

SCIENCE IN BRIEF: OMAI

ASSESSING ACIDIFICATION



Science in brief: OMAI – Assessing acidification in the Baltic Sea, monitoring and scientific basis

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Emissions.

Photo: catazul, Pixabay.

Summary

In marine and brackish waters, the acidity of the water is mainly controlled by the inorganic carbon system (see Fact Box 1). Anthropogenic CO₂ emissions will – unless reduced – gradually move the Baltic Sea towards a state where acidification becomes harmful for some organisms. The effect is caused by the uptake of CO₂ in the water, but can be further enhanced by other climate effects, such as increased water temperature and a possible freshening of the sea water. This is expected to lead to changes in species composition, both directly (competitive advantages/disadvantages) and indirectly (altered food availability), potentially influencing ecosystem functioning.

Coastal seas, such as the Baltic Sea, are highly influenced by their catchment areas, which means that pH dynamics is generally more complex than in the open ocean. The reason is that pH, in addition to the response to increasing CO₂, is also influenced by changes in hydrology and changes in the supply of carbon and nutrients. High-productive waters typically experience larger seasonal pH variations than low-productive waters, with higher pH peaks in spring/summer and also a more pronounced pH decline in winter. The comparatively weak long-term acidification trend can be masked behind much larger short-term variations. Furthermore, since acidification is a slow process, organisms can to varying degrees adapt to the changes.

Model simulations performed as a part of the OMAI (Operational Marine Acidification Indicator) project indicate that the expected acidification in the Baltic Sea generally follows the same trajectory as the open oceans, with a pH decline of almost 0.4 by year 2100 and a further decline of 0.3 by year 2300 in the worst-case scenario. Due to large regional differences in the area, the annual mean pH in the Bothnian Bay might decline from present-day 7.8 to 7.4 by year 2100, whereas in the Gotland Sea and Southern Kattegat mean pH could decline from present-day 8.1 to 7.7. The degree of eutrophication has a comparatively small effect on the annual mean pH, but on the other hand a considerable impact on the seasonal amplitude and thus minimum and maximum values.

The complex situation in the Baltic Sea gives a strong incentive to improve the temporal and spatial coverage of acidification monitoring. This would broaden the

understanding of current acidification trends and also improve the capacity to predict future changes. An indicator for acidification in the Baltic Sea is currently under development. Monitoring of parameters relevant for acidification, i.e., the inorganic carbon system parameters, would as an added value also provide an additional handle in terms of assessing changes in primary production and eutrophication trends.



A fraction of the anthropogenic CO₂ emissions is absorbed by the oceans, causing ocean acidification.

Photo: Steffen Wachsmuth, Pixabay.

Ocean acidification – the evil twin of global warming

Fossil fuel burning and other industrial processes have caused a rapid increase of the CO₂ level in the atmosphere since the mid-19th century. The concentration now exceeds 400 ppm (Figure 1), which can be compared to an estimated range of 180-280 ppm over the last 800000 years, prior to the onset of industrialization. A fraction of the anthropogenic CO₂ emissions is absorbed by the oceans, leading to a gradual pH decline – ocean acidification.

IPCC has presented several possible scenarios (Representative Concentration Pathways, or RCPs) for the future development, corresponding to e.g. different levels of CO₂ emissions. RCP 2.6, for example, is a scenario where heavily reduced CO₂ emissions result in declining atmospheric CO₂ and increasing surface water pH before the end of this century. RCP 8.5, on the other hand, is a worst-case scenario where the atmospheric CO₂ will not start to level out until the first half of the 23rd century, at a point where the CO₂ level has reached almost 2000 ppm, and surface water pH has on average declined by more than 0.6 units compared to today (Figure 1).

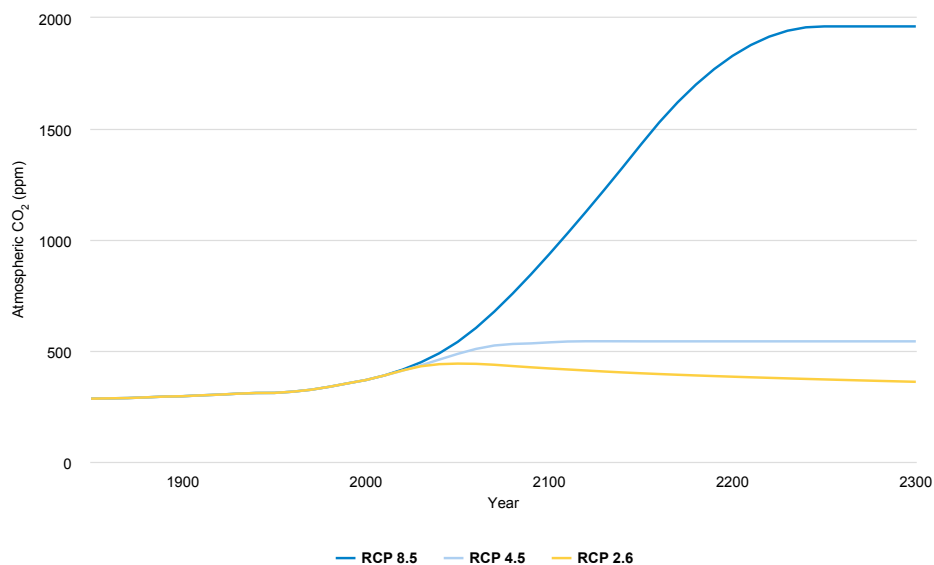


Figure 1 a. Historical and possible future development of annual mean atmospheric CO₂ according to the three IPCC emission scenarios RCP 8.5, RCP 4.5, and RCP 2.6, respectively.

