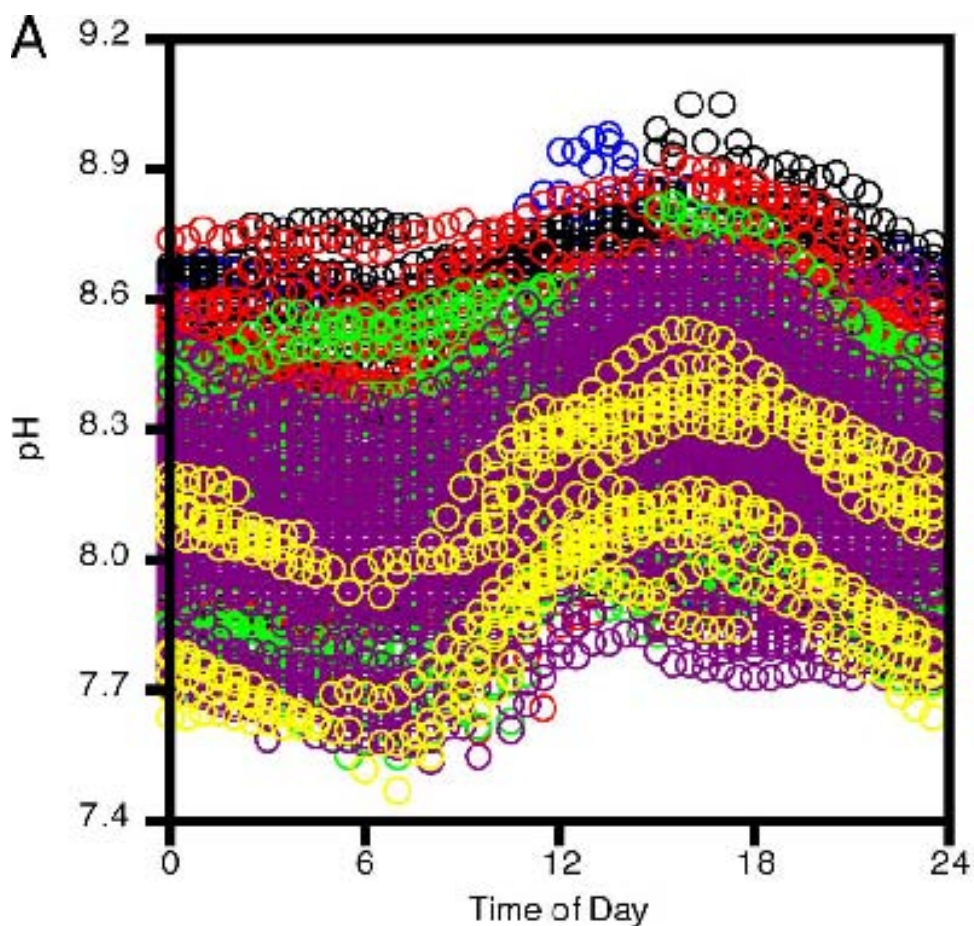


Ocean acidification and carbonate system parameters measurements

A Review



Døgn- og årsvariasjoner i pH i havet på samme sted (Wootton et al., 2008)

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Abstract
 This document summarizes the most recent estimates of the ocean acidification and carbonate system parameters measurements on the basis of the available reviews prepared by international and national organizations (IPCC, NOAA/NSF/USGS, ICES, Royal Society, OSPAR, WBGU), with additional information from research papers of relevance to the activity of NIVA.

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3. Målinger	3. Measurements
4. Modellering	4. Modelling



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Ocean acidification and carbonate system parameters measurements

A Review

Preface

NIVA initiated this project due to the increased focus on Ocean Acidification in international and national projects. The aim is to estimate the potential consequences of acidification for the marine environment and human activities.

This document summarizes the most recent estimates on the basis of the available reviews prepared by international and national organizations (IPCC, NOAA/NSF/USGS, ICES, Royal Society, OSPAR, WBGU), with additional information from research papers of relevance to the activity of NIVA.

The project is funded by NIVA.

Projectleader Evgeniy Yakushev and Kai Sørensen have participated.

Oslo, 30.01.2010

Evgeniy Yakushev

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Sammendrag

Oversikter over situasjonen for hav-forsuring kan finnes i en lang rekke publikasjoner; både nasjonale og internasjonale, bl.a.:

- IPCC, International Panel of Climate Change (IPCC, 2001, 2007)
- NOAA/NSF/USGS (Kleypas, 2006),
- ICES, International Council for the Exploration of the Sea, (Fernand, L., and Brewer, P., 2008),
- Royal Society (Royal Society (2005)),
- OSPAR Commission, protecting and conserving the North-East Atlantic and its resources (OSPAR, 2006).
- WBGU, German Advisory Council for Climate Change, (WBGU, 2006),
- NIVA-rapport l.nr. 5526-2008

De fleste av disse er tilgjengelig på Internet.

Økende partialtrykk av CO₂ i atmosfæren fører til økt CO₂-opptak fra luft til vann og økende karbon-konsentrasjoner i havet. Dette øker surheten i havet uttrykt som pH. pH i overflatevannet i verdenshavene har allerede avtatt med ca. 0.1 pH-enheter. Det ventes ytterligere reduksjon i pH på 0.2-0.3 pH-enheter innen år 2100, og videre forsuring senere avhengig av fremtidige utslipps-scenarier. Forsuring opptrer først i havets blandede overflatevann, typisk ned til 50 – 200 meters dyp, og etterhvert til dypere vannmasser. I områder med effektiv utveksling med dypere vannmasser, slik som f.eks. i Grønlandshavet, kan vann helt ned til flere tusen meter påvirkes av forsuringen i dette århundre opp mot det en vil finne i overflatevannet.

Endringer i havenes karbon-kjemi pga. forhøyet CO₂ i atmosfæren er ikke begrenset til redusert pH. Økt konsentrasjon av løst CO₂ i sjøvann fører også til redusert konsentrasjon av karbonat-ioner. Dette har konsekvenser for karbonat-metningen i sjøvann og fører til at det blir gradvis vanskeligere for marine organismer med kalkskall. Koraller, inklusive de som lever i kalde farvann, og noen pelagiske organismer, som potensielle nøkkelorganismer av planteplankton og dyreplankton, vil trolig bli negativt påvirket av den pågående forsuringen.

Dagens endringer i havenes karbon-kjemi er raske, minst 100 ganger raskere enn andre endringer i løpet av de siste 100 000 år. Enkelte arter kan ha vanskelig for å tilpasse seg endrede forhold, mens arter med forskjellige livs-stadier med og uten kalkskall kan presses til større dominans av sistnevnte. Økosystemer vil trolig endres, men det er foreløpig ikke mulig å forutsi hvordan. Subpolare marine økosystemer er karakterisert med lange generasjonstider og få nøkkelarter. Kjemiske egenskaper i det relativt kalde vannet medfører en raskere reduksjon i karbonat-metning enn ved lavere breddegrader (OSPAR, 2006).

Et problem ved vurderingen av hav-forsuring ut fra pH-målinger er at variasjonene fra år-til-år er påvirket av store korttids-variasjoner (over døgn og sesong) og stor romlig variasjon (f.eks. ved frontsoner). I tillegg har den normalt brukte metoden for pH-målinger (potensiometrisk metode) svært dårlig presisjon og nøyaktighet (dårligere enn >0.020) sammenliknet med observerte trender. Dette gjør det svært vanskelig å sammenlikne data fra forskjellige kilder. Det er derfor nødvendig både å innføre nye og mer nøyaktige målemetoder og å få høyere oppløsning på målingene over tid og rom, f.eks. ved å bruke kontinuerlige målinger ombord i ferger o.l. (Ships of Opportunity).

I denne rapporten har vi samlet en oversikt over eksisterende metoder for bestemmelse av karbonat-systemet med spesiell vekt på fotometriske måleteknikker. Vi presenterer også eksisterende alternative metoder som er i bruk i NIVA og argumenterer for videre utviklingsbehov.

Summary

Estimates of the present state of the ocean acidification can be found in a large number of research papers and reviews that are published periodically by the international and national bodies, including:

- IPCC, International Panel of Climate Change (IPCC, 2001, 2007)
- NOAA/NSF/USGS (Kleypas, 2006),
- ICES, International Council for the Exploration of the Sea, (Fernand, L., and Brewer, P., 2008),
- Royal Society (Royal Society (2005)),
- OSPAR Commission, protecting and conserving the North-East Atlantic and its resources (OSPAR, 2006).
- WBGU, German Advisory Council for Climate Change, (WBGU, 2006),
- NIVA report no. 5526-2008

The majority of these reviews are available on the Internet.

Increasing partial pressure of CO₂ in the atmosphere leads to CO₂ uptake across the air-sea interface and increased carbon concentrations in the ocean. This increases the acidity of the seawater, expressed by a reduced pH. Surface waters of the world oceans have already experienced a pH reduction of about 0.1 pH units. Further reductions of the order of 0.2-0.3 pH units by 2100, are expected and even larger reductions may occur thereafter, depending on future emission scenarios. The acidification occurs first in the surface mixed layer which is typically 50 – 200 m deep and with some delay to deeper waters. In regions with efficient ventilation to great depths, such as in the Greenland Sea, waters down to several thousand meters depth may experience acidification rates in this century approaching those of near surface water.

Changes in ocean carbon chemistry due to elevated atmospheric CO₂ are not restricted to increased acidity, i.e. reduced pH. An increased concentration of dissolved CO₂ in seawater also implies reduced concentration of carbonate ions. This has consequences for the carbonate saturation state of the seawater and implies that it is becoming gradually more difficult for marine organisms to build carbonate shells. Corals including those living in cold water coral reefs, and some pelagic organisms, including potential key species of phytoplankton and zooplankton, are likely to be significantly negatively affected by the ongoing acidification.

Present changes in ocean carbon chemistry are rapid, at least 100 times more rapid than any experienced over the past 100 000 years. Individual species which may be especially vulnerable have little possibility to adapt, but some species that may exist in different forms e.g. with and without carbonate shells, may shift towards dominance of the latter. Ecosystems are likely to change but in yet unpredictable ways. Subpolar marine ecosystems are characterized by long generation times and few key species. Chemical properties of the relatively cold water implies a more rapidly reducing carbonate saturation state than at lower latitudes (OSPAR, 2006).

The problem of estimation of the ocean acidification using pH measurements is that the interannual changes of pH are superposed with large temporal (daily and seasonal) variability and spatial variability (for example at the frontal zones). Besides this, the commonly applied potentiometric technique has a very poor precision and accuracy (worse than >0.020) compared with the observed trends, that makes it difficult to compare data from different sources.

Implementation of new approaches is required. It is necessary to measure pH with higher accuracy and with better spatial and temporal coverage, for example by using Ships Of Opportunity (SOOP) program facilities.

In this document we reviewed the existing methods of the determination of the carbonate system parameters with a special attention to the photometric pH technique.

We also discuss the techniques that are in use at NIVA and justify the necessary development.

1. Ocean acidification: definitions; estimates; potential consequences

1.1 Introduction

Ocean acidification is the name given to the ongoing decrease in the pH of the Earth's oceans, caused by their uptake of anthropogenic carbon dioxide from the atmosphere (Cicerone et al., 2004).

The consequences of acidification might change the saturation state of the oceans with respect to calcium carbonate (CaCO_3), affect marine calcifying organisms, which build their external skeletal material out of calcium carbonate, change the community structure of carbonate ecosystems and affect the capacity of the Ocean to consume anthropogenic CO_2 .

On the base of some estimates, pH has decreased by - 0.075 from 8.179 in 1751 to 8.104 in 1994, a period of 243 yrs (Feely et al., 2004, Doney et al., 2006), pH may decrease by 0.770 from 2007 to 2250 (Caldeira and Wickett, 2003).

Direct pH measurements during time series programs testify to the presence of a negative trend in some areas (-0.02 per decade during the last 10-20 years (IPCC, 2007)) while in other cases such trends are unclear.

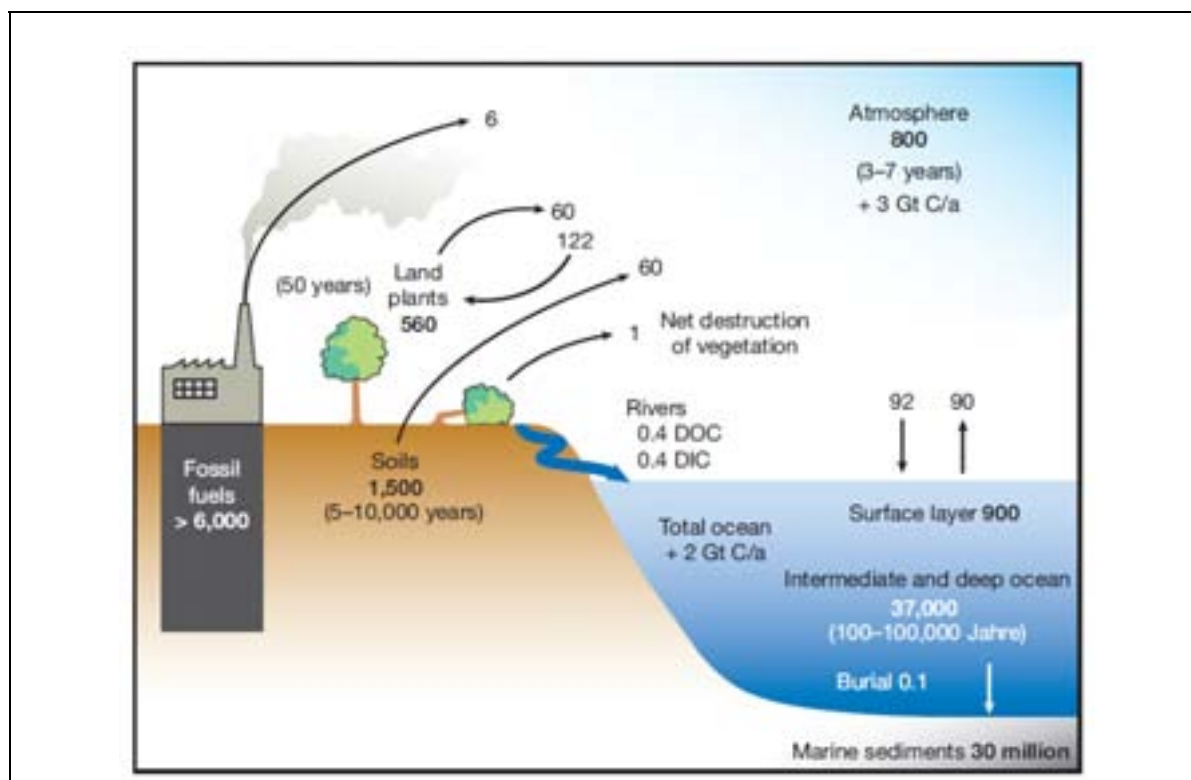


Figure 1.1.1.1 Overview of the global carbon cycle. Values for the carbon reservoirs are given in Gt C (numbers in bold print). Values for the average carbon fluxes are given in Gt C per year (numbers in normal-print). Mean residence times are in parentheses. Flux into soils amounts to around 1.5Gt C per year. DOC = dissolved organic carbon, DIC = dissolved inorganic carbon. Sources: adapted after Schlesinger, 1997 and WBGU, 2003. Numbers expanded and updated for ocean and fossil fuels: Sabine et al., 2003; marine sediments: Raven et al., 2005; atmosphere: NOAA-ESRL, 2006 (WBGU, 2006).

The problem of estimation of the ocean acidification using pH measurements is that the interannual changes of pH are superposed with large temporal (daily and seasonal) variability and spatial variability (for example at the frontal zones). Besides this, the commonly applied potentiometric technique has a very bad precision and accuracy (worse than >0.020 (Grasshoff et al., 1999)) compared with the observed trends, that makes it difficult to compare data from different sources.

Implementation of new approaches is required. It is necessary to measure pH with higher accuracy and with better spatial and temporal coverage, for example by using Ships Of Opportunity (SOOP) program facilities.

1.1.1 Oceanic carbon cycle

Estimates of the present state of the ocean acidification can be found in a large number of research papers and several reviews that are available through the Internet: German Advisory Council for Climate Change (The Future Ocean, 2006), NOAA/NSF/USGS (Kleypas, 2006); ICES (Fernand, L., and Brewer, P., 2008); Royal Society (2005); OSPAR (2006). The International Panel of Climate Change (IPCC) publishes reports with the recent estimates connected with the climate forced changes in the Ocean system.

Present estimates are that the oceans hold around 38,000 gigatonnes of carbon (Gt C). They presently store about 50 times more CO₂ than the atmosphere and 20 times more than the terrestrial biosphere and soils (Fig. 1.1.1.1). The present estimates on the Ocean carbon budget from different sources varies in estimation of the values and the residence time. (Fig. 1.1.1.1 and Fig. 1.1.1.2).

The ocean is not only an important CO₂ reservoir, but probably also the most important long-term CO₂ sink.

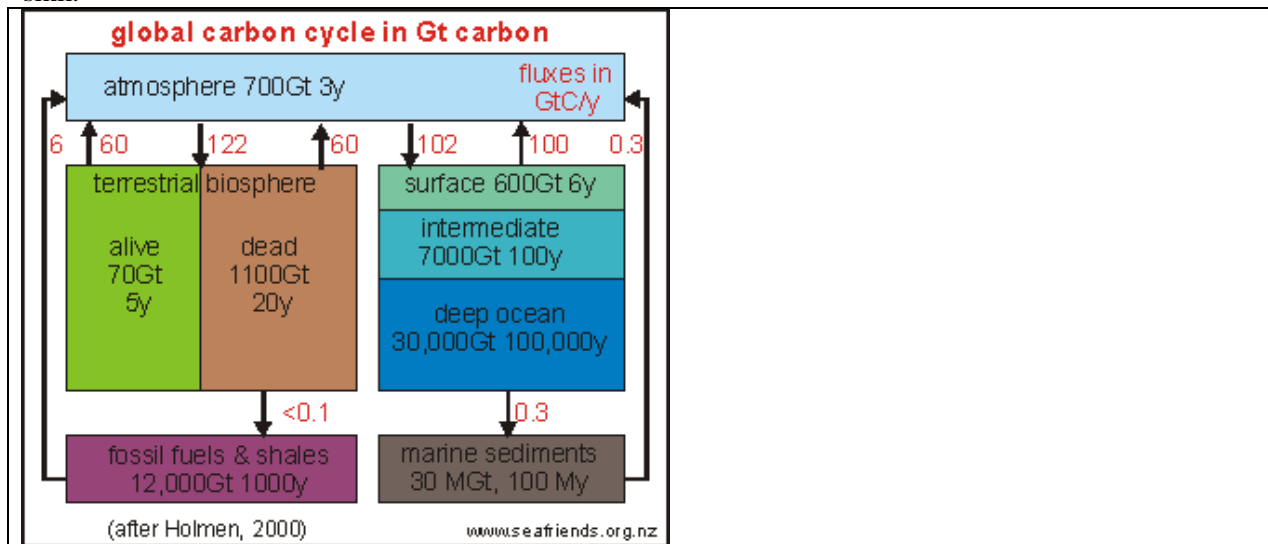


Figure 1.1.1.2 Global carbon cycle (from www.seafriends.org.nz after Holmen, 2000)

The increase in atmospheric CO₂ causes additional CO₂ to dissolve in the ocean. Changes in temperature and salinity also affect the solubility and chemical equilibria of gases. Changes in circulation affect the supply of carbon and nutrients from below, the ventilation of oxygen-depleted waters and the downward penetration of anthropogenic carbon. The combined physical and biogeochemical changes also affect biological activity, with further consequences for the biogeochemical cycles. (IPCC, 2007).

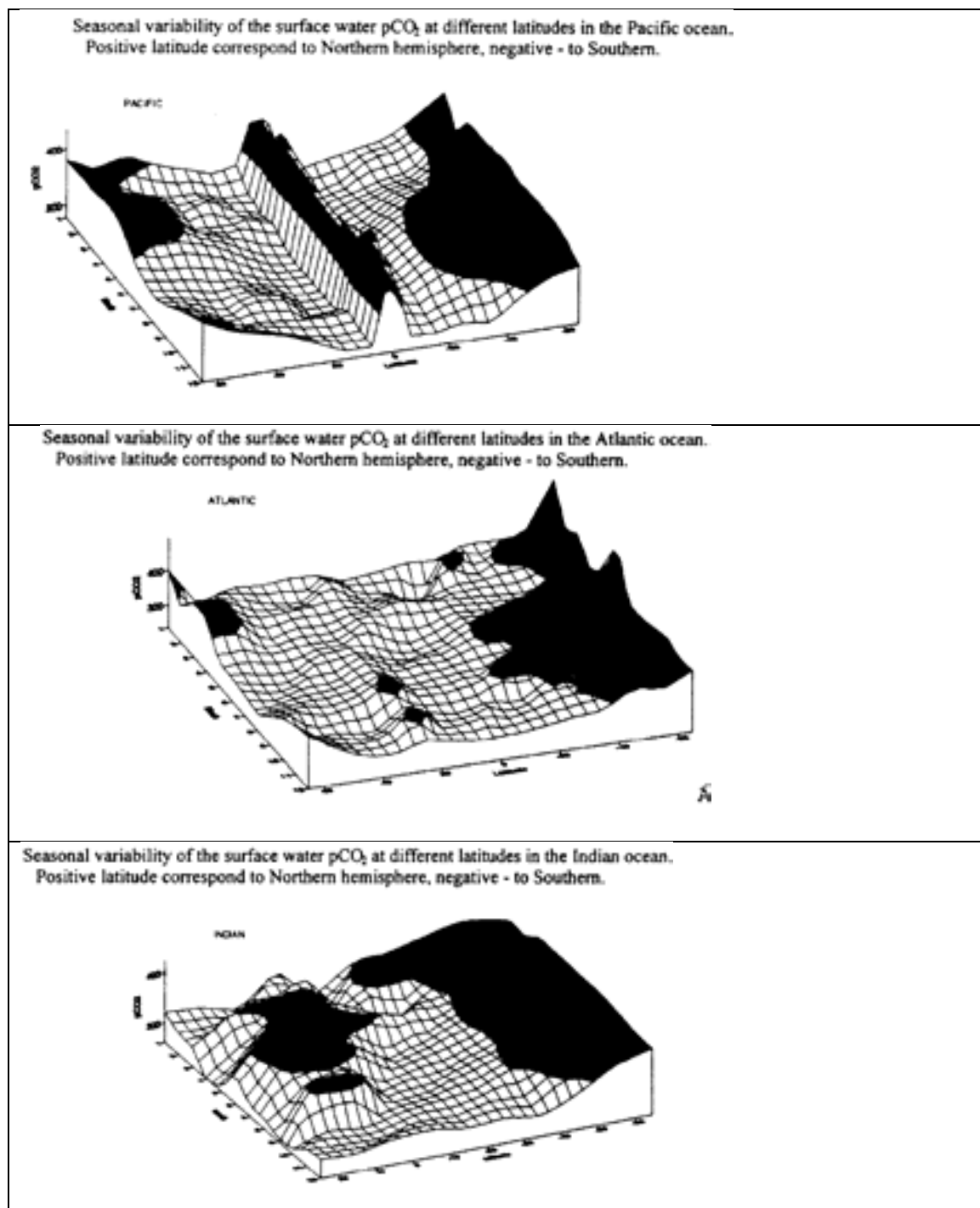


Figure 1.1.1.3 Seasonal variability of the surface water $p\text{CO}_2$ at different latitudes of the Ocean. Zones oversaturated with CO_2 are marked with Black (figure from Makkaveev, Yakushev, 1998).

The surface CO_2 is characterized by the zones permanently saturated with CO_2 (equator and polar regions), undersaturated (tropics) and zones that are oversaturated or undersaturated seasonally (Fig. 1.1.1.3). This results in different capacities of different latitudes bands of the oceans to take up the atmospheric CO_2 . The most undersaturated region from this point of view is the North Atlantic because this is the starting point of the deep loop of the Oceanic Conveyor Belt, where Ocean intermediate and deep water forms.

