G., Grant, J., Guyondet, T., Jansen, H.M., Landry, T., McKindsey, C.W., Petersen, J.K., Reid, G.K., Robinson, S.M.C., Smaal, A., Sonier, R., Strand, Strohmeier, T., 2015. An integrated ecosystem approach for assessing the potential role of cultivated bivalve shells as part of the carbon trading system. Mar. Ecol. Prog. Ser. 518, 281–287. https://doi.org/10.3354/meps11048

Frankignoulle, M., Canon, C., Gattuso, J.P., 1994. Marine calcification as a source of carbon dioxide: Positive feedback of increasing atmospheric CO_2. Limnol. Oceanogr. 39, 458–462. https://doi.org/10.4319/lo.1994.39.2.0458

Fuentes, A., Fernández-Segovia, I., Escriche, I., Serra, J.A., 2009. Comparison of physico-chemical parameters and composition of mussels (*Mytilus galloprovincialis* Lmk.) from different Spanish origins. Food Chem. 112, 295–302. https://doi.org/10.1016/j.foodchem.2008.05.064

Gattuso, J.P., Pichon, M., Frankignoulle, M., 1995. Biological control of air-sea CO_2 fluxes: effects of photosynthetic and calcifying marine organisms and ecosystems. Mar. Ecol. Prog. Ser. 129, 307–312. https://doi.org/10.3354/meps129307

Godfray, H.C.J., Beddington, J.R., Crute, I.R., Haddad, L., Lawrence, D., Muir, J.F., Pretty, J., Robinson, S., Thomas, S.M., Toulmin, C., 2010. Food security: The challenge of feeding 9 billion people. Science (80). 327, 812–818. https://doi.org/10.1126/science.1185383

Granada, L., Sousa, N., Lopes, S., Lemos, M.F.L., 2015. Is integrated multitrophic aquaculture the solution to the sectors' major challenges? - a review. Rev. Aquac. 6, 1–18. https://doi.org/10.1111/raq.12093

Hartman, S., Humphreys, M., Kivimäe, C., Woodward, M., Kitidis, V., McGrath, T., Hydes, D., Greenwood, N., Ostle, C., Pearce, D., Sivyer, D., Stewart, B., Walsham, P., McGovern, E., Harris, C., Griffiths, A., Smilenova, A., Clarke, J., Davis, C., Nightingale, P., *In press*.

Seasonality and spatial heterogeneity of the surface water carbonate system on the NW European shelf. Prog. Oceanogr. https://doi.org/10.1016/j.pocean.2018.05.001

Hartmann, J., West, A.J., Renforth, P., Köhler, P., Rocha, C.L.D. La, Wolf-Gladrow, D.A, Dürr, H.H., Scheffran, J., 2013. Enhanced chemical weathering as a geoengineering strategy to reduce atmospheric carbon dioxide, supply nutrients, and mitigate ocean acidification. Rev. Geophys. 51, 113–149. https://doi.org/10.1002/rog.20004.1.Institute

Hickey, J., 2009. Carbon sequestration potential of shellfish. http://www.thefishsite.com/articles/615/carbon-sequestration-potential-of-shellfish/ Accessed on 06/09/2018

Hjalmarsson, S., Wesslander, K., Anderson, L.G., Omstedt, A., Perttilä, M., Mintrop, L., 2008. Distribution, long-term development and mass balance calculation of total alkalinity in the Baltic Sea. Cont. Shelf Res. 28, 593–601. https://doi.org/10.1016/j.csr.2007.11.010

Humphreys, M.P., 2017. Climate sensitivity and the rate of ocean acidification: future impacts, and implications for experimental design. ICES J. Mar. Sci. 74, 934–940. https://doi.org/10.1093/icesjms/fsw189

Humphreys, M.P., Achterberg, E.P., Chowdhury, M.Z.H., Griffiths, A.M., Hartman, S.E., Hopkins, J.E., Hull, T., Kivimäe, C., Smilenova, A., Wihsgott, J., Woodward, E.M.S., Moore, C.M., *in press*. Mechanisms for a nutrient-conserving carbon pump in a seasonally stratified, temperate continental shelf sea. Prog. Oceanogr. https://doi.org/10.1016/j.pocean.2018.05.001

