



Causes and Consequences of Ocean Acidification

with special emphasis on the Dutch territorial waters



2018-04

Algemene inleiding

De uitstoot van kooldioxide door de verbranding van fossiele brandstoffen warmt de aarde op. Een tweede, maar minder bekend, effect van de toename in broeikasgassen is een gestage verzuring van het oceaanwater. Wat voor effecten deze verzuring heeft op het leven in de zee, is grotendeels onbekend. In het slechtst denkbare scenario, kunnen zogenaamde ecologische 'key species' zich niet op tijd aanpassen en leidt hun uitsterven tot een ecologische ramp. In een gunstiger scenario lukt het de meeste flora en fauna wel degelijk om zich aan te passen aan de veranderende omstandigheden en zullen de ecosystemen in zee weinig last hebben van verzuring. Deze ecosystemen spelen op hun beurt weer een belangrijke rol in de opname van CO₂ uit de atmosfeer naar de oceaan (biologische pomp) en daarmee het globale broeikas effect. Een gebrek aan fundamentele kennis weerhoudt ons er op dit moment nog van om een reële inschatting te maken van het gevaar van oceaanverzuring. Dit rapport vat onze huidige kennis omtrent oceaanverzuring samen, identificeert hiaten daarin en brengt in kaart welke rol de wetenschap in het algemeen, en die in Nederland in het bijzonder, kan spelen in het opvullen daarvan. In dit rapport wordt een aantal vaktermen gebruikt, die uitgelegd staan aan het eind van sectie 1 (pagina 13).

Samenvatting

De door de mens veroorzaakte toename in atmosferische CO₂ is voor een groot deel (±30%) opgenomen door de oceanen. In het marine milieu zorgt de opname van extra CO₂ voor een verschuiving in het carbonaat evenwicht, ook wel oceaanzuring genoemd. Deze oceaanzuring is zeer goed voorspelbaar voor de open oceaan aan de hand van het chemisch evenwicht, maar kan van de globale trend afwijken in kustzeeën, zoals de Noordzee, door veranderingen in nutriënten en door de toevoer vanaf het land of de kuststrook. Ook in de Caraïben kan oceaanzuring zich anders ontwikkelen door de sterke samenhang van de zeewater chemie met de lokale riffen en eutrofiering. Omdat sommige organismen voor het bouwen van hun kalkskelet sterk afhankelijk zijn van de oceanische CO₂ speciatie is het voor de biologie en ecologie belangrijk om deze te monitoren. Ook staat voor veel organismen het effect van oceaanzuring nog niet vast. De economische impact van oceaanzuring zal afhangen van zowel de ontwikkeling daarvan in de verschillende gebieden als de gevoeligheid van de relevante organismen.

In de ons omringende landen en ook wereldwijd hebben de afgelopen jaren een groot aantal onderzoeken naar zowel oceaanzuring zelf als naar de effecten van oceaanzuring op de verschillende organismen plaatsgevonden. Bij gebrek aan een Nederlands programma gebruikt dit rapport deze onderzoeken en vertaalt een aantal zaken naar de Nederlandse context (Noordzee en de Caraïben) en voor Nederland relevante organismen. Tot de meest relevante organismen behoren diegenen die een economische waarde vertegenwoordigen (vis, schaal- en schelpdieren, etc.) en het is dan ook voor die soorten in het bijzonder relevant te weten in welke mate zij zich kunnen aanpassen aan de veranderende omstandigheden. Daarnaast is het met name voor kustregio's en ondiepe zeeën (zoals de Noordzee) niet zonder

meer te voorspellen hoe oceaanzuring exact zal verlopen vanwege de (variabele) toevoer van nutriënten en door seizoensgebonden effecten op verzuring (die wellicht ook veranderen met toenemende opwarming). Dit maakt dat met name voor kustregio's het essentieel is om de chemische condities nauwkeurig en langdurig te monitoren.

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Part 1 – Ocean Acidification

1.1. Introduction

Anthropogenic CO₂ emissions since the industrial revolution resulted in atmospheric CO₂ to increase from 280 ppm to over 400 ppm (2015). Also the ocean has absorbed a considerable part of the carbon dioxide emitted by fossil fuel burning since the industrial revolution (figure 1). Without oceans on Earth, current atmospheric carbon dioxide concentrations would have been about 30% higher (Sabine & Tanhua, 2010), with increased global warming as a result. At the same time the uptake of CO₂ also changes the chemistry of the sea water, decreasing pH and resulting in a suite of chemical changes known as ocean acidification. Ocean acidification is increasingly recognized as a global problem that will intensify with continued CO₂ emissions

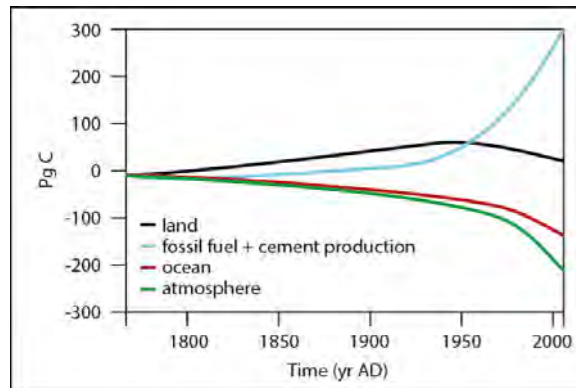


Figure 1: changes in anthropogenic CO₂ source and sinks since the beginning of the industrial revolution. Positive values (fossil fuel burning and cement production, in blue) indicate the source of added CO₂, whereas the atmosphere (in green) and the ocean (in red) act as reservoirs where this CO₂ is stored (i.e. acting as a sink for the emitted carbon dioxide). The difference between the source and the two sinks represents the terrestrial source (in black). This figure shows the fate, over time, of the carbon dioxide emitted by fossil fuel burning. Modified from (Khaliwala, Primeau, & Hall, 2009).

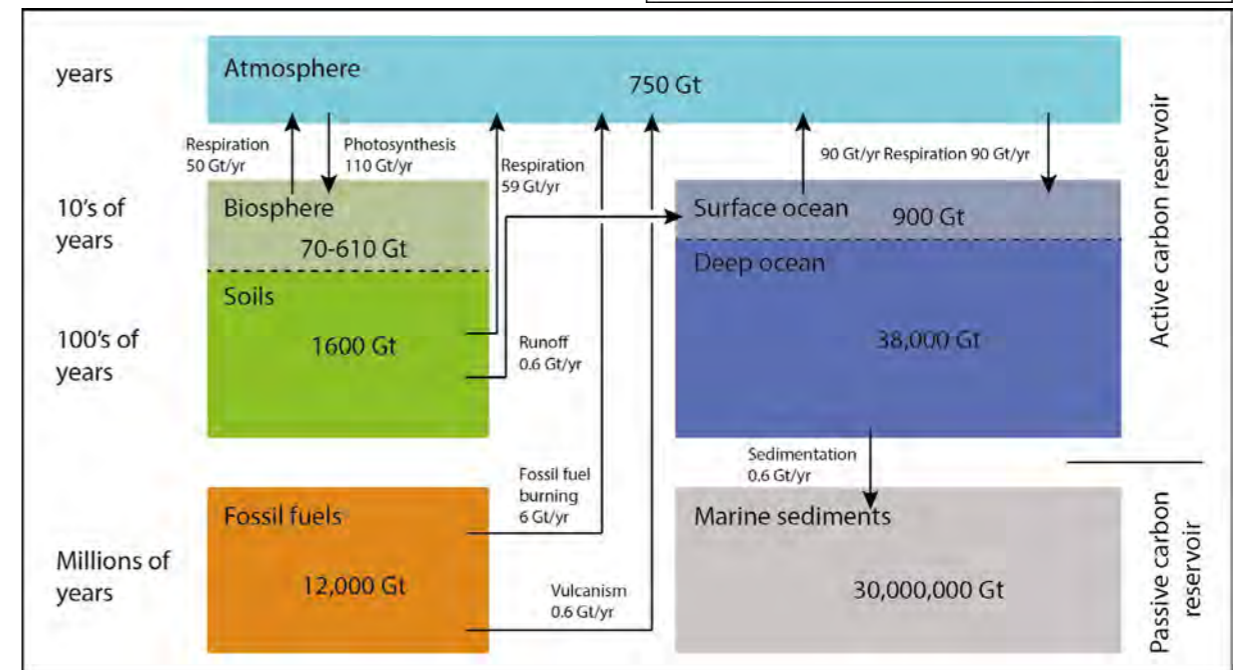
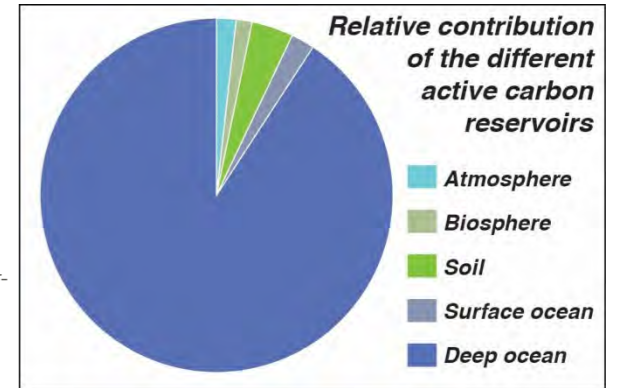
and which potentially will affect marine ecosystems and hence benefits of these ecosystems to society.