CO₂ data were downloaded from the RCP database (<https://tntcat.iiasa.ac.at/RcpDb/dsd?Action=htmlpage&page=download>)

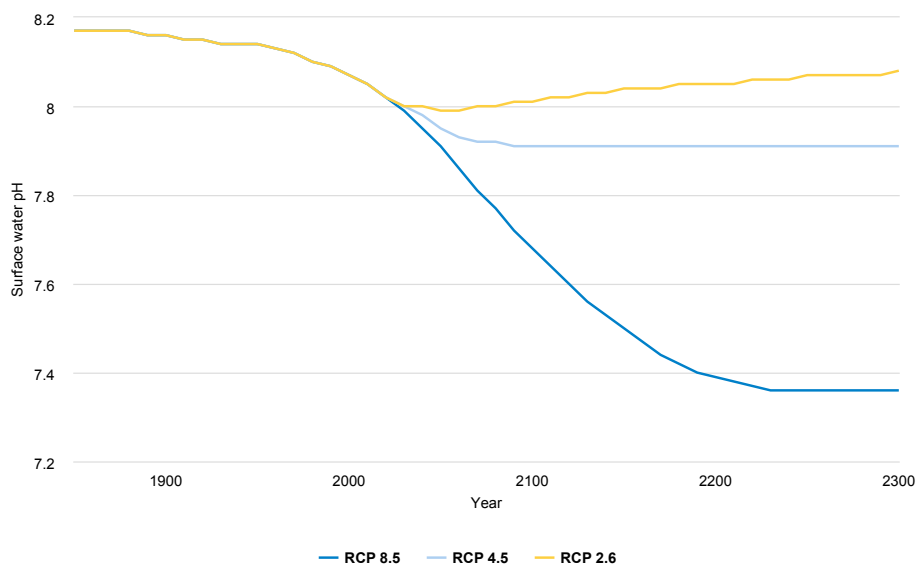


Figure 1 b. Corresponding annual mean pH development in central Baltic Sea surface water – assuming the water is in a steady state.

pH response was computed as part of the OMAI project.

In 2015, the so called Paris Agreement was signed. One goal of this agreement is to reduce greenhouse gas emissions so that global warming can be kept below 2 °C – and preferably below 1.5 °C – compared to preindustrial levels. To realize this goal, even larger emission reductions than in the RCP 2.6 scenario will likely be required.



Acidification can become an additional pressure for organism that already have to cope with other stressors, such as fishery and eutrophication issues.

Photo: Ricardo Resende, Unsplash.

Complex situation in the Baltic Sea

Ocean acidification is predictable in surface water of the open oceans, because pH change is largely controlled by the development of atmospheric CO₂. Coastal areas are on the other hand influenced by inputs of river water, nutrients and carbon from their catchments – changes in supplies can strongly influence pH. The acidification driven by increasing atmospheric CO₂ can be either enhanced or counteracted by processes such as:

1. Changes in precipitation/runoff and thus salinity – a reduced buffer capacity or “CO₂ storage capacity” of fresher water would result in an additional future pH decline.
2. Changes in nutrient supply and thus productivity – the degree of eutrophication and magnitude of plankton blooms influence both the seasonal variability and to a lesser degree annual mean levels of e.g. pH.
3. Changes in inorganic carbon supply and thus total alkalinity/buffer capacity: changes in buffer capacity lead to a gradual shift in the baseline, or in other words alter the typical levels of e.g. pH that naturally occur in a certain water body.
4. Changes in water temperature – warming results in higher dissociation of dissolved inorganic carbon constituents, which produces more protons and decreasing pH.

In the Baltic Sea, pH trends over the last couple of decades have been shown to be heavily site-dependent. Observations indicate that acidification has been partly counteracted in the open Baltic Proper and in the Gulf of Bothnia by increased alkalinity (buffer capacity). Contrasting development has, however, been observed in Danish estuaries as well as in the Laajalahti Bay near Helsinki – at these sites pH has declined faster than what could be explained by increasing atmospheric CO₂ alone.



Blue mussels form biogenic reefs. They are also important both as prey and for human consumption.

Photo: Anna Ventura, Pixabay

Future development of Baltic Sea waters

Model simulations were used to investigate the differences between past, present, and possible future conditions with regards to surface water partial pressure of CO_2 ($p\text{CO}_2$), pH, and calcite saturation level (Ω_{Ca}) in three different Baltic Sea sub-basins (the Southern Kattegat, the Gotland Sea, and the Bothnian Bay, respectively). The following six cases (a–f) were considered:

- a. "Pristine", corresponding to the conditions in the second half of the 19th century, i.e., before the large impact of anthropogenic CO_2 emissions and nutrient supply.
- b. Present-day (early 21st century) conditions in terms of CO_2 level and nutrient supply.

Scenarios c–f indicate possible future conditions towards the end of the 21st century depending on both CO_2 emission scenarios and nutrient load scenarios:

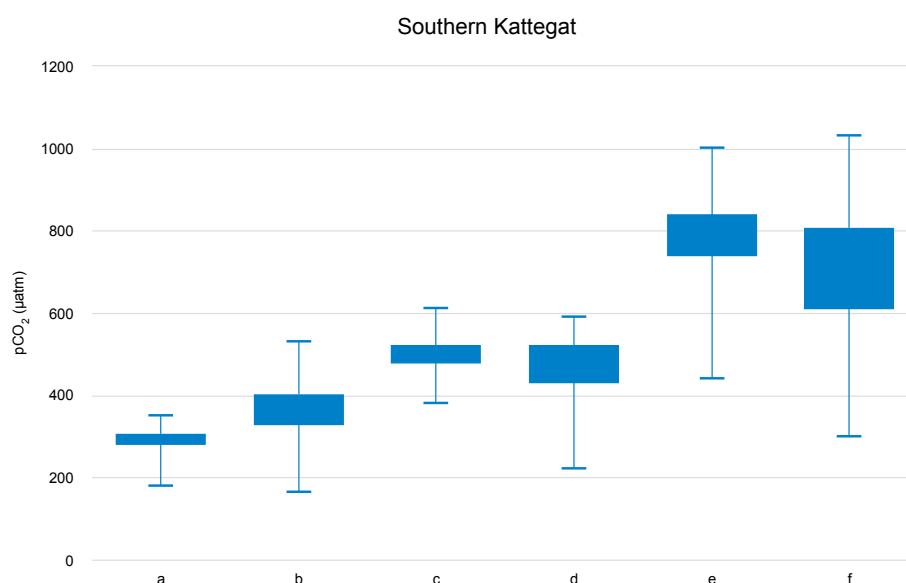
- c. Future scenario with a moderate increase in CO_2 (RCP 4.5), and low nutrient loads resulting in oligotrophic conditions.
- d. Future scenario with a moderate increase in CO_2 (RCP 4.5), and high nutrient loads resulting in eutrophic conditions.
- e. Future scenario with a high increase in CO_2 (RCP 8.5), and low nutrient loads resulting in oligotrophic conditions.
- f. Future scenario with a high increase in CO_2 (RCP 8.5), and high nutrient loads resulting in eutrophic conditions.

