

Kyle Angle is a doctoral candidate and **Vicki Grassian** is a distinguished professor, both at the University of California, San Diego, in La Jolla. **Andrew Ault** is an associate professor at the University of Michigan in Ann Arbor.



The rapid acidification of sea spray aerosols

Kyle J. Angle, Vicki H. Grassian, and Andrew P. Ault

The ocean has a nearly neutral pH. But the same can't be said of the microscopic drops churned up from its surface.

Atmospheric aerosols, tiny solid and liquid particles suspended in the air, have profound effects on the world. High in the atmosphere, they seed clouds and thus influence weather and climate. Closer to ground, aerosols in the US have been regulated for many years by the Environmental Protection Agency because breathing high aerosol concentrations is connected to negative effects on the lungs, brain, and tissues. And aqueous aerosols produced by speech and coughing have made the news in the past two years as the dominant route of the spread of SARS-CoV-2.

With oceans covering 70% of Earth's surface, sea spray aerosols (SSAs) are one of the most prevalent types of atmospheric aerosols. More than just salt water, SSAs contain a rich variety of compounds, including fatty acids and other organic molecules that originate from living creatures, in greater concentrations than the bulk ocean. The chemical makeup of SSAs is important because it affects their role in climate—only certain types of aerosols can efficiently seed clouds—and human health.

A fundamental chemical property is acidity. For human health, aerosol acidity is particularly important because more acidic aerosols are correlated with increased lung stress.

Aerosol acidity also affects solid material solubility, aerosol reactivity, and gas transfer into and out of particles. For example, sulfur dioxide oxidization and conversion to particulate sulfate—a potential cloud seed—occurs at the interface of acidic aerosols only. Biogenic molecules in SSAs include active enzymes that function differently at acidic pH levels. Fatty acids in acidic SSAs can become protonated and act as surfactants. Despite the importance of aerosol pH, only recently have scientists begun to devise ways to measure it.

Studying sea spray with a smartphone

Fortunately, the same pH strips used in first-year chemistry labs can be used to measure aerosol pH! The strips are ordinarily thought of as a semiquantitative tool for estimating pH based on the color they turn when dipped into a bulk solution. But as one of us (Ault) and colleagues at the University of Michigan recently found, more detailed analysis can quantitatively relate color and acidity. By depositing aerosol particles onto pH paper and photographing the paper with a smartphone, one can calculate the acidity from the red, green, and blue values in the image. We found that pH decreases with size for atmospheric ammonium sulfate aerosols.

