OCEAN ACIDIFICATION

Starting with the Science

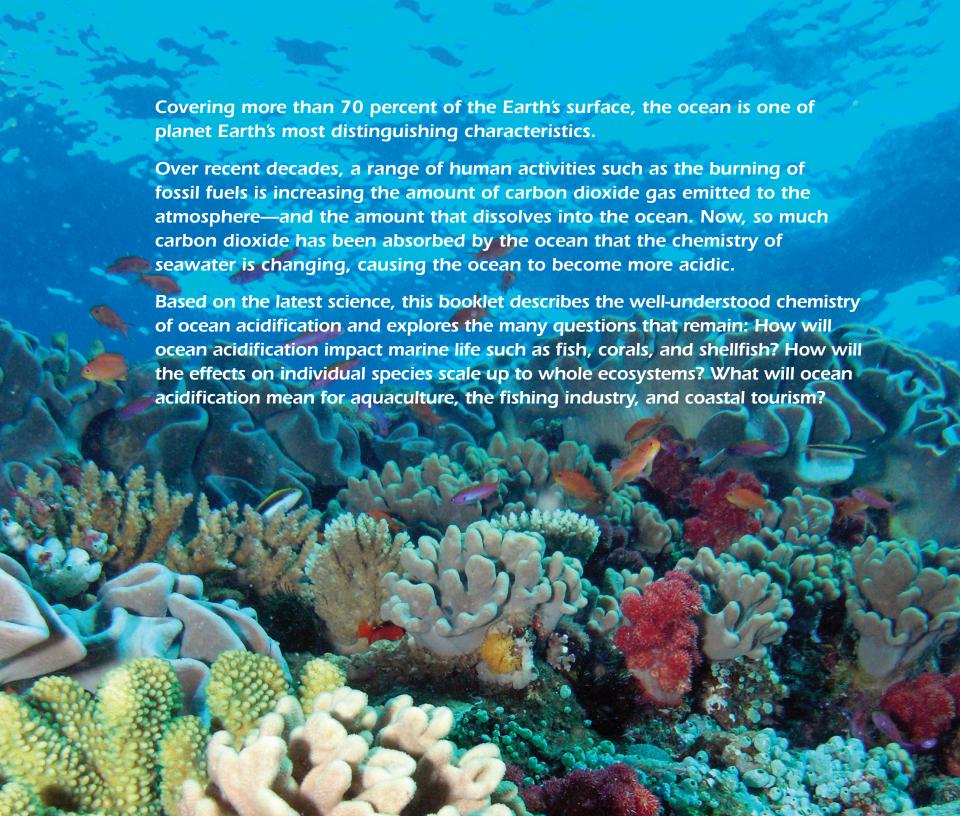






NATIONAL RESEARCH COUNCIL
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THE CARBON CYCLE

Carbon dioxide is a natural part of Earth's atmosphere and one of several gases that contribute to the "greenhouse effect," which traps heat and helps make Earth habitable. Normally, the Earth's carbon cycle maintains a natural balance of carbon in the atmosphere, land, and ocean through the "breathing of the planet" (see Box 1). However, since the beginning of the industrial era, emissions of carbon dioxide have climbed rapidly, and now are exceeding the capacity of the carbon cycle to maintain an equilibrium between the atmosphere and ocean. Excess carbon dioxide traps more heat in the atmosphere, which changes the Earth's climate.

Not all of the excess carbon dioxide stays in the atmosphere. Scientists estimate that one-third of all the carbon dioxide produced by human activities has been absorbed by the ocean. The ocean's removal of carbon dioxide from the atmosphere has undoubtedly helped curb the extent of climate change—but this benefit has come at a cost. The absorption of carbon dioxide is fundamentally changing the chemistry of the ocean by triggering reactions that make seawater more acidic, a phenomenon called ocean acidification. In fact, the ocean has become nearly 30 percent more acidic than it was at the beginning of the industrial era—a change larger and more rapid than seen in the fossil record going back at least 800,000 years, before the appearance of vertebrates and plants in the fossil record.



