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Changing pH in the Surface Ocean

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SPECIAL ISSUE ON CHANGING OCEAN CHEMISTRY »
ANTHROPOCENE: THE FUTURE…SO FAR

Changing pH in the Surface Ocean

BY MICHAEL E.Q. PILSON

In 1896, Arrhenius provided the first roughly quantitative sense of the plausible magnitude of human-induced changes in the concentration of CO_2 in the atmosphere. Since then, all chemists could be aware that increasing CO_2 in the atmosphere must lead to increasing amounts in the ocean and a corresponding increase in acidity. For a long time, however, no one appears to have thought much about this latter consequence, probably because the likely effects were small and were, in any case, rather troublesome to calculate. It was only in 1909 that Sørensen proposed the concept of the pH scale. The negligible level of concern about the effect of CO_2 on Earth's heat balance was not much affected by the work of Callendar (1938), who argued that the increasing concentrations in the atmosphere could be observed and would be significant. The radiative balance calculations of Plass (1956), published in *Tellus*, began to influence those who read such journals, and the beginnings of the Keeling curve brought widespread attention to the increasing atmospheric CO_2 concentration.

Bolin and Eeriksson (1959) quantitatively worked out the uptake of CO_2 by the ocean corresponding to increases in atmospheric concentrations. They showed that a change in the partial pressure of CO_2 also changes the pH of seawater and, consequently, its carbonate ion concentration. While it was certainly pointed out by Smith and Buddemeier (1992, and references therein) that increasing CO_2 would lead to decreasing saturation of surface seawater with calcium carbonate, and that this could cause problems for calcifying organisms, the large degree to which such seawater was supersaturated then (and still today) suggested that the situation might not be serious. Indeed, Smith and Buddemeier calculated that even at 600 ppmv CO_2, corals would still be bathed in water 2.4 times saturated with respect to aragonite.

During the 1990s, increasing evidence of a decrease in calcification by most calcifying organisms with a reduction in the level of supersaturation (Gattuso et al., 1998; Kleypas et al., 1999, and references therein; Langdon et al., 2000) led to widespread concern about the possible effects of decreasing pH and the associated decrease in carbonate ion concentration. Plausible pH changes over the next 3,000 years, explored by Caldeira and Wickett (2003), led to even more widespread recognition of the potential consequences of ocean acidification, resulting in the publication of a major report by The Royal Society (2005); a workshop report sponsored by the National Science Foundation, the National Oceanic and Atmospheric Administration (NOAA), and the US Geological Survey (Kleypas et al. 2006); and numerous publications since.

Not only will biological and chemical processes change in response to changing pH, but even the absorption of sound within the ocean will decrease (Hester et al., 2008). It should be noted, perhaps, that multiple chemical changes are associated with increasing CO_2: concentrations (and activities) of hydrogen ions and bicarbonate ions increase, while concentrations of carbonate ion and borate ion decrease. It is generally believed that the decreasing rates of calcification are due to decreasing carbonate ion concentrations, but there is little information on the biological effects of changing hydrogen ion or bicarbonate concentrations or changing partial pressures of CO_2. Certainly, these changes affect many other chemical equilibria.

Figure 1 shows pH changes in surface seawater in equilibrium with the atmosphere, as atmospheric CO_2 concentrations change from a minimum during the last glaciation up to and beyond

> “DURING THE 1990s, INCREASING EVIDENCE OF A DECREASE IN CALCIFICATION BY MOST CALCIFYING ORGANISMS WITH A REDUCTION IN THE LEVEL OF SUPERSATURATION LED TO WIDESPREAD CONCERN ABOUT THE POSSIBLE EFFECTS OF DECREASING pH AND THE ASSOCIATED DECREASE IN CARBONATE ION CONCENTRATION.”

values that could plausibly be reached before the end of the present century. The calculation is straightforward, the only assumptions being that the surface ocean is in equilibrium with the CO_2 in the atmosphere and that variations of salinity and salinity-normalized alkalinity of the ocean are too small to make a significant difference during the time span considered. Ice core data provide an estimate of about 180 ppmv of CO_2 in the atmosphere 20,000 years ago, and data from Keeling and NOAA (Tans and Keeling, 2013) show concentrations from 1959 until the present. The vertical lines indicate appropriate values for four dates. No dates are listed for times in the future, because the trajectory of changing atmospheric concentrations will depend on the amount of fossil fuel burned, release of CO_2 from other sources, possible changes in ocean circulation and temperature, and exchange processes between the atmosphere and the land and the sea. None of these uncertainties (except changes in the amount of fossil fuel burned) will likely have a major impact on the concentration of CO_2 in the atmosphere, so plausible projections suggest that atmospheric concentrations could approach 600 ppmv or more by the end of this