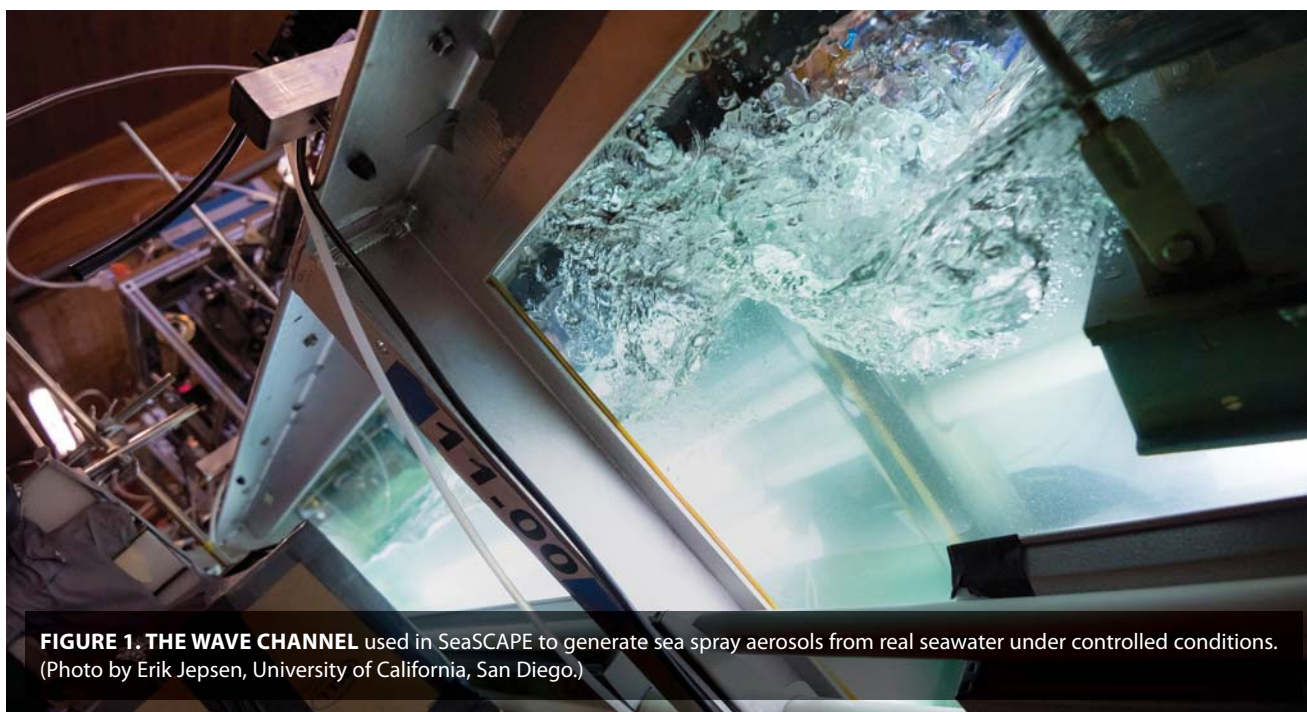


FIGURE 1. THE WAVE CHANNEL used in SeaSCAPE to generate sea spray aerosols from real seawater under controlled conditions. (Photo by Erik Jepsen, University of California, San Diego.)

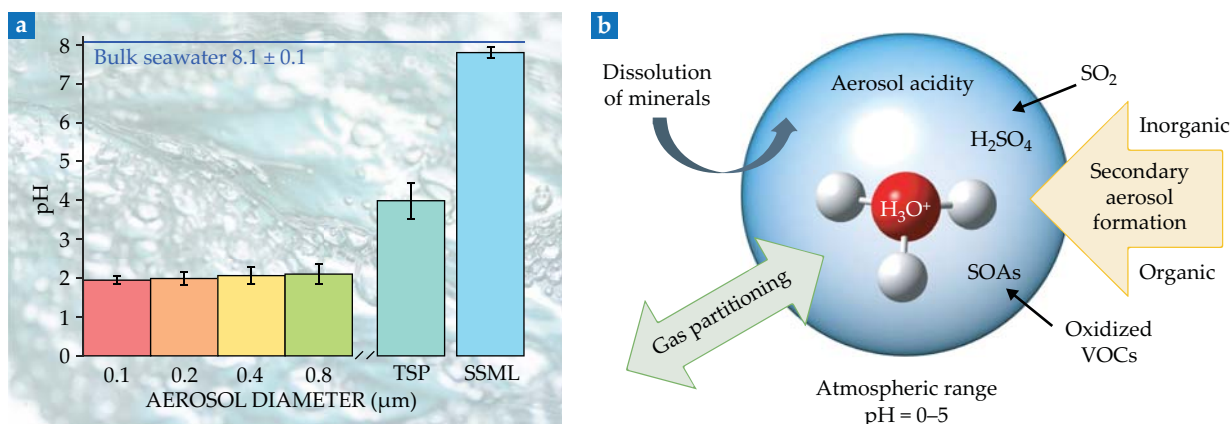


FIGURE 2. ACIDITY of sea spray aerosols (SSAs). **(a)** The pH of size-separated SSAs is shown by the four leftmost bars. Submicron SSAs are found to be orders of magnitude more acidic than the total suspended particles (TSP, mainly a measure of aerosols larger than 1 μm), the sea surface microlayer (SSML, the topmost layer of the ocean), and the ocean itself. (Background photo by Nigella Hillgarth.) **(b)** Aerosol acidity influences various phenomena, including the oxidation of sulfur dioxide into sulfuric acid, the dissolution of minerals, gas partitioning into and out of the aerosol, and the chemical reactions that produce secondary organic aerosols (SOAs) from volatile and semi-volatile organic compounds (VOCs) in the atmosphere.

