GEOPHYSICAL INSTITUTE - UNIVERSITY OF BERGEN - NORWAY

REPORTS IN METEOROLOGY AND OCEANOGRAPHY

2 - 2004

Peter M. Haugan

POSSIBLE EFFECTS OF OCEAN ACIDIFICATION

"REPORTS IN METEOROLOGY AND OCEANOGRAPHY"
is a report series maintained by the Geophysical Institute, University of Bergen.
Its objective is to publish work by people affiliated with the institute.

Address: "Reports in Meteorology and Oceanography",
Geophysical Institute, Allégaten 70, N-5007 Bergen, Norway

REPORTS IN METEOROLOGY AND OCEANOGRAPHY
UNIVERSITY OF BERGEN
REPORT NO. 2 - 2004

Peter M. Haugan

POSSIBLE EFFECTS OF OCEAN ACIDIFICATION

Geophysical Institute,
Allégaten 70,
N-5007 Bergen, Norway
REPORT NO. 2 - 2004

REPORTS IN METEOROLOGY AND OCEANOGRAPHY
UNIVERSITY OF BERGEN
REPORT NO. 2 - 2004
ISSN 1502-5519
ISBN 82-8116-002-0

Foreword

This report has been written with support from the Norwegian Ministry of Environment. Thanks also to Christoph Heinze from the Geophysical Institute, Richard Bellerby from the Bjerknes Centre for Climate Research and Lars Golmen from NIVA for comments to an early draft. However, responsibility rests solely with the author. Hopefully the report can be useful for further research and assessments. The report is written with a Norwegian perspective and regional emphasis, but is provided in English for the benefit of non-Norwegian readers.

Peter M Haugan

POSSIBLE EFFECTS OF OCEAN ACIDIFICATION

Peter M. Haugan

December 2004

Abstract

Emissions of carbon dioxide (CO_2) to the atmosphere lead to increased carbon concentration and acidification (reduced pH) in the ocean. Near the ocean surface, the acidification is even over most of the world oceans, with a reduction of just over 0.1 pH units since the start of the industrial revolution and expected reduction of 0.3 pH units or more over the present century. At depth (more than 1000-1500 m) large geographical differences prevail. The acidification will penetrate most rapidly down in areas with strong vertical mixing, generally in the North Atlantic, particularly in the Norwegian Sea, the Barents Sea and the Greenland Sea and in certain areas in Antarctica.

Experiments with important algal species and calcifying organisms like corals show significant disturbances when exposed to CO_2 levels which are expected in the present century. Calcium carbonate shells form later and more slowly or not at all. The vertical transport to the deep sea is significantly reduced. Experiments also show that competion between different algal species will change depending on the ability to sequester carbon from the water. The structure of large marine ecosystems can be expected to change. The carbon levels are not high enough to give acute problems for organisms like fish, but eggs and larvae seem to be more sensitive.

At larger depths the natural variations are smaller in amplitude than the change which has already happened at the surface and which is penetrating downwards. We know very little about which effects to expect for deep-sea organisms. Natural changes over time have happened much more slowly than the anthropogenic supply taking place now. Special ecosystems associated with natural seeps of CO_2 through the seafloor do exist, but most deep-sea organisms are not adapted to the CO_2 levels which are approaching.

There is a lot we do not know about effects of CO_2 on the oceans, e.g. via changed nutrient uptake and availability of trace elements. The ecosystems are complicated and it is difficult to get an overview of all consequences. However, there are some relatively simple but important direct effects which have already been documented and are at least partially understood. During the present century, the ocean will change significantly because of the added CO_2.

Introduction

The issue and some background

It has been well established that CO_2 is a greenhouse gas and that increased levels of CO_2 in the atmosphere lead to global warming. The Intergovernmental Panel on Climate Change (IPCC) has assessed causes, possible abatement options and effects of climate change. A complicated interplay between indirect effects on the marine environment and marine organisms via changes in ocean temperature, sea level, wind, ice extent and possibly in ocean currents, has been considered. Up to now, the oceans have taken up at least 1/3 of the total emissions to the atmosphere. After 1000 years at least 2/3 of the cumulative emissions to the atmosphere are expected to reside in the oceans. The direct chemical changes in the marine environment due to increased carbon concentration can be calculated accurately. But direct impacts, caused by a changed chemical environment and independent of greenhouse effect and climate change, have not been included in the assessments, neither by the IPCC nor e.g. the Arctic Climate Impact Assessment (ACIA).

