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Effects of an increasing atmospheric CO₂
concentration on the pH of the Baltic Sea

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Abstract

Ocean acidification is a consequence of the anthropogenic release of carbon dioxide (CO₂) to the atmosphere. When CO₂ is dissolved in water it affects the composition of ions and lowers the pH of the water. As the partial CO₂ pressure in the atmosphere increases a new balance is reached with the surface waters which causes the pH of the surface oceans to decrease. For small shallow seas this effect may be worse than in the oceans because of the limited vertical mixing of deep water and the limited buffering capability (alkalinity). A decrease in ocean pH may have direct effects on ecosystems and indirect effects where the saturation states of calcium carbonates are the most important.

This project aims to model projections of future pH of the Baltic Sea surface waters from several CO₂ scenarios suggested by the IPCC. A predictive, deterministic model was constructed to project future changes in pH based on the atmospheric CO₂ partial pressure, alkalinity and the equilibrium of ions. From the model the ion concentrations can be calculated and used to calculate projections of the saturation state of calcite and aragonite of the Baltic Sea surface waters.

Projections of Baltic Sea pH during the 21st century have been made using the model and the CO₂ scenarios A1FI, A2 and B2 described by the IPCC. For these scenarios the projections show a decrease in pH by 0.2-0.4 units. If possible changes in alkalinity, which may be a result of changes in river run off to the Baltic Sea, are included the decrease in pH may be as large as 0.5 units.

Projections for calcium carbonate indicate that it is possible that calcite becomes under saturated in spring and autumn during the 2050's but is not likely to become under saturated during summers. Aragonite is in our model projected to become under saturated in all seasons already in the 2040's.

The magnitude of our projected changes in pH and saturation states of calcite and aragonite has been reported by SMHI to cause negative effects on calcifying organisms and may have effects on the ecosystem as a whole.

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1. Aim

The aim of this project is to model ocean acidification in the Baltic Sea and estimate what pH values can be expected in the present century with CO₂ increases as suggested by the international panel on climate change (IPCC).

It is expected that a change in climate leads to changes in the hydrology of the Baltic Sea. Therefore the project aims also to give an estimate of the effect on Baltic Sea pH from an increase in river runoff.

2. Introduction

Acidification refers to a decrease in pH which is a measure of the concentration of hydrogen ions (H^+). Since H^+ is very reactive, organic compounds are sensitive to changes in pH. Ocean acidification is referred to as the process where the pH of the oceans decreases as a result of uptake of anthropogenic carbon dioxide released in e.g. burning of fossil fuels. The carbon dioxide dissolves into carbonic acid and ions which results in an increase of hydrogen ions in the oceans. A change in pH would have a major effect on biological organisms and the marine life (Gatusso and Hansson, 2011).

Climate change and anthropogenic emission of CO_2

The climate varies naturally on our planet and there have been both warm periods and colder periods. These changes are caused by variations in solar output, orbital variations, volcanic eruptions, i.e. these are natural causes. Today humans are increasing the concentration of greenhouse gases due to emissions from burning of fossil fuels and cement production (Seinfeld and Pandis, 2006). These emissions are called anthropogenic and impact the climate and are two aspects of what is often referred to as the anthropogenic climate change. The Swedish physicist, Svante Arrhenius, found already in the nineteenth century that an increase in greenhouse gases would lead to an increase in global temperature. Later in the 1950's Charles David Keeling started measuring the concentration of carbon dioxide in the atmosphere from an observatory on the Hawaiian islands. He discovered that the concentration of carbon dioxide was increasing and concluded that it probably was a result due to anthropogenic emissions. Keeling kept doing his measurements from the Hawaiian islands. His results, displayed in a graph, later became known as the Keeling Curve (figure 1) and shows the annual increase and decrease in carbon dioxide as well as the total increase.

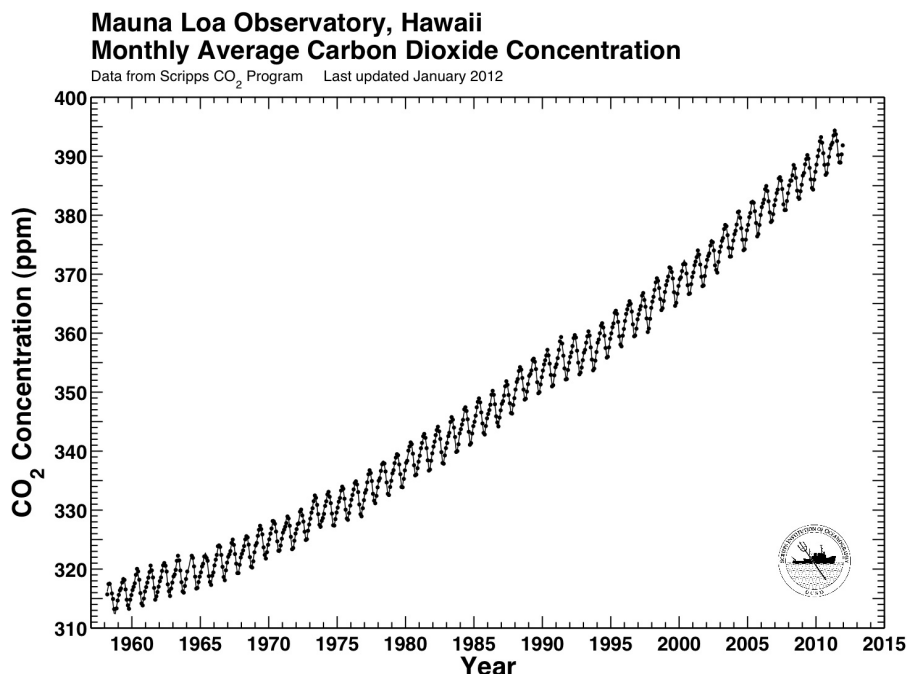
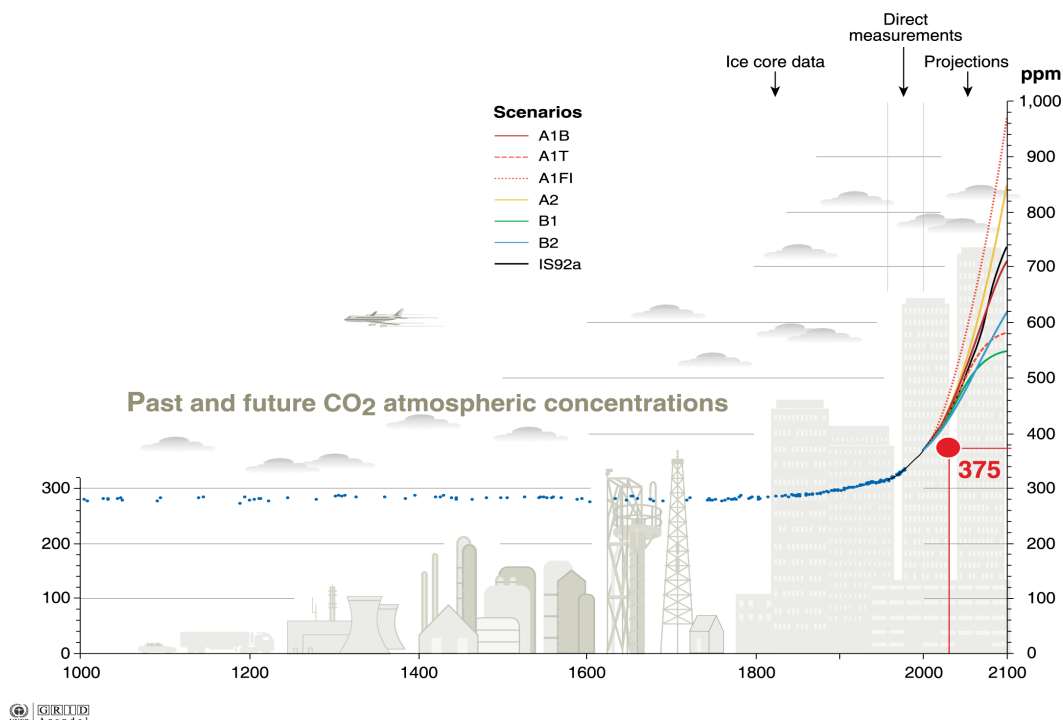


Figure 1: The Keeling curve shows the increase of atmospheric carbon dioxide from 1958 up to present. (Reproduced with permission from Ralph Keeling, Scripps Institution of Oceanography, 2012.)
http://scrippsco2.ucsd.edu/graphics_gallery/mauna_loa_record/mauna_loa_record.html

The annual variation in concentration of carbon dioxide is due to the change in vegetation in the northern hemisphere. When the northern hemisphere is tilted towards the sun the vegetation starts to grow and the photosynthesis is larger than respiration and carbon dioxide is consumed. During our fall and winter the northern hemisphere is tilted away from the sun and leaves and plants defoliate and thereby the photosynthesis decreases and carbon dioxide concentration increases (Taylor, 2005).

From the Keeling Curve, the change in atmospheric CO₂ concentration can be observed since the measurements began in the 1950's. To be able to study the CO₂ concentration further back in time other methods are used. By drilling thousands of meters down in the Antarctic ice and collecting ice samples, the CO₂ concentration can be measured from the year the snow fell. There are records of CO₂ concentration derived from ice core data several hundred thousand years back and the concentration has never been as high as it is today (Taylor, 2005). Today the concentration is around 390 ppm (IPCC, 2011) and before the industrial revolution it was around 280 ppm (Seinfeld and Pandis, 2006).

Attempts to predict future CO₂ concentrations have been made by research groups coordinated by the IPCC in the special report on emission scenarios (SRES). The results have been set together to several plausible socio-economic developments that will lead to different CO₂ scenarios. There are no probabilities assigned to the different scenarios and no best guess exist. Therefore when producing new data based on these emission scenarios it is important to use several scenarios (SRES, 2000). The projections for the future CO₂ scenarios shown in figure 2 have a wide spread which means that the scenarios reflect both conditions that will lead to extreme CO₂ concentrations and conditions which lead to values not so far from present concentrations. But it is worth recalling that it is not possible to say which scenario is extreme since no probability is available. Scenarios with very high CO₂ concentration the year 2100 are the A1FI and A2. Scenarios with lower concentration are the B1 and B2 scenarios. The higher concentrations are in the range of 800-1000 ppm and the lower range between 500-700 ppm. Since today's CO₂ concentration is approximately 400 ppm all scenarios shown in figure 2 represent a 25 percent or more increase in concentration.



GRID-Arendal

Figure 2: SRES emission scenarios from the IPCC.

(Reproduced with permission from Philippe Rekacewicz, Emmanuelle Bournay, UNEP/GRID-Arendal. http://www.grida.no/graphicslib/detail/past-and-future-co2-concentrations_a92d#)

Carbon cycle

Carbon is stored in many different ways on the earth with only a very small part of the total budget found in the atmosphere (Table 1). Still, the carbon dioxide found in the atmosphere is essential to all living organisms as it both provides the source for carbon in the photosynthesis and absorbs enough infra-red radiation that heats the surface of the earth considerably. Carbon is cycled between these reservoirs and the anthropogenic use of fossil fuels are currently increasing the concentration in the atmosphere. Compared to the atmosphere is the ocean a huge reservoir of carbon, but the carbon is not evenly distributed in the ocean since carbon dioxide is more soluble in cold water. The deep cold water of the ocean contains almost all the carbon stored in the ocean. There is also an increase with depth due to transport of organic carbon from the surface waters to the deep waters accounting for as much as 10% of the increase with depth (Williams and Follows, 2011). It could be assumed that since the ocean stores so much carbon a small change in concentration of the atmospheric carbon dioxide will not change the concentration in the ocean much. This is true on long time scales but the time it takes to reach equilibrium between the atmosphere and the surface waters is much faster than the vertical mixing of the ocean. This means that the upper mixed layer of the ocean where almost all biomass exist in the ocean will experience a large increase of dissolved inorganic carbon (DIC).

Table 1: Approximate reservoirs of carbon, rocks not included. (Sarmiento and Gruber, 2002).

Reservoir	Mass of carbon (Pg)
Atmosphere	600
Vegetation and soil	2300
Fossil fuels	3700
Oceans	38000

Ocean acidification and uptake of CO₂

Since the beginning of the industrial era approximately half of the anthropogenic carbon released to the atmosphere has been taken up by the ocean (Sabine, 2004). Over time it is believed that as much as 90% of the anthropogenic emissions will be stored in the ocean (IPCC, 2011). This uptake of carbon dioxide by the ocean is positive in the sense that it lowers atmospheric concentrations and thus slows down the increase of greenhouse gases. The negative effect is due to carbon dioxide being a weak acid. Therefore an increase of atmospheric carbon dioxide leads to a lowering of the ocean pH i.e. the ocean becoming more acidic. The ultimate removal of CO₂ from the atmosphere-ocean reservoirs are believed to occur through the reaction with calcium carbonate (CaCO₃) in marine sediments (Zeebe and Wolf-Gladrow, 2001).

Recent studies that were compiled in the IPCC fourth assessment in 2007 show that since the beginning of the industrial era the uptake of anthropogenic CO₂ by the ocean has lead to a decrease of ocean surface water pH of approximately 0.1 units reflecting a 30% increase of hydrogen ions. With an unchanged burning of fossil fuels the change in pH in this century can be as much as 0.4 units and in the next few hundred years 0.6-0.8 units. A change of order that is believed not have been seen in a few hundred million years and it is believed that the ocean pH has never been lower than 0.6 units from today's value, at least not in the last 300 million years (IPCC, 2007).