More than half of the anthropogenic carbon can still be found in the upper 400 m, and it is undetectable in most of the deep ocean water (Fig. 1.1.1.4), because of the limited rate of vertical transport in the ocean, according to the model estimates (ICCP, 2007)

The deeper penetration of anthropogenic carbon in these regions is consistent with similar features observed in the oceanic distribution of chlorofluorocarbons (CFCs) of atmospheric origin (Willey et al., 2004), confirming that it takes from decades to many centuries to transport carbon from the surface into the thermocline and into the deep ocean.

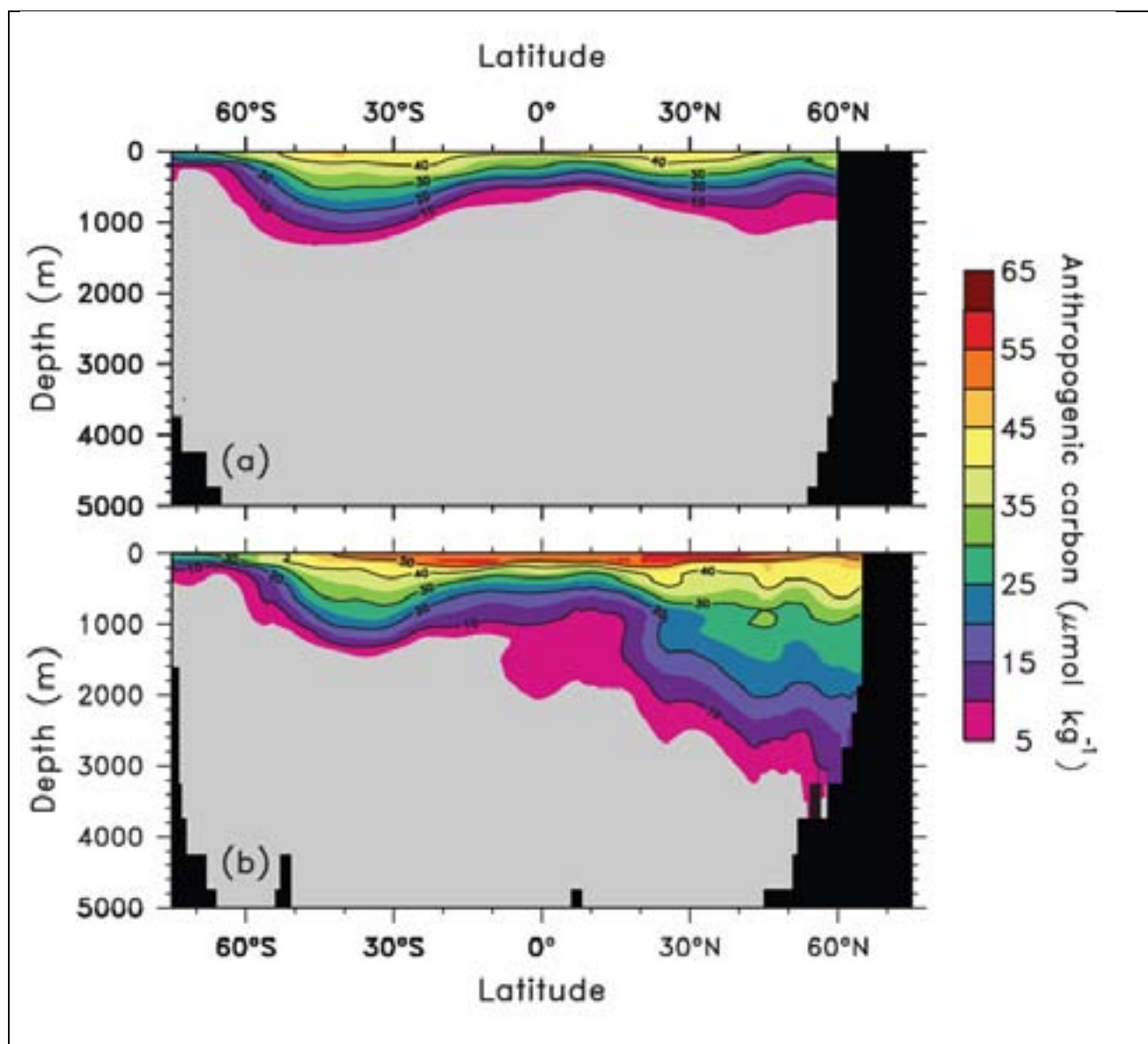


Figure 1.1.1.4 Mean concentration of anthropogenic carbon as of 1994 in $\mu\text{mol kg}^{-1}$ from Sabine et al. (2004b) averaged over (a) the Pacific and Indian Oceans and (b) the Atlantic Ocean (ICCP, 2007)

There has already been a demonstrable increase in CO_2 concentrations in the upper layer of the sea over recent decades (Sabine et al., 2004) that can be attributed to the proportional rise of CO_2 in the atmosphere. Direct surface pCO_2 observations have been used to compute a global air-sea CO_2 flux of $1.6 \pm 1 \text{ Gt C yr}^{-1}$ for the year 1995 (Takahashi et al., 2002). The ocean is presently taking up 2 Gt of

carbon annually, which is equivalent to about 30 per cent of the anthropogenic CO₂ emissions (IPCC, 2001, IPCC, 2007). Altogether, between 1800 and 1995, the oceans have absorbed around 118 Gt C ± 19 Gt C. That figure corresponds to about 48 per cent of the cumulative CO₂ emissions from fossil fuels (including cement production), or 27–34 per cent of the total anthropogenic CO₂ emissions (including those from land-use changes; Sabine et al., 2004). The anthropogenic CO₂ signal in the sea can be traced, on the average, to a water depth of approximately 1000 m. Due to the slow mixing of ocean layers it has not yet reached the deep sea in most parts of the ocean. However, in the North Atlantic due to the formation of deep water there, the anthropogenic CO₂ signal already extends down to 3000 m (Fig. 1.1.1.5).

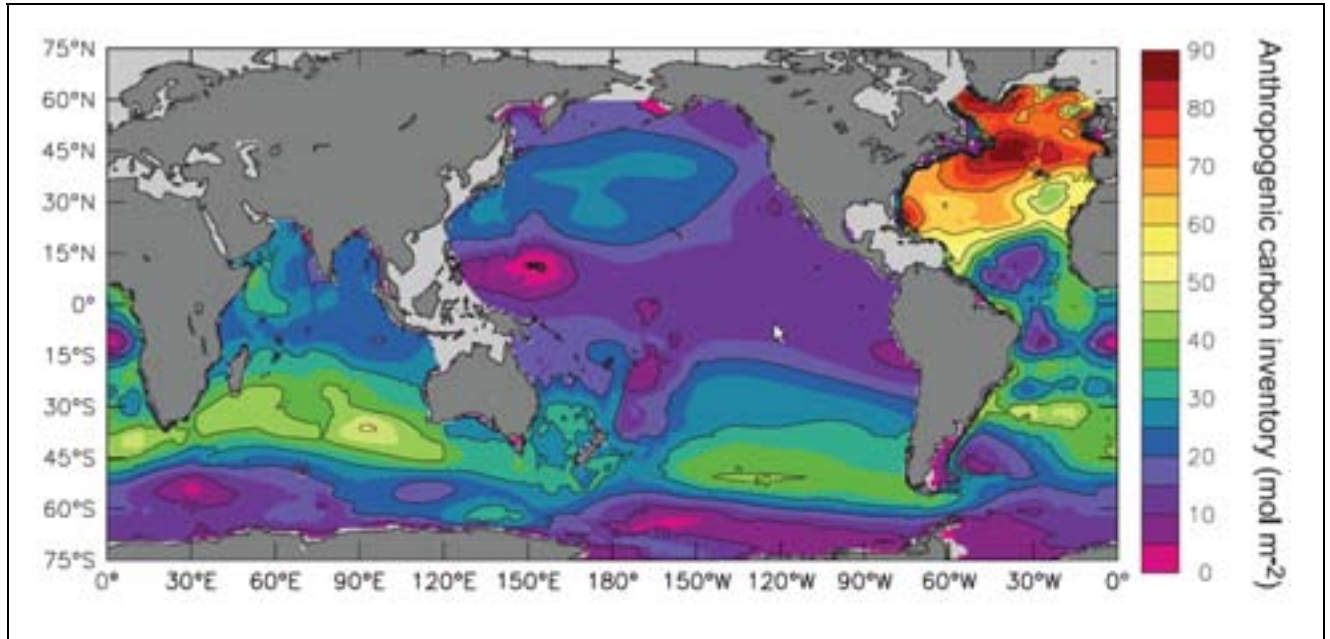


Figure 1.1.1.5 Column inventory of anthropogenic carbon (mol m^{-2}) as of 1994 from Sabine et al. (2004b). Anthropogenic carbon is estimated indirectly by correcting the measured DIC for the contributions of organic matter decomposition and dissolution of carbonate minerals, and taking into account the DIC concentration the water had in the pre-industrial ocean when it was last in contact with the atmosphere. The global inventory of anthropogenic carbon taken up by the ocean between 1750 and 1994 is estimated to be $118 \pm 19 \text{ GtC}$. (ICCP, 2007).

The buffer capacity of the seawater can be characterized by so-called “Revelle factor” (after Roger Revelle):

$$RF_0 = \left(\frac{d[\text{CO}_2]}{[\text{CO}_2]} / \frac{d\text{DIC}}{\text{DIC}} \right)_{TA=\text{const}}$$

This factor (Zeebe, Wolf-Gladrow, 2001) describes how the partial pressure of CO₂ in seawater ($p\text{CO}_2$) changes for a given change in DIC (Sabine et al. 2004). Its value is proportional to the ratio between DIC and alkalinity, where the latter term describes the ocean charge balance (Sabine et al. 2004). Low Revelle factors are found in the warm tropical and subtropical waters and high Revelle factors are found in the cold, high latitudes.

Direct observations of oceanic dissolved inorganic carbon (DIC; i.e., the sum of CO₂ plus carbonate and bicarbonate) reflect changes in both the natural carbon cycle and the uptake of anthropogenic CO₂ from the atmosphere (Bindoff et al., 2007). These observations show that variability in the content of natural DIC in the ocean has occurred in association with climate variability.

Longer observations exist for the $p\text{CO}_2$ at the surface only. Over more than two decades, the oceanic $p\text{CO}_2$ increase and pH decrease were generally followed the atmospheric CO_2 within the given uncertainty, although regional differences have been observed (Feely et al., 1999; Takahashi et al., 2006). (IPCC, 2007)

From observed DIC changes between surveys in the 1970s and the 1990s, an increase in anthropogenic carbon has been inferred down to depths of 1,100 m in the North Pacific (Peng et al., 2003; Sabine et al., 2004), 200 to 1,200 m in the Indian Ocean (Peng et al., 1998; Sabine et al., 1999) and 1,900 m in the Southern Ocean (McNeil et al., 2003).

In the atmosphere, CO_2 shows chemically inert behaviour, that is, it does not react with other gases, but it contributes to climate change through its strong interaction with infrared radiation. However, in the ocean CO_2 is chemically active and is not a conservative component of the sea water. Dissolved CO_2 contributes to the reduction of the pH value, or an **acidification of seawater**. This effect can already be detected: since the onset of industrialization the pH value of the ocean surface water has dropped by an average of about 0.11 units. This is equivalent to an increase in the concentration of hydrogen ions (H^+ ions) by around 30 per cent. Starting from a slightly alkaline pre-industrial pH value of 8.18, the acidity of the ocean has thus increased at the surface.

1.2 pH changes assessments

A decrease of pH is reported from different sources that can be divided into 3 groups: (1) results of the regular direct measurements in the frames of time series programmes, (2) calculations on the base of correlation of pH with other data and (3) mathematical modelling.

1.2.1 Time series direct measurements.

The time series of direct pH measurements usually cover the period of last 10-30 years. The analysis of these measurements is problematic since pH has a large daily (up to 0.700) and seasonal (up to 1.300) variability (Fig. 1.2.1.1), that is comparable with the existing estimates of the interannual changes.

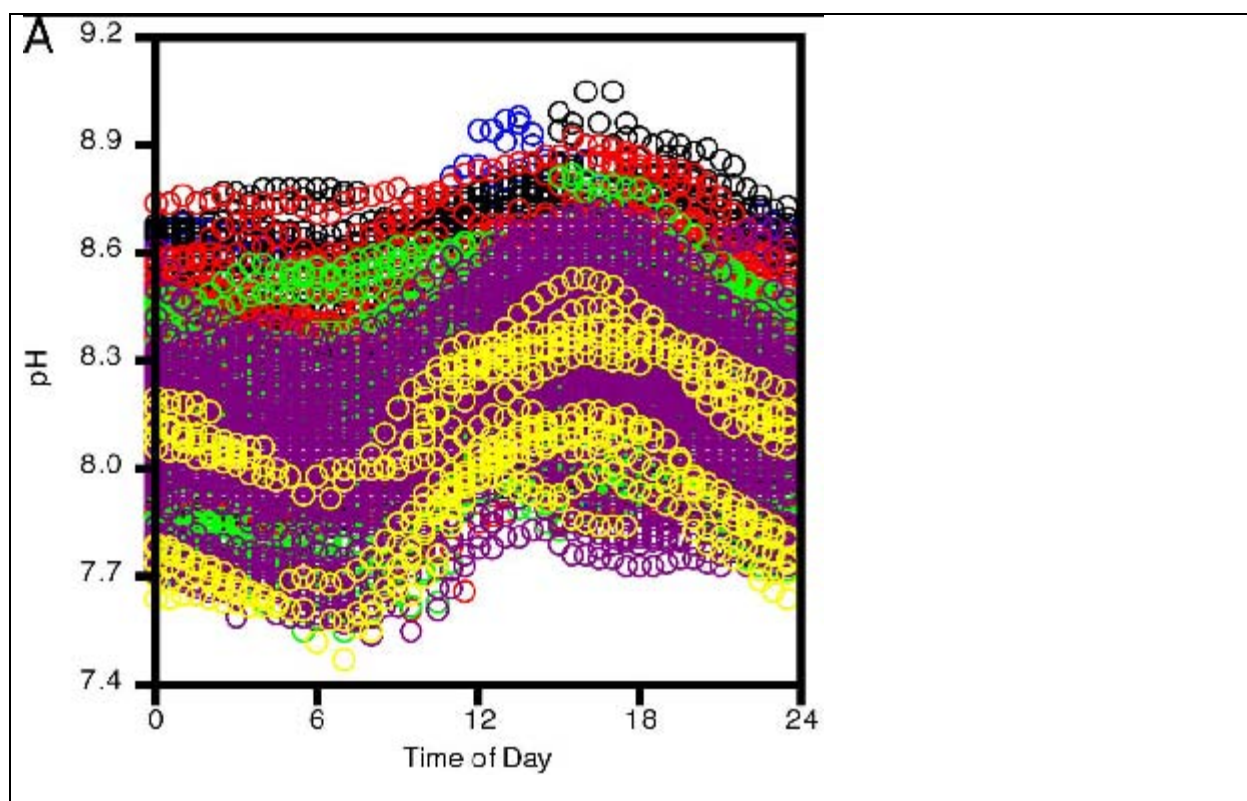
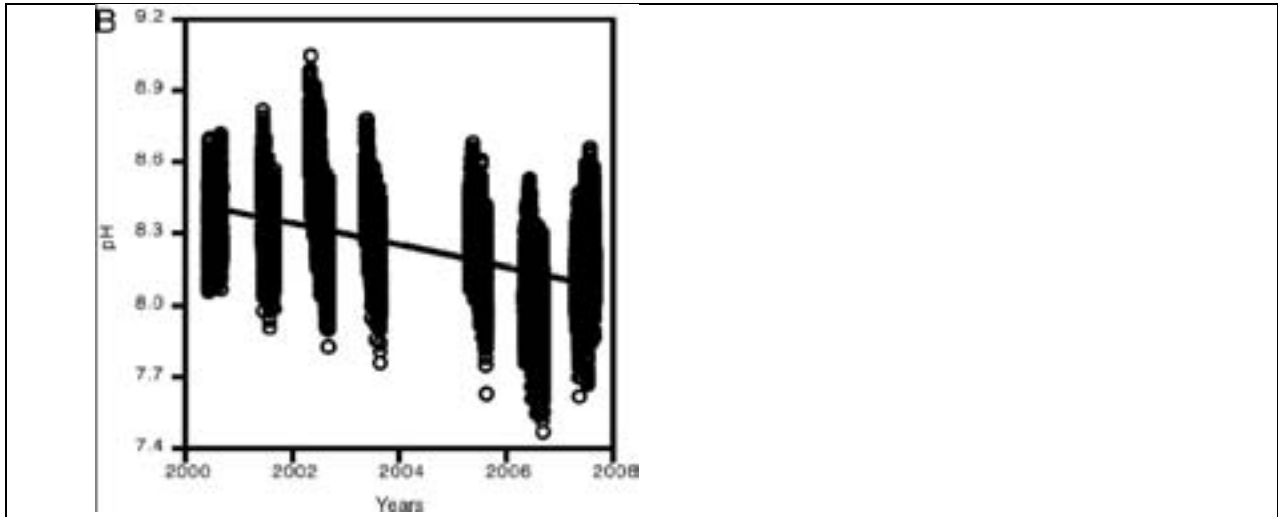
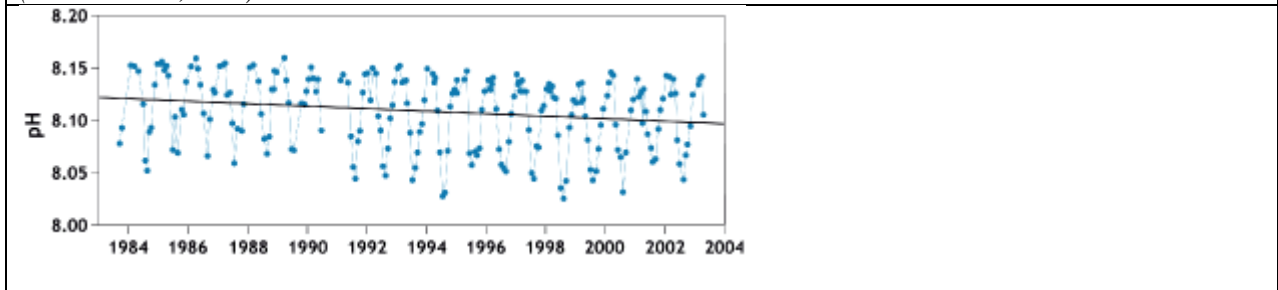


Figure 1.2.1.1 Patterns of ocean pH through time at Tatoosh Island (N_24,519). (A) Daily cycle of pH arising from photosynthetic uptake of CO₂ by algal primary producers. Colours indicate month that the data were collected (blue, April; black, May; red, June; green, July; purple, August; yellow, September). (B) pH readings as a function of date and time taken between 2000 and 2007. The decline is significant ($P < 0.05$). (Wootton et al., 2008)

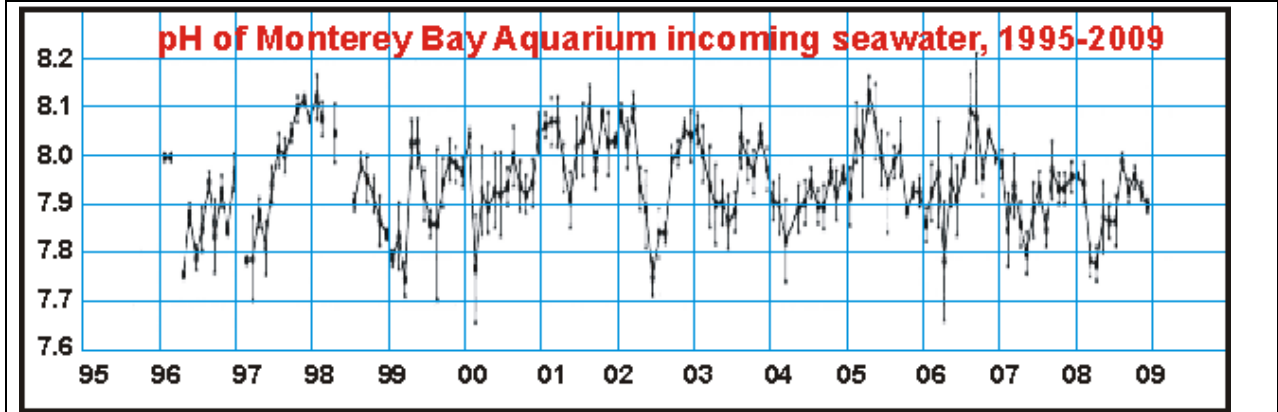
The results of direct measurements performed in different regions are given in Fig. 1.2.1.2, 1.2.1.3.



A. Tatoosh Island ($N_{24,519}$) pH readings as a function of date and time taken between 2000 and 2007.. (Wootton et al,2007)



B. BATS (Bermuda Atlantic Time-series Study (from F. Anthoni, 2007)



C. The Monterey Bay marine aquariums have been monitoring seawater pH at the depth of the intake, near the thermocline,

Figure 1.2.1.2 Examples of the direct pH measurements from different regions: Tatoosh Island (A), Bermuda station (B), The Monterey Bay marine aquariums (C).

Results from time series stations include not only the increase in anthropogenic carbon, but also other changes due to local physical and biological variability, and therefore differs in different regions. According to the IPCC conclusions, the observations at the time series stations testify to a decrease in pH of 0.02 per decade during the last decades (IPCC, 2007).