Carbon is continually exchanged between the atmosphere, ocean, biosphere, and land. There are short- and long-term cycles at work. **BOX 1 THE CARBON CYCLE** $C0_2$ **Fossil Fuel** Exchange of CO₂ **Emissions Volcanic Eruptions** Weathering of Rocks **Waste and Decay** 3 of Dead Organisms **Fossil Fuels**, Limestone (Calcium Carbonate) Coal, Oil, and Gas Long Term **Photosynthesis Marine Deposits** Respiration Exchange

Short-Term Cycles

Carbon dioxide is exchanged rapidly between plants and animals through respiration and photosynthesis, and between the ocean and the atmosphere through gas exchange. The burning of fossil fuels releases carbon dioxide to the atmosphere.

Long-Term Cycle

Over millions of years, carbon dioxide in the air combines with rainwater to form weak acids that very slowly dissolve rocks. Rivers and streams carry these minerals to the oceans where they are used by animals to form coral reefs and shells and help balance the pH of the ocean. Over even longer time periods, organic carbon (formed from the remains of marine life) becomes stored deep within the Earth's crust and forms fossil fuels, such as oil and natural gas. Some of this carbon will be released back into the atmosphere by volcanoes, completing the cycle.

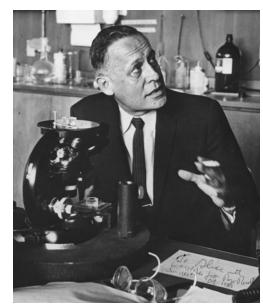
EVIDENCE OF EXCESS CARBON DIOXIDE

For the first half of the twentieth century, scientists thought the excess carbon dioxide from fossil fuel emissions would be taken up by vegetation and absorbed by the immense ocean without accumulating in the atmosphere. But a key paper published in 1957 by Roger Revelle, director of the Scripps Institution of Oceanography, together with chemist Hans Suess, hypothesized that the ocean would absorb carbon dioxide at a much slower rate than was previously thought.

The paper is widely regarded as the initial study of global warming because it recognized that if the ocean could not take up all of the carbon dioxide from fossil fuels, the excess must be accumulating in the atmosphere.

To help test this hypothesis, Revelle hired Charles David Keeling, a young researcher who had developed the first instrument for accurately measuring atmospheric carbon dioxide levels while he was a postdoctoral fellow at the California Institute of Technology. Keeling set up his equipment at the Mauna Loa Observatory in Hawaii, far from the localized effects of fossil fuels, to take precise, daily measurements of atmospheric carbon dioxide levels. The now famous "Keeling Curve" documents a steady increase in atmospheric carbon dioxide that continues today, providing evidence that natural carbon cycling is not keeping pace with human carbon dioxide emissions.

With evidence of carbon dioxide accumulating in the atmosphere, oceanographers decided they should track carbon concentrations in the ocean to see if carbon dioxide was also accumulating there. Studies that began in the mid 1980s have shown that the concentration of carbon dioxide in the ocean is increasing in parallel with the rise in atmospheric carbon dioxide (see Figure 1). At the same time, the pH of the ocean is decreasing (becoming more acidic), indicating that carbon dioxide levels have exceeded the ocean's natural capacity to buffer pH.

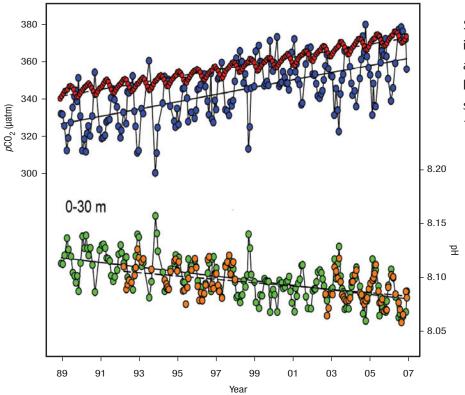




(Above) Charles David Keeling points to carbon dioxide data records now called the "Keeling Curve"

(Left) Roger Revelle works in his laboratory

Figure 1. Ocean carbon dioxide and pH measurements near Hawaii at Station ALOHA. 1988-2007

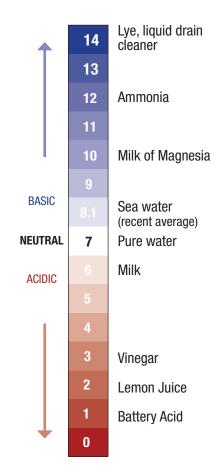


This figure demonstrates that as carbon dioxide in the air and ocean increases over time, the pH in the seawater decreases (Dore et al., 2009). Top: Calculated partial pressure of carbon dioxide in seawater (blue •), and in air at nearby Mauna Loa (red •)*. Bottom: Direct measurement of pH in surface seawater (orange •) compared with calculated pH (green •)*. Scientists measure "partial pressure" of carbon dioxide (pCO₂), the pressure that carbon dioxide gas exerts if it were alone in a container instead of being a component of the mixture of gases in the atmosphere or ocean, in units called microatmospheres.