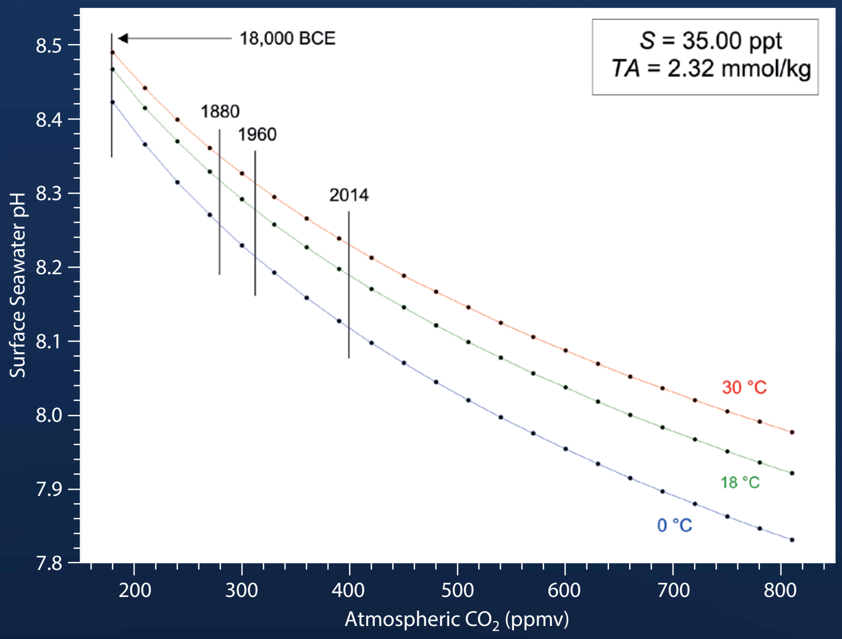

Figure 1. Calculated pH of surface seawater in equilibrium with CO_2 in the atmosphere, updated from figures published in Pilson (1998, 2013). The atmospheric concentration is expressed as ppmv: parts per million by volume in a dry atmosphere. This unit is the same as the mole fraction: moles of CO_2 per total moles of all gases except water. Table 1 provides some details of the calculation. Results for three temperatures are plotted: those for 18°C because that is approximately the area-weighted average for the world ocean (Levitus, 1982), and for 0°C and 30°C to span nearly the range in the world ocean. The value of 180 ppmv of CO_2 corresponds approximately to the low value at the height of the last glaciation. Dates are entered to show the values for the year 1880 (from ice core data) and for 1960 and for 2014, predicted from the Keeling curve and NOAA data (http://www.esrl.noaa.gov/gmd/ccgg/trends). NOAA also publishes global monthly averages near sea level on that same website; the Mauna Loa data were used here because the series is longer and the average values differ by less than 1 ppmv. At the height of glaciation, the average salinity of the world ocean may have been greater by about 3.5%; the resulting pH at 18°C would accordingly have been about 0.005 greater. No adjustment for such changes is attempted here.

century. In due course, over several hundred to several thousand years, the total alkalinity of the ocean must slowly increase (due to reduced calcification in the ocean and increased dissolution of carbonates on land and in the ocean), and thereby influence the pH, but such considerations are beyond the scope of this paper.

The pH of seawater at equilibrium with the atmosphere depends on its salinity, temperature, and total alkalinity, and the partial pressure (properly the fugacity) of atmospheric CO_2. The usual unit for expressing the concentration of CO_2 in the atmosphere (commonly plotted over time as the famous Keeling Curve; Figure 2) is *parts per million by volume* (ppmv), equivalent to the *mixing ratio* or the *mole fraction*. For quick calculation, the numerical ppmv values are sometimes treated as the partial pressure at sea level, but they are not exactly the same. The concentration is expressed on the basis of a dry atmosphere, but the atmosphere exactly at the ocean's surface must be saturated with water vapor. The water vapor pressure must be taken into account in considering the equilibrium with seawater. A sample calculation in Table 1 includes this effect, and also a small correction to yield the fugacity. Table 1 also provides brief estimates of the sensitivity of the calculation to variations in salinity and atmospheric pressure. The calculations shown in Figure 1 were all carried out for a salinity of 35, as a common convention, close to the world average surface salinity of 34.63 reported by Levitus (1982).