There has been some research on direct impacts of elevated CO_2 level on terrestrial biological systems. Some plants react positively to increased CO_2 up to a certain level, others do not. The ocean accounts for approximately the same amount of primary production (from solar energy to biomass) as the land surface. Because of the special carbon chemistry of seawater, the environmental changes in the ocean due to increased CO_2 are in many ways more dramatic than those due to increase of the CO_2 level in the air. Experiments with increased CO_2 have only been done with very few marine species and not on an ecosystem scale. During 2004, however, research results have been put forward indicating that the ongoing changes may be dramatic in a 100 year perspective both for large scale biogeochemical processes in the world oceans, for key species of phytoplankton and for organisms such as coral reefs.

It is likely that already when the atmospheric CO_2 level reaches 450 ppm (which will happen soon regardless of scenario; we are now at 380 ppm, up from 280 in pre-industrial times) there will be direct effects on ocean ecosystems. The changes in acidity measured in units of reduced pH may not seem dramatic compared to pH variations which are known e.g. from fresh water and certain marine environments. This may be why they have not been taken seriously up to now. But the changes are large and rapid compared to natural changes over geological time scales and they occur in all oceans. Sensitive algae that need to stay near the ocean surface to find nutrients and sunlight for photosynthesis, have no way to escape. Other organisms like fish and marine animals are subject to other types of physiological stress when CO_2 levels increase.

In order to put the concentrations and environmental changes into perspective, it may be mentioned that a working group appointed by Norwegian public health authorities has recommended 1000 ppm as the maximum acceptable CO_2 level in air indoor, e.g. in classrooms in public schools. It is not unrealistic that we may reach such levels outdoor all over the globe in the present century. Before we get there, and before we have figured out the regional effects of climate change, what happens to marine life?

A primer on some relevant carbon chemistry of seawater

The most important chemical changes occurring when CO_2 is added to seawater (salt water) may be summarized by two reactions.
The first leads to production of bicarbonate ion (HCO_3^-) by consuming carbonate ion (CO_3^{2-}):

$CO_2 + H_2O + CO_3^{2-} \rightarrow 2HCO_3^-$.

So there will be less carbonate and more bicarbonate. As the carbonate reserves begin to be depleted, much of the added CO_2 will remain simply as dissolved CO_2. But bicarbonate will also by produced by reaction directly with water:

$CO_2 + H_2O \rightarrow H^+ + HCO^-$.

This reaction has increased concentration of hydrogen ion (H^+) as a byproduct. That means reduced pH, since pH is defined as the negative logarithm of the concentration of H^+ measured in mol/kg. So a reduction of 1 pH unit corresponds to a 10-fold increase in the concentration of H^+. (Several different pH scales are in practical use depending on how the measurements are performed. These pH scales give significantly different numerical values for absolute pH measured in any given system. But one can always convert from one scale to another when the system is characterized. The relative pH changes addressed here are independent of scale and measurement technique.) Seawater normally has a pH value around 8. The chemical reactions are quite different in freshwater. It is practical to measure the environmental change by the pH reduction, and a certain body of knowledge exists concerning effects of pH changes. But the effects of CO_2 can be larger than those experienced by similar pH changes from other additives, such as HCl. Carbon may be taken up by organisms in different ways than other materials. Reduced carbonate concentration and increased CO_2 concentration may in some cases be at least as important as the reduced pH.

The above reactions equilibrate rapidly (few minutes) after addition of CO_2. They involve carbonic acid (H_2CO_3) in an intermediate stage, and normally we do not distinguish between concentrations of carbonic acid and dissolved CO_2. The total carbon concentration in seawater (the sum of carbonate, bicarbonate and carbonic acid/CO_2) is around 2 mol/kg = 2000 µmol/kg. Most of the carbon dissolved in seawater is in the form of bicarbonate, some in the form of carbonate and only about 1% is in the form of dissolved CO_2, see the figure on the following page. In the atmosphere, CO_2 is almost chemically inert. All carbon that is transformed directly from the atmosphere to the ocean (not via river runoff) do so in the form of CO_2.

