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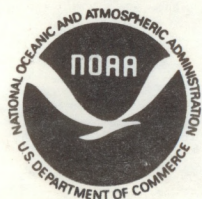


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ON THE CONTRIBUTION OF BUBBLES AND WAVES TO AIR-SEA
CO₂ FLUX, WITH IMPLICATIONS FOR REMOTE SENSING

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Boulder, Colorado
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**UNITED STATES
DEPARTMENT OF COMMERCE**

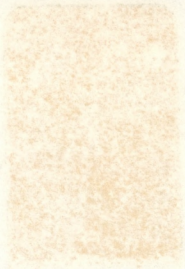
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Abstract

The concepts behind the simple one-dimensional models for gas transfer are described and the important parameters are defined. Two models for gas transport through bubbles are discussed, and relevant laboratory and field measurements are presented. The importance of the wave field is also discussed. The report concludes with a summary of the current state of our understanding of air-sea gas exchange and the implications for remote sensing of CO₂ flux.

1. INTRODUCTION

Gas exchange across the air-sea interface has a major role in establishing gas concentrations in the atmosphere, which in turn affect global conditions. In particular, it is believed that the ocean takes up much of the increase in carbon dioxide caused by human activities (e.g., Broecker et al., 1979; Siegenthaler, 1983). Without the ocean as a CO₂ reservoir, phenomena such as the "greenhouse effect" would probably occur much more rapidly. The physics of gas exchange across the ocean surface is, however, likely to be quite complicated. In addition, gas flux is a difficult quantity to measure directly.

Our basic understanding of air-sea gas exchange is based on simple one-dimensional diffusion models. In recent years, however, attention has been focused on the possible importance of wind waves, breaking waves, and bubbles to gas transfer between the atmosphere and ocean. My motivation for researching and writing this review stems from some fascinating underwater acoustic observations of ocean bubbles generated by breaking waves (e.g., Thorpe, 1982; Crawford and Farmer, 1987). I wished to evaluate the potential for estimating gas flux (in particular, CO₂ flux) from such observations.

2. GAS DIFFUSION MODELS

In most studies of gas exchange between the atmosphere and the ocean, a simple one-dimensional conceptual model has been used. The interface is treated as a system of two thin layers (films) through which gases pass continuously (Liss and Slater, 1974; Deacon, 1977; Hasse and Liss, 1980; also, see Fig. 1). The main body of each fluid is presumed to be well-mixed by turbulent diffusion, and molecular diffusion is assumed to dominate gas transport in the interfacial layers (i.e., viscous sublayers). The greatest resistance to gas exchange occurs near the interface, since molecular diffusion usually takes place much more slowly than turbulent diffusion. For gases that have rapid chemical reactivity or are highly soluble, such as SO_2 and H_2O , the greatest resistance occurs in the atmospheric sublayer; for most other gases, including O_2 , N_2 , and CO_2 , it occurs in the liquid sublayer. In the following, we consider only the latter group.

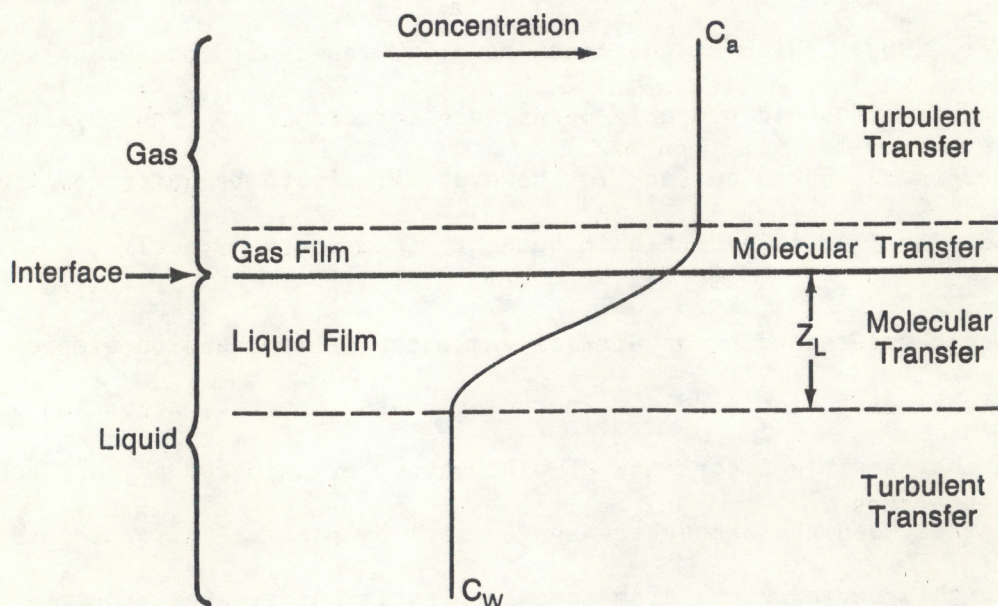


Figure 1. A two-layer model of a gas-liquid interface (after Liss and Slater, 1974). We assume that the greatest resistance to gas transfer across the interface occurs in the liquid sublayer (i.e., the gas film is much thinner than the liquid film). Greater turbulence in the liquid will reduce the liquid film thickness.

In a simple one-dimensional model, the gas flux F through the liquid sublayer is given by

$$F = -D \frac{dC}{dz} \quad (1)$$

where D is the (molecular) diffusion coefficient for the gas in question and C is the gas concentration. Historically, this is rewritten in terms of the difference in concentration across the layer (of thickness Z_L) and a transfer velocity (also known as a piston velocity) V :

$$\begin{aligned} F &= -V (C_{\text{air}} - C_{\text{water}}) \\ &= -V K (p_{\text{air}} - p_{\text{water}}) \\ &= -0.01 s V K X P \end{aligned} \quad (2)$$

where

$$V = D/Z_L, \quad (3)$$

$$s = 100 (p_{\text{water}} - p_{\text{air}})/p_{\text{air}} \quad (4)$$

is the percentage of supersaturation of the gas in water, P is atmospheric pressure, X is the mole fraction of the gas in the air, K is the gas solubility in water, p_{air} and p_{water} are the partial pressures of the gas in the air and ocean, and C_{air} and C_{water} are the mean concentrations of CO_2 in the air and in the ocean. The sign of the flux indicates upward (positive) or downward (negative) gas transport.

Many techniques for studying gas transfer measure the gas exchange rate, G , where

$$F = -0.01 s G. \quad (5)$$

(Note that the gas exchange rate has the same units as gas flux although the two are quite different measurements. Care must be taken when comparing obser-

vations from different studies.) Providing one can determine V (or G) under a given set of conditions, the gas flux can be evaluated from (2)--or (5)--by measuring the partial pressure of the gas in the air and in the near-surface ocean.

Several models have been proposed in the literature, suggesting that the transfer velocity should be proportional to some power of the Schmidt number, Sc^{-n} , where $Sc = \nu/D$ and ν is the kinematic viscosity of the water (alternatively, we could re-write the proportionality as D^n , since ν is constant). In the stagnant-film model described above, $n = 1$ (Liss, 1973; Broecker and Peng, 1974); for a smooth liquid surface, Deacon postulated $n = 2/3$. Most theoretical and laboratory results favor $n = 1/2$; field observations favor $n = 1$. Table 1 lists solubilities and diffusivities for several gases studied.

Table 1. Solubilities and diffusivities for several gases

Gas species	Molecular weight (g/mol)	Solubility in sea water* (mol m ⁻² atm ⁻¹ , at 24°C)	Diffusion coefficient* ($\times 10^{-5}$ cm ² s ⁻¹ at 24°C)
N ₂	28	0.52	2.1
O ₂	32	1.06	2.3
Ar	40	1.16	1.5
Rn	222	8.3	1.4
CO ₂	44	30	1.9
N ₂ O	44	22	2.0

* After Broecker and Peng (1982).

3. MODELS OF GAS FLUX DUE TO BUBBLES

At first inspection, it may appear that bubbles simply constitute an additional surface area through which gas transfer can occur. However, each bubble has a finite quantity of each composite gas. The direction and magnitude of flux for each gas depends on the relative proportion of each gas in the bubble and in the water, the solubility of each gas, and the depth of the bubble. Both the depth and the relative proportion of each gas will change in time, owing to gas diffusion and bubble motion. The net gas transfer for a bubble will be the flux integrated over the lifetime of the bubble in the water. Large bubbles will rise back to the surface within a short time of injection and then burst; small bubbles may dissolve before this occurs. The models discussed below are based on the work on bubble dynamics by Levich (1962) and Garrettson (1973).

Merlivat and Memery (1983) developed a gas diffusion model that included forces on bubbles due to hydrostatic pressure, drag, and an added mass effect (due to the inertia of the liquid in the presence of accelerated relative motion of the bubbles). The bubbles are assumed to comprise two gases: air and the gas of interest. In the model, the bubbles are injected at a depth of 0.1 m and then rise toward the surface. Turbulence and other upper ocean dynamical processes are ignored, but wave action can be included.

Using this model, Merlivat and Memery found that the bubbles become enriched in gases less soluble than air and depleted in those more soluble. Under calm conditions (with no surface waves present), the transfer velocity was proportional to $KD^{1/2}$. In the presence of a single frequency wave (which imparts an orbital motion on bubbles), the model predicts an enhancement of the exchange rate, the increase being larger for longer waves.

In order to determine the amount of gas transferred by bubbles, the two researchers used a bubble size distribution of the form

$$\phi \propto U_{10}^m r^{-b} e^{-cz} ,$$

where U_{10} is the wind speed measured 10 m above the water surface, r is the bubble radius, z is the depth, $m = 4.5$, $b = 4$ and $c = 0.1 \text{ m}^{-1}$ (from Wu 1981). Only bubbles with radii between 50 μm and 1000 μm were considered. Using a combination of laboratory observations and modeling results, Merlivat and Memery determined that the contribution of bubbles to the total gas transfer was as much as 60% for N_2O and up to 80% for Ar. The model predicts that for an equilibrium condition, in which there is no net gas transfer, the ocean is slightly supersaturated. The degree of supersaturation is higher for less soluble gases (assuming negligible difference in diffusivity). The results of Merlivat and Memery's modeling are for the most part in good agreement with their laboratory observations (Merlivat and Memery, 1983) except at the highest wind speeds studied, at which point wave-breaking was intense.

Thorpe (1982,1984a) developed a turbulent diffusion model of bubble dynamics that allows for a net downward component of velocity in addition to the buoyant rise speed of the bubbles. The gas inside each bubble is assumed to be nitrogen, oxygen, or a combination of the two. The model accounts for the effects of gas diffusion, hydrostatic pressure, surface tension, and advection on bubble size, and the mole fraction of each gas within a bubble. Thorpe (1984b) combined this model with observations of the acoustic scattering cross section from bubbles under conditions of a long fetch and estimated the flux of O_2 or N_2 through bubbles to be

$$F_b = M_o D K \left(\frac{2g}{9Dv}\right)^{1/3} P X \exp(0.74 U_{10}) s_1 (s_1 - s)$$

for $U_{10} < 14 \text{ m s}^{-1}$, where $M_o = 1.7 \times 10^{-8} \text{ m}^{-1}$, D is the diffusivity of the gas in water, g is the acceleration due to gravity, s is the percentage of supersaturation of the gas in water, and

$$s_1 = 1.5 + 0.5 U_{10}.$$

This indicates that there is a flux of gas into the water even when $s = 0$, which implies that the bubble flux produces supersaturated conditions in the water (as Merlivat and Memery [1983] also found). Thorpe also calculated an "equivalent piston velocity" for bubbles,

$$V_1 = 100 M_o D \left(\frac{2g}{9Dv}\right)^{1/3} \exp(0.74 U_{10}) s_1,$$

and showed that equilibrium is reached when the percentage of gas supersaturation in the water reaches

$$s_e = s_1 V_1 / (V_1 + V).$$

Thorpe suggested that steady winds of about 13 m s^{-1} are needed to maintain the observed 3% average supersaturation of O_2 in the ocean (more recently, Thorpe (1985) reduced this required wind speed estimate to 8 m s^{-1}). He cautioned, however, that the model is not applicable to the exchange of other gases, such as CO_2 , because their concentration may change significantly during the lifetime of bubbles.

Kitaigorodskii (1984) developed a theory focusing on the effect of wave-breaking on gas transfer. He argued that the turbulence generated by breaking waves plays an important role in gas transfer, and he developed a theory indi-

cating that the transfer velocity is proportional to $Sc^{-1/2} (\nu \epsilon_0)^{1/4}$, where ϵ_0 is the rate of turbulent energy dissipation uniformly distributed in the upper part of the turbulent patch. This theory does not appear to have been used yet in any study of the relationship between gas transfer and environmental parameters.

4. LABORATORY MEASUREMENTS

Most laboratory studies of gas flux across an air-water interface have been done in sealed wind-wave tanks. Waves are generated by a fan blowing across the water. Often, mechanically generated waves can also be added. The gases to be studied can be initially dissolved in the water or injected into the air above. Careful monitoring of gas concentration in the air and water as a function of time leads to gas flux estimates.

A number of early wind-wave tunnel experiments indicated that the gas transfer rate increased as the square of the wind speed (e.g., Downing and Truesdale, 1955; Kanwisher, 1963; Liss, 1973). More recent laboratory measurements (e.g., Broecker et al., 1978; Jahne et al., 1979) suggest that the exchange rate increases linearly with wind speed. Broecker et al. (1978) found that the presence of a surface-active film at the air-water interface inhibits wave growth and gas transfer. It is not clear if the latter effect is purely due to the reduced wave growth or if the film also acts as a barrier for gas exchange.

Most laboratory studies of air-sea gas exchange have stopped short of conditions under which wave-breaking and bubble entrainment occur. In recent years, however, there has been more interest in examining these higher wind

speed regimes. Merlivat and Memery (1983) performed a series of gas exchange measurements with Ar and N_2O in a wind-water tunnel. The water surface was covered with wind-driven waves. In addition, single-frequency mechanical waves could be superimposed (presumably to initiate the effect of swell, although the wavelengths are only on the order of 10 cm to 1 m). They found a linear variation between transfer velocity and wind speed for both gases for winds up to 9 m s^{-1} . The presence of the mechanically generated waves enhanced the transfer velocity by up to 30%. At higher wind speeds, V jumped by as much as a factor of 3, first for Ar and then for N_2O . This result was considered due to the onset of breaking waves and bubble entrainment.

Jahne et al. (1985) performed a series of gas exchange measurements in a large wind-wave facility, using He and Rn. They observed much lower transfer velocities than those obtained in other facilities. In addition, the wave growth rate was much lower than rates in other wind tunnels. Jahne et al. attributed the differences in transfer velocities to differences in the wave field arising from the presence or absence of currents and/or surface contaminants. Wave-breaking was not present at wind speeds lower than 12 m s^{-1} , and even at the greatest wind speed studied (13.8 m s^{-1}), wave-breaking was not intense. Concentrations of bubble distributions generated by breaking waves were low, leading to the authors' conclusion that bubbles did not contribute more than 4% to gas exchange.

It has often been assumed that the gas transfer rate is proportional to the square root of the Schmidt number of the gas being studied. This relation is used for intercomparison of studies using different gases. Merlivat and Memery (1983) concluded that this relation breaks down at high wind speeds, when wave

breaking is intense and large amounts of bubbles are entrained. They stated that in these regimes there is no straightforward method of computing exchange rates from one gas from measurements obtained for another. They found that an increase in gas transfer rate due to the presence of breaking waves occurred, first for Ar and at a higher wind speed for N_2O , in the presence of a "background" mechanically generated wave. They noted that Ar is the less soluble of the two gases. A similar result was obtained by Broecker and Siems (1984), who combined theoretical results with observations of bubble spectra in a wind-wave tank. They determined that bubbles start to enhance the gas exchange rate at lower wind speeds for O_2 , (which is less soluble than CO_2), than for CO_2 .

5. OCEAN MEASUREMENTS

Gas flux across the ocean surface is a difficult quantity to measure directly. Most researchers have attempted to measure instead the gas concentration difference and gas exchange rate (or piston velocity) and then infer the flux from (5)--or (2). The exchange rate is usually determined from radioisotope measurements, in particular, measurements of carbon-14 or radon-222 (see Broecker and Peng 1974, 1982; Jones 1980). Below, we describe briefly the concepts behind the isotopic measurements of CO_2 exchange.

Carbon-14 is a radioactive isotope with a half-life of about 6000 years. It is generated in the atmosphere (by cosmic rays and, more recently, by nuclear explosions), enters the ocean as a part of the CO_2 molecule, and usually decays within the ocean. The concentration of this isotope is usually measured in terms of the ratio of ^{14}C atoms to ^{12}C (natural carbon) atoms, $^{14}C/^{12}C$. The

flux of ^{14}C across the ocean surface depends on the gas exchange rate of CO_2 and on the air-sea $^{14}\text{C}/^{12}\text{C}$ difference. It is generally assumed that there was a steady-state distribution of ^{14}C before the Industrial Revolution, so that the decay of ^{14}C in the ocean was balanced by an influx from the atmosphere. Estimates of pre-anthropogenic $^{14}\text{C}/^{12}\text{C}$ in the atmosphere have been made from tree-ring samples; estimates for the ocean have been made from pre-nuclear testing of sea water and shells. From these numbers and from the decay rate of ^{14}C in the ocean, the CO_2 gas exchange rate has been estimated to be $17 \pm 4 \text{ mol m}^{-2} \text{ yr}^{-1}$ in pre-anthropogenic times and $20 \pm 5 \text{ mol m}^{-2} \text{ yr}^{-1}$ between 1970 and 1980 (Broecker et al., 1986). The fractional supersaturation (i.e., $s/100$) of dissolved CO_2 is usually much less than 1, so the CO_2 flux is much less than the exchange rate.

The CO_2 transfer rate can also be determined from the distribution of bomb-produced ^{14}C , specifically from the quantity of bomb ^{14}C in the ocean at one time and the history of the difference between bomb contributions to $^{14}\text{C}/^{12}\text{C}$ for atmospheric CO_2 and for the total CO_2 concentration in the surface water, ΣCO_2 (since CO_2 reacts with water, the total CO_2 concentration is the sum of the concentrations of CO_2 , HCO_3^- , and CO_3^{2-}). Broecker et al. (1980; 1985) showed that the inventory of bomb ^{14}C atoms can be estimated from vertical profiles of $^{14}\text{C}/^{12}\text{C}$, ΣCO_2 , and ^3H . The history of $^{14}\text{C}/^{12}\text{C}$ in the atmosphere is well documented, and bomb contributions to this ratio can be estimated from this information and from pre-bomb measurements; the history of $^{14}\text{C}/^{12}\text{C}$ for CO_2 dissolved in surface waters can be inferred from measurements on corals in some regions. On the basis of these bomb-produced radiocarbon data, Broecker et al. (1986) estimated the mean CO_2 exchange rate for the world's oceans to be about $20 \pm 3 \text{ mol m}^{-2} \text{ yr}^{-1}$. They also obtained more localized estimates for the

Indian, Pacific, and Atlantic Oceans, all of which are within 20% of the global exchange rate.

A third measurement technique is based on measurements of the ratio of radon-222 to radium-226. The radon isotope is a daughter of radium and has a half-life of about 4 days. It is therefore suitable for measurements on a much shorter time scale than ^{14}C . In the open ocean, the radon present in the ocean mixed layer is the result of in situ decay of ^{226}Ra dissolved in sea water, which is usually assumed to be uniformly distributed in the upper regions of the ocean (all natural waters contain ^{226}Ra). By measuring the ratio of ^{222}Rn to ^{226}Ra activity in mixed layer samples, one can determine the relative amount of radon escaping to the atmosphere and hence the radon evasion rate (that is, the rate at which radon escapes from the ocean into the atmosphere). The mixed layer thickness and the radon evasion rate vary with meteorological conditions, however, so researchers average results from several stations or several times to obtain a steady-state estimate. Peng et al. (1979) obtained an average world radon evasion rate and Broecker et al. (1986) used this value to obtain a mean global CO_2 exchange rate estimate of $16 \pm 4 \text{ mol m}^{-2} \text{ yr}^{-1}$ for an atmospheric CO_2 partial pressure of $3.3 \times 10^{-4} \text{ atm}$.

Peng et al. (1979) analyzed Rn observations over much of the Atlantic and Pacific Ocean. They found no clear relation between CO_2 exchange rate and the wind speed. More recently, Smethie et al. (1985) performed a similar study in the tropical Atlantic and found that the piston velocity was correlated with a (weighted-average) wind speed. Estimates of CO_2 flux varied between $1.4 \text{ mol m}^{-2} \text{ yr}^{-1}$ into the ocean to $2.7 \text{ mol m}^{-2} \text{ yr}^{-1}$ out of the ocean. Other researchers (e.g., Roos and Gravenhorst, 1984; Andrie et al., 1986) made local measurements

of the wind speed, inferring a piston velocity from laboratory results, and obtained comparable estimates of flux levels. Generally, the ocean absorbs CO_2 at high latitudes and releases CO_2 at low latitudes. Roos and Gravenhorst (1984) estimated that the total net global flux of CO_2 is into the oceans and accounts for about 13% of the anthropogenic emission of this gas. Broecker et al. (1986), in evaluating measurements from several types of isotope studies, indicated that estimates of zonal average net CO_2 fluxes vary from $-3 \text{ mol m}^{-2} \text{ yr}^{-1}$ to $3 \text{ mol m}^{-2} \text{ yr}^{-1}$.

The estimates of CO_2 exchange rates and fluxes obtained using isotopic measurements have response times on the order of a few days to several thousand years. None of these techniques is capable of measuring variations with time scales on the order of hours. In the past few years, however, a more direct technique has been developed using the method of eddy correlation, otherwise known as the micrometeorologic method. In this case, the flux of CO_2 is given by

$$F = \overline{w'c'} + E_H + E_Q ,$$

where w' is the fluctuation in vertical velocity about its mean w , c' is the fluctuation in CO_2 concentration (in mass/volume) about the mean concentration c , and E_H and E_Q are corrections for CO_2 entrained by a small mean vertical flow associated with heat and water vapor, respectively (see Smith and Jones, 1985). The correlation of w' and c' gives the vertical flux of CO_2 , after applying these corrections. Fluctuations in CO_2 concentration are determined by passing infrared light across a small path, which is open to the wind, and determining the amount of electromagnetic energy absorbed by the CO_2 absorption band centered at a wavelength of $4.3 \mu\text{m}$. Velocity fluctuations within the same

volume are obtained using sonic anemometers or other fast-response, high-resolution velocity sensors. Data are typically collected at 10 Hz or faster, but estimates are made about every half hour in order to get a statistically significant correlation.

The eddy correlation method has been used successfully for measuring CO₂ flux over vegetated fields (e.g., Ohtaki, 1984), where net fluxes ranged from 100 to 1000 mol m⁻² yr⁻¹. The values obtained compare very favorably with theoretical estimates. The detection threshold is about 10 mol m⁻² yr⁻¹. Jones and Smith (1977) measured CO₂ flux across the air-sea interface from a beach site and in light winds, obtaining upward fluxes between 16 and 25 mol m⁻² yr⁻¹. Wesely et al. (1982) obtained upward CO₂ fluxes of 35 to 230 mol m⁻² yr⁻¹ over shallow coastal waters at a wind speed of 3 to 10 m s⁻¹. The fluxes increased roughly linearly with wind speed. Bingham (1982) made measurements off the coast of San Diego, California, from an aircraft and reported fluxes of about 100 mol m⁻² yr⁻¹. Greenhut (1985) obtained vertical profiles of CO₂ flux over the ocean using an airborne system, and found significant vertical structure. Most recently, Smith and Jones (1985) found the mean flux to be near zero, although the surface water was supersaturated with CO₂ by about 15%. The range of fluxes they observed varied between -32 mol m⁻² yr⁻¹ and 17 mol m⁻² yr⁻¹. They also found that the flux was well-correlated with hourly variations in wind speed and they suggested that additional CO₂ is driven into the ocean by wave breaking and the downward mixing of bubbles when the wind speed increases.

The micrometeorologic measurements are quite controversial. Broecker et al. (1986) presented a detailed comparison of micrometeorologic measurements, isotopic measurements of CO₂ flux in the ocean, and laboratory measurements.

They noted that the maximum micrometeorologic measurements of flux are greater than all others by at least an order of magnitude. They showed that, to the best of our current understanding, the enhancement of CO₂ flux due to bubbles is not enough to explain these differences and they questioned the technique Smith and Jones (1985) used to measure CO₂ partial pressure in the ocean.

Smith and Jones (1986) responded to these criticisms by pointing out that their results describe short-term enhanced fluxes, related to changes in the wind speed, and that their mean observed flux was near zero (below the detection threshold). They added that the eddy correlation technique can respond much faster to changes in flux than can the isotopic methods, which have a response time on the order of the appropriate isotope half-life (a few days to thousands of years). Wesely (1986) suggested that vigorous near-shore wave and current action, greater than that implied from wind measurements alone, may have been responsible for a reduced sublayer thickness, Z_L , and hence for the large CO₂ fluxes observed by Jones and Smith (1977), Smith and Jones (1985), and Wesely et al. (1982). Smith and Jones (1985, 1986) postulated that the breaking waves and bubbles provide an additional component to the average or effective atmospheric pressure (and hence to the partial pressure of CO₂ in the air) that increases gas flux. They referred to this extra pressure as a "pumping pressure" and suggested that it is due to dynamic and hydrostatic pressure and surface tension effects on the entrained bubbles. Their results show that this is a transient phenomenon, which depends on changes in wind speed. More measurements and comparisons are needed before we can fully understand the discrepancies between the different measurements.

6. DISCUSSION

Wind speed does not appear to be the only parameter affecting the gas transfer rate and, hence, gas flux. Much of the recent laboratory work (e.g., Merlivat and Memery 1983; Jahne et al., 1985) indicates that gas transfer is strongly affected by the wave field. This in itself is some function of friction velocity, fetch, and surface contamination. On the other hand, in an analysis of several researchers' laboratory measurements, Broecker et al. (1986) found no clear dependence of V on fetch. Furthermore, although there is much variability among measurements of V in both laboratory and (isotopic) field studies, they are of the same order of magnitude and show comparable levels of scatter (Broecker et al., 1986; also, Fig. 2). There is an obvious need for studies to relate gas flux measurements with some measure of the actual wave field.

How do waves affect gas transfer? Hasse and Liss (1980) discussed the effects of surface waves on the simple gas diffusion model. They concluded that gravity waves have little effect except under high wind conditions, when breaking waves, spray, and bubble formation may become important. On the other hand, they suggested an increase in the transfer velocity of up to a factor of 2 in the presence of capillary waves, due to the increase in surface area and the periodic reduction in the thickness of the viscous sublayers. Merlivat and Memery (1983) showed that gas flux due to bubbles can be increased by wave action. Their results (theoretical and experimental) indicate that longer waves produce greater enhancement of gas exchange.

The contribution of bubbles to gas transfer across the air-sea interface continues to be a controversial subject. The field suffers from a lack of

measurements of bubble distributions and dynamics in the lab and in the ocean. There are few studies indeed where gas exchange and bubble measurements have been carried out simultaneously in either environment. The most recent laboratory and theoretical studies indicate that bubbles do not begin to have an important role in CO₂ transfer until the wind speed reaches about 13 m s⁻¹ (Merlivat and Memery 1983; Broecker and Siems 1984). Field measurements using isotopic methods show no significant relationship between fluxes and bubbles; micrometeorologic measurements by Smith and Jones (1985) suggest large transient variations in CO₂ flux due to changes in the wind speed, which may be related to the changing bubble distribution as the system reaches a new equilibrium.

In spite of the controversy between isotopic and micrometeorologic measurements, the former appear to be useful for determining the longer-term characteristics of CO₂ flux. It is not clear what the significance of short-term (i.e., hourly), localized variability is to long-term global scales, but the micrometeorologic studies may tell us more about the actual physics of gas transfer. It is also not clear what (if any) differences there are between CO₂ fluxes near shore, where most of the micrometeorologic observations have been made, and far offshore, where most isotopic studies have been carried out.

Of the two models of gas diffusion through bubbles summarized here, Thorpe's (1982, 1984a) work is the most consistent with recent observations of bubble distributions in the ocean. Clouds of bubbles can extend down to depths of 10 m and more in winds on the order of 10 m s⁻¹ and higher (Thorpe 1982; Crawford and Farmer 1987). Thorpe's models allow for a downward velocity component for bubbles, while Merlivat and Memery's (1983) model assumes that the bubbles are injected at a depth of 0.1 m and then rise back to the surface. However, as

noted previously, Thorpe's model is not appropriate for estimating CO_2 flux. The next step in the modeling process seems to be the incorporation of both a downward velocity component and surface wave action (which Merlivat and Memery found to be important in both their experimental and modeling results of gas exchange through bubbles). Initial bubble distributions for these models should be based on breaking wave studies (e.g., Cipriano and Blanchard, 1981), which suggest that more large bubbles are injected into the near-surface ocean than have been observed in background bubble distributions. Thorpe's model should be modified to allow calculation of CO_2 fluxes due to bubbles. Further model improvement may also be required to account for the biological uptake of CO_2 (e.g., Walsh et al., 1981).

Recent laboratory and theoretical studies indicate that, once wave-breaking and bubble entrainment become important, it is inappropriate to infer gas transfer rates for one gas from measurements for another gas by assuming a simple Schmidt number power-law relationship. This result brings into question some of the comparisons among different laboratory and field measurements. Often measurements for different gases are "normalized" to measurements for one gas using this relationship, as in Fig. 2, in order to compare results. This "normalization" may not be valid under conditions in which wave-breaking is present, particularly when gases with significantly different physicochemical properties are being compared.

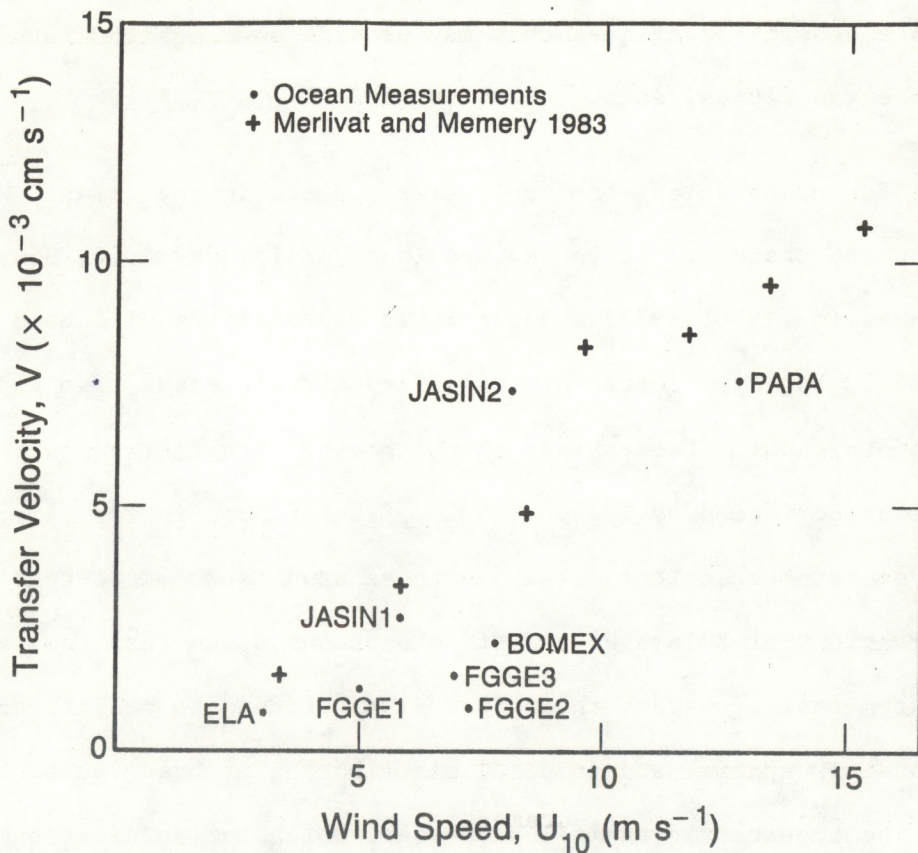


Figure 2. A comparison between laboratory and field gas transfer velocities for CO_2 (after Broecker et al., 1986). The field values are based on radon transfer velocity measurements and have been converted to CO_2 transfer velocities assuming a $Sc^{-1/2}$ dependence. The wind speeds and transfer velocities are averaged over several days. The data points correspond to different sets of experiments: ELA (Torgersen et al., 1982); FGGE 1, 2, and 3 (Kromer and Roether, 1983); BOMEX (Broecker and Peng, 1971); JASIN 1 and 2 (Kromer and Roether, 1983); PAPA (Peng et al., 1974). The laboratory results from Merlivat and Memery (1983) are provided for comparison. The inferred wind speed (at 10 m height) for the laboratory data was calculated from the friction velocity, assuming a drag coefficient of 1.3×10^{-3} .

7. REMOTE SENSING OF CO_2 FLUX ACROSS THE AIR-SEA INTERFACE

Although there is still some uncertainty, bubbles do not appear to have a significant role in the long-term CO_2 flux across the air-sea interface at low-to-moderate wind speeds. At high wind speeds, it is expected that the bubble contribution will be much more important. Unfortunately, there is little work,

either experimental or theoretical, in this regime. I describe below some potential remote sensing techniques that may provide some insight into bubble dynamics, bubble gas fluxes, and CO₂ flux in general.

There are few observations of bubble size spectra in the ocean. Most have been obtained using photographic techniques (e.g., Kolovayev 1976; Johnson and Cooke 1979). Medwin (1970, 1977) made acoustic measurements of bubble spectra in coastal waters, but his spectra are significantly different from those derived from photographic observations in the ocean. Single-frequency acoustic studies have been performed by Thorpe (1982), Crawford and Farmer (1987), and others. Analyses of backscatter levels in these studies are more consistent with the observations of Kolovayev and of Johnson and Cooke than they are with Medwin's measurements. However, there is a distinct need to measure both the size spectra and the spatial and temporal distribution of ocean bubbles in order to understand the important dynamical processes, which influence strongly the gas flux between the bubbles and the water. Measurements will need to be coupled to dynamical models to determine gas fluxes.

Acoustic techniques appear to be the most promising remote sensing tool for bubble studies. A multi-frequency acoustic system for mounting on a subsurface buoy has recently been developed at the Institute of Ocean Sciences and will provide estimates of bubble spectra as a function of space and time (D. Farmer; Institute of Ocean Sciences, Sidney, Canada; personal communication, 1987).

Future studies should investigate velocity structure of bubble plumes and correlate the plumes with breaking waves. In any Doppler system, there is a trade-off between spatial and velocity resolution. Acoustics offers a higher accuracy in this regard than does electromagnetics. The expected vertical

velocity scales are on the order of a few cm s^{-1} . One would like spatial resolution in the vertical of about 10 cm or so. This suggests that a coherent Doppler system is required (i.e., a system with phase coherence between pulses). One could take advantage of the wealth of research on Doppler radar techniques to devise a scheme for measuring bubble velocity profiles. One could also choose to investigate parametric transducer designs to increase the horizontal resolution of an upward-pointing Doppler system, although at reasonably high acoustic frequencies and reasonable transducer sizes the acoustic beam becomes quite narrow.

Although lidar systems will not provide simultaneously the required velocity and spatial resolution to measure velocity profiles of bubbles, they might prove useful for obtaining bubble concentrations (and, with multiple frequencies, perhaps bubble spectra) with very accurate spatial resolution. J. Churnside (NOAA) has found a commercial dye laser that can pulse 100 times per second with a pulse width of about 10 cm and a spot diameter on the ocean surface of about 10 cm (with the laser mounted on a plane at an altitude of about 50 m). The frequency is adjustable over some range. Initial estimates suggest that a sufficient signal level can be obtained with bubble concentrations on the order of 10^3 m^{-3} (J. Churnside; WPL, Boulder, Colorado; personal communication, 1987). The advantