Chemical methods

Minerals for enhanced carbon dioxide uptake by the ocean

The amount of carbon dioxide that the ocean can absorb without becoming highly acidic depends on the alkalinity of its surface water. This term refers to the amount of acid-binding mineral components that were previously dissolved from weathered rock and washed into the ocean. The question now is: could a targeted input of such minerals help to increase the marine carbon dioxide uptake without unbalancing the chemistry and life in the ocean? This approach does work in simple model calculations. However, field experiments are still lacking, as are realistic simulations and detailed knowledge about the consequences and risks of an increase in alkalinity. The research mission CDRmare investigates the potentials, feasibility and side effects of the various methods.

The big climate goal: a net zero of carbon dioxide emissions

There is a consensus in scientific climate research that humanity will only mitigate climate change and its growing impacts and risks, if it reduces the amount of its annual carbon dioxide emissions into the atmosphere to net zero.

Human-induced carbon dioxide emissions result from the burning of fossil raw materials such as crude oil, natural gas and coal, as well as from changes in land use. So far, nobody knows how mankind can avoid these emissions in the future in an ecologically and socially acceptable way. Experts rather assume that humanity will still be emitting residual amounts of carbon dioxide by the middle of the 21st century. These are expected to amount to 5 to 15 percent of current emissions.

The remaining emissions must be offset. There are various approaches to remove carbon dioxide from the atmosphere in order to achieve this offset. One basic idea is to accelerate the carbon dioxide uptake of natural carbon sinks. Besides forests, savannahs and wetlands on land, these primarily include the ocean. Its water masses already contain more than 50 times as much carbon as the Earth's atmosphere and have absorbed a quarter of the carbon dioxide emissions caused by humans in recent decades, thus significantly slowing down global warming.

Chalk cliffs on Rügen. Example of natural erosion and weathering.
Photo: Felix Mittermeier, Pixabay.com

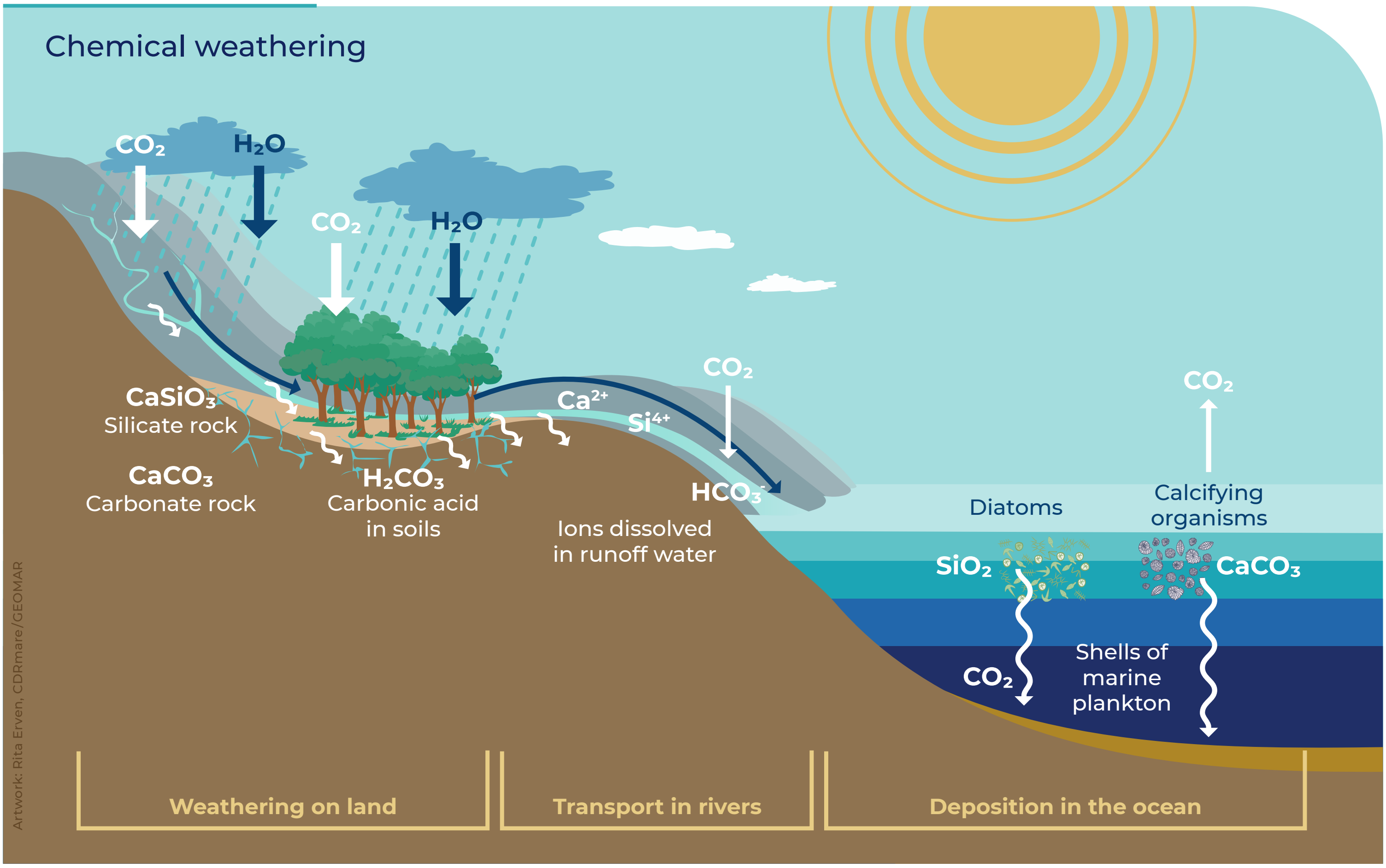
The laws of marine chemistry

The ocean's carbon dioxide uptake occurs at the sea surface and is possible because there is a constant exchange of gases between the surface water and the atmosphere, which equalises any pressure differences between the carbon dioxide dissolved in the seawater and the carbon dioxide in the atmosphere. If the carbon dioxide concentration in the atmosphere increases, the ocean also absorbs more carbon dioxide.

As carbon dioxide dissolves in seawater, a part of the gas undergoes a series of chemical reactions during which the dissolved gas, which could escape back into the atmosphere at any time, is chemically bound in the seawater in the form of hydrogen carbonates and carbonates. As such, re-emission into the atmosphere is impossible. At the same time, the chemical reaction lowers the concentration of carbon dioxide dissolved in the surface water and the ocean can absorb new carbon dioxide from the atmosphere again.

However, in the course of this reaction chain, so-called protons (hydrogen ions) are also produced, which acidify the ocean when they are released. The extent to which they are released depends on the acid binding capacity of the water. Experts also speak of the degree of alkalinity in this context.

The alkalinity of seawater is primarily determined by the amount of acid-binding mineral components (hydrogen carbonate, carbonate, borate) that were previously dissolved from weathered rock on land over the course of many millions of years and carried into the ocean by rainwater via streams and rivers. If their proportion is high, many of the protons are not released, but are immediately bound by the minerals in the course of the chain reaction. This means that the acidification of the water is buffered. However, if the water contains only a few minerals, its acid-binding capacity is limited. The number of free protons rises and the sea becomes increasingly acidic, which means a deterioration of living conditions for many marine organisms.



The degree of alkalinity of seawater is determined by two basic processes: on the one hand, by the input of acid-binding solution products of rock weathering dissolved in the water; on the other hand, by the natural uptake and further processing of these solution products by marine organisms such as calcifiers (carbonates) or diatoms (silicates), with part of the previously bound carbon dioxide (CO_2) being released again during calcification ($CaCO_3$).

Graphic: Rita Erven, CDRmare/GEOMAR

The idea: an acceleration of natural weathering

Rock weathering and the associated dissolution of minerals in the ocean are comparatively slow natural processes and influence the Earth's climate over periods of thousands of years and more. Every year, they remove about 1 billion tonnes of carbon dioxide from the atmosphere. This amount corresponds, on a long-term average, to the amount of carbon dioxide that enters the atmosphere through volcanic activity and mineralisation processes in the Earth's mantle and in the ocean. To increase this carbon dioxide removal and thus compensate for unavoidable man-made residual carbon dioxide emissions, natural weathering would have to be accelerated by a factor of about 5.

According to model studies, an increase would be quite possible if natural rock weathering was accelerated and the degree of alkalinity of the seawater deliberately increased. Such an intervention in ocean chemistry would have the advantage that the ocean could absorb more carbon dioxide without further acidification. At the same time, in marine regions with high ocean acidification, this chemical process, which is harmful to many marine organisms, could be reversed, which could facilitate the restoration of coral reefs and mussel beds.