Oceans cover approximately 70% of the surface of our planet and contribute a similar amount as the land surface to global net primary productivity (Field, Behrenfeld, Randerson, & Falkowski, 1998) and the global carbon cycle. More importantly, of all biological available carbon (i.e. CO₂, sea water dissolved carbon, soil carbon and the entire biosphere) more than 90% is present in sea water (figure 2). Most of this carbon is dissolved in the deep sea in the form of bicarbonate ion and this large oceanic reservoir is also the key to the oceans' buffering capacity to global change. Under normal conditions the slow release and/or uptake of CO₂ from this vast oceanic reservoir determines the changes in global climate on a glacial-interglacial time scale. It is basically the ocean that sets atmospheric pCO₂ levels and the atmosphere responds. Only by the present massive release of CO₂ by anthropogenic activities this equilibrium has started to change and nowadays the ocean is responding to the enhanced inputs of CO₂ by changing its carbon partitioning.

1.2. Ocean acidification as a process

Every day, approximately 24 million tons of CO₂ are taken up by the oceans (Le Quere et al., 2007) (Takahashi et al., 2009). As a result of this CO₂ uptake the acidity of the (surface) ocean has steadily increased. In addition to global warming, this is considered to be the second largest impact of CO₂ on our climate and is hence dubbed "the other CO₂ problem" (Turley, 2005). This does not imply that the oceans have become acidic, but indicates a shift in the

Figure 2: relative partitioning of carbon between the different active (right) and absolute numbers for the active and passive reservoirs (below). Arrows between the reservoirs indicate the estimated flow of carbon between them. The difference between active and passive reservoirs is based on the time scale involved in their carbon cycling, which differs several orders of magnitude. Numbers are based on Holmen et al. (2000), (Sundquist, 1993), and Raven et al. (2005).



carbon partitioning within the oceans (see box 1). Although the oceans do not become acidic as such, this does have a major impact on ocean chemistry and also on the biology. This is due to the reaction of CO₂ with water which forms carbonic acid (H₂CO₃). This is an unstable molecule and therefore dissociates into bicarbonate (HCO₃⁻) and protons (H⁺). The ongoing uptake of carbon dioxide by our oceans therefore, increases the concentration of protons and thereby decreases the pH: a process also known as Ocean Acidification (figure 2).

The relation between the so-called inorganic carbon species (carbon dioxide or CO₂, bicarbonate or HCO₃⁻ and carbonate or CO₃²⁻) is closely related to the pH of the seawater (figure box 1.2). At high pH (i.e. low [H⁺]), most of the inorganic carbon is present in the form of carbonate, whereas at low pH, the balance shifts towards CO₂. This means that with ongoing CO₂ uptake and subsequent lowering of the pH, relatively less carbonate ions will be available. This in turn, lowers the so-called saturation state for CaCO₃, which is the most common mineral precipitated for the production of shells and skele-

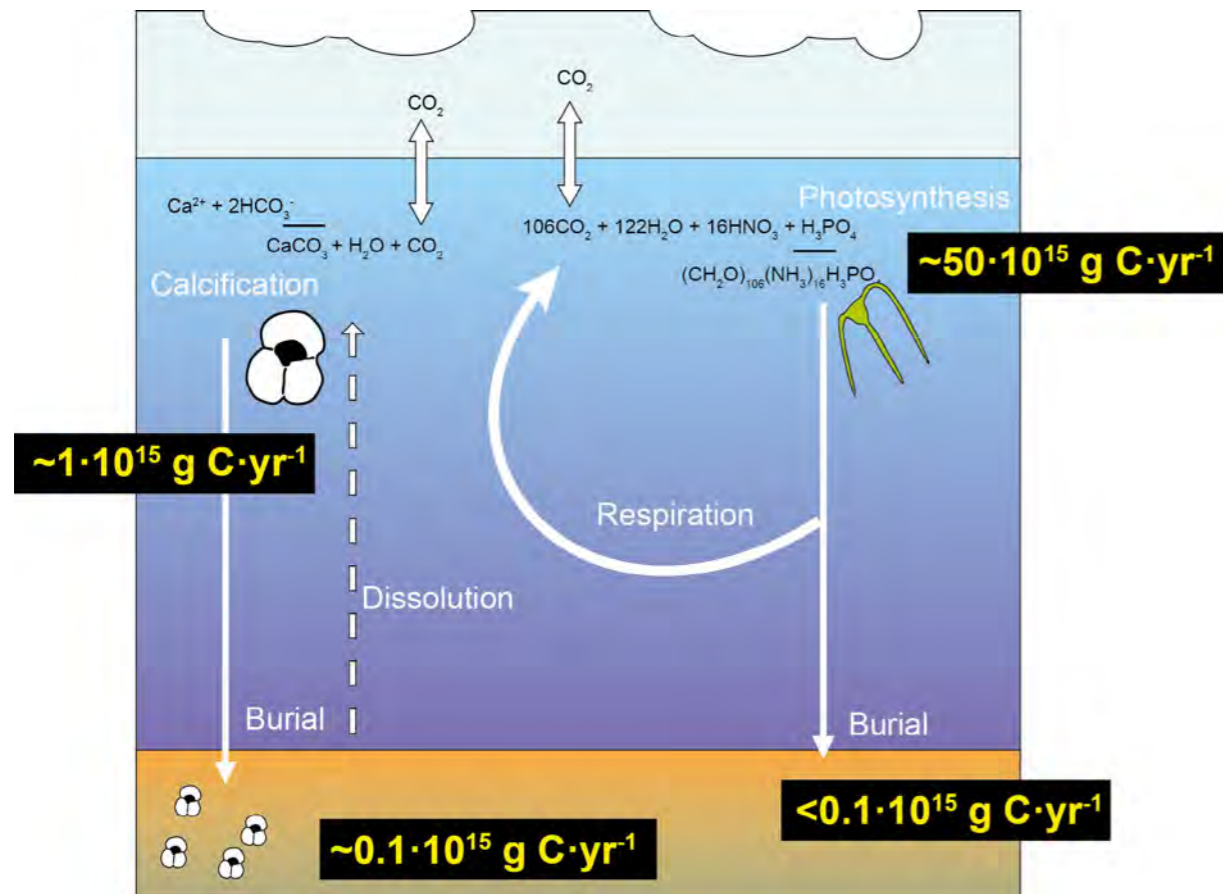


Figure 3: the so-called carbonate pump (left) and biological pump (right). Dissolved inorganic carbon is taken up either by calcification (often noted as a consumption of HCO_3^-) or by photosynthesis (by CO_2 uptake). Although the inorganic carbon uptake by algae exceeds that of uptake by calcifying organisms by approximately 50 times, the majority of the produced organic carbon is respired. Comparing the resulting fluxes of carbon to the seafloor (i.e. the net export), the contribution of calcification exceeds that of the biological pump (i.e. photosynthesis). Note that the use of 'biological' here is misleading: CaCO_3 production is also a biological process.

tons. This in turn, has given rise to the concern that ongoing ocean acidification will decrease the ability of many organisms to form their hard parts (section 2). Oceanic inorganic carbon is also linked to the organic carbon system by respiration and primary production: respiration transforms organic to inorganic carbon (CO_2), whereas primary productivity relies on inorganic carbon to form biomass. The biological contribution to the net uptake of CO_2 from the ocean's surface and transport to the seafloor, is

called the biological pump. This is often distinguished from the so-called carbonate pump that represents the production and export of particular inorganic carbon (PIC) in the form of (small) CaCO_3 shells (figure 3).