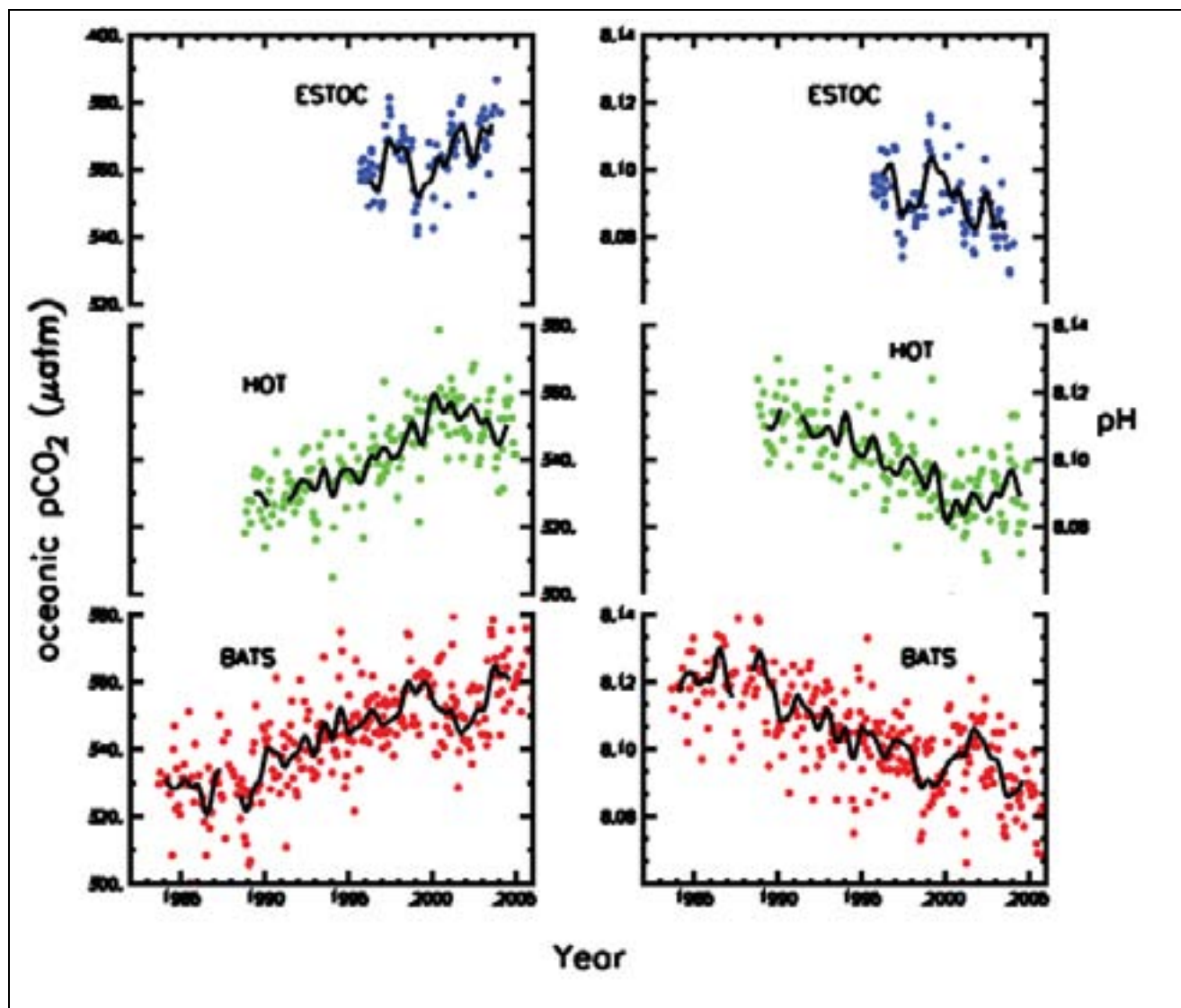


Figure 1.2.1.3 Changes in surface oceanic $p\text{CO}_2$ (left; in μatm) and pH (right) from three time series stations: Blue: European Station for Time-series in the Ocean (ESTOC, 29°N , 15°W ; Gonzalez-Dávila et al., 2003); green: Hawaii Ocean Time-Series (HOT, 23°N , 158°W ; Dore et al., 2003); red: Bermuda Atlantic Time-series Study (BATS, $31/32^\circ\text{N}$, 64°W ; Bates et al., 2002; Gruber et al., 2002). Values of $p\text{CO}_2$ and pH were calculated from DIC and alkalinity at HOT and BATS; pH was directly measured at ESTOC and $p\text{CO}_2$ was calculated from pH and alkalinity. The mean seasonal cycle was removed from all data. The thick black line is smoothed and does not contain variability less than 0.5 years period (from IPCC, 2007).

1.2.2 Indirect estimates

Indirect estimates are based on the analysis of the relationship between pH with other carbonate system parameters. For example, a 300-y reconstruction of surface-ocean pH at Flinders Reef, Australia is based on boron isotope ($\delta^{11}\text{B}$) data retrieved from a 300-y-old *Porites* coral (Fig. 1.2.2.1).

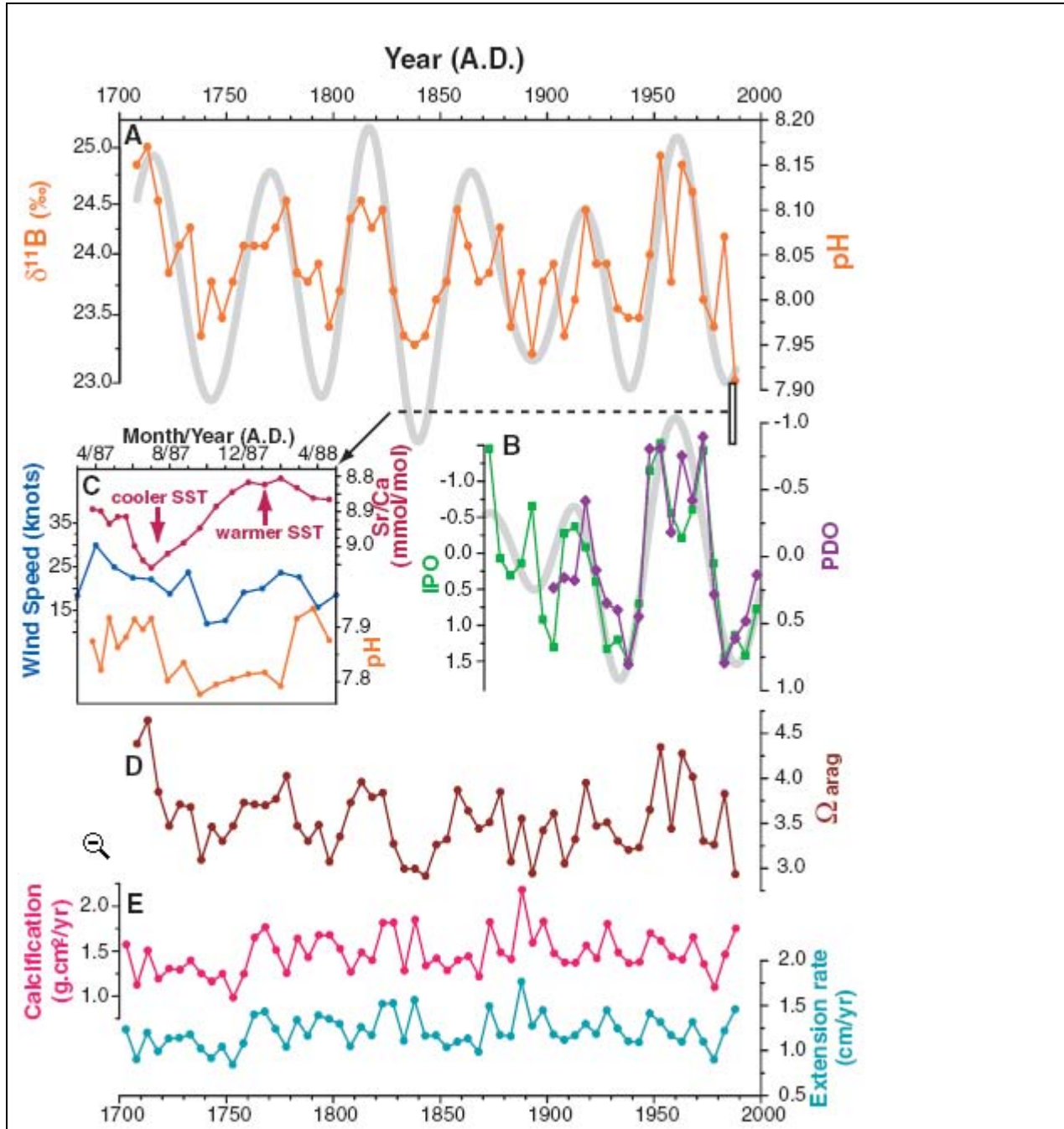


Figure 1.2.2.1. . A 300-y reconstruction of surface-ocean pH at Flinders Reef, Australia, based on boron isotope ($\delta^{11}\text{B}$) data retrieved from a 300-y-old *Porites* coral. Gray line in top figure is the Interdecadal Pacific Oscillation (IPO). Also shown are aragonite saturation state (Ω_{arag}) calculated from the boron isotope-derived pH and assuming constant alkalinity, and the measured extension and calcification rates of the corals (reprinted from Pelejero et al., 2005, copyright AAAS).

One of the most commonly cited estimates is that between 1751 and 1994 surface ocean pH is estimated to have decreased from approximately 8.179 to 8.104 (a change of -0.075). (Doney et al., 2006, Feely et al., 2004).

1.2.3 Modeling

The uptake of anthropogenic carbon by the ocean changes the carbonate equilibrium of the ocean. Dissolved CO_2 forms a weak acid. As CO_2 increases, pH decreases, that is, the ocean becomes more acidic. Ocean pH can be computed from measurements of DIC and alkalinity. A decrease in surface pH of 0.1 over the global ocean was calculated from the estimated uptake of anthropogenic carbon between 1750 and 1994 (Sabine et al., 2004b; Raven et al., 2005), with the lowest decrease (0.06) in the tropics and subtropics, and the highest decrease (0.12) at high latitudes, consistent with the lower buffer capacity of the high latitudes compared to the low latitudes. The mean pH of surface waters ranges between 7.9 and 8.3 in the open ocean, so the ocean remains alkaline ($\text{pH} > 7$) even after these decreases.

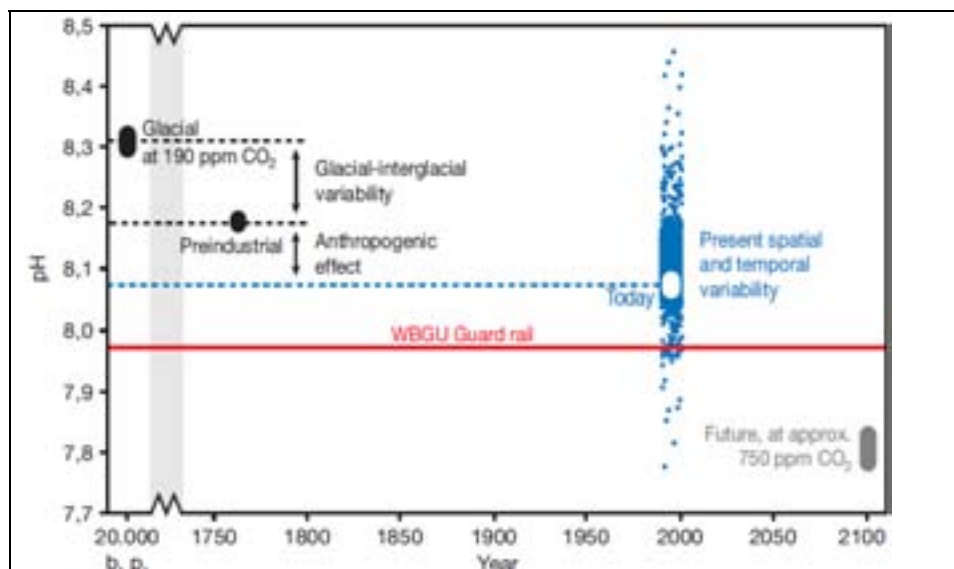


Figure 1.2.3.1. Variability of the average pH value of the oceans in the past and present, as well as a projection for the future for an atmospheric CO_2 concentration of approx. 750 ppm. The red line indicates the WBGU guard rail. Source: after IMBER, 2005. (WBGU, 2006).

For comparison, pH was higher by 0.1 unit during glaciations, and there is no evidence of pH values more than 0.6 units below the pre-industrial pH during the past 300 million years (Caldeira and Wickett, 2003). A decrease in ocean pH of 0.1 units corresponds to a 30% increase in the concentration of H^+ in seawater, assuming that alkalinity and temperature remain constant. Changes in surface temperature may have induced an additional decrease in pH of <0.01 .

The estimates received with the models regarding so-called WBGU Guard rail level, a level of conservation of sustainable development of the ecosystem is shown in Fig. 1.2.3.1. To prevent undesirable or high-risk changes to the marine food web due to aragonite undersaturation (Section 4.3), the pH value of near surface waters should not drop more than 0.2 units below the preindustrial average value of 8.18 in any larger ocean region (nor in the global mean). A pH drop of 0.2 units would correspond to an increase in the H^+ ion concentration of around 60 per cent compared to pre-industrial values (The Future Ocean, 2006).

The various IPCC emission scenarios indicate that if the atmospheric CO_2 concentration reaches 650 ppm by the year 2100, a decrease in the average pH value by 0.30 units can be expected compared to pre-industrial values. With an atmospheric concentration of 970 ppm, the pH value would drop by 0.46 units. But if the CO_2 in the atmosphere can be limited to 450 ppm, then the pH reduction will only amount to 0.17 units (Caldeira and Wickett, 2005).

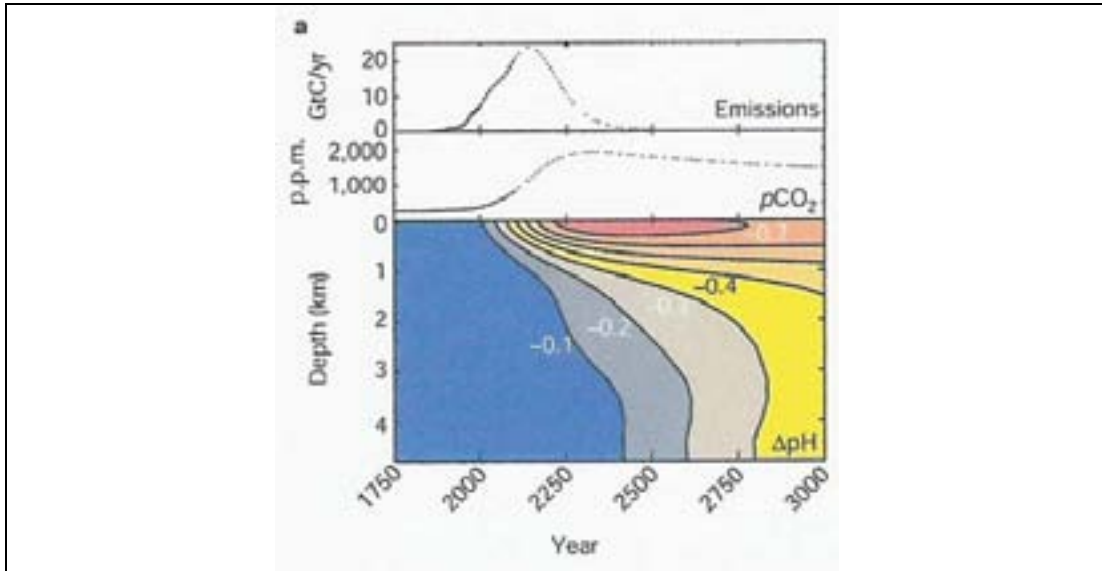


Figure 1.2.3.2. Modeled changes in ocean pH from prior to the Industrial Era into the future, lower panel; note depth scale on the y-axis (vertical). The upper two panels respectively show the history of anthropogenic CO₂ emissions and atmospheric CO₂ concentration over the same time scale. The surface ocean pH decrease will reach its maximum magnitude of -0.77 units by 2250 and will drop thereafter due to ocean mixing with a stabilized atmospheric concentration. With normal ocean mixing, there is little drop in deep ocean pH until about 2500. (From Caldeira and Wickett, 2003).

Jacobson (2005) performed equilibrium calculations based on known equilibrium constants, assuming that the ocean is in equilibrium with the atmosphere for scenarios 275, 375, 750 ppm CO₂ and 0-25 °C aiming to model for future pH. They found that whereas surface ocean pH is estimated to have dropped from near 8.25 to near 8.14 between 1751 and 2004, it is forecasted to decrease to near 7.85 in 2100, for a factor of 2.5 increase in H⁺ in 2100 relative to 1751.

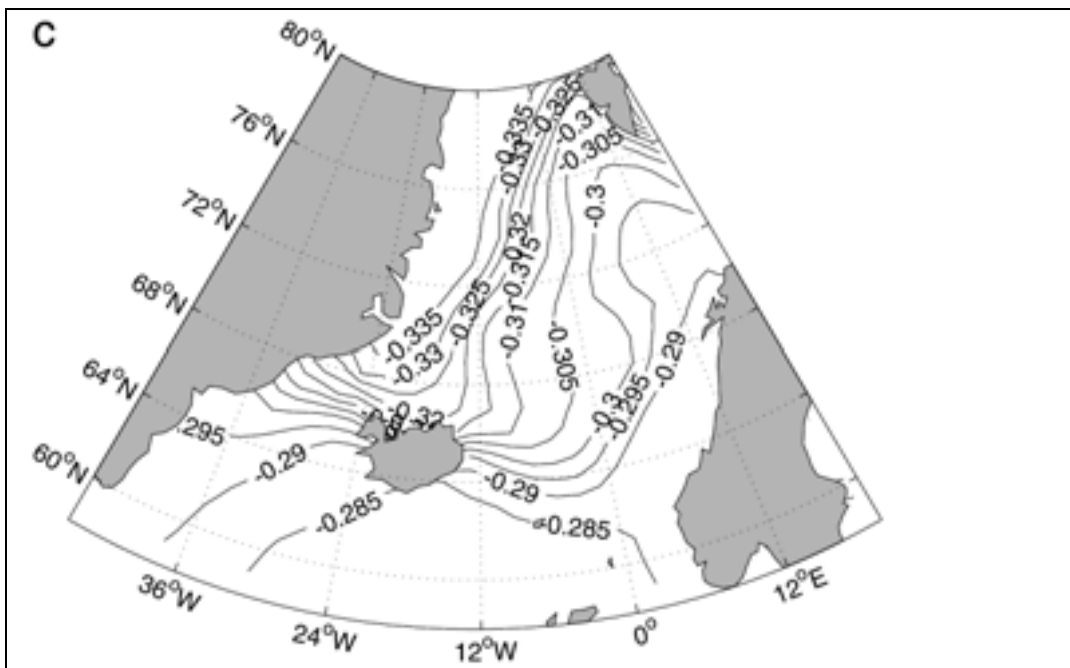


Figure 1.2.3.3. Predicted reduction in surface pH from 1997 to 2067 in a scenario in which atmospheric CO₂ doubles during that time (approximately 1% increase per year). The physical ocean

state is taken from coupled climate model run and the surface ocean carbon chemistry from empirical correlations with the physical state. From Bellerby et al. (2005).

Bellerby et al. (2005, Fig. 1.2.3.3) focussed on an area relevant to OSPAR (OSPAR, 2006), and found that the future pH changes are not expected to be uniform. The main regional gradients are associated with the transition between Atlantic and Arctic waters. In this model he used the IPCC scenario in which atmospheric CO₂ doubles during that time from 1997 to 2067. In his model he considered only physical factors but not ignored the role of processes of production and destruction of organic matter (OM).

Models allow analyzing the role of natural factors. Makkaveev (2009) modelled the pH variability during the last 500 000 years with a model forced by the estimates on magma de-gassing and rates of carbon accumulation in the sediments (Fig.1.2.3.4). He found 80-120 Ky cycles coupled with 20-30 Ky cycles. The surface layer pH variability was asymmetric – the decrease of pH occurs much faster in a time period compared to its following increase. Generally the values of the surface pH remained in the frames from 7.95 to 8.32 (NBS).

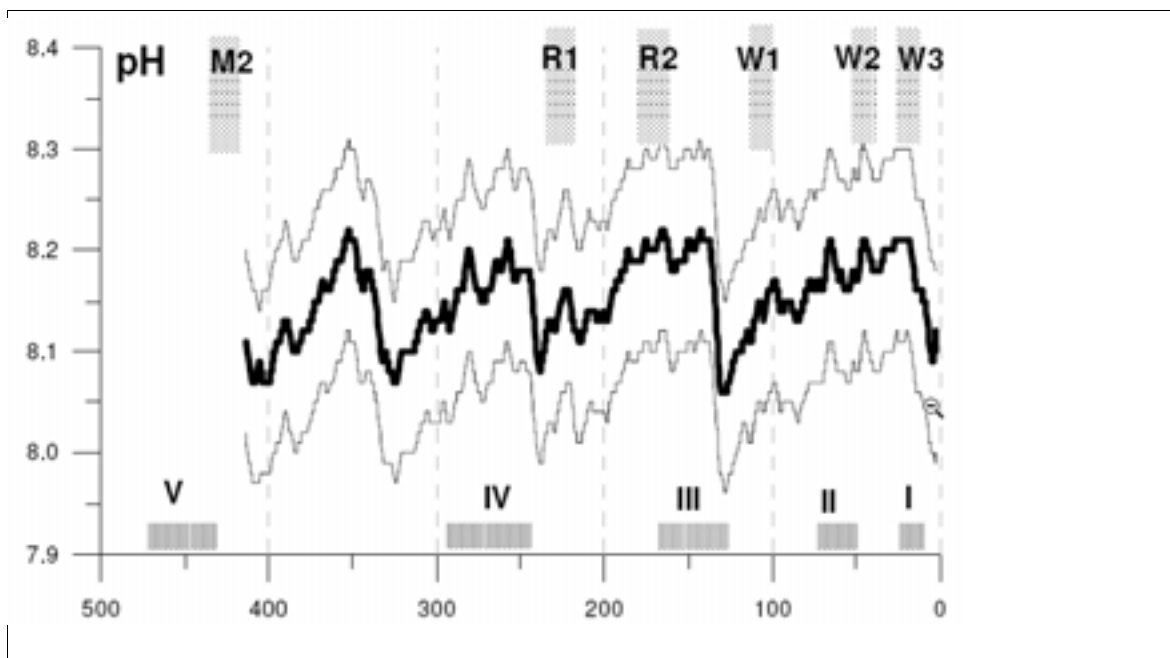


Figure 1.2.3.4. Model estimates of the pH variability in the upper layer of the Ocean during the last 500 Ky (Makkaveev, 2009). The possible range is shown in thin line, and an averaged values as a thick line. The ice ages are marked with grey colour.

One more factor that should affect the pCO₂ in the ocean and the atmosphere is the rate of mineralization of organic matter and position of so-called “remineralization depth” (Fig. 1.2.3.5). This depth at which this sinking carbon is converted back to carbon dioxide depends on the balance between particle sinking speeds and their rate of decay. This effect was analysed with the model (Kwon et al., 2009); they found that atmospheric carbon dioxide concentrations are highly sensitive to the potential changes in remineralization depth that may be caused by climate change. This is an example of the natural process that contributes to the observed pCO₂ dynamics.

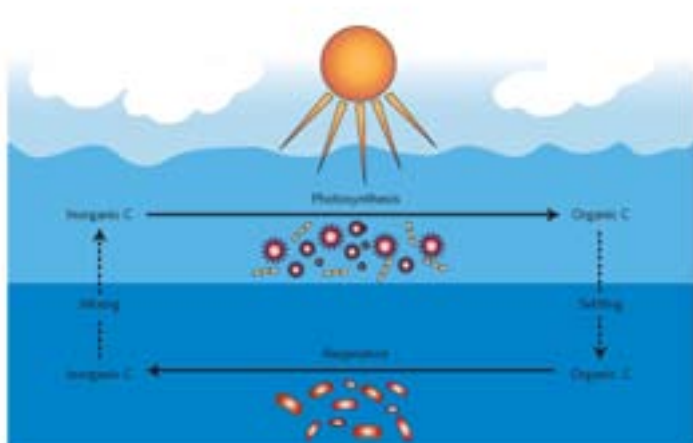


Figure 1.2.3.4. *The oceanic biological pump. During photosynthesis, phytoplankton capture inorganic carbon from the surface ocean and atmosphere, and convert it into organic carbon. When phytoplankton die they sink through the water column, carrying the organic carbon to deeper waters with them. Bacteria and zooplankton degrade this sinking carbon, converting it back to inorganic forms in a process termed remineralization. Some of this inorganic carbon is then released back to the atmosphere. Kwon and colleagues (2009) use a three-dimensional global ocean biogeochemistry model to show that the depth at which particulate organic carbon is remineralized has a strong effect on atmospheric carbon dioxide concentrations (Najjar, 2009).*

Nevertheless, the application of prognostic multi-decadal or multi-centurial mathematical models face with some criticism, i.e. “Much has been done with computer models, but these are only as valid as their underlying assumptions, and can neither be proved right nor wrong” (Anthoni, 2007)

An overview of the potential changes of the ocean carbonate system based on IPCC IS92a CO₂ (IPCC, 2007) emission scenario is given in Table 1.2.3.1.

In addition to acting as a greenhouse gas and increasing atmospheric temperature and consequently sea surface temperature, carbon dioxide also affects marine systems directly. Simulations for the next century project a further reduction of 0.3 to 0.5 units, depending on which IPCC scenario is adopted in the calculation (Orr et al., 2005, Caldeira and Wickett, 2005). The increased concentration of dissolved CO₂ will lower the saturation levels of carbonate minerals such as calcite, aragonite, and high-magnesium calcite, which will decrease the availability of materials used to form the supporting skeletal structures of many major groups of marine organisms. Using the IPCC IS92a scenario, Southern Ocean winter time aragonite saturation is expected to occur at an atmospheric CO₂ concentration of 450 ppm or by the year 2030 and no later than 2038 (McNeil and Matear, 2008).