WHY CARBON DIOXIDE MAKES

SEAWATER MORE ACIDIC

Scientists use pH—a measure of the concentration of hydrogen ions using a logarithmic scale—as an indicator of the acidity of a solution. As the hydrogen ion concentration increases, a solution becomes more acidic and its pH decreases. Because the scale is logarithmic, a decrease of one pH unit corresponds to a 10-fold increase in acidity.



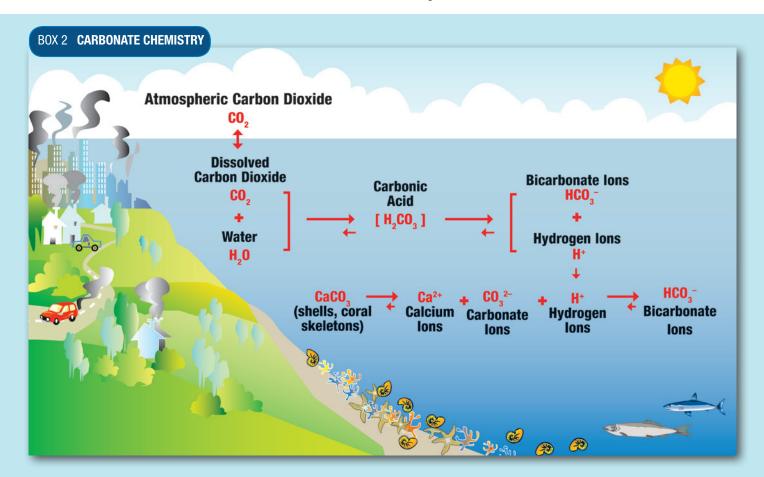
^{*} calculated partial pressure CO₂ and pH are based on measurements of the chemical properties of seawater at Station ALOHA. Please see Dore et al., 2009 for more details; full citation on inside back cover of booklet.

THE CHEMISTRY OF OCEAN ACIDIFICATION

Atmospheric carbon dioxide is absorbed by the ocean, where it reacts with seawater to form carbonic acid (H₂CO₃). Almost immediately, carbonic acid dissociates to form bicarbonate ions (HCO₃⁻) and hydrogen ions (H⁺). As the concentration of hydrogen ions increases, the water becomes more acidic.

Some of the extra hydrogen ions react with carbonate ions (CO₃²⁻) to form more bicarbonate. This makes carbonate ions less abundant—a problem for many marine species that absorb carbonate from seawater and use it to build calcium carbonate shells and skeletons in a process called calcification. As carbonate becomes less abundant, these organisms, such as corals and clams, have more difficulty building and maintaining their shells and skeletons.

Increased acidity can even cause some carbonate shells and skeletons to dissolve. Hydrogen ions react with the solid calcium carbonate ($CaCO_3$) and convert it to soluble bicarbonate (HCO_3^{-1}) and (Ca^{2+}) ions.



BIOLOGICAL PROCESSES AFFECTED BY OCEAN ACIDIFICATION

Increasing acidity, which also changes the carbonate chemistry of seawater, combined with other environmental stressors like increasing ocean temperature and pollution, has the potential to affect many biological processes.



Building Shells

Many animals and some algae use carbonate ions to make calcium carbonate shells and skeletons. Because ocean acidification decreases the availability of carbonate ions, these organisms will have to work harder to produce shells.

Maintaining Metabolism

Many physiological processes are finetuned to operate within a narrow pH range; outside of that range, the biochemical reactions may be too slow or inefficient to keep the organism healthy. Although many species can adjust to changes in their surroundings by actively maintaining a constant internal environment, this maintenance requires a significant expenditure of energy. An adult fish may be able to compensate by eating more, but fish eggs and larvae have limited energy reserves and, therefore, may have less capacity to adjust to more acidic conditions. Recently, scientists discovered that lower pH can also affect neurological processes in adult fish (see Neurological Effects on page 9) -indicating that a broader range of physiological processes may be sensitive to pH, with potentially others yet to be discovered.





