Print

OCB-OA: Introduction to OA

On this page:

What is ocean acidification?
What is the difference between pH and acidity?
Why are scientists concerned about such a seemingly small change in ocean pH?
Common misunderstandings about pH and ocean acidification
Ocean acidification chemistry 101

What is ocean acidification?

Basic: Ocean acidification (OA) is a long-term decrease in the pH of ocean water. Wastes from some human activities, like carbon dioxide (CO_2) from fossil fuel use, are causing OA around the world today.

Intermediate: International experts define ocean acidification (OA) as a decrease in ocean pH over decades or more that is caused primarily by uptake of CO_2 from the atmosphere. Because human activities are releasing CO_2 into the atmosphere very quickly, the ocean is taking up CO_2faster today than it has in the past. This is causing global ocean chemistry to change more quickly than ocean systems can handle.

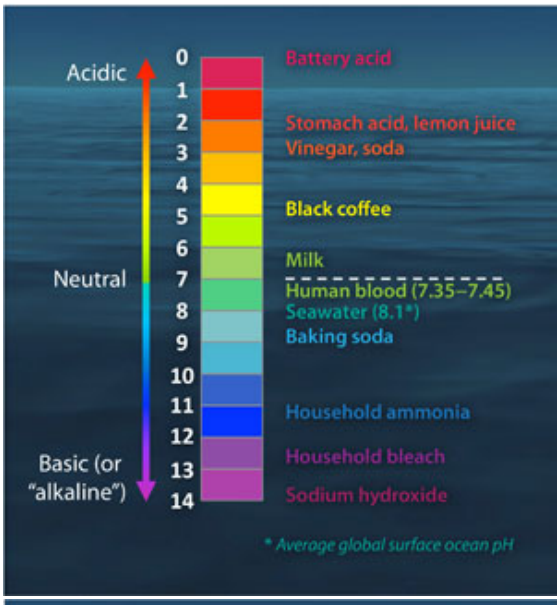
Advanced: The Intergovernmental Panel on Climate Change (IPCC) Workshop on Impacts of Ocean Acidification on Marine Biology and Ecosystems defines ocean acidification (OA) as *"a reduction in the pH of the ocean over an extended period, typically decades or longer, which is caused primarily by uptake of carbon dioxide (*CO_2*) from the atmosphere, but can also be caused by other chemical additions or subtractions from the ocean."* Ocean acidification can also be caused by other chemical additions or subtractions from the oceans that are natural (e.g., increased volcanic activity, methane hydrate releases, long-term changes in net respiration) or human-induced (e.g., release of nitrogen and sulphur compounds into the atmosphere). Anthropogenic ocean acidification refers to the component of pH reduction that is caused by human activity. When this document refers ocean acidification, it primarily focuses on the anthropogenic portion caused by atmospheric carbon dioxide released by human industrial development. —R. Feely

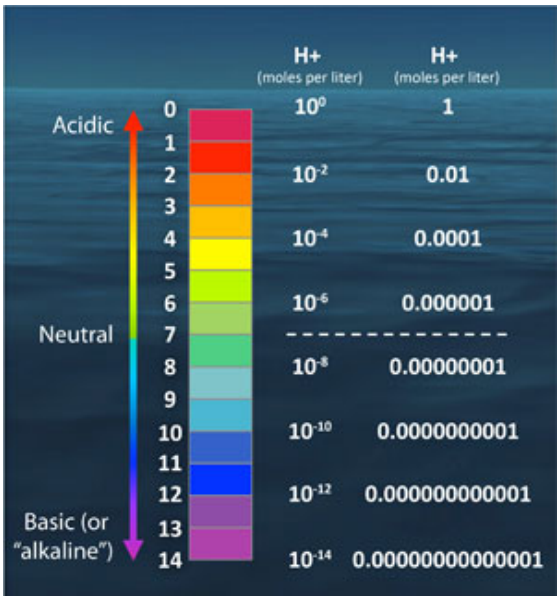
What is the difference between pH and acidity?

Basic: pH is the scale on which acidity is measured, and so it describes how much acid is in a liquid. This is similar to how degrees Celsius are used to measure temperature. The amount of hydrogen ions in a liquid determines how acidic the liquid is. But hydrogen ions can be present in a range from 1 down to extremely small numbers (0.00000000000001) (Figure 1). To avoid error from writing down all the zeros, scientists use a logarithmic scale and call this scale pH. Because it is logarithmic, one step up or down on the pH scale is the same as multiplying or dividing by ten on the hydrogen ion scale. (See Figure 1)