The decrease in ocean pH is seen as particularly severe because it has been relatively stable for the past 300 million years (Caldeira and Wickett, 2003), it will take a very long time to reverse the trend, and it could fundamentally alter the lowest levels of the marine food-web with unpredictable consequences for higher trophic levels. The 450 ppm atmospheric CO₂ is considered a tipping point for ocean acidification and has resulted in the Monaco declaration (see e.g. <http://www.igbp.net/documents/MonacoDeclaration2009.pdf>). This was made in October 2008 by 155 scientists from 26 countries stating that:

- o Ocean acidification is underway
- o It is accelerating and severe damages are imminent
- o It will have socioeconomic impacts
- o Is rapid, but recovery will be slow
- o It can only be controlled by reducing atmospheric CO₂ concentrations

Table 1.2.3.1. Projected changes in surface ocean carbonate chemistry based on IPCC IS92a CO₂ emission scenario (Houghton *et al.*, 2001)

Parameter	Symbol	Unit	Glacial	Preindustrial	Present	2 × CO ₂	3 × CO ₂
Temperature	T	°C	15.7	19	19.7	20.7	22.7
Salinity	S		35.5	34.5	34.5	34.5	34.5
Total alkalinity	A _T	μmol kg ⁻¹	2356	2287	2287	2287	2287
pCO ₂ in seawater	pCO ₂	μatm	180	280	380	560	840
Carbonic acid	H ₂ CO ₃	μmol kg ⁻¹	(-56)	(0)	(35.7)	(100)	(200)
Bicarbonate ion	HCO ₃ ⁻	μmol kg ⁻¹	7	9	13	18	25
Carbonate ion	CO ₃ ²⁻	μmol kg ⁻¹	(-29)	(0)	(44)	(100)	(178)
Hydrogen ion	H ⁺	μmol kg ⁻¹	1666	1739	1827	1925	2004
Calcite saturation	Ω _{calc}		(-4)	(0)	(5)	(11)	(15)
Aragonite saturation	Ω _{arag}		279	222	186	146	115
Dissolved inorganic carbon	DIC	μmol kg ⁻¹	(20)	(0)	(-16)	(-34)	(-48)
Total pH	pH _T		4.79 × 10 ⁻³	6.92 × 10 ⁻³	8.92 × 10 ⁻³	1.23 × 10 ⁻²	1.74 × 10 ⁻²
			(-45)	(0)	(29)	(78)	(151)
			6.63	5.32	4.46	3.52	2.77
			(20)	(0)	(-16)	(-34)	(-48)
			4.26	3.44	2.9	2.29	1.81
			(19)	(0)	(-16)	(-33)	(-47)
			1952	1970	2026	2090	2144
			(-1)	(0)	(2.8)	(6.1)	(8.8)
			8.32	8.16	8.05	7.91	7.76

^aWe assume that PO₄ = 0.5 μmol L⁻¹ and Si = 4.8 μmol L⁻¹, and use the carbonic acid dissociation constants of Mehrbach *et al.* (1973) as refit by Dickson and Millero (1987). pH_T is based on seawater scale. Percent change from preindustrial values are in parentheses. After Feely *et al.* (2008).

1.3 Changes in the carbonate budget

A mechanism of the changes in the ocean water carbonate budget can be explained with Fig. 1.3.1 (from Feely et al., 2004). An increase of $p\text{CO}_2$ from preindustrial atmospheric level to the present day resulted in an increase of total dissolved inorganic carbon (DIC) bicarbonate ion (HCO_3^-) but decrease in the carbonate ion (CO_3^{2-}) concentration and the calcite species saturation.

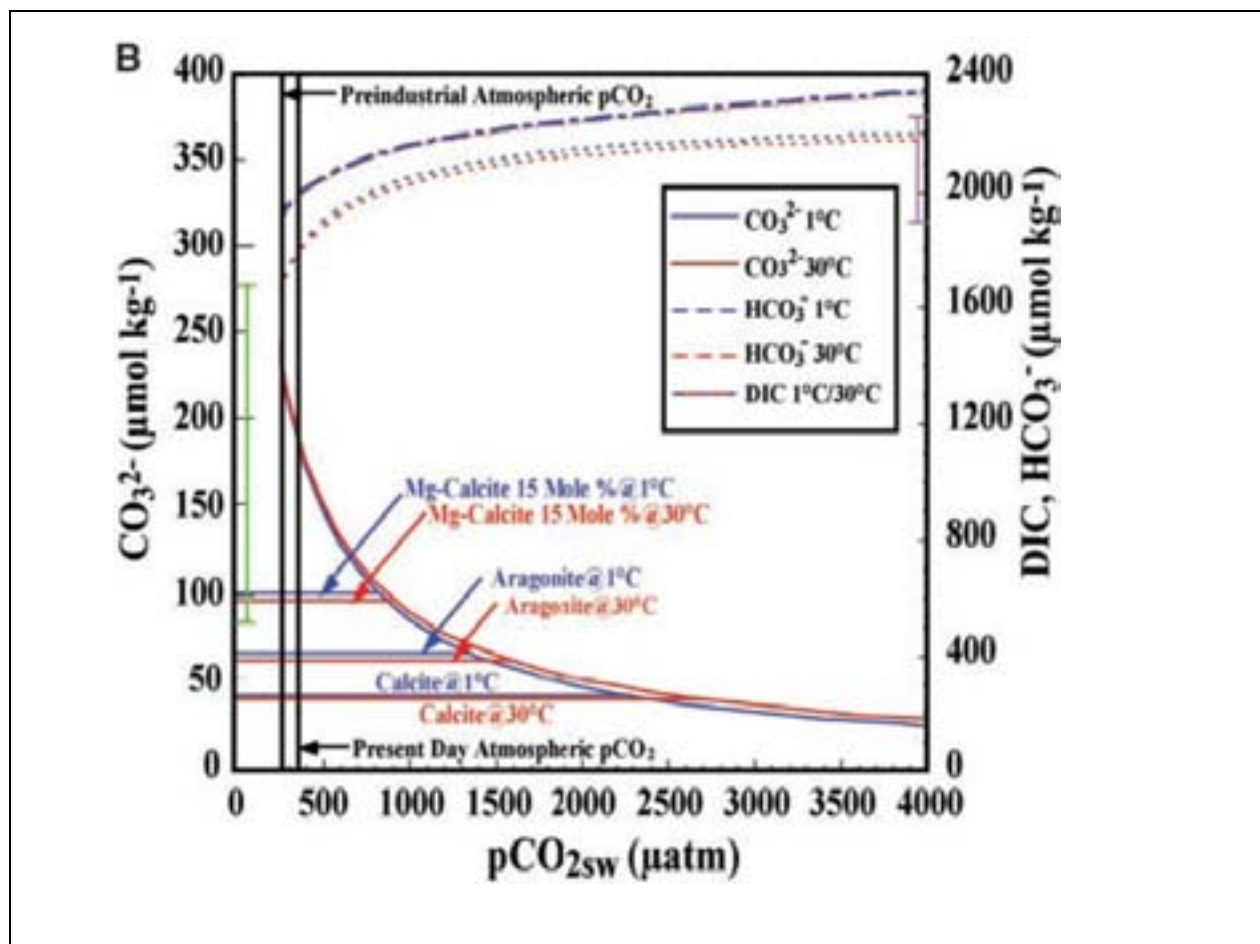


Figure 1.3.1. Relation between the concentrations of carbonate species in surface waters at constant salinity and TA for surface waters spanning the approximate range of temperatures observed in the oceans as a function of the surface ocean $p\text{CO}_2$ in μatm . The solid vertical light green line shows the range of carbonate ion concentrations observed in the present-day oceans, and the solid vertical magenta line shows the range of dissolved inorganic carbon concentrations. The three sets of parallel horizontal lines show the equilibrium carbonate ion concentrations for magnesian calcite, aragonite, and calcite saturation, respectively (Feely et al., 2004).

The saturation of seawater with carbonate ions is especially important for marine organisms that build their shells or skeletons with lime (calcium carbonate, CaCO_3). Calcium carbonate occurs in marine organisms primarily in the forms of aragonite and calcite, which differ in their crystal structures. Seawater is supersaturated with respect to the more easily dissolved aragonite when the carbonate concentration lies above $66 \mu\text{mol}$ per kilogram. If it falls below this value the aragonite formed by the organisms stops forming – this is referred to as aragonite undersaturation. Because of the increasing solubility of calcium carbonate with decreasing temperature and increasing pressure, the deeper layers of the sea are, as a rule, undersaturated, that is, sinking CaCO_3 dissolves in the water at greater depths.

The boundary between the undersaturated and super-saturated layers is referred to as the **saturation horizon** ($\Omega=1$) (Fig. 1.3.2).

Due to the uptake of anthropogenic CO_2 , the carbonate concentration in the ocean surface layer has already dropped by 10 per cent compared to the pre-industrial level (Orr et al., 2005).

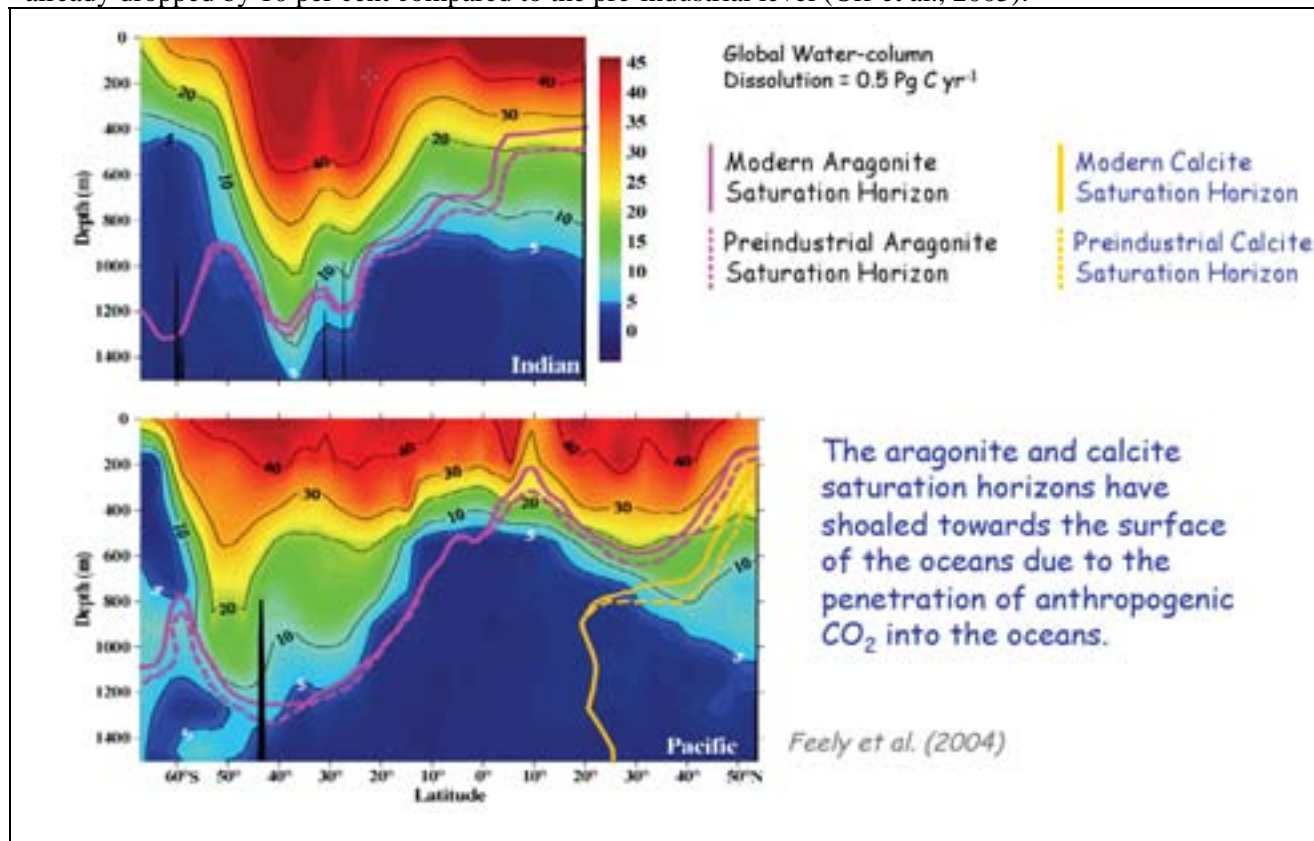


Figure 1.3.2. Modern and pre-industrial levels of aragonite and calcite saturation horizons (Feely et al., 2004).

The present carbonate concentration in the sea surface layer varies among regions: the highest concentrations (averaging $240 \mu\text{mol per kilogram}$) occur in the tropics, while values in the Southern Ocean average only $105 \mu\text{mol per kilogram}$ (Orr et al., 2005). With progressive CO_2 input into the sea, therefore, the marine organisms in the Southern Ocean are the first to be threatened by aragonite undersaturation. Orr et al. (2005) calculate the possible future development of the carbonate concentration of the Southern Ocean for various emission scenarios. According to these calculations, under a ‘business-as-usual’ scenario it could already be undersaturated with respect to aragonite by the middle of this century (Fig. 1.3.3). With an atmospheric CO_2 concentration of approximately 600 ppm or more, the greater part of the surface layer of the Southern Ocean would be undersaturated. But even before this threshold is reached the saturation horizon drifts upward, that is, the upper layer of the sea that is supersaturated with respect to aragonite becomes thinner, and CaCO_3 formation becomes more difficult. Individual parts of the surface layer would be affected even earlier. With respect to the less-soluble calcite the surface layer remains saturated despite higher CO_2 concentrations, but the calcite saturation horizon also shifts upward. With the displacement of the saturation horizon the conditions for biogenic CaCO_3 formation change, which can have considerable consequences for marine organisms and ecosystems.

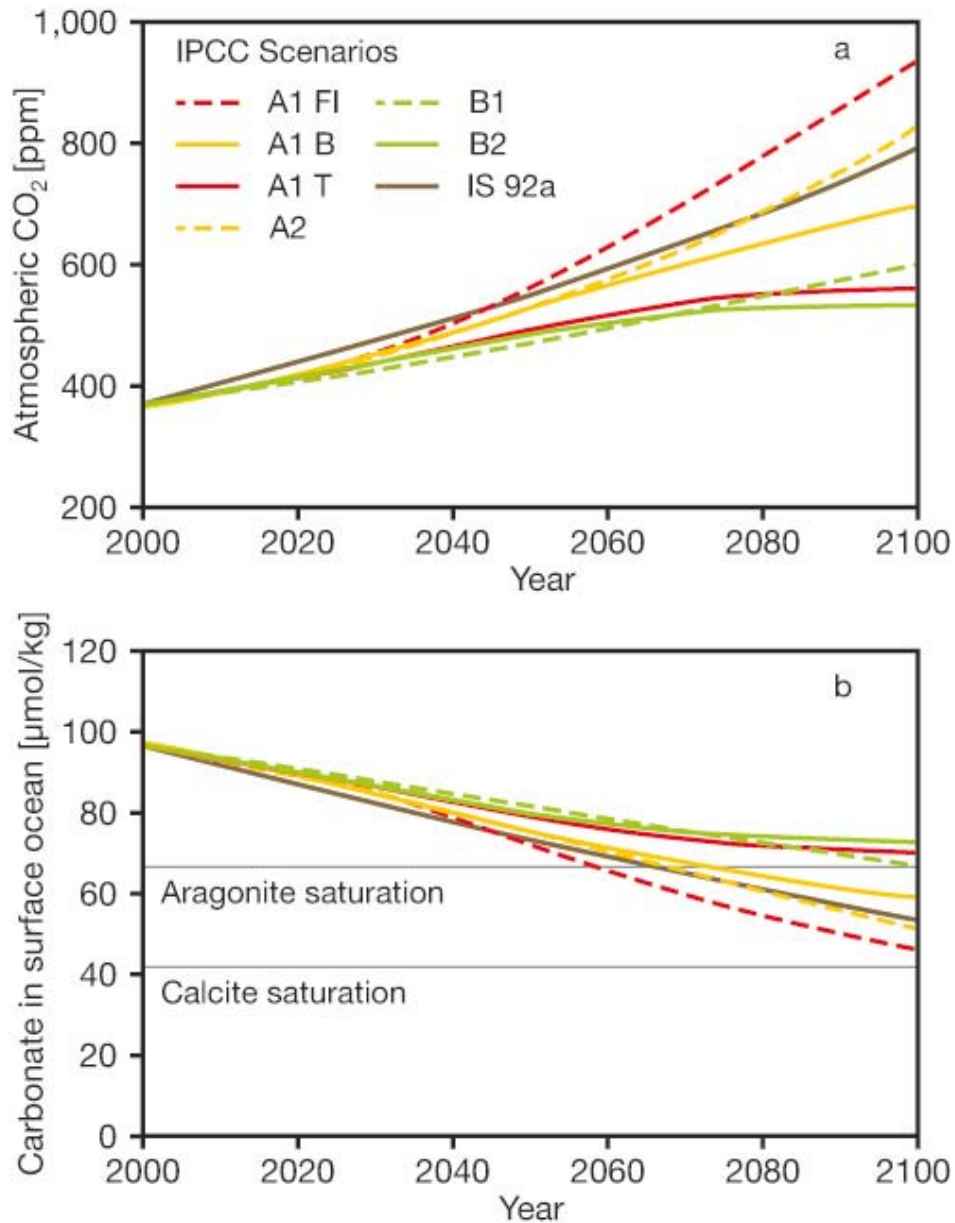


Figure 1.3.2. Projections of different CO₂ concentrations (a) and their effects on the carbonate budget of the Southern Ocean (b). The variation according to various IPCC scenarios is shown. (Source: Orr et al., 2005).

The saturation horizon for aragonite and calcite has shifted 50 to 200 meters closer to the surface since the industrial revolution and it is predicted to shift even closer to the surface in the next 100 years. In cold waters, especially polar areas, the saturation horizon is expected to be non-existent and all of the waters will be undersaturated with respect to aragonite by the end of this century.

Shallowing of the aragonite saturation horizon has been observed in all ocean basins based on alkalinity, DIC and oxygen measurements (Feely et al., 2004, Sabine et al., 2004, Sarma et al., 2002). The amplitude and direction of the signal was everywhere consistent with the uptake of anthropogenic carbon, with potentially smaller contributions from changes in circulation, temperature and biology. Feely et al. (2004) calculated that the uptake of anthropogenic carbon alone has caused a shoaling of the aragonite saturation horizon between 1750 and 1994 by 30 to 200 m in the eastern Atlantic (50°S–15°N), the North Pacific and the North Indian Ocean, and a shoaling of the calcite saturation horizon

by 40 to 100 m in the Pacific (north of 20°N). This calculation is based on the anthropogenic DIC increase estimated by Sabine et al. (2004a), on a global compilation of biogeochemical data and on carbonate chemistry equations. Furthermore, an increase in total alkalinity (primarily controlled by carbonate and bicarbonate) at the depth of the aragonite saturation horizon between 1970 and 1990 has been reported (Sarma et al., 2002). These results are consistent with the calculated increase in CaCO₃ dissolution as a result of the shoaling of the aragonite saturation horizon, but with large uncertainty.

1.4 Consequences in marine ecosystems and feedbacks

The effects of ocean acidification in the marine ecosystem was reviewed in several sources (WBGU, 2006, OSPAR 2006, NIVA nr. 5526-2008).

1.4.1 Physiological effects on marine organisms

Numerous changes in marine organisms have been identified, for example, in the productivity of algae, metabolic rates of zooplankton and fish, oxygen supply of squid, reproduction in clams, nitrification by microorganisms, and the uptake of metals (for a survey, see Pörtner, 2005). Many of these experiments, however, were carried out with CO₂ concentrations much higher than what could be expected in emission scenarios under discussion today for the time frame up to 2100. (WBGU, 2006).

Doubling the present CO₂ concentration leads to an increase in the rate of photosynthesis in many phytoplankton species by about 10 per cent (Raven et al., 2005). However, the various groups of phytoplankton exhibit different sensitivities to increased CO₂ concentrations with respect to photosynthesis, which is due to differences in carbon uptake (CO₂ versus HCO₃⁻) and a different saturation behaviour of the photosynthetic rates. The interactions between photosynthesis, primary production of phytoplankton, microbial respiration, and the resulting effects on the food web are, however, compounded by a number of other factors (temperature, light and nutrient supply, disparate feeding risk from zooplankton, adaptive processes, etc.). With the present state of knowledge no clear conclusions can be drawn regarding the effects of acidification on growth rates and assemblage compositions of the phytoplankton. (WBGU, 2006).

1.4.2 Effects in calcifying organisms

Next to photosynthesis, calcification is the most important physiological process influenced by the increase of CO₂ concentration. For their skeletons or shell structure, many marine organisms use calcium carbonate, which has to be extracted from seawater. This is only possible while the seawater is supersaturated with calcium carbonate, which is why the increasing CO₂ concentration and falling pH value hampers calcification (Raven et al., 2005).

Organisms such as coccolithophores, foraminifera, coralline algae, and pteropods use aragonite and magnesium calcite shells, so they will be affected first. The effects of lowered pH range from decreased growth rates to dissolution of their shells, depending on the amount of change. These organisms are also important links in several marine food webs, so their predators could also be significantly impacted by the lack of food.

Around three-quarters of the global marine calcium carbonate production is carried out by planktonic organisms, primarily coccolithophores, foraminifera, and pteropods. In experiments with both monocultures and natural plankton communities it has been shown that the calcification by coccolithophores clearly decreases with increased atmospheric CO₂ concentrations (Riebesell et al., 2000; Riebesell, 2004). There is great uncertainty about the capacity of the organisms to adapt to these changes, as too few long-term experiments have been carried out (Raven et al., 2005; Pörtner, 2005, WBGU, 2006)

The recruitment rate and growth of crustose coralline algae were severely inhibited in the elevated carbon dioxide mesocosms (added HCl). These findings suggest that ocean acidification due to human activities could cause significant change to benthic community structure in shallow-warm-water carbonate ecosystems (Kufner et al., 2007).

Nevertheless, some studies (Iglesias-Rodriguez et al., 2008) revealed that, over the past 220 years, coccolithophores have increased the mass of calcium carbonate they each produce by around 40 per cent. These results are in agreement with previous observations that coccolithophores are abundant through past periods of ocean acidification such as 55 million years ago – the Paleocene Eocene Thermal Maximum.

1.4.3 Ecosystem structure and higher trophic layers

Acidification impacts on the food web are also conceivable. Different responses to increased CO₂ concentrations, with respect to growth rates or reproduction of an organism, could change the spatial as well as temporal distributions of the species through changes in competition (Rost and Sültemeyer, 2003). In long-term studies in the North Atlantic, it has been observed that changes in the phytoplankton, due to the close coupling with their predators, can be passed on first to the algae-feeding zooplankton and then further to the predatory zooplankton (Richardson and Schoeman, 2004). A change in the species composition of the phytoplankton can thus impact on the zooplankton. In polar ecosystems it is conceivable that reduced calcification by pteropods has effects on the higher levels of the food web, although this is speculative and not easily predictable (Orr et al., 2005)...

The Ocean acidification could cause significant changes in the structure and diversity of coastal sediment communities. Lowered seawater pH could also affect nutrient cycling directly by altering bacterial communities and indirectly through impacts on the abundance and activity of key bioturbators (Widdicombe et al., 2009)

As bad as conditions are expected to be for many marine organisms, there will be some winners, too. Right now very little of the carbon in seawater takes the form of dissolved carbon dioxide, and this scarcity limits the growth of some types of phytoplankton. Many of these species devote precious energy to concentrate carbon dioxide inside their cells, so one might guess that increases in dissolved carbon dioxide will be beneficial to them. Perhaps that will be the case. Not enough is known, however, about this “fertilization” effect to make firm predictions for the future of phytoplankton or to say whether higher carbon dioxide levels will benefit the photosynthetic algae that live inside corals. Many species of marine phytoplankton use HCO₃⁻ for photosynthesis. And because the concentration of this ion will remain largely unchanged, biologists do not expect that these organisms will experience a significant boost. Some higher plants (sea grasses, for example) use dissolved carbon dioxide directly and probably will benefit from its rising levels, just as plants on land are expected to gain as the atmospheric concentration of this gas increases (Doney, 2006).

