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Effect of Air Bubble Solution on Air-Sea Gas Exchange

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Recent data on ambient wave generated oceanic bubble spectra (Medwin, 1970) permit the calculation of the influence of bubble solution on air-sea gas exchange. Schulkin's formula is used to estimate the depth variation of bubbles, and a square law is used to estimate the increase of bubble volume with wind speed. Calculations indicate that bubble solution can be a very significant factor in gas exchange. Bubble solution enhances gas input and retards degassing of the water column. Preliminary data show a lag time of about 5 hours in the response of the water column to an atmospheric pressure change.

Although there have been few measurements of air-sea gas exchange, nearly all reports on such measurements point out the possible participation of bubbles; Redfield [1948] calculated gas exchange coefficients for the Gulf of Maine and felt that the seasonal variation in the gas exchange coefficient could be explained by 'waves, spindrift, and the bubbles.' In his summary of gas exchange measurements in tanks Kanwisher [1963] mentions that bubbles must be important in gas exchange, and he stresses the need to know the volume flux of bubbles under various sea conditions. There have been several experimental tank measurements of gas exchange coefficients; there is a revealing difference between these experimental measurements and coefficients measured (often very indirectly) in the ocean. Schink *et al.* [1970] summarized the experimental and oceanic measurements; the higher gas exchange coefficients were attained in natural conditions. The one characteristic definitely missing from experimental measurements is the large breaking wave with resultant bubble production.

Measurements of oceanic gas concentrations have led to speculation and recently to some definite evidence for gas concentration control by bubble solution. Benson and Parker [1961, p. 249] felt that, although their N_2/Ar data were near N_2'/Ar' , '... it is interesting to note

that the experimental curve (N_2/Ar) lies above the theoretical curve (N_2'/Ar') at high temperatures where most surface waters are represented. This would be expected if trapping of air bubbles from surface turbulence were significant. . . ' Bieri [1971] and Craig and Weiss [1971] presented values of up to 10% for the amount of air injected into the water by bubble solution.

The production of bubbles by breaking waves and the presence of bubbles in the upper few meters of the ocean are facts accepted by anyone who has had the opportunity to be at sea. In a stormy sea the position of a breaking wave is marked for minutes by a greenish blue patch of bubble-laden water contrasted against the normal oceanic blue. As the wind speed rises, the sea surface becomes increasingly covered with foam patches until, during hurricane conditions, the sea surface becomes undefinable because of the confusion of breaking waves, bubbles, and spray. Bubbles produced by a breaking wave are carried down the water column by vertical turbulence. Visual observations from the bow port of the R.V. *Atlantis* led Kanwisher [1963] to estimate that bubbles penetrated the water column to a depth equal to 2-3 times the wave height. On the average, especially at a higher wind speed and a higher density of breaking waves, the bubble density at a given locality in the water column will remain constant, even though bubbles are constantly passing through the given locality. Under normal circumstances these bubbles will go into solution because of hydrostatic pressure and

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surface tension. Therefore they represent a source of dissolved gas distributed throughout the water column. This paper demonstrates the magnitude and characteristics of bubble solution of air-sea gas exchange.

SPECTRA AND SOLUTION RATES OF BUBBLES

Because of recent advancements in underwater acoustical research, limited data are available on the size-frequency relationship of bubbles in the surface layer of the ocean; unfortunately, acoustical methods are not reliable at high bubble populations, and no measurements have been made above sea state 2 (wind speed $U = 3$ m/sec). Medwin [1965, 1970] used both attenuation and backscattering techniques to measure spectra of bubbles in an isothermal oceanic surface layer during sea state 2. His observations agree qualitatively with results of wind tank experiments by Glotov *et al.* [1962]; a maximum is found at 0.005–0.0150 cm. Medwin's results compare quantitatively with the visual observations of Blanchard and Woodcock [1957] (see Medwin [1970, Figure 6]). This agreement exists even though the Blanchard and Woodcock observations were in the surf zone and Medwin's were during sea state 2 in the open ocean, when few waves are breaking. Monahan [1971] has shown that no breaking waves are present at wind speeds of <3.6 m/sec. If this is true, Medwin's values at a wind speed of about 3 m/sec may be fortuitous, but regardless these values do agree with Blanchard and Woodcock's and will adequately serve as a base for the following calculations. Figure 1 shows a typical oceanic bubble spectrum adapted from Medwin [1970, Figure 6]; the maximum frequency at about 0.01 cm is a result of the high solution rates of small bubbles and the high buoyancy of larger bubbles. Turner [1961] has shown that bubbles with a radius of <0.0050 cm are stable; although they may appear in a measured spectrum, they are not contributing gas to the water column via bubble solution. The $N(r, U, z)$ refers to the number of bubbles of radius r during wind speed U at depth z . The radius bandwidth dr is 0.0001 cm (1 μ m).