Intermediate: “Acidity” is the concentration of hydrogen ions (H^+) in a liquid, and pH is the scale on which this concentration is generally measured. The amount of hydrogen ions in a liquid determines how acidic the liquid is. Some common examples are shown in Figure 1. The concentration of hydrogen ions can vary across many multiples of ten, or “orders of magnitude”—from 1 to 0.00000000000001 moles per liter. Because it is difficult to write down all the zeros accurately, we express acidity on a logarithmic scale called the pH scale. Because the pH scale is logarithmic ($pH = -\log[H^+]$), one step up or down on the pH scale corresponds to multiplying or dividing by ten on the hydrogen ion scale (Figure 1).—S. Alin, H. Findlay

Figure 1: pH measures the acidity of a liquid. (a) The pH scale, with examples of common solutions and their pH values. (b) The pH scale is logarithmic, meaning that a change of one pH unit represents an order of magnitude change in the hydrogen ion (H+) concentration. Here the hydrogen ion concentrations are shown in both scientific notation and decimal form. (c) The percent change in acidity with falling pH values is calculated as the percent change in hydrogen ion (H+) concentration relative to the starting concentration. In this figure, the concentrations of H+ ions are shown in decimal notation (middle column) for every tenth of a pH unit from 8.2 down to 7.2. The numbers in the percent change in acidity column reflect the percent increase in H+ concentrations between the starting point (8.2) and each successive number. Average global surface ocean pH has already fallen from a pre-industrial value of 8.21 to 8.10, corresponding to an increase in acidity of 28.8%. Values of 7.8–7.9 are expected by 2100, representing a 100–150% increase in acidity.





pH	H+ (moles per liter)	change in acidity
7.2	6.3×10^{-8}	+900%
7.3	5.0×10^{-8}	+694%
7.4	4.0×10^{-8}	+531%
7.5	3.2×10^{-8}	+401%
7.6	2.5×10^{-8}	+298%
7.7	2.0×10^{-8}	+216%
7.8	1.6×10^{-8}	+151%
7.9	1.3×10^{-8}	+100%
8.0	1.0×10^{-8}	+58%
8.1	7.9×10^{-9}	+26%
8.2	6.3×10^{-9}	

Why are scientists concerned about such a seemingly small change in ocean pH?

Basic: Many organisms on land and in the oceans are very sensitive to small changes in pH. Marine organisms that are used to stable seawater chemistry will experience changing conditions because of ocean acidification. Research shows that this change could harm certain species.

Intermediate: Many organisms are very sensitive to seemingly small changes in pH. For example, in humans, arterial blood pH normally falls within the range 7.35–7.45. A drop of 0.2-0.3 pH units in human blood pH can result in rather profound health consequences, including seizures, heart arrhythmia, or even coma (a process called "acidosis"). Similarly, many marine organisms are very sensitive to either direct or indirect effects of the change in acidity (or H^+ concentration) in the marine environment. Fundamental physiological processes such as respiration, calcification (shell/skeleton building), photosynthesis, and reproduction respond to the magnitude of changes in CO_2 concentrations in seawater, along with the resultant changes in pH and carbonate ion concentrations that are expected over the next century. —S. Alin

Common misunderstandings about pH and ocean acidification

Misunderstanding: Percent change in acidity isn't the same as percent change in pH.

When acid is added to a solution, the concentration of hydrogen ions (acidity) increases, and the pH decreases. People frequently confuse pH with acidity—pH is the scale on which acidity is expressed, but it is not the same as acidity. We can correctly compare the acidity at two different pH values by expressing the relative percentage change of the H^+ concentration between the two pH levels, as in Figure 1. For example, the present pH decrease of 0.11 from ocean acidification equals a 28.8% change in acidity (H^+ concentration) when calculated in this way.

Misunderstanding: Liquids with high pH values don't have acidity; they only have alkalinity.

pH values above 7 are commonly referred to as "basic" or "alkaline." These common terms can be confusing, because pH values do not

directly measure the concentration of bases in the solution. pH values above 7 still measure the *acidity* of that liquid, but in that case, the liquid's acidity (H^+ concentration) is very, very low (less than 10^{-7} (or 0.0000001) moles per liter, to be specific). High pH values also do not measure *alkalinity*. Alkalinity actually measures the acid neutralization capacity of seawater. To determine the alkalinity of a solution, a separate, detailed laboratory analysis must be done. It is incorrect to characterize the change in hydrogen ion concentration as a decrease in alkalinity.

Misunderstanding: Calling this phenomenon "ocean acidification" when surface seawater will remain "basic" under future emissions scenarios is alarmist.

Just as we describe an increase in temperature from -20°C to 0°C as warming, even though neither the starting nor the ending temperature is "warm," the term "acidification" describes the increase in the level of acidity in the global oceans. Both "warming" and "acidification" do not refer to absolute end points. When CO_2 is added to seawater, it reacts with water to form carbonic acid (H_2CO_3). Therefore, acid is being added to seawater, which is acidifying it.