A study of the influence of a volcanic CO₂ vents on the boundary bottom layer properties was performed by Hall-Spencer et al. (2008) along a small islet/peninsula of the island of Ischia, on Italy’s west coast. They chose for their studies a bottom area near shallow coastal sites where volcanic ‘cool’ CO₂ vents lower the pH of the water column.

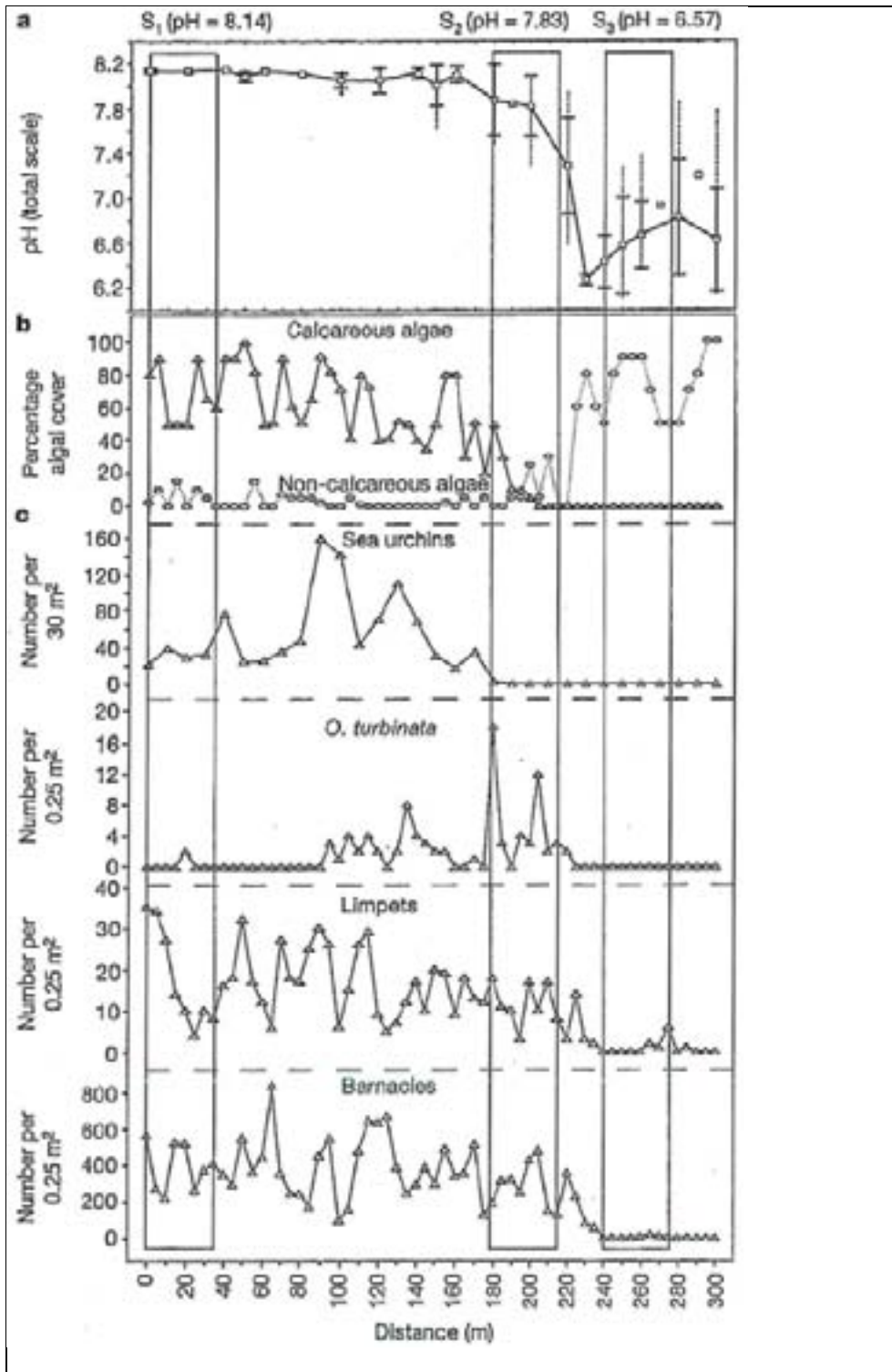


Figure 1.4.3.1 Results of studies of the influence of a cold CO_2 vents on pH and ecological community (from Hall-Spencer et al., 2008).

The graph (Fig. 1.4.3.1) summarizes the findings of the study. From left to right the transect distance along the rocky shore, moving landward towards the field of CO_2 bubblers on right. In this field the pH varies considerably between 6.0 and 7.5. The gas was nearly pure CO_2 , capable of acidifying the water locally 1000-fold to a pH of 5. However, mixing through turbulence, currents and waves soon dilutes the acid, even though an area of over 50m remains consistently highly acidic. Within a distance

of a mere 25 m, average acidity changes from 6.5 to 7.7, accompanied by a critical change in the environment, affecting in particular grazing sea urchins, snails and limpets. In their absence while fed by higher CO₂ levels, non-calcareous (edible) algae multiply.

The study shows that along a daily fluctuating gradient from normal sea water (pH=8.14) to acidic water (pH=6.57), species diversity suddenly drops at around pH=6.8 (about 20 times more acidic than present). It affects mainly calcareous algae, sea urchins, limpets, grazing snails and barnacles. Sea-grass production was highest in an area at mean pH 7.6 (1,827 μ atmp CO₂) where coralline algal biomass was significantly reduced and gastropod shells were dissolving due to periods of carbonate sub-saturation.

1.4.4 Effect on fisheries

Acidification may also directly affect the growth and reproduction rates of fish, as well as affecting the plankton populations which they rely on for food, with potentially disastrous consequences for marine food webs (quoted from F. Anthoni, 2007).

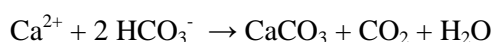
Direct toxic effects of increased atmospheric CO₂ concentrations on fish are not expected because the threshold of acute sensitivity of fish to CO₂ is beyond the predicted concentrations (Pörtner, 2005). When calcification is reduced, however, this can trigger changes in the species composition of the phytoplankton, and this, in turn, can have an impact all the way to the upper layers of the food web through trophic coupling (Richardson and Schoeman, 2004). It cannot be ruled out that this kind of change in the structure and function of the marine ecosystems can have an impact on the pelagic fisheries, but with the present state of knowledge the prognosis remains very speculative (Raven et al., 2005). Lowered pH-values in the water impair reproduction of animals in fresh water and in the sea. A low pH in the water leads to smaller egg sizes and delayed hatching (WBGU, 2006).

Because cold waters are naturally less supersaturated than warm ones for the various forms of calcium carbonate, high latitude and deep water ecosystems may be the first to suffer from ocean acidification. Polar surface waters most likely will become undersaturated for aragonite before the end of this century. One worrisome possibility, based on the work of Victoria J. Fabry of California State University, San Marcos (Doney, 2006), is that polar pteropods will simply disappear altogether. Or perhaps they will be forced to migrate to lower, warmer latitudes, assuming that they can adapt to those environments. No one knows how a sharp decrease in pteropod numbers will affect other parts of the marine ecosystem. But the fact that these small snails are a key link in the food chain in the Southern Ocean (which supports large populations of fish, whales and seabirds) is ample cause for concern (Doney, 2006).

Changes in growth and competitive conditions for the species in tropical coral reefs will probably also affect another important branch of fishery: millions of people depend on subsistence fishery on coral reefs for their protein supply (Raven, et al., 2005), and the coral reefs themselves are threatened by acidification. A large-scale loss of coral habitats would doubtless have adverse effects upon this fishery, with socioeconomic consequences that are difficult to predict. (The Future Ocean, 2006)

1.4.5 Feedback of changes in calcification on the carbon cycle

The annual primary production in the ocean is approximately 50 Gt C, of which approximately 10 Gt is exported to the deep sea by the biological pump. For this important process in the global carbon cycle, which contributes to the sink function of the ocean, it makes a great difference whether the production is by calcifying species like coccolithophores or by noncalcifying species, for example, siliceous algae. Calcification by marine organisms always involves CO₂ production:



This carbonate ‘counter-pump’ becomes stronger with increasing atmospheric CO₂ concentration as a consequence of the altered carbonate buffer capacity. Assuming constant calcification, this would cause a future weakening of the sink effect of the sea. But if biogenic carbonate formation is reduced as a result of a pH decrease, then this effect can be overcompensated so that the sink effect may even be strengthened. This would, however, only have a minor impact on the CO₂ uptake by the ocean (Zondervan et al., 2001). (WBGU, 2006).

1.5 Forcing. Factors affecting acidification

The ocean acidification development depends on the content of CO₂ in the atmosphere and temperature of the surface water. Both of these factors affect the air-water flux of CO₂.

1.5.1 Atmospheric CO₂

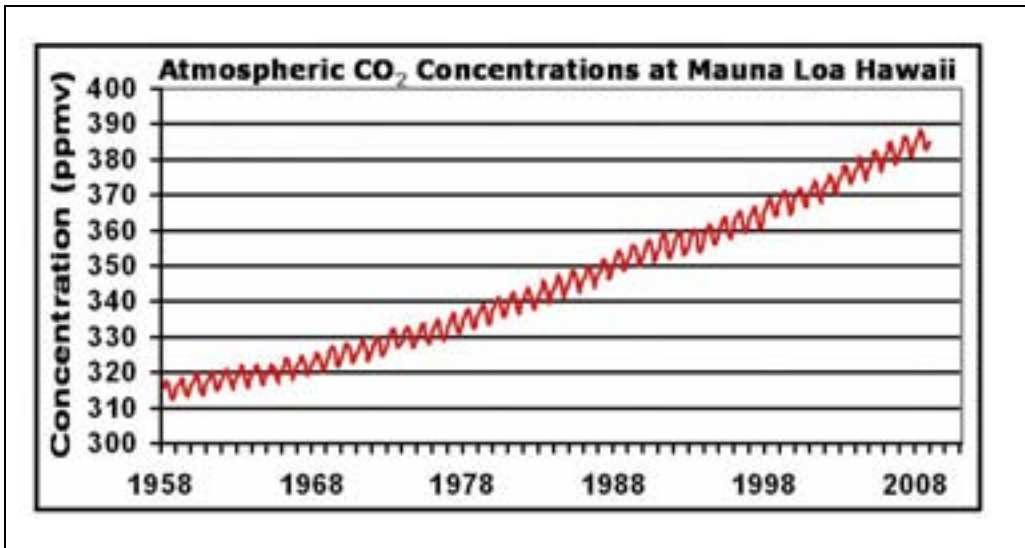


Figure 1.5.1.1. Interannual variability of pCO₂ at Mauna Loa Hawaii (CDIAC website).

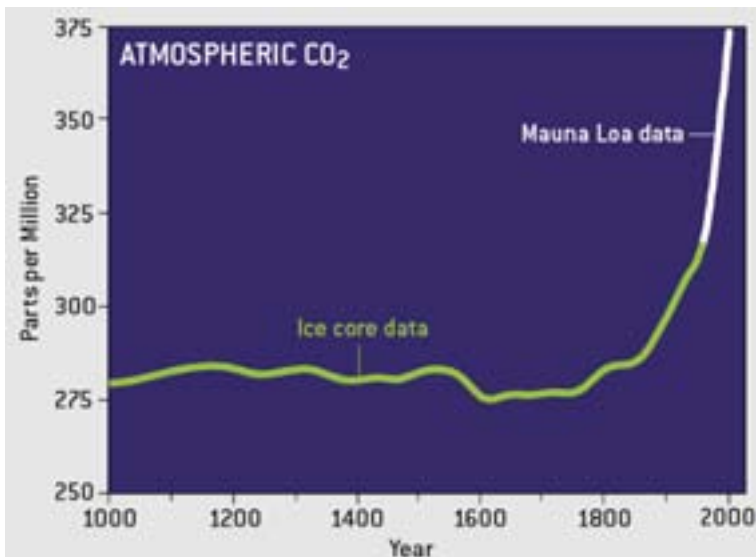


Figure 1.5.1.2 The concentration of carbon dioxide in the atmosphere has mounted considerably over the past century or so. This worrisome trend is well documented (right) by a combination of two techniques: the examination of air bubbles trapped in glacial ice (green segment, which shows 75-year averages) as well as direct measurements of the atmosphere (white segment, which reflects the annual average determined at a weather station situated atop Mauna Loa on the big island of Hawaii). (Doney, 2006).

The results of observations on the $p\text{CO}_2$ interannual dynamics are available at the Carbon Dioxide Information Analysis Center, which includes the World Data Center for Atmospheric Trace Gases. CDIAC responds to data and information requests from users worldwide investigating the greenhouse effect and global climate change.

The Mauna Loa atmospheric CO_2 measurements (Fig. 1.5.1.1) constitute the longest continuous record of atmospheric CO_2 concentrations available in the world.

The observations from all the points present in the CDIAC data base confirm the global trend of $p\text{CO}_2$ increase.

The estimates on the atmospheric content of CO_2 in the previous centuries can be obtained on the base of examination of air bubbles trapped in glacial ice (Fig. 1.5.1.2).

The changes shown in Fig. 1.5.1.1 and 1.5.1.2 demonstrate monotonous growth of concentrations during the last 50 years.

1.5.2 Temperature

The sea surface temperature dynamics is available from 1860 (Fig. 1.5.2.1). The general trend of warming is superimposed with the periods of cooling. It was able to demonstrate an interconnection with the atmospheric temperature variations and the climate modes, Fig. 1.5.2.2. (Swanson, Tsonis, 2009). The nature of these past shifts in climate state suggests the possibility of near constant temperature lasting a decade or more into the future must at least be entertained.

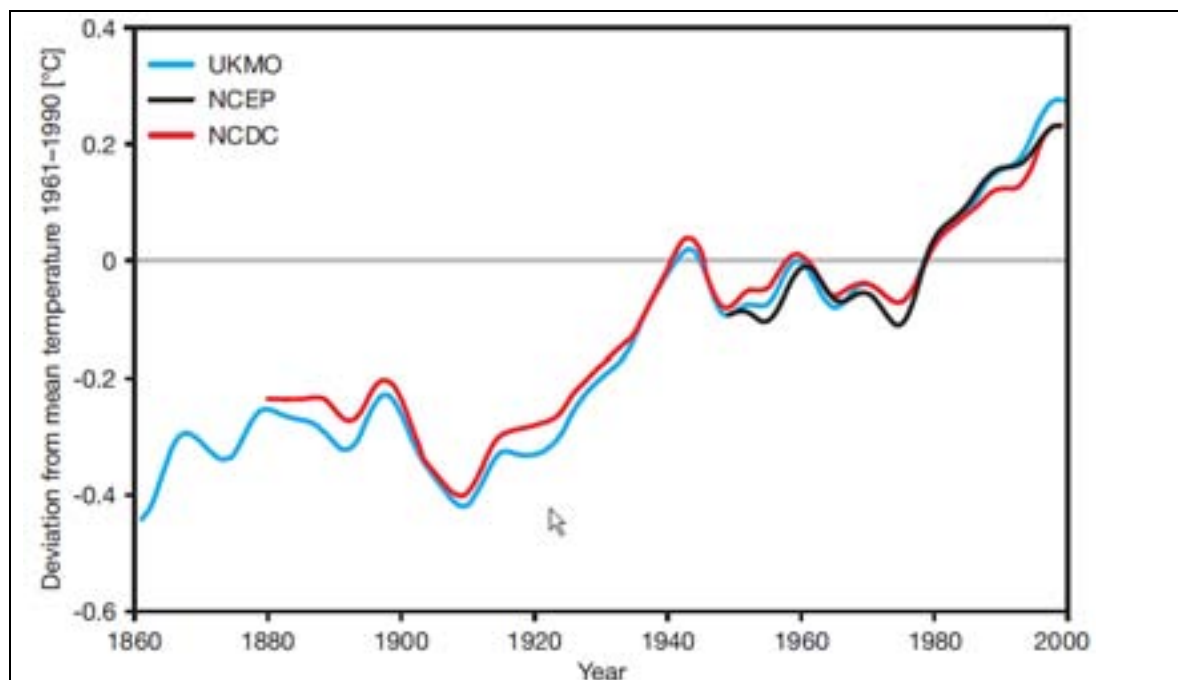


Figure 1.5.2.1 Globally averaged sea surface temperature, according to three data centres: The UK Met Office (UKMO, blue), the US National Center for Environmental Prediction (NCEP, black), and the US National Climatic Data Center (NCDC, red). Source: IPCC, 2001a (WBGU, 2006).

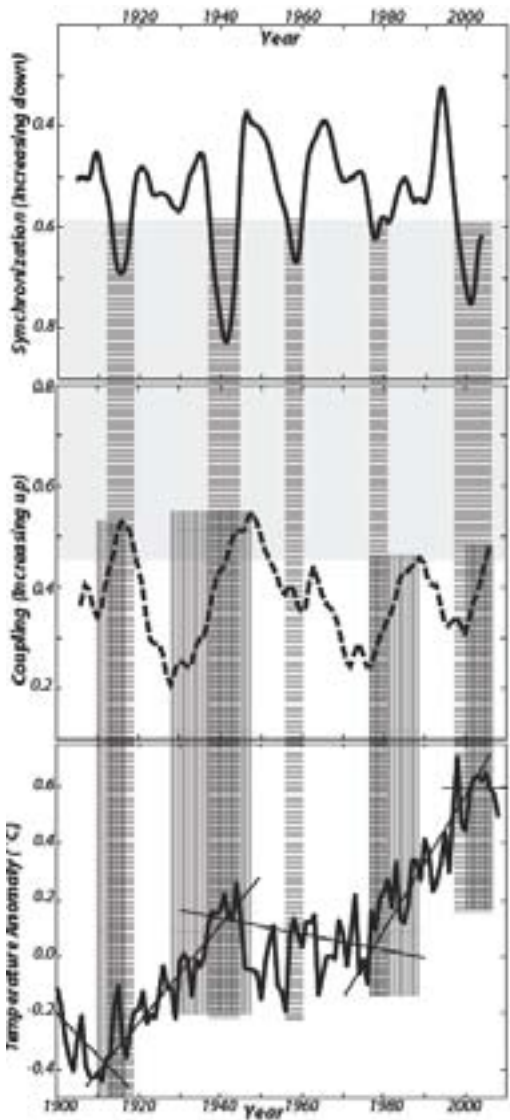


Figure 1.5.2.2 *Top panel:* Synchronization as measured by the root-mean-square correlation coefficient between all pairs of modes over a 7-year running window. Note the reversed ordinate; synchronization increases downward in the panel. High synchronization at the $p = 0.95$ level is denoted by shading, tested by generation of surrogate data as described in Tsonis et al. (2007). *Middle panel:* Coupling as measured by the fraction of consistently increasing or decreasing mode time series described in (Swanson, Tsonis, 2009). The shaded region denotes coupling at the $p = 0.95$ level as calculated from the surrogate data used for the confidence intervals in the top panel. *Bottom panel:* HadCRUT3g global mean temperature over the 20th century, with approximate breaks in temperature indicated. The cross-hatched areas indicated time periods when synchronization is accompanied by increasing coupling.

As it follows from Figures 1.5.2.1, 1.5.2.2, the growth of World’s temperature is not constant. There are periods of fast warming and periods of slower warming or even cooling. Some data (Robinson et al., 2007) testify that the average temperature of Earth varied within a range of about 3° during the last 3000 years (Fig. 1.5.2.3). The connection between the anthropogenic CO₂ increase signal and change of the Earth temperature is not so clear (Fig. 1.5.2.4), because there are some other factors (e.g. solar activity) that affect the variability of climate.

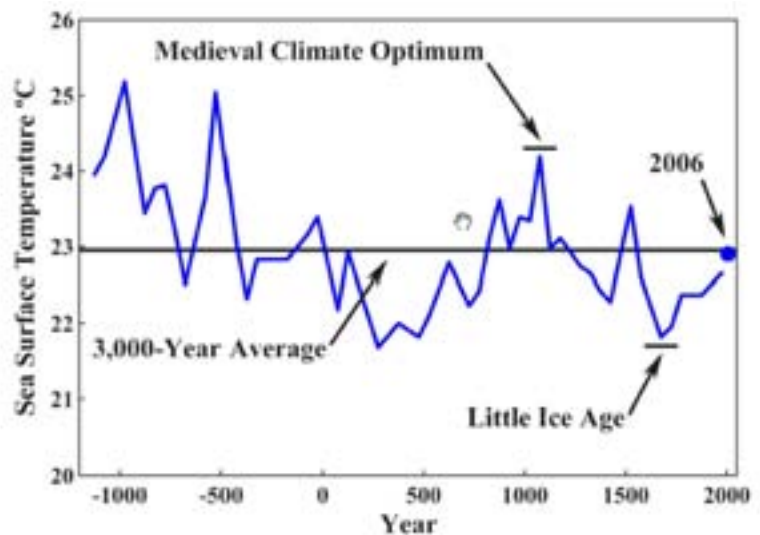


Figure 1.5.2.3. Surface temperatures in the Sargasso Sea, a 2 million square mile region of the Atlantic Ocean, with time resolution of 50 to 100 years and ending in 1975, as determined by isotope ratios of marine organism remains in sediment at the bottom of the sea (3). The horizontal line is the average temperature for this 3,000-year period. The Little Ice Age and Medieval Climate Optimum were naturally occurring, extended intervals of climate departures from the mean. A value of 0.25 °C, which is the change in Sargasso Sea temperature between 1975 and 2006, has been added to the 1975 data in order to provide a 2006 temperature value (Robinson et al., 2007).

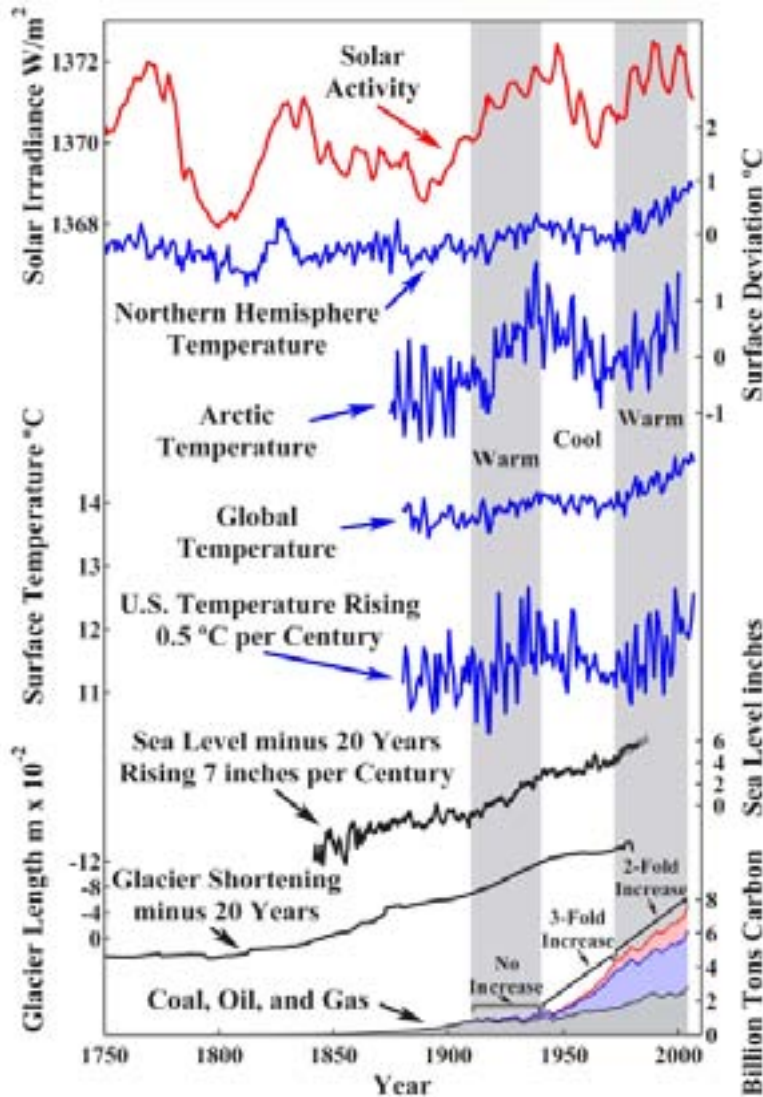


Fig. 1.5.2.4. Seven independent records – solar activity; Northern Hemisphere, Arctic, global, and U.S. annual surface air temperatures; sea level; and glacier length– all qualitatively confirm each other by exhibiting three intermediate trends – warmer, cooler, and warmer. Sea level and glacier length are shown minus 20 years, correcting for their 20-year lag of atmospheric temperature. Solar activity, Northern Hemisphere temperature, and glacier lengths show a low in about 1800. Hydrocarbon use is uncorrelated with temperature. Temperature rose for a century before significant hydrocarbon use. Temperature rose between 1910 and 1940, while hydrocarbon use was almost unchanged. Temperature then fell between 1940 and 1972, while hydrocarbon use rose by 330%. Also, the 150 to 200-year slopes of the sea level and glacier trends were unchanged by the very large increase in hydrocarbon use after 1940 (Robinson et al., 2007).

The study, done by Knorr (2009), shows that the relationship between airborne and absorbed carbon dioxide has been almost silent since 1850. This despite the fact that carbon dioxide emissions have increased from around 2 billion tonnes in 1850 to today's 35 billion tonnes a year. The study is thus across years of research showing that the earth and the sea's ability to absorb carbon dioxide will go down as the emissions increase (Knorr, 2009).

2. Carbonate system theory

Carbon is present in the seawater in the form inorganic carbon (dissolved and particulate) organic carbon (dissolved and particulate) and in small quantities as carbohydrate (i.e. methane).

The modern theory of the sea water carbonate system and the equilibrium constants dependences on the different conditions can be found in (Dickson, 1981, Dickson, Millero, 1987, Millero, F., 1995, Dickson et al., 2007).

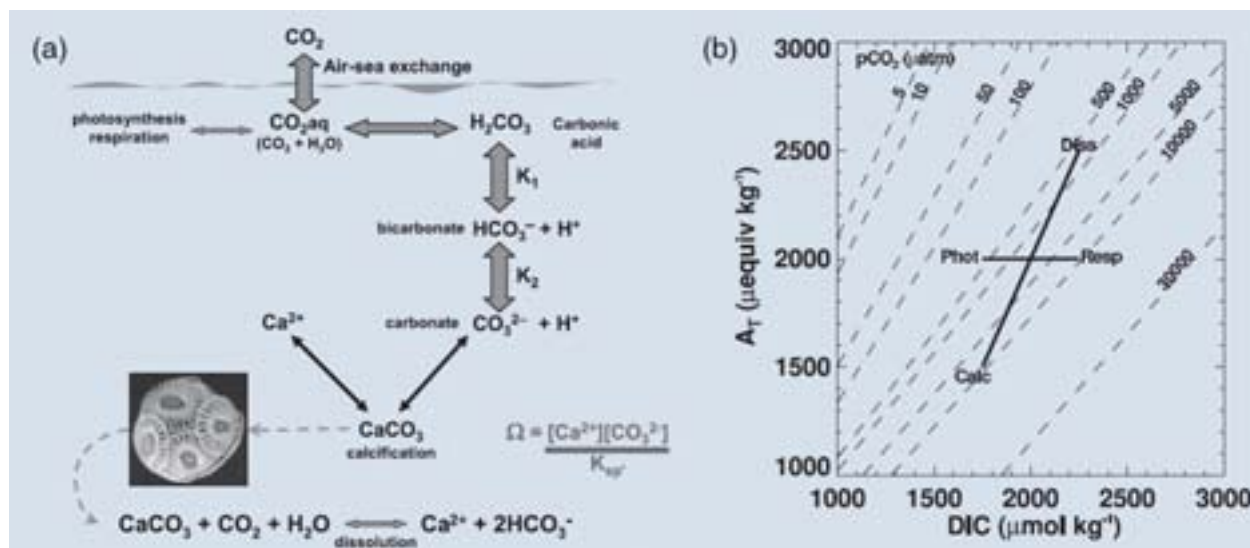
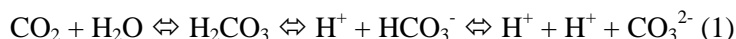


Figure 2.1 (a) A simplified diagram of the carbonate system in seawater. K_1 and K_2 are the dissociation constants for H_2CO_3 and HCO_3^- , respectively. (b) $p\text{CO}_2$ concentration (dashed lines) as a function of AT and DIC. Photosynthesis and respiration affect only DIC, while calcification and dissolution affect both DIC and AT (Kleypas et al., 2006)

An overview of the oceanic carbonate system is summarized in Fig. 2.1. In the seawater carbon is represented by gaseous carbon dioxide (CO_2), carbonic acid (H_2CO_3), bicarbonate ion (HCO_3^-) and carbonate ion (CO_3^{2-}).



The chemical reaction represented by double arrows \Leftrightarrow denotes a chemical equilibrium that can shift in both directions. At the seawater conditions carbon dioxide CO_2 is a mere 1%, bicarbonate HCO_3^- is 93% and carbonate CO_3^{2-} 8%. The amount of undissolved H_2CO_3 is negligible.

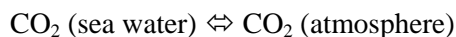
The carbonate system determines the state of two very important parameters of the sea water – concentration of hydrogen ions H^+ (characterized via pH, that is cologarithm of the activity of dissolved hydrogen ions (H^+)) and the carbonate alkalinity $\text{AC} = \text{HCO}_3^- + 2\text{CO}_3^{2-}$. The carbonate alkalinity represents about 96% of the total alkalinity (AT) (Millero, 1979) and therefore determine the buffer capacity of the sea water. Marine pH is governed by the CO_2 system, which can be explained by a classical buffer concept consisting of carbonate salts and carbonic acid.

It is assumed that the processes of production and degradation of organic matter (Corg) result in the consumption and release of neutrally charged CO_2 :



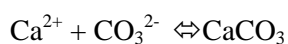
These processes do not affect alkalinity (“Phot-Resp” in Fig. 2.1 b) but significantly affect pH because of shifting the balance of the equilibrium of the carbonate system.

In a similar way the process of gas exchange between the sea water and the atmosphere also doesn't affect alkalinity:



A supply of CO₂ from a seep (or a leakage from a storage reservoir) should also not affect the alkalinity.

The processes of carbonate mineral formation and dissolution change both alkalinity and pH (“Calc and Diss.” in Fig. 1b):



According to (Canfield et al., 2005) the concentrations of dissolved organic carbon (DOC) are 100-500 μM in the coastal waters and 40-80 μM in the open ocean, and concentrations of carbohydrate vary from 20-80 μM in the coastal waters to 5-15 μM in the open ocean. Kepkay (2000) partitioned the carbon pools for the world ocean (in Gt C) as: DOC (200-700); POC (20); phytoplankton (1-11); and other biota (0.4). He further partitioned the DOC pool into a refractory low molecular weight component (120-630) and a bioavailable colloidal component (20-280). The combined DOC + POC is often referred to as “detritus” and represents a major source of carbon for the microbial food web.

Table 2.1 Typical concentrations (ranges of concentrations) of carbon species (in μM) in the seawater (in μM).

	Concentration, μM	Source
AT	2400	(Millero, 1979)
AC	2305	(Millero, 1979)
TIC	2111	(Millero, 1979)
[HCO ₃ ⁻]	1890	(Millero, 1979)
[CO ₃ ²⁻]	208	(Millero, 1979)
[CO ₂]	13	(Millero, 1979)
[H ⁺] (pH=8.151 NBS)	7 x 10 ⁻⁶	(Millero, 1979)
DOC	40-500	(Canfield et al., 2005, Kepkay, 2000)
POC	4-50	(Kepkay, 2000)
Carbohydrate	5-80	(Canfield et al., 2005)
CH ₄ (oxic waters)	0.006-0.050	(Egorov, 2002, Schubert et al., 2006)
CH ₄ (anoxic waters)	16	(Reeburgh et al., 1991, Egorov, 2002),

Methane in the water column can be produced by methanogenesis during the process of degradation of organic matter and can be oxidized by oxygen or in anoxic conditions by sulphate. All these processes are mediated by bacteria. Marine sediments are the main source of methane in the seawater (Canfield et al., 2005). Concentrations of methane in the oxic waters are about 6- 50 nM (Egorov, 2002, Schubert et al., 2006). The maximum concentrations of methane in the water column observed in anoxic waters of the Black Sea are 0.016 mmol kg⁻¹ (16 μM) (Egorov, 2002).

The characteristic values of concentrations of carbonate system parameters, organic carbon and methane in the same units are summarized in Table 1. The distribution of the sea-surface TIC is shown in Fig. 2.1.

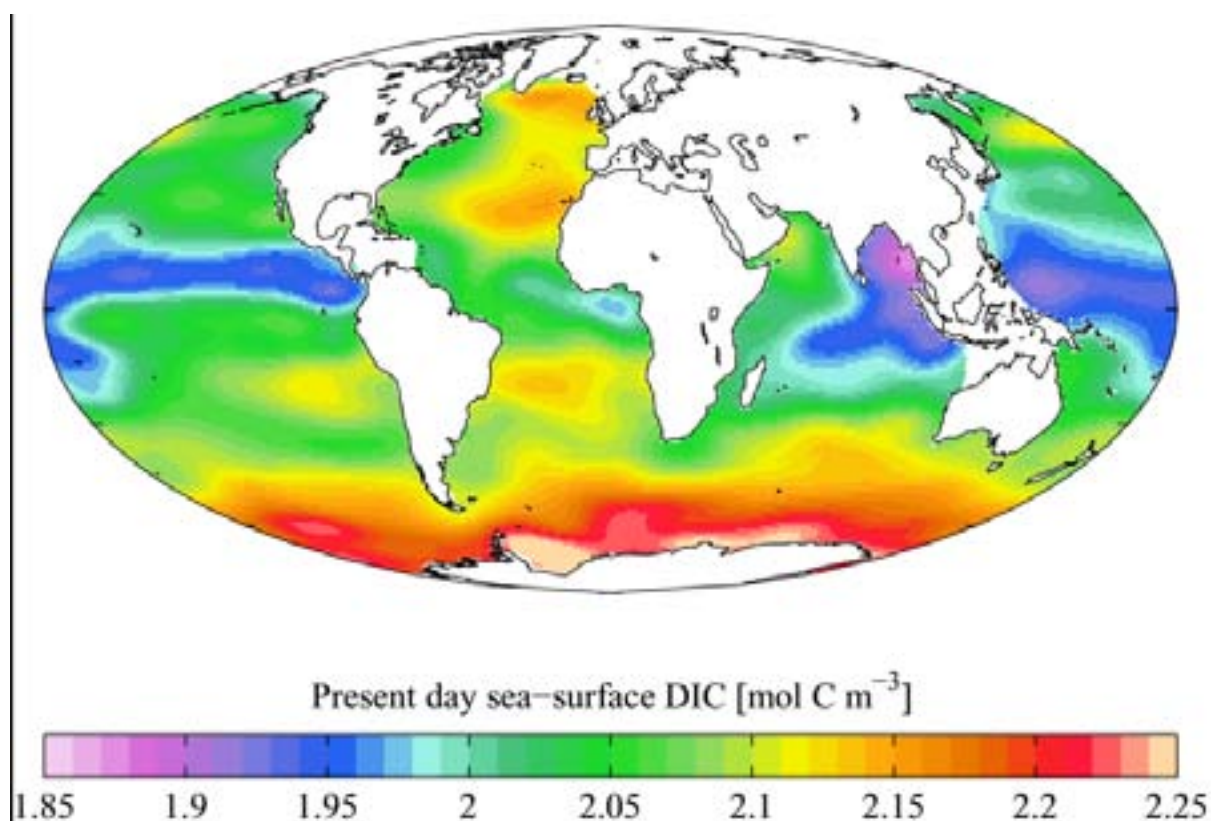


Fig. 2.1. Distribution of the sea-surface TIC (μM) in the surface layer of the Ocean <http://cdiac.esd.ornl.gov/oceans/glodap/Glopintrod.htm>.

It is necessary to remind that the carbonate species have a very small percentage share of the total salts dissolved in the sea water and don't contribute significantly to the density variations of the seawater (Table 2.1.).

Table 2.1. Concentrations of main cations and anions of the seawater (from Golmen et al., 2008)

Kationar, g/kg *		Anionar, g/kg *	
Natrium, Na ⁺	10.76	Klorid, Cl ⁻	19.35
Magnesium, Mg ²⁺	1.30	Sulfat, SO ₄ ²⁻	2.71
Kalsium, Ca ²⁺	0.41	Bikarbonat, HCO ₃ ⁻	0.15
Kalium, K ⁺	0.40	Bromid, Br ⁻	0.07
Strontium, Sr ²⁺	0.008	Borat, H ₂ BO ₃ ⁻	0.005
		Fluorid, F ⁻	0.001
Relativ fordeling, ca:**	12.6 ‰		21.9 ‰

*) For sjøvann med 35.0 i salinitet. Practical handbook. Marine Science. CRD Press, 1994.

***) Seawater: It's composition, properties and behaviour. Open Univ. Press, 1997.

2.1 pH

pH was originally defined by Sørensen (1909) in terms of the concentration of hydrogen ions (in modern nomenclature) as $\text{pH} = -\lg(c\text{H}/c_0)$ where $c\text{H}$ is the hydrogen ion concentration in mol dm^{-3} , and $c_0 = 1 \text{ mol dm}^{-3}$. Subsequently (Sørensen and Linderstrøm-Lang, 1924), it has been accepted that it is more satisfactory to define pH in terms of the relative activity of hydrogen ions in solution $\text{pH} = -\lg a\text{H} = -\lg(m\text{H}\gamma\text{H}/m_0)$

where $a\text{H}$ is the relative (molality basis) activity and γH is the molal activity coefficient of the hydrogen ion H^+ at the molality $m\text{H}$, and m_0 is the molality standard state exhibiting infinitely diluted behaviour.

pH involves a single ion quantity, the activity of the hydrogen ion, which is immeasurable by any thermodynamically valid method and requires a convention for its evaluation (Buck et al., 2001).

2.1.1 pH scales

The pH scale is not an absolute scale; it is relative to a set of standard solutions whose pH is established by international agreement.

Distinct pH scales exist depending on the method of determination.

1. NBS Scale, denoted pH_{NBS} . This scale is useful for pH determinations by galvanic cells calibrated with NBS/NIST (National Bureau of Standards/National Institute of Standards and Technology) standards. Unfortunately, the ionic strength of the standard buffer solutions are much lower (~0.1 M) than that of seawater (~0.7 M). Consequently, a strong liquid junction potential perturbation leaves the pH_{NBS} scale not recommended for use with seawater pH determinations.
2. The *Total* scale, denoted pH_{T} . A set of buffers based on artificial seawater was developed. This pH scale is referred to as the total scale, denoted by pH_{T} . The total scale was defined using a medium containing sulfate ions, which are subject to the proton absorbing equilibrium $\text{H}^+ + \text{SO}_4^{2-} \rightleftharpoons \text{HSO}_4^-$.
3. The *Free* scale, denoted pH_{F} . This scale omits the effect of ions and focuses solely on $[\text{H}^+]_{\text{F}}$, in principle making it a simpler representation of hydrogen ion concentration. Analytically, only $[\text{H}^+]_{\text{T}}$ can be determined, therefore, $[\text{H}^+]_{\text{F}}$ must be estimated using the $[\text{SO}_4^{2-}]$ and the dissociation constant constant of HSO_4^- . The utility of this scale is limited by the complexity of the calculations. pH values measured on the free scale differ by up to 0.12 pH units from both the total and seawater scales.
4. The *Seawater* scale, denoted pH_{SWS} . Lastly, the seawater scale takes into account of the fact that hydrogen fluoride is a weak acid, $\text{H}^+ + \text{F}^- \rightleftharpoons \text{HF}$. However, the concentration of ions is about 400 times larger than the concentration of fluoride, so the difference between the total and seawater scales is very small.

The offset between the free and NBS scales is small and not well known (Culberson, 1981; Zeebe and Wolf-Gladrow, 2001). Strickland (1958) states that a precision <0.02 is achievable under seagoing conditions, so the offset between the NBS and free scales is insignificant by comparison.

The offset between the free and total scales arises from the inclusion of HSO_4^- in the definition of the “total” hydrogen ion concentration and can be estimated from total sulfate concentration (S_{T}) and the equilibrium constant for dissociation of HSO_4^- (K_{S}), which can in turn be estimated from temperature

and salinity as described by Zeebe and Wolf-Gladrow (2001) and Dickson et al. (2007). The offset is $\log_{10}(1 + S_T / K_S)$.

The various pH scales are inter-related by the following equations (Lewis, and Wallace, 1998):

$$a_H = 10^{(-\text{pH}_{\text{NBS}})} = f_H * H_{\text{sws}},$$

and

$$H_{\text{free}} = H_{\text{tot}} / (1 + \text{TS}/K_{\text{SO4}}) = H_{\text{sws}} / (1 + \text{TS}/K_{\text{SO4}} + \text{TF}/K_{\text{F}}),$$

where

a_H is the activity and f_H is the activity coefficient of the H^+ ion (this includes liquid junction effects), TS and TF are the concentrations of SO_4^{2-} and fluoride, and K_{SO4} and K_{F} are the dissociation constants of HSO_4^- and HF in seawater.

The conversions depend on temperature, salinity, and pressure. At 20°C, salinity 35, and 1 atm, pH values on the total scale are about (Lewis, and Wallace, 1998):

- 0.09 units lower than those on the free scale
- 0.01 units higher than those on the seawater scale
- 0.13 units lower than those on the NBS scale

The similar difference between the pH scales was roughly estimates by Zeebe and Wolf-Gladrow, 2001) (Table 2.1.1).

Table 2.1.1. *The pH scales and differences between them (from Zeebe and Wolf-Gladrow, 2001)*

pH scale	Applicable in	Reference state	Difference at S=35, Tc= 25 °C to free scale $\text{pH}_F - \text{pH}_i$
pH_{NBS}	Freshwater	Pure water	
pH_F	Seawater	Artificial seawater	
pH_T	Seawater	Artificial seawater	~0.11
pH_{SWS}	Seawater	Artificial seawater	~0.12

Lewis, and Wallace (1998) evaluated several computer programs that performed calculations relating the seawater CO_2 system parameters. These programs differed in the values of the constants used and in what contributions to the alkalinity were considered. To get an idea of the differences, they ran three programs with the following inputs: TA = 2300 $\mu\text{mol/kg-SW}$; $\text{TCO}_2 = 2000 \mu\text{mol/kg-SW}$; no phosphate or silicate (two of the programs did not have an option to include these); and temperature (°C), salinity [on the Practical Salinity Scale (PSS)], and pressure (in dbar) equal to 20, 35, and 0, respectively. The results were as follows:

Program	pCO_2 (μatm)	pH	pH scale	HCO_3^- ($\mu\text{mol/kg}$)	CO_3^{2-} ($\mu\text{mol/kg}$)
1	336	8.229	Free	1767	223
2	351	8.088	Seawater	1772	216
3	330	8.247	NBS	1782	208

As can be seen, the pH values are on different pH scales and thus are difficult to compare. The values for pCO_2 , though, should be the same regardless of pH scale, as should the values for the concentrations of HCO_3^- and CO_3^{2-} .

2.2 Alkalinity

Alkalinity or A_T is a measure of the ability of a solution to neutralize acids to the equivalence point of carbonate or bicarbonate. Alkalinity is closely related to the acid neutralizing capacity (ANC) of a solution and ANC is often incorrectly used to refer to alkalinity. The alkalinity is equal to the stoichiometric sum of the bases in solution. In the natural environment carbonate alkalinity tends to make up most of the total alkalinity due to the common occurrence and dissolution of carbonate rocks and presence of carbon dioxide in the atmosphere. Other common natural components that can contribute to alkalinity include borate, hydroxide, phosphate, silicate, nitrate, dissolved ammonia, the conjugate bases of some organic acids and sulfide. Solutions produced in a laboratory may contain a virtually limitless number of bases that contribute to alkalinity. Alkalinity is usually given in the unit mEq/L (milliequivalent per liter) or $\mu\text{mol/kg}$ or μM .

The following equations demonstrate the relative contributions of each component to the alkalinity of a typical seawater sample. Contributions are in $\mu\text{mol}\cdot\text{kg}^{-1}\cdot\text{soln}^{-1}$ and are obtained from *A Handbook of Methods for the analysis of carbon dioxide parameters in seawater* Salinity = 35, pH = 8.1, Temperature = 25°C).

$$A_T = [\text{HCO}_3^-]_T + 2[\text{CO}_3^{2-}]_T + [\text{B}(\text{OH})_4^-]_T + [\text{OH}^-]_T + 3[\text{PO}_4^{3-}]_T + [\text{HPO}_4^{2-}]_T + [\text{SiO}(\text{OH})_3^-]_T - [\text{H}^+] - [\text{HSO}_4^-] - [\text{HF}]$$

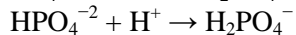
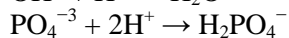
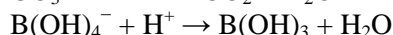
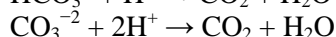
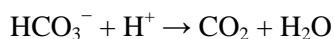
Phosphates and silicate, being nutrients, are typically negligible. At pH = 8.1 $[\text{HSO}_4^-]$ and $[\text{HF}]$ are also negligible. So,

$$A_T = [\text{HCO}_3^-]_T + 2[\text{CO}_3^{2-}]_T + [\text{B}(\text{OH})_4^-]_T + [\text{OH}^-]_T - [\text{H}^+]$$

$$A_T = 1830 + 2 \cdot 270 + 100 + 10 - 0.01$$

$$A_T = 2480 \mu\text{mol}\cdot\text{kg}^{-1}\cdot\text{soln}^{-1}$$

Alkalinity can be measured by titrating a sample with a strong acid until all the buffering capacity of the aforementioned ions above the pH of bicarbonate or carbonate is consumed. This point is functionally set to pH 4.5. At this point, all the bases of interest have been protonated to the zero level species, hence they no longer cause alkalinity. For example, the following reactions take place during the addition of acid to a typical seawater solution:



It can be seen from the above protonation reactions that most bases consume one proton (H^+) to become a neutral species, thus increasing alkalinity by one per equivalent. CO_3^{2-} however, will consume two protons before becoming a zero level species (CO_2), thus it increases alkalinity by two per mole of CO_3^{2-} . $[\text{H}^+]$ and $[\text{HSO}_4^-]$ decrease, as they act as sources of protons. They are often represented collectively as $[\text{H}^+]_T$.

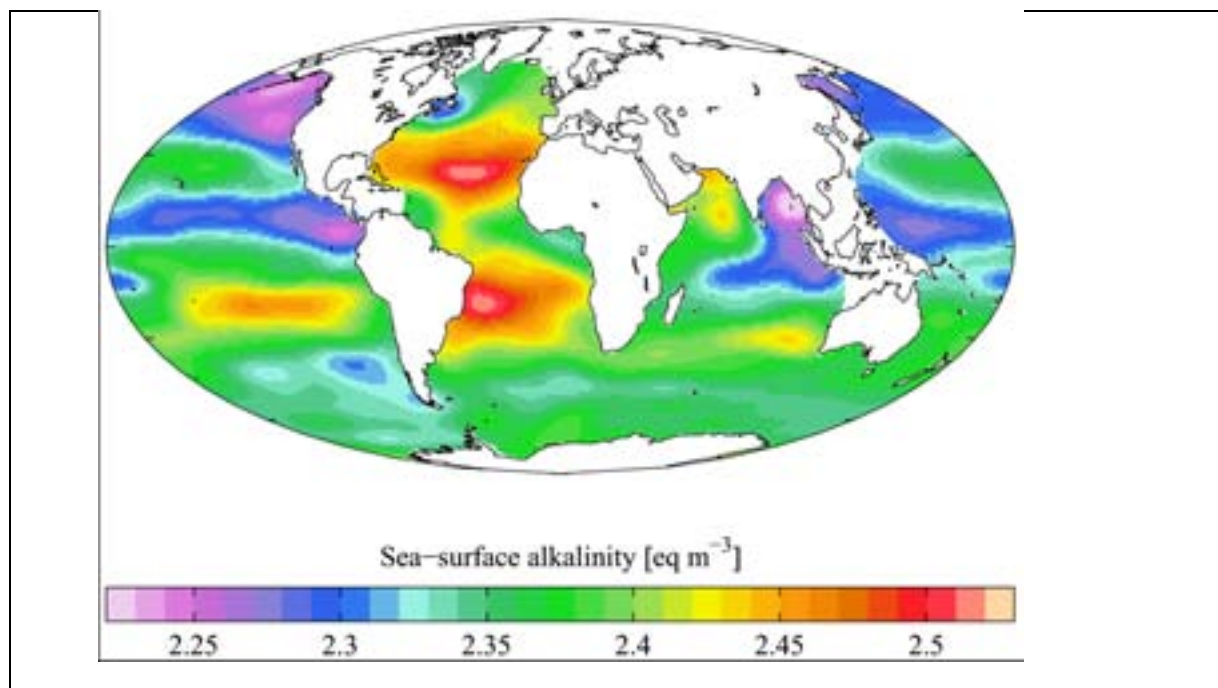
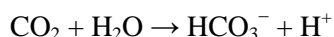


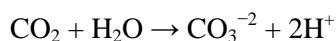
Figure 2.2.1 Sea surface alkalinity

The addition (or removal) of CO_2 to a solution does not change the alkalinity. This is because the net reaction produces the same number of equivalents of positively contributing species (H^+) as negative contributing species (HCO_3^- and/or CO_3^{2-}).

At neutral pH's:



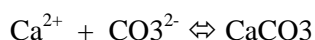
At high pH's:



Addition of CO_2 to a solution in contact with a solid can affect the alkalinity, especially for carbonate minerals in contact with groundwater or seawater. The dissolution (or precipitation) of carbonate rock has a strong influence on the alkalinity. This is because carbonate rock is composed of CaCO_3 and its dissociation will add Ca^{2+} and CO_3^{2-} into solution. Ca^{2+} will not influence alkalinity, but CO_3^{2-} will increase alkalinity by 2 units.

2.3 Carbonate mineral formation and dissolution

This equation is a gross simplification of the seawater system because seawater has many more elements that are likely to play a role. One of these is Calcium (Ca^{2+}) which 'binds' with CO_3^{2-} like:



to form limestone as in corals and shells. There exist several forms of limestone, but this is only a finer point (aragonite, calcite, magnesium calcite, ...). The production of limestone by organisms is called *calcification*. *De-calcification* on the other hand can be done either by organisms who calcify (echinoderms for instance) or those who dissolve limestone (boring sponges, worms, molluscs, many bacteria) and it can also happen chemically without organisms (coral sand dissolving back into sea water).

Calcite and aragonite saturation in the global oceans. The degree of saturation of seawater with respect to aragonite and calcite (Ω_{arg} or Ω_{cal}) is the ion product of the concentrations of calcium and carbonate ions, at the in situ temperature, salinity, and pressure, divided by the stoichiometric solubility product (K^*_{sp}) for those conditions

$$\Omega_{\text{arg}} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] / K^*_{\text{sparg}}$$

$$\Omega_{\text{cal}} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] / K^*_{\text{spcal}}$$

where the calcium concentration is estimated from the salinity, and the carbonate ion concentration is calculated from the DIC and TA data. Because the calcium-to-salinity ratio in seawater does not vary by more than 1.5%, variations in the ratio of $[\text{CO}_3^{2-}]$ to the stoichiometric solubility product primarily govern the degree of saturation of seawater with respect to aragonite and calcite (Feely et al., 2004).

2.4. Bjerrum Plot

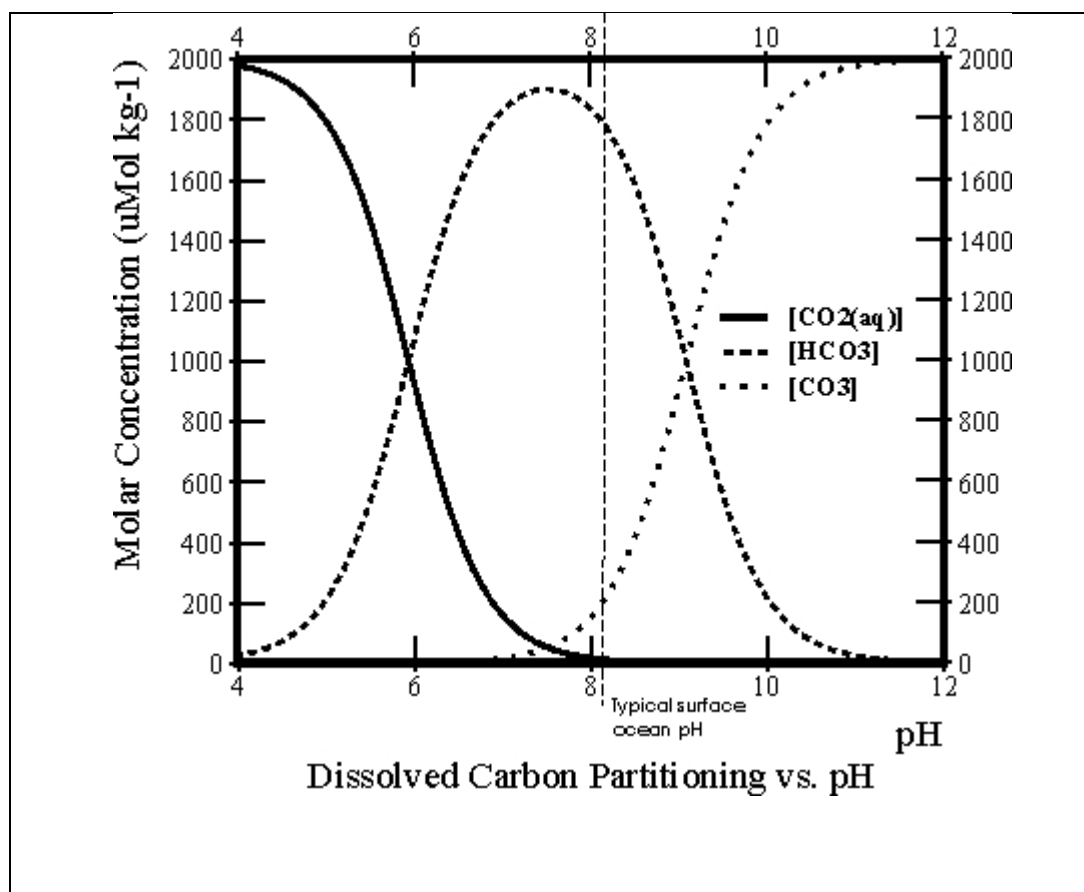


Figure 2.4.1 Carbonate system of seawater (Bjerrum Plot). Relative proportions of the three inorganic components CO_2 , HCO_3^- and CO_3^{2-} . The dashed line shows schematically the pH range that occurs in today's surface ocean.

The diagram shown in Fig. 2.4.1 (so called **Bjerrum Plot**, named after N Bjerrum (1914) who invented this diagram) allows visually representing the equilibrium between the three carbonate species CO_2 , HCO_3^- and CO_3^{2-} . It is possible to illustrate how the decrease of pH is connected with the decrease of carbonate and increase of carbon dioxide. The shown in Fig. 2.4.2. dependence illustrate the changes in the typical ranges of oceanic pH.

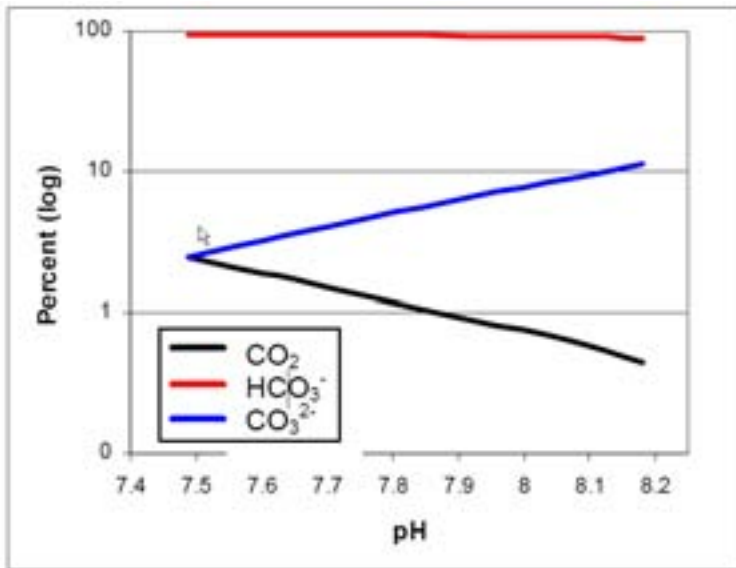


Figure 2.4.2 The percentage changes of concentrations of CO_2 , HCO_3^- and CO_3^{2-} in the typical oceanic pH. (from Golmen et al., 2008)

3. Carbonate system parameters measurement techniques and possibilities in NIVA.

The carbonate chemistry of seawater is so complex that it can be a challenge to accurately measure changes and attribute observed changes to specific mechanisms. Currently there are four measurable parameters: CO₂ partial pressure (pCO₂), total alkalinity (AT or TA), total dissolved inorganic carbon (DIC), and pH. Using the thermodynamic dissociation constants and assumptions about the composition of seawater as a function of salinity, the distribution of all the carbonate species can be calculated from the concentrations of any two of these measurable quantities (Millero, 1979).

The detailed description of the modern techniques for the ocean carbonate system measurements can be found in the “Guide to best practices for ocean CO₂ measurements” (Dickson et al., 2007), that is available at http://cdiac.ornl.gov/oceans/Handbook_2007.html.

The following terms are used to characterize the analytical techniques:

Precision Closeness of agreement between independent test results obtained under stipulated conditions

Repeatability Precision under repeatability conditions – observation conditions where independent test results are obtained with the same method on identical test items in the same test facility by the same operator using the same equipment within short intervals of time.

Reproducibility Precision under reproducibility conditions – observation conditions where independent test results are obtained with the same method on identical test items in different test facilities with different operators using different equipment.

Uncertainty (of measurement) Parameter, associated with the result of a measurement, that characterizes the dispersion of the values that could reasonably be attributed to the measurand.

Accuracy (of measurement) The closeness of the agreement between the result of a measurement and a true value of the particular quantity subjected to measurement (measurand).

The most common measurements for open-ocean discrete water samples are DIC and AT. (Kleypas et al., 2006).

3.1 Methodology of pH measurement and determination

The pH of seawater can be determined using pH electrodes, or more precisely, with a spectrophotometric method (Clayton and Byrne, 1993). Historically, pH potentiometric measurements in sea water have shown a precision of about 0.02 pH units which combined with the lack of convention over which pH scale to use has resulted in pH remaining a rarely reported parameter in oceanography. Discrete potentiometric methods of pH measurements have been shown to be very precise with precisions better than 0.005 pH units. This has been exceeded using continuous flow techniques where precisions better than 0.003 pH units have been reported. However, the high flow rates used to obtain this high precision may have seriously compromised the accuracy due to the calibration difficulties of such systems which suffer from problems associated with unknown residual liquid junction potentials, electrode drift, standing potentials and inaccurate buffer composition. A

recent intercalibration of discrete potentiometric techniques showed differences of 0.2 pH (NBS) units and 0.02- 0.03 pH(SWS) units between investigators.

Classic **potentiometric** methods of pH measurements are described in (Grasshoff et al., 1999) as well as in international (<http://132.239.122.17/co2qc/handbook/sop06.pdf>) and national handbooks of the Seawater analyses.

The **photometric** pH technique is based on measurements of absorbance at 3 wave length (separately at 730 nm and simultaneously at 578 and 434 nm) after addition of the m-cresol purple dye. (Determination of the pH of sea water using the indicator dye m-cresol purple (Version 3.01 SOP 6b — Spectrophotometric pH January 28,2009 http://cdiac.ornl.gov/ftp/oceans/Handbook_2007/sop06b.pdf). A similar technique is described by Wedborg et al. (1999). A **photometric flow-injection technique** description is given in (Bellerby et al., 1995).

In combination with an adequate thermodynamic model of seawater, knowledge of the dissociation constants of carbonic acid, any combination of two CO₂ parameters allows the calculation of the other two. For this purpose high accuracy (at least 0.001 pH units) automated pH measurements are required which can not be reached by conventional pH glass electrodes. Such long-term precision is equivalent to a deviation of $\pm 1.1\text{-}2.2 \mu\text{mol kg}^{-1}$ in total dissolved inorganic carbon (TCO₂) and $\pm 1.4\text{-}2.1 \mu\text{mol kg}^{-1}$ in total alkalinity (TA), depending on temperature and the TCO₂/TA ratio. Spectrophotometric pH determination is based on the absorbance spectra of a pH indicator dye, which has a pK value centered in the expected oceanic pH and colored protonated and deprotonated forms.

The spectrophotometric technique involves adding a pH sensitive indicator (usually m-cresol purple) to a “fresh” seawater sample and looking at the relative absorbance of the protonated and un-protonated species using either a scanning or diode array spectrophotometer. Variability in the spectrophotometer response is corrected by looking at wavelengths outside of the range of the indicating dye. The results are also a function of the temperature and pressure of the sample at the time of measurement. Seawater pH is not a common open ocean measurement because samples cannot be preserved and must be measured soon after collection, but **it does provide a key variable for calcification studies** (Kleypas et al., 2006).

Discrete spectrophotometric pH techniques, using selected sulphonephthalein indicators, have been shown to exhibit very high precisions of better than 0.001 pH. Although faster than measurements of the other carbonate system parameters, these methods are slow and labour intensive and cannot provide the high density measurements necessary to monitor small-scale spatial changes in the carbon dioxide system. There is, therefore, a need for the development of a continuous, real-time spectrophotometric method of sea water pH measurement (Bellerby et al., 1995).

The description of the technique of the modern approaches of photometric pH measurements can be found in a large number of sources:

Dickson, A.G., Sabine, C.L. and Christian, J.R. (Eds.) 2007. Guide to best practices for ocean CO₂ measurements. PICES Special Publication 3, 191 pp.

DOE (1994) *Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water*. Version 2, A. G. Dickson & C. Goyet, eds. ORNL/CDIAC-74

Grasshoff et al., 1999

There were provided some experimental studies and measurements in different regions (Byrne et al., 1988, Dickson, 1993, Chierici et al., 1999, Clayton, Byrne, 1993, Mosley et al., 2004, Yao et al., 2007, Ohline et al., 2007, Millero et al., 2009).

3.1.1 Methods in use at NIVA

At NIVA a standard **potentiometric** technique is used. Sample's pH is determined with pH-meter equipped with combined glass / calomel electrode. Reading of the measurement is made when the sample is in approximate equilibrium with the environment, and preferably at 25 ° C. The pH in the range 10 to 14 is corrected for "sodium error" by using the table for the electrode. The measurements of pH are performed using the following instruments: Radiometer PHM 210 Standard pH meter. Combined glass electrode type GK 2401 C from Radiometer, PHM 93 Reference pH meter, PHM 220 Lab pH meter, Jenway 3045 Ion Analyzer and Metrohm Titrator type Titrino 799 GPT.

The description of the potentiometric technique used at NIVA is given in: (NS 4720. Måling av pH. 1979, 2. utg.). The certificates for the buffers we use indicates that the uncertainty is ± 0.010 pH units at 25 ° C when the coverage factor is 2 This corresponds to a standard deviation of 0.005 pH units.

We started the installation of photometric pH technique in NIVA in the framework of the Project 29083. We used a HACH DR-2800 photometer to measure the absorption at 3 wave length in a 5 cm cell. The preliminary data show good correlation with the traditionally measured pH (Fig. 3.1.1) but there is difference in the absolute values, connected with the using of different scales and some questions with the application of the reagent correction for the photometric results.

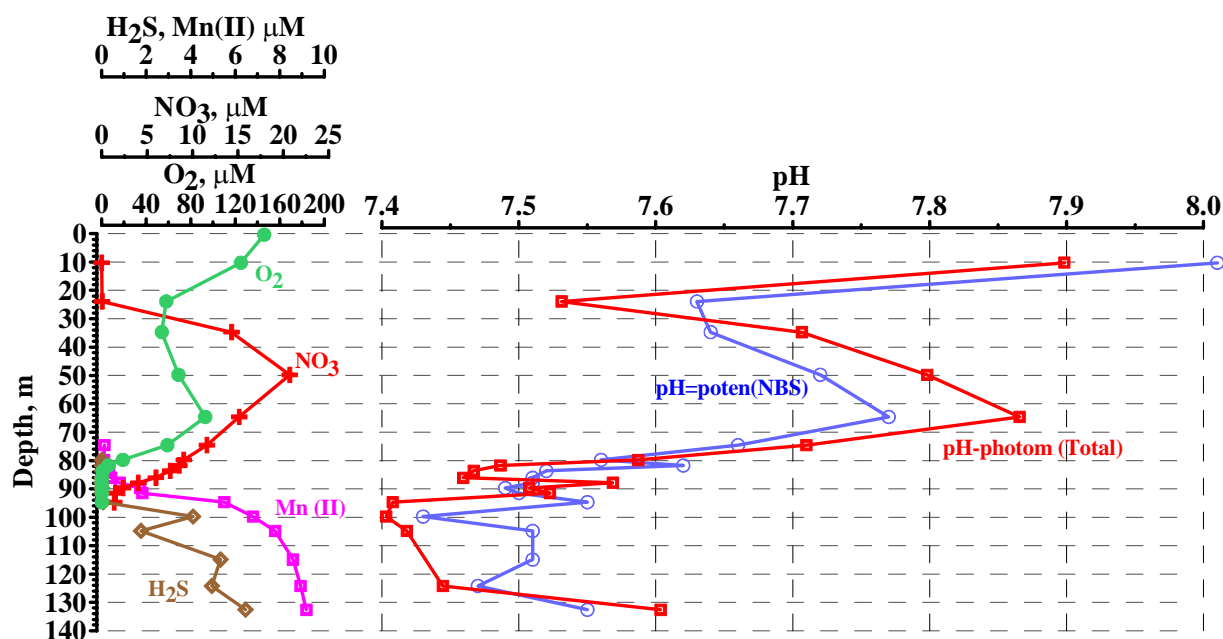


Fig. 3.1.1. Preliminary data on vertical distribution of dissolved oxygen, potentiometric pH (given in NBS scale) and photometric pH (given in Total scale, without correction for reagent) in Bunnefjord 20.08.2009,

3.2 Total alkalinity

Total alkalinity (AT) measurements are made by potentiometric titration (using a titrate and a potentiometer). AT can be determined either by characterizing a full titration curve (Brewer et al., 1986; Millero et al., 1993;) or by a single-point titration (Perez and Raga, 1987). Common analytical differences between systems are in the volume of sample analyzed, the use of either an open or closed titration cell, and the calibration methods. Results can also be obtained from different curve-fitting techniques such as Grin plots, nonlinear fitting, or single-point analysis. Typical open-ocean accuracy and precision are $\pm 2-4$ µmol/kg.

3.2.1 Methods in use at NIVA

Determination of alkalinity at NIVA is performed with automated potentiometric titration with 789 Robot sample carousel. The method applies to the determination of alkalinity in natural and polluted water, and includes both freshwater and seawater. The minimum value that can be determined by this method is 0.01 mmol/l. The method is modified in relation to standards in that it used 50 ml instead of 100 ml sample. The measurement used Metrohm Titrator Titrino 799 GPT are performed with a combined glass electrode GK 2401 from Radiometer, connected to a 789 analysis robot. The description of the using at NIVA technique is given in: (NS-EN ISO 9963-1. Determination of alkalinity. Part 1 Determination of total and composite alkalinity. 1. Issue 1996.)

3.3 Dissolved Inorganic Carbon

Dissolved Inorganic Carbon (DIC) is typically measured using a coulometric titration with a semi-automated sample delivery system. The most common system, a single-operator multi-parameter metabolic analyzer (SOMMA), is fitted with a 20- to 30-mL pipette and calibrated by filling a gas loop with a known volume of pure CO₂ gas, then introducing the gas into the carrier gas stream and performing coulometric titration (Johnson et al., 1987; Johnson et al., 1993). Some systems are calibrated by analyzing sodium carbonate standards. DIC systems that are not coupled with a semi-automated sample analyzer typically introduce the sample manually with a pipette or a syringe. Typical open-ocean accuracy and precision are $\pm 1-2$ $\mu\text{mol/kg}$.

3.3.1 Methods in use at NIVA

Determination of inorganic carbon in freshwater and seawater is performed at NIVA with Dohrmann Phoenix 8000 TOC-TC analyzer, with automatic sample changer.

This method involves the determination of inorganic bound carbon in freshwater and seawater. Samples containing large particles can cause problems in the provision due to the re-sealing of tubes and valves. Range of concentration area for the direct measurement is split in two, 0.2 to 20 mg/l and 20 - 100 mg/l. At higher concentrations, the samples must be diluted. The practical detection limit is 0.2 mg/l C. The samples should be taken in 125 ml or 250 ml glass bottles with slip and glass cork. It is important that the sample bottle contains no air bubbles. 4 ml subsample should be injected into an IC-chamber and 0.5 ml 21% phosphoric acid should be added. The inorganic bound carbon (IC) from carbonates, bicarbonate and CO₂ should be released, and performed with nitrogen as a carrying gas to a NDIR detector where the amount of CO₂ be measured quantitatively.

The description of the using at NIVA technique is given in: (NS-EN 1484 Guidelines for determination of total organic carbon (TOC) and solved organic carbon (DOC) 1997-01.)

3.4 Free CO₂

Two different types of instruments are typically used to measure discrete CO₂ samples. The main difference between the systems is the sample size. One system uses 500 mL samples equilibrated by bubbling a recirculated 50 mL headspace gas through the sample. There is also a small volume technique which equilibrates a 10 mL headspace with a 120 ml sample. With each, an aliquot of seawater is equilibrated at a constant temperature of either 4 or 20°C with a head space of known initial CO₂ content. Subsequently, the head space CO₂ concentration is determined by a nondispersive infrared (NDIR) analyzer or by quantitatively converting the CO₂ to CH₄ and analyzing the concentration using a gas chromatograph (GC) with a flame ionization detector. The initial pCO₂ in the water is determined after correcting for loss (or gain) of CO₂ during the equilibration process. This correction can be significant for large initial pCO₂ differences between the head space and the water,

and for systems with a large head-space to- water volume ratio (Chen et al., 1995). Estimates of precision duplicate samples range from 0.1 to 1%, depending on pCO₂ level and the measurement procedure, with higher pCO₂ levels on the small volume system (>700 µatm), being the least reproducible (Chen et al., 1995).

3.4.1 Methods in use at NIVA

Determination of free CO₂ in freshwater and seawater is performed at NIVA with Dohrmann Phoenix 8000 TOC-TC analyzer with sample carousel STS 8000.