Acidic aerosols have been observed in various contexts and by various methods, and researchers have found that aerosols that experience longer atmospheric aging often have lower pH levels. Inspired by Ault's simple and inexpensive way to determine aerosol pH, the other two of us (Angle and Grassian) at the University of California, San Diego, took on an unsolved question: What is the pH of *fresh* SSAs?

Seawater has a pH of 8.1 (a value that is slowly decreasing as more and more carbon dioxide dissolves in the ocean), so one might expect newly created SSAs to have the same pH. But as SSAs are emitted from the ocean surface when waves crash and bubbles burst, they quickly mix with the surrounding air, which contains gases and other aerosols. It is therefore difficult to determine their native acidity, and past studies were unable to distinguish between fresh and aged SSAs.

The solution was to mimic sea spray in a controlled environment. Measurements were performed during a sampling project called SeaSCAPE (Sea Spray Chemistry and Particle Evolution) carried out by the NSF Center for Aerosol Impacts on Chemistry of the Environment (CAICE). At the Hydraulics Laboratory at the Scripps Institution of Oceanography, the CAICE team filled a 33-meter-long glass tank, shown in figure 1, with real seawater. Aerosols were generated by a specialized paddle and were airborne for less than two minutes before being collected onto pH paper.

The results are shown in figure 2, with the measured pH plotted as a function of the aerosol-particle diameter. As the figure shows, even freshly created SSAs are far more acidic than the bulk ocean. Just as in a bulk solution, acidity in aqueous aerosols is measured on a logarithmic pH scale: A decrease in one pH unit means a 10-fold increase in acidity. The smallest aerosols, at pH 2, become a million times more acidic than bulk seawater in just two minutes!

Acid-base chemistry, microscopically

The rapid acidification of SSAs is likely due to several reasons, including their interaction with acidic atmospheric gases. Just as dissolved CO_2 acidifies the ocean, atmospheric CO_2 , SO_2 , and even hydrogen chloride produced by chemical reactions with

salts in SSAs can all lead to more acidic aerosols. In fact, acidic gases are a major factor in controlling atmospheric pH levels in general. The gases dissolve in fog and cloud droplets, making them slightly acidic, and the effect is amplified for aerosols because of their greater surface-to-volume ratio.

If acidic gases create more acidic aerosols, one might think that alkaline gases such as ammonia—released into the atmosphere from ammonium nitrate fertilizer—could counteract the effect. Unfortunately, intuitions about acid-base balance do not necessarily hold for atmospheric aerosols. A recent publication in *Science* (see "Additional resources") demonstrated that ammonia can actually buffer aqueous aerosols and maintain their acidic pH.

Exciting progress has been made in recent years. But it remains an outstanding analytical challenge to measure the pH of individual SSAs on the fly in the real atmosphere. If portable, streamlined aerosol acidity sensors can be developed, they would enable more accurate assessments of aerosols as well as air quality.

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Additional resources

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- G. Zheng et al., "Multiphase buffer theory explains contrasts in atmospheric aerosol acidity," *Science* **369**, 1374 (2020).
- V. Grassian, "What's really in the air we breathe," TEDxSanDiego, www.youtube.com/watch?v=yWv18fV6tdQ.
- "Sea spray: Complex chemistry with big effects on climate," Science Nation, NSF video series, www.youtube.com/watch?v=kYQc2IjQqRU.
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