Box 1 – Seawater inorganic carbonate chemistry and ocean acidification.

Atmospheric CO_2 is in equilibrium with seawater dissolved CO_2 . Most of this CO_2 reacts with water to form carbonic acid, which dissociates into bicarbonate and protons. Depending on the pH of the seawater, a proportion of the bicarbonate dissociates further into carbonate ions and protons. This implies that ongoing CO_2 emissions will decrease seawater pH, a process known as ocean acidification (Figure box 1.1).

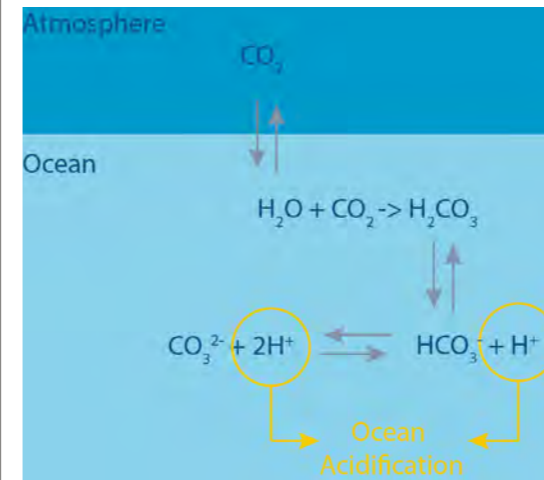


Figure box 1.1: the fate of dissolved carbon dioxide in seawater. Increased uptake of CO_2 leads to an increase in DIC and an increase in H^+

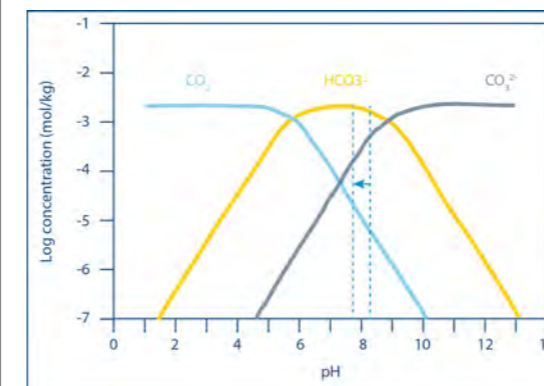


Figure box 1.2: the relation between inorganic carbon species (carbon dioxide, bicarbonate and carbonate ions) and seawater pH. The forecasted reduction in pH (dashed lines) will shift the balance between CO_3^{2-} and HCO_3^- .

Ocean acidification links seawater pH and speciation of inorganic carbon species (i.e. CO_2 , HCO_3^- and CO_3^{2-}), which can be plotted in a so-called Bjerrum plot (Figure b). Such a plot shows that at high seawater pH, most inorganic carbon is present in the form of carbonate ions, whereas carbon dioxide dominates at (very) low seawater pH. With ongoing acidification, the balance between CO_3^{2-} and HCO_3^- changes, with a relative (and absolute) increase in the latter of the two. As a consequence, the reduced $[\text{CO}_3^{2-}]$ decreases saturation state (Ω) with respect to calcium carbonate.

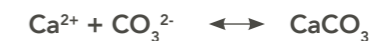
Inorganic carbon dissolved carbon occurs in sea water basically in 3 forms: dissolved carbon dioxide ($\text{CO}_2 \text{ aq}$), bicarbonate ion (HCO_3^-) and carbonate ion (CO_3^{2-}). In (sea) water CO_2 acts as an acid, providing hydrogen ions (H^+) to form bicarbonate:



The H^+ produced is subsequently taken up by the CO_3^{2-} , which acts as a base, to also form HCO_3^- :



These reactions are reversible, with relative amounts of the species produced depending on the equilibrium constants. Although calcium carbonate by organisms is not necessarily produced according to the reaction



Saturation state is defined as follows:

$$\Omega = \frac{[\text{Ca}^{2+}]_{\text{sw}} * [\text{CO}_3^{2-}]_{\text{sw}}}{[\text{Ca}^{2+}]_{\text{sat}} * [\text{CO}_3^{2-}]_{\text{sat}}}$$

Under current sea water pH conditions sea water is supersaturated with respect to CaCO_3 in most surface waters. Calcium concentration varies little in the open ocean, but the ocean acidification decreases CO_3^{2-} concentration and thereby degree of supersaturation.

1.3. Ocean acidification in the past decennia and the coming century

Ocean Acidification is a process recorded in ongoing measurements of seawater pH (figure 4) although the time series is just long enough to observe this trend. The increase in atmospheric $p\text{CO}_2$ of more than 120 ppm since the beginning of the industrial revolution, resulted in a decrease in surface ocean pH of 0.1 units. Although this seems a very modest decrease, because of the logarithmic nature of the pH scale this equals an increase in H^+ concentration of more than 25%. Importantly also the relative distribution of the carbon species important for organism in sea water shifts (Box 1).

With projected atmospheric $p\text{CO}_2$ scenarios, it is relatively straightforward to predict the development of seawater pH for the coming century for open ocean areas. Depending on the scenario this results in a decrease in pH of 0.2-0.3 units by the year 2100 (Caldeira & Wickett, 2005). Such a shift implies that the ocean would be about 100-150% more acidic at that time compared to the beginning of the industrial revolution. Besides this absolute shift in acidity and changes in carbonate chemistry, also the rate of change is alarming: it is estimated that the current rate of acidification is at least

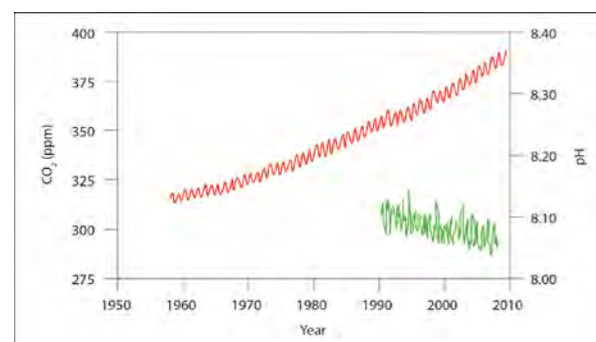


Figure 4: measured atmospheric CO_2 (in red), and surface ocean pH (in green) over the course of the last decades from Mauna ALOHA and Hawaii ocean time series station, ALOHA, Hawaii. Data from NOAA PMEL program.

10 times higher than at any time over the last 55 million years (Honisch et al., 2012).

In shelf seas, such as the North Sea and also large parts of the Dutch Caribbean territories the impact of ocean acidification is much less easy to predict compared to the open ocean for several, very different, reasons. First, the impact of local biology is currently changing because of environmental mitigation measures. The North Sea is getting less eutrophic because of the decline in artificial fertilizers, which enhances the impact of ocean acidification as less CO_2 is used by biological productivity. In contrast eutrophication is still an ongoing issue in the Dutch Caribbean territories, which on the one hand would dampen the effect of ocean acidification, but on the other hand may indirectly enhance the impact of acidification via stimulating bioerosion of coral reefs by excavating sponges. In the North Sea factors like the addition of alkalinity from anoxic intra-tidal areas and carbonate rich river waters offset carbonate parameters from what would be expected in an open ocean setting. These last two factors make it especially difficult to predict the future development of ocean acidification in the North Sea and calls for careful and detailed monitoring.