Range of concentrations for the direct determination is from 0.1 to 20 mg C/l. The detection limit is 0.1 mg/l.

The sampling should be performed in the oxygen flasks with fixation with conservation with HgCl₂. Then the samples should be purged with nitrogen without addition of acid so that the free CO₂ should be driven off and detected. The measurements are performed in an NDIR detector.

The description of the using at NIVA technique is given in: (Standard Methods, 4500-CO₂, 4-12-4-18.).

As it described above four different measurement parameters are available to describe the CO₂ system: the partial pressure of CO₂ (pCO₂), total dissolved inorganic carbon (TCO₂), total alkalinity (TA), and pH. In combination with an adequate thermodynamic model of seawater, and knowledge of the dissociation constants of carbonic acid, any combination of two CO₂ parameters allows calculation of the other two. For this purpose high accuracy (at least 0.001 pH units) automated pH measurements are required which can not be reached by conventional pH glass electrodes. Such long-term precision is equivalent to a deviation of ±1.1-2.2 µmol kg⁻¹ in total dissolved inorganic carbon (TCO₂) and ±1.4-2.1 µmol kg⁻¹ in total alkalinity (TA), depending on temperature and the TCO₂/TA ratio. The estimated accuracy of the spectrophotometric method is ±0.002, although individual precision estimates using this technique may be much better.

Table 3.1 Accuracy and precision of the carbonate system parameters techniques.

Parameter	Accuracy and precision (Kleypas et al., 2006)	At NIVA
DIC	±1–2 µmol/kg.	2 µmol/kg.
AT	±2–4 µmol/kg.	2.6 µmol/kg.
pCO ₂	0.1 to 1%	0,016% *
pH potentiometric	0.02 pH units	0.046 **
pH photometric	±0.002 pH units	Technique in preparation

*repeatability, calculated as 2 x STD (0.087 mg/L)

**repeatability

4. Technique of autonomous measurements

Although the mentioned techniques are very useful for mesocosm or water column studies from ships, some of the studies outlined in this report require sampling at much higher frequencies or over longer temporal ranges. These measurements can be obtained with autonomous instruments.

4.1 pCO₂

Carbon researchers have been making high-resolution surface pCO₂ measurements from moving ships for decades using semiautonomous instruments. These typically use an equilibrator that equilibrates a small, fixed volume of air with essentially an infinite volume of water. The equilibrated air is then analyzed in a manner similar to the discrete pCO₂ measurement using either an infrared detector or a GC (e.g., Wanninkhof and Thoning, 1993; Feely et al., 1998). These systems are regularly calibrated by analyzing gas from a series of known CO₂ concentrations. This technology has also been adapted for use on moorings with a surface buoy. This technique was successfully used in the Institute for Baltic Sea Research Warnemuende (Körtzinger et al., 1996, Schneider et al., 2006, 2007, 2009) for the ferrybox system installed onboard Luebeck-Helsinki ferry. Such observations allowed to obtain detailed data on the temporal and spatial variability of pCO₂ for seasonal and interannual scales (Fig. 4.1.1).

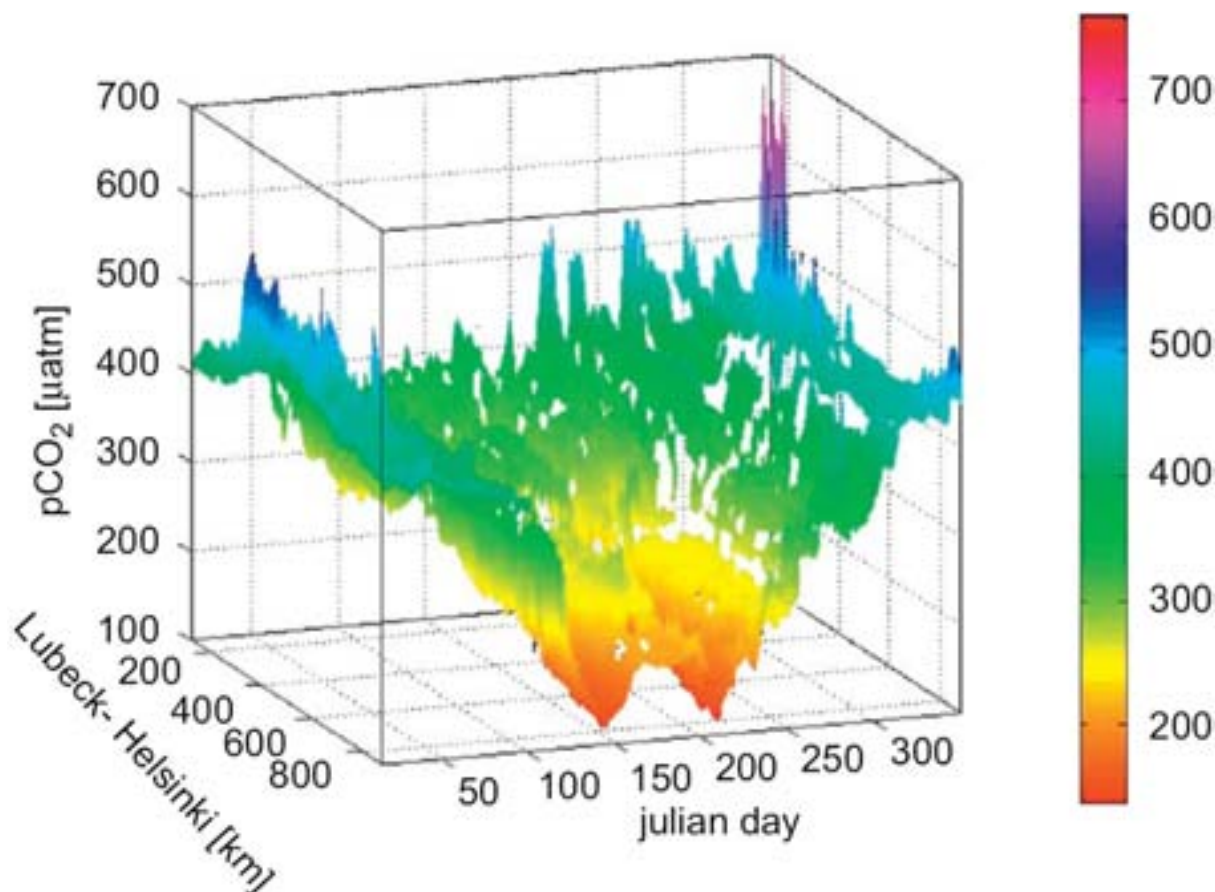


Figure 4.2.1 Seasonality of the CO₂ partial pressure, pCO₂, between the southwestern (Luebeck) and the northeastern (Helsinki) of the Baltic Sea (from Schneider et al., 2009).

4.2 pH

Underway shipboard pH measurements have also been made using the spectrophotometric method. This technique mixes a colorimetric dye into a flowing seawater stream which is then run through the spectrophotometer. The system is “calibrated” by looking at the wavelengths that are not affected by the dye. This basic principle has also been adapted for a variety of autonomous instruments.

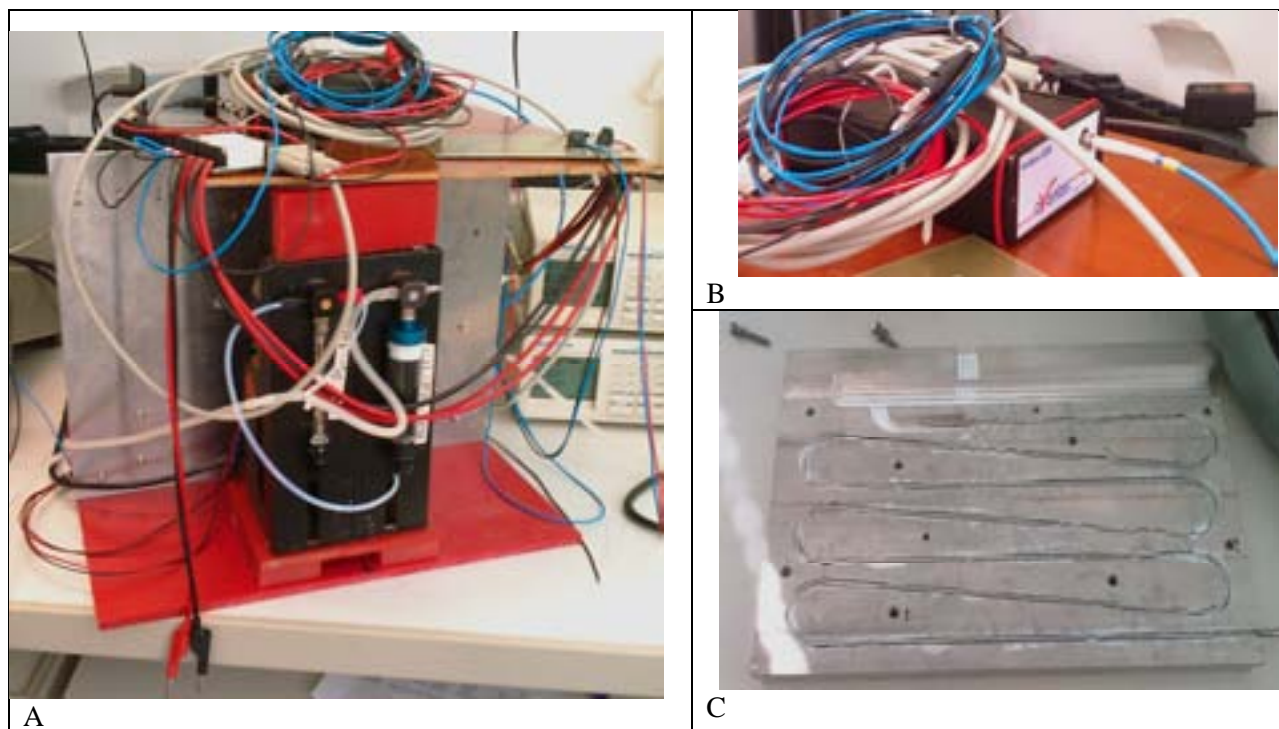


Figure 4.2.1 Constructed in GKSS device for underway shipboard pH measurements. A- main block with two syringes for addition of dye (front side), photometer (on top) and flow cell (back side), B – photometer, C – thermostated flowcell.

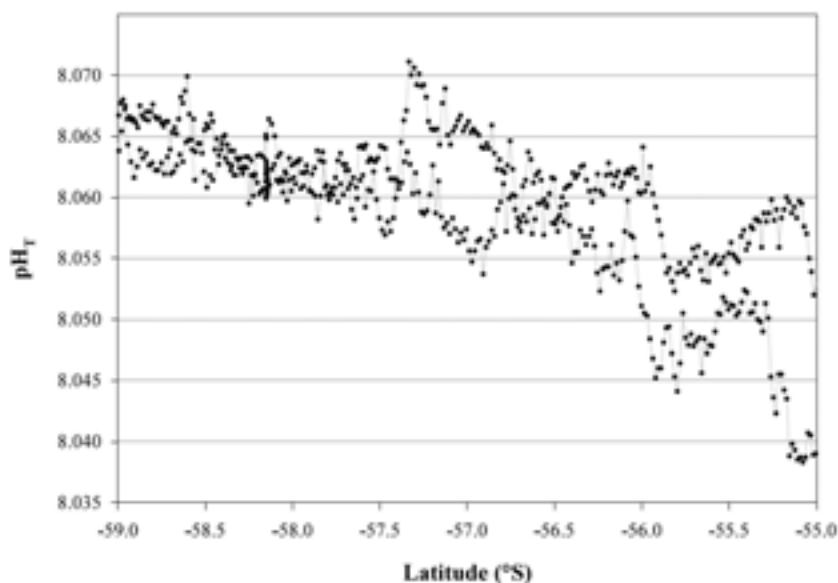


Figure 4.2.2 Surface in situ profile of pH_T through the Weddell Sea. Data is from the ANTXVI/3 expedition during the Austral Spring (Bellerby et al., 2004).

There are several institutions that work on the implementation of the photometric pH technique. Some examples of the devices, constructed for the onboard continuous pH measurements can be found in (Bellerby et al., 1995, 2002, Tapp et al., 2000, Friis et al., 2004, Saito et al., 2008).

The GKSS Research Centre (Petersen et al., 2005) uses a device constructed following a general scheme described in (Grasshoff et al., 1999). Two syringes are used to mix the seawater and dye, the measurements are performed with a optical fiber equipped photometer Avantes Ava Spect-2048 in a thermostated flowcell (Fig. 4.2.1). For the future modifications they plan to purchase a HAMAMATSU photometer (http://jp.hamamatsu.com/resources/products/sys/pdf/eng/e_pma12.pdf). For applications on the ships it is necessary to use a power stabilizer.

The photometric pH measurements were successfully implemented at the Bjerknes Centre for Climate Research (Bellerby et al. 1995, 2002) (An example of the measurements at a frontal zone is presented in Fig. 4.2.2). Nowadays they are working at the autonomous 12 V-based photometric pH measuring system for installation at a probe with a flow cell (Fig. 4.2.3).



Figure 4.2.3 *Flow cell for in situ pH measurements using at the Bjerknes Centre for Climate Research.*

Another example of simultaneous measurements of seawater pH and CO₂ performed with the instrumentation designed in The University of Montana (Seidel, 2006) is shown in Fig. 4.2.4.

New developments by measuring pH spectrophotometrically have been tested in the lab and aboard research vessels (Friis et al, 2004). This first generation prototype will be further developed in the laboratory and tested. In addition this device will be extended by an automatic titration system in order to measure alkalinity. Such an instrument will then be further developed as an automated device connected to the FerryBox observatory system.

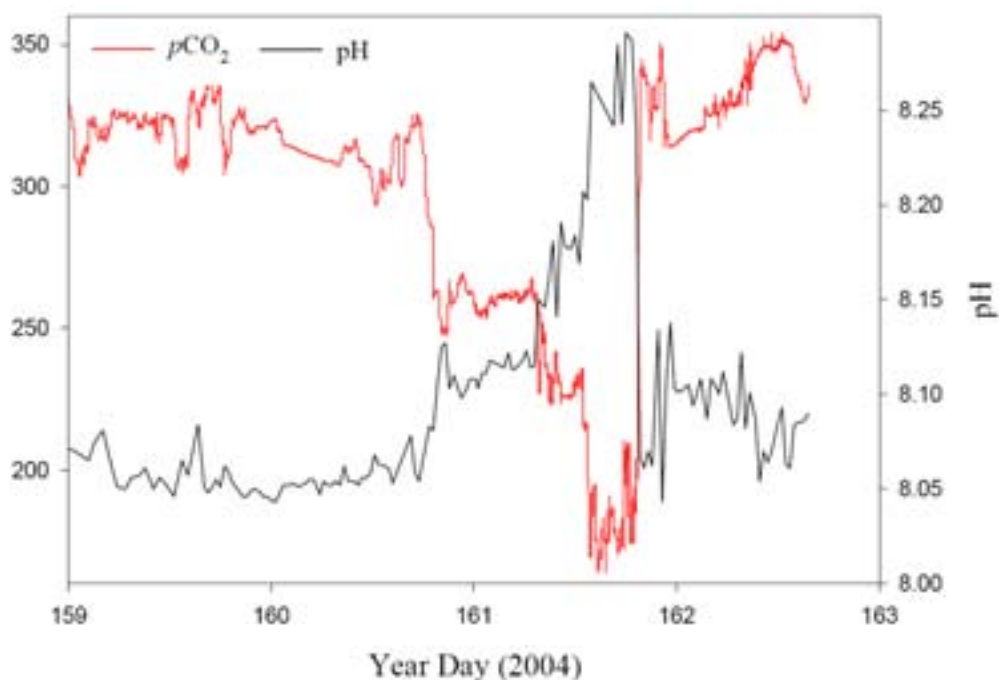


Figure 4.2.4. SAMI-pH and SAMI-pCO₂ profiles collected using underway sampling systems on the R/V Endeavor during a 4-day period. pCO₂ and pH profiles are inversely related due to increased acidity of the seawater with increased pCO₂ (Seidel, 2006).

4.3 Dissolved Inorganic Carbon and Total Alkalinity

Continuous-flow-through analyzers have been developed for DIC (Kimoto et al., 2002) and AT (Watanabe et al., 2004), for use in shallow-water coastal zones. The continuous DIC analyzer strips CO₂ from an acidified sample, and the CO₂ is then measured with an NDIR analyzer. The flow-through AT analyzer is continuous potentiometric measurements. These systems can measure DIC and AT at frequencies of 1–5 minutes, with precisions and accuracies of about 2 $\mu\text{mol kg}^{-1}$ in the laboratory (Watanabe et al., 2004). These instruments have been incorporated into an integrated carbonate chemistry monitoring system that additionally measures temperature, pH conductivity, and dissolved oxygen (Kayanne et al., 2002). The integrated system has been used successfully to obtain continuous measurements on reef flats from an anchored boat in Ishigaki and Palau for 6–10 days (Kayanne et al., 2005). The spectrophotometric method has also been adapted for making underway AT and DIC measurements by comparing acidified water samples to un-acidified samples. Although a few prototype systems have been demonstrated to work, they have not been developed for common oceanographic use.

5. Carbonate system parameters calculations and modeling

The CO₂ system in seawater is characterized by four measurable parameters: the total alkalinity (TA); the total inorganic CO₂ (TIC) (i.e., the sum of the dissolved CO₂, the carbonate, and the bicarbonate); the pH; and either the fugacity of CO₂ (fCO₂) or the partial pressure of CO₂ (pCO₂).

TA and TIC are independent of temperature and pressure; fCO₂, pCO₂, and pH are not. The knowledge of any two of these parameters, along with the temperature, salinity, pressure, abundances of other constituents of seawater, and the relevant equilibrium constants, allows the determination of the other two.

It is assumed, that the accuracy of the carbonate system equilibrium calculations is very high, and they are widely used. But such calculations can be based on different carbonic acid dissociation constants analyzed in (Dickson, Millero, 1987) i.e. Buch, Lyman, Mehrbach, Hannson. Besides, there are several scales for pH measurements (Dickson, 1984) and different definitions of TA (Dickson, 1981): the contribution of some ions (i.e. phosphate, ammonia, sulphide) can be considered or neglected. The majority of modern calculations are based on the approaches available in (SOP3, 2007).

The estimated accuracy of these calculations (after Grasshoff et al., 1999) is given in Table 5.1.

Table 5.2 *Estimated accuracy of calculated CO₂ parameters (after Grasshoff et al., 1999).*

Measured parameter	Accuracy of calculated parameter
pH, A_T	4 $\mu\text{mol/kg } C_T$, 5.3 $\mu\text{atm } f(\text{CO}_2)$
pH, $f(\text{CO}_2)$	30 $\mu\text{mol/kg } C_T$, 40 $\mu\text{mol/kg } A_T$
pH, C_T	5 $\mu\text{mol/kg } A_T$, 5 $\mu\text{atm } f(\text{CO}_2)$
A_T , C_T	0.010 pH, 9 $\mu\text{atm } f(\text{CO}_2)$
A_T , $f(\text{CO}_2)$	0.003 pH, 4 $\mu\text{mol/kg } C_T$
C_T , $f(\text{CO}_2)$	0.003 pH, 2 $\mu\text{mol/kg } A_T$

Carbon system calculations software for BASIC, Excel and MATLAB (CO2SYS) is available at the web page of the Carbon Dioxide Information Analysis Center (CDIAC): <http://cdiac.ornl.gov/ftp/co2sys/>.

A FORTRAN code for the carbonate system parameters calculations was recently published by (Follows et al., 2006). In this approach like in the others, an iteration procedure is recommended, because the rates of reactions between the carbonate system parameters are much faster (the equilibrium constants are less than 0.05 s^{-1} (Emerson, 1995)) than of hydrophysical or biogeochemical processes considered in the models.

Besides the chemical transformation in the carbonate system it is necessary to parameterise the changes connected with (1) processes of production and destruction of organic carbon, (2) processes of gas exchange with the atmosphere and (3) processes of dissolution and precipitation of carbonates (only for the large temporal scale models).

To parameterise the processes of production and destruction of organic carbon it is possible to use an ecological model. It is possible to modify such a model by an addition of a compartment for TIC (that might change similar to the model's limiting nutrient according to the Redfield stoichiometry). It is possible also to assume that estimate the changes in TA on the base of a constant Salt/Alk ratio, and therefore receive 2 independent variables necessary for the calculation the all the carbonate system parameters.

Such an approach was used in: (Blackford, Gilbert, 2006) and (Kuznetsov et al., 2009). Salt/Alk ratio can be assumed constant for the oceanic waters. It is not clear either such an approach can be used for the natural seeps studying, but it can probably be accepted for the estimating of the leakages.

The gas exchange processes are also very fast and can be modelled on the base of the Henry's law, that is represented by a linear equation.

6. Conclusions

Even though ocean acidification has happened in the past, during previous episodes of high atmospheric CO₂ levels, the current changes are much more likely to be very detrimental to the ocean ecosystems and especially biodiversity. The last recorded period of low ocean pH and high atmospheric CO₂ was during the Paleocene-Eocene Thermal Maximum about 55 million years ago. During this period, many marine species became extinct. This was a slow, natural increase in atmospheric CO₂, which would have allowed species time to adapt. The current change in atmospheric CO₂ levels and ocean pH is happening much more quickly than the episode 55 million years ago, so it is likely that many more species will become extinct because they will not have time to adapt. Since many species are likely to become extinct, the entire ocean ecosystem will be affected with decreased biodiversity.

The concern of many scientists today is that the current episode of acidification is taking place more rapidly than anything that has transpired in the past, leaving oceanic species no time to adapt. Although the effects may be hidden from people's view, dramatic alterations in the marine environment appear to be inevitable. (Doney, 2006)

Theoretically there are 2 reasons of the growth of CO₂ content in the atmosphere and in the upper layer of the Ocean:

- (1) CO₂ in the atmosphere can increase because of land sources (including anthropogenic influence) and after that penetrate to the Ocean's surface waters
- (2) CO₂ in the atmosphere can increase because of the growth of the Ocean temperature, the following decrease of the gas solubility, shallowing of the remineralization depth and therefore increasing flux from the Ocean to the atmosphere.

Of course, a short time of observations doesn't allow to filter the data from climatic decadal signals such as NAO (appr. 11 years) and AMO (appr. 60 years). Another factor is the insufficient accuracy of the carbonate system parameters measurements, first of all, pH.

As it is seen from direct comparison between the Fig. 1.4.1.1 and 1.4.2.2 there is no direct linear correlation between the growth of temperature and atmospheric pCO₂ at the scales of several years-several decades, but nevertheless it is necessary to agree with the conclusions of (Hall-Spencer et al., 2008) *"This opportunity to observe the tipping points at which principal groups of marine organisms are affected by lowered pH proves that, even without global warming, the projected rise in atmospheric CO₂ concentration is hazardous, as ocean acidification will probably bring about reductions in biodiversity and radically alter ecosystems."*

We suppose that there is a gap of knowledge in the estimating of the present rate of the acidification development in connection with the climatic patterns. We need an establishment of more accurate and more regular system of measurements based on new technique (first of all photometric pH measurements) and new facilities (SOOP). We also need application of more realistic models for the period from several years to several decades (AMO and NAO signals) that will simulate combined influence of hydrophysical and biogeochemical processes incondition of forcing by atmospheric CO₂ and climatic (temperature) patterns.

The using at NIVA techniques of the carbonate system measurements (pH, Alk, DIC, CO₂) are up-to-date and correspond to the modern levels of accuracy and precision.

Nevertheless, NIVA requires an establishment of a new technique of photometric pH measurements. This will allow to implement the existing and planned SOOP systems. The necessary equipment can be either constructed at NIVA or purchased.

This will strengthen NIVA in deep knowledge of the ocean acidification studies and thereby increase NIVA's contribution to the ongoing and future projects with national and international institutes.

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