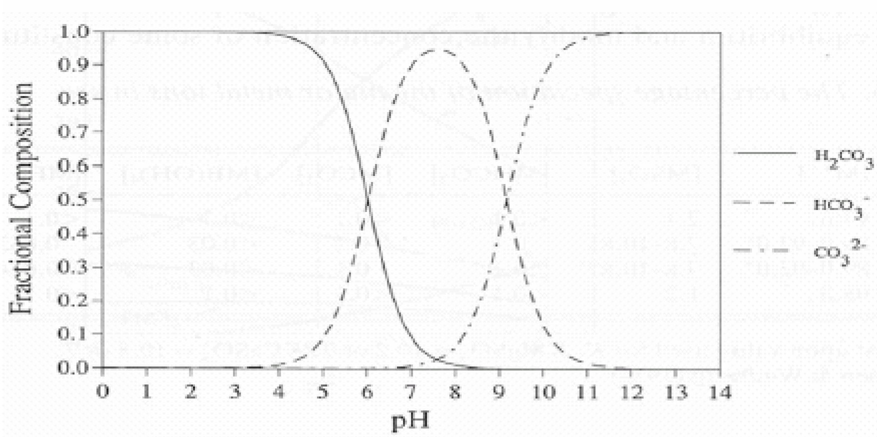
Biological matter is formed primarily from carbon (C) and nutrients such as phosphorus (P), nitrogen (N) and in some cases silicon (Si). In addition, trace elements like iron (Fe) can be important. Calcium (Ca) is important for some organisms such as coral reefs and some algal species, preferrably in the form of calcium carbonate ($CaCO_3$). Biological production of calcium carbonate requires the availability of sufficient amounts of carbonate (CO_3^{2-}). Production takes place near the ocean surface and dissolution at depths when dead matter sinks down, but this export may be reduced in high CO_2 conditions.

Scenarios for CO_2 and acidification (pH)

The situation today

Since pre-industrial times, i.e. during the last 200 years, the atmospheric CO_2 concentration has increased from 280 ppm (parts per million) to 380 ppm. The increased partial pressure of CO_2 in the atmosphere drives the gas into seawater. During the last 20 years there has been a partial pressure difference of 8 ppm between air and water and a net uptake of CO_2 in the ocean of about 2 PgC (= 7 $PgCO_2$) per year corresponding to about 1/3 of the annual emissions. Almost everywhere in the surface mixed layer (normally 50-200m deep), the pH has therefore reduced by about 0.1 pH units, the carbonate concentration has reduced by about 40 µmol/kg, while the total carbon concentration has increased by about 60 µmol/kg since pre-industrial times.

It is only in very special areas, e.g. upwelling areas where the carbon concentration is already high, or permanently ice covered areas, that these changes near the surface have not occurred.



Fractional compositionof the carbon system

The exchange between the surface and deeper layers occurs slowly with a turnover time that is counted in hundreds to a thousand years. So anthropogenic CO_2 is mostly confined to the upper layers down to 500-1000 m. Exceptions can be found in special areas where surface water is cooled and/or gets higher salinity (by ice freezing or evaporation) so that it becomes heavier and sinks down. The water becomes especially dense and sinks especially deep (more than 1000m) from certain limited areas in the Arctic and Antarctic. The vertical mixing is also strong and can reach down to 500-600m every winter in the Norwegian Atlantic Current along the Norwegian continental slope, and to the bottom in the shallower Barents Sea. Cooling also increases the ability to take up CO_2 (by reducing the partial pressure), but most of the increased carbon content in these waters has been taken up from the atmosphere further south in the Atlantic and transported into the area past the Faroe Islands. Dense water with high anthropogenic carbon content is formed in the Nordic Seas. This water flows southward at depth across the Greenland-Scotland ridge and thereby contributes to increase the carbon content of deep water also further south. Of all the world oceans, the North Atlantic has the highest content of anthropogenic carbon per area.