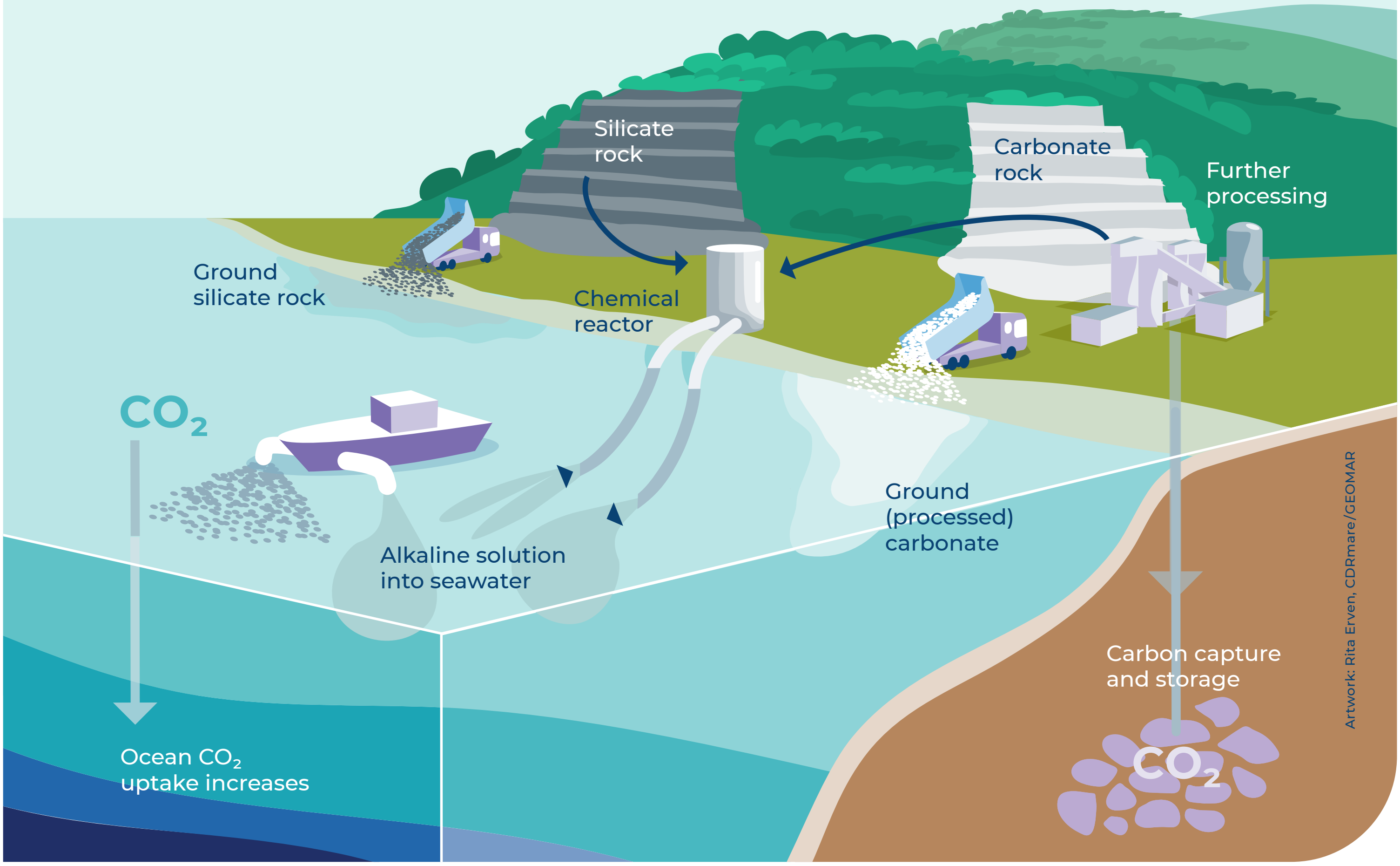
Marine alkalinity enhancement

Costs:
Estimates range from **US$40 to US$260 per tonne of carbon dioxide**

Scalability:
Carbon dioxide extraction on an industrial scale is theoretically possible. Alkalinity enhancement processes are already being used in practice, e.g. in Lusatia for the remediation (neutralisation) of acidic mining lakes.

Duration of storage:
Many hundreds to hundreds of thousands of years

Technical state of development:
For the ocean, the method has so far **only been simulated in computer models and tested in individual laboratory experiments.** Extensive laboratory and field tests as well as **knowledge on risks and side effects for humans and the environment are lacking**.



