# An overview of the potential consequences for cetaceans of oceanic acidification.

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#### Abstract

There has been a recent increase in research dedicated to understanding the complex effects of ocean acidification on marine ecosystems and organisms. Whilst study in this area is very much in its infancy, there is a clear message from a range of scientists and research institutions that this could have serious implications for cetaceans, with high latitude species likely to experience changes in their food web structure within this century. This paper provides a summary of the key peer-reviewed literature on ocean acidification with reference to consequences for cetaceans, their food webs or habitats. Drawing on assertions made in these papers, it is our contention that the potential impacts of ocean acidification on cetaceans merit future in-depth consideration from the Scientific Committee of the IWC and may have implications for the management of whale populations.

# Introduction

#### The role of the oceans in the carbon cycle

Carbon dioxide in the atmosphere dissolves in the oceans and can be released back into the atmosphere, making the oceans an important exchange point in the carbon cycle (Raven *et al.*, 2005). Although terrestrial systems have a higher biological uptake of  $CO_2$  per unit area, the overall biological absorption by the oceans is almost as large as absorption by terrestrial systems due to the much greater surface area of the surface oceans (Field *et al.*, 1998).

#### Increases in carbon dioxide and lowered ocean pH

Analysis of ice cores shows that atmospheric  $CO_2$  concentrations oscillated between 200 and 280 parts per million (ppm) over the 400,000 years pre-industrialisation (Doney, 2006). Current atmospheric concentrations of  $CO_2$  are now approaching 380 ppm as a result of anthropogenic emissions (Feely *et al.*, 2004; Raven *et a.l*, 2005) and  $CO_2$  is now around 30% more abundant in the atmosphere than it was in the 18<sup>th</sup> century (Doney, 2006). Based on current trends it is predicted that  $CO_2$  emissions could be up to 50% higher by 2030 (Turley *et al.*, 2006). Estimates of future atmospheric  $CO_2$  concentrations, based on the Intergovernmental Panel on Climate Change emission scenarios, suggest that by the end of the 21<sup>st</sup> century  $CO_2$  levels could be over 800 ppm (Prentice *et al.*, 2001).

'Ocean acidification' is the term given to the ongoing decrease in the pH of the Earth's oceans, caused by their uptake of anthropogenic carbon dioxide from the atmosphere.  $CO_2$  in the atmosphere is relatively inert, but in seawater it participates in a range of chemical, biological and geological reactions meaning that elevated  $CO_2$  can affect many processes in marine biogeochemistry, with the effects likely to be non-linear and complex, potentially including positive and negative feedback reactions. The pH or pristine seawater is between 8 and 8.3, making it naturally alkaline (Raven et al., 2005). When  $CO_2$  dissolves, it reacts with water to form a balance of ionic and non-ionic chemical species (H<sub>2</sub>CO<sub>3</sub> (Carbonic acid) + HCO<sub>3</sub><sup>-</sup> and  $CO_3^{2-}$ 

(bicarbonate and carbonate ions) +  $H^+$  +  $CO_{2 (aq)}$ ). Dissolved atmospheric  $CO_2$  increases the hydrogen ion  $(H^+)$  concentration in the ocean, and thus reduces ocean pH.

The world's oceans have taken up around 50% of the anthropogenic  $CO_2$  released to the atmosphere since the industrial revolution (Sabine *et al.*, 2004; Raven *et al.*, 2005; Doney, 2006) and are known to act as a buffer for atmospheric  $CO_2$  concentrations.

Between 1951 and 2004, ocean pH is estimated to have dropped by approximately 0.1 units from approximately 8.25 to 8.14, equivalent to a 30% increase in the concentration of hydrogen ions (Jacobson, 2005; Raven *et al.*, 2005) and it is estimated that it will drop by a further 0.3 - 0.4 units (Haugan and Drange, 1996; Brewer, 1997; Raven *et al.*, 2005; Orr *et al.*, 2005) by 2100. This will result in larger and more rapid pH changes over the next several centuries than any experienced over the last 20 million years and perhaps longer (Seibel and Fabry, 2003; Caldeira and Wickett, 2003; Raven *et al.*, 2005; Turley *et al.* 2006). Unabated release of fossil-fuel CO<sub>2</sub> into the atmosphere could lead to a pH reduction in surface waters of 0.77 units by 2250 (IPCC, 2001; Caldeira and Wickett, 2003). As the ocean's CO<sub>2</sub> uptake increases, so its capacity to act as a buffer to atmospheric CO<sub>2</sub> levels decreases (Turley *et al.*, 2006).