There is a natural geographical variation in the carbon system in the world oceans with lowest pH in the socalled oxygen minimum layer around 500-1500m depth, where bacterial decomposition has consumed oxygen and released carbon so that the pH is reduced by about 0.3 pH units compared to natural levels at the surface. In the Southern Ocean south of about 50 ºS, the pH is close to 8 and generally very homogeneous in all sectors and at all depths.

Further development into the future

A doubling of atmospheric CO_2 from 280 to 560 ppm will lead to a 30% reduction of the carbonate concentration, 60% increase in the hydrogen ion concentration and more than a doubling of the free CO_2 concentration (CO_2 and H_2CO_3) in seawater which is in contact with the atmosphere. A more detailed particular scenario is given in the table.

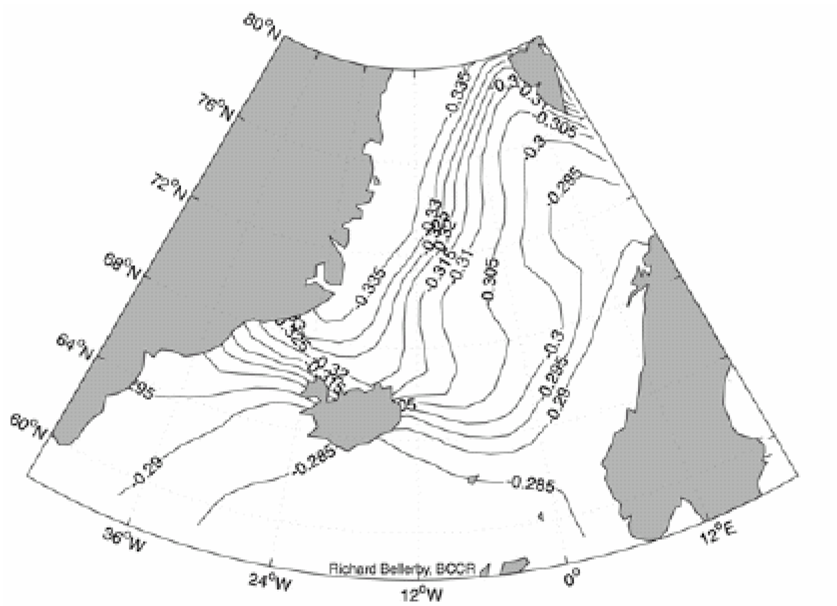
Numerical climate models can be used to estimate future scenarios for different carbon related parameters. Near the surface, the response is primarily determined by atmospheric CO_2 (which has very little geographical variation, only a few ppm), and ocean temperature and salinity, which among other things depend on ocean vertical mixing. We see from the figure that projections with the global coupled "Bergen Climate Model" gives changes of about 0.3 pH units in the surface of the Nordic Seas, strongest in the Greeland Sea (0.335), and a bit less in the North Atlantic (0.285).

The figure shows changes relative to today (1997) for a doubling of atmospheric CO_2 in year 2070 relative to atmospheric CO_2 today. In this calculation, the result is also influenced by changes in the chemical composition of Atlantic and Arctic waters.

Table 2. The evolving chemistry of surface sea water under "Business as Usual"

Time	pCO_2 year	Total CO_2 µatm	pH	HCO_3 µmol kg^{-1}	CO_3^{2} µmol kg^{-1}	H_2CO_3 µmol kg^{-1}
1800	280	2017	8.191	1789	217	10.5
1996	360	2067	8.101	1869	184	13.5
2020	440	2105	8.028	1928	161	16.5
2040	510	2131	7.972	1968	144	19.1
2060	600	2158	7.911	2008	128	22.5
2080	700	2182	7.851	2043	113	26.2
2100	850	2212	7.775	2083	97	31.8

FromBrewer (1997)



Estimated changes in pH in surface waters at doubled CO_2 (from Bellerby et al., 2005)

In deep water there are large geographical differences among the world oceans. It is fair to say that ocean areas of special interest to Norway are among those parts of the world oceans which first will experience increased carbon concentration, reduced pH and reduced carbonate concentration at depth. In tropical areas and generally at low latitudes, except special frontal areas with downwelling, it will take up to 1000 years for the anthropogenic carbon signal to penetrate much deeper than 1000m.