Alkalinity enhancement: A method in its infancy

Various processes are currently being developed that could accelerate the natural weathering of mineral-bearing rocks and increase the alkalinity of seawater. These include the idea of mining limestone and chalk or siliceous rocks such as basalts and olivine on land, then crushing them to increase the surface area for weathering (chemical reactions) and distributing the rock flour on beaches or directly on the ocean. Residual materials or waste products from cement production could also be used for the same purpose.

A second approach aims to install chemical reactors on the coast or on ships or platforms in the ocean. In these reactors, the rock flour would weather particularly quickly under controlled conditions and produce an alkaline solution that would then be discharged into the ocean. This would primarily increase the concentration of hydrogen carbonates and, depending on the weathered rock, the proportion of calcium, magnesium or even silicate in the seawater.

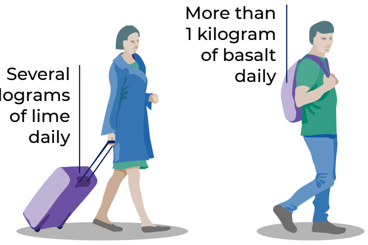
All these compounds are already present in high concentrations in seawater today, so that the relative changes caused by a targeted mineral input would be in the range of a few percent. The effects of these concentration changes on marine ecosystems must nevertheless be studied in detail.

Conclusive laboratory or field studies on risks and side effects are lacking

Much of the knowledge about the chemical and biological consequences of alkalinity enhancement has so far come from model studies (computer simulations). However, conclusive laboratory or field studies on the local, regional and global effects of industrial-scale mineral inputs on humans and the environment are still lacking. Science is therefore faced with a multitude of important questions that are to be answered within the framework of the interdisciplinary research mission CDRmare.

How many tonnes of rock would be needed to offset residual emissions through an increase in alkalinity, and which of the envisaged methods are the most promising?

One thing is certain: A large amount of rock or alkaline mineral products would be needed to increase the alkalinity of the surface water in a way that would have an impact on the climate. Previous estimates assume that in practice half a tonne to five tonnes of mineral products would have to be used per tonne of carbon dioxide removed.



One tonne of carbon dioxide corresponds roughly to the annual residual emissions that would be attributable to each inhabitant of Germany by the middle of the century if, as planned, the greenhouse gas emissions of Germany were to be reduced to net zero by 2045. If every citizen wanted to compensate for these residual emissions solely by increasing the alkalinity of the ocean, he or she would have to dissolve more than one kilogram of basalt or several kilograms of lime per day. Extrapolated to all inhabitants of Germany, there would be an additional demand of basalt of up to 32 million tonnes or a demand of lime of 100 million tonnes per year, correspondingly less if the compensation is divided among several carbon dioxide removal methods. From a global perspective, less than one fifth of the rock and sand quantities mined worldwide today would have to be provided as feedstock for alkalinisation measures on the scale required.

Both, limestone and silicate rock occur in the subsoil in far more than sufficient quantities. The latter are even the most common rocks in the earth's crust. However, it is still unclear how much energy and investment would be needed to extract the rocks on an industrial scale, process them, transport them to the coast and later out to the ocean, and what greenhouse gas emissions would arise from that.

Chalk mining in Lägerdorf. Photo: Joachim Müllerchen, Wiki Commons

Limestone does not readily dissolve in seawater because the surface water of the ocean is usually chemically supersaturated with carbonates. An exception are acidic and oxygen-poor water masses that occur, for example, in some deep areas of the Baltic Sea. The water in surface sediments is also often very acidic, so that carbonate minerals can be dissolved there as well. In contrast, seawater is extensively undersaturated with silicates, which is why silicate rock would dissolve in principle. To increase the alkalinity of the ocean as quickly as possible, the silicate rock would have to be ground into a very fine powder and distributed in shallow coastal waters or be dissolved in seawater in chemical reactors.

However, limestone and silicate rock are not the only options. There are now promising minerals extracted from rocks, such as magnesium-calcium minerals, whose extraction or production requires less energy than the mining and processing of limestone and silicate rock.

In the research mission CDRmare, researchers investigate various materials and processes for marine alkalinity enhancement in terms of their potential and impact on the marine environment, their technical implementation and the respective cost framework – from the input of rock flour, to the production of the best possible alkaline solutions, to the distribution of mineral-containing materials on beaches and rocky shores. For example, they investigate which materials weather the fastest and also test new materials for their suitability.