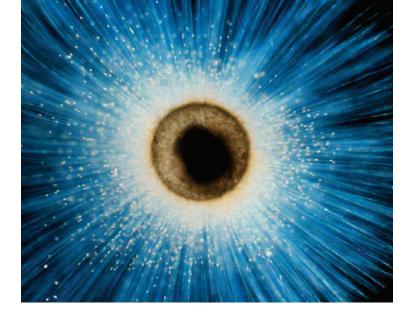
Boosting Photosynthesis

Carbon dioxide can stimulate plant growth by boosting the rate of photosynthesis. Many plants, including seagrasses, grow more rapidly under elevated carbon dioxide conditions. Although seagrasses provide valuable habitat, this could be too much of a good thing, if these plants overgrow less robust species and reduce the ecosystem's biodiversity.

Obtaining Essential Minerals and Nutrients

Ocean acidification could make it harder for marine organisms to absorb nitrogen, phosphorus, iron, and other elements essential for growth. For example, when seawater becomes more acidic, iron attaches to organic compounds, preventing marine life from using this essential element.





EFFECTS ON SHELLFISH, CORALS, AND OTHER CALCIFIERS

Calcifiers—organisms with shells or skeletons made from calcium carbonate—are among the most abundant forms of marine life. Ranging from tiny plankton species such as pteropods and foraminifera (pictured above) that form the basis of marine food chains, to the vast coral reefs that provide habitat for many ocean animals, calcifiers are an essential part of many marine ecosystems.

Because ocean acidification decreases the availability of carbonate ions, many researchers focused on studying the effects of acidification on organisms with calcium carbonate shells. These studies found that organisms must work harder to produce shells, and as a result, have less energy left to find food, to reproduce, or to defend against disease or predators. As the ocean becomes more acidic, populations of some species could decline, and others may even go extinct.

COULD OCEAN ACIDIFICATION THREATEN EARTH'S LARGEST CORAL REEF?

Ocean acidification could be contributing to the decline in coral growth. Every coral reef begins with tiny coral polyps that use the carbonate ions naturally found in seawater to form a hard calcium carbonate skeleton. Over time, the skeletons of many coral polyps will build up the structure of the reef. But ocean acidification, together with other stressors such as rising ocean temperature and pollution, is likely to make it harder for corals to grow or repair damage (see Box on page 6).

Although scientists are just beginning to piece together the relative impact of each factor, it is clear that such a combination of stressors will ultimately threaten the health of the reef system.



Australia's Great Barrier Reef is a massive coral ecosystem that is the largest biological structure in the world, visible even from space. The reef provides habitat for more than 1,500 species of fish and 400 species of coral—but recently, scientific studies have shown that the growth of the Great Barrier Reef's coral colonies has decreased by 14 percent since 1990. If growth rates continue to decline to the point that damage and erosion outpace repair, the reef system may begin to shrink.

DISSOLVING PTEROPOD SHELLS

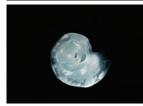
Amongst the mixture of tiny plants and animals that make up plankton lives a tiny sea snail called the pteropod. Despite their small size, pteropods are an important source of food for many species, including fish, seals, and whales (see "The Open Ocean," page 12).

But pteropods have delicate calcium carbonate shells that are vulnerable to ocean acidification. In a series of experiments, pteropod shells were placed in seawater at the pH (acidity) projected for the Southern Ocean by 2100. Within 48 hours, the pteropod shells began to dissolve.

Pteropod shells arranged from top (most intact) to bottom (most dissolved) illustrate the increasing stages of dissolution in seawater with elevated carbon dioxide.











NEUROLOGICAL EFFECTS

Recent research suggests that ocean acidification could muddle fishes' sense of smell and alter their behavior. Scientists found that in more acidic conditions, young clownfish lost the ability to navigate home using their sense of smell. The fish also became attracted to odors they normally avoid, such as the scent of predators, and displayed uncharacteristically bold behaviors such as roaming far from their home reef.

These changes could be due to altered patterns of neurotransmitter function in high carbon dioxide conditions. In a series of experiments with clownfish and damselfish, researchers found the abnormal behaviors could be reversed by treatment with a chemical that muted the action of the GABA-A receptor, a major neurotransmitter in the vertebrate brain. Given the ubiquity of the GABA-A receptors in vertebrate brains, the researchers think elevated carbon dioxide levels could cause similar sensory and behavioral impairment in a wide range of marine species.



