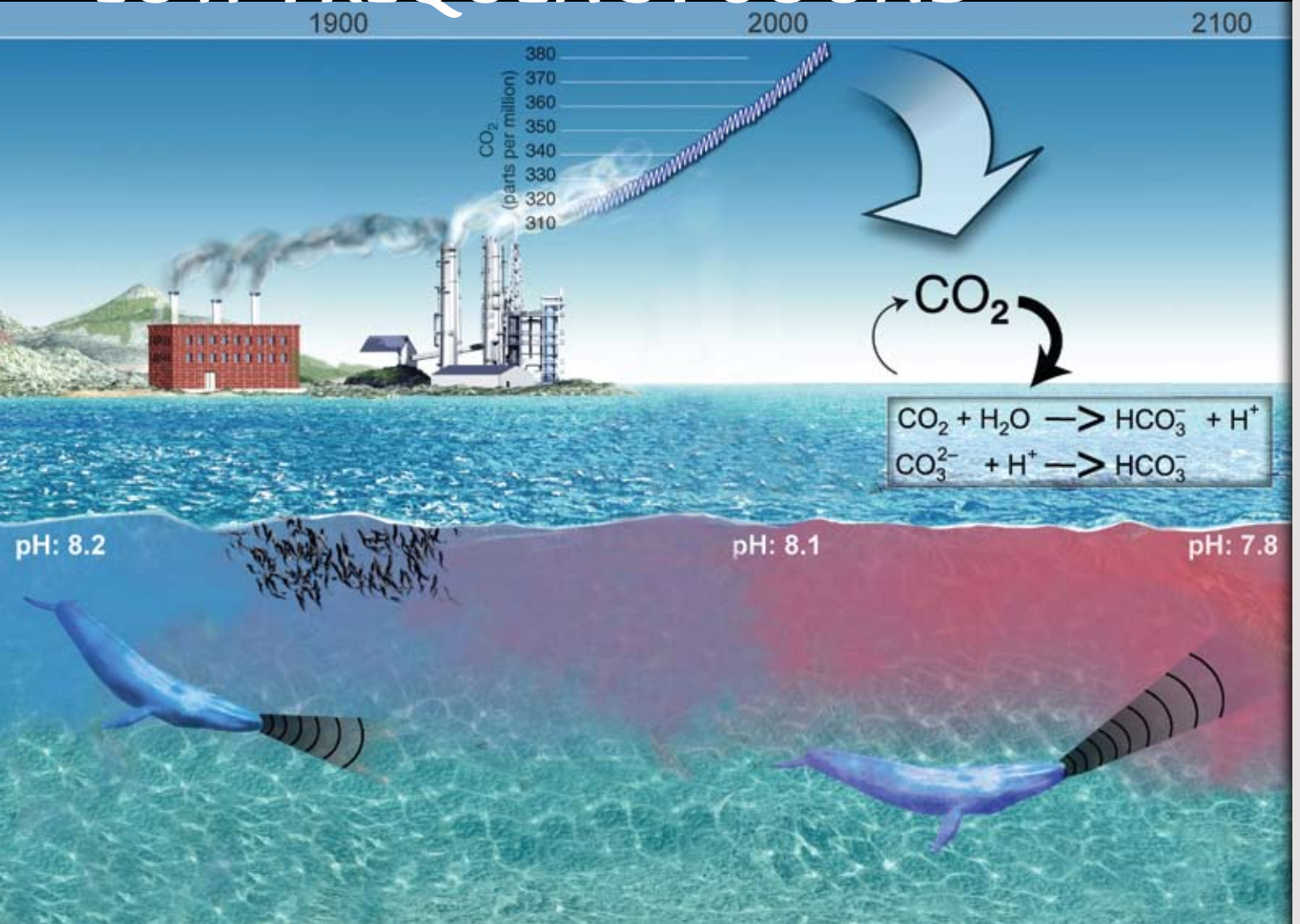


BY PETER G. BREWER AND KEITH HESTER

OCEAN ACIDIFICATION AND THE INCREASING TRANSPARENCY OF THE OCEAN TO LOW-FREQUENCY SOUND



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ABSTRACT. As the ocean becomes more acidic, low-frequency (~ 1–3 kHz and below) sound travels much farther due to changes in the amounts of pH-dependent species such as dissolved borate and carbonate ions, which absorb acoustic waves. The effect is quite large; a decline in pH of only 0.3 causes a 40% decrease in the intrinsic sound absorption properties of surface seawater. Because acoustic properties are measured on a logarithmic scale, and neglecting other losses, sound at frequencies important for marine mammals and for naval and industrial interests will travel some 70% farther with the ocean pH change expected from a doubling of CO₂. This change will occur in surface ocean waters by mid century. The military and environmental consequences of these changes have yet to be fully evaluated. The physical basis for this effect is well known: if a sound wave encounters a charged molecule such as a borate ion that can be “squeezed” into a lower-volume state, a resonance can occur so that sound energy is lost, after which the molecule returns to its normal state. Ocean acousticians recognized this pH-sound linkage in the early 1970s, but the connection to global change and environmental science is in its infancy. Changes in pH in the deep sound channel will be large, and very-low-frequency sound originating there can travel far. In practice, it is the frequency range of ~ 300 Hz–10 kHz and the distance range of ~ 200–900 km that are of interest here.

BACKGROUND

One of the more remarkable effects of the ocean’s rapidly changing CO₂ status is the impact on low-frequency sound absorption (Hester et al., 2008). Doubling of atmospheric CO₂ will result in about a 40% decrease in the intrinsic sound absorption properties of surface seawater at frequencies of about 10 kHz and below. This frequency range is important for marine mammal communication and is of significant naval and industrial interest. What is the chemistry behind this effect? How was it discovered? How sure are we of projections for the future? And what demands might this knowledge place on scientists and policymakers?

Acousticians in the late 1960s to early 1970s discovered that increasing ocean sound absorption at ~ 1 kHz and below occurred relative to pure water, and that

this absorbing component showed strong interocean and regional differences; the Pacific was far more transparent to low-frequency sound (i.e., sound could travel farther) than the Atlantic (Mellen and Browning, 1976). From exploring simple correlations with hydrographic data, it