The spontaneous formation of new minerals during the dissolution of silicate rocks is also being investigated, as the efficiency of carbon dioxide uptake can be reduced by these new mineral formations. Moreover, it is analysed what quantities of the respective material would be required and could be used in an ecologically reasonable way; how expensive their production, transport and use would be, what undesirable constituents were to be released during their dissolution in seawater and how their quantity could be reduced. In addition, CDRmare scientists calculate in what quantities and over what area of the ocean the respective materials would have to be applied if a significant contribution is to be made towards offsetting the residual emissions through marine alkalinity enhancement.

Basalt rocks.
Photo: Zorion, Wiki Commons

For how long would the ocean store the additional absorbed carbon dioxide?

As a result of the increase in alkalinity, the surface water can absorb more carbon dioxide, which is chemically bound and then stored primarily in the form of hydrogen carbonate. The hydrogen carbonates dissolved in the surface water and other solution products of weathering are distributed throughout the global ocean including great depths by ocean currents. In this way, the entire ocean becomes a reservoir for the carbon taken up at the sea surface. Depending on the depth of the water and the ocean circulation, it takes decades or even centuries for the carbon-rich water to return naturally to the surface.

Up to now, water whose alkalinity has not yet been increased by humans has continuously risen to the sea surface in the so-called upwelling areas of the world ocean. It would therefore still have the full uptake potential for a targeted increase in alkalinity and the resulting carbon dioxide uptake. And even if one day water masses rise to the surface again that have already experienced targeted alkalinity enhancement and thereby stored carbon dioxide released by humans in the form of dissolved carbon dioxide or hydrogen carbonate, the hydrogen carbonates will remain in the water for a period of the order of 100,000 years. This means that the carbon bound in them could not outgas into the atmosphere in the form of carbon dioxide. Only the dissolved carbon dioxide would escape.

How long the additional hydrogen carbonates remain dissolved in the ocean depends mainly on chemical and biological processes: The higher alkalinity reduces the acidity of the water, which leads to a reduced dissolution of calcareous sediments on the seabed and may also make it easier for calcifying species to produce calcareous shells. Thus, less calcareous sediments are dissolved and more calcareous shells tend to be formed.

Calcification, in turn, is the reverse process of weathering. In the chemical reaction, hydrogen carbonates are consumed, reducing the alkalinity of seawater and producing dissolved carbon dioxide. The latter results in an increase in the carbon dioxide concentration in the water. At the next contact with the sea surface, this dissolved carbon dioxide can escape into the atmosphere.

These chemical effects on carbonate dissolution and formation thus represent leakages of stored carbon. The dissolution of calcareous sediments occurs on time scales of tens of thousands of years, while the formation of calcareous shells in organisms can occur within a few days, for example when environmental conditions allow calcareous algal blooms. It can therefore be quite decisive in which marine regions of the world possible measures to increase alkalinity are carried out.

Repeated alkalinity enhancement of water masses that have already been alkalinised could eventually lead to supersaturation and spontaneous precipitation of carbonates, releasing carbon dioxide again. Alkalinity enhancement as a measure to increase the ocean's natural carbon dioxide uptake could therefore probably be carried out "only" for many decades to a few centuries. Nevertheless, such an effort should be sufficient to offset the residual emissions and thus stabilise the climate.

In the research mission CDRmare, scientists investigate how much additional carbon dioxide the ocean would absorb through targeted alkalinity enhancement and for how long this carbon dioxide would be stored in the water. To do this, they simulate the local but also the large-scale application of suitable methods in various ocean regions of the world – including German and European coastal waters as well as the Labrador Sea and the Southern Ocean. The latter are ocean regions in which deep waters are formed, which then circulate in the deep ocean for centuries to millennia before they rise to the ocean surface again and can enter into gas exchange with the atmosphere.

What are known risks and side effects of alkalinity enhancement and how could these be minimised?