1.4. Regional differences in ocean acidification and its causes

Whereas OA in the open ocean is relatively easy to predict as a function of future atmospheric CO_2 levels and based on inorganic carbon chemistry (see also Box 1), coastal areas are impacted by varying amounts of terrestrial/riverine input and strong differences in seasonal biological activity. Coastal seas are characterized by high primary productivity and thus increased atmosphere-sea CO_2 fluxes through the 'continental shelf pump' (Thomas, Bozec, Elkalay, & de Baar, 2004; Tsunogai, Watanabe, & Sato, 1999). High primary productivity enables CO_2 drawdown, increasing the (sub)surface

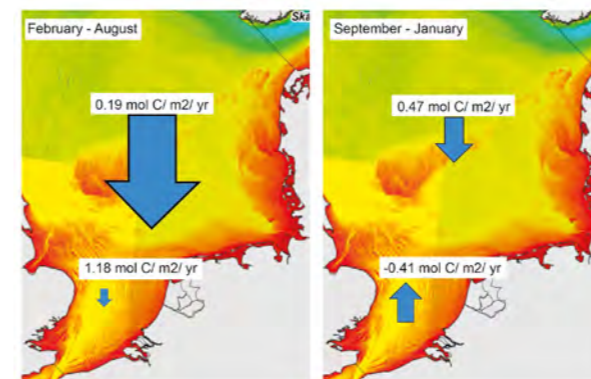


Figure 5: seasonal variability in CO_2 air-sea flux. The southern North Sea acts as a net CO_2 sink in spring and summer (left panel), whereas in autumn and winter, there is an opposite flux of CO_2 (i.e. to the atmosphere). The northern North Sea acts as a CO_2 sink all year round, with higher uptake rates in Feb-August than in Sep-Jan. Colours indicate the depth of the seafloor. Modified from (Thomas, Bozec, Elkalay, et al., 2005).

$p\text{CO}_2$ which contributes to the intermediate layers of the open ocean by open ocean-shelf sea exchange.

In the North Sea, more than 99% of the present carbon is exported to the North Atlantic Ocean, whereas less than 1% is buried in sediments (Thomas, Bozec, de Baar, et al., 2005). Of all the exported carbon, approximately 97% is in the form of DIC, with the increase in North Sea DIC being caused by uptake of atmospheric CO_2 and by local conversion of DOC into DIC (Thomas, Bozec, de Baar, et al., 2005). Within the North Sea, there is a distinction between the northern and central parts which act as a CO_2 -sink all year round and the southern part, which is characterized by a high seasonal (spring) primary production, and thereby a temporal high CO_2 uptake (figure 5). At an annual scale, differences in temperature and biological activities result in major changes, with either of the two processes being dominant. The southern part is dominated by temperature effects, with an increase of $p\text{CO}_2$ in summer, while the northern part is clearly dominated by biological processes with a summer decrease of $p\text{CO}_2$ typical for mid and high latitude waters. The highest seasonal amplitude in $p\text{CO}_2$ is observed in the central part as a consequence of early stratification and high biological activity (Thomas, Bozec, Elkalay, et al., 2005).

The North Sea CO_2 system and hence ocean acidification not only has large differences spa-

tially and on a seasonal cycle, but also showed major changes over the last decades, which are not always in line with known global trends. Whereas the global ocean showed a steady decrease in pH, the North Sea is influenced by several factor inherent to its setting. Differences in circulation related to the North Atlantic Oscillation affects exchange with the North Atlantic and hence residence time of the waters in the North Sea on a multi annual time scale (Salt et al., 2013). Longer residence times subsequently result a higher proportion of metabolic CO_2 to build up. Over the 2001- 2011 decade, when the carbonate system was monitored on a bi-annual basis, the $\Delta p\text{CO}_2$ (difference between atmosphere and sea water) in the northern North Sea became less negative. Although it is difficult to distinguish multi-annual trends from seasonal signals, due to the limited time resolution of the data sets available, the observed trend is in line with a gradual decrease in productivity related to a reduction of nutrients entering the North Sea (Borges & Gypens, 2010; Provoost, van Heuven, Soetaert, Laane, & Middelburg, 2010). This would preferentially impact the southern North Sea, similar to what is observed. Also temperature has a major effect on the $p\text{CO}_2$ in the North Sea, explaining much of the observed inter annual variability (CARGO, Salt, Thomas, & de Baar, 2015). Overall, in the northern North Sea, mean abiotic pH decreased over the 2001-2011 decade from 8.0819 to

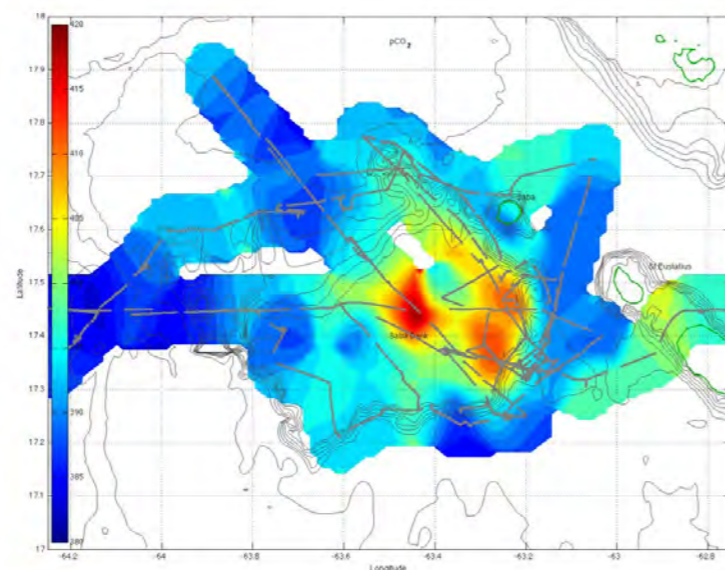
8.0606, which corresponds to an annual increase in $[H^+]$ of $4.1630 \times 10^{-11} \text{ mol yr}^{-1}$. At a pH level of 8.0819 (2001), this corresponds to a pH change of $-0.0022 \text{ pH units yr}^{-1}$ (Clargo et al., 2015). In the southern North Sea, mean abiotic pH decreased from 8.0859 to 8.0638, which corresponds to an annual increase in $[H^+]$ of $4.2840 \times 10^{-11} \text{ mol yr}^{-1}$. This results in a comparable pH change of $0.0023 \text{ pH units yr}^{-1}$ (Clargo et al., 2015).

For the North Sea also the addition of alkalinity from coastal areas, via Baltic sea water and from rivers offsets the carbonate system (Burt et al., 2016; Salt, Thomas, Bozec, Borges, & de Baar, 2016). Since changes in alkalinity directly affect the acid-base buffering capacity these fluxes also impact the sensitivity of the North Sea to ocean acidification. These inputs vary spatially, on a seasonal scale and, most likely, also on a multi annual time scale (Burt et al., 2016). This does not only require monitoring of the sea water carbonate system with a high enough spatial resolution, but also with enough spatial and temporal coverage as well as detailed analyses of the carbonate system to be able to disentangle the different relevant parameters. In the Caribbean, sea water is much more

supersaturated with respect to calcium carbonate and generally under natural conditions oligotrophic. This would imply that the buffering capacity locally would be much higher with respect to ocean acidification. However, the dominant calcifying organisms produce aragonite instead of calcite, a calcium carbonate mineral phase which dissolves much easier in seawater compared to calcite. Hence potential impact of ocean acidification on aragonite producing organisms, such as corals, will occur already at higher pH. Moreover, photosynthesis (fixing CO_2 into organic matter), decreases DIC and increases pH and hence the opposite (respiration) reduces the sea water saturation state. Eutrophication, although initially removing CO_2 , ultimately enhances carbonate dissolution. This is potentially even more enhanced by bioeroding sponges which thrive under higher productivity conditions. A recent expedition into the Dutch territorial waters (figure 6) specifically targeted such a potential impact on the Saba Bank. Because the Saba bank is relatively undisturbed during this expedition it was shown that the reefs in this area are still net carbonate producing, i.e. calcium carbonate growth is exceeding dissolution.