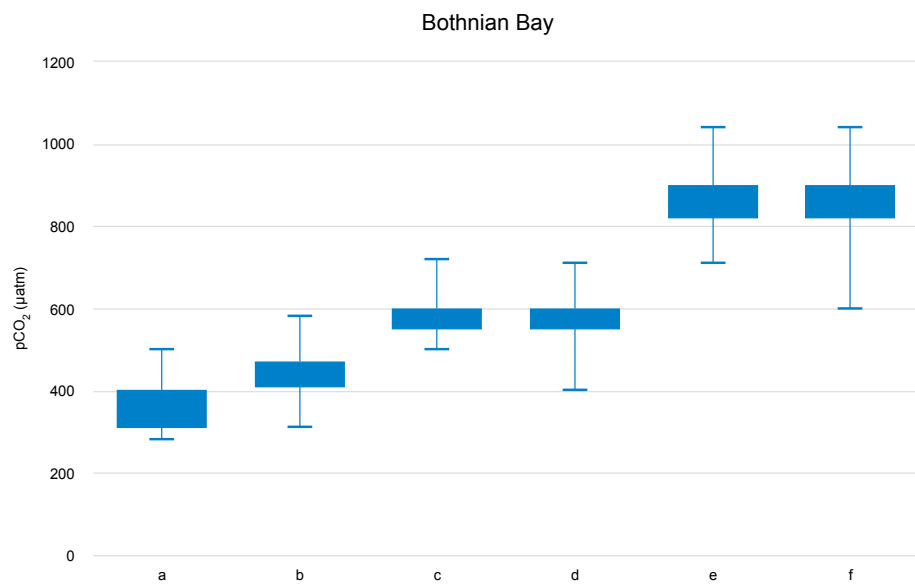
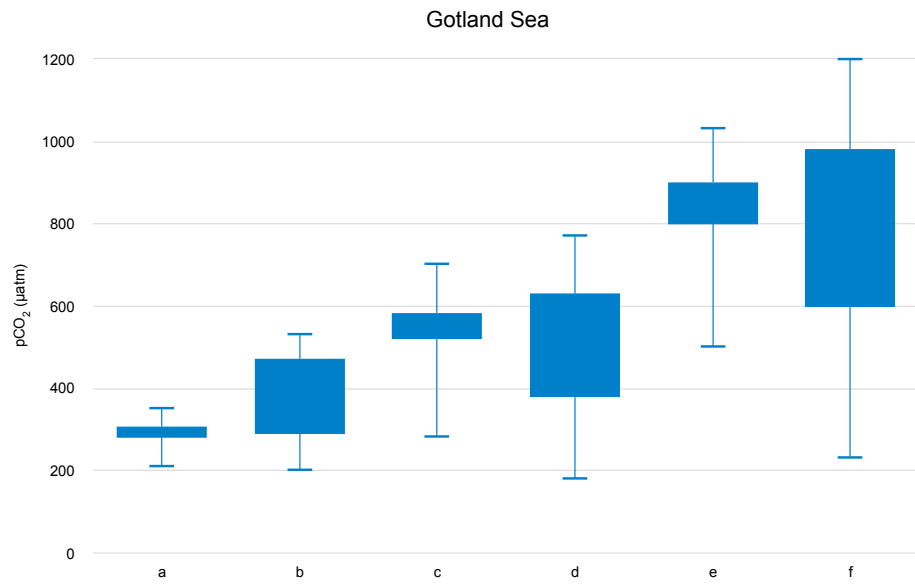
The simulations demonstrate how the rising atmospheric CO₂ level is the main factor that causes changes in the baseline, or typical average values, of e.g. pH (Figure 2). The partial pressure of CO₂ (pCO₂) in surface water tends to follow the atmospheric pCO₂. In a worst-case scenario, pH in Baltic Sea surface waters might decrease by almost 0.4 units compared to present-day conditions before the end of the 21st century. If these scenarios were extended into the 23rd century, pH could decrease by another 0.3 units according to the RCP 8.5 scenario, as shown in Figure 1.