The ocean and coastal seas (shelf seas) like the Baltic Sea may not react to acidification in the same way. Differences in salinity, alkalinity, riverine input, precipitation and vertical and horizontal mixing times may cause regional variabilities in the amplitude of the acidification. Only about 9% of the ocean surface is located over shelf seas. However, observations show that 20% to 25% of the total biological primary production takes place in shelf seas. Roughly 40% of the human population

lives within 100km from the coast and of all the fish we eat about 90% comes from shelf seas (Simpson and Sharples, 2012). To evaluate the magnitude and the effects of ocean acidification in these areas are therefore of great importance.

Consequences of ocean acidification

Today the surface ocean is saturated with respect to calcium carbonate (SMHI, 2008). A lowered pH and an increasing concentration of dissolved CO₂ changes the concentrations of bicarbonate and carbonate ions. This change influences the saturation level of different calcium carbonates, essential for calcifying organisms (Gatusso and Hansson, 2011). Calcium carbonate is mainly precipitated as calcite and aragonite in the ocean. Marine organisms incorporate calcite and aragonite to develop their shells and skeletons. This is an important process and requires the seawater to be super-saturated so that the shells do not dissolve back into ions once formed.

With today's increase of atmospheric CO₂ the concentration of carbonate ions by the year 2100 may be lowered to 50% of its pre-industrial value (Tyrrell, 2008a). Thereby will also the saturation level, of aragonite and calcite, be lowered to half its pre-industrial value.

An important sink of carbon is a species which belong to the phytoplankton group coccolithophorids. It deposits carbon on the ocean floor by sedimentation of its calcareous shell. The coccolithophorids fix carbon in two ways, both by photosynthesis and through the calcification process. If the pH decrease the calcification process will be haltered and its calcite shell may dissolve (SMHI, 2008).

A decrease in pH by 0.2 units has been shown to cause a complete extinction of a common brittlestar larvae. While larvae of other common brittlestars have reduced survival or increased generation times. On some organisms like jelly fishes the effect of a more acidic ocean may have positive or negligible effect. Organisms that are carbon limited may also be positively affected by the acidification (SMHI, 2008).

Calcifying species in Swedish waters with major impact on ecology of the Baltic Sea and Skagerrak/Kattegat include the coccolithophorid, blue mussels, barnacles, cold water corals, crustaceans and echinoderms. Acidification of the ocean is likely to have significant effect on the ecosystem as a whole. Projected decreases in coastal ocean pH may change the ecological dominance of for example blue mussels in the Baltic proper and cause a complete extinction of cold water corals in these waters (SMHI, 2008).

River run-off and dissolved organic carbon

Decomposition of organic material results in organic carbon which ends up in the soil. When it comes in contact with water it dissolves and is carried out to sea by streams and rivers. Dissolved organic carbon (DOC) is the largest reservoir of organic carbon in the oceans and has a major role in the ocean carbon cycle (Kulinski and Pempkowiak, 2008).

A relatively small shallow sea like the Baltic Sea is especially affected by the DOC because of its high contribution from river run-off. The yearly input from river water is about 2% of the total volume of the Baltic sea (Kulinski and Pempkowiak, 2011). This results in a sea with very low salinity and a high concentration of DOC. The concentration of DOC is 3-4 times higher in the Baltic Sea compared to the oceans (Kulinski and Pempkowiak, 2008). The degradation of DOC releases carbon dioxide in the ocean. This effect, together with today's high concentration of DOC, results in an over saturation of dissolved CO₂ with respect to atmospheric concentrations in many parts of the Baltic Sea (Kulinski and Pempkowiak, 2011).

3. Theory

The amount of CO₂ that the ocean can hold depends on the atmospheric partial pressure and the temperature of the ocean (Gatusso and Hansson, 2011). The change in pH due to CO₂ can therefore be described as a function of partial pressure and temperature. It is also necessary to account for the oceans ability to buffer. The buffering capability is linked to the alkalinity of the ocean which can be measured and included in calculations.

Air-sea interaction

The interaction between the surface of the ocean and the atmosphere includes both transport of heat and particles in both directions. The particular exchange influences the atmosphere and changes the chemistry of the oceans. The oceans are large sources of cloud condensation nuclei's (CCN) to the atmosphere which are essential for the condensation of water vapour into clouds. The heat transported within the oceans are transported over large distances and has great impact on the climate of both coastal and inland areas. Particles are transported to the ocean surface both by dry and wet deposition. The solubility of gaseous species determines how much of a gas will be dissolved in the ocean.

Chemical equilibrium

The equilibrium between the gaseous and the aqueous phase of a gas is described by Henry's law $[A(aq)] = k_A p_A$ where the concentration of a species A is given by Henry's law constant k_A and its atmospheric partial pressure p_A (Seinfeld and Pandis, 2006). Henry's law constant, k_A , is a function of temperature and thus the concentration dissolved in water depends on both pressure and temperature. If a species dissolves and the dissolved complex forms ions this may increase the solubility of the species; this is the case with CO₂.

pH

The most simple definition of $\text{pH} = -\log_{10}(\text{H}^+)$. In reality free hydrogen ions in aqueous solutions are rare and H⁺ refers to complexes such as H₃O⁺ instead (Zeebe and Wolf-Gladrow, 2001).

In water a reversible reaction occurs where the H₂O-molecule dissociates into ions, one hydrogen ion and one hydroxide ion (Wallace and Hobbs, 2006). The concentration of the three molecules quickly reaches equilibrium (equation 1).



The equilibrium constant k'_w is equal to a factor of 10^{-16} M at a temperature of 298 K and since the concentration of pure water molecules is around 55 M the concentration of dissolved ions is approximately 10^{-14} M (Seinfeld and Pandis, 2006).

$$k'_w = \frac{[\text{OH}^-][\text{H}^+]}{[\text{H}_2\text{O}]} \approx 10^{-16} \text{ M} \quad (2)$$

$$[\text{H}_2\text{O}] \approx 55 \text{ M} \Rightarrow k_w = [\text{OH}^-][\text{H}^+] \approx 10^{-14} \text{ M} \quad (3)$$

Each water molecule that undergoes hydrolysis forms one hydrogen ion and one hydroxide ion,

$$[\text{H}^+] \approx 10^{-7} \text{ M} \quad (4)$$

Hence the pH-value for pure natural water will be equal to 7.0.

$$\text{pH} = -\log_{10} 10^{-7} = 7 \quad (5)$$

For seawater three different pH-scales exist, the total scale (pH_T), the free scale (pH_F) and the seawater scale (pH_{sws}).

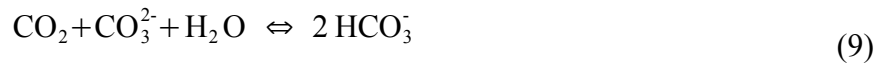
Carbon dioxide

Dissolved carbon dioxide, bicarbonate and carbonate are referred to as dissolved inorganic carbon (DIC). More than 99% of the DIC is made up of bicarbonate and carbonate ions and bicarbonate is by far the largest reservoir of carbon in the oceans (Gatusso and Hansson, 2011).

When carbon dioxide dissolves in water (equation 6) it forms carbonic acid or dissolved carbon dioxide.



The carbonic acid quickly dissolves forming bicarbonate ions (equation 7) which subsequently dissolves forming carbonate ions (equation 8) releasing one hydrogen ion in both reactions. The carbonate ions may react directly with dissolved carbon dioxide and form two bicarbonate ions (equation 9).



When CO_2 concentrations increase, equation 9 describes the reaction most likely to occur. The net effect of the equilibrium equations 6-9 that describes the dissolution of CO_2 in water results in an accumulation of carbon stored as bicarbonate ions with only a very small contribution to the H^+ concentration. However it is important to realize that the amount of hydrogen ions in the ocean is negligibly small compared to the concentration of DIC. Therefore even if only a very small percentage of the CO_2 contributes to the hydrogen ion concentration it still has an effect on the pH. This is the effect that makes CO_2 a weak acid since only a very small part of the dissolved CO_2 contributes to the H^+ concentration.

Alkalinity

Ocean water consists of many different substances that can react with acids and thereby become neutralized. The most common bases in the oceans are bicarbonate, carbonate, boron and hydroxide (Zeebe and Wolf-Gladrow, 2001). The ability for a solution to neutralize acids is called alkalinity. The following reactions shows the neutralization with some bases in the oceans.





Alkalinity is additive so the total alkalinity is (equation 17):

$$A_T = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B}(\text{OH})_4^-] + [\text{OH}^-] + 2[\text{PO}_4^{3-}] + [\text{HPO}_4^{2-}] + [\text{SiO}(\text{OH})_3^-] - [\text{H}^+] - [\text{HSO}_4^-] \quad (17)$$

Alkalinity can be quite difficult to use in calculations involving natural seawater since there are many bases that depend on each other in complex ways. That is why it is common to use a simplified expression for the total alkalinity when dealing with practical calculations.

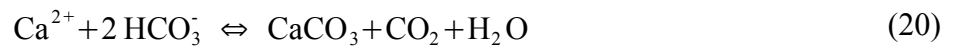
$$A_T = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B}(\text{OH})_4^-] + [\text{OH}^-] - [\text{H}^+] = PA \quad (18)$$

This approximation is shown to be very good when dealing with problems with natural seawater with a pH value above 8.0 (Zeebe and Wolf-Gladrow, 2001). This expression for total alkalinity is called practical alkalinity (*PA*) and used from now on in calculations throughout this project.

The alkalinity of the Baltic Sea varies with the seasons and the different areas. Long time series of measurements of the alkalinity show that the Baltic Proper has an average total alkalinity of approximately 1550 $\mu\text{mol/kg}$ (Hjalmarsson, 2008). The regional variations in alkalinity ranges from 770 $\mu\text{mol/kg}$ in the Bothnian bay to more than 2000 $\mu\text{mol/kg}$ in the Kattegat.

Calcium carbonate

Calcium carbonate, $\text{CaCO}_3(\text{s})$ is created through reactions involving calcium ions. Equation 19 shows the reaction between the calcium and carbonate ions in the aqueous phase as well as the formation of solid calcium carbonate.



Calcium carbonate can also be formed through bicarbonate ion binding with calcium ion (equation 20). However this is not the reaction that controls the CaCO_3 concentration in the oceans (Gattuso and Hansson, 2011). The production is highly dependent on the concentration of calcium and carbonate ions. Calcium ions come from weathering of rocks and is carried out to sea with rivers and streams. The concentration of carbonate ions is dependent on the amount of carbon dioxide dissolved in the ocean. An increase of dissolved carbon dioxide leads to an increase of bicarbonate ions and in a decrease of carbonate ion concentration. This has a negative effect on the production of CaCO_3 .

The saturation level for CaCO_3 is defined as the concentration of carbonate and calcium ions divided by the solubility product constant K_{sp} for CaCO_3 (equation 21). The value for K_{sp} depends on the temperature, salinity and pressure. The two most common types of carbonate minerals are aragonite and calcite. These have different saturation levels, where aragonite always has a lower saturation level than calcite.

$$\Omega = \frac{[\text{CO}_3^{2-}] \cdot [\text{Ca}^{2+}]}{K_{sp}} \quad (21)$$

Since the calcium carbonate is easily dissolved in water, i.e. dissolve into one calcium ion and one carbonate ion, the saturation state is extremely important. CaCO_3 is under saturated if $\Omega < 1$ and supersaturated if $\Omega > 1$ (Gattuso and Hansson, 2011).

Like alkalinity, calcium carbonate acts to buffer the effect of increased CO_2 levels. When the pH decreases the carbonate ion concentration decreases as a result of the balance shifting towards bicarbonate. This will dissolve CaCO_3 found in sediments on the ocean floor. Through mixing of the water column Ca^{2+} will be transported to the surface waters where it may react with carbonate ions again to form calcium carbonate. The mixing of the water column may take hundreds to thousands of years and is generally much too slow to buffer effectively.

4. **Baltic Sea water experiment**

Baltic Sea surface water from Vik, Österlen on the Swedish south east coast was collected on a day with offshore winds and clear water. River water was collected from the river mouth of Höje å located in Lomma. CO₂ was gathered in a tube from air in a bottle containing highly carbonated water.

Experimental set-up

The experiment was set up in a climate chamber which allowed us to control temperature and avoid sunlight which may cause photosynthesis in plankton naturally found in surface waters. An air tight box of 50 L with the shape of an aquarium was used to contain the water and gas (air). 5 Litres of Baltic Sea water was added to the box. To speed up the equilibration time the water was continuously bubbled using an air pump. The water was also slowly stirred using a magnetic stirrer to create a current and minimize local differences in pH. pH was measured with a digital pH-meter. Temperature of both air and water was measured using a digital thermometer. Finally the CO₂ concentration was monitored using a gas-monitor with high accuracy and which automatically compensates for water vapour. The salinity of the water was measured using a conductivity-meter.