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was soon realized that the changing low-frequency effect was associated with the intensity of the oxygen/pH minimum in the ocean water column. Yeager et al. (1973) hypothesized a pH connection

that Fisher and Simmons (1977) later identified as primarily a borate species relaxation effect.

Boron exists in seawater in two forms—the B(OH)₄⁻ ion and the un-ionized form B(OH)₃; their ratio is set by the pH of bulk seawater, and as seawater becomes more acidic, the fraction of the ionized B(OH)₄⁻ form decreases. Plainly, the B(OH)₄⁻ species is a bigger molecule than B(OH)₃ and, because of its charge, also carries with it associated water molecules as a loose assemblage. This weakly associated complex can be temporarily compressed into a lower-volume form by the passage of a sound wave; there is just enough energy in a sound wave to do it. This compression takes work and thus robs the sound wave of some of its energy. Once the wave front has passed by, the B(OH)₄⁻ molecules return to their original volumes. Thus, in a more acidic ocean with fewer of the larger borate ions to absorb sound energy, sound waves will travel farther.

The thesis by Simmons (Fisher and Simmons, 1977) confirmed this effect through resonator and temperature-jump experiments, and from them they proposed a sound absorption equation

incorporating the borate term. The effect was found to be quite large; for example, Fisher and Simmons (1977) noted that at 200 kHz, sound absorption in seawater was 300 times greater than in pure water.

The absorption of sound by the borate ion is not challenged today, and it is incorporated into all equations now in use to describe and predict ocean sound absorption. But it is not the complete story, and there is strong evidence for a small “unknown” term (Garland et al., 1973; Mellen et al., 1979; Fisher, 1979), probably a carbonate ion, extending pH-dependent effects out to about 3 kHz.

The exact mechanism for how the borate ion absorbs sound is still unknown, but it is clear that the $B(OH)_4^-$ species is the primary active agent. Today, we are experiencing reduced low-frequency ocean sound absorption as a result of ocean acidification, and pH-dependent terms are included in all modern formulations of ocean sound absorption (Mellen et al., 1987), typically as an addition of all the chemical species as in:

Total absorption = (boric acid + magnesium sulfate + pure water) contributions.

The effect can be seen graphically in Figure 1.

