

2200

pH value



Unfavorable prognosis: According to simulations of researchers at the Max Planck Institute in Hamburg, the pH value of the oceanic surface layer will be considerably lower in 2200 than in 1950, visible in the color shift within the area shown in red (left). The oceans are becoming more acidic.

When the Air Turns the Oceans **Sour**

Human society has begun an ominous large-scale experiment, the full consequences of which will not be foreseeable for some time yet. Massive emissions of man-made carbon dioxide are heating up the Earth. But that's not all: the increased concentration of this greenhouse gas in the atmosphere is also acidifying the oceans. **Tatiana Ilyina** and her staff at the **Max Planck Institute for Meteorology** in Hamburg are researching the consequences this could have.

TEXT **TIM SCHRÖDER**

They're called "sea butterflies" because they float in the ocean like a small winged creature. However, pteropods belong to the gastropod class of mollusks. They paddle through the water with shells as small as a baby's fingernail, and strangely transparent skin. Though tiny, they are tremendously important because there are billions of them. Fish – whales, too – swallow them down in vast quantities.

Pteropods are nautical nibbles.

American zoologists simply call them the "potato chips of the sea." But it seems that the supply of pteropods is endangered. Climate change, or more precisely, ocean acidification, may pose serious problems for them in the future.

It is common knowledge today that carbon dioxide emissions

are warming the Earth like a greenhouse. Less well known is the fact that the rising concentration of carbon dioxide in the atmosphere also leads to the oceans slowly becoming more acidic. This is because the oceans absorb a large portion of the carbon dioxide from the atmosphere. Put simply, the gas forms carbonic acid in the water. The more carbon dioxide humans expel into the air, the more CO_2 is dissolved in water, and the more carbonic acid forms. The pH level, which indicates how alkaline or acidic the water is, falls. That becomes a problem for the pteropods and other living creatures because, at lower pH values, they can hardly generate any calcium carbonate for constructing their shells. What consequences this will have for life and the food chain in the sea is still largely unknown.

Today, the pH value of seawater is 8.1, making it, strictly speaking, a weak base rather than an acid. The term acidification applies nevertheless, because the pH value has fallen toward acidic

1950

» By absorbing carbon dioxide from the atmosphere, the sea decreases the greenhouse effect.

by a bit more than 0.1 since the start of the industrial revolution. Although 0.1 doesn't sound like much, the pH value scales logarithmically, so it actually represents an increase in the acidity of water by about 30 percent already.

SEARCHING FOR ANSWERS WITH THE COMPUTER

When water reacts with carbon dioxide, it can be expressed in a simple chemical equation. However, the oceanic pathway of carbon dioxide and the carbon it contains is so complex that researchers haven't yet been able to fully estimate how the oceans will change. How quickly will various re-

gions of the ocean acidify? What effect will high levels of carbon dioxide have on the survival of phytoplankton, the microscopic algae that are the basis for all life in the oceans? Will the uptake of carbon dioxide slow down in the future? All of these questions still need to be answered.

Tatiana Ilyina is attempting to find the answers with the aid of the computer. The oceanographer works at the Max Planck Institute for Meteorology in Hamburg, where simulations of the Earth's climate and calculations of climate change have been carried out for many years. Ilyina's work focuses primarily on the carbon pathway from the atmosphere into the oceans, be-

cause this strongly influences climate change: by absorbing carbon dioxide from the atmosphere, the ocean reduces the greenhouse effect.

Ilyina's specialty is simulating the biogeochemistry of the oceans. This includes the chemical processes that occur in seawater, the seafloor and between substances that marine organisms absorb and release. Carbon is an important biogeochemical component, and carbon dioxide therefore has a major impact on the biogeochemistry. Ilyina has spent a lot of time in the past few years translating biogeochemical processes into mathematical rules and incorporating them into the climate models of her colleagues, espe-



Sea butterflies (*Limacina helicina*) are predatory marine snails and represent a keystone species of plankton. Ocean acidification etches their shells made of calcium carbonate.

cially into the standard ocean chemistry model known as HAMOCC, which has been well established for many years now. The computer simulations have since produced several interesting insights.