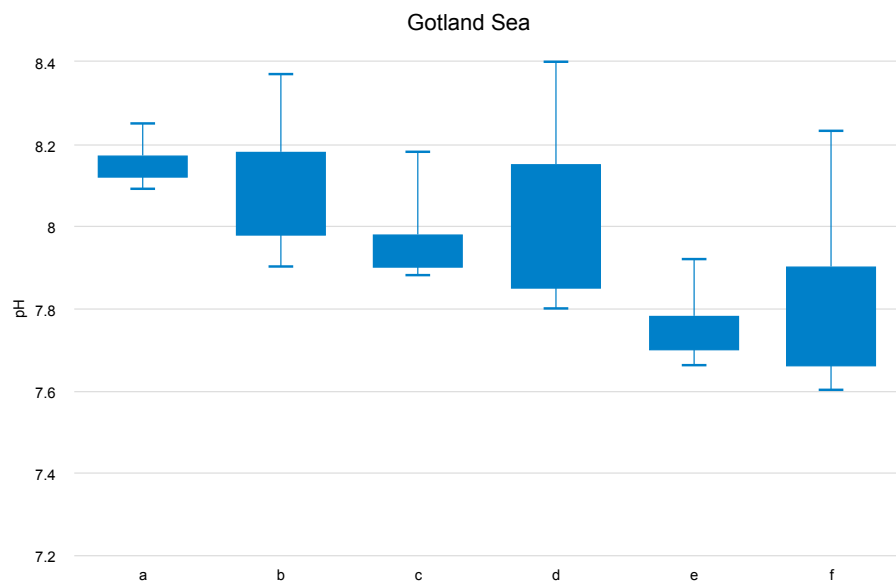
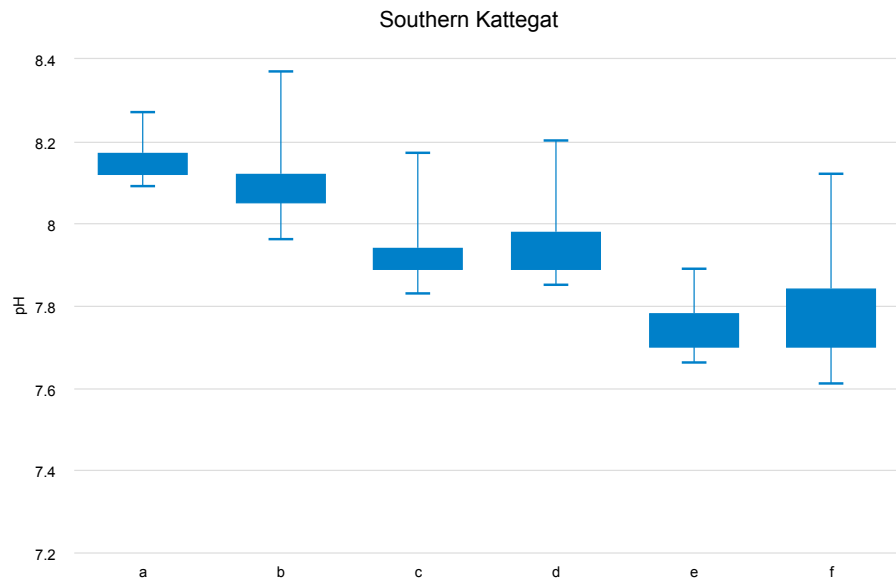
Acidification also influences the saturation state of calcium carbonate minerals such as calcite (Ω_{Ca}). The saturation state is a measure of the tendency for the mineral to either form or dissolve, with values below 1 favoring dissolution and values above 1 favoring production of shells and skeletons. Calcifying organisms, such as mussels and corals, are particularly vulnerable to ocean acidification because of the gradually decreased saturation states of calcium carbonate minerals. In the Baltic Sea there are large regional differences; Bothnian Bay surface waters are naturally undersaturated in calcite saturation level, whereas Kattegat surface waters are oversaturated. Gotland Sea surface waters fluctuate between undersaturation in winter and oversaturation in summer, but with an increasing tendency towards undersaturation in scenarios with high CO₂ emissions (Figure 2).

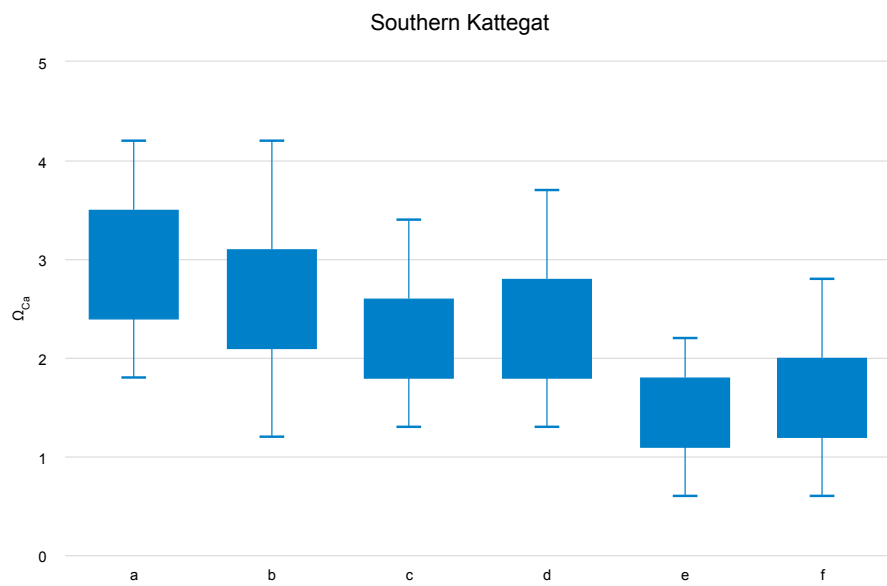
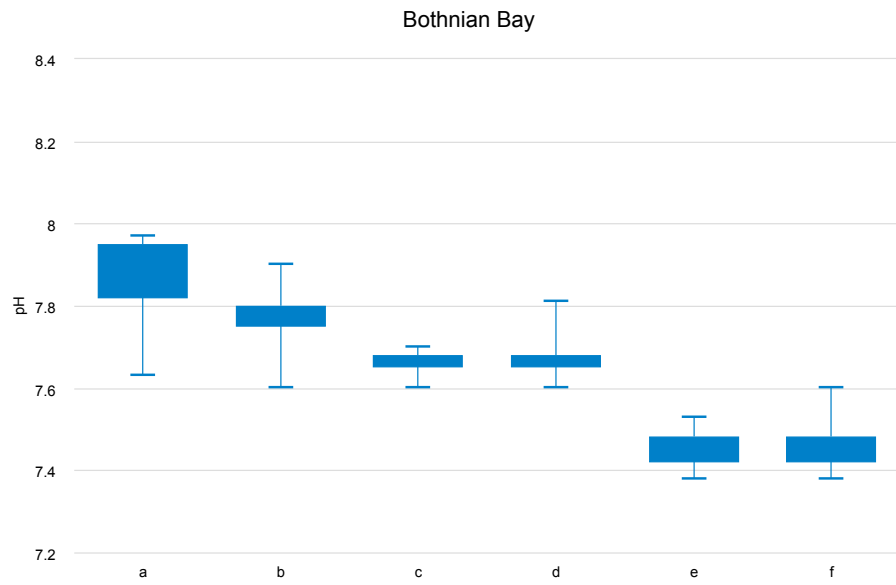
Changes in nutrient loads and thus productivity mainly affect the range of seasonal variations (amplitude), and accordingly also extremes towards "both ends". In the case of a highly eutrophied Baltic Sea, the seasonal variations of pCO₂ and pH are thus more pronounced than in a more oligotrophic case (see Fact Box 2).

