

OCB-OA: Measurements and observations

On this page:

[What evidence suggests that OA is happening and results from human activity?](#)

[How do OA's effects relate to those of other human activities?](#)

[Does "ocean" acidification also affect bodies of fresh water, like lakes?](#)

[Why is the current rate of change in pH concerning?](#)

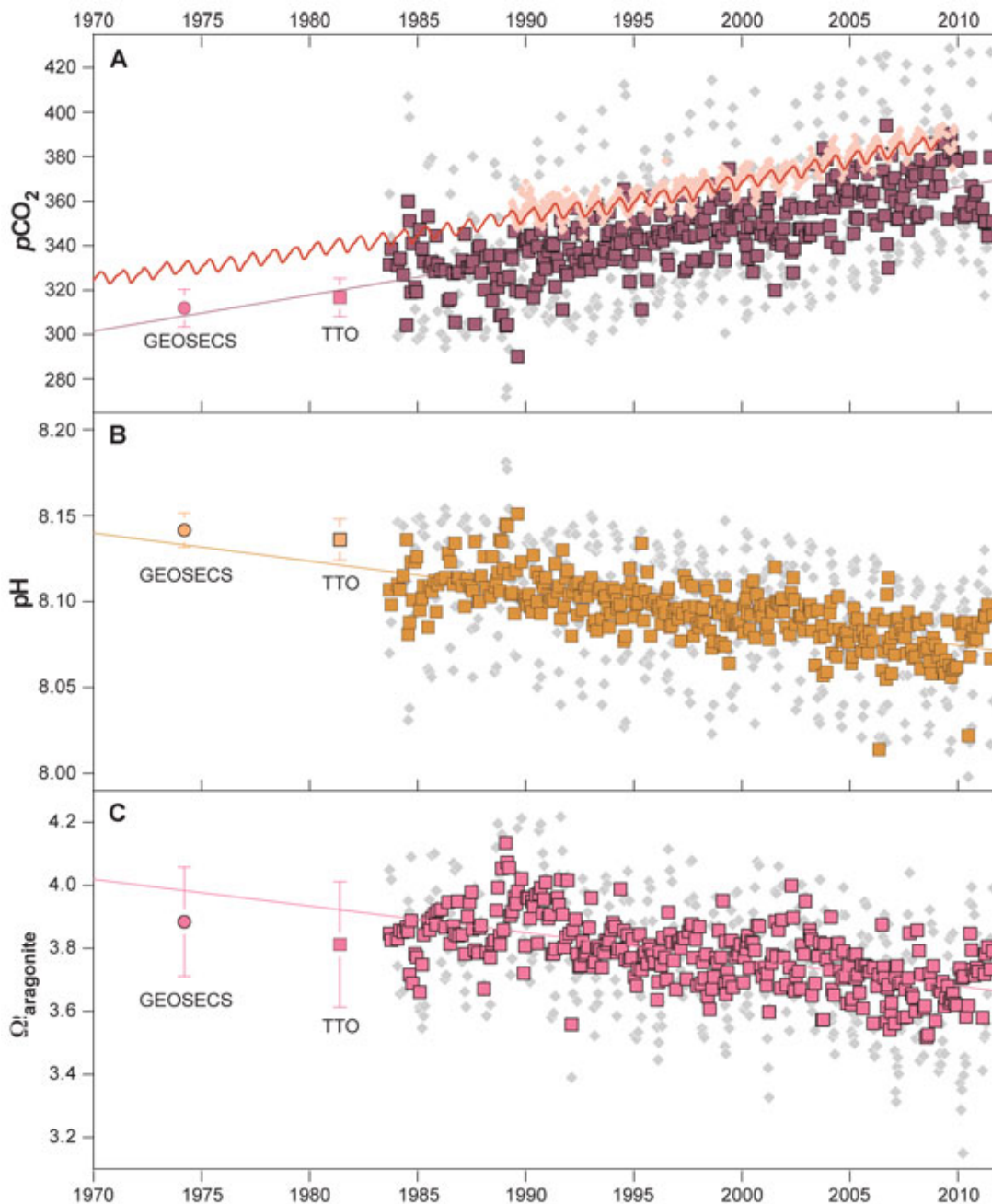
[How certain are we about ocean acidification?](#)

What evidence suggests that OA is happening and results from human activity?

Basic/Intermediate: Semi-continuous measurements of surface seawater acidity have been made in the Pacific and Atlantic Oceans for the past 20-30 years. These datasets have shown that the hydrogen ion concentration has been increasing. The observed increase in acidity agrees with estimates of the oceanic uptake of CO₂ that comes from human activities. —C. Turley, J. Kleypas, N. Bates