The uptake of atmospheric CO_2 decreases the pH of seawater (Figure 1), and this has had and will have many consequences. Figure 3 illustrates one of them. As seawater absorbs CO_2, its capacity to take up more of this gas diminishes. Seawater at 18°C in equilibrium with an atmosphere containing about 200 ppmv of CO_2 will take up 1.17 µmol of CO_2 into each kilogram of seawater if the atmospheric concentration increases to 201 ppmv. This year, with an atmospheric concentration of 400 ppmv, an increase to 401 ppmv will lead to an uptake of less than 0.5 µmol of CO_2 into each kilogram. The effect is not trivial in the global mass balance, or as an entry in the list of processes associated with the absorption of CO_2 into the ocean. For a quantitative perspective, consider the top 100 m of the world ocean; this has a mass of about 35×10^{18} kg. In the atmosphere, 1 ppmv amounts to 2.128 Gt of carbon. At 18°C and an atmospheric concentration of 200 ppmv, an increase of 1 ppmv leads to the absorption of 0.49 Gt of C into the top 100 m of the world ocean, or about 23% of the atmospheric increase. At 400 ppmv, the increase of 1 ppmv leads to the absorption of only 0.21 Gt C, or 9.7% of the atmospheric increase. The surface layers are, of course, gradually mixed with and replaced by subsurface waters, but the rates are locally variable and the global average rate is not well known.

It is likely that the most important consequence of CO_2 uptake and decreasing pH is the consequent decrease in carbonate ion concentration (Figure 4). This is important because the saturation state of calcium carbonate in seawater depends largely on the concentration of carbonate ion (the concentration of calcium is always present in nearly constant proportion to the salinity). The solubility product constant, $K_{sp} = [Ca^{2+}][CO_3^{2-}]$, has a

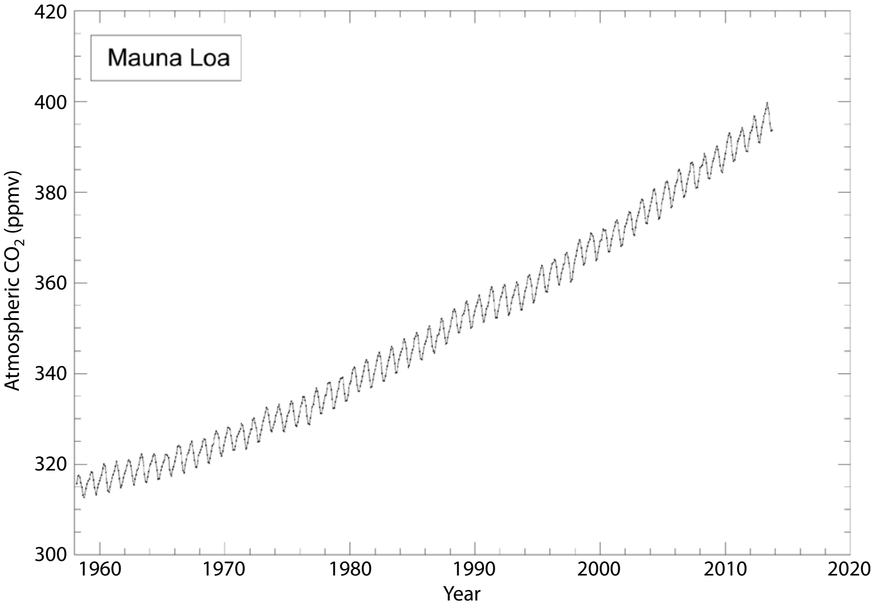

Figure 2. The concentration of CO_2 in the atmosphere at a measurement station located near the top of Mauna Loa, Hawaii. Concentrations are measured many times per day; the monthly average values (see http://www.esrl.noaa.gov/gmd/ccgg/trends) are plotted here starting from the time in 1958 that Charles David Keeling began this set of observations. NOAA has continued recording these measurements since 1974. From ice core data, the value in 1880 would have been about 280 ppmv.

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substantial dependence on salinity, but a very weak dependence on temperature (Mucci, 1983). Although it may seem that the equilibrium concentration of carbonate ion is currently well above that required for the equilibrium solubility of aragonite in seawater, it is observed that many (though not all) organisms apparently will only secrete their carbonate shells or skeletons at a healthy rate if the carbonate ion concentration is well above that required for saturation (Kleypas et al., 1999, 2006; Ries et al., 2009).