# Effects of increased CO<sub>2</sub>

Dissolved atmospheric  $CO_2$  results in a higher concentration of H+ ions in solution. In simple terms, H+ ions combine with carbonate ions, making bicarbonate ions, leaving a net decrease of carbonate ions. Oceanic carbonate ion concentration is expected to drop by half over this century (Doney, 2006).

Many organisms depend on the presence of carbonate ions to build their calcium carbonate (CaCO<sub>3</sub>) shells (Doney, 2006). Calcium carbonate (CaCO<sub>3</sub>) exists in two main structures; aragonite and calcite, the latter being less soluble due to its structure. Oceanic water is termed 'undersaturated with respect to CaCO<sub>3</sub> (aragonite, calcite or both) when there is insufficient  $CaCO_3^{2-}$  available in solution to prevent CaCO<sub>3</sub> dissolving in sea water. Depending on the level of under-saturation, it may also mean that there is insufficient  $CaCO_3$  structures (Raven et al., 2005).

#### Reduced calcification

Laboratory studies suggest that some oceanic plankton are highly sensitive to changes in  $CO_2$  concentrations in sea water. The calcification rate of all calcifying organisms investigated to date decreased in response to a decreased calcium carbonate saturation state (Feely *et al.*, 2004; Raven *et al.*, 2005). Calcifying organisms that may be affected include the coccolithophores, pteropods, gastropods and foraminifera; all of which are major food sources for fish and some whale species (Riebesell *et al.*, 2000; Doney, 2006).

Research has already found that pteropods experience reduced calcification when exposed to elevated  $CO_2$  (Orr *et al.*, 2005). Increased  $CO_2$  (lowered pH) also results in reduced calcite production in cultures of two dominant marine calcifying species, the coccolothophorids *Emiliania huxleyi* and *Gephryrocapsa oceanica*. These unicelluclar microalgae are important primary producers and an important part of marine ecosystems. *E. Huxley* is one of the most prominent producers of calcium carbonate in temperate and sub-polar oceans. (Riebesell *et al.*, 2000). Regional variations in pH will mean that by 2100 the process of calcification may have become extremely difficult for some of these groups of organisms, particularly in the Southern Ocean (Raven *et al.*, 2005; Orr *et al.*, 2005).

# Saturation horizons and dissolution of calcifying organisms

Deep, cold waters are undersaturated with calcium carbonate ions, causing  $H^+$  ions to dissolve CaCO<sub>3</sub> in the shells of calcifying organisms, hence these organisms are not found in deep, cold waters. Surface waters,

supersaturated with carbonate ions (CO3<sup>2-</sup>) do not dissolve calcifying organisms (Doney, 2006). The 'saturation horizon' is the level below which CaCO<sub>3</sub> begins to dissolve, and below which calcifying organisms are not able to exist. As atmospheric CO<sub>2</sub> dissolves in surface waters so the concentration of  $H^+_{(aq)}$  ions increases. These H+ ions combine with carbonate ions to form bicarbonate ions and carbonic acid and so a net reduction in the amount of CO3<sup>2-</sup> (carbonate) ions in surface waters occurs. This has the effect of artificially under-saturating the water with respect to carbonate ions, leaving structures made of calcium carbonate vulnerable to dissolution at shallower depths, as the saturation horizon rises vertically in the water column (Orr *et al.*, 2005; Doney, 2006). The calcite and aragonite saturation horizon has moved closer to the surface by 50-200m compared to where it was in the 1800s (Doney, 2006).

Laboratory experiments readily show the deleterious effects (including growth stunting and reduced reproduction) of increased CO<sub>2</sub> (and associated fall in pH) for all major groups of marine organisms that have parts made of CaCO<sub>3</sub> (Doney, 2006). Coccolithophore algae (Riebesell *et al.*, 2000) and pteropods (Orr *et al.*, 2005) exhibit enhanced dissolution when exposed to elevated CO<sub>2</sub>.

# Changes in the high latitudes

Cold polar waters are naturally less supersaturated with respect to carbonate ions than warm waters, so high-latitudes will be the first to suffer measurable impacts of ocean acidification, including reduced carbonate availability and decreased volume of habitat suitable for calcifying plankton due to rising saturation horizons (Doney, 2006).

Pteropods are prominent components of the upper-ocean biota in the Southern Ocean, Arctic Ocean and subarctic Pacific Ocean and are the major planktonic producers of aragonite (Orr et al., 2005). These pelagic molluscs are an important food source for marine predators in the Antarctic food web and are known to replace krill as the dominant zooplankton group in parts of the Southern Ocean (Cabal *et al.*, 2002; Seibel and Dierssen, 2003).