Ocean sound absorption is quite difficult to measure. Changes in frequency and phase can be measured with high precision, but measuring changes in

amplitude is hard and requires careful calibration. Nonetheless, the interest in this problem is strong, and it has been pursued as a strategy for obtaining mean pH over a very large volume of seawater. For example, Jin and Worcester (1989) examined the feasibility of acoustic measurement of pH at 550 Hz over a 750-km path length; they suggested that in order to obtain a precision of 0.05 pH, some 100 independent samples would be required for a Pacific experiment, and 60 for the Atlantic because of its higher absorption coefficient. Sound waves travel through the ocean acoustic waveguide in a typically concertina-like folded path, and the pH signal obtained would thus be a vertically integrated mean over several hundred meters depth.

More recently, Duda (2009) very carefully re-examined the problem and suggested using differential acoustic measurements at two or more frequencies below 600 Hz in order to determine pH with a precision of ± 0.05 . He noted that a significantly greater number of samples would be required. The acoustic strictures on such an observing technique were analyzed in detail, including coping with scintillation created by the ocean internal wave field, which caused fluctuations in the sound channel.

PREDICTING THE EFFECT OF OCEAN ACIDIFICATION

Ocean acidification is now proceeding apace caused not only by fossil fuel CO_2 invasion from the surface but also by the rapid emergence of an increased

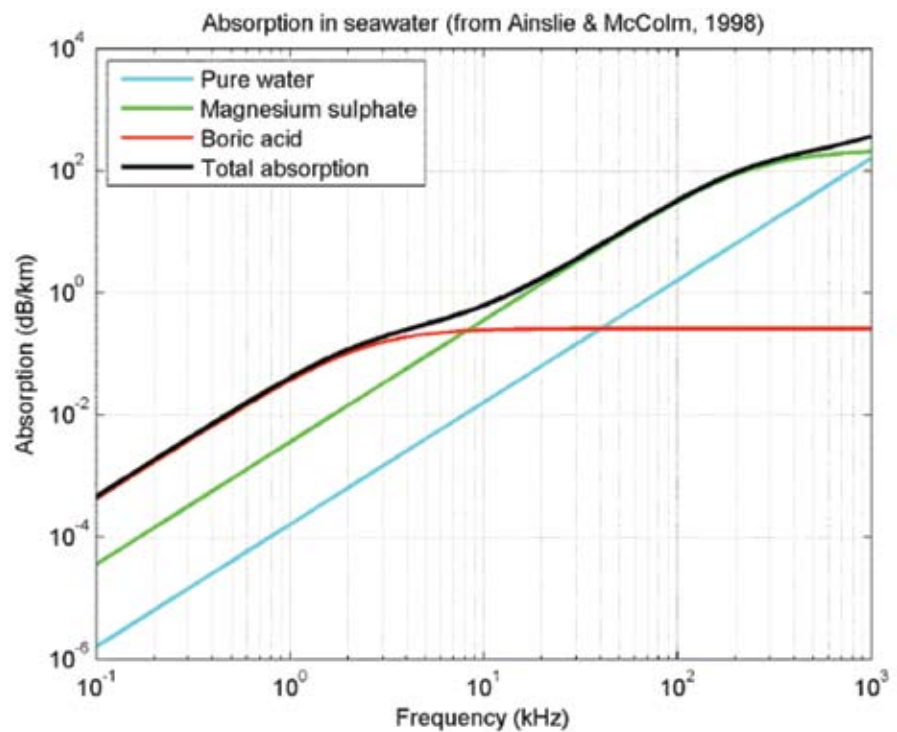


Figure 1. Sound absorption in seawater as a function of frequency, showing the additive effect of the three primary chemical species. The pH effects associated with the boric acid term begin to be significant at about 10 kHz and below. From Ainslie and McColm (1998)

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respiratory CO₂ signal at depth, which also reduces pH (Hester et al., 2008). This increase of CO₂ at depth arises in large part from physical climate change, which is causing milder winters and reducing ocean ventilation by the atmosphere. Declining oxygen (and therefore increasing CO₂) trends at depth have been noted around the world (e.g., Stramma et al., 2008). The net result is a faster and greater appearance of pH change at depth than would result from fossil fuel CO₂ changes alone (Brewer and Peltzer, 2009).

Hester et al. (2008) calculate the predicted changes in sound absorption as a function of anticipated changes in pH from the fossil fuel CO₂ signal (Figure 2). These results show a remarkable change in the absorption coefficient of 40% or

more with a pH change of -0.3. Surface waters can reasonably be expected to show such change by mid century, and larger changes at depth are very likely.