DEPTH DEPENDENCE OF BUBBLE SPECTRA

Schulkin [1969] used the following equation as an estimate of the depth dependence of

bubble spectra:

$$N(r, U, z) = N(r, U, 1)$$

$$\cdot (1 - z/L)^{1/2} (1 + z/11)^{1/2} z^{-1/2} \quad (1)$$

where z is the depth in yards and $N(r, U, 1)$ is the bubble density of radius r at the surface ($z = \text{yard}$). For dimensional correctness, $z^{-1/2}$ is understood to mean $(z/1 \text{ yd})^{-1/2}$. According to Schulkin, $(1 - z/L)^{1/2}$ represents the mixing property of the isothermal layer, $z^{-1/2}$ is the natural decay of bubble density with depth, and $(1 + z/11)^{1/2}$ is the contribution of deeper non-surface bubble sources or bubbles released in air-saturated water by decompression at the crests of internal waves. The actual importance of the decompression process in bubble production is unknown; however, the $(1 + z/11)^{1/2}$ term makes a relatively small contribution to $N(r, U, z)$ and will be retained for completeness. The $z^{-1/2}$ term creates a problem because, as z approaches 0 from 1, $z^{-1/2}$ approaches infinity. This could be avoided by using e^{-z} , but, for the sake of using Schulkin's complete formula, $z^{-1/2}$ will be retained. It must be remembered that the surface refers to 1 meter or 1 yard. For the purposes of the study it is assumed that meters and yards are equivalent. Equation 1 is shown in Figure 2 for a mixed layer depth of 10 and 20 meters. Bubble fre-

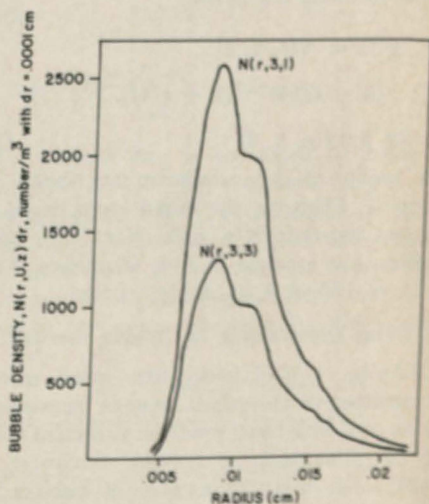


Fig. 1. Medwin's $N(r, 3, 3)$ size frequency bubble spectrum and the calculated surface spectrum.

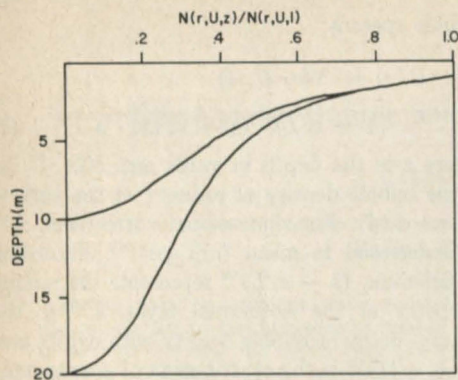


Fig. 2. Bubble frequency versus depth normalized to the surface spectra $N(r, U, 1)$.

quency is expressed as a fraction of the frequency at 1 meter. There is a rapid drop of bubble density in the first 5 meters, then a more gradual decrease to the bottom of the mixed layer.

CALCULATIONS OF SURFACE BUBBLE SPECTRA

The only data of any use in calculating surface bubble spectra are from *Medwin* [1970, Figure 6]. These data are from sea state 2 ($U = 3$ m/sec) and a depth of 3 meters ($z = 3$ meters). If we use (1) and a mixed layer depth of 10 meters ($L = 10$ meters), *Medwin's* data are converted to a $U = 3$ surface spectrum by the following calculation:

$$\begin{aligned} N(r, 3, 1) &= N(r, 3, 3) \\ &\cdot (1 - z/10)^{-1/2} (1 + z/11)^{-1/2} 3^{-1/2} \\ &\cong 2.0N(r, 3, 3) \end{aligned} \quad (2)$$

The results of this calculation are shown in Figure 1. Changing the mixed layer depth L changes the ratio $N(r, 3, 1)/N(r, 3, 3)$ only slightly. For example, if $L = 20$ meters, $N(r, 3, 1) = 1.8N(r, 3, 3)$, a 10% change.