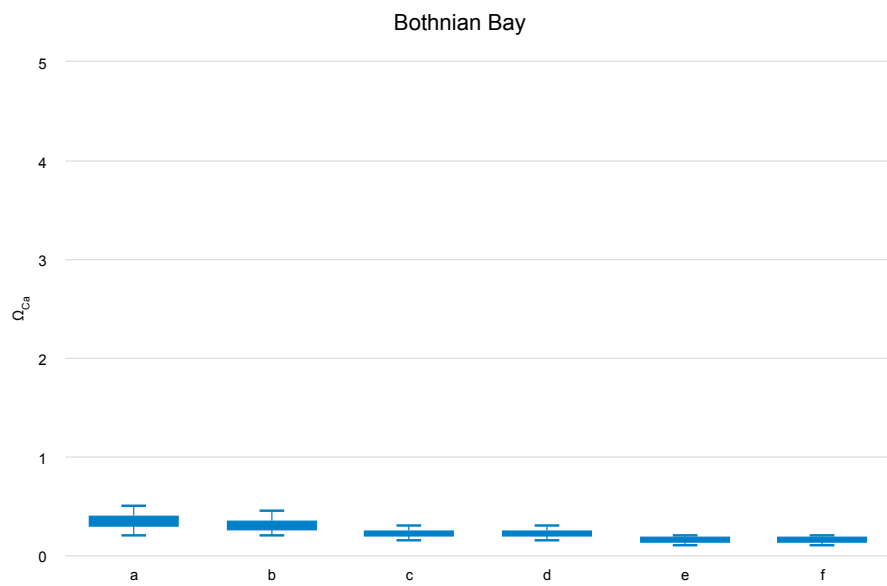
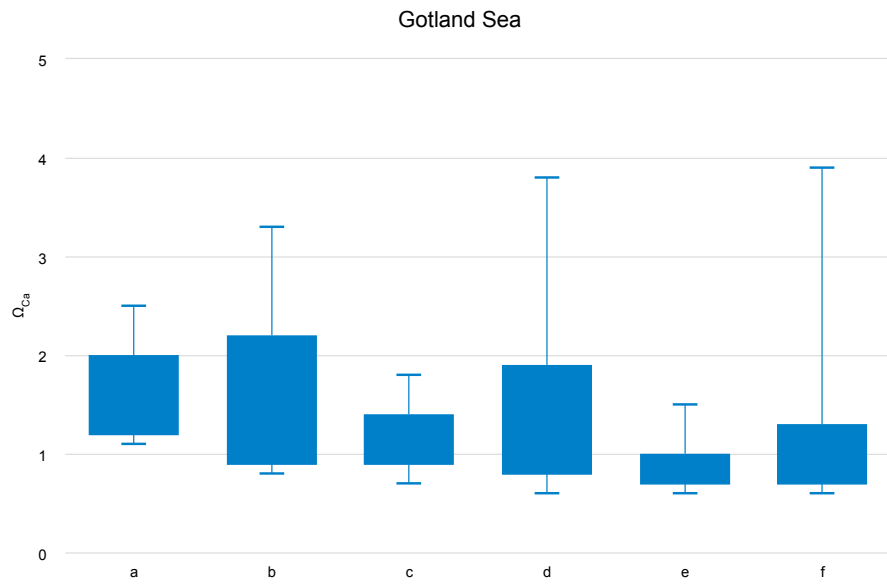
Figure 2. Pristine, contemporary, and potential future pCO₂, pH, and calcite saturation in surface waters of the Southern Kattegat, the Gotland Sea and the Bothnian Bay, respectively. The whiskers indicate the ranges of the datasets (i.e., the span between minimum and maximum values), whereas the boxes represent the interquartile range. For explanations of the different scenarios (a–f), see text. Data from model simulations performed in the OMAI project.

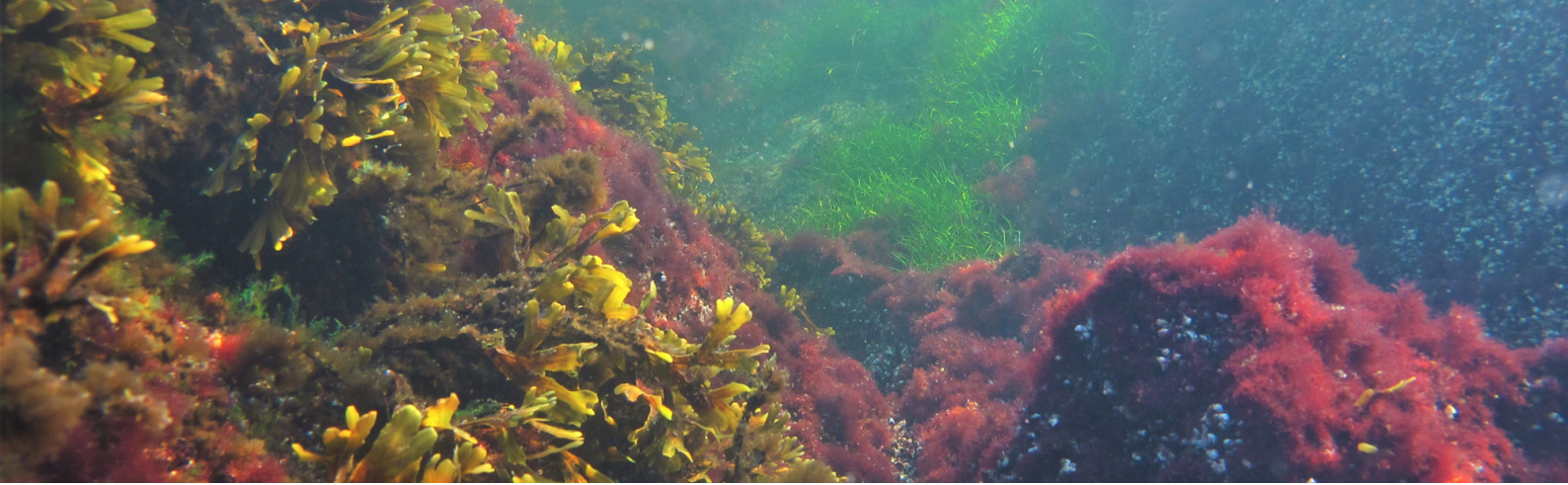












Benthic environment

Photo: Julia Nyström, Metsähallitus

Effects of acidification on marine life

Many marine species are threatened by the ongoing ocean acidification, while other species appear unaffected or might even benefit from the increasing CO_2 in the environment.