Humphreys, M.P., Daniels, C.J., Wolf-Gladrow, D.A., Tyrrell, T., Achterberg, E.P., 2018. On the influence of marine biogeochemical processes over CO_2 exchange between the atmosphere and ocean. Mar. Chem. 199, 1–11. https://doi.org/10.1016/j.marchem.2017.12.006

IPCC., 2014: Climate Change 2014: Synthesis Report. Contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change, in: IPCC, 2014: Climate Change. http://www.ipcc.ch/report/ar5/syr/ Accessed on 17/06/2018

Jacquet, J., Sebo, J., Elder, M., 2017. Seafood in the future: Bivalves are better. Solut. J. 8, 27–32. https://www.thesolutionsjournal.com/article/seafood-future-bivalves-better/

Jones, D.C., Ito, T., Takano, Y., Hsu, W.C., 2014. Spatial and seasonal variability of the air-sea equilibration timescale of carbon dioxide. Global Biogeochem. Cycles 28, 1163–1178. https://doi.org/10.1002/2014GB004813

Klinger, D., Naylor, R., 2012. Searching for solutions in aquaculture: charting a sustainable course. Annu. Rev. Environ. Resour. 37, 247–276. https://doi.org/10.1146/annurev-environ-021111-161531

Köhler, P., Hartmann, J., Wolf-Gladrow, D.A., 2010. Geoengineering potential of artificially enhanced silicate weathering of olivine. Proc. Natl. Acad. Sci. U.S.A. 107, 20228–20233. https://doi.org/10.1073/pnas.1000545107

Kuhn, D.D., Angier, M.W., Barbour, S.L., Smith, S.A., Flick, G.J., 2013. Culture feasibility of eastern oysters (*Crassostrea virginica*) in zero-water exchange recirculating aquaculture systems using synthetically derived seawater and live feeds. Aquac. Eng. 54, 45–48. https://doi.org/10.1016/j.aquaeng.2012.10.008

Lee, K., Kim, T.W., Byrne, R.H., Millero, F.J., Feely, R.A., Liu, Y.-M., 2010. The universal ratio of boron to chlorinity for the North Pacific and North Atlantic oceans. Geochim. Cosmochim. Acta 74, 1801–1811. https://doi.org/10.1016/j.gca.2009.12.027

Lennartz, S.T., Lehmann, A., Herrford, J., Malien, F., Hansen, H.P., Biester, H., Bange, H.W., 2014. Long-term trends at the Boknis Eck time series station (Baltic Sea), 1957-2013: Does climate change counteract the decline in eutrophication? Biogeosciences 11, 6323–6339. https://doi.org/10.5194/bg-11-6323-2014

Lueker, T.J., Dickson, A.G., Keeling, C.D., 2000. Ocean pCO_2 calculated from dissolved inorganic carbon, alkalinity, and equations for K1 and K2: validation based on laboratory measurements of CO_2 in gas and seawater at equilibrium. Mar. Chem. 70, 105–119. https://doi.org/10.1016/S0304-4203(00)00022-0

Lyngsgaard, M.M., Svensson, H., Carl, J.D., Dolmer, P., Wallach, T., Leibach, A., 2017. Substrate test at Musholm 2016: Mussel growth in the western Baltic sea. Submariner network report: available at: https://www.submariner-network.eu/images/projects/bbg/reports/BalticBlueGrowth_Substrate_test_Musholm2016.pdf Accessed on: 06/09/2018.

McGrath, T., McGovern, E., Cave, R.R., Kivimäe, C., 2016. The Inorganic Carbon Chemistry in Coastal and Shelf Waters Around Ireland. Estuaries and Coasts 39, 27–39. https://doi.org/10.1007/s12237-015-9950-6

Michalek, K., Ventura, A., Sanders, T., 2016. *Mytilus* hybridisation and impact on aquaculture: A minireview. Mar. Genomics 27, 3–7. https://doi.org/10.1016/j.margen.2016.04.008

Mistri, M., Munari, C., 2013. The invasive bag mussel *Arcuatula senhousia* is a CO_2 generator in near-shore coastal ecosystems. J. Exp. Mar. Bio. Ecol. 440, 164–168. https://doi.org/10.1016/j.jembe.2012.11.019

Mistri, M., Munari, C., 2012. Clam farming generates CO_2: A study case in the Marinetta lagoon (Italy). Mar. Pollut. Bull. 64, 2261–2264. https://doi.org/10.1016/j.marpolbul.2012.07.010