It is important to recognize that the intrinsic effect we are describing here is a very small component of overall sound loss in the ocean, and that losses from physical absorption at the surface and the seafloor far exceed these terms. The pH effect is not easily detectable at short range, and sound intensity drops off very quickly with distance, first from spherical spreading losses and then in inverse square form from cylindrical spreading of the acoustic wave.

The definition of “long range” is subjective, but a realistic answer is given by the length scales employed by the early experimentalists who first

uncovered these effects by using explosive sources. Typical length scales used earlier ranged from about 200–900 km. Today, length scales of ≥ 100 km would likely be required. The paper by Duda (2009) notes that the connection implies “a straightforward means of measuring ocean acidity continuously over extended paths (hundreds to thousands of kilometers in length) by measuring sound attenuation.”

HOW VALID IS THE OCEAN CHEMISTRY DATABASE NOW USED?

The ocean acoustics community has done a remarkable job of unraveling the physical basis for the absorption of low-frequency sound by chemical species in the ocean, despite the unusual observational pH data set on which these equations were based. Although the result is internally consistent in that all ocean acousticians have used the same historical pH data source, the fields used bear little relationship to the remarkable progress made in global ocean CO₂ chemistry over the last 40 years and the hard-won knowledge from the classic GEOSECS-TTO-JGOFS-WOCE¹ experimental series. Instead, we have a house of cards. Ocean chemists and acousticians simply proceeded along separate paths for about 35 years.

Ocean acousticians’ results cannot be very badly wrong—otherwise no useful correlations would have been found; however, the fields used were so coarse, and enormous gaps in documentation exist, so that very basic questions now

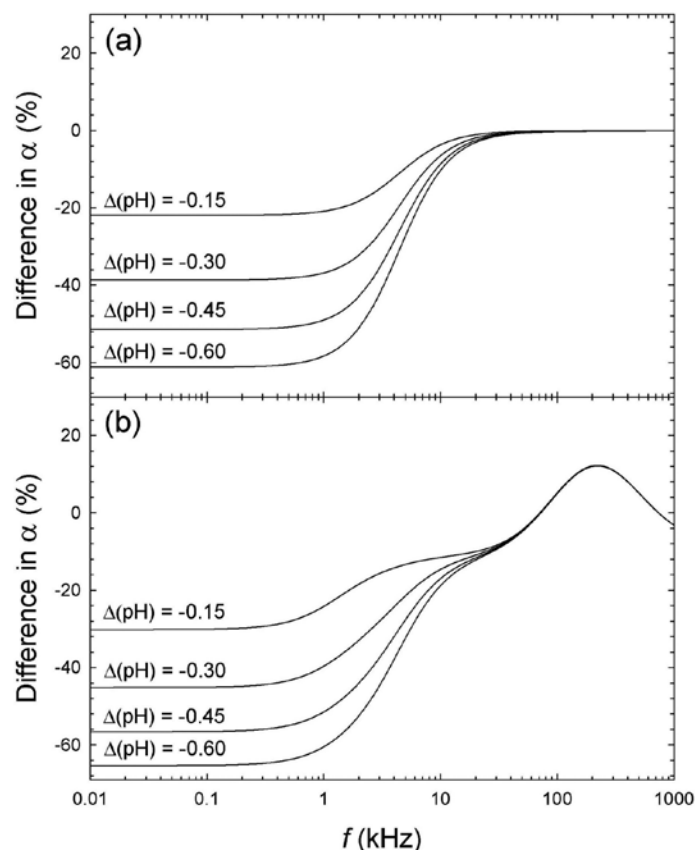


Figure 2. Predicted changes in the sound absorption coefficient (dB km^{-1}) as a function of pH based upon the equations of Francois and Garrison (1982) for fossil fuel CO₂ projections only (Panel a) and with changing temperature included (Panel b). From Hester et al. (2008)

¹ GEOSECS: Geochemical Ocean Sections Study (1968–1978). TTO: Transient Tracers in the Ocean (1981–1983). JGOFS: Joint Global Ocean Flux Study (1987–2003 [US JGOFS continued to 2005]). WOCE: World Ocean Circulation Experiment (1990–2002).

arise as we begin to deal with changing ocean pH in a high-CO₂ world.

The question of how and why this disconnect between two important ocean science communities arose and persisted for so long is of interest. Although no published record exists, it is possible to piece together a credible account.