Calcifying organisms are particularly threatened by the ocean acidification, but the increasing pCO_2 in the marine environment also affects a range of physiological processes. Such effects are not limited to calcifiers. There are no universal thresholds for acidification parameters that apply to all organisms. Responses can vary significantly between species and communities, and there are still large knowledge gaps in terms of ecological effects of acidification. Primary producers may benefit from the improved carbon uptake energetics, whereas negative effects are most common in macrozoobenthos and potentially fish.

Studies from the Baltic Sea indicate that many of the organisms are not sensitive to moderate-to-large changes in CO_2 level and pH, partly because of the naturally very large seasonal variations, and partly because of the ability to adapt to the slowly developing acidification. However, a gradual shift in pH and the acid-base system over time will both be directly harmful to some organisms (at least in the more pessimistic CO_2 emission scenarios) and favor/disfavor some species more than others, leading to altered communities.

In addition, the effects of acidification are strongly modified by interactions with other drivers, including warming, enhanced stratification, and deoxygenation. This means that acidification can become an additional pressure on top of the other ones. To minimize the impact of acidification, it is for that reason important to alleviate other pressures that organisms have to cope with.



The Sea

Photo: Michal Jarmoluk, Pixabay

Improved monitoring is needed

For historical reasons, acidification in coastal seas is rather poorly studied, although dedicated studies have emerged in recent years. In the Baltic Sea, relevant measurements have been limited to the open sea monitoring stations and a few coastal sites. To improve the understanding of gradually emerging signs of acidification – particularly concerning the potentially contrasting trends between different areas – it is necessary to expand the existing marine monitoring programs with regard to inorganic carbon system parameters, and further to ensure measurements of high quality.

Marine monitoring should include inorganic carbon system parameters for assessing acidification in the Baltic Sea. The technology required for precise measurements of pH and the other inorganic carbon system parameters (i.e., A_T , C_T , and pCO_2 , see Fact Box 1) is in place. To assess acidification, at least two but preferably three of the inorganic carbon system parameters should be measured. Historically, pH and A_T have been measured most regularly. pCO_2 -measurements are nowadays automated in a way that they can be operated continuously on commercial vessels, allowing to trace productivity with a unique spatiotemporal resolution.

Measurements of inorganic carbon system parameters are necessary to monitor acidification in the Baltic Sea. An added value of such measurements is that they can also be used to quantify primary production directly based on CO_2 uptake and release, providing a robust estimate of eutrophication trends and in extension insight into the linkage between primary production and deep water oxygen demand.

Development of an indicator for acidification in the Baltic Sea is currently under the auspice of HELCOM EN Eutrophication.



Blue mussel (*Mytilus edulis*) shell

Photo: JØNAS, Unsplash

Key messages

- Anthropogenic CO₂ emissions will, unless they are reduced, bring about a planetwide acidification of marine ecosystems.
- Ecosystem effects of acidification are currently small in the Baltic Sea, but CO₂ emissions could in a worst-case scenario lead to a pH decline of more than 0.6 units and probably large changes in species composition in the coming two hundred years.
- Coastal seas are influenced by processes in their catchment areas, leading to significant regional differences and also to much larger natural variations than in the open ocean – such processes can either enhance or counteract acidification.
- To assess acidification and to broaden the understanding of drivers of acidification in different areas of the Baltic Sea, it is necessary to improve the temporal and spatial coverage of acidification monitoring.
- In addition to a broadened understanding of current acidification trends and possible future development, monitoring of acidification provides insight into changes in productivity patterns.
- An indicator for acidification in the Baltic Sea is currently under development.

Further reading

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Fact box 1:

The marine inorganic carbon system

The oceans play a central role in the global carbon cycle because of processes in seawater that influence air-sea CO_2 exchange. When gaseous CO_2 dissolves in seawater, it reacts with water and forms carbonic acid (H_2CO_3). The protons (H^+) of the carbonic acid may partly dissociate, changing the concentrations of bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) through chemical equilibrium reactions.

When added CO_2 equilibrates with the large pool of dissolved inorganic carbon (C_T) in seawater (i.e., the sum of aqueous CO_2 , carbonic acid, bicarbonate, and carbonate), the bicarbonate concentration increases while on the other hand pH, carbonate, and also the saturation levels of calcium carbonate minerals (CaCO_3) decrease. Carbonate (mobilized by dissolution of calcium carbonate minerals) can form bicarbonate by reacting with either CO_2 or H^+ – added carbonate thus functions as a buffer by increasing the seawater's capacity to neutralize acids.

The chemical reactions that follow additions of e.g. CO_2 or carbonate continue until new equilibria between the dissolved inorganic carbon species are established (proportions of the different C_T species as a function of pH are indicated in Figure 3). This complex chemical system is often referred to as the marine inorganic carbon system. In marine and brackish waters, the inorganic carbon system exerts the main control on pH.

Analytically, the inorganic carbon system is determined by four measurable parameters;

1. total concentration of dissolved inorganic carbon (C_T), representing the sum of all inorganic carbon forms in seawater,
2. total alkalinity (A_T), defined as the excess of proton acceptors over donors, which is dominated by the carbonate and bicarbonate species, and can be seen as a measure for the buffer capacity of the water
3. partial pressure of carbon dioxide (pCO_2), determines the flux direction of CO_2 at the sea-air interface, and
4. pH, the negative decadic logarithm of the H^+ activity and thus the variable most closely related to the seawater "acidity".