In McMurdo Sound, the pteropod *Limacina helicina* can constitute more than 20% of the zooplankton biomass (Siebel and Dierssen, 2003). *L. helicina* is an important prey item for a number of Antarctic species, including whales and myctophid and notothenioid fishes (Foster and Montgomery, 1993), the latter being important components in the diet of penguins and certain mammals including toothed cetaceans (Davis *et al.*, 1999).

Orr *et al.* (2005) predict that some polar and subpolar surface waters will become undersaturated with respect to aragonite when atmospheric  $CO_2$  levels reach twice the pre-industrial levels, probably within the next 50 years in a "business as usual" scenario. A recent experimental study showed that the shells of live pteropods dissolve rapidly once surface waters become undersaturated with respect to aragonite (Feely *et al.*, 2004). If pteropods are restricted to aragonite-saturated waters, their habitat will become increasingly marginalised latitudinally and vertically as the aragonite saturation horizon moves closer to the oceans' surface (Siebel and Fabry, 2003; Raven *et al.*, 2005).

Several authors have indicated the possibility that polar pteropods such as *Clio pyramidata* could disappear completely under the surface water conditions predicted for the year 2100 (Seibel and Fabry, 2003; Orr *et al.*, 2005). The disappearance of pteropods would have an immediate affect on their direct predators, such as the zooplankton *gymnosome*, which feed exclusively on pteropods (Seibel, & Dierssen, 2003). Pteropods are also a key primary link in the Southern Ocean food chain, contributing to the diets of many species of zooplankton, North-Pacific salmon, mackerel, herring, cod and baleen whales (Lalli and Gilmer, 1989; Seibel and Dierssen, 2003; Orr *et al.*, 2005). The state of pteropod populations is presently taken as an indicator of overall ecosystem "health" in the Ross Sea (Seibel and Dierssen, 2003) and their removal could have catastrophic impacts on the entire food chain of the Southern Ocean.

The food web implications for the disappearance of a prominent primary calcifying producer are potentially huge. Non-calcifying organisms may take advantage of this newly vacated niche and so change the structure and processes occurring in the ecosystem as a whole (Riebesell *et al.*, 2000; Turley *et al.*, 2004; Raven *et al.*, 2005). Lowering of pH also has the potential to inhibit nitrification, which may also cause changes in the dominant phytoplankton species composition. This in turn is likely to affect the grazer community, including economically important species (Turley *et al.*, 2006).

# Effects of ocean acidification on multicellular animals

Climate change scenarios that involve three- to fourfold increases in atmospheric  $CO_2$  may also result in stress to the physiology of multi-cellular organisms with high metabolic rates, such as squid, with the potential for growth reduction and increased mortality (Ishimatsu *et al.*, 2004; Raven *et al.*, 2005). The influence of ocean acidification on marine organisms other than calcifiers, could include decreased reproductive potential, slower growth or increased susceptibility to disease. These responses could have cascading effects through food webs, with possible consequences for ecosystem structure (Raven *et al.*, 2005). The importance of cephalopods as primary prey species for many cetaceans is well established and, therefore, the predicted negative impact for populations of these predators deserves further attention.

# Conclusions

Raven et al. (2005) have recently commented that:

"Marine ecosystems are likely to become less robust as a result of the changes to the ocean chemistry and these will be more vulnerable to other environmental impacts (such as climate change, water quality, coastal deforestation, fisheries and pollution). The increased fragility and sensitivity of marine ecosystems needs to be taken into consideration during the development of any policies that relate to their conservation, sustainable use and exploitation, or the communities that depend on them."

And Turley et al. (2006) state that:

"...marine acidification seems inevitable and effects on the marine ecosystem are likely to be measurable. We, the scientific community, are far from being able to predict with certainty the extent of impact and whether an appreciable decline in resource base may occur."

This review highlights both the concerns raised by the expert community and our inability to clearly predict implications for whales and marine species, although those that are dependent on cephalopods and certain planctivores may be especially vulnerable. The inevitable changes in high-latitude seawater chemistry by the end of the century are predicted to alter the structure and biodiversity of high-latitude ecosystems, with large-scale ramifications for the Southern Ocean ecosystems on which many cetacean species are dependent.

The issue of ocean acidification has been - and continues to be - rapidly gaining attention within the scientific community. That an eminent team of experts (Raven *et al.*, 2005) and an international convention (OSPAR) have called on marine resource managers to take ocean acidification into consideration when developing policies is a clear indication of the potential seriousness of the situation, and a sign that this issue merits thorough attention from the IWC.

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