DISCORD IN THE US OCEAN COMMUNITY

At the very same time that acousticians were uncovering the 1-kHz sound absorption anomaly (Thorp, 1965, 1967) and its relationship to pH/borate (Yeager et al., 1973), ocean chemists were struggling with incoherent measurements of ocean CO₂ system properties. One of the earliest challenges for the GEOSECS program, initiated in 1968, was to tackle ocean CO₂ chemistry. It was realized that no single laboratory could accomplish the task of a global survey, and thus an intercalibration exercise was set up to examine the accuracy and coherence of the pH-pCO₂-TCO₂-Alk measurement capabilities and the constants that relate the properties to each other. The

test cruise was carried out in September 1969 offshore San Diego (Craig and Weiss, 1970). In December 1969, and within a few miles of that same location, a major ocean sound absorption experiment took place (Lovett, 1975). The experiments were not connected and the teams had little or no awareness of each other's work.

There were good reasons for this split: acousticians were still uncovering the chemical connections to their work and not yet sure of the way forward, and the GEOSECS test cruise was a legendary debacle for ocean chemistry. When the CO₂ system measurements were digested (Takahashi et al., 1970; Figure 3), significant errors were revealed. In a brave attempt at compromise, Takahashi wrote that “the discrepancy can be eliminated if a 30% error in the second apparent dissociation constant for carbonic acid is assumed,” but that was not to be.

As a result, no routine, direct pH measurements were taken during the GEOSECS program, and the significant discrepancy between measured and computed CO₂ properties continued

for a full decade. The discord and confusion this discrepancy created was widely known. It was not until after the untimely death of Arnold Bainbridge, the GEOSECS technical leader, that the difficult reverse engineering of the code he wrote was possible, thereby uncovering basic errors in the formulation used for the titrimetric analysis (Bradshaw et al., 1981). This correction provided—for the first time—an accurate titrimetric chemical model and code that is in worldwide use to this day.

THE SOVIET OPTION

The decade of conflict over an accurate rendition of ocean pH data during the formative years of this branch of ocean acoustics took its toll. Ocean acousticians, seeking simplicity and a refuge from the unresolved and messy chemical debate surrounding GEOSECS, chose the Soviet-era Gorshkov atlas (Gorshkov, 1978), which conveniently provided apparently clear maps of the observed ocean pH field (Figure 4). Contoured to 0.1 pH intervals, and thereby constraining the sound absorption coefficient to within about 30%, the fields this atlas provided, although coarse by modern standards, were sufficient to show interocean differences that could be correlated with widely spaced sound absorption experiments. While it is odd to think of the US acoustics-Navy community choosing, in the midst of the Cold War, a Soviet data set over the results from US geochemists, this was so. And while it was a temporary convenience, the use of these data has had long-lasting repercussions.

Though not specified, the pH scale used in the Gorshkov atlas was probably based on the US National Bureau of

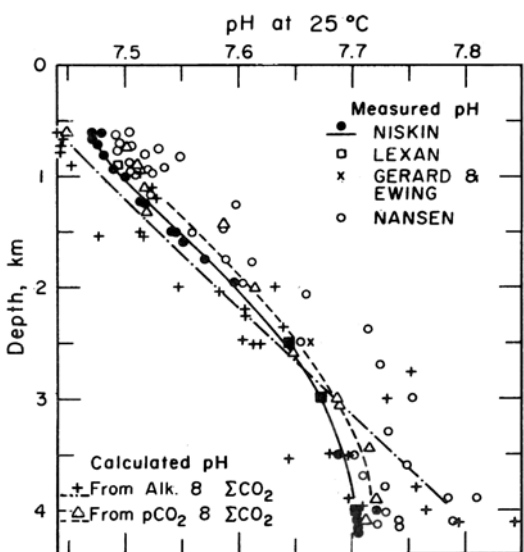


Figure 3. The pH data obtained at the 1969 GEOSECS test station (Takahashi et al., 1970). The problems in this data set resulted in widespread distrust of direct pH measurements by US scientists for a decade or more. Acousticians of the 1970s era who were faced with this issue, and had pressing needs, simply chose another source of pH data.