Advanced: Scientists have collected semi-continuous records of seawater carbon dioxide (CO₂) content and pH in the Pacific and Atlantic Oceans over the last 20-30 years. These ocean time-series records from near the islands of Hawaii (Dore et al., 2009), Bermuda (Bates et al., 2012), Iceland (Olafsson et al., 2009) and the Canary Islands (González-Dávila et al., 2010) show that seawater pCO₂ (i.e., the partial pressure of CO₂ in seawater) of surface waters is mirroring the increase in atmospheric CO₂ concentrations and that ocean pH is decreasing. There is no doubt the increase in atmospheric CO₂ originates from human activity as the majority of this gas is produced from burning of fossil fuels, which contains no ¹⁴C and is depleted in ¹³C causing a dilution of the atmospheric ¹⁴CO₂ and ¹³CO₂ commonly called the Suess effect (Tans et al., 1979). Over the last 40 years, seawater pCO₂ has increased by more than 20% near Bermuda (Bates et al., 2012) (Figure 4A) due to the uptake of CO₂ from the atmosphere (Sabine et al., 2004). Other time-series records (Dore et al., 2008; Olafsson et al., 2009; González-Dávila et al., 2010; Byrne et al., 2010) show similar increases in the CO₂ content of seawater in accordance with rising atmospheric CO₂ concentrations. While the ocean remains mildly alkaline (pH>7) at present, the uptake of CO₂ changes the chemical balance of seawater resulting in gradual acidification of seawater. As the CO₂ content of seawater increases, the pH, carbonate ion concentration [CO₃²⁻] and saturation state of calcium carbonate (CaCO₃) minerals such as calcite and aragonite decreases. Ocean time-series have indeed confirmed that the pH and saturation state for aragonite ($\omega_{\text{aragonite}}$) have decreased with observations near Bermuda extending back nearly forty years (Figure 4B,C). Similar decreases have been recorded in the Pacific (Dore et al., 2009; Byrne et al., 2010) and the Atlantic Oceans (Olafsson et al., 2009; González-Dávila et al., 2010). —C. Turley, J. Kleypas, N. Bates

Figure 4: Time series data from the surface ocean. Time-series of atmospheric and ocean pCO₂, pH and aragonite saturation states from Bates et al., 2012, Biogeosciences, doi:10.5194/bg-9-2509-2012. (a) Time-series of atmospheric pCO₂ (ppm) from Mauna Loa, Hawaii (red line), and Bermuda (pink symbols), and surface ocean seawater pCO₂ (µatm) at the Bermuda Atlantic Time-series Study (BATS) site off Bermuda. Observed (grey) and seasonally detrended (purple) surface ocean seawater pCO₂ levels are shown. Earlier seawater data from the GEOSECS (Geochemical Sections) and TTO (Transient Tracers in the Ocean) expeditions in the North Atlantic Ocean are also shown in this and following panels. (b) Time-series of surface ocean seawater pH at the BATS site off Bermuda. Observed (grey) and seasonally detrended (orange) seawater pH are shown. (c) Time-series of surface ocean aragonite saturation state ($\omega_{\text{aragonite}}$) for calcium carbonate at the BATS site off Bermuda. Observed (purple) and seasonally detrended (purple line) seawater $\omega_{\text{aragonite}}$ are shown.



How do OA's effects relate to those of other human activities?

Basic: Many human activities and the products of these activities, like acid rain and nutrient runoff, change seawater chemistry and acidity locally. But ocean acidification is happening around the world, and it is due to one cause: human emissions of CO₂.

Intermediate: Other human activities certainly are affecting seawater chemistry and the ocean's acid-base balance, but not nearly to the extent of atmospheric CO₂-driven acidification. Acid rain, which contains sulfuric and nitric acids originally derived from fossil fuel combustion, falls on the coastal oceans. The impact of acid rain on surface ocean chemistry may be important locally and regionally, but it is small globally and its total effects equal only a few percent of the changes driven by rising atmospheric CO₂. Coastal waters are also affected by excess nutrient inputs, mostly nitrogen, from agriculture, fertilizers and sewage. The resulting chemical changes lead to large plankton blooms, and when these blooms collapse and sink below the surface layer the resulting respiration from bacteria leads to a drawdown in seawater oxygen and an increase in CO₂, which decreases pH and calcium carbonate saturation state even more in subsurface coastal waters.

One of the major differences between OA and these types of human effects is that OA's influence is truly global in scale, affecting pH-sensitive and calcifying organisms in every ocean basin from the equator to the poles. At present, the effects are restricted primarily to the upper 200-500m of the ocean, but every year the effects penetrate to deeper depths. Many of the other impacts of human activities are more local in nature.—S. Doney, C. Langdon, J. Mathis, R. Feely

Does "ocean" acidification also affect bodies of fresh water, like lakes?

Basic: Fresh water also takes up carbon dioxide from the atmosphere, which can lower pH. At the same time, lakes and rivers are acidified by acid rain, nutrient runoff, and other human-caused pollution. Freshwater does not contain the "salts" that seawater has which can "buffer" changes in pH. This means that fresh water pH varies over a larger range than seawater, but progressive acidification is also possible.