Misunderstanding: Because natural pH variability is greater than long-term pH change, ocean acidification is nothing to worry about.

Many scientists have observed that natural variability in seawater acidity (and thus pH) over days, weeks, and months is strong. This short-term variability can be much larger than the recent and forecasted changes in acidity that will take place over decades to centuries because of ocean acidification. The reason that scientists are concerned about this slow, long-term change is that it changes the environmental baseline. This means that the natural variability in acidity due to photosynthesis, respiration, upwelling, and many other processes will be overlaid on an ever-increasing average concentration of H^+. Even though this change in the baseline is slow and steady relative to human time scales, this change is very fast relative to geological time scales. Ocean acidification is more rapid than any change in ocean acidity documented over the last 300 million years, so organisms that tolerate a certain narrow range of conditions may encounter increasingly stressful, or even lethal, conditions in the coming decades. (Also see Individuals and Ecosystems section.)

Ocean acidification chemistry 101

—S. Alin

Carbon dioxide (CO_2) naturally exchanges between the atmosphere and the surface of the ocean. The CO_2 content of the upper ocean has been increasing in parallel with the CO_2 in the atmosphere since the Industrial Revolution, with the rate of increase becoming more rapid over the last half century as human-caused CO_2 emissions have accelerated.

When CO_2 dissolves in seawater, it has several consequences for the chemistry of the seawater. Some of the CO_2 that dissolves in seawater will remain in the form of a dissolved gas that can freely exchange with the atmosphere and be taken up directly by marine plants and phytoplankton. This fraction is usually referred to as dissolved or aqueous carbon dioxide, and it is typically expressed as the partial pressure of CO_2 [abbreviated pCO_2, in units of microatmospheres (µatm)].

Some of the molecules of CO_2 dissolved in seawater combine with molecules of water (H_2O) to form a weak acid, called carbonic acid (H_2CO_3), the same acid that is in carbonated beverages like seltzer water (Figure 2). This reaction can be depicted as:

CO_2 + H_2O ? H_2CO_3

carbon dioxide — water — carbonic acid

When acids are dissolved in water, they "dissociate," which means that they break apart into their constituent ions, in this case a hydrogen ion (H^+) and a bicarbonate ion (HCO_3^-, as is found in baking soda).

H_2CO_3 ? H^+ + HCO_3^-

carbonic acid — hydrogen ion — bicarbonate ion

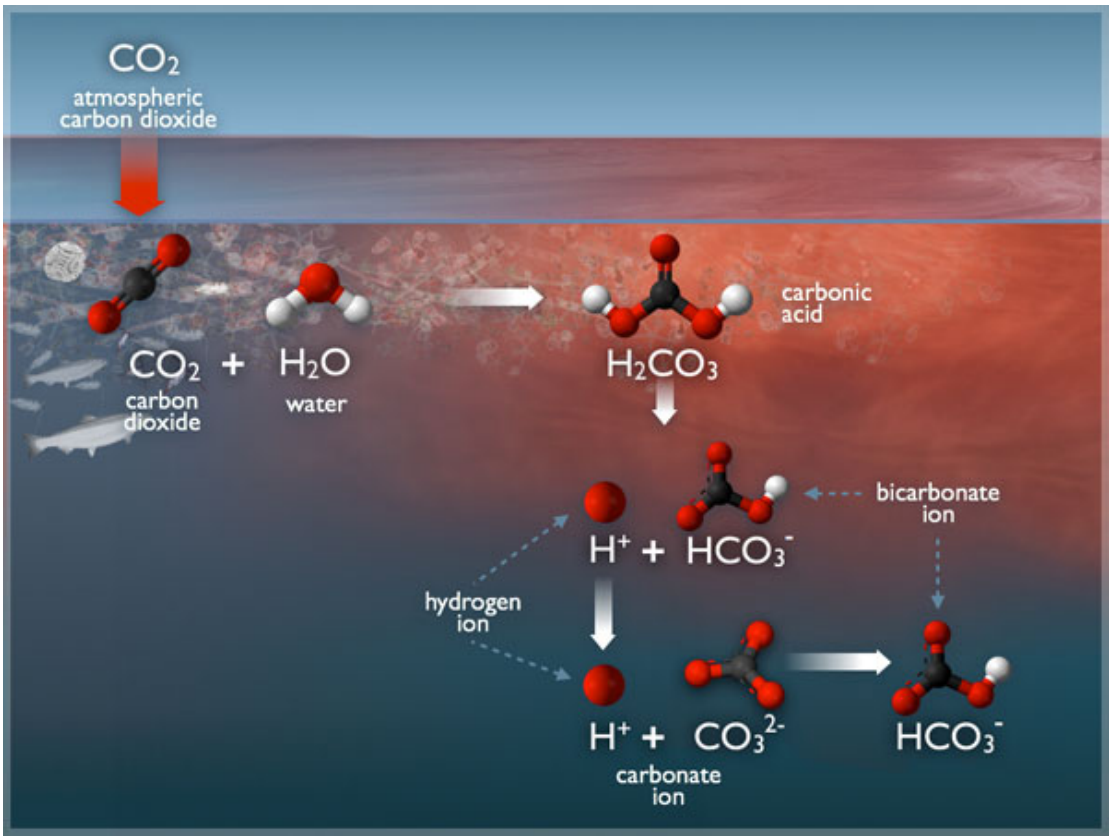
At typical seawater pH values, some of the hydrogen ions will remain as hydrogen ions, thus increasing the acidity and lowering the pH of the seawater. However, most of the hydrogen ions created through the previous reaction will subsequently combine with carbonate ions (CO^{2-}) to form additional bicarbonate ions, thereby reducing the pool of carbonate ions.