Figure 6: the Saba Bank is a shallow submerged carbonate platform (above) characterized by a higher surface pCO_2 (right), which is indicative of a net calcification on the bank.



Glossary

pCO_2

the partial pressure of CO_2 (in parts per million or $\mu\text{atmosphere}$)

DIC

Dissolved Inorganic Carbon, equalling $[CO_2] + [HCO_3^-] + [CO_3^{2-}]$. Sometimes also referred to as total inorganic carbon, TCO_2 or Σ

pH

$-\log [H^+]$, a measure for the concentration of protons (H^+) in (sea)water. Water with a pH of 7 contains 10 times as many protons as water with a pH of 8.

total alkalinity

a measure expressing the capacity of water to resist changes in pH

calcium carbonate saturation state (Ω)

the product of the concentrations of calcium and carbonate, divided by the solubility constant K_{sp} , which is a function of the $CaCO_3$ polymorph, temperature and pressure

calcite

a crystalline $CaCO_3$ polymorph, precipitated by coccolithophores, most foraminifera and many bivalves

aragonite

a crystalline $CaCO_3$ polymorph, less dense than calcite, precipitated by (amongst others) corals and pteropods. At a given concentration of carbonate ions ($[CO_3^{2-}]$), the saturation state (Ω) for aragonite is lower than that of calcite, which implies that with steadily increasing atmospheric (and hence dissolved) CO_2 concentrations, shells and skeletons of aragonite will dissolve sooner than those composed of calcite.

carbonic acid (H_2CO_3)

a molecule that forms by the reaction of CO_2 with H_2O and readily dissociates into bicarbonate (HCO_3^-) and a proton. Since this is an equilibrium reaction, the reverse may also occur (e.g. when a process locally alkalizes the seawater). Due to its instability, carbonic acid always accounts for a small amount of the dissolved inorganic carbon.



Part 2 – Impact of Ocean Acidification on Biology

Whereas the changes in pH seem to be rather small, changes in speciation for especially carbon are large. This inevitably affects calcifying organisms, which are widely assumed to be directly influenced by the saturation state of seawater with respect to calcite or aragonite. This is expressed as the omega (Ω) and equals the product of the concentrations of carbonate ions and calcium ($[\text{CO}_3^{2-}]$ and $[\text{Ca}^{2+}]$), divided by the K_{sp} , the solubility constant. Since a small decrease in pH in the range of 7-8 already greatly reduces the $[\text{CO}_3^{2-}]$ and thereby the saturation state, organisms that form CaCO_3 shells and skeletons are particularly vulnerable to ocean acidification.

Whereas the impact of ocean acidification on the ocean inorganic carbonate system is generally well understood and can be accurately predicted for the global ocean based on CO_2 emission scenarios, the impact of ocean acidification on different organisms is largely unknown. Still, there is general consensus that calcifying organisms are directly affected by the predicted changes in saturation state (Fabry, Seibel, Feely, & Orr, 2008; J. B. Ries, Cohen, & McCorkle, 2009). Studies have shown responses of a decrease in calcification rates in coccolithophores, pteropods (Maas, Lawson, Bergan, & Tarrant, 2018), bivalves (Gazeau et al., 2007), foraminifera (Bijma, Hönisch, & Zeebe, 2002; Spero, Bijma, Lea, & Bemis, 1997), sea urchins (Miles, Widdicombe, Spicer, & Hall-Spencer, 2007), corals (Gattuso, Frankignoulle, Bourge, Romaine, & Buddemeier, 1998; C. Langdon, 2005; Chris Langdon et al., 2003; Chris Langdon et al., 2000; Leclercq, Gattuso, & Jaubert, 2002; Marubini, Barnett, Langdon, & Atkinson, 2001; Marubini, Ferrier-Pages, & Cuif, 2003; Ohde & Hossain, 2004; Schneider & Erez, 2006;

Silverman, Lazar, & Erez, 2007) and coralline algae (Kuffner, Andersson, Jokiel, Rodgers, & Mackenzie, 2008). Some of these organisms respond already to minor changes in saturation state, others are only affected by shift of > 0.5 units (Fabry et al., 2008; J. B. Ries et al., 2009).

Besides the relatively obvious relation between the formation of CaCO_3 and saturation state, a variety of other biological processes are impacted by ocean acidification. For instance, some organisms, such as cyanobacteria (Lomas et al., 2012), macro algae and sea grasses (Koch, Bowes, Ross, & Zhang, 2013)(and references therein) have been shown to profit from the ongoing changes in carbonate chemistry. Hence, ocean acidification most likely has the capacity to alter ecosystems, biogeochemical functioning and biodiversity. One of the less apparent, but by no means unimportant effects of AO, is that it appears to make organisms more vulnerable to other environmental changes (Harvey, Gwynn-Jones, & Moore, 2013; Portner & Farrell, 2008). This has, for example, been estimated to affect fish catches (Lam, Cheung, & Sumaila, 2016).

2.1 What organismal and ecological processes are negatively (and which positively?) affected by OA?

Accumulation of CO_2 in animal bodies negatively affects fitness and physiology (Fabry et al., 2008; Portner, 2012) and for example, hampers growth rates in fish larvae (Baumann, Talmage, & Gobler, 2012). Changes in fish behaviour as a function of $p\text{CO}_2$ is also reported (Munday, Donelson, Dixon, & Endo, 2009). Marine plants and phytoplankton, on the other hand are reported to profit from extra CO_2 , reflected in

higher photosynthesis and growth rates (Bach et al., 2013), which is also reflected by high abundances of marine plants in the vicinity of natural CO_2 vents (Hall-Spencer et al., 2008). Extrapolating the effects on individual species to community- or ecosystem-level is challenging since those larger-scale systems cannot be studied under controlled conditions. Loss of species or ecological functional groups likely alters the structure of marine food webs and nutrient cycling. Impact will, however, strongly vary between different areas. Whereas some areas are relatively well-buffered, such as the Caribbean, other areas, such as the North Sea, are not. Still, organisms inhabiting the well-buffered areas are generally less well adapted to such changes (J. A. Kleyvas, 1999).

2.2 Which organisms are vulnerable to ocean acidification?

Another type of response to ocean acidification includes a reduced buffering capacity for CO_2 in the tissue of marine organisms. With increased environmental CO_2 , the removal of carbon dioxide from muscle tissue may cost more energy due to the reduced CO_2 gradient from inside to outside the organism (Seibel & Walsh, 2003). Similarly, the increased seawater $[\text{H}^+]$ may reduce the ability to regulate the ion exchange across membranes (Burnett, Terwilliger, Carroll, Jorgensen, & Scholnick, 2002; Miles et al., 2007; Spicer, 1995). One of the consequences of a reduced internal pH is the decrease in the oxygen-binding capacity with arrested muscle functioning as a consequence (Childress & Seibel, 1998; Hourdez & Weber, 2005). Organisms that suffer from such metabolic perturbations include many higher organisms including cnidaria, arthropods, sea urchins and bivalves (Kurihara & Shirayama, 2004; Miles et al., 2007; Pane & Barry, 2007). Particularly, hatching and larval stages of many species (Ishimatsu, Kikkawa, Hayashi, Lee, & Kita, 2004; Kurihara & Shirayama, 2004),

as well as organisms with high metabolic rates (Reipschlagler & Portner, 1996) are vulnerable to changes in their ionic-metabolic household. At the same time, a number of fish appear to be tolerant to high environmental CO_2 levels (Kikkawa, Kita, & Ishimatsu, 2004; Kikkawa, Sato, Kita, & Ishimatsu, 2006).

2.3 What are the predicted effects of ocean acidification on biodiversity?

Ocean acidification has the potential to impact marine ecosystems through a variety of pathways. Inter-species differences in response to reduced saturation state likely will lead to ecological losers and winners, and affect ecological interactions between species. For example, species may migrate to other latitudes (poleward or towards the tropics) or to different water depths (e.g. North Sea fish: (Perry, Low, Ellis, & Reynolds, 2005)), species may locally suffer extinction (Portner & Knust, 2007) and the timing of biological events may change between the seasons (e.g. (Wiltshire & Manly, 2004)). Such changes can, for example, result in a mismatch with the preferential thermal window and hence, occurrence of predators and preys, like documented in the North Sea for juvenile cod and zooplankton, respectively (Portner & Farrell, 2008).