So far, little is known about the risks and possible environmental impacts of all measures and processes associated with alkalinity enhancement. On the one hand, it is known that the extraction of minerals in quarries often leads to land-use conflicts in the affected areas, to interventions in local ecosystems, and to increased traffic volumes and rising noise and dust pollution. On the other hand, it is known that silicate rocks contain certain nutrients (silicon, iron) and heavy metals (nickel, chromium, zinc). The former can influence marine nutrient cycles and the growth of certain algae (especially diatoms). The latter could be toxic and thus have harmful effects on ocean ecosystems. However, there is hope that harmful side effects of alkalinity enhancement could be prevented through the production of synthetic minerals. Detailed knowledge about the respective effects on the chemical and biological processes of the ocean, however, is still largely lacking.

In the research mission CDRmare, scientists use various laboratory and mesocosm experiments to investigate the extent to which the input of mineral-containing material or the weathering of rocks on the seabed would influence the coastal ecosystems of the North Sea and Baltic Sea and the threshold values up to which negative effects of alkalinity enhancement for the biotic communities of the ocean could be prevented. To do this, they are analysing the physiological and ecological responses of key species such as phyto- and zooplankton as well as selected organisms living on or in the seabed. The so-called mesocosms – which are self-contained seawater basins whose environmental parameters can be changed – allow experiments with natural ecosystems under realistic conditions in which the dynamics resulting from the interactions between the organisms and their physical and chemical environment can be investigated.

The local research results are extrapolated to the regional and global level with the help of numerical models. These models are used to simulate the deployment of measures to increase alkalinity in German territorial waters and in other marine areas. In this way, the experts can identify risks, name critical threshold values, test concepts for monitoring procedures and derive corresponding options for action for the local, national and international level.

In such mesocosms, also called benthocosms, the reactions of living organisms on the seabed (benthos) are studied.
Photo: Sonja Geilert, CDRmare/GEOMAR

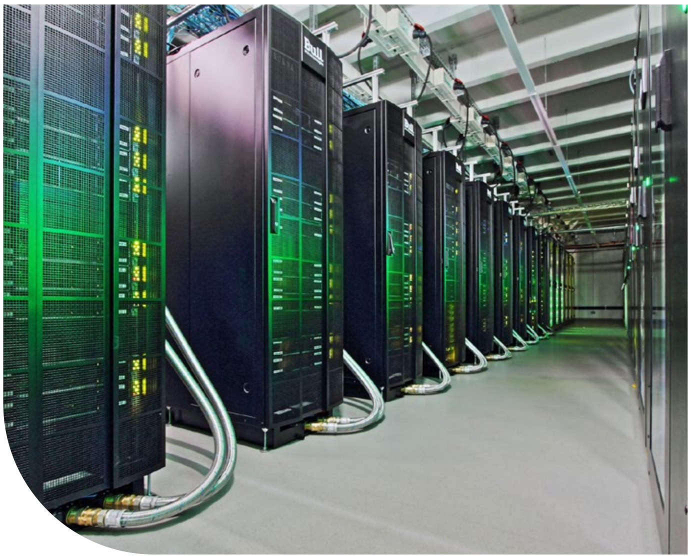
Would the widespread use of alkalinity enhancement measures have a negative impact on fish stocks?

Fish and seafood are among the most traded commodities in the world. Around the globe, around 3.3 billion people depend on fish for a balanced diet and sufficient animal protein. It is therefore important to know the potential impacts of alkalinity enhancement on global fish stocks before discussing the possible application of the various methods.

In the research mission CDRmare, scientists investigate the possible effects of alkalinity enhancement on biomass production in the world's oceans – from phytoplankton to fish populations. For this purpose, they combine scenarios for further climate development with modelling of alkalinity enhancement on a large scale. They then analyse the consequences of possible population increases or collapses in certain marine regions on global trade flows and determine which nations would particularly benefit or suffer losses. They focus in particular on fish stocks in the Baltic Sea and the North Sea. Behind all this research is the big question of whether a widespread increase in alkalinity would endanger food security in certain regions of the world and thus make it more difficult to achieve the UN sustainability goal of »No Hunger«.

How could carbon dioxide uptake by the ocean, achieved by alkalinity enhancement, be measured and monitored?

Increasing the alkalinity of the ocean only makes sense if the desired effects can also be measured and attributed to the mineral input. In this context, experts speak of the verification and attribution of a change – in this case, a change in the alkalinity and increase in the carbon content of the ocean. Measuring these, distinguishing them from natural fluctuations and attributing them to individual measures is a major scientific challenge for which there is no reliable method to date.