Morris, J.P., Backeljau, T., Chapelle, G., 2018. Shells from aquaculture: a valuable biomaterial, not a nuisance waste product. Rev. Aquacult. *early online* https://doi.org/10.1111/raq.12225

Morse, J.W., Arvidson, R.S., Lüttge, A., 2007. Calcium carbonate formation and dissolution. Chem. Rev. 107, 342–381. https://doi.org/10.1021/cr050358j

Munari, C., Rossetti, E., Mistri, M., 2013. Shell formation in cultivated bivalves cannot be part of carbon trading systems: A study case with *Mytilus galloprovincialis*. Mar. Environ. Res. 92, 264–267. https://doi.org/10.1016/j.marenvres.2013.10.006

Okumu, I., Stirling, H.P., 1998. Seasonal variations in the meat weight, condition index and biochemical composition of mussels *Mytilus edulis* L./ in suspended culture in two Scottish sea lochs. Aquaculture. 159, 249-261. https://doi.org/10.1016/S0044-8486(97)00206-8

Olsen, A., Key, R.M., Heuven, S. van, Lauvset, S.K., Velo, A., Lin, X., Schirnick, C., Kozyr, A., Tanhua, T., Hoppema, M., Jutterström, S., Steinfeldt, R., Jeansson, E., Ishii, M., Pérez, F.F., Suzuki, T., 2016. The Global Ocean Data Analysis Project version 2 (GLODAPv2) – an internally consistent data product for the world ocean. Earth Syst. Sci. Data 8, 297–323. https://doi.org/10.5194/essd-8-297-2016

Ozturk, S., Sozdemir, A., Ulger, O., 2013. The real crisis waiting for the world: oil problem and energy security. Int. J. Energy Econ. Policy 3, 74–79. http://www.econjournals.com/index.php/ijeep/article/view/581/331

Parker, L.M., Ross, P.M., O'Connor, W.A., Pörtner, H.O., Scanes, E., Wright, J.M., 2013. Predicting the response of molluscs to the impact of ocean acidification. Biol. 2, 651–692. https://doi.org/10.3390/biology2020651

Pi-hai, G., Jiao, L.I., Chang-tao, G., Meng-jie, L.I., Chao, L.I.U., 2014. Estimation and experiment of carbon sequestration by oysters attached to the enhancement artificial reefs in Laizhou Bay, Shandong, China. Yingyong Shengtai Xuebao 25. https://www.ncbi.nlm.nih.gov/pubmed/25796916

Rau, G.H., 2014. Enhancing the Ocean's Role in CO_2 mitigation. Glob. Environ. Chang. 1, 817–824. https://doi.org/10.1007/978-94-007-5784-4

Rau, G.H., 2008. Electrochemical splitting of calcium carbonate to increase solution alkalinity: implications for mitigation of carbon dioxide and ocean acidity. Environ. Sci. Technol. 42, 8935–8940. Https://doi.org/10.1021/es800366q

Rau, G.H., Caldeira, K., 1999. Enhanced carbonate dissolution: a means of sequestering waste CO_2 as ocean bicarbonate. Energy Convers. Manag. 40, 1803–1813. https://doi.org/10.1016/S0196-8904(99)00071-0

Renworth, P., Henderson, G., 2017. Assessing ocean alkalinity for carbon sequestration. Rev. Geophys. 55, 636–674. https://doi.org/10.1002/2016RG000533

Royal-Society, 2009. Geoengineering the climate: Science, governance and uncertainty, RS Policy document 10/09. https://doi.org/10.1007/s10098-010-0287-3

Scanes, E., Parker, L.M., Connor, W.A.O., Stapp, L.S., Ross, P.M., 2017. Intertidal oysters reach their physiological limit in a future high-CO_2 world. J. Exp. Biol. 220, 765–774. https://doi.org/10.1242/jeb.151365

Shumway, S.E., Davis, C., Downey, R., Karney, R., Kraeuter, J., Parsons, J., Rheault, R., Wikfors, G., 2003. Shellfish aquaculture — In praise of sustainable economies and environments. World Aquac. 34, 15–17. http://agris.fao.org/agris-search/search.do?recordID=US201300949523 Accessed on: 06/09/2018

Śmietanka, B., Burzyński, A., 2017. Disruption of doubly uniparental inheritance of mitochondrial DNA associated with hybridization area of European *Mytilus edulis* and *Mytilus trossulus* in Norway. Mar. Biol. 164, 1–11. https://doi.org/10.1007/s00227-017-3235-5