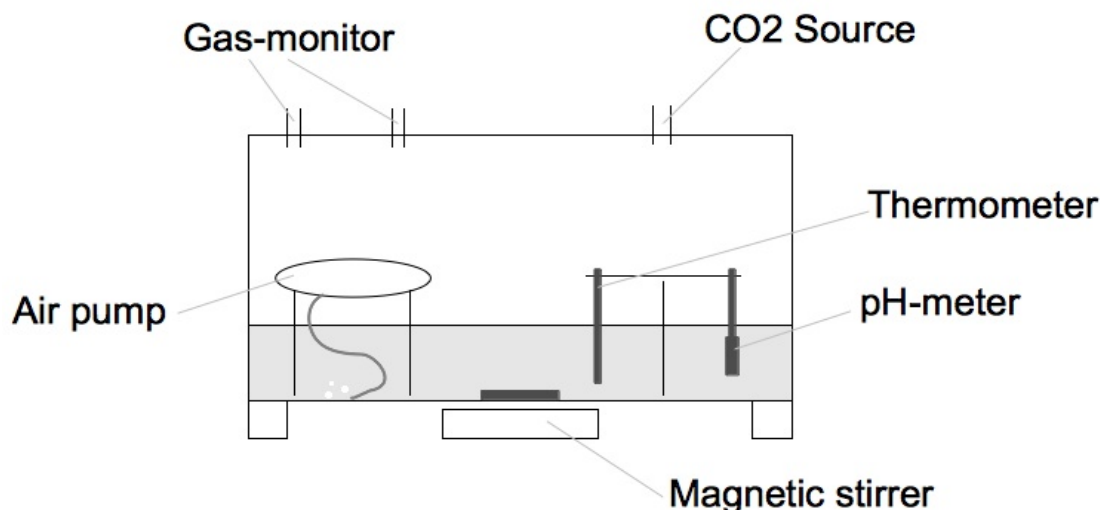


Figure 3: *Experimental set up.*

Procedure

Initially a calibration of the pH-meter was carried out using solutions with pH 4 and 7.

In the first attempt, four measurements of pH were done for CO₂ concentrations close to 500 ppm, 1000 ppm, 1500 ppm and 2000 ppm. The CO₂ was added to the system through a tube into the box and approximately 5000 seconds were allowed for equilibration between water and air. Temperature was kept constant around $4 \pm 1^\circ\text{C}$. The CO₂ concentration and pH were then simultaneously measured and the averages of approximately the last 10 minutes were taken as equilibrium levels. The climate chamber was kept closed and without light during the experiment with the exception when the injections of CO₂ were done and the doors had to be opened for shorter times.

In an attempt to measure the effect of an increase in riverine input, river water was added to the seawater. The amount of river water corresponds to a large additional increase of riverine input and amounts to approximately 250ml river water in 5L sea water.

Measurements were then done for CO₂ concentrations close to 500 ppm, 1000 ppm, 1500 ppm and 2000 ppm at temperature 4C ±1°C. The results were compared with the measurements on pure Baltic Sea water.

Results

The salinity of the water was measured to be 12.16 psu. The pH-meter was calibrated and the following calibration equation was used when measuring the pH.

$$\text{pH} = 3.8551 x + 13.619 \quad (22)$$

The collected data of how pH varies with time after a sharp rise (injection) in ambient CO₂ is shown in figure 4, 5, 6 and 7. Figure 4 shows 500 ppm which was left overnight in order to estimate the time it takes to establish an equilibrium between gas and water. Approximately 70% of the reduction in pH is reached after 5000 seconds in figure 4. Figure 5 shows 1000 ppm which has a minimum near 4000 seconds. Both figure 6 and 7 have near constant recordings for about 2000 seconds from 2000 seconds and onwards.

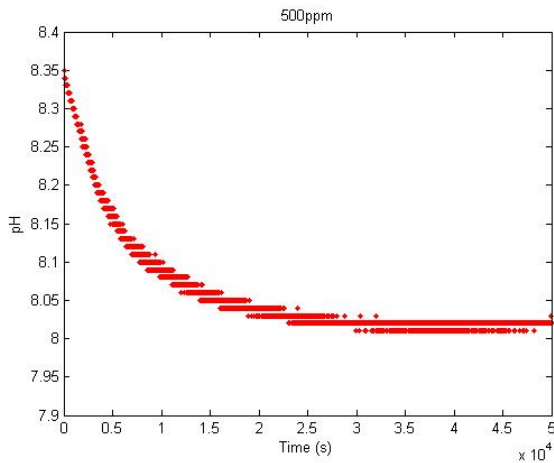


Figure 4: 500 ppm CO₂. Calibration: default

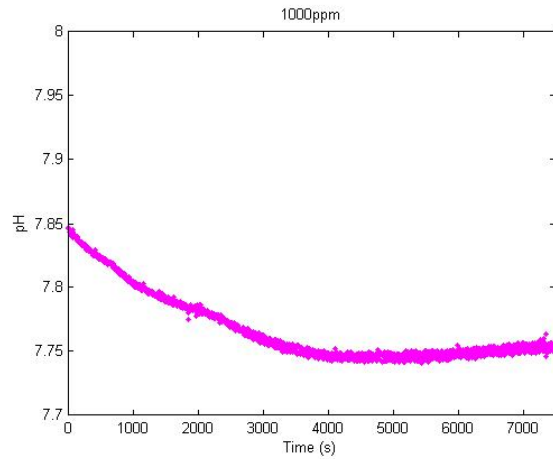


Figure 5: 1000 ppm CO₂. Calibration: default

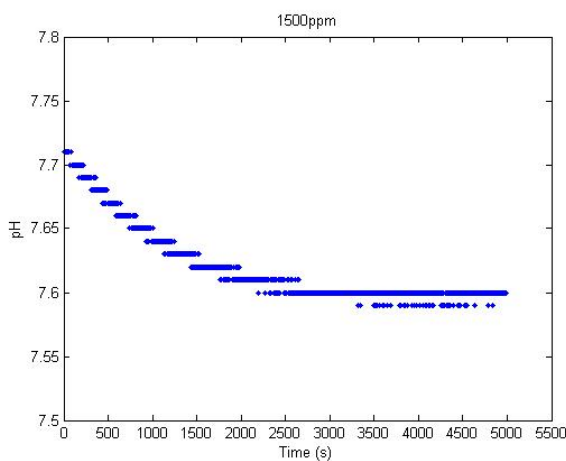


Figure 6: 1500 ppm CO₂. Calibration: default

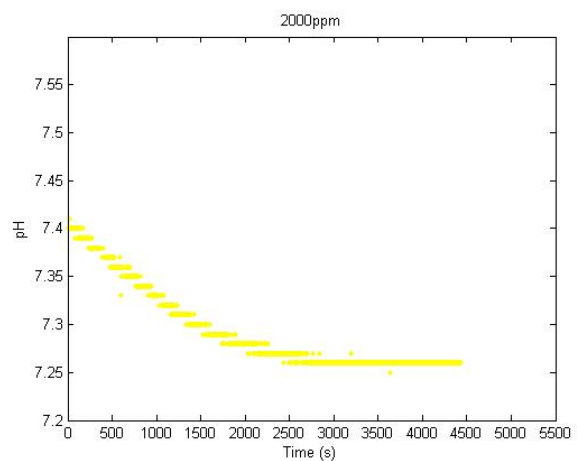


Figure 7: 2000 ppm CO₂. Calibration: equation 22

The pH values of table 2, experiment 1, differ from those in figure 4-7 since the calibration was set to default. The calibration is linear and easily recalculated with the result as shown in table 2.

Table 2: Measurement of ambient CO₂ concentration and pH on Baltic Sea water (experiment 1) and with added river water (experiment 2). Temperature 4°C.

CO ₂ (ppm)	pH
Experiment 1: No river water	
475	7.83
962	7.56
1392	7.41
1971	7.26
Experiment 2: Added river water	
582	7.77
1028	7.60
1430	7.45
1907	7.30

The results of the measurements on Baltic Sea water with and without added river water are shown in figure 8. They both show decreasing pH with higher CO₂ concentrations. They differ in magnitude and non-linearity of the curve.

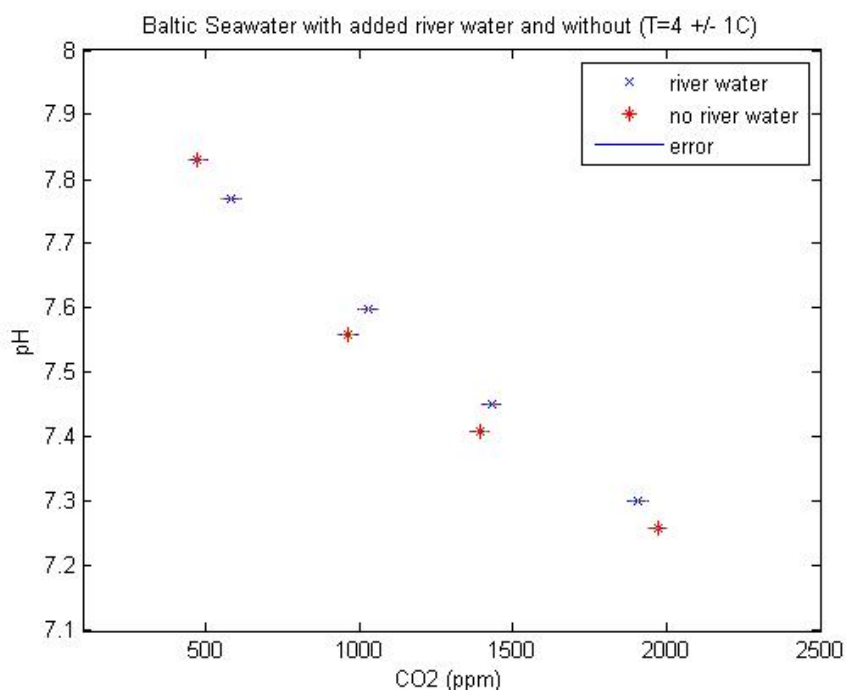


Figure 8: Measurement of Baltic Sea water pH with and without added river water. Error shown is two standard deviations (CO₂ only).

The results show that without added river water the response of increasing atmospheric CO₂ concentration to 1000 ppm of Baltic Sea water is a decrease in pH close to pH 7.5. The decrease in pH represents an increase of H⁺ ion concentration of approximately 300%. Continued increase of CO₂ lowers the pH further but at a slower rate. At 1970 ppm CO₂ the pH is as low as 7.26.

Discussion of the experiment results

The results of experiment 1 show an obviously non-linear relationship between atmospheric partial CO₂ pressure and pH of Baltic Sea water. Measurements on Baltic Sea water shown in figure 8 suggest a lowering of the pH to between 7.5 and 7.6 if atmospheric CO₂ concentrations rise to 1000 ppm. The decrease from pH 8.0 to pH 7.5 represents an increase in acidity and H⁺ ion concentration of more than 300%. The response of the water to CO₂ concentrations close to 2000 ppm is to lower the pH to approximately 7.25. The decrease in pH is slowing down as CO₂ rises but at 2000 ppm the rate of the decrease is still considerable and the concentration of H⁺ ions has then risen with almost 600% from a pH 8.0.

The results of experiment 2, where river water was added to the system, show that the decrease in pH is not as large as for pure Baltic Sea water. The pH is approximately 0.05 units of pH higher for the same CO₂ concentration compared to the experiment on pure Baltic Sea water. The most plausible explanation to the result is that the river water adds to the alkalinity and thereby increases the buffering capacity of the water. This is also supported by measurements on Høje river which show a high alkalinity (Høje Å Vattenråd, 2012).

The experiment indicates that changes in the freshwater inflow to the Baltic Sea can have a significant effect on the pH of the water. The characteristics of Høje river may not be representative of the rivers flowing into the Baltic Sea today. However it does show that changes of riverine input may change the alkalinity of the Baltic Sea. The resulting change in alkalinity from changes in riverine input could therefore have a large effect on the pH of the Baltic Sea.

Errors

The errors related to the measurements are accuracy of the equipment and from errors occurring from reading off the equipment. The accuracy of the equipment is given by the manufacturer and given in the appendix A.

The experiment also suffers from uncertainties where the effect is more difficult to estimate. One suggestion for increasing the quality of the experiment is related to the time allowed for equilibration, approximately 5000 seconds. Figure 5-7 suggest that equilibrium is reached after this time while figure 4 indicates that the equilibrium time may be much longer. In order to carry out this experiment within reasonable time we have assumed that equilibrium has been reached after the time reached in figure 5-7. There may therefore be errors in the results which can be eliminated if the experiment is allowed to have longer equilibration time.

The pH is measured in a single point in a bath of water measuring 30x50 cm. To avoid pH sinking faster in one end of the box a magnetic stirrer was used to create a continuous stirring of the water. There may still be errors in pH measurement from only measuring in one point and other solutions for measuring the pH may increase the accuracy. Stirring the water may also change the equilibrium level of CO₂ since this may cause the CO₂ to out-gas again. Since oceans are seldom in rest and currents of less than 1 and up to a few knots are likely, we believe that a light stirring simulates ocean conditions better than a totally calm water.

The measurements of pH and CO₂ are averages over 10 minutes and during this time the gas-monitor fluctuates by a few ppm. The pH is almost constant and within 0.01 units pH. The sample standard deviation (equation 23) has been calculated for all measurements of CO₂ (table 3).

$$s = \sqrt{\frac{1}{N-1} \sum_i (x_i - \bar{x})^2} \quad (23)$$

Table 3: Standard deviation of the measurements.

Measurement (ppm)	Standard deviation, s
Experiment 1: No river water	
475	2.162
962	2.352
1392	15.98
1971	14.18
Experiment 2: Added river water	
582	6.547
1028	6.061
1430	5.123
1907	4.832

The error related to the accuracy of the instruments is less than 2% in the measured interval for CO₂ and 0.01 unit of pH (table 4).