Direct effects on calcifying organisms

Coral reefs, both tropical corals and cold water corals which are present in Norwegian waters, use calcium (Ca) in order to build calcium carbonate ($CaCO_3$). Certain microalgae, especially coccoliths including the key species *Emiliania huxleyi*, also produce calcium carbonate shells. As long as there is free $CO3^{2-}$ in the seawater, i.e. for moderate pH changes, one used to think that this production would not be affected by variations in pH. However, recent research has shown that coccoliths may reduce the production of shells by 20-40% at doubled CO_2 levels. Corals and coralline algae respond with 15-85% reduced growth at doubled CO_2. Clearly, it becomes difficult for some species to utilize the carbon that is present in the seawater when the carbonate concentration is reduced as a consequence of increased CO_2.

Other effects

CO_2 penetrates into organisms and lead to physiological changes. The acid-base regulation in body fluids is affected. The metabolism depend on enzymes which normally work over a very narrow pH range. To compensate for acidification and maintain ionic balance, osmo-regulation may be affected so that more salt (NaCl) is taken up in fish exposed to high CO_2. In extreme cases this can lead to death. Animals which breathe in air can relatively easily reduce increased carbon level in their body by hyperventilation. However, animals which breathe in seawater have a carbon content much closer to that of the seawater, so that increased pumping of seawater through the gills will be less effective in reducing the carbon content.

Changes in pH also lead to changes in access to nutrients. NH_3 will reduce significantly while NH_4 will increase when the pH is reduced from just over 8 down towards 7. In a similar fashion certain phosporous and silicon nutrients will reduce and others increase in concentration. Higher CO_2 levels may also lead to higher ratio of carbon to nitrogen and phosphorous in biological material. Among the trace elements, Fe (III) will decrease and Fe(II) will increase, while Pb(I) will decrease and Pb(II) will increase. These environmental changes may have effects on productivity and toxicity, but there is very little information on how large the consequences will be on individual organisms.

In recent years, experiments have been performed exposing different marine organisms to elevated CO_2 concentrations. Some of these experiments have been done with concentrations which are larger than those mentioned in the scenarios for uptake from the atmosphere. Not all effects which have been reported in the literature will be relevant for carbon system changes corresponding to pH reductions around 0.3 or a doubling or tripling of the atmospheric CO_2. But it is a conspicious common feature of many studies with different types of organisms that the sensitivity to increased CO_2 is larger in long term experiments than in short term experiments, and the effects are larger on eggs, larvae and early life cycles than on adults. One may therefore fear that reduced reproduction and increased mortality is to be expected also for moderate pH changes even if this has not been confirmed in the experiments performed to date.

Possible consequences and indirect effects of changed biology

Because calcification becomes less effective and saturation conditions for different forms of calcium (or "chalk") changes, the vertical transport of biologically fixed calcium carbonate from the surface to depth (the export production) is expected to be significantly reduced (order 50% depending on scenario). Also chalk in sediments on the seafloor will dissolve more easily. Both the changed vertical transport and the changed chemical state of the seawater will have consequences for the environment at depth. These changes affect the exchange of CO_2 between atmosphere and ocean in the direction of increased uptake, but this effect is small (few percent) compared to the total uptake.

At higher CO_2 levels, algae which can utilize dissolved CO_2 or bicarbonate directly in the photosynthesis, will have a competitive edge. Some species are able to do this via not yet fully understood carbon concentration processes. One important species, *Emiliania huxleyi*, is able to grow strains without calcium carbonate shell in conditions with increased CO_2 levels. How this and other changes affecting the balance between important species will influence the larger ecosystem, is generally hard to say. Both the access to food for higher organisms and decomposition processes may be influenced.

Complex organisms are generally more sensitive to temperature extrema than simple organisms. Many of the same physiological mechanisms which are influenced by temperature and oxygen are also influenced by CO_2. Increased CO_2 is expected to lead to reduced tolerance to temperature extrema. Estimates have been made for expected reduction in extent of tropical coral reefs due to global warming and acidification. Up to now, warming has been more focussed, but the contribution from acidification is significant.