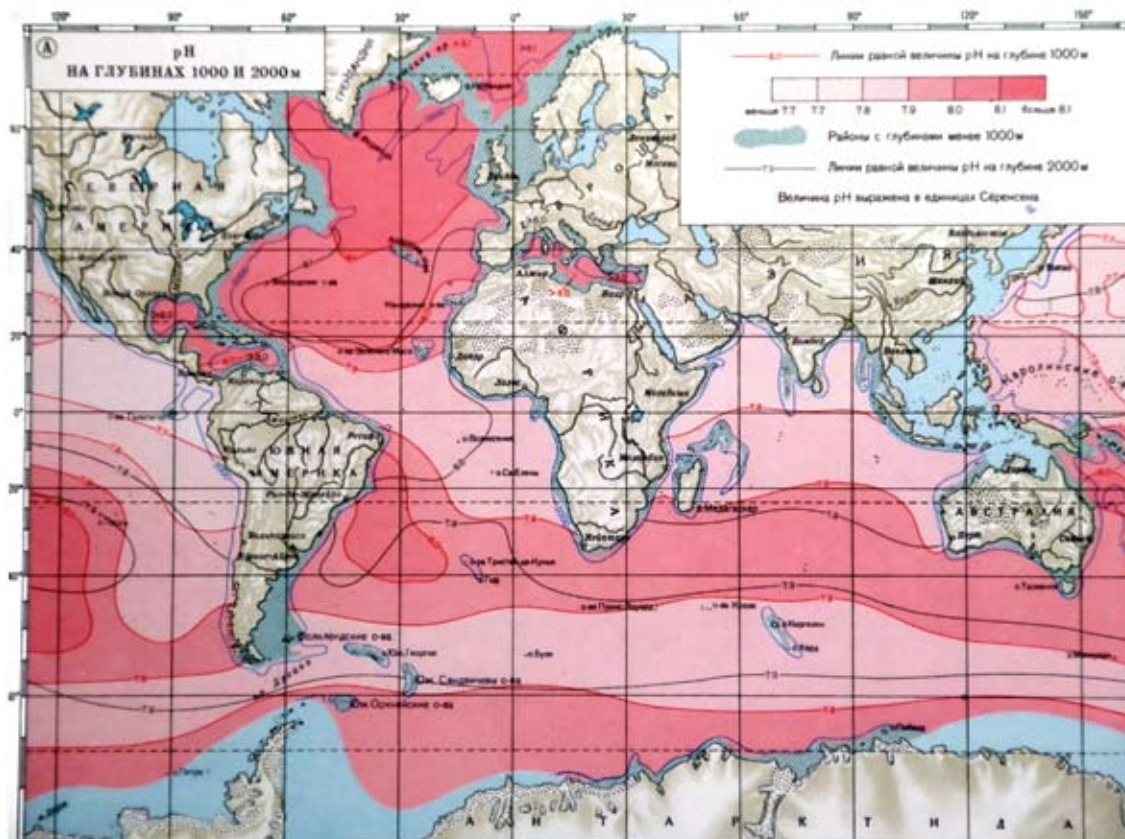


Figure 4. A specimen page from the Gorshkov atlas (1978) showing contours of pH for the Atlantic and Indian oceans at 1000-m and 2000-m depth from 1960s to early 1970s observations; the contour interval is 0.1 pH units. The pH scale used is not reported, although it is likely to be the National Bureau of Standards scale because the more modern scales had not yet been invented. Acousticians picked points from these pages to define the pH vs. sound absorption relationship.

Standards (NBS; now National Institute of Standards and Technology) scale; the other pH scales for seawater in common use today had not yet been invented. Although the Soviet political system was tragically flawed, it is very likely that the technical staff who served through long voyages at sea was as dedicated and careful as possible, and took great pride in their work. Thus, through these devoted efforts, a respectable though coarsely rendered description of the ocean pH field circa the 1960s was produced.

But there were fundamental limits posed by the technology of the times; those who visited Soviet ships of that

era recall with mild astonishment the pH apparatus used. This predigital age required the reading of a galvanometer needle that was subjected to ship accelerations. But most memorable was the large (several liter) reservoir of potassium chloride attached above the electrode system and connected to it by a rubber hose. This reservoir accommodated the significant flow rate through the liquid junction, and it was refilled when necessary. Wisely, care was taken not to titrate the sample for chlorinity after pH measurement so as to avoid the excess chloride that had leaked in.