The total alkalinity (salinity normalized) does vary somewhat over the surface ocean, being maintained at slightly lower than average values in latitudes where $CaCO_3$ is actively precipitated. The total alkalinity of seawater is likely to increase over time in response to elevated atmospheric CO_2 (due to decreased precipitation of calcium carbonate in surface waters and increased dissolution at depth), ameliorating, to some extent, the effects of increasing atmospheric CO_2 by increasing the carbonate ion concentration and increasing

Table 1. Data needed for a sample calculation, and sensitivity to some variables.

Item	Value	Notes
Concentration of CO_2	400 ppmv	in a dry atmosphere
Temperature of water	18°C	
Salinity	35.00	$\equiv S_P$, Practical salinity
Total alkalinity (TA)	2.320 mmol kg^{-1}	Close to global average
Atmospheric pressure	101,325 Pa	1 standard atmosphere
Water vapor pressure*	2,032 Pa	603 Pa @ 0°C; 4,179 @ 30°C
Atm. Pressure, dry atmosphere	99,293 Pa	
Partial pressure (pp) CO_2	39.717 Pa	
Fugacity adjustment to pp (−0.142 Pa)*	39.575 Pa	= 390.6 µatm
pH calculated with CO_2 equations*		
for 390.6 µatm	8.189	

Sensitivity to salinity at 18°C,
$[CO_2]$ = 400 ppmv, and
atmospheric pressure = 101,325 Pa

S = 33	pH = 8.175
S = 35	pH = 8.189
S = 37	pH = 8.201

Sensitivity to atmospheric pressure at 18°C,
$[CO_2]$ = 400 ppmv, and S = 35
(due to consequent changes in
the partial pressure of CO_2)

Atm pressure = 98,000 Pa	pH = 8.201
Atm pressure = 101,325 Pa	pH = 8.189
Atm pressure = 105,000 Pa	pH = 8.176

*Two factors are needed to enter the equations to calculate all components of the CO_2 system. I used TA and fugacity of atmospheric CO_2, ignoring small corrections to total alkalinity due to variations in nutrient concentrations. There are several sources for the data and equations used here. It was convenient to use those in Pilson (2013). The fugacity calculation is from Dickson et al. (2007). Atmospheric CO_2 values were obtained from http://www.esrl.noaa.gov/gmd/ccgg/trends. The pH values in Figure 1 are based on the widely familiar NBS (now NIST) scale. Conversions among the various pH scales, importantly the "total" scale common for open ocean calculations, are very conveniently done using the "CO2calc" program (Robbins et al., 2010). It really would be advisable for all CO_2 partial pressures to be expressed in pascals, and the CO_2 equations to be entered with that unit, but it is still common to use µatm.

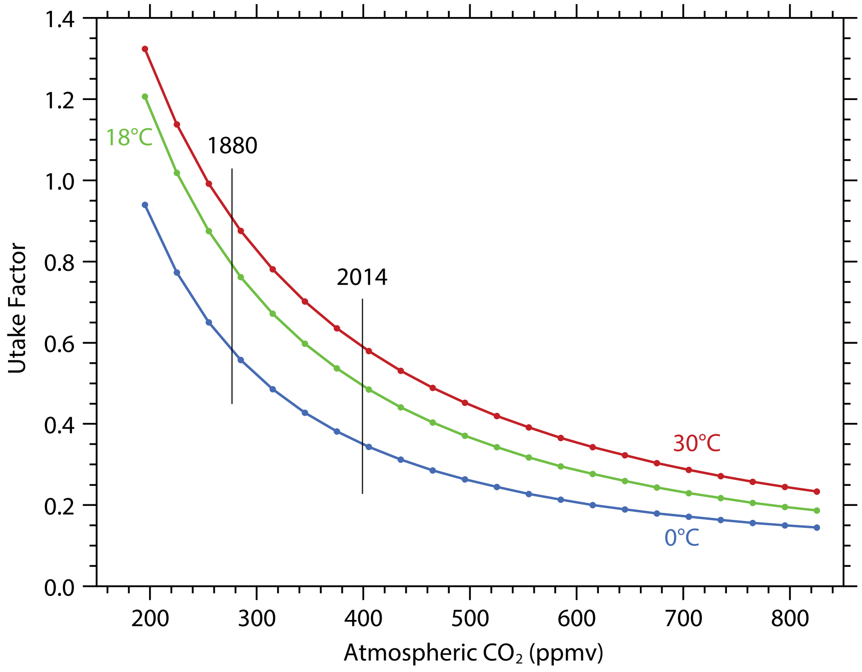

Figure 3. The uptake factor is the incremental increase in the concentration of total CO_2 in seawater, in equilibrium with the atmosphere, corresponding to an incremental increase in the atmospheric concentration of CO_2 (Pilson, 2013), and is expressed as