WIND DEPENDENCE OF BUBBLE SPECTRA

Schulkin [1969] found that sound energy transmitted in the mixed layer is increasingly attenuated with rising wind; he attributed much of the attenuation to bubbles. *Glotov et al.* [1962] felt that the number of bubbles increased exponentially with wind speed during his tank experiments, although other lines of evidence would justify the use of a square extrap-

olation to estimate the increase of bubble density with wind speed. For example, it is well known that wind stress increases with approximately the square of the wind speed, and *Kanwisher* [1963] and *Downing and Truesdale* [1955] found gas exchange rates to increase with the square of the wind speed. *Blanchard* [1963] found a square law dependence of white-cap coverage on wind speed. More recently, *Monahan* [1971] has demonstrated a dependence on the 3.3 power of the wind.

To calculate the surface bubble spectra for wind speeds other than 3 m/sec, a square law is used to keep the calculation as conservative as possible.

$$N(r, U, 1) = aU^2 \quad (3)$$

where a is a radius dependent proportionality coefficient. No doubt a is some function of wind speed; at higher wind speeds large bubbles stay in suspension longer as increased turbulence overcomes buoyancy forces. The exact relationship is not known and will have to be ignored in this study. Here a is calculated for each radius at $U = 3$ then used to calculate $N(r, U, 1)$ for various values of U . That is,

$$\begin{aligned} a &= N(r, 3, 1)/3^2 \\ N(r, U, 1) &= N(r, 3, 1)U^2/3^2 \end{aligned} \quad (4)$$

A table was then prepared listing surface bubble spectra versus wind speed.

SOLUTION RATE OF BUBBLES

Bubble solution rates are quite well known, and the following derivations are from *Wyman et al.* [1952] and *Blanchard and Woodcock* [1957]. According to the general gas law,

$$n = 4\pi r^3 p / 3RT \quad (5)$$

where n is the number of moles of gas in the bubble, R is the gas constant, T is the absolute temperature, r is the bubble radius, and p is the pressure in the bubble. If the surface tension is included, as it should be, the pressure in the bubble will be atmospheric pressure plus hydrostatic pressure plus $2\gamma/r$, the pressure due to surface tension. According to Fick's law of diffusion,

$$dn/dt = -\delta 4\pi r^2 (p + 2\gamma/r - p_0) \quad (6)$$

where $2\gamma/r$, the pressure due to surface tension, is included, p_0 is the partial pressure of air in the bulk water, and δ is a constant defined by $\Delta s/d$, where Δ is the diffusion constant of air in water, s is the solubility of air in water, and d is the shell thickness of water around the bubble across which the diffusion gradient occurs. Differentiating (5) with respect to time and then equating that with (6) and substituting $dV = 4\pi r^2 dr$, we obtain the following equation:

$$dV/dt = -\delta RT 12\pi r^2 [r(p - p_0) + 2\gamma]/(3pr + 4\gamma) \quad (7)$$

If we use the values $RT = 2.4 \times 10^4 \text{ cm}^3 \text{ atm/mole}$, $\gamma = 76 \times 10^{-8} \text{ atm cm}$, $\delta = 5 \times 10^{-9} \text{ mole/cm}^2 \text{ sec atm}$ [Wyman *et al.*, 1952] and let $p = 1 + (z/10)$, (7) reduces to

$$dV/dt = 4.52 \times 10^{-3} r^{-3} [z/10 + 1 - p_0 + 2(76 \times 10^{-6})/r]/[3(z/10 + 1)r + 4(76 \times 10^{-6})] \quad (8)$$

The sign was changed to denote input of gas to the water column. Here p_0 will normally be near 1 atm, and thus it is indicated that the water is saturated.