Changes in species composition of algae may change the release of dimethylsulphide (DMS) from the ocean to the atmosphere. DMS is important for cloud formation, so changes may give feedbacks to climate. Also release of other climate relevant trace elements from the ocean to the atmosphere, including organo-halogenes, may change. Very little is known about such effects at present.

Comparison to natural variations

In the littoral zone, bottom dwelling organisms may be exposed to larger natural variations in pH every day between high and low tide than the pH change that is expected 100 years into the future. There are also considerable diurnal variations in the biologically active surface layer when solar radiation governs primary production and the biological transformation of carbon. Seasonal changes, however, are small in most places. As mentioned previously, low pH is found in the oxygen minimum layer, normally around 1000-1500m depth. There are also geographical variations with relatively high pH in the Atlantic and low pH in the Pacific. This can be explained by the natural transport pathways, biological decomposition and the age of the water masses.

Normally very stable pH prevails at greater depths, but there are some exceptions. Special environments with natural seeps of CO_2 and other dissolved gases exist several places in the deep oceans. Specially adapted organisms exist in such areas. It is assumed that they have evolved over long time scales, and that "normal" organisms will not be able to adapt in a similar fashion to the present rapid changes.

The changes that are now occurring in ocean carbon chemistry are larger than changes over the past 20 million years. Even further back in time such as around 55 million years ago, dramatic environmental changes occurred with extinction of many species in a relatively short period of time, of order 1000 years. Some mass extinction events are associated with both increased CO_2

(decreased $CO3^{2-}$) and increased temperature. Since low $CO3^{2-}$ in seawater and high temperature often are correlated in time, it is difficult to conclude which factor has had largest biological effect. Recently several researchers have proposed that reduced $CO3^{2-}$may have been more important than previously understood. This also applies to studies of the connection between temperature and growth of corals.

Conclusion

Anthropogenic supply of CO_2 to the oceans leads to massive changes in the carbon chemistry state of seawater. The biogeochemical processes connected to formation of calcium carbonate shells and their dissolution are directly affected by these changes.

Addition of CO_2 also leads to changes in the competition between different algal species. These and other effects may induce biogeochemical feedbacks which are less well known and understood, but can alter the structure and functioning of large marine ecosystems.

Different means to abate and adapt to climate changes are presently discussed. However, the direct effects of CO_2 on the marine environment can only be avoided by drastic limitations to the expected CO_2 level in the atmosphere in this century.

References and selected literature

Bellerby, R.G.J. et al 2005. Response of the surface ocean CO_2 system in the Nordic Seas and North Atlantic to climate change. Accepted in H. Drange, T.M. Dokken, T. Furevik, R. Gerdes, and W. Berger (Eds): *Climate Variability in the Nordic Seas*, Geophysical Monograph Series, AGU.

Brewer, P. G. 1997. Ocean chemistry of the fossil fuel CO_2 signal: The haline signal of "business as usual". *Geophysical Research Letters* **24** (11), 1367-1369.

Caldeira, K. and M.E. Wickett 2003. Anthropogenic carbon and ocean pH. *Nature* **425**, 365.

Cicerone, R. et al 2004. The Ocean in a High-CO_2 World, SCOR/IOC Symposium, http://ioc.unesco.org/iocweb/co2panel/HighOceanCO2.htm , and articles submitted to *J.geoph.res.*

Feely, R.A. et al 2004. Impact of Anthropogenic CO_2 on the $CaCO_3$ System in the Oceans, *Science* **305**, 362-366.

Haugan, P.M. and H. Drange 1996. Effects of CO_2 on the ocean environment. *Energy Convers. Mgmt.* **37** (6-8), 1019-1022.

Heinze, C. 2004. Simulating $CaCO_3$ export production in the greenhouse. *Geophysical Research Letters* **31** L16308, doi:10.1029/2004GL020613.

Sabine, C.L. et al 2004. The Oceanic Sink for Anthropogenic CO_2, *Science* **305**, 367-371.

Shirayama, Y. et al 2004. Special Section on Advances in Biological Research for CO_2 Ocean Sequestration, *Journal of Oceanography* **60 (4)**, 691-816, including several independent arcticles by Riebesell, Poertner and others.