Monitoring Ocean Carbon and Ocean Acidification

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Atmospheric carbon dioxide (CO_2) concentration has increased by 42% since the onset of the industrial revolution due to emissions from fossil fuel burning, cement production and land-use change, as reported in the WMO Greenhouse Gas Bulletin No. 10. As of 2010, the oceans had absorbed an estimated 155 ± 30 petagrams (Pg, 1 petagram = 1015 grams-force) of anthropogenic CO_2 [Khatiwala et al., 2013], the equivalent of 28% of the total CO_2 emissions during the same time. This factor limited the increase of CO_2 in the atmosphere. ==Although this ocean CO_2 uptake reduces climate change, it also comes with severe consequences for ocean chemistry and biology.==

Since the beginning of the industrial era, human activity has added 4 kg of carbon dioxide per day per person on average to the ocean. This

anthropogenic CO_2 reacts with water to form an acid. As atmospheric CO_2 continues to increase, more and more CO_2 enters the ocean, which reduces pH (pH is a measure of acidity, the lower the pH, the more acidic the liquid) in a process referred to as ocean acidification. Along with the increase in acidity (higher concentrations of hydrogen ions, H+), there is also a simultaneous decrease in concentrations of carbonate ion (CO_3^{2-}). Reductions in CO_3^{2-} reduce the chemical capacity of the ocean to take up further CO_2 while also degrading the ability of many marine organisms to produce and maintain shell and skeletal material.

Declines in surface ocean pH due to ocean acidification are already detectable and accelerating. Measurements gathered at biogeochemical time-series sites around the world reveal similar decreasing trends in ocean pH (reductions between 0.0015 and 0.0024 pH units per year), but datasets are only available for the last few decades. To estimate earlier changes, scientists have used both models and data-based extrapolations. Both approaches converge to indicate that since 1860, the pH of the ocean surface has dropped from 8.2 to 8.1, corresponding to a 26% increase in H+. The present rate of change can be put into context by looking at the paleoclimatic record. The current change appears to be the fastest in at least 300 million years, with the fastest known natural acidification event – occurring 55 million years ago – being probably ten times slower.

Under most emission scenarios, Earth system models project an acceleration in acidification at least until mid-century. When forced by the latest scenarios from the [Intergovernmental Panel on Climate Change (IPCC)](#), Earth system models that participated in Phase 5 of the [Coupled Model Intercomparison Project (CMIP5)](#) consistently indicated that reductions in surface pH will depend almost solely on the atmospheric CO_2 pathway that will be taken. Between 1850 and 2100, under the most conservative IPCC scenario for the trajectory of greenhouse gas concentrations, the decline in global-mean surface pH among models ranges from 0.12 to 0.14, a 36% increase in acidity; under the worst scenario, it ranges from 0.41 to 0.43, a 165% increase in acidity. But pH is not the only concern.

Enhanced ocean CO_2 uptake alters the marine carbonate system, which controls seawater acidity. As CO_2 dissolves in seawater it forms carbonic

acid (H_2CO_3), a weak acid that dissociates into bicarbonate (HCO_3^-) and hydrogen ions (H+). Increased H+ means increased acidity (lower pH). The rate of the ocean's acidification is slowed by the presence of CO_3^{2-}, which binds up most of the newly formed H+, forming bicarbonate. But that buffering reaction consumes CO_3^{2-}, reducing the chemical capacity of the near-surface ocean to take up more CO_2. Currently, that capacity is only 70% of what it was at the beginning of the industrial era, it may well be reduced to only 20% by the end of the century. The same models project that CO_3^{2-} concentrations will reach levels that are so low by mid-century that tropical coral growth may become unsustainable. In the cold polar oceans, where CO_3^{2-} is naturally less abundant, CO_3^{2-} concentrations have already begun to dip below a critical level in which waters become corrosive to the calcium carbonate ($CaCO_3$) mineral known as aragonite – the main component of shells, pearls, the exoskeleton of crustaceans, etc. By the end of the century, these corrosive conditions are predicted to expand throughout the polar oceans, causing concern for the fate of organisms such as pteropods – snails – that secrete aragonite to build their shells, and for food security, as many economically important organisms depend on availability of CO_3^{2-} to survive.

Despite remarkably consistent projections for changes in surface ocean pH, there is less agreement among models about the magnitude of subsurface changes. Furthermore, current Earth system models have coarse resolution and are not designed to study changes in the coastal ocean where other anthropogenic influences can also affect changes in pH.

Biological impacts

The potential consequences of ocean acidification on marine organisms are inherently complicated. The first studies concentrated on calcifying organisms, such as mollusks, corals, coralline algae, and some plankton, because their ability to build shell or skeletal material (via calcification) was shown to depend on the abundance of CO_3^{2-}. But there is another concern that changes in ocean pH could affect physiological processes that depend on stable intracellular chemistry. For example, marine organisms

would have to use more energy to regulate chemistry within their cells, which would result in less energy available for other biological processes such as growth or reproduction.