As opposed to the effects of OA on individual species, it is very difficult to predict the effects on communities and ecosystems. It is generally assumed that higher trophic levels, like most fish species will be sensitive to ocean acidification through changes in the food web, even though these fish are able to cope with (moderate) levels of ocean acidification by adjusting their physiology. A number of ecosystems are thought to be particularly vulnerable to ocean acidification: these include: tropical reefs, open ocean plankton ecosystem, coastal, high latitude and deep sea ecosystems. Tropical reef ecosystems, for example, are projected to

suffer from acidification by reduced calcification, lower reproduction and recruitment. Bioerosion, the dissolution and mechanical degradation of reefs, by sponges, algae, etc. may also increase due to acidification and thereby further degrade reefs. A prime example of the reduction in calcification rates due to a reduced saturation state (in combination with increased temperature), is the Great Barrier Reef, which is reported to have experienced a reduction in calcification rate by approximately 14% between 1990 and 2015 (De'ath, Fabricius, Sweatman, & Puotinen, 2012). This decrease fits several experimental studies documenting a 10-60% reduction in calcification rate for a doubling in $p\text{CO}_2$ from pre-industrial values (Doney, Fabry, Feely, & Kleypas, 2009; Joan A. Kleypas, Anthony, & Gattuso, 2011; C. Langdon, 2005). Warming has a synergistic effect on reduced calcification, which is known from studies with coralline algae (Anthony, Kline, Diaz-Pulido, Dove, & Hoegh-Guldberg, 2008; Reynaud et al., 2003). Such experimental studies are validated by field studies showing a decrease in coralline algae in the vicinity of natural CO_2 vents (Hall-Spencer et al., 2008; Martin et al., 2008). Replacement of corals by macroalgae and reduced settlement of new coral colonies by dominance of these algae poses another threat to tropical coral reef ecosystems, an effect which again is hypothesized from a combination of acidification and warming.

Open ocean planktonic ecosystems are affected by ocean acidification in several key processes, including calcification, photosynthesis and nitrogen fixation. These in turn, may affect organic and inorganic carbon cycling, oxygen, nutrient and trace element cycling. Finally, changes in open ocean planktonic communities may affect the $p\text{CO}_2$ of surface ocean waters and thereby provide an important feedback loop for seawater-atmospheric CO_2 exchange. The magnitude of the sum of these processes as a feedback is difficult to predict accurately. Even

the contribution of individual components may be difficult to estimate: the calcification- CO_2 uptake feedback, for example, will crucially rely on future changes in the balance between particular inorganic carbon (i.e. calcite shells) and particulate organic carbon (figure 3). Depending on the modelled scenario, however, the effect of changes in calcification on oceanic CO_2 uptake feedback could be of the same magnitude as the effect of warming (Zhang & Cao, 2016). Coccolithophores, foraminifera and pteropods are the three main producers of open ocean calcium carbonate and are all known to respond to a reduction in saturation state (Bergan, Lawson, Maas, & Wang, 2017; Bijma et al., 2002; Fabry et al., 2008; Iglesias-Rodriguez et al., 2008; Moy, Howard, Bray, & Trull, 2009; Riebesell et al., 2000; Spero et al., 1997), although the response is known to be highly species-specific (Keul, Langer, de Nooijer, & Bijma, 2013; Gerald Langer et al., 2006; G. Langer, Nehrke, Probert, Ly, & Ziveri, 2009; Ridgwell et al., 2009; Rost, Zondervan, & Wolf-Gladrow, 2008). A change in open ocean calcium carbonate production will in turn affect the global carbon cycling by reducing the ballasting and hence export of organic matter from the surface waters. Ocean acidification can increase phytoplankton growth, primary production and the release of extracellular organic matter (Bellerby, 2017; Fu, Warner, Zhang, Feng, & Hutchins, 2007; Hutchins, Mulholland, & Fu, 2009). Changes in the C:P:N ratio were observed for plankton grown in mesocosms at elevated $p\text{CO}_2$ (Riebesell et al., 2007), which may in turn affect their nutritional value and thereby impact those organisms that depend on them in the field (Sternner et al., 2008). In addition, phytoplankton with an elevated C:N ratio effectively increases transport of carbon to the seafloor (Riebesell et al., 2007). Carbon and nitrogen fixation can increase in cyanobacteria as a function of $p\text{CO}_2$ (Hutchins et al., 2007; Kranz, Sultemeyer, Richter, & Rost, 2009; Levitan et al., 2007; Ramos,

Biswas, Schulz, LaRoche, & Riebesell, 2007). This increases availability of nitrogen in the surface ocean, which is usually nitrogen-limited and hence primary productivity increases and thus also carbon uptake. Similar to the reports for calcification responses to CO_2 , some cyanobacteria also show an opposite response in their nitrogen fixation rate (and growth rate) with increasing $p\text{CO}_2$ (Czerny, Ramos, & Riebesell, 2009).

Coastal ecosystem are threatened by acidification in a number of ways. Most prominently, reduced calcification by bivalves including scallops, clams, oysters and mussels (Green, Jones, Boudreau, Moore, & Westman, 2004; Green, Waldbusser, Reilly, Emerson, & O'Donnell, 2009; Kurihara, 2008; Kurihara, Kato, & Ishimatsu, 2007; Miller, Reynolds, Sobrino, & Riedel, 2009; Salisbury et al., 2008; Talmage & Gobler, 2009; Watson, Southgate, Tyler, & Peck, 2009). Juveniles of some lobsters, shrimps and sea urchins are reported to be negatively affected by ocean acidification (Arnold, Findlay, Spicer, Daniels, & Boothroyd, 2009; Kurihara, 2008; Kurihara & Shirayama, 2004), whereas others are positively affected (J. B. Ries et al., 2009). Such effects may be important for the basis of coastal food webs, and for example, in the ecosystem engineering role that oyster beds play for a variety of species and for example, the settlement of larvae. Acidification and low oxygen levels may

enhance each other in their effects on reduced respiration levels by aerobic organisms. This could particularly affect coastal upwelling regions, where organisms are already affected by seasonally corrosive conditions.

2.4 What are the hiatuses in our current knowledge?

The responses of calcifying organisms to changes in saturation state are mixed. Some species calcify less-well under elevated $p\text{CO}_2$, some respond positively and others have highest calcification or growth rates at intermediate CO_2 concentrations (J. B. Ries et al., 2009). These mixed responses may well result from differences in the way that organisms maintain a pH gradient between their calcifying fluid and surrounding seawater (Justin B. Ries, 2011). This may indicate that although a variety of organisms employ basically the same mechanism, the 'strength' by which they employ this mechanism (i.e. proton pumping), varies between species and hence determines their response to ongoing ocean acidification.