Intermediate: Fresh water takes up carbon dioxide from the atmosphere through the same mechanism as seawater, and carbon dioxide in fresh water reacts with water molecules in the same chemical reactions as in seawater. But fresh water alkalinity tends to be much lower than that of seawater, so pH changes in bodies of fresh water tend to be greater, because the newly released H⁺ ions are not being buffered by as many bicarbonate ions. Therefore, aquatic life in fresh water can sometimes be more accustomed to wider pH changes than organisms in salt water. However, the examples of damage to fresh water lakes in the 1980s because of acid rain (caused by deposition of nitrogen and sulfur from fossil fuel use and industry) showed that bodies of fresh water can become progressively acidified and this process damages aquatic ecosystems. Fresh water ecosystems may also be experiencing nutrient loading that increases the rates of photosynthesis and respiration there, magnifying CO₂ drawdown and release. Local acidification from these other large-amplitude processes may mask atmospheric CO₂-driven acidification until longer time-series records are collected.—S. Alin

Advanced: During the 1980s, a large body of paleolimnological and ecological research demonstrated that freshwater ecosystems in North America and Europe had experienced marked declines in pH in response to increasing atmospheric deposition of acidic nitrogen and sulfur species ("acid rain") through the 20th century (see, for example, special issues on acid deposition and ecosystem impacts

in *Water, Air, and Soil Pollution* (1986, vol. 31[3–4] and 1987, vol. 35[1–2]), *Ambio* (1993, vol. 22[5]), and *Journal of Paleolimnology* (1990, vol. 3[3]). The magnitude of the pH change observed in lakes was related to both the magnitude of acid deposition as well as the underlying watershed geology, with lakes in poorly-buffered granitic watersheds showing the strongest pH changes and those in relatively well-buffered carbonate-dominated watersheds showing limited or undetectable declines in freshwater pH values in response to 20th century atmospheric acid deposition (Driscoll et al. 2001 and references therein). This historical "experiment" demonstrated that acidic atmospheric inputs can acidify freshwater systems. A few differences between acidic N and S deposition and a steadily increasing atmospheric CO₂ burden are worth considering with respect to projecting potential CO₂-driven acidification on freshwater systems; while the N and S species associated with acid rain are stronger acids, their atmospheric lifetimes are much shorter, reducing their geographic dispersion. Also, emissions of compounds associated with acid rain have been greatly reduced in many regions. Thus, any CO₂-driven acidification of freshwater systems may be more gradual, but also may not be reversible on a similarly short timescale.

The freshwater scientific literature also shows that most lakes and rivers tend to be supersaturated with CO₂ at the surface in most observations, so scientists typically think of freshwater systems as outgassing CO₂, rather than taking up CO₂ from the atmosphere (e.g. Cole et al. 1994, Richey et al. 2002, Alin & Johnson 2007, Alin et al. 2011, Butman & Raymond 2011). However, increasing atmospheric CO₂ can still result in the acidification of freshwater ecosystems by decreasing the air-water gradient of CO₂, which exerts a major control on the rate of outgassing of CO₂ from aquatic ecosystems. Finally, additional factors may influence whether anthropogenic CO₂-driven acidification will affect freshwater ecosystems: 1) Many freshwater ecosystems have experienced eutrophication as a result of other anthropogenic inputs (or other environmental stressors, such as species invasions) that may mask chemical changes due to CO₂-driven acidification (e.g. Trolle et al. 2012, Barbiero et al. 2006). 2) Many freshwater organisms may have broader tolerance ranges for environmental acidity (or other chemical factors), as a result of having evolved in less well-buffered ecosystems than the marine environment.—S. Alin

Why is the current rate of change in pH concerning?

Basic: Today's rate of pH change in the ocean is concerning because it is thought to be ten to a hundred times faster than any time in the past 50 million years. Today's change may be unlike any previous ocean pH change in Earth's history.

Intermediate: The current rate of decrease in pH is thought to be ten to a hundred times faster than anytime in the past 50 million years, and it may be unprecedented in Earth's history. Marine life that exists today has never experienced such a rapid change in average pH, and many important species like corals, oysters, mussels, clams, crabs and plankton may be adversely impacted and may not have sufficient time to evolve mechanisms to cope with this changing chemistry. During a much slower acidification event that occurred 55 million years ago (the Paleocene-Eocene Thermal Maximum), there was a mass extinction of marine life, especially in benthic species.—S. Alin

How certain are we about ocean acidification?

Basic: It is certain that atmospheric carbon dioxide is causing seawater pH to decrease. The biological effects of this change are less certain, because ocean acidification has both big and small effects on marine organisms.

Intermediate: There is no argument that seawater chemistry is changing. The root cause is rising atmospheric CO₂ released by human combustion of fossil fuels and deforestation. These changes are well documented by observations from repeat research cruises conducted throughout the world oceans over several decades, and from a number of time series data collection stations in the major ocean basins. There is less certainty about the possible biological impacts of ocean acidification, but this primarily is because different groups of marine organisms express a wide range of sensitivity to changing seawater chemistry. Some of the different responses exhibited by members of the same species in lab studies may simply reflect the natural variability in wild populations, because specimens have been collected from different areas, populations, or strains. Nevertheless, there is broad agreement among the scientific community that ocean acidification is occurring and that it likely will have significant effects, some positive and some negative, on a large number of marine organisms. — S. Doney, S. Widdicombe, J. Mathis, R. Feely

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