In the last decade, there has been an exponential growth in research and publications aimed at assessing the effects of elevated CO_2 on marine organisms. Doubling every 2 or 3 years, the number of annual publications focused on ocean acidification reached 540 in 2013 (IAEA OA-ICC bibliographic database). In 2013, Thompson-Reuters labelled ocean acidification the number one research front in Ecology and Environmental Sciences. Although encouraging, such growth has made it more and more difficult to synthesize results. Scientists have recently moved to using a statistical technique known as meta-analysis to quantitatively summarize results from hundreds of studies by extracting mean trends in responses and experimental variability about the means. One meta-analysis indicated that a pH reduction of up to 0.5 units lead to significant reductions in survival, calcification, growth and development, resulting in scarcity across a wide range of organisms, but that responses differ greatly between groups. Another meta-analysis demonstrated that some groups (echinoderms, bivalves, gastropods, and corals) show harmful effects at much lower CO_2 levels than others (crustaceans and cephalopods). The same study revealed that negative effects from acidification were also observed on the brain function and behaviour of fish; however, such studies have been limited only to coral reef fish.

Most of the research conducted to date has focused on responses at the individual level, but some have captured multiple organisms for weeks or months at a time in large containers (mesocosms) that either float in a water column or are fixed above bottom sediments. Mesocosm chemical conditions can be manipulated to match what is projected for the future, enabling researchers to study future potential effects of ocean acidification on the organisms tested. Another promising approach has been to study the long-term effects of acidification on entire ecosystems by exploiting natural sites where pure CO_2 has been found to bubble out of the seafloor. In one such study, near Mt. Vesuvius in the Bay of Naples, the CO_2-enriched, low-pH region showed much less biodiversity than adjacent regions, (e.g., many fewer calcifiers), and the shells that did exist were found to be more fragile. These long-term acidification ecosystems effects are consistent with what has been observed from short-term lab and field experiments on individual organisms.
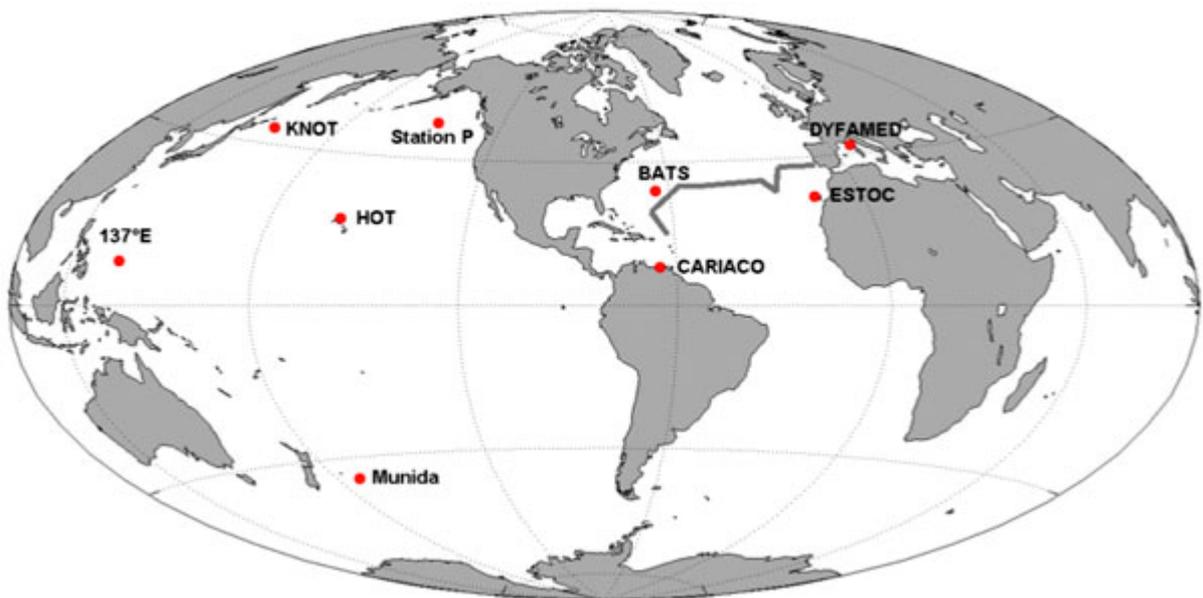
Feedbacks and other stressors

Ocean acidification is occurring along with other large-scale changes, such as warming, increasing stratification (in the ocean, stratification, or water density distribution, is governed mainly by variations in water temperature and salinity) and reductions in subsurface oxygen concentrations, all

related to climate change. Warming and stratification generally have little effect on acidification. Warming counteracts less than 10% of the change from CO_2 increase due to the carbonate chemistry and solubility of CO_2. But freshening from enhanced ice melt does worsen projected acidification, especially in locations where the rate of ice loss is significant, such as in the Arctic.