Researchers like Tatiana Ilyina always try to simplify reality in their simulations, yet still include the key processes in their models. In the case of biogeochemistry, this is very challenging because carbon has many pathways. Even the transport of the carbon dioxide into the sea is complex, because how much gas dissolves in seawater, among other factors, depends, for instance, on the water temperature. Cold water absorbs more gas than warm water. The Arctic Ocean, as the simulations show, is thus likely to acidify considerably faster over the coming decades than, for example, the subtropical and tropical regions of the oceans.

CARBON DIOXIDE WITH THE WEIGHT OF 500,000 CARS

When carbon dioxide (CO_2) from the air passes into the sea, it reacts with water (H_2O) to form carbonic acid. This, in turn, reacts with the carbonate ions (CO_3^{2-}) naturally contained in water to form bicarbonate (HCO_3^-). Since CO_2 is quickly converted into ions and thus becomes unavailable for the exchange with the air above, the ocean can continually absorb large quantities of CO_2 . The oceans swallow a mass of CO_2 equivalent to the weight of 500,000 automobiles every day. The various ions are in equilibrium and can be transformed into one another when environmental conditions change. The pH value also influences this equilibrium.

Ilyina's simulations showed that acidification shifts the equilibrium toward bicarbonate. For many sea creatures, the accompanying decline in carbonate ions may be fatal, because carbonate is an important component of mollusk and snail shells. If more and more CO_2 enters the oceans, the quantity of carbonate ions could decline so far that calcium carbonate production is impaired. If the amount of carbonate falls further still, shells made of calcium carbonate may even dissolve.

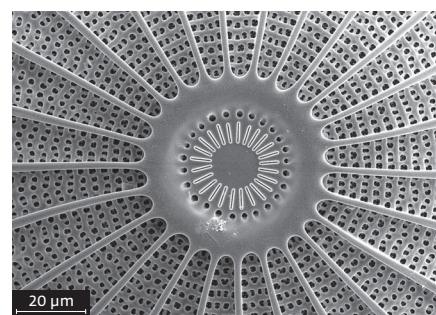
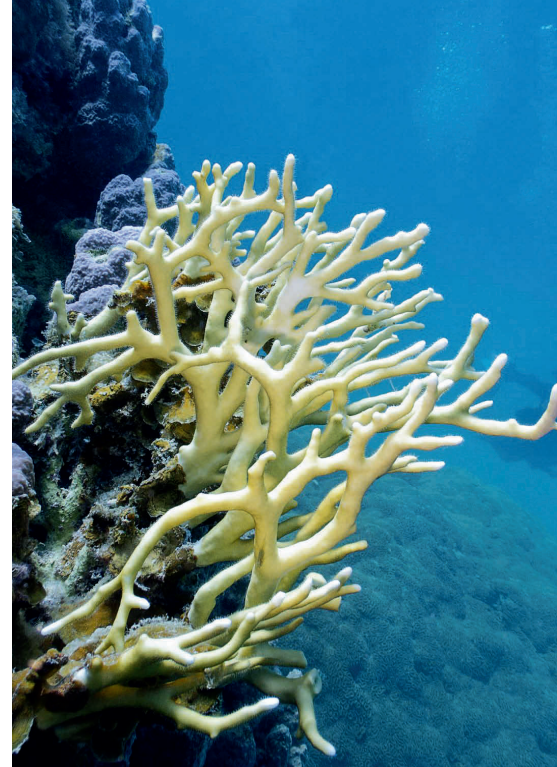
The findings from Ilyina's group are also important for the upcoming report of the Intergovernmental Panel on Climate Change (IPCC). The Max Planck Institute for Meteorology in Hamburg is one of about twenty research institutions around the world whose climate simulations form the scientific basis of this report. The different simulations are so important because each of them yields slightly different results.

The experts of the Intergovernmental Panel on Climate Change (IPCC) are responsible for distilling something like a scientific consensus from these models. This international climate model comparison project is called Coupled Model Intercomparison Project Phase 5 (CMIP5). For a long time, simulations with climate models focused only on currents and temperatures. After the influence of ocean biogeochemistry was recognized, biogeochemical computations were included in CMIP5 for the first time. "Although the models differ slightly from one another, they all agree that, from a global perspective, the oceans are acidifying," says Ilyina.