Subasinghe, R., Soto, D., Jia, J., 2009. Global aquaculture and its role in sustainable development. Rev. Aquac. 1, 2–9. https://doi.org/10.1111/j.1753-5131.2008.01002.x

Takahashi, T., Sutherland, S.C., Chipman, D.W., Goddard, J.G., Ho, C., Newberger, T., Sweeney, C., Munro, D.R., 2014. Climatological distributions of pH, pCO_2, total CO_2, alkalinity, and $CaCO_3$ saturation in the global surface ocean, and temporal changes at selected locations. Mar. Chem. 164, 95–125. https://doi.org/10.1016/j.marchem.2014.06.004

Takahashi, T., Sutherland, S.C., Wanninkhof, R., Sweeney, C., Feely, R.A., Chipman, D.W., Hales, B., Friederich, G., Chavez, F., Sabine, C., Watson, A., Bakker, D.C.E., Schuster, U., Metzl, N., Yoshikawa-Inoue, H., Ishii, M., Midorikawa, T., Nojiri, Y., Körtzinger, A., Steinhoff, T., Hoppema, M., Olafsson, J., Arnarson, T.S., Tilbrook, B., Johannessen, T., Olsen, A., Bellerby, R., Wong, C.S., Delille, B., Bates, N.R., de Baar, H.J.W., 2009. Climatological mean and decadal change in surface ocean pCO_2, and net sea–air CO_2 flux over the global oceans. Deep Sea Res. Part II Top. Stud. Oceanogr. 56, 554–577. https://doi.org/10.1016/j.dsr2.2008.12.009

Tang, Q., Zhang, J., Fang, J., 2011. Shellfish and seaweed mariculture increase atmospheric CO_2 absorption by coastal ecosystems. Mar. Ecol. Prog. Ser. 424, 97–104. https://doi.org/10.3354/meps08979

Thomas, H., Schiettecatte, L.-S., Suykens, K., Koné, Y.J.M., Shadwick, E.H., Prowe, A.E.F., Bozec, Y., de Baar, H.J.W., Borges, A. V, 2009. Enhanced ocean carbon storage from anaerobic alkalinity generation in coastal sediments. Biogeosciences. 6, 227–267. https://doi.org/10.5194/bg-6-267-2009

Tjiputra, J.F., Olsen, A., Bopp, L., Lenton, A., Pfeil, B., Roy, T., Segschneider, J., Totterdell, I., Heinze, C., 2014. Long-term surface pCO_2 trends from observations and models. Tellus B 66, 23083. https://doi.org/10.3402/tellusb.v66.23083

van Heuven, S., Pierrot, D., Rae, J.W.B., Lewis, E., Wallace, D.W.R., 2011. CO_2SYS v 1.1, MATLAB program developed for CO_2 system calculations. ORNL/CDIAC-105b. Carbon Dioxide Inf. Anal. Center, Oak Ridge Natl. Lab., U.S. Dep. Energy, Oak Ridge, TN, USA. https://doi.org/10.3334/CDIAC/otg

Vaughan, N.E., Lenton, T.M., 2011. A review of climate geoengineering appraisals. Clim. Change 109, 745–790. https://doi.org/10.1002/wcc.197

Wang, H., Ge, C., Mao, Y., Huang, Y., Sui, H., 2016. Effect of hybrid abalone, *Haliotis discus hannai* x *Haliotis discus discus*, cultivation on the carbon cycle: carbon source/sink. J. World Aquac. Soc. 47, 720–728. https://doi.org/10.1111/jwas.12311

Wolf-Gladrow, D.A., Zeebe, R.E., Klaas, C., Körtzinger, A., Dickson, A.G., 2007. Total alkalinity: The explicit conservative expression and its application to biogeochemical processes. Mar. Chem. 106, 287–300. https://doi.org/10.1016/j.marchem.2007.01.006

Zeebe, R.E., Wolf-Gladrow, D., 2001. CO_2 in Seawater: Equilibrium, Kinetics, Isotopes, Elsevier Oceanography Series 65. Elsevier B.V., Amsterdam, The Netherlands. https://www.elsevier.com/books/co2-in-seawater-equilibrium-kinetics-isotopes/zeebe/978-0-444-50946-8