SOURCE STRENGTH CALCULATION

The source strength $S(z)$ is the time rate of diffusion of a volume of gas bubbles with a radius between r and $r + dr$ per unit volume of liquid at depth. At each depth, $S(z)$ is

$$S(z) = \int_0^\infty \left(\frac{dV}{dt} \right)_{z,r} N(r, U, z) dr \quad (9)$$

To apply this integral to the data derived from Medwin's observations, the following summation is used:

$$S(z) = \sum_{r=0.0043}^{0.02} 5 \left(\frac{dV}{dt} \right)_{z,r} N(r, U, z) \quad (10)$$

The surface spectrum was digitized at 0.0005-cm intervals, and so the 5 is placed in (10) to change to a 0.0001-cm interval for summation. The dV/dt is calculated by using (8). Figure 3 shows the results of these calculations for $L = 20$ meters and $U = 10, 20, 30$, and 40 m/sec. Between 0 and 1 meter, $S(z)$ cannot be calculated because, as was mentioned earlier, the

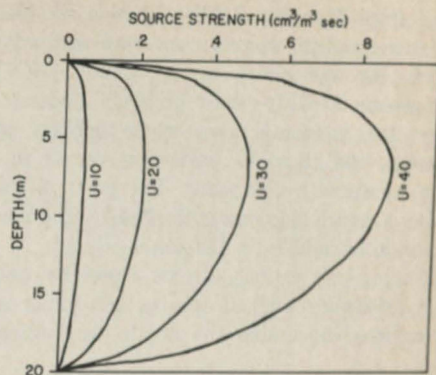


Fig. 3. Source strength versus depth at various wind speeds.

depth distribution equation (1) goes to infinity between 1 and 0. Intuitively, I feel that the source strength must be very near 0 at the surface, since the bubble solution rate dV/dt as calculated by equation (8) is near 0 at $z = 0$. Therefore $S(z)$ is extrapolated from $S(1)$ to $S(0) = 0$.

ESTIMATE OF FLUX DUE TO BUBBLE SOLUTION

The source strength at each depth also represents a flux of gas across the air-sea interface. By integrating the source strength (9) with depth, a surface flux can be calculated:

$$\begin{aligned} \text{Flux} &= \int_0^L S(z) dz \\ &= \int_0^L \int_0^\infty \left(\frac{dV}{dt} \right)_{z,r} N(r, U, z) dr dz \quad (11) \end{aligned}$$

The surface flux is calculated by using the estimate of (10) for the inner integral. The results are in Table 1. Since this flux is only in the area where whitecaps (and thus bubbles) occur, it must be corrected to represent an average flux for each square centimeter of the surface of the sea. The corrected flux is calcu-

TABLE 1. Calculated Flux at Various Wind Speeds for $L = 20$ Meters

Wind, m/sec	Flux, $\text{cm}^3/\text{cm}^2 \text{ sec}$	Corrected Flux, $\text{cm}^3/\text{cm}^2 \text{ sec}$
10	0.7×10^{-4}	0.017×10^{-4}
20	3.5×10^{-4}	0.9×10^{-4}
30	7.3×10^{-4}	7.3×10^{-4}
40	13.9×10^{-4}	13.9×10^{-4}

lated from Monahan [1971, equation 6]. This equation predicts whitecap coverage with wind speed. As was noted by Blanchard [1971], Monahan's [1971] values probably underestimate the horizontal area where bubbles are present, and thus the correction results in a very conservative estimate. The point is that quite a respectable flux is implied by the mere presence of bubbles in the water column.

Similar implications can be found by using only Medwin's original spectra and minor assumptions concerning the depth distribution.

COMPARISON WITH A STORM REQUIRED FLUX

During the passage of a typical storm the atmospheric pressure may fall and rise 10 to 20 mm Hg or about 1-2%. During the pressure change, gas will transfer from one phase to another at a rate dependent on the partial pressure difference and wind. If we assume a 20-mm Hg pressure drop during 12 hours and a 20-meter mixed layer, a flux of -1.8×10^{-4} cm³ air/cm² sec would be required to maintain equilibrium. Then, as the pressure rises, the flux would be $+1.8 \times 10^{-4}$ cm³ air/cm² sec. If the wind speed is 20 m/sec on the average, the solution of bubbles can contribute approximately 0.9×10^{-4} cm³/cm² sec, or half the flux required to maintain equilibrium. It is clear that the solution of bubbles significantly affects the flux of air in and out of the water column. In fact, bubbles may be a severe impediment to degassing of the water column.

COMPARISON WITH SEASONALLY REQUIRED FLUX

The normal seasonal heating and cooling of the water column causes gas to move across the interface. The flux is dependent on the amount of heating or cooling. In temperate latitudes the mixed water column may vary 20°C. If we assume a 20-meter water column and a normal salinity, the seasonal change would cause a flux of 8.5×10^{-7} cm³/cm² sec. Of course, this is the average for a season, and it could be expected that at times of extreme heating or cooling the required flux could be much higher. Redfield [1948] found the annual exchange in the Gulf of Maine to be 1.9×10^{-6} cm³/cm² sec. These values are again much less than the $\sim 10^{-4}$ -cm³/cm² sec flux resulting from bubble solution.