The largest feedback of ocean acidification on climate (via atmospheric CO_2) is chemical. Increases in CO_2 reduce CO_3^{2-}, which in turn reduces the ocean's capacity to buffer further increases in CO_2. For a 1 part per million (ppm) increase in atmospheric CO_2, today's associated ocean carbon uptake is only 70% of the capacity it had at the beginning of the industrial era. If atmospheric CO_2 doubles from its pre-industrial level to 560 ppm, ocean carbon uptake will only be at 40%, and if it reaches 800 ppm, it will only be 26%. Other feedbacks are uncertain but much smaller.

In coastal regions, there will also be additional stresses acting more locally, for example, eutrophication (excessive amounts of nutrients which stimulate rampant algae growth that deplete water of oxygen as they die and are eaten by bacteria), enhanced freshwater delivery and atmospheric deposition of anthropogenic nitrogen and sulfur. It remains a challenge to address how biological impacts differ when multiple stressors act together or individually.

Changes in ocean carbonate chemistry

The decreasing pH and increasing pCO_2 trends due to uptake of anthropogenic carbon are observable in the ocean. As anthropogenic CO_2 enters the ocean at its surface, the trends should be strongest there, but the signal tends to be masked by large temporal variability, mainly in the form of seasonal cycles, though both longer and shorter variability are present. Thus, time-series of relatively frequent observations and considerable length are needed to observe such trends. There are a few sustained ocean-time-series observations around the globe which provide the long – at least

10 years of measurements – temporally-resolved datasets needed to characterize changes in ocean biogeochemistry and ecosystems. The stations where these time-series are collected (see globe on page 50) are to be representative of the larger ocean regions.

At all locations, surface pCO_2 has increased and pH has decreased with time due to the rise of anthropogenic CO_2 (see graph below). To assess such change, we deseasonalized the surface data using the procedures recommended by the [WMO Global Atmosphere Watch (GAW)](#) and fitted them with a linear trend over the range of measurements to provide comparable decadal changes for each station. While there are seasonal and inter-annual variations in CO_2 dissolved in ocean water, pCO_2, this has increased at a rate of 1.3 to 2.8 microatmospheres (µatm) per year (for comparison, the atmospheric content increased at an average rate of 2.1 ppm per year during last 10 years), while ocean surface pH has decreased during the period of observations at an average rate of -0.0013 per year to -0.0024 per year, depending on the location. The rate of these changes depends not only on the chemistry, but also on other, both physical and biological, factors particular to each region. ESTOC, HOT and BATS (see figures on page 50), the rates of increase in surface pCO_2 match the rise in atmospheric CO_2 concentration - at DYFAMED those changes are impacted by the changes in the Mediterranean circulation. At CARIACO, change of surface pCO_2 was one of the highest measured, which can be attributed to warming of surface waters linked to a reduction in upwelling that leads in turn to lower biological productivity. The sub-polar time-series displayed some of the highest temporal variability, caused in part by the large seasonal differences in temperature and biological productivity.

While we focus here on surface observations, a large portion of the water column is being affected by the anthropogenic carbon uptake and associated changes in ocean chemistry. The largest signal of pCO_2 increase and ocean acidification is typically encountered in the surface ocean, but the main long-term control mechanism for ocean uptake of anthropogenic carbon is the transport from the surface mixed layer to the ocean. This is typically regulated by physical processes that "ventilate" the ocean. Currently, changes in deeper (below surface) ocean carbonate chemistry,

such as in dissolved carbon and pH trends, can only be assessed by repeatedly collecting measurements from ships across the same ocean sections. For that, a global-scale network of cruises must be repeated roughly every decade. The lower frequency of sampling is because the deeper ocean is much less variable than the ocean surface; however, corrections for small-scale variability, such as eddies, are still needed.

Currently, few conduct regular CO_2 observations in the ocean, and several major ocean regimes have no systematic carbon measurements at all. Maintaining sustained measurements in the ocean is a logistical challenge, particularly for developing countries, and this poses significant obstacles to quantify trends in ocean acidification and carbonate chemistry. Close monitoring of the ocean uptake of CO_2 is important for the understanding of the global carbon budget – Where does the fossil fuel CO_2 end up? Today, only a few ocean provinces are covered by systematic continuous observations, impeding understanding of temporal and spatial variability and trends of the carbon uptake by the ocean. CO_2 observations from ocean stations, together with surface and interior ocean measurements from ships, need to be sustained and extended.

Related Links

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