This also directly relates to our own, recent observations that foraminifera promote calcification by creating a strong pH gradient during calcification (de Nooijer, Toyofuku, & Kitazato, 2009; Glas, Langer, & Keul, 2012; Toyofuku et al., 2017). This, amongst others, results in a

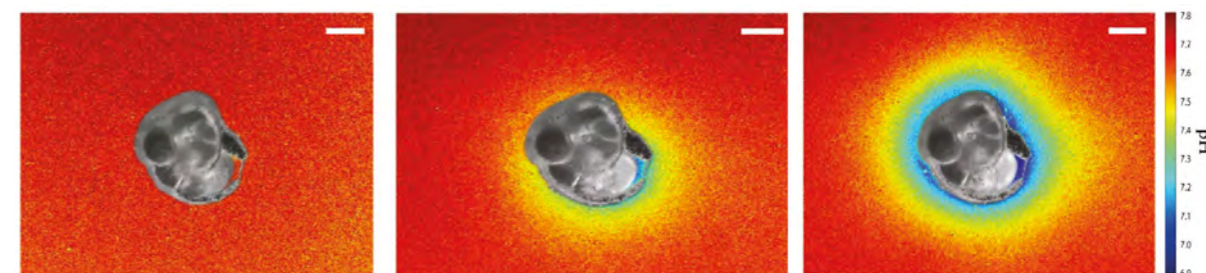


Figure 7: acidification of the foraminiferal microenvironment due to outward proton pumping (modified from (Toyofuku et al., 2017)). At the beginning of chamber formation (left) the pH in the foraminiferal microenvironment is similar to that of the ambient seawater. When calcification begins (middle) and the chamber wall starts to form, pH in the direct vicinity of the newly formed chamber decreases and remains low throughout the course of chamber formation (right). This decrease in pH can be as much as 1.5 pH units compared to that of the surrounding seawater.

conversion of (bi)carbonate into carbon dioxide, which diffuses inward and is used for calcification (after subsequent conversion into CO_3^{2-} at the site of calcification: figure 7). These results imply that it is irrelevant for the foraminifera in what form the inorganic carbon is available, but that they are able to convert it into the appropriate form when necessary. This, in turn, implies that an increase in seawater [DIC], i.e. due to ocean acidification may actually be beneficial for calcification, or at least partly counter-effects the negative impact of a lowered saturation state due to an increase in seawater $p\text{CO}_2$ (figure box 1.1).

A further unknown is the balance between the negative and positive effects that OA has on organisms and hence, the overall impact of

ocean acidification on marine organisms. For example, the inferred increased photosynthetic rates at higher CO_2 (e.g. (Hopkinson, Dupont, Allen, & Morel, 2011)) may outweigh the potential negative effects of lowered saturation state on calcification in for example, coccolithophores that harbour both of these processes.ww

2.5 Are there large differences between organisms in their response to ongoing OA?

So far, there are no apparent universal relations between the response (negative, positive or mixed) of individual organisms to ocean acidification and their phylogeny: some urchins have an optimum calcification rate at intermediate $p\text{CO}_2$, whereas others calcify more at higher

saturation states. Similar variability in responses are reported for snails (figure 8).

It should be stressed that the variability in responses outlined above only focus on one aspect of the biology of these organisms. This may or may not match their responses in terms of reproductive success, survival, etc. as a function of $p\text{CO}_2$. Hence, the sum of these responses (i.e. their balance), plus their interactions is needed to predict the large-scale (i.e. ecosystem) impacts of ocean acidification.

2.6 Do global warming, eutrophication, etc. enhance the effects of OA?

With ongoing warming, surface oceans are projected to become more stratified, which likely will limit the transport of nutrients from deeper waters. Whether such changes, in combination with the effects of ocean acidification, will have synergistic, antagonistic, or additive effects is unknown, but multiple stressors are likely to affect marine ecosystems at multiple scales. The interplay between these effects is virtually impossible to predict with the fragmented knowledge currently available. To start predicting the large-scale effects of OA and the additional impacts of other stressors, experimental results (see sections 2.2 and 2.3) and mesocosm studies need to be scaled up and most sensitive organisms need to be identified. Analogues from other environmental perturbations may provide clues to ecosystem-wide responses to the collapse of food webs: overfishing for example, can locally lead to an explosive dominance of sea urchins and dramatically alter nutrient cycling. This effectively tips the state of an ecosystem to another equilibrium from which it is hard, if not impossible, to recover. More analogues are for such tipping points are known from lake systems, and increasingly are also suggested relevant for the marine realm. Equally relevant is studying the adaptability of organisms to acidification, warming, deoxygen-

ation and eutrophication. Combined impact (i.e. multi-stressor) is a still understudied scientific subject, also because of the intrinsic large scientific effort involved, and is the only way to place species' and ecosystem's responses in a realistic context.

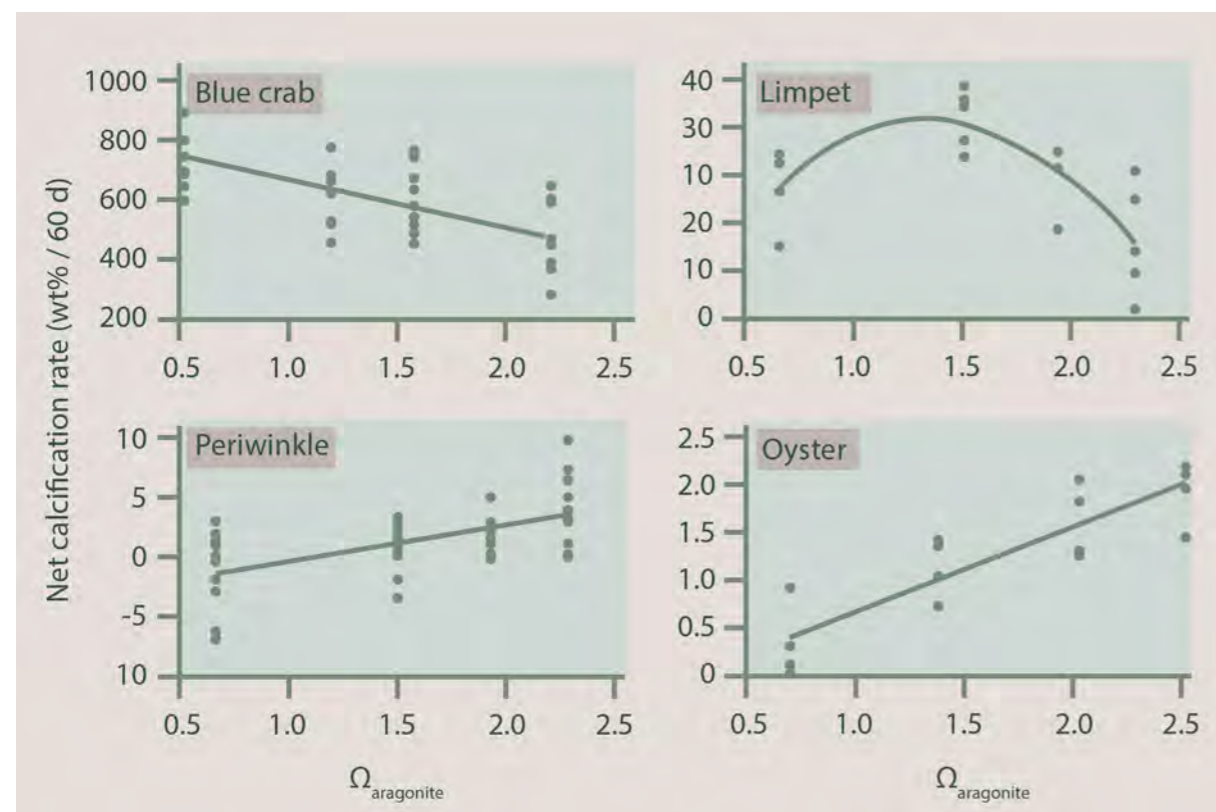


Figure 8: a selection of responses in terms of calcification rates as a function of saturation state (Ries et al., 2009). On the vertical axis is given the net calcification rate (in increase in weight% for 60 days), on the horizontal axis is plotted the aragonite saturation state.



Part 3 – Societal and Economic Impacts of OA

The marine environment is important for humans as it provides goods and services, including seafood and other natural products, it plays a key role in global biogeochemical cycling (and thus also carbon cycling), it protects communities from flooding and coastal erosion, it offers recreational opportunities, and there are many more difficult to assess values such as continued marine biodiversity. Ocean acidification is expected to have major socio-economic impacts because of several reasons. First several economically important marine resources, including fish stocks and shellfish will be impacted and hence also those depending on these resources for their sustenance. Second, also coral reefs will be impacted, limiting their role in tourism and also as coastal protection. Third, invasive species which are better able to cope with ocean acidification, could profit from the new conditions over indigenous species (potentially causing harmful algal blooms). Ultimately impacts on human societies will depend on vulnerability, resilience and adaptation capacity of these specific communities. Ocean acidification most likely will impact the uptake capacity of the ocean of added anthropogenic CO₂, but to what extent is heavily dependent in how different species and ecosystems are affected. Expressed in carbon storage equivalents the cost of this could easily add up to billions of euros annually. Because ocean acidification and global warming are both directly linked to increases in CO₂, it is also important to realize that the combined impact of global warming and ocean acidification might become relevant before the damage of ocean acidification alone is fully expressed.