$$UF = \frac{\Delta \mu mol\ TCO_2\ kg^{-1}}{\Delta ppmv\ CO_2}$$

The calculation was done over small increments and plotted at the mid-point of each increment. Conditions were: seawater with S = 35 and total alkalinity = 2.32 µmol kg^{-1}, a standard atmospheric pressure of 101,325 Pa, and the fugacity at each temperature and atmospheric concentration. Values appropriate for the years 1880 and 2014 are indicated.

the capacity of seawater to take up CO_2. Whether alkalinity will be measurably altered during the rest of this century is uncertain. Any change will not significantly affect the projected average values in the figures shown here.

It is likely that no place in the surface ocean is ever exactly in equilibrium with the atmosphere with regard to CO_2 except by chance. Temperature changes daily and seasonally, and CO_2 exchanges more slowly than does heat, so the CO_2 concentration changes required to reach equilibrium will commonly lag changes in temperature. More importantly, the balance between biological processes of photosynthesis and respiration, as phytoplankton blooms come and go, varies much faster than the exchange of CO_2 with the atmosphere can keep up. In extreme examples, especially in inshore waters, the observed range of pH may be greater than the total range shown in Figure 1. Thus, the values shown here in all the figures (except Figure 2) are equilibrium targets that ocean water in any given place and time will usually be moving toward, at rates controlled by the chemical history of the water and physical conditions such as water turbulence and local wind strength. It is reasonable to assume that observed average values in the ocean will center around equilibrium values, allowing for some likelihood that there will be asymmetry in the rates of approach from undersaturation versus oversaturation. Measurements of pH provide sensitive and important assessments of current and recent past conditions in any body of water.

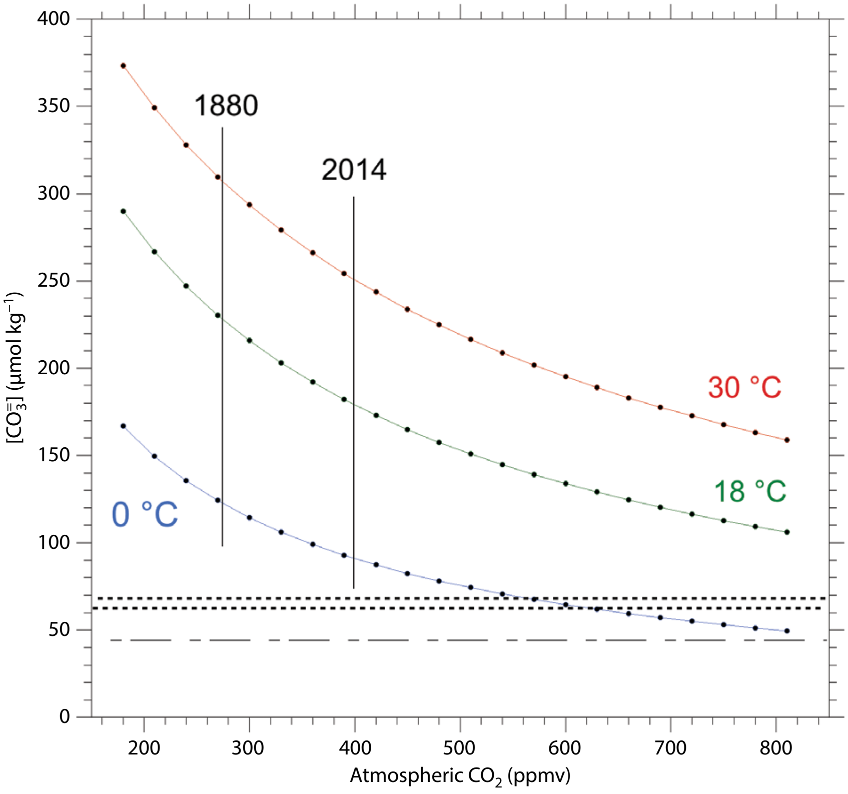

Figure 4. Concentration of carbonate ion in seawater characterized by S = 35 and TA = 2.032 μmol kg^{-1} at three temperatures and at equilibrium with a range of atmospheric concentrations of CO_2. The two horizontal dotted lines show the carbonate ion concentration at saturation with aragonite, the upper one at 0°C and the lower one at 30°C. The one horizontal dashed line (there is not much temperature effect) shows the carbonate ion concentration at saturation with calcite (calculated from Mucci, 1983). The vertical lines indicate the equilibrium conditions for the years indicated.