ONE-WAY EFFECT AND LAG TIME

Clearly, one of the incongruities in considering the role of bubbles in interfacial mass transfer is the one-way effect. Bubbles and their solution cause a transfer of gas into the water column because, once a bubble enters the main part of the water column, it will never reach the surface. Only bubbles that penetrate just the upper meter or so have any chance of reaching the surface before disappearing because of solution. Thus the effect of bubble solution on gas transfer from air to water is much easier to visualize than that from water to air. In this paper, only the air-water route will be considered. Since the object of this paper is to show that bubbles can indeed affect gas transfer in a substantial way, this limitation is valid. A theoretical development that considers the motion of a bubble in the velocity field of a breaking wave and turbulent mixed layer could lead to new insight into the problem.

If we assume a steadily changing atmospheric pressure, the gas content of the water column should decrease or increase correspondingly. Figure 4 shows how the expected integrated gas content of the mixed water column changes with time in response to changing atmospheric pressure. As atmospheric pressure drops, the total gas in the water column begins to decrease but lags behind the pressure drop. This lag results from the gas input by bubble solution and the mixing characteristics of the water column. As the atmospheric pressure begins to rise again, the water column gas content increases but again lags behind the rise in atmospheric pressure by an amount less than that during degassing. The lag here is caused by the

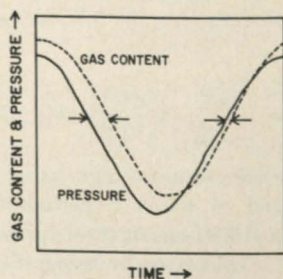


Fig. 4. Variation of mixed-layer gas content with changing pressure. Left center arrows indicate gassing lag, and right center arrows indicate degassing lag. Units are arbitrary.

mixing characteristics of the water column.

Data obtained from the offshore oil rig Sedneth-1 give an indication of the effect of lag time. Figure 5 shows a plot of the difference between the averages of the 0- and 4-meter and the 8- and 12-meter N_2 samples. With a pressure drop of 17 mb the gas content in the 0- to 6-meter interval drops in relation to the 6- to 12-meter interval, and thus it is indicated that the deeper waters of the mixed layer are not in contact with the interface as much as the surface water, as would be expected. The wind during the period started at 25 m/sec, fell to 9 m/sec, and toward the end rose to 16 m/sec. The data show how the water column does not act as a thoroughly mixed bulk water-interface water system but rather the waters of the mixed layer have sporadic depth dependent encounters with the surface. A lag time of approximately 5 hours is indicated.

CONCLUSION

The simple calculations that were made clearly indicate a potential gas flux into the

water column resulting from a bubble solution of about 10^{-4} cm^3/cm^2 sec. With even more conservative estimates of bubble populations and lower solution rates because of organic films, the potential flux is still considerable. The one-way effect surely causes higher rates of ingassing relative to degassing. Further theoretical treatment could consider the motions of bubbles in the turbulent mixed layer. This approach would be analogous to particle motion theories with the added complications of buoyancy and depth and radius dependent solution rates. The implications of air bubble solution on the distribution of gases in the mixed layer is discussed by Atkinson [1972], and a paper is being prepared on the subject.

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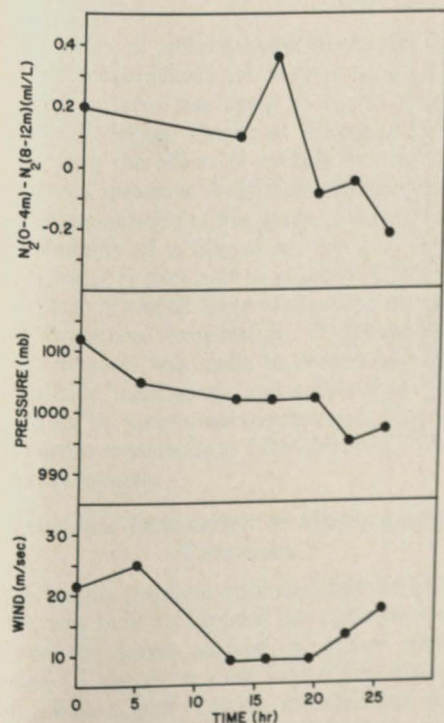


Fig. 5. Change of relative amounts of N_2 in the water column in response to dropping pressure.

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