3.1 What are the impacts for fishery and tourism considering the organismal and ecosystem-level changes?

Direct impacts of ocean acidification on fisheries and the human communities they support, are largely unknown. Although it has been suggested that ocean acidification may have a major impact, also indirectly by affecting important food sources for fish, other factors such as fishing pressure are most likely much more important in determining fish stocks in the North Sea. Shell fish (e.g. bivalves) on the other hand are known to be impacted by ocean acidification and in many countries ocean acidification is monitored to prevent loss of e.g. oyster, mussel and clam larvae. Bivalves and other molluscs also provide an indirect economic value since they are an important food source for fish (for example salmon). Although crustaceans are likely less vulnerable to ocean acidification, they play a major role in local fisheries and in the Caribbean often closely linked to the well-being of the local reef environment. They also provide a connection between phytoplankton (eaten by e.g. copepods) and their predators (fish and mammals). For the Caribbean, health of the coral reefs also plays an important role for the fish stocks as healthy reefs provide essential habitats and nurseries for commercially important fish stocks and are of vital importance for the tourist industry.

Studies on the impact of ocean acidification on fisheries in the North Atlantic have shown that the impact of warming (also due to increased pCO₂) is most likely larger than that of ocean acidification. Recently, however, a study in the UK into potential impacts of the combined effects of ocean acidification and warming on fisheries catches showed that this combined

effect was much larger than that of ocean warming alone (Fernandes et al., 2017). This study suggested that standing stocks for the UK could decline by as much as 10-60% by 2050, with appreciable losses in employment in fisheries and related industries. Potential combined impacts in other areas than the UK coastal zone are currently not known, but can be assumed of a similar order for the remainder of the North Sea. Due to the poorly quantified and challenging to predict (indirect) effects of OA on fish stocks, estimates for reduced fisheries incomes are highly uncertain. Confidence is higher for shellfisheries, for which estimates include a ~13% reduction in mollusc harvests in the USA for the year 2060 (Cooley & Doney, 2009), although economically relevant species may be more (or less) vulnerable. Oyster larvae in the Pacific, because of the lower saturation state locally, are generally more sensitive to OA and are already reported to be affected by lower seawater pH (Barton, Hales, Waldbusser, Langdon, & Feely, 2012; Waldbusser et al., 2013). The deterioration of (shell)fish catches in the UK are estimated at about 97 million US Dollar annually by the year 2100 (Narita, Rehdanz, & Tol, 2012).

3.2 Do the Caribbean Netherlands differ from the North Sea?

Because ocean acidification seems to favor cyanobacterial and macro algal growth this provides another potentially important threat to the economy of the (Dutch) Caribbean. Cyanobacterial blooms today occur infrequently, mostly related to waters exported from the Orinoco and Amazon rivers, but seriously hamper the local tourist and especially diving industry. These blooms block visibility in the water and create organic debris covering the coral reefs, which effectively make recreational diving impossible at those times. On-going ocean acidification is expected to make such blooms more frequent and more intense. These blooms sometimes de-



Figure 9: The coast of Tobago covered by mats of plant matter that attract biting sand fleas and smell like rotten eggs. Major effort is involved in the cleaning operations and tourists have cancelled their travel due to the foul smelling seaweed. (picture from The Guardian, August 10, 2015)

velop into massive growth of brown sea weed, known as Sargassum, which washes up on the local beaches, making the islands unattractive also for all other tourists (figure 9). These so-called “harmful algal blooms” can also wipe out local fish populations, and even cause coastal dead zones (hypoxia).

Reduced coral growth and increased bioerosion of coral reefs due to ongoing ocean acidification are other hazards, which may affect the Caribbean Netherlands in particular. For instance conchs at St Eustatius, the lobster population at Saba and the coral reefs at Bonaire/ Curacao/ Saba might all be of rather limited economic importance, but are closely linked to the cultural identity of these islands and their populations. Coral reefs are expected to deteriorate, partly a consequence of ocean acidification, but currently the impact is difficult to isolate from the effects of eutrophication and warming on these ecosystems. Deconvolving these effects is of crucial importance to allow knowledge-based policy making for the most relevant mitigation measures.

3.3 What needs to be specifically monitored/measured to assess and predict the effects of Ocean Acidification?

Although the effects of CO₂ uptake are relatively straightforward to predict (see 1.2 and 1.3), the impacts on biology are relatively uncertain (2.1-2.5). Inorganic carbon chemistry in shelf seas such as the North Sea are more complicated due to riverine input and exchange with adjacent seas and oceans (1.4) and therefore require specific criteria when setting up monitoring programs (3.4). Most clear effects of ocean acidification are known for certain physiological processes (i.e. calcification or respiration), but for functioning of entire specimens, populations or even ecosystems, effects are increasingly more difficult to predict. Future research should specifically target population- or ecosystem-level vulnerability towards ocean acidification. This requires a mechanistic understanding of processes involved in order to be able to extrapolate knowledge on species level to ecosystems. An important unknown is the trade-off between the (potential) beneficial effects of increased inorganic carbon availability (e.g. for photosynthesis) and the (likely) negative impacts of lowered pH (e.g. for calcification).

3.4 What quality requirements should a monitoring program meet?

In 2009 the European Science Foundation recommended that all European marine sites, including those already in the European Ocean Observatory Network, would act as oceanic carbon system data providers. This should include the North-East Atlantic and northern North Atlantic Ocean areas from 20°N to 70°N, together with the Baltic, Mediterranean and North Seas. Because the diverse European coastal ecosystems will likely show a similar diversity in responses to ocean acidification it was recommended that a broad spatial coverage would be maintained. It was furthermore recommended

that at that time existing long-time series should be maintained and new sensors and sampling/collecting devices should be developed. These recommendations resulted in several national programs (e.g. Bioacid in Germany; Cefas Smart Bouys in UK), but were not followed up as such in the Netherlands. Currently monitoring of ocean acidification relies on individual scientists receiving grants to investigate specific parts of the ocean carbon system. This makes it currently difficult to link the results collected elsewhere to the Netherlands.

For the Dutch North Sea, there is currently no long-running program to monitor ocean acidification and assess potential (biological) consequences. To disentangle the effect of increasing atmospheric CO₂ from other factors (e.g. eutrophication) and to isolate the impact of ocean acidification from other environmental changes, such a monitoring program requires measuring a suite of parameters in addition to the marine inorganic carbon system (salinity, temperature, nutrient concentrations, oxygen). For reasons outlined in 1.4, the temporal resolution of such a monitoring program should be able to distinguish seasonal variability in pCO₂, [DIC], O₂, etc. (fig. 4). Importantly, these analyses have to be of ocean-going research accuracy to allow disentangling effects on the different parameters of the carbonate system and to be able to monitor the gradual changes foreseen. The outcomes of a multi-decadal monitoring program should ideally be linked to similar programs carried out in the UK, Germany and Denmark to, I) add the results of the Dutch national monitoring to the wider context and II) to identify the effects of national measures.

A monitoring program for the North Sea, initiated by the WKN (Werkgroep Kennis en Noordzee) has recently started and encompasses measurements of the inorganic carbon system parameters, salinity, dissolved oxygen, nutrients and temperature. This program also aims at identifying particularly vulnerable areas within

the North Sea and should allow determining the effects of ongoing changes in the North Sea. To cover the necessary spatial and temporal resolution, a total of 18 stations are visited monthly within this program. The total length of the program should be sufficiently to account for longer term environmental variability as a function of multi-annual climate oscillations (like the NAO cyclicity), which likely influences the North Sea's inorganic carbon system (see also section 1.4).

For the Dutch Caribbean waters, there is hardly oceanographic data available, except from bathymetry and sea surface temperatures. This is especially clear when comparing data on acidification available from the large area of the EEZ of the Caribbean Netherlands compared with the Dutch North Sea. The marine inorganic carbon system around the BES-islands urgently needs to be monitored to understand their current and future behaviour in response to environmental change.

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