Table 4: Errors related to accuracy of the equipment.

Unit	Error
CO ₂ (ppm)	±30
pH	±0.01

Two standard deviations where the deviation calculated is the largest should give a good estimate of the error of the CO₂ measurement which is $2s \approx \pm 32\text{ppm}$ and is close to the the error related to the accuracy of the instruments.

5. Modelling ocean acidification

Method

All calculations present in the model are found in appendix B together with an explanation to the physical relations modelled.

To model the ocean pH for different CO₂ scenarios, equations for alkalinity, equilibrium between dissolved ions and CO₂ gas pressure was used. From these equations the H⁺ concentration and pH were derived. The equations found in chapter 3 are the basis for calculating pH in sea water.

The equilibrium constants are well known and can be found in literature (Zeebe and Wolf-Gladrow, 2001). The equilibrium constants are temperature and salinity dependent. Therefore in addition to CO₂, future changes in salinity and temperature as well as alkalinity have an impact on ocean pH and needs to be considered in models. Equations for the equilibrium constants derived from empiric measurements can be found in the book by Zeebe and Wolf-Gladrow (2001). There are several different pH scales and in this model all equilibrium constants used have been measured with the total scale (pH_T).

To address the issue of future alkalinity and salinity levels, varying today's average values by 20% in the model gives a rough idea of the impact from variations in alkalinity.

In modelling the pH of the coming century, the CO₂ scenarios A1FI, A2 and B2 from the IPCC have been used.

Matlab

The model was programmed in Matlab. The equilibrium constants have been calculated from 0°C-25°C. Alkalinity and salinity remain constant in the calculations but may be changed to obtain different scenarios. Equation 24 is then solved for a set range of CO₂ concentrations and the H⁺ ion concentration is obtained. The solution to equation 24 is taken to be the point where the function changes sign. This is then converted to pH which gives a relationship between CO₂ and pH.

$$\Rightarrow [H^+]^4 + (k_B + A_T)[H^+]^3 - (k_B B_T + k_1 H_{CO_2} P_{CO_2} + k_w - k_B A_T)[H^+]^2 - (k_B k_1 H_{CO_2} P_{CO_2} + 2k_1 k_2 H_{CO_2} P_{CO_2} + k_w k_B)[H^+] - 2k_B k_1 k_2 H_{CO_2} P_{CO_2} = 0 \quad (24)$$

The solution to equation 24 is solved numerically to three decimals accuracy. This is done to ensure a minimum accuracy of two decimals throughout the modelling.

Model sensitivity and behaviour

As atmospheric CO₂ concentrations increase, the pH of the ocean decrease. The model has been run for different temperatures, alkalinities and salinities. To best measure the effect of temperature on pH, the model was run keeping salinity constant at 7.5 psu and alkalinity constant at 1550 μmol/kg while varying the temperature from 0 to 20 degrees Celsius (figure 9). The spread of the results illustrates the effect on pH. The lowest pH refers to the coldest temperature. In the Baltic Sea, a temperature change from 0 to 20 degrees Celsius is approximately what can be expected during normal seasonal variations. The natural variation in pH due to temperature changes is approximately 0.1 unit. However the difference in pH from temperature increases with increasing CO₂ concentration and is therefore not constant (table 5). This effect is still relatively small and does not cause dramatic effects on the results but has to be included in projections of future pH.

Table 5: Difference in pH from variations in temperature. Alkalinity 1550 $\mu\text{mol/kg}$, salinity 7.5 psu.

[CO ₂]	250 ppm	1000 ppm	2500 ppm
0°C	8.26	7.58	7.19
20°C	8.31	7.66	7.28
Difference	0.05	0.08	0.09

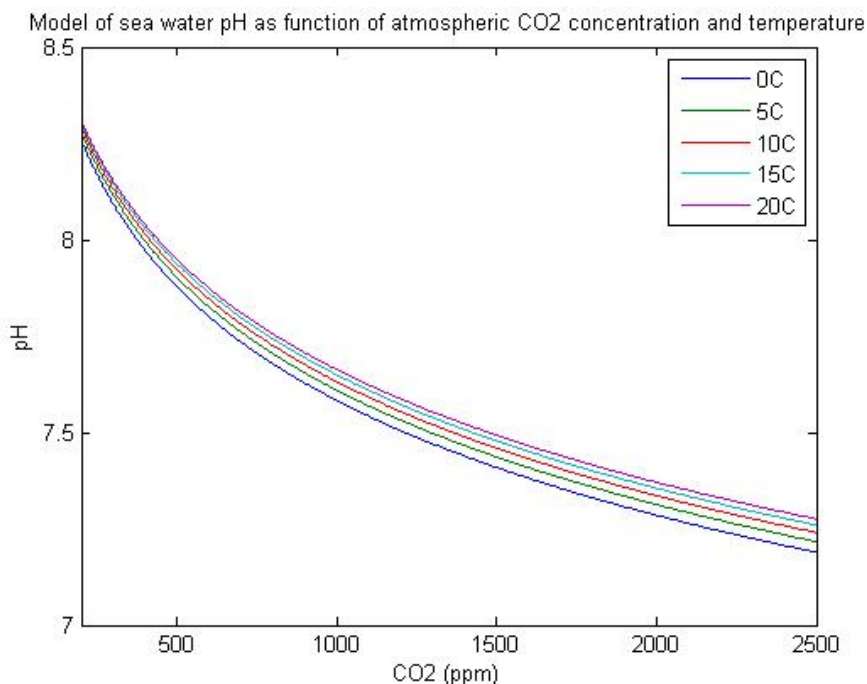


Figure 9: Model of pH dependence on CO₂ and temperature. Alkalinity constant at 1550 $\mu\text{mol/kg}$. Salinity constant at 7.5 psu.

We assume that an increase in dissolved carbon dioxide does not change the alkalinity and as expected the effect on pH from changes in alkalinity is practically independent of CO₂ concentration and temperature.

Changes in alkalinity result in large change in pH (table 6 and figure 10). Varying the alkalinity by 20% from today's average of 1550 $\mu\text{mol/kg}$ changes the pH by almost as much as 0.1 unit. The change in pH from alkalinity may therefore be as large as the seasonal variations due to temperature.

Table 6: Change in pH due to a 20% change in alkalinity. CO₂ concentration 1000 ppm, temperature 4°C.

Alkalinity ($\mu\text{mol/kg}$)	1240	1550	1860
pH	7.51	7.60	7.68

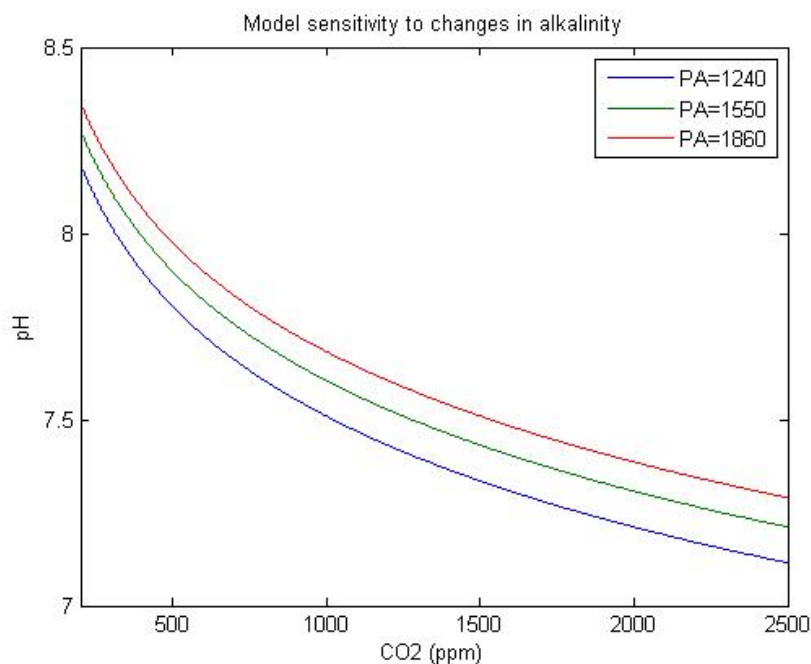


Figure 10: Illustration of the resulting change in pH from a change in alkalinity. PA in $\mu\text{mol/kg}$, salinity 7.5 psu, temperature 4°C .

The effect of varying salinity (figure 11) is smaller than for variations in alkalinity. Varying the salinity from 6.0 psu to 9.0 psu with alkalinity constant at 1550 $\mu\text{mol/kg}$ the difference in pH is only 0.013 units. Relatively small changes in salinity of a few psu are therefore not as important as changes in alkalinity. Should the salinity vary by more than 10 psu, the effect becomes important but it is first when varying the salinity from the Baltic Sea average of 7.5 psu to 30 psu that the change in pH is of the same order as a 20% change in alkalinity (table 7). Such large changes in salinity over a short period of time are not unthinkable since inflowing water from the Kattegatt has a salinity above 20 psu.

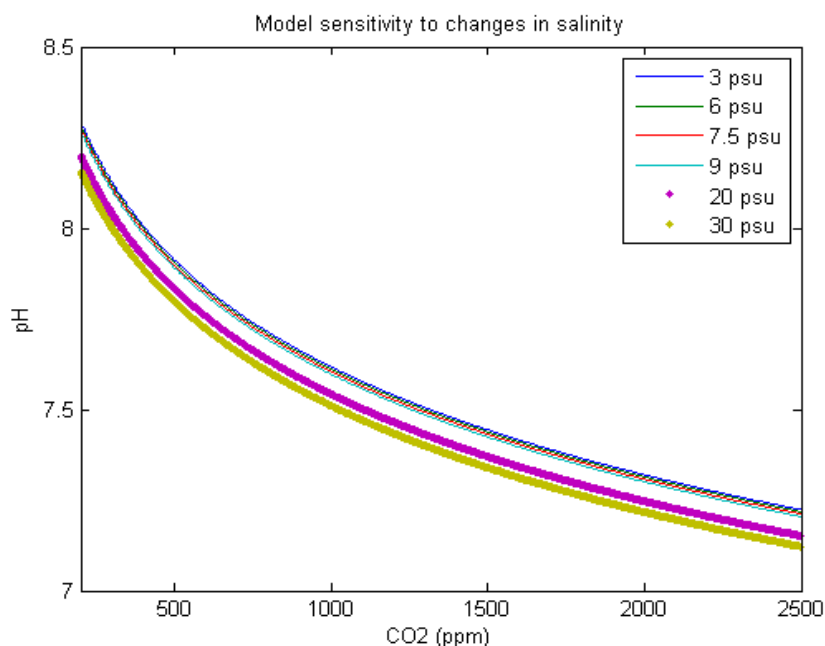


Figure 11: Model sensitivity to changes in salinity. Notice how higher salinity is equivalent with lower pH. Alkalinity 1550 $\mu\text{mol/kg}$, temperature 4°C .

Table 7: Salinity dependence. Modelled pH at CO₂ concentration of 1000 ppm, alkalinity 1550 μmol/kg, temperature 4°C.

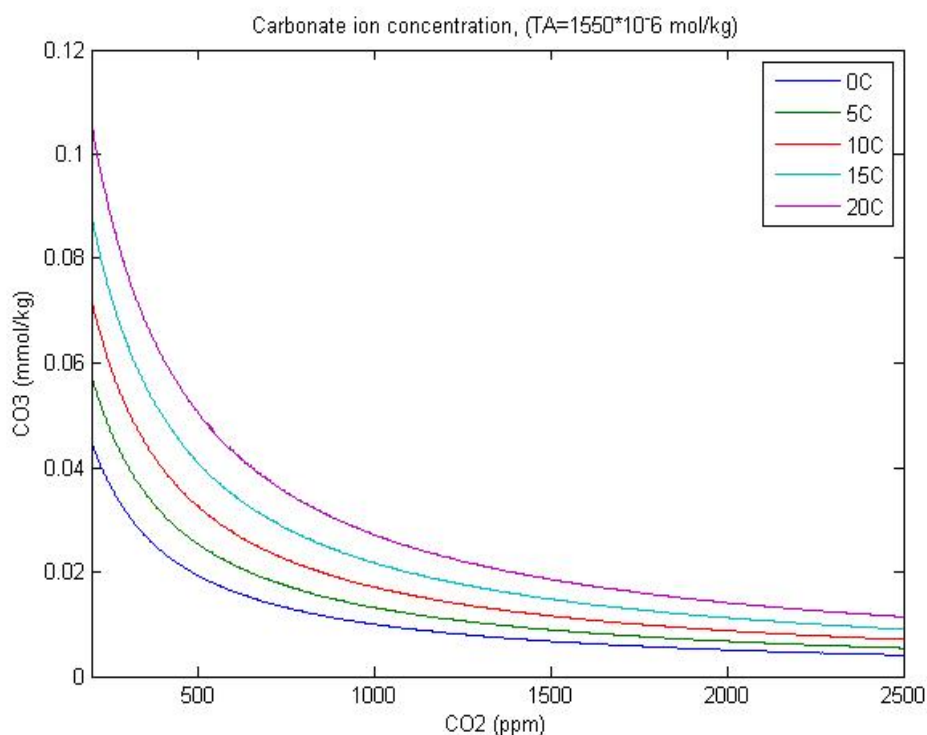
Salinity	3	6	7.5	9	20	30
pH	7.618	7.612	7.605	7.598	7.542	7.510