In the research mission CDRmare, scientists develop monitoring strategies that can be used to detect and attribute the effects of alkalinity enhancement in the ocean. On the one hand, they carry out chemical measurements, statistical analyses, modelling and process observations, on the basis of which the understanding of the different measures is improved so that statements can be made on the verification and attribution of an artificial increase in alkalinity. On the other hand, the scientists simulate the application of different chemical measures in coastal models that cover marine regions such as the North Sea, the Baltic Sea, the Wadden Sea and the Northwest European shelf at a spatial resolution of 10,000 to 10 metres. In doing so, they examine the extent to which the respective methods for alkalinity enhancement change the carbon uptake of the ocean and have an impact on ecosystems.

Based on their results, decision-makers should then be able to assess whether and how a possible increase in alkalinity could be reconciled with the goals of climate, environmental and nature protection.

High-performance computers like these supercomputers of the HLRN network at the University of Göttingen are employed to carry out the large model simulations on alkalinity enhancement of the ocean.
Photo: Gesellschaft für wissenschaftliche Datenverarbeitung mbH Göttingen (GWDG)

What would be the global impact of a widespread increase in alkalinity?

The world ocean is a global, interconnected system: changes in one ocean area lead to interactions with other areas. This includes features of marine chemistry. For this reason, local changes in alkalinity can be expected to have impacts that not only extend far beyond the boundaries of the targeted marine area, but can also last over very long periods of time. However, it has not yet been precisely clarified what concrete global effects the local input of minerals could entail.

In the research mission CDRmare, scientists therefore establish a global context. Using global models that resolve the global carbon cycle, they simulate how much additional carbon dioxide *the world ocean would absorb in selected areas if the alkalinity was increased in European coastal waters as well as in selected ocean regions where deep water is formed. They also address the question which consequences alkalinity enhancement would have on the carbonate chemistry in deeper waters and to what extent a further increase in atmospheric carbon dioxide concentrations would affect the effectiveness of alkalinity enhancement measures.*

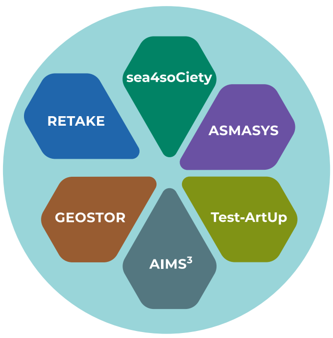
Model uncertainties are estimated by using different models and different settings of poorly known model parameters. Knowledge about model uncertainties is an important building block for the development of robust methods for monitoring, detection and attribution of alkalinisation measures. At the same time, it is needed to develop methods for "carbon accounting" – i.e. methods of "book keeping" – as well as to define the legal framework of possible deployments.

Would international climate policy change if its actors could fall back to the option of alkalinity enhancement, and would the potential benefits of using it justify the resulting costs and side effects?

In international climate negotiations, governments and experts often consult socio-economic models. These can be used to calculate what economic gains and losses climate change would bring at different levels of warming and whether investments in emission reductions will actually pay off in the end. The results of this modelling are thus an important tool for developing options for action in international climate policy.

So far, however, such models are not able to take into account a possible use of various marine alkalinity enhancement measures in their calculations. It is therefore completely unclear what long-term options for action would result if these procedures were deployed. Would their use make sense from a socio-economic perspective, or would other approaches for increasing carbon uptake by the ocean or land areas be more effective? Corresponding studies have not been possible so far, especially because basic knowledge about the costs, risks and side effects of alkalinity enhancement is lacking.

In the research mission CDRmare, scientists compile new and already existing basic knowledge on the various methods of alkalinity enhancement and incorporate it as a new variable into a socio-economic model for the first time. They then examine whether new options for action for climate policy arise in the course of the model calculations and what these options would be. The experts also analyse to what extent the benefits of alkalinity enhancement would justify the costs and side effects that would arise and whether other methods for strengthening natural carbon sinks would be better suited than the large-scale input of minerals into the ocean.



All research activities described here are carried out within the CDRmare consortium »RETAKE – CO_2 removal by alkalinity enhancement: potential, benefits and risks« .

Within the research mission CDRmare of the German Alliance for Marine Research (DAM), which involves about 200 researchers in 6 consortia, different methods of marine CO_2 removal and storage (alkalinisation, blue carbon, artificial upwelling, CCS) are investigated with respect to their potential, risks and trade-offs and brought together in a transdisciplinary assessment framework. CDRmare has been funded by the German Federal Ministry of Education and Research with 26 million euros since August 2021 and will run for three years.

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