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POTENTIAL IMPACTS ON **ECOSYSTEMS**

As important as it is to understand how ocean acidification will affect individual organisms,

how these changes may shift the balance in marine ecosystems. Because ecosystems represent an intricate network among organisms and their interactions with the environment, a disturbance to one part can have cascading effects throughout the system. Marine ecosystems provide critical services that humans depend on, such as supporting healthy fisheries and shellfish farms, recreation, commerce, and protec-

Many species known to be vulnerable to ocean acidification play critical roles in ecosystems, such as the corals and seagrasses that form habitat for diverse communities of organisms. When ocean acidification triggers even a relatively subtle change in an organism's performance, it can scale up to a change in the size of the population (e.g. through changes in survival, growth, or reproductive success), altering the composition of an ecological community, and potentially the entire marine ecosystem.

tion from storm surges.

One of the challenges scientists face is the difficulty of scaling up laboratory experiments on single species for a short period of time to the complex interactions of species in an ecosystem over many generations. Some insights can be gleaned from waters naturally high in carbon dioxide and past events in the Earth's geological record.



INSIGHTS FROM UNUSUAL ECOSYSTEMS: UNDERWATER VOLCANIC CARBON DIOXIDE VENTS

Beneath the Mediterranean Sea, and a few other sites around the world, carbon dioxide bubbles from volcanic vents in the seafloor, making the water around the vents more acidic—and offering scientists an opportunity to conduct natural experiments to investigate the effects of acidified seawater. Although the vents do not fully replicate the conditions of global ocean acidification, they do provide some clues as to how marine ecosystems might respond to the expected changes in ocean chemistry.

In the waters off Italy, researchers found that overall biodiversity was lower at the carbon dioxide vent sites, with a notable decrease in the abundance of calcifying organisms such as sea urchins, corals, and calcified algae. These studies also indicate that there are ecological winners and losers: although overall diversity declined at sites with lower pH, some organisms were better suited to tolerate acidic conditions than others. For example, seagrasses and brown algae were abundant at the vents, seeming to thrive in the high carbon dioxide water.

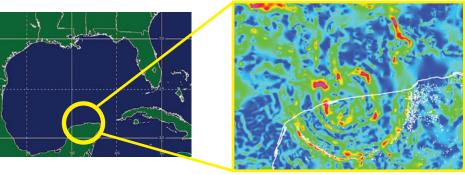
One recent study looked at corals growing along the coast-line of the Yucatan Peninsula, where underwater springs naturally lower the pH of seawater. Scientists found that ocean acidification reduced the density of coral skeletons, making them more vulnerable to erosion during storms, to organisms that bore into corals, and to parrotfish, which sometimes feed on corals. This could lead to a weakening of the reef framework and degradation of the coral reef ecosystem.

INSIGHTS FROM **EARTH'S GEOLOGIC PAST**

About 65 million years ago, an asteroid slammed into the Yucatan Peninsula, just north of what is now the city of Merida, Mexico. The asteroid, perhaps six miles in diameter, ejected enough soot and dust into the atmosphere to block out the sun for months or longer, contributing to the widespread death of plants and animals. This event, called the Cretaceous-Tertiary boundary extinction, is famous for the demise of the dinosaurs and roughly sixty percent of all species on Earth disappeared as a result of this cataclysm.

Oceanic species were particularly vulnerable to the effects of the asteroid impact. Many marine organisms went extinct, including marine species that built shells or skeletons out of calcium carbonate. A look at the fossil record shows that corals became rare, shell-forming plankton went extinct, and many species of mussels disappeared.

Why did these marine organisms die out? It turns out that the Yucatan Peninsula is largely a giant block of calcium carbonate and calcium sulfate, formed by the remnants of ancient



This map (a gravity anomaly map) reveals a crater roughly 180 km in diameter, produced when an asteroid struck the Yucatan Peninsula, Mexico more than 65 million years ago. The white line shows the Yucatan coast. The largest green, yellow, and red circles mark the rim of the crater.





Before the asteroid hit Earth, marine bivalves called rudists (left) were so abundant they formed reefs. Ammonites (right) were also plentiful. Both species vanished in the Cretaceous-Tertiary boundary extinction.

marine organisms. When the asteroid struck, the heat and pressure of the impact caused the release of sulfur dioxide, nitrates, and other compounds into the atmosphere. There, the compounds reacted with oxygen and water to form acid (e.g., sulfuric acid and nitric acid), which rained down into the ocean. The surface waters of the ocean became so acidic that marine organisms could not maintain their calcium carbonate shells and skeletons. Only organisms able to withstand the acidic conditions persisted, typically species without calcareous shells such as diatoms, a type of planktonic plant with a shell made of silica, rather than calcium carbonate.