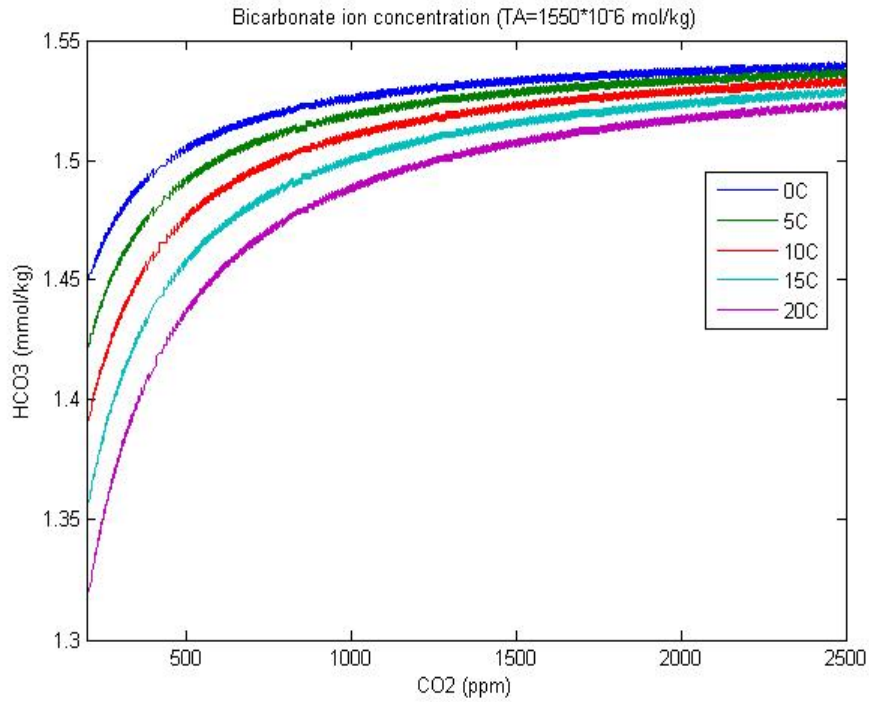
The model shows that the pH of the water is more dependent on alkalinity than salinity and a 20% change in alkalinity results in almost 0.1 pH units while for a 20% change in salinity the result is only a change of 0.01 pH units.

The effect due to temperature is also greater as CO₂ concentrations increase. Therefore seasonal variations of pH will be greater as the CO₂ concentration rises. The uncertainties in future plausible temperature increases will also lead to a greater uncertainty in the projections of future pH.

From the model the concentrations of carbonate and bicarbonate ions may be extracted. As pH decrease the concentration of carbonate ions decreases while the bicarbonate ion concentration increases. The increase in bicarbonate is a result of equation 9 and large changes in CO₂ concentration will have large impact on the respective ion concentrations (figure 12 and 13).

The carbonate ion concentration at a CO₂ concentration of 500 ppm is half of that for a CO₂ concentration of 200 ppm. The temperature dependence is also quite significant as a change in temperature from 0°C to 20°C yields a change in carbonate ion concentration of approximately twice the initial value. However, the effect of temperature (measured in mol/kg) is decreasing as CO₂ levels increases and the carbonate ion concentration is lowered.





Since the saturation state of the different calcium carbonates, aragonite and calcite in seawater is determined by the Ca^{2+} and the CO_3^{2-} concentrations the saturation state of the water may be calculated with respect to the different compounds and CO_2 (figure 14 to 16). The Ca^{2+} concentration was calculated (equation 25) for the Baltic Sea from Dyrssen (1993).

$$[\text{Ca}^{2+}] = (0.330 * S + 0.197) / 1000 \quad (\text{mol/kg}) \quad (25)$$

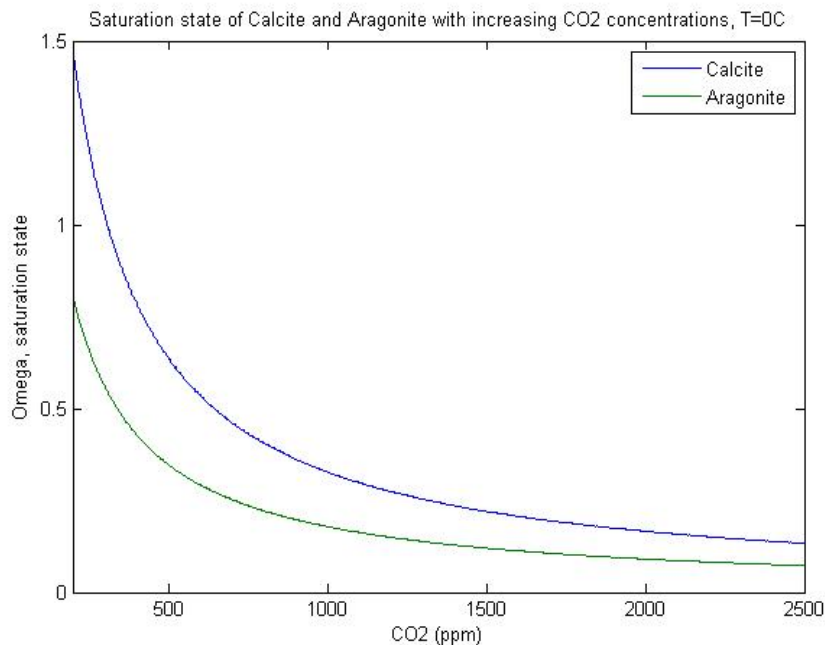


Figure 14: Saturation state of calcite and aragonite. Temperature 0°C and alkalinity 1550 μmol/kg.

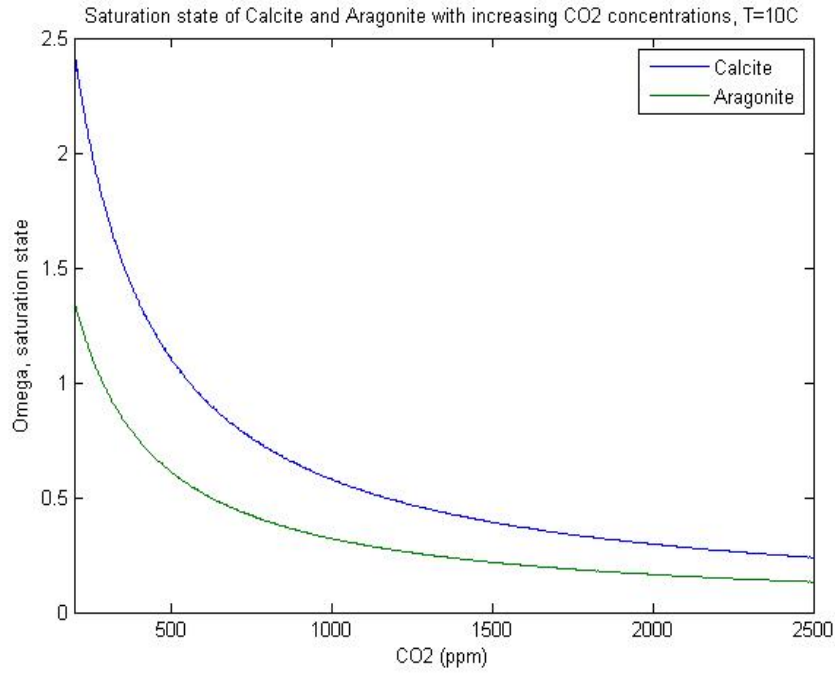


Figure 15: Saturation state of calcite and aragonite. Temperature 10°C and alkalinity 1550 $\mu\text{mol/kg}$.

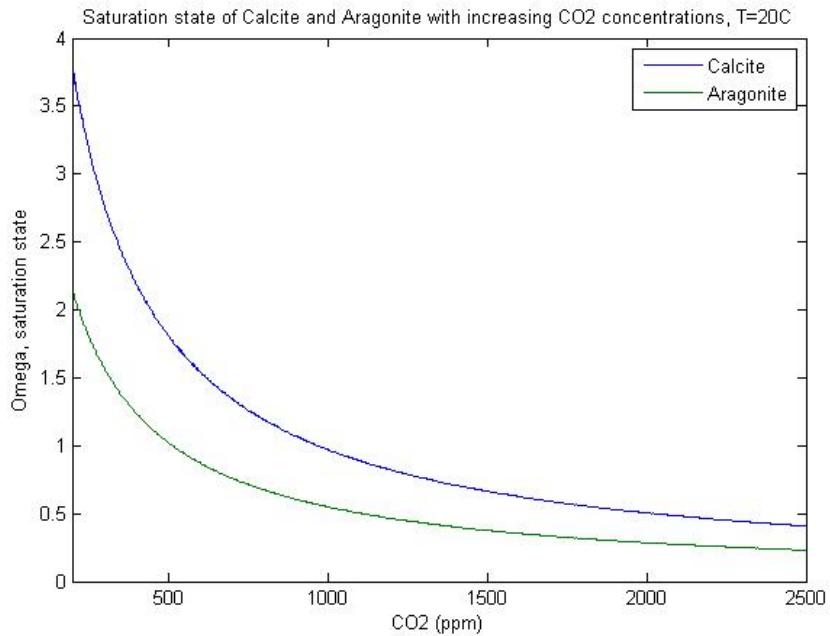


Figure 16: Saturation state of calcite and aragonite. Temperature 20°C and alkalinity 1550 $\mu\text{mol/kg}$.

The temperature has a large influence on the saturation state. For 0°C both the aragonite and the calcite are under saturated at present CO₂ concentrations. When the temperature increases considerably to 20°C the saturation state is supersaturated at present CO₂ concentration. As discussed in both the introduction and theory, super saturated conditions are required for calcifying organisms or else their shells may dissolve. Our results indicate that today, summertime will have super saturated waters of both aragonite and calcite while winter time will have under saturated conditions for aragonite and possibly calcite as well.

Model and measurement comparison

There is a need to try and test the model before modelling projections for pH levels almost 100 years into the future. Therefore this requires that experiments and model calculations show the same behaviour and preferably agree, although there are factors limiting the accuracy of experiments such as changes in buffer capacity, primary production and respiration etc. Comparing the model with the experimental results of chapter 4 reveals a similar relation between CO₂ concentrations and pH (figure 17).

A good fit to the measurements is obtained for an alkalinity of 1400 $\mu\text{mol/kg}$. The salinity of the model is set to 12.16 psu which was measured in the experiment. The model fits the data very well and the results indicate that using practical alkalinity is a good approximation in calculations.

For an alkalinity of 1550 $\mu\text{mol/kg}$, the Baltic proper average alkalinity, the modelled pH is consistently too high. Unfortunately no measurement of alkalinity was made in the experiment. An alkalinity of 1400 $\mu\text{mol/kg}$ is plausible for the water measured on. Should the alkalinity of the water be closer to 1550 $\mu\text{mol/kg}$ then our model is most likely yielding a pH that is too high compared to reality. In this case the model is likely to underestimate the magnitude of the ocean acidification.

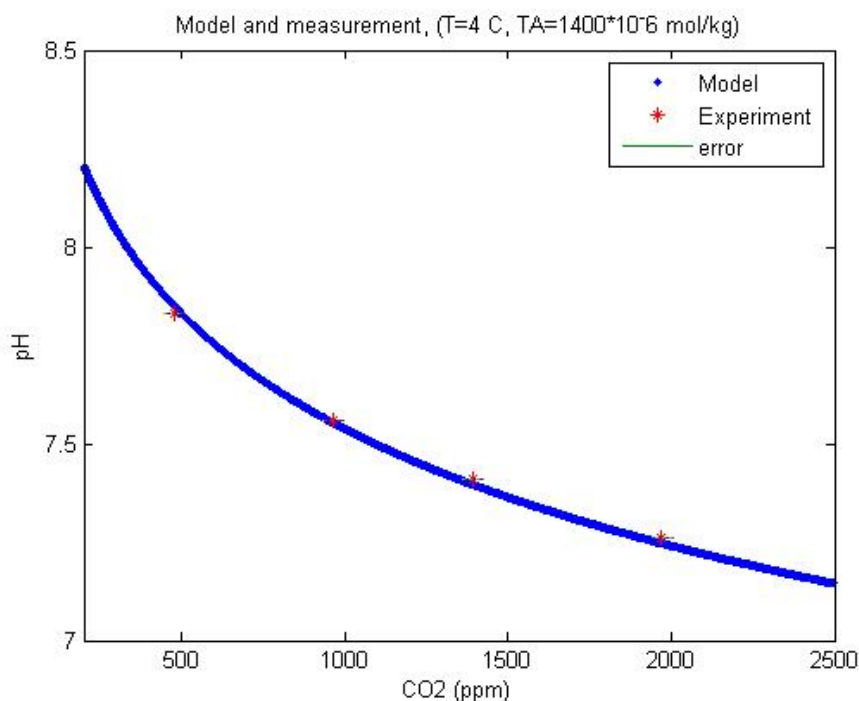


Figure 17: Modelled and experimental pH. Alkalinity 1400 $\mu\text{mol/kg}$. Salinity 12.16 psu.

The model may also be used to fit a curve to the experiment with river water added to the Baltic Sea water (figure 18). When adding river water to the seawater one must remember that the model is based on the assumption that the total alkalinity can be approximated as practical alkalinity. This means that if the river water adds alkalinity in form of other ions than the ones included in the practical alkalinity then the reaction of an increase in CO₂ concentration does not have to be the same. This follows from the fact that the model assumes a constant relationship between the ions and this assumption may not be accurate if other ions also react with the DIC.