Deviations arise primarily when the various models treat individual regions – that is, when regional details become important. Simulations show that there will be winners and losers among the phytoplankton. Several calculations even predict that phytoplankton in some ocean regions, such as the Arctic, will flourish more than previously. The reason: the receding ice allows more sunlight to penetrate the water, which is exactly what plankton algae need, just like plants on land.

However, most of the simulations predict the opposite: that ocean acidification will, on the whole, bring disadvantages to these sea creatures. The mechanisms behind this are still not completely understood, but some experiments show that the growth of algae may be impaired. Accordingly, the quantity of plankton is expected to decline in the coming decades.

In addition, a physical effect could also contribute to the algae starving. The surface layer of the oceans will warm up further due to global warming. This would form a warm body of



Ocean acidification threatens corals (*Millepora spec.*, above), important for reef formation, and the pelagic microscopic diatom algae (*Arachnoidiscus spec.*, below).

water that floats on top of the deeper, cold water. The mixing between these bodies of water will then be slower, as the boundary between warm and cold acts like a separation layer. The result is that the transport of deep, nutrient-rich water to the surface is interrupted. However, these nutrients are essential for the growth of the phytoplankton. The data from Ilyina's research group also indicate a decline in phytoplankton.

The decline of the phytoplankton population affects not only the food chain in the oceans; it also directly affects the carbon cycle. The phytoplankton absorb large amounts of carbon dioxide and transform it into biomass. When the algae die, they sink into the deep. In this way, large amounts of CO_2 are ultimately withdrawn from the upper layers of the ocean and removed from the CO_2 exchange with the atmosphere for long periods. Climatologists

» Our simulations show that the oceans' capacity to absorb CO₂ will indeed decline in the coming years.

refer to the oceans as a carbon sink. But it will shrink if the phytoplankton concentration declines.

Physics, too, plays a role in the decrease of CO₂ being sequestered into the deep ocean. Within the relatively well mixed water of the North Atlantic today, there is strong circulation and mixing taking place, transporting large quantities of CO₂ into the deep ocean. Enhanced thermal ocean stratification could weaken this transport considerably in the future.

SULFUR COMPOUND IS A RAINMAKER

"Our simulations show that the oceans' capacity to absorb CO₂ will indeed decline in the coming years," says Ilyina. "Unfortunately, we don't yet know what factors play the most critical role in this." How great is the influence of the phytoplankton and the biological transport of CO₂ into the deep? How strong is the effect of the physical trans-

port? What role does the equilibrium of the ions and the pH value of the water play?

Ilyina now wants to attempt to focus on individual aspects of her simulations to determine their role in the oceanic carbon cycle. The problem is this: "If we switch off certain parameters, we have to make sure that the simulation still corresponds to reality and delivers plausible results." Tatiana Ilyina is the right person in the right place for this. Not only is she an oceanographer, but she also has many years of experience in constructing models. "I simply enjoy constructing models," she admits. The climatologist also has the right tools for transforming complex processes involved in ocean biogeochemistry into algorithms for climate simulations.

Just how important ocean biogeochemistry is can be seen from a further experiment that Ilyina conducted in collaboration with her colleague Katharina Six: simulating the future release

and transport of dimethyl sulfide gas. Anyone who has trudged through seaweed on the beaches of the Baltic knows the musty smell of this substance. It is generated when algae die and decompose. Dimethyl sulfide is one of the rainmakers. It rises high into the atmosphere above the oceans and ultimately, via several intermediate steps, contributes to the formation of clouds there. Emission of dimethyl sulfide from the ocean is the largest source of sulfur in the atmosphere.

The simulation shows that the flux of dimethyl sulfide into the atmosphere decreases due to ocean acidification. This results in fewer clouds, which reflect the Sun's energy. Consequently, the Earth becomes warmer.