The rapid environmental change due to the asteroid provides a clue to what might happen with present day ocean acidification, but it is not directly analogous. One of the differences is that dust from the impact darkened the sky, thus inhibiting plant growth and cooling the atmosphere. Also, the increase in ocean acidity from the asteroid was relatively short lived, lasting just hundreds of years, because mixing of the acidified surface with deeper waters restored the chemical balance of the upper ocean. Even so, fossil evidence indicates that many species never recovered and coral reefs did not reappear for another two million years. Today's acidification, caused by the steep climb in carbon dioxide emissions over the last 200 years, will likely affect marine ecosystems from the surface to the deep and will persist for many centuries to come.

POTENTIAL EFFECTS ON ECOSYSTEMS AROUND THE GLOBE

The specific effects of ocean acidification will vary from place to place, depending on the habitat and the types of organisms in the ecosystem. Below are descriptions of how ocean acidification might affect a variety of ocean ecosystems.

THE OPEN OCEAN

Open ocean ecosystems are based on plankton, a mixture of tiny free-floating plants and animals that live and grow in sunlit surface waters and serve as the foundation of the marine food chain. A number of planktonic species, including coccolithophores, foraminifera, and pteropods, need carbonate ions to build their shells. If ocean acidification in-



creases, these carbonate-based plankton species may decline – and that means that a range of species, including fish, seals, and whales, could lose their preferred foods, or have less food altogether.

TROPICAL CORAL REEFS

In the natural world, corals must grow rapidly to outpace predation by fish and other organisms, and to compete for space with algae and sea grasses. Experiments show that ocean acidification prevents reefbuilding corals from growing fast enough to escape predation and competition, or to repair physical damage sufficiently. Slowed



growth is not the only impact that ocean acidification could have on coral reefs – some scientists think that more acidic conditions could also contribute to coral bleaching.





POLAR ECOSYSTEMS

The polar waters of the Arctic and Southern oceans harbor many protected and endangered marine mammals and support some of the most productive fisheries in the world. Carbon dioxide dissolves more readily in cold water, acidifying polar waters faster than in lower

latitudes. In fact, scientists have determined that the surface waters of the Southern Ocean will begin to become corrosive to some types of carbonate structures by the year 2050 if carbon dioxide emissions continue to increase at the current rate.



DEEP WATER CORAL REEFS

Corals are not only found in warm, shallow, tropical waters—these animals are also found in the deep sea, up to 1000 meters (about 3281 feet) below the surface of the ocean, where they create habitat for many species of fish. Ocean acidification is expected to take longer to reach the deeper waters, but just as for tropical

reefs, over time it could reduce calcification, decreasing the rate of growth of deep-water corals. Furthermore, deep-water species may be less able to tolerate changing conditions than their shallow water counterparts. Many deep-dwelling organisms are adapted to the unvarying conditions that characterize the deep sea and may be less able to cope with change, such as increasing ocean acidity.

HOW WILL CHANGING ECOSYSTEMS IMPACT PEOPLE?

As the ocean's ecosystems change, so too will the services they provide to society. For example, every year, millions of scuba divers and snorkelers visit coral reefs to enjoy their beauty and abundant sea life. Local businesses generate income by offering diving tours and recreational fishing trips, and hotels, restaurants, and other businesses based near the reef ecosystems also benefit from the influx of visitors. One estimate places the total global value of coral-reef based recreation and tourism at \$9.6 billion. Ocean acidification threatens the survival of these beautiful and valuable ecosystems.





IMPACTS ON WILD FISHERIES

In 2007, the wild fish and shellfish harvested by the U.S. fishing industry were valued at \$3.7 billion. Ocean acidification could jeopardize this industry by altering the growth and development of economically important species of fish, either directly or through effects on the ecosystems of which these species are a part. The bottom line could be a reduction in the yield of commercial fisheries, affecting livelihoods of fishermen and the availability of seafood in markets and restaurants.