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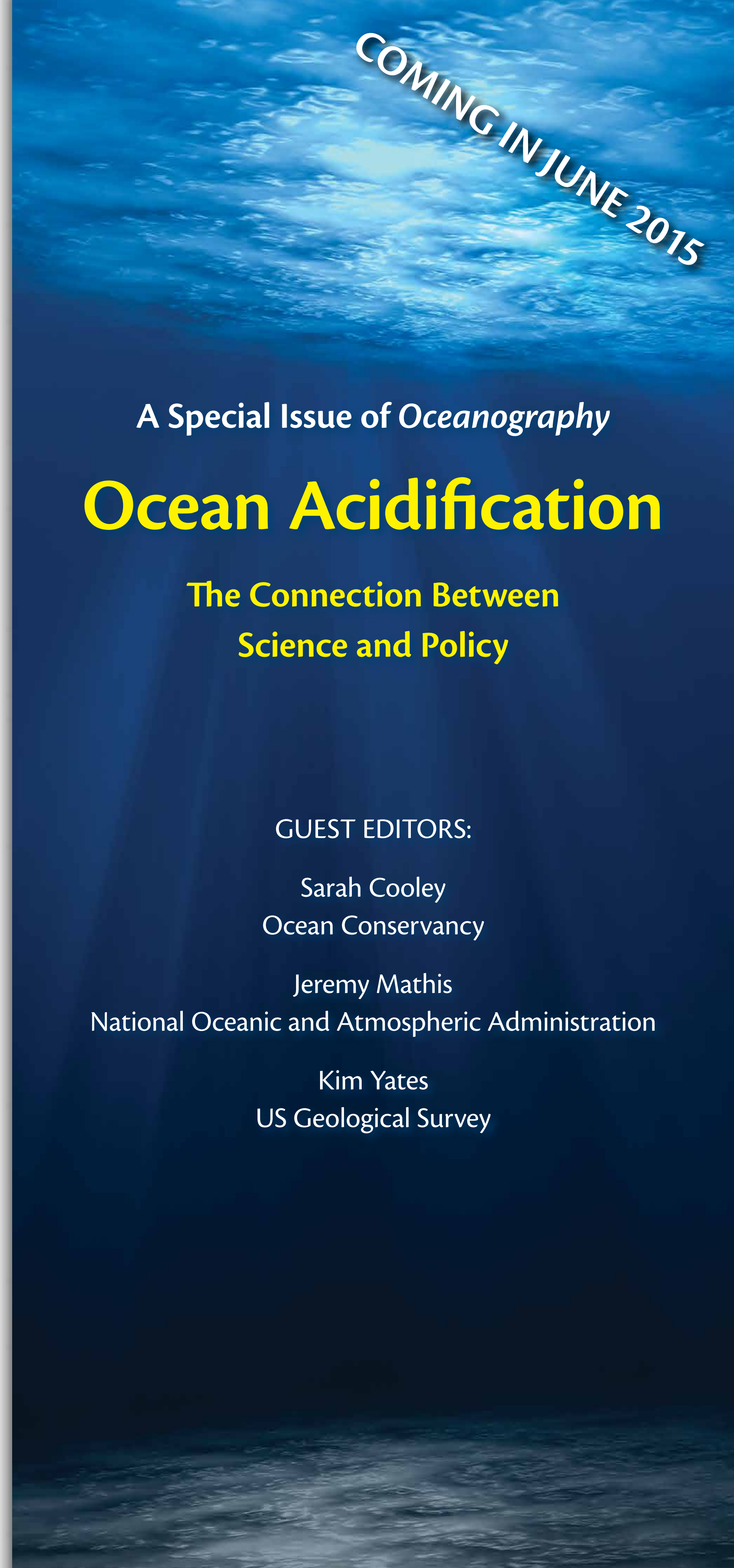

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