The consequences of increased CO₂ concentrations in the ocean are not yet fully understood. Researchers now refer to global warming and ocean acidification as the evil twins. The relationships become even more intricate when one considers that the carbon cycle in-

Carbonate saturation (indicated by the Ω value) in the ocean for 1950 (left) and 2200 (right). The blue regions display a condition of undersaturation, while the red areas are supersaturated with respect to calcite – a mineral form of calcium carbonate. In 1950, the blue regions in which calcite dissolved were located only in the depths of the Pacific Ocean. Through 2200, these areas will become much more widespread.



fluences other cycles in the ocean, such as the nitrogen cycle. This cycle is driven by, among other things, cyanobacteria – the phytoplankton known as blue-green algae.

Cyanobacteria have existed for hundreds of millions of years. They developed during a time when little oxygen was present in the Earth's atmosphere, but a lot of CO₂. These microbes absolutely love CO₂. Increased CO₂ concentrations drive them to high levels of activity. Cyanobacteria are one of the few life forms that are able to convert gaseous N₂ into other nitrogen compounds, such as those that plants use for nutrition.

CONSEQUENCES OF ALKALINITY ENHANCEMENT UNFORESEEABLE

Thus, more CO₂ means more nitrogen compounds. No one can say with certainty yet whether that will prove advantageous or disadvantageous for life in the ocean. There is no doubt that cyanobacteria profit from the added CO₂ in the oceans. Mainly, however, the example shows how difficult it is to fully comprehend the biogeochemical processes and transfer them to a simulation.

This also applies to the calculations Tatiana Ilyina's group is developing to simulate the idea of halting ocean acidification artificially. There is a natural process that serves as a model for this: Carbonate ions that are supplied in the ocean from the weathering of, for instance, limestone, aren't accompanied by acidification of seawater, but exactly the opposite. Carbonate ions that derive from eroded rock and other alkaline ions neutralize acids, thus buffering the effect of CO₂. This has been happening for millions of years. For years now, the question of whether ocean acidification can be slowed down has been a topic of discussion – whether we could fertilize the oceans with additional alkaline compounds, such as calcium hydroxide, or hydrated lime.

Researchers call these methods of artificial mitigation of climate change geoengineering. Ilyina has checked whether this would be feasible at all. The results of the simulation were sobering. One would have to pour into



Simulating the future of the oceans: Tatiana Ilyina (left) and Katharina Six discuss their latest results.

the oceans 200 times the quantity of ions that are deposited globally by natural weathering. This would require some 70 to 100 billion tons of limestone. That is quite expensive.

Initially, though, the pH value would climb to 8.7 at the locations where the alkalinity was added to the seawater, until the currents distributed it. That would be too much of a good thing, and a massive intervention in the eco-

system. The consequences for living creatures would be unforeseeable. For this reason, Ilyina thinks that global alkalinity enhancement wouldn't make much sense. Especially since her research makes it clear that the relationships between biogeochemistry and climate are too complex for humans to monitor and control the effects if they destabilize individual processes, such as the carbon cycle. ◀

TO THE POINT

- The increasing concentration of carbon dioxide in the atmosphere is not only changing the climate, it is also acidifying the oceans.
- The concentration of carbonate ions is decreasing in seawater with decreasing pH values, making it harder for all organisms with calcareous shells to construct these shells.
- Ocean acidification causes feedback that can amplify the greenhouse effect.
- Model simulations show that primary production by phytoplankton in the oceans may decline as a result of climate change, and the oceans may absorb less CO₂ from the atmosphere. At the same time, the oceans would release less dimethyl sulfide, impairing cloud formation and allowing more thermal radiation from the Sun to reach the Earth's surface.
- Slowing down ocean acidification by geoengineering could be expensive and have unforeseeable consequences for biogeochemistry, the ecology of the oceans, and the climate.

GLOSSARY

CMIP5: In the *Coupled Model Intercomparison Project Phase 5*, climatologists are examining the results of climate simulations that were undertaken by more than twenty institutions worldwide. The conclusions will be distilled into a scientific consensus for a report to the Intergovernmental Panel on Climate Change (IPCC).

Phytoplankton: Microorganisms in the ocean, such as green, brown and blue algae, that, like plants, utilize the energy of sunlight through photosynthesis. Phytoplankton is the first link in the food chain of the oceans.