H^+ + CO_3^{2-} ? HCO_3^-

hydrogen ion carbonate ion bicarbonate ion

In summary, the chemical changes in seawater resulting from increased atmospheric CO_2 concentrations include *increases* in the concentrations of dissolved (or aqueous) carbon dioxide, hydrogen ions, and bicarbonate ions, and *decreases* in the carbonate ion concentration and pH.

Figure 2: Chemistry of ocean acidification. As carbon dioxide (CO_2) dissolves into seawater (left), it creates carbonic acid (right). Through a series of chemical reactions, carbonic acid releases hydrogen ions (H^+), which decreases seawater pH, and decreases the concentration of carbonate ions (CO_3^{2-}), which provide chemical building blocks for marine organisms' shells and skeletons.



Impacts of changes in seawater chemistry on biology

Organisms may be affected directly or indirectly by changes in the concentrations of any of the forms of inorganic carbon (CO_2, HCO_3^-, CO_3^{2-}) discussed above, as well as by acidity levels. However, most research to date has focused on characterizing the response of organisms that build hard parts out of calcium carbonate—such as shells, skeletons, or tests—to decreases in the abundance of carbonate ions. Many organisms synthesize hard structures out of various forms of the biomineral calcium carbonate, including aragonite, calcite, and amorphous calcium carbonate. To build these solid structures, they must extract dissolved calcium and bicarbonate ions from seawater:

Ca^2 + $2HCO_3^-$? $CaCO_3$ + CO_2 + H_2O

calcium ion (dissolved) bicarbonate ion (dissolved) calcium carbonate (solid) carbon dioxide (gas) water (liquid)

The net effect of forming calcium carbonate is to emit more carbon dioxide into the water, which creates carbonic acid and reduces the

pool of carbonate ions as described above. For simplicity, many chemists sum together the above chemical reactions and write the formation of calcium carbonate as:

Ca^{2} + CO_3^{2-} ? $CaCO_3$

calcium ion (dissolved)	carbonate ion (dissolved)	calcium carbonate (solid)

To compare how easy or difficult it should be for organisms to build their calcium carbonate hard parts in waters with different chemistries, scientists use calcium carbonate saturation states (represented by the symbol ? (omega)) as an index:

$?_{form}$ = $[Ca^{2+}]$ x $[CO_3^{2-}]$ ÷ K_{sp}'

saturation state for a specific form of $CaCO_3$	calcium ion concentration	carbonate ion concentration	solubility factor under environmental conditions

In the above equation, *form* refers to the specific crystal type of calcium carbonate the organism makes. Different crystal forms include aragonite, calcite, or amorphous calcium carbonate. The term K_{sp}' is the "apparent solubility product." This simply indicates the solubility of that type of calcium carbonate at the actual temperature, salinity, and depth of interest. At omega values greater than one, calcium carbonate is supersaturated, meaning that shell-building should be relatively easy and calcium carbonate structures will stay intact. At omega values below one, conditions are undersaturated, meaning that shell-building would be more difficult and the seawater would naturally break down that type of solid calcium carbonate. A value of one for omega indicates that the saturation state is at a threshold between solid calcium carbonate being favored (above one) and dissolved ions being favored (below one).

However, it is critical to note that saturation state is a chemical index, and different organisms have a wide range of tolerances to saturation states. Scientists are just beginning to learn more about the biological thresholds of different species. Although knowing the exact value of the saturation state will not necessarily help predict how a particular organism will respond, saturation state is a helpful chemical measure that can allow scientists to compare sensitivity across species and in varied environments. Having such a universal measure is key for letting us understand and predict how species that are ecologically or economically important will be affected by ocean acidification.

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