The best model fit to the experiment is obtained for an alkalinity of 1550 $\mu\text{mol/kg}$ (figure 18).

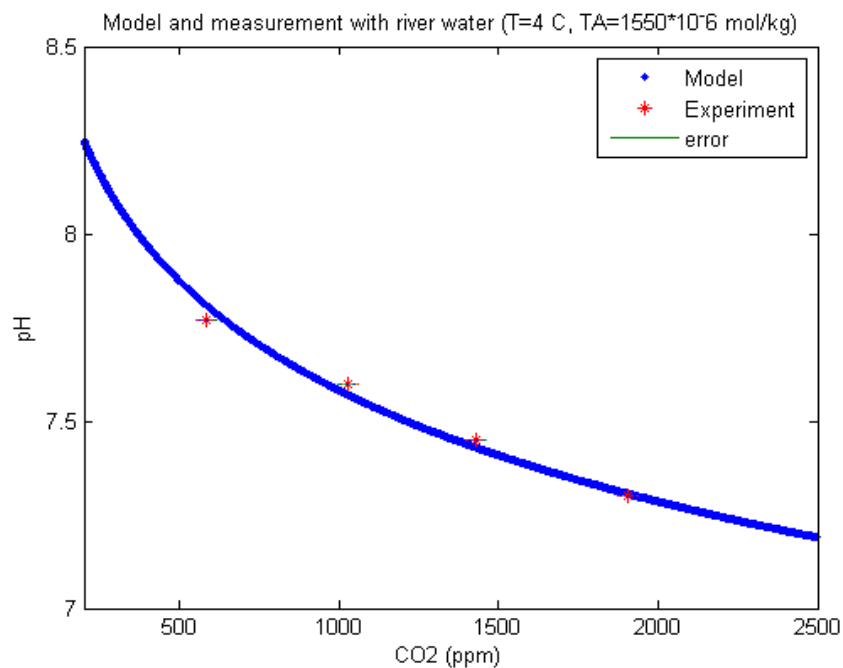


Figure 18: Modelled and experimental pH with river water added to the seawater. Notice how the model indicates an increase in the alkalinity of the water. Alkalinity 1550 $\mu\text{mol/kg}$. Salinity 12 psu.

6. Future projections of ocean acidification

Projected changes in pH

The IPCC reports two different carbon cycle models to calculate the CO₂ projections. The worst case scenario A1FI run by the ISAM model predicts a CO₂ concentration of 970 ppm by the year 2100. The BERN model for the A1FI scenario predicts a concentration of 958 ppm at the end of the century. Since the A1FI scenario run by the ISAM model indicates the highest CO₂ concentration it is an important scenario because it indicates a lower limit of the decrease in pH. If we can withstand the burning of fossil fuels that leads to concentrations as high as projected by the A1FI scenario the pH of the ocean is also likely to not decrease as much as modelled using the A1FI scenario and the impact on ecology will be less severe.

The expected changes in salinity have only minor impacts on the model and the salinity is remained constant at the mean Baltic Sea surface salinity of 7.5 psu.

Figure 19 shows the modelled decrease in pH using the A1FI scenario as CO₂ reference. The alkalinity is constant at 1550 μmol/kg and salinity is constant at 7.5 psu. The temperature dependence is illustrated by the 5 lines at 5°C interval. The seasonal variation is likely to be within this temperature range and is on the order of 0.1 unit of pH.

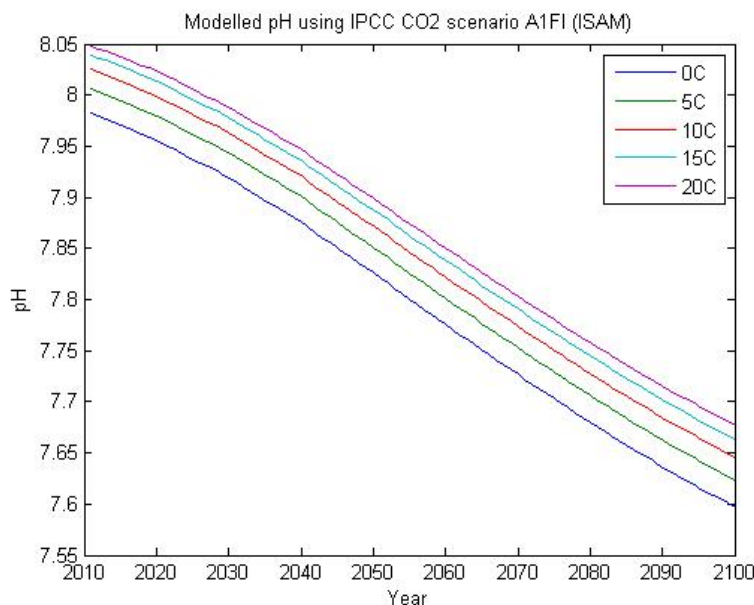


figure 19: Model of future surface pH of the Baltic Sea. CO₂ from the A1FI scenario (ISAM). Alkalinity 1550 μmol/kg. Salinity 7.5 psu.

The model of the A1FI scenario indicates a lowering of the pH from today's pH just above 8 to pH 7.6 at the year 2100. For a given temperature the lowering is therefore almost 0.4 units of pH. The lowest pH can be expected during the winter when temperatures are the lowest.

The emission scenarios A2 and B2 are often used in modelling for example by SMHI. Modelling the future pH for these scenarios are therefore interesting since comparison is made easier.

In the A2 scenario (figure 20) the CO₂ concentration in 2100 is 856 ppm. The model projects a decrease in pH to around 7.70 and as low as 7.65 in the wintertime (alkalinity 1550 μmol/kg).

The B2 scenario (figure 21) features much lower CO₂ emissions and subsequently the reduction in pH is not as large. In the B2 scenario without any change in alkalinity and salinity the pH may decrease to 7.8.

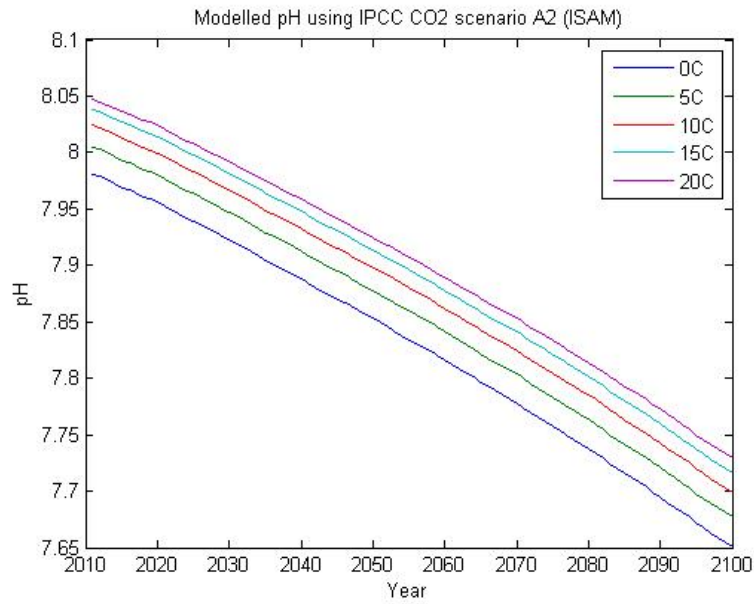


Figure 20: A2 scenario (ISAM). Alkalinity 1550 $\mu\text{mol/kg}$. Salinity 7.5 psu.

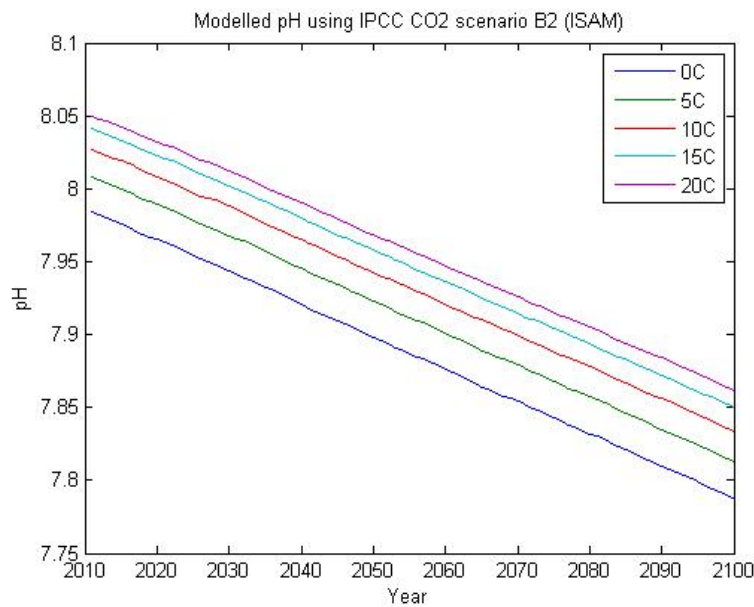


Figure 21: B2 scenario (ISAM). Alkalinity 1550 $\mu\text{mol/kg}$. Salinity 7.5 psu.

The temperature during spring and autumn is near 10°C. With no changes in alkalinity, the model shows that the pH may be as low as 7.65 for the A1FI scenario and 7.83 for the less severe B2 scenario (table 8).

Table 8: Modelled spring and autumn pH. The difference between the scenarios is almost 0.2 units of pH by the year 2100. Temperature 10°C, alkalinity 1550 $\mu\text{mol/kg}$, salinity 7.5 psu.

Year	2011	2020	2030	2040	2050	2060	2070	2080	2090	2100
A1FI	8.03	8.00	7.96	7.92	7.87	7.82	7.77	7.73	7.69	7.65
B2	8.03	8.01	7.99	7.97	7.94	7.92	7.90	7.88	7.86	7.83
A2	8.02	8.00	7.97	7.93	7.90	7.86	7.82	7.79	7.74	7.70

The sensitivity of the model to changes in alkalinity is high. It has been shown that the effect from changes in alkalinity is nearly independent of CO₂ concentration. Therefore we may estimate the effect from changes in alkalinity directly by applying our previous results. With alkalinity 20% lower than today's average, the pH may decrease a further 0.1 units of pH. This means that in the worst case scenario the pH may reach as low as 7.50 by the year 2100. If the alkalinity instead increases by 20% from today the pH in the B2 scenario may not go much lower than 7.9 even during winter temperatures.

The results of our projections suggest that the pH by the year 2100 is likely to range from a pH of 7.6-7.8 in the winter and including changes in alkalinity could be as low as pH 7.5. During summer temperatures the pH will decrease to 7.70-7.85. The results equals a lowering of 0.2-0.5 units pH from today.

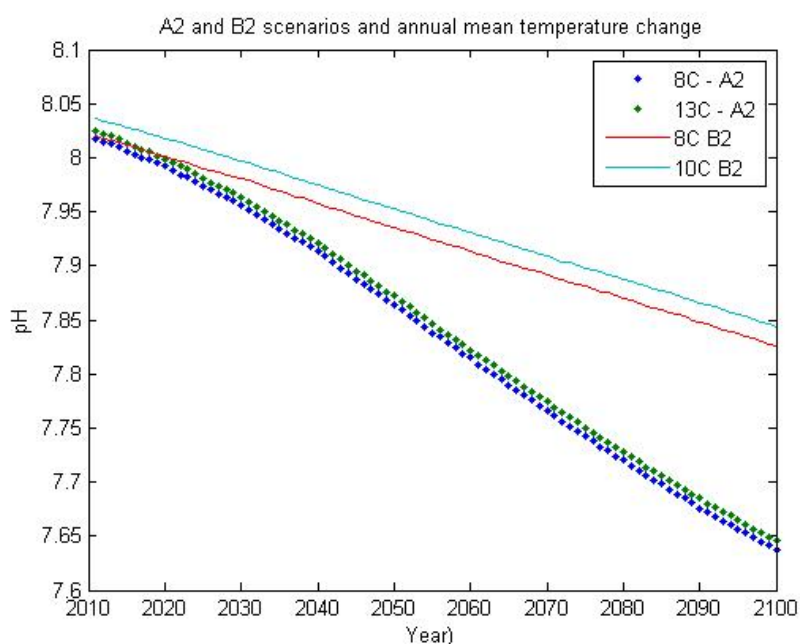


Figure 22: B2 and A2 scenarios, 8°C unchanged annual mean SST. Projected future annual mean SST for A2-13°C and B2-10°C. The upper two are the B2 and the lower two the A2 scenario.

The annual mean sea surface temperature (SST) of the southern Baltic Sea ranges from 7-10°C (SMHI, 2002). Projections for future SST of the Baltic Sea for the A2 and B2 scenarios indicate a warming of between 3-5°C for the A2 scenario and 1-2°C for the B2 scenario (BACC, 2008). The warming results in a slightly higher pH and for the B2 scenario the mean annual pH increases from 7.83 to 7.84 the year 2100. For the A2 scenario the mean annual pH changes from 7.69 to 7.71 if the change in temperature is 5°C (figure 22). These changes are small and in relation to seasonal temperature changes and in relation to uncertainties in future changes in alkalinity very small.