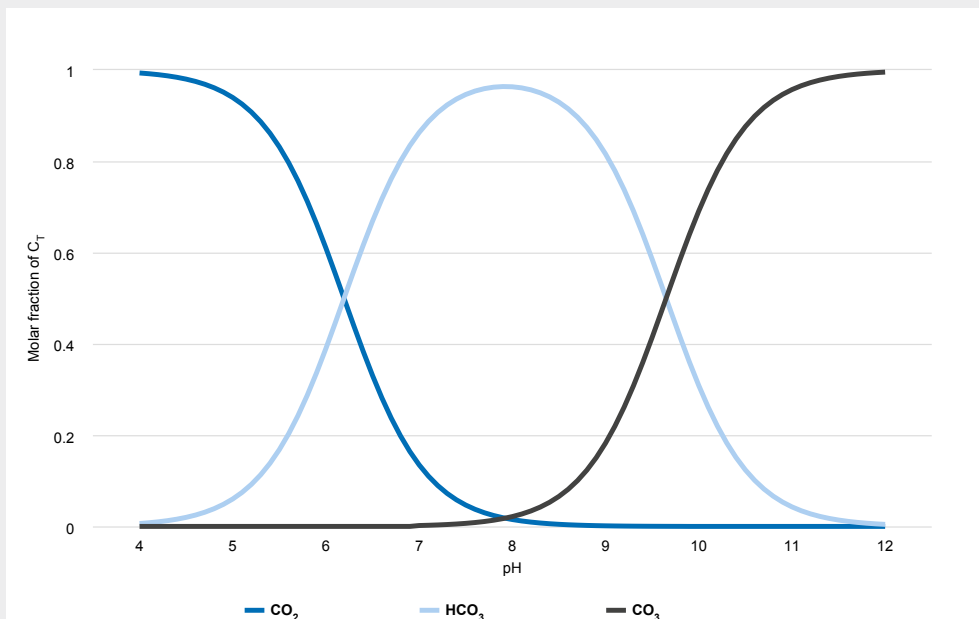


Figure 3. Bjerrum plot showing relative proportions of the different C_T species as function of pH. In surface waters of the Baltic Sea, pH naturally spans a large range, approximately 7.6–8.7. This value depends both on location (lower values in the poorly buffered Bothnian Bay, higher values in the strongly buffered Gulf of Riga) and on time of the season (lower values in winter, higher values in summer; see Fact Box 2).

Fact box 2:

Main drivers of the marine inorganic carbon system

The inorganic carbon system parameters undergo changes on different time-scales. There are processes that mainly affect short-term variations of e.g. pH, including daily and seasonal changes of production/respiration patterns (Figure 4–5), and there are processes that drive long-term changes, resulting in a gradually shifting baseline of pH, or in other words a change of the normal operation space experienced by marine organisms. The main process driving such changes is the uptake of anthropogenic CO₂, but changes in A_T concentration/buffer capacity can also produce long-term pH changes (Figure 6).

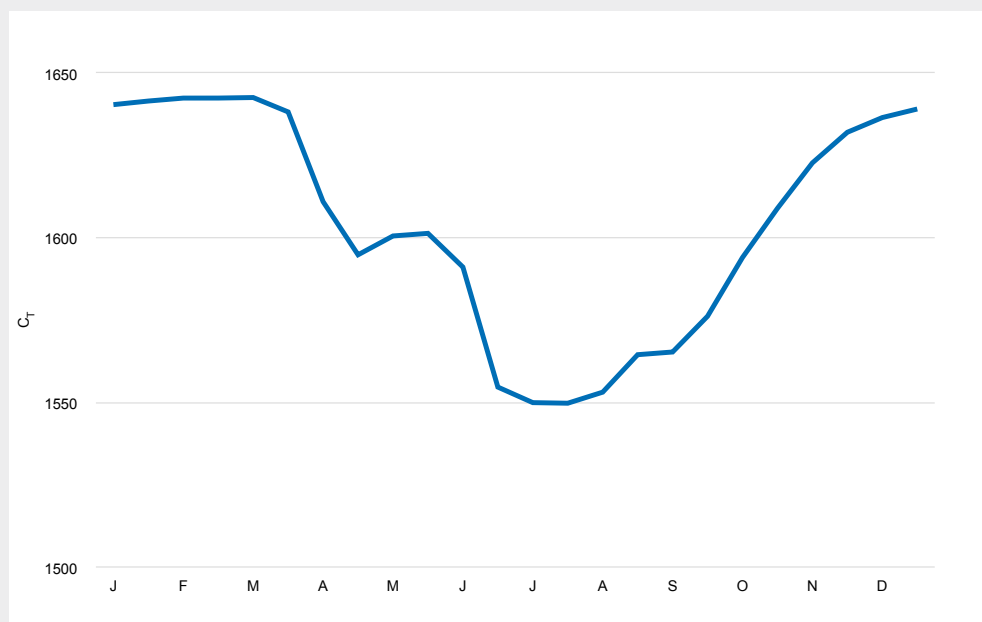


Figure 4 a. CO₂ fixation by primary producers reduce the C_T concentration in surface waters.