US ocean acousticians seized upon this opportunity, picked points off the

Gorshkov atlas pages, and prepared a table of data to match the locations of sound absorption experiments. The conversion of the Gorshkov atlas pages into numerical data sets that served the community well in uncovering these effects was carried out by Lovett (1980), who noted, “In Figs. 1 and 2, as in any contour chart, some level of subjectivity occurs, induced partly by the necessity to interpolate from available pH contour charts spaced at 500- to 1000-m intervals. Indeed the Atlases (which fail to cite original sources) state that for certain areas, the pH data were relatively sparse. Despite the above limitations, these charts should provide a good basis for

the prediction of low-frequency sound absorption in the ice-free World oceans.”

Astonishingly, this atlas has served until today as the primary pH data resource. For comparison, modern pH

$H^+ + SO_4^{2-} \leftrightarrow HSO_4^-$ equilibrium, important for defining seawater, is correctly represented. There is a difference of about 0.12 pH units between the two scales (Brewer et al., 1995). The modern

a vertically integrated section of the ocean water column over hundreds of kilometers. It is possible to recognize the ray traveling at the sound speed minimum and also other paths taken that integrate greater depth zones.

The unknown chemical species that appears as a third term in fitting data to models is of some concern because the exact species is not known. Because the CO_3^{2-} ion is the most likely candidate, the effect of pH change could be large.

“ IT IS WELL PAST TIME TO BRING TOGETHER THE ACOUSTIC AND GEOCHEMICAL COMMUNITIES, WHO HAVE COMPLEMENTARY SKILLS, TO TACKLE THIS MATTER. ”

measurements, now fully reconciled with the complete set of seawater CO_2 system components, are reported with 100-fold greater precision and elegantly reveal the changing nature of the CO_2 status of the ocean (Dore et al., 2009).

PROBLEMS ARISE

Brewer et al. (1995) first investigated the problems in correlating the Gorshkov atlas pH data set with modern results. They found significant differences in the North Atlantic and also drew attention to the problem of the admittedly confusing pH scales used. This mixing of scales is very common and interconversion is still difficult. Duda (2009) used the standard absorption-pH equations derived from the Gorshkov atlas to examine the feasibility of acoustic pH measurement and selected the data set of Terner et al. (2001) as a test case. But the Terner et al. (2001) pH data are reported on the pH_T scale (i.e., total scale), and the sound absorption equations are based on the old NBS scale. The pH_T scale is based on the definition of buffer solutions that contain sulfate ions so that the

definition and measurement of pH has been examined exhaustively; Buck et al. (2002) is the authoritative reference.

Although pH scale issues are confusing, the technical concerns are fairly small; of greater interest is the lack of a time scale to account for the changing ocean pH—some 60% of all fossil fuel CO_2 emissions have occurred since the 1969 sound absorption measurements reported by Lovett (1975). Also of concern is the accuracy with which future changes can be predicted (Figure 3; Hester et al., 2008) as we move into a high- CO_2 world far removed from the Gorshkov atlas and data sets and correlations taken almost a half century ago.

It is unclear what segment of the oceanic water column the single pH values (Francois and Garrison, 1982) associated with early sound absorption experiments in the acoustic literature refer to, but it is most likely the value at the sound speed minimum. Typically, ocean sound ray paths are bent in folded, concertina-type wave forms formed by the sound channel and thus “sample”

THE SITUATION TODAY

It is well past time to bring together the acoustic and geochemical communities, who have complementary skills, to tackle this matter. One of their early tasks should be to re-examine the early sound absorption experiments, and to assign to those a pH field based upon modern knowledge. This task will require stripping the fossil fuel CO_2 signal and providing profiles appropriate for the time of measurement and for the ray paths taken.

The second challenge will be to investigate the fit of the revised pH-borate-acoustic data to the likelihood of an “unknown” term (Garland et al., 1973; Fisher, 1979) that has been ascribed to both carbonate and bicarbonate ions—these ions will have opposite effects because bicarbonate will increase and carbonate will decrease in our future ocean. Which is correct?

A third task will be to seriously engage the environmental community, which has become a potent force on policy. There are, for example, groups now pressing for mandatory noise reduction from ships for marine mammal protection. How does the changing sound absorption phenomenon fit

into this scenario? Is it a significant factor? How will marine mammals respond to this changed environment that is being skewed to easier transmission, but greater background noise, at the lower frequencies of their range? These issues are international because sound travels far and many groups have interest in this field. How will this new community evolve?

Finally, we will have to advance this field in new ways, engaging with Navy-supported communities, and investigating with care the new form of combined acoustic and geochemical experiments and skills that will be required to understand and accurately predict this strange phenomenon. ☒

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