Projected calcite and aragonite saturation states

The projections above lead to sinking pH and a change in the chemistry of the Baltic Sea. This change leads to a change in the saturation state of the calcium carbonates as discussed in the model results. Projections for the saturation state have been made for the same CO₂ and pH scenarios as above. The results are shown in figure 23-25 which show projections for different temperatures meant to visualise the seasonal change. Since the solubility of CaCO₃ increases with pressure and the model has a constant pressure of 1 atmosphere the saturation state shown in figure 23-25 refers strictly to surface waters of the Baltic Sea.

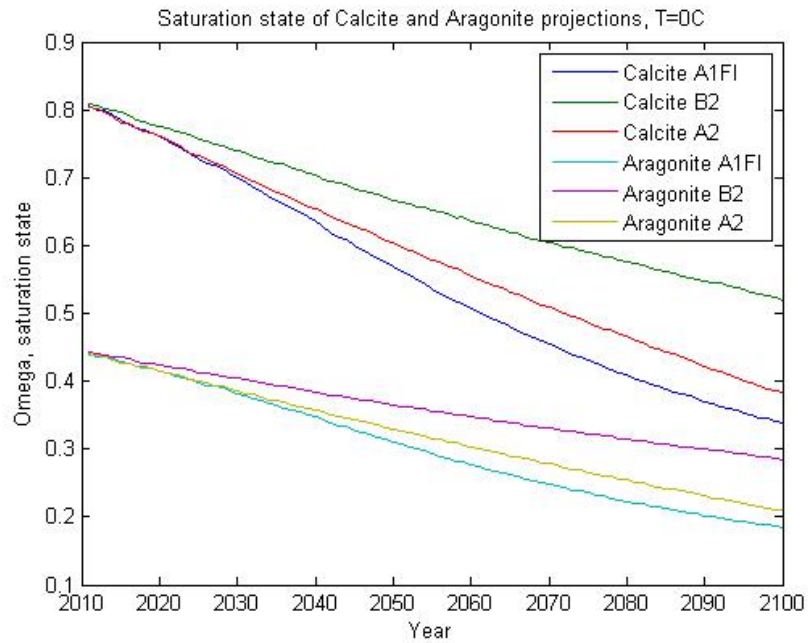


Figure 23: Temperature 0°C. Saturation state of calcite and aragonite modelled using the A1FI, B2 and A2 scenarios. Alkalinity 1550 $\mu\text{mol/kg}$.

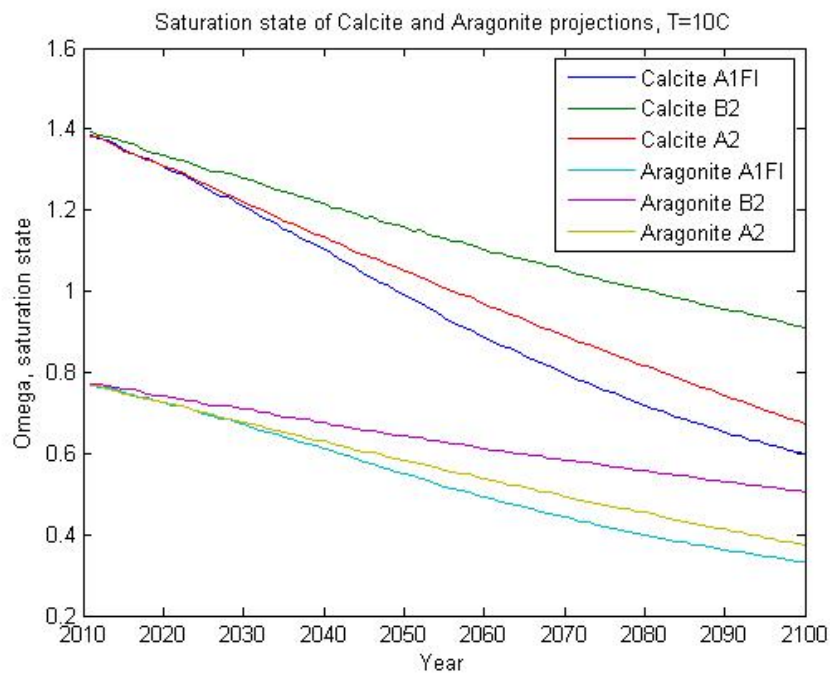


Figure 24: Temperature 10°C. Saturation state of calcite and aragonite modelled using the A1FI, B2 and A2 scenarios. Alkalinity 1550 $\mu\text{mol/kg}$.

Our model projections indicate that already at present day CO_2 concentrations there are wintertime under saturation with respect to both aragonite and calcite. During both spring and autumn the aragonite is with today's CO_2 concentrations also under saturated while projections show that calcite may become under saturated within 30-40 years time around the year 2050.

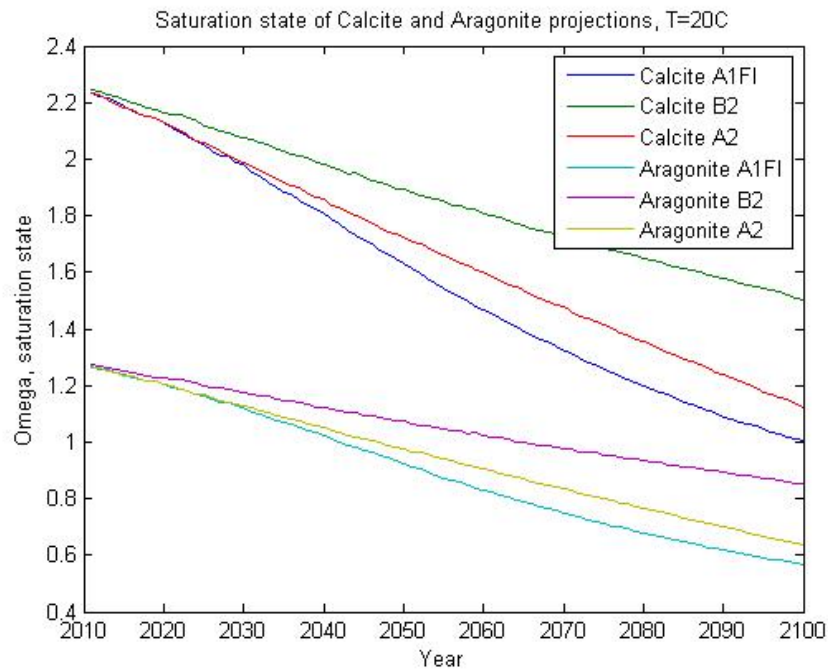


Figure 25: Temperature 20°C. Saturation state of calcite and aragonite modelled using the A1FI, B2 and A2 scenarios. Alkalinity 1550 $\mu\text{mol/kg}$.

During summer both aragonite and calcite are super saturated with present day CO_2 concentrations. With future increases in CO_2 as suggested by the B2 scenario, calcite will stay super saturated for the whole projected time but will be very near a saturation state of 1 by 2100. Aragonite will risk becoming under saturated in the 2070's. For the A1FI and A2 scenarios aragonite may become under saturated already by 2040.

7. Discussion

Modelling

The method used in answering the project aim has both limitations and advantages. The model constructed relies heavily on the accuracy of the approximations done to simplify the equations involved in the processes. However the approximations done are known to be good and therefore turns a very complex dependence into an equation that is manageable and has relatively few variables that it depends on.

Initially an experiment is carried out to be used as a tool when testing the reliability of the model. As has been shown that the model can be used to fit the experiment data and the model lies within the error of the experiment. However some uncertainties still remain about the alkalinity since no measurements of alkalinity were carried out on the experiment water, but the best fit was obtained at an alkalinity of 1400 $\mu\text{mol/kg}$ is a reasonable alkalinity for the water sample. Also presented is the model fit to the experiment data with river water added to the Baltic Sea water. It is clear from the figure that this fit is not as good as for pure Baltic Sea water. This is likely an effect of the approximations used in the modelling and such mixing of river water is therefore not modelled very well.

Our model fits the experimental data well and while it is difficult to set a specific accuracy on the model it is most likely well within 0.1 units pH. The physical aspects of the model are most probably well described but as physical forcing may change the chemistry of the ocean so may

biological activity. This effect makes comparisons between the modelled pH and the experiment uncertain since in this study no means to survey the biological activity during the experiment has been taken.

The equilibrium constants used may not be optimized for brackish water and to determine these to a very good precision also for water with almost no salinity may therefore improve the accuracy of the model. Determining what ions must be included for a good approximation of the alkalinity of the Baltic Sea is also needed because of the large riverine input.

Acknowledging the results and discussion above and given that the ions considered are to a very large extent the ones determining the pH balance of the ocean, the accuracy of our model of the Baltic Sea surface water pH ought to be good. However errors related to uncertainties in future CO₂ concentrations, changes in alkalinity and temperatures of the Baltic region will always yield the projections to be in some sense, inaccurate.

Modelled and measured saturation states

Tyrell et al. (2008b) have measured saturation states for both aragonite and calcite in the central Baltic and present results from March to November (table 9). The saturation state of today's Baltic Sea with respect to calcite is in March (T=2.7°C) close to 1.0 and with respect to aragonite less than 0.6. These results are in line with our modelled saturation states. Our results are for a water temperature of 0°C and since the solubility of calcium carbonate increases with lower temperature our results are also slightly lower than the ones measured by Tyrell et al (2008b).

The measured saturation level in November (T=9.89°C) shows good agreement with the modelled levels with a measured calcite saturation of 1.44 compared to the modelled saturation state of 1.44 at 10°C. For aragonite the measured saturation state of 0.79 is close compared to the modelled saturation state just below 0.80.

The largest difference between modelled and measured saturation states occurs at temperatures around 20°C where the measured saturation states are more than twice that of the modelled levels. But the measurement from June 2001 with water temperatures of 18.9°C also has a measured pH of 8.42 while the model has a pH of 8.04 at the same temperature. This difference in pH will naturally influence the CO₃²⁻ concentration which has as large effect on the saturation state as the concentration of Ca²⁺ and may explain the difference between measured and modelled saturation state. The pH for March and November measurements are close to the modelled pH near a pH 8.

Table 9: Measured saturation states by Tyrell et al (2008b) and modelled saturation states at different temperatures and corresponding pH at a CO₂ concentration of 400ppm.

	November		March		June	
Measured (Tyrell et al., 2008b)	T=9.89°C and pH=8.01		T=2.71°C and pH=7.99		T=18.91 pH=8.42	
	$\Omega_C=1.44$	$\Omega_A=0.79$	$\Omega_C=1.03$	$\Omega_A=0.57$	$\Omega_C=4.94$	$\Omega_A=2.78$
Modelled	T=10°C and pH=8.02		T=0°C and pH=7.97		T=20°C and pH=8.04	
	$\Omega_C=1.44$	$\Omega_A=0.80$	$\Omega_C=0.80$	$\Omega_A=0.43$	$\Omega_C=2.19$	$\Omega_A=1.24$

Comparison to other model projections

There are of today not many reports on future projections for pH of the Baltic Sea. Many reports focus on the oceans and do not include projections for small seas like the Baltic Sea. There are also differences in the CO₂ scenarios chosen to model. This makes a comparison of our results to other projections of future pH limited. However our model itself could be used to project changes in pH of the oceans as well as smaller seas like the Baltic Sea.

Despite limitations to a comparison, comparing our results to other model projections for ocean acidification of the 21st century shows that the decline in pH that is the result of our model is in line with other models. Orr et. Al (2005) models the pH of the surface ocean to decrease by 0.3-0.4 units by the year 2100 in a business as usual CO₂ scenario. The Royal society (2005) concludes in their report on ocean acidification that if humans continue the following trend in CO₂ emission the pH could fall by 0.5 units by the year 2100. The IPCC (2007) states that the different CO₂ emission scenarios projected will lead to a direct lowering of the surface ocean pH ranging from 0.14 to 0.35 units depending on the CO₂ scenario. The IPCC also concludes that the southern ocean surface waters are likely to become under saturated with regard to calcium carbonate for CO₂ concentrations higher than 600 ppm. More recent studies by McNeil and Matear (2008) have shown that the Southern Ocean is likely to become under saturated during winters with respect to aragonite already at CO₂ concentrations of 450 ppm. Other projections for the pH of the Baltic Sea are calculations done by SMHI (2008) which show a decrease in pH to 7.81 in the southern Baltic proper by the year 2100. However these calculations have been done through statistical trends and simple linear regression and are not based on chemical models. The calculated Baltic Sea surface pH by the model presented by Omstedt et al. (2009) projects a pH of 7.6 at wintertime temperatures if CO₂ concentration rise to 970 ppm. This relates to one of most severe climate scenarios by the year 2100, A1FI (IPCC 2007).

Our projections for the Baltic Sea indicates a lowering of the pH ranging from 0.2-0.5 units by the year 2100 depending on which CO₂ scenario is used. This is consistent with the projections from other models but could indicate that our model yields a pH slightly higher compared to other models since the alkalinity of the Baltic Sea is much lower than in the oceans. The projections for future saturation states of calcium carbonate is also similar to the results reported by IPCC and McNeil and Matear. Our model projects a wintertime under saturation of both aragonite and calcite in the Baltic Sea already today. The cold winter temperatures of the Baltic region are most likely the cause of the very low saturation states. For warmer seasons the projections are consistent with other models and predicts under saturated conditions for aragonite within a few decades and for calcite within 50 years time.

8. Summary and conclusions

The most important conclusions obtained from our model results are stated below. Important observations regarding the model behaviour and ideas for improving the model are also listed.