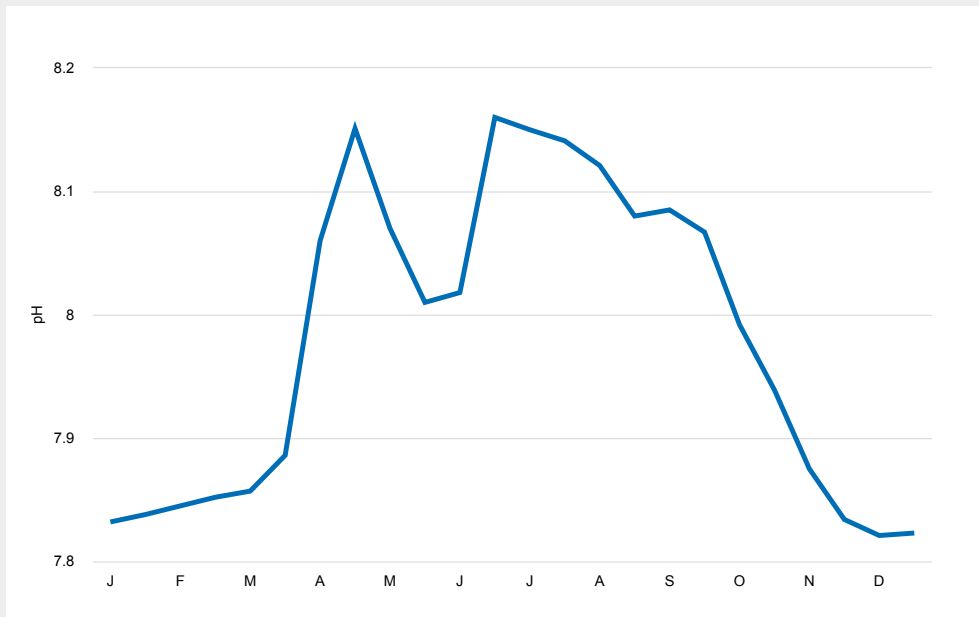


Figure 4 b. CO_2 fixation by primary producers reduce the C_T concentration in surface waters. In the central Baltic Sea, two main periods of C_T drawdown are observed, one during the spring bloom in March, and a second during the mid-summer bloom. C_T increases again as a result of a net CO_2 release to the water in autumn and winter when mineralization dominates over production because of unfavorable light conditions. The C_T drawdowns are mirrored by pH peaks during major plankton blooms, while the net CO_2 release to the water in autumn and winter results in a pH decline. Data from model simulations performed in the OMAI project.

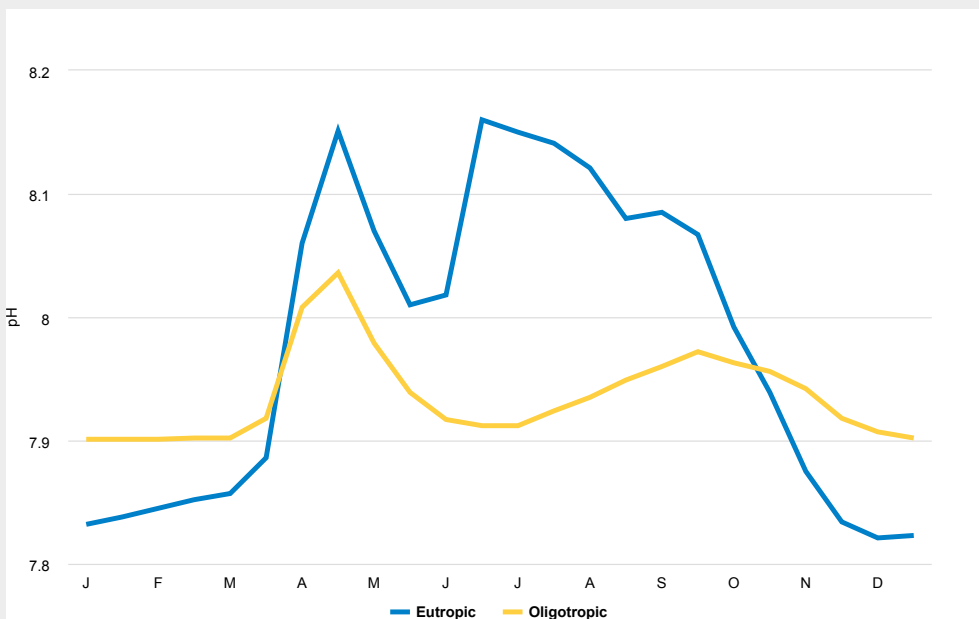


Figure 5. Seasonal pH variations are larger in eutrophic than oligotrophic waters. More CO_2 is fixed for photosynthesis in eutrophic waters during the productive season (increasing pH), and more CO_2 is subsequently released (decreasing pH) when mineralization of the organic matter outpaces production. Oligotrophic waters exhibit considerably smaller pH variations due to smaller imbalances between production and respiration. Data from model simulations performed in the OMAI project.

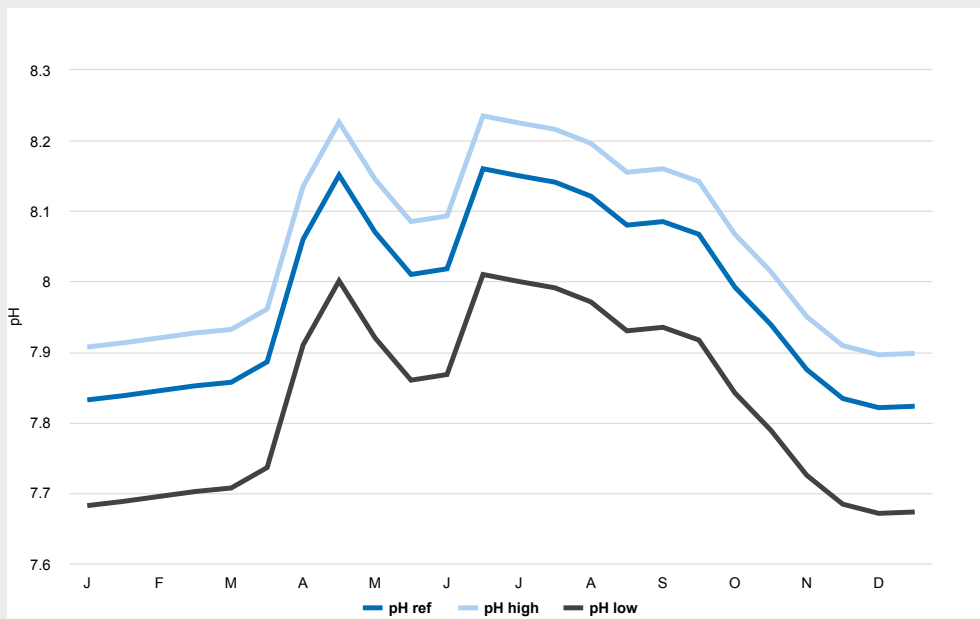


Figure 6. Increasing atmospheric CO_2 drives a shift of the pH baseline – or “natural” state – towards generally lower values. This could result in dramatic changes over the next century unless CO_2 emissions are curbed (see Figure 1). The pH baseline can also be altered from changes in A_T , characterizing the system’s capacity to neutralize acids. If A_T increases, pH will shift towards higher values. In contrast, decreasing A_T enhances acidification induced by CO_2 emissions. Data from model simulations performed in the OMAI project.

About this publication

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