WARNING SIGNS FROM THE OYSTER INDUSTRY

The Pacific Northwest is home to a \$111 million shellfish industry, but in recent years, several of the region's oyster hatcheries have reported that oyster larvae are dying. Some oyster hatcheries have experienced 70 to 80 percent decreases in production due to massive losses of oyster larvae, and wild oysters in some regions have not successfully reproduced since 2005. Now, some researchers and oyster farmers are attributing this loss to ocean acidification.

In 2008, researchers noticed that die-offs on the outer coast tended to happen after coastal upwelling events—when winds push coastal surface waters offshore, causing an upsurge of deep water which is colder and more acidic. Another link between the

oyster larvae deaths and ocean acidification was identified when a group of researchers found that Puget Sound, where many of the region's oyster farms are located, was becoming acidic more quickly than the surrounding waters.

A 2013 study began to document why oysters are so sensitive to ocean acidification. The researchers found that water high in carbon dioxide alters shell formation rates, energy usage, and ultimately, the growth and survival of young oysters.

The researchers found that although adult oysters and other bivalves may respond to more acidic conditions by growing more slowly, oyster larvae don't have this option. Once eggs are fertilized,

oyster larvae are in a race against time to quickly build a calcium carbonate shell and develop the structures necessary for feeding before energy from the egg runs out. Exposure to acidified water, however, makes it more difficult for oysters to build shells. Working at the Whiskey Creek Shellfish Hatchery in Netarts Bay, Oregon, researchers found that oyster larvae were still relying on egg-derived energy until they were 11 days old—slowing their growth and jeopardizing their survival.

Some shellfish farms have already taken steps to protect oyster larvae from more acidic water, for example by buffering the water surrounding larvae to control pH. However, it would be premature to conclude that ocean acidification is the sole cause of the oyster hatchery failures. Other factors, such as nutrient pollution from runoff, or bacterial and viral infections, could also play a role. Research to better understand the cause, or causes, of the oyster larvae deaths will require more research—and until then, the Northwest's shellfish farmers will continue to struggle to find a way to keep their oysters, and hence their livelihoods, healthy and productive.



Herrold Oyster Company workers picking oysters in Willapa Bay, Washington.



WHERE DO WE GO FROM HERE? PROTECTING OUR OCEAN

Mounting evidence suggests that ocean acidification has the potential to alter ecosystems, the health of coral reefs, shellfish, and fisheries; and affect society and the economy on a global scale. Even if carbon dioxide emissions were curtailed immediately, the ocean would still become more acidic, as it continues to absorb the recently increased carbon dioxide levels in the atmosphere for many years to come. So what can we do?

A better understanding of the potential effects of ocean acidification, as well as the ability to anticipate these changes, will be needed for fishery managers, industries, and communities to plan and adapt. Ocean acidification research is still in its infancy, but the United States government has taken steps to establish a national ocean acidification research program to support this emerging field.

To more fully understand and address the threat that ocean acidification poses, two recent reports from the National Research council make recommendations on the development of a coordinated, cooperative system for collecting and analyzing ocean data. Documenting changes over time—akin to the Keeling Curve—is particularly important. Establishment of a global effort to regularly sample ocean chemistry and collect biological data such as the rate of coral growth or the abundance of various types of plankton at sites throughout the ocean would form the core of an ocean acidification research program.

Like climate change, ocean acidification is a global phenomenon with global consequences. Since further ocean acidification seems inevitable, adaptation to such change will be necessary. Work to investigate this problem and to develop ways to adapt will require cooperation and coordination at the international, national, regional, state, and local levels, as well as collaboration among scientists and researchers in a wide range of disciplines.



There's more online...

How did scientists become interested in studying ocean acidification?

How do animals behave when they encounter high carbon dioxide levels in the deep ocean?

What can crabs teach us about ocean ecosystems?

Discover the answers to these questions and much more at our website, http://nas-sites.org/oceanacidification where you'll find interviews with ocean scientists and photos illustrating their research.



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This booklet was prepared by the National Research Council based on the following reports:

Ocean Acidification: A National Strategy to Meet the Challenges of a Changing Ocean (2010)

Sponsored by: The National Oceanic and Atmospheric Administration, NASA, the National Science Foundation, and the U.S. Geological Survey.

Review of the Federal Ocean Acidification Research and Monitoring Plan (2013)

Sponsored by: NOAA and the National Science Foundation.

These and other reports are available from the National Academies Press, 500 Fifth Street, NW, Washington DC 20001; 800-624-6242; http://www.nap.edu.

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