- The decrease in pH of the Baltic Sea surface waters due to the ocean acidification is modelled to be in the range of 0.2-0.5 units of pH during 21st century. This result is comparable to other studies (not necessarily projections for the Baltic Sea) which together set the decrease in pH to be in the range of 0.14-0.5 units of pH within the 21st century.
- The model may be used to fit the data measured in the experiment on Baltic Sea water and lies within two standard deviations. However caution is necessary since uncertainties remain regarding the alkalinity, but the results are plausible.

- If riverine input changes the alkalinity of the Baltic Sea this may lead to large changes in pH. These effects need to be considered in models of Baltic Sea pH and approximating alkalinity with practical alkalinity may therefore be a poor approximation.
- Aragonite risks becoming under saturated throughout the year by the year 2040. Calcite is likely to stay super saturated during summer throughout the 21st century but may become under saturated by the year 2050.
- The projected changes in pH and subsequent changes in the saturation state of calcite and aragonite may lead to extinction of certain species, especially calcifying organisms are vulnerable, and may cause chain effects throughout the food chain (SMHI, 2008).

To summarise our projections for the Baltic Sea pH, the year 2100 will have a Baltic Sea with pH 7.60 in the wintertime for the most severe CO₂ scenario. All scenarios result in a significant decrease in pH and although the temperature increases more in the more severe scenarios this temperature change has only minor effects on the resulting pH.

Large changes in alkalinity could lead to very large changes in pH and a reduction of 20% in alkalinity coupled with high CO₂ emissions could lead to a pH of 7.5 by the year 2100. The change in pH from today may range from a decrease of 0.2-0.5 units if changes in both CO₂ and alkalinity are taken into account.

The saturation state of aragonite remains under saturated throughout winter and autumn/spring in all projections. If enough CO₂ is released as suggested by the A2 and A1FI scenarios then even during summer temperatures under saturation is likely to occur already by year 2040. Any calcifying organism with shells of aragonite are then in these scenarios likely to be largely affected by ocean acidification already within the coming 30 years.

Calcite is likely to stay super saturated during the whole projected time during summers, but may become under saturated during winters in the 2050's.

Our modelled projections suggest that ocean acidification will have a large impact on calcifying species in the Baltic Sea by the 2040's and 2050's if no action is taken to minimize the CO₂ emissions. This threat to certain species may lead to chain effects through the food chain and potentially cause changes to the whole ecosystem (SMHI, 2008). Ocean acidification is therefore an effect of anthropogenic CO₂ emissions that may have large consequences on the ecology of the Baltic Sea.

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11. Appendix A

Most of the equipment used in the Baltic Sea experiment was borrowed from the department of physics and the department of physical geography and ecosystem science at Lund University. Below follows a list of equipment used for the experiment.

Climate chamber

Environmental control room, i.e. climate chamber, which was used to regulate and control the temperature during the experiment.

Water and airtight box

The box used during the experiment was made out of an old aquarium glass tank. The lid was made out of hard plastic. Silicon was spread on the edge around the glass tank to make it air tight. Holes were cut for the hoses to the gas-monitor, cords and for injection of CO₂. Dimensions: 30x30x50 (cm), approximately 50 litres.

pH-meter

A digital pH-meter was attached to a stand in the tank with the sensor placed in the water. The pH-meter was connected to a computer where the measured values were observed and saved. Resolution: 0,005 pH units. Vernier.

Gas-monitor

The carbon dioxide concentration in the tank was measured using a Gaset DX-4030 gas-monitor. The gas was lead through hose into the gas-monitor where the concentration was measured and then lead back into the tank. The gas-monitor was connected to a computer where all the data were observed and saved. The software used to study the result was the Calcmeter 4030 Analysis Software PRO. Deviation: <2% of measuring range.

Digital thermometer

A digital thermometer was attached to a stand and placed in the tank to measure the water temperature. A second digital thermometer was placed outside the tank in the climate chamber to measure the surrounding air temperature. The thermometers were connected to a computer where the data was observed and saved. Accuracy: ±0,2°C. Vernier.

Air pump

An aquarium air pump to bubble the CO₂ into the water. The air pump was attached on to a stand and placed in the tank. Two hoses were connected to the pump and placed in the water. Capacity: 200 litres/min.

Magnetic stirrer

An magnetic stirrer was used to mix the water in the tank.

Conductivity-meter

A conductivity-meter was used to measure the salinity of the Baltic Sea water. Accuracy: ±1% of full-scale reading to each range. Vernier.

12. Appendix B

Calculations

To calculate the pH, the practical alkalinity (PA) includes all relevant bases (ions) for the conditions in the Baltic sea. Therefore PA is used to derive the equation that describes how the concentration of hydrogen ions depends on the atmospheric carbon dioxide, water temperature and salinity. Using the equilibrium constants for dissolved carbon dioxide and ion equilibrium equations, variations in pH from atmospheric changes in CO_2 concentration can be modelled and studied. The change in alkalinity as a result of the dissolution of CO_2 is negligible and can therefore be treated as a constant only related to the properties of the water.

Practical alkalinity is defined in equation (A1) and rearranging yields equation (A2) and the concentration of H^+ ions.

$$PA = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] - [H^+] \quad (A1)$$

$$\Rightarrow [H^+] = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] - PA \quad (A2)$$

The only equations needed to consider are therefore those that describe the relationship between these ion concentrations. The equilibrium constants H_{CO_2} , k_1 , k_2 , k_B and k_w describe the ion concentration distributions in the equilibrium relations. Equation (A3) to equation (A7) show the considered reactions and their equilibrium relations.

$$CO_2^* = H_{CO_2} P_{CO_2} \quad H_{CO_2} = \frac{[CO_2^*]}{P_{CO_2}} \quad (A3)$$

$$CO_2^* \Leftrightarrow H^+ + HCO_3^- \quad k_1 = \frac{[H^+][HCO_3^-]}{[CO_2^*]} \quad (A4)$$

$$HCO_3^- \Leftrightarrow H^+ + CO_3^{2-} \quad k_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \quad (A5)$$

$$B(OH)_3 + H_2O \Leftrightarrow H^+ + B(OH)_4^- \quad k_B = \frac{[H^+][B(OH)_4^-]}{[B(OH)_3]} \quad (A6)$$

$$H_2O \Leftrightarrow H^+ + OH^- \quad k_w = [H^+][OH^-] \quad (A7)$$

Equation (A8), which is the Henry's law for carbon dioxide, is substituted into equation (A9) and rearranged.

$$[CO_2^*] = H_{CO_2} P_{CO_2} \quad (A8)$$

$$k_1 = \frac{[H^+][HCO_3^-]}{H_{CO_2} P_{CO_2}} \Rightarrow [HCO_3^-] = \frac{k_1 H_{CO_2} P_{CO_2}}{[H^+]} \quad (A9)$$

Equation (A8) above yields the bicarbonate concentration which is then substituted into equation (A9) and rearranged.

$$k_2 = \frac{[\text{H}^+]^2 [\text{CO}_3^{2-}]}{k_1 H_{\text{CO}_2} P_{\text{CO}_2}} \Rightarrow [\text{CO}_3^{2-}] = \frac{k_1 k_2 H_{\text{CO}_2} P_{\text{CO}_2}}{[\text{H}^+]^2} \quad (\text{A10})$$

Equation (A9) and (A10) now describe the concentration of bicarbonate and carbonate ions respectively which only depend on the concentration of hydrogen ions, partial pressure and the equilibrium constants.

The total concentration of boron B_T is the sum of tetrahydroxy borate, B(OH)_4^- and hydrogen borate, B(OH)_3 .

$$B_T = [\text{B(OH)}_4^-] + [\text{B(OH)}_3] \Rightarrow [\text{B(OH)}_4^-] = B_T - [\text{B(OH)}_3] \quad (\text{A11})$$

Equation (A11) is substituted into equation (A12), which describes the equilibrium constant for boron k_B , and then rearranged to receive an expression for the hydrogen borate concentration.

$$k_B = \frac{[\text{H}^+](B_T - [\text{B(OH)}_3])}{[\text{B(OH)}_3]} = \frac{[\text{H}^+]B_T}{[\text{B(OH)}_3]} - [\text{H}^+] \Rightarrow [\text{B(OH)}_3] = \frac{B_T[\text{H}^+]}{k_B + [\text{H}^+]} \quad (\text{A12})$$

Equation (A12) is substituted into equation (A11) and rearranged. Finally this yields equation (A13) that describes the concentration of tetrahydroxy borate as a function of hydrogen ion concentration, equilibrium constant k_B and the total concentration of boron.

$$\Rightarrow [\text{B(OH)}_4^-] = \frac{k_B B_T [\text{H}^+]}{[\text{H}^+] k_B + [\text{H}^+]} = \frac{k_B B_T}{k_B + [\text{H}^+]} \quad (\text{A13})$$

An expression for hydroxide ion concentration is obtained by rearrangement of equation (31).

$$k_w = [\text{H}^+][\text{OH}^-] \Rightarrow [\text{OH}^-] = \frac{k_w}{[\text{H}^+]} \quad (\text{A14})$$

Equations (A9), (A10), (A13) and (A14) are substituted into equation (A2). This eliminates all unwanted variables and equation (A14) for the hydrogen ion concentration is obtained.

$$[\text{H}^+] = \frac{k_1 H_{\text{CO}_2} P_{\text{CO}_2}}{[\text{H}^+]} + \frac{2k_1 k_2 H_{\text{CO}_2} P_{\text{CO}_2}}{[\text{H}^+]^2} + \frac{k_B B_T}{k_B + [\text{H}^+]} + \frac{k_w}{[\text{H}^+]} - A_T \quad (\text{A15})$$

The equation is rearranged so no variables remain in the denominators.

$$\Rightarrow [\text{H}^+]^2 + k_B [\text{H}^+] = (k_B + [\text{H}^+]) \left(\frac{k_1 H_{\text{CO}_2} P_{\text{CO}_2}}{[\text{H}^+]} + \frac{2k_1 k_2 H_{\text{CO}_2} P_{\text{CO}_2}}{[\text{H}^+]^2} + \frac{k_B B_T}{k_B + [\text{H}^+]} + \frac{k_w}{[\text{H}^+]} - A_T \right) \quad (\text{A16})$$

$$\begin{aligned} \Rightarrow [\text{H}^+]^4 + k_B [\text{H}^+]^3 &= [\text{H}^+]^2 (k_B + [\text{H}^+]) \frac{k_1 H_{\text{CO}_2} P_{\text{CO}_2}}{[\text{H}^+]} \\ &+ [\text{H}^+]^2 (k_B + [\text{H}^+]) \frac{2k_1 k_2 H_{\text{CO}_2} P_{\text{CO}_2}}{[\text{H}^+]^2} + k_B B_T [\text{H}^+]^2 \\ &+ \frac{k_w [\text{H}^+]^2}{[\text{H}^+]} (k_B + [\text{H}^+]) - [\text{H}^+]^2 A_T (k_B + [\text{H}^+]) \end{aligned} \quad (\text{A17})$$

Finally all parts of the equation is moved to the left side and rearranged. This yield a fourth order equation. The solutions to equation A18 will describe the hydrogen ion concentration as a function of the equilibrium constants, total boron concentration and the carbon dioxide concentration.

$$\Rightarrow [\text{H}^+]^4 + (k_B + A_T)[\text{H}^+]^3 - (k_B B_T + k_1 H_{\text{CO}_2} P_{\text{CO}_2} + k_w - k_B A_T)[\text{H}^+]^2 - (k_B k_1 H_{\text{CO}_2} P_{\text{CO}_2} + 2k_1 k_2 H_{\text{CO}_2} P_{\text{CO}_2} + k_w k_B)[\text{H}^+] - 2k_B k_1 k_2 H_{\text{CO}_2} P_{\text{CO}_2} = 0 \quad (\text{A18})$$

Equilibrium constants

The value of the equilibrium constants depends on temperature (T) and salinity (S). In our model the following equations have been used to calculate the equilibrium constants. These constants have been derived from measurements done in artificial seawater and uses pH_T as scale (Zeebe and Wolf-Gladrow, 2001).

$$\ln H_{\text{CO}_2} = 9345.17/T - 60.2409 + 23.3585 \ln(T/100) + S(0.023517 - 0.00023656T + 0.0047036(T/100)^2) \quad (\text{A19})$$

$$\ln k_1 = 2.83655 - 2307.1266/T - 1.5529413 \ln T - (0.207608410 + 4.0484/T) \sqrt{S} + 0.1130822S - 0.00846934 S^{3/2} + \ln(1 - 0.001005S) \quad (\text{A20})$$

$$\ln k_2 = -9.226508 - 3351.6106/T - 0.2005743 \ln T - (0.106901773 + 23.9722/T) \sqrt{S} + 0.1130822S - 0.00846934 S^{3/2} + \ln(1 - 0.001005S) \quad (\text{A21})$$

$$\ln k_B = (-8966.90 - 2890.53 S^{1/2} - 77.942S + 1.728 S^{3/2} - 0.0996 S^2)/T + 148.0248 + 137.1942 S^{1/2} + 1.62142 S - (24.4344 + 25.085 S^{1/2} + 0.2474S) \ln T + 0.053105 S^{1/2} T \quad (\text{A22})$$

$$\ln k_w = 148.96502 - 13847.26/T - 23.6521 \ln T + (118.67/T - 5.977 + 1.0495 \ln T) S^{1/2} - 0.01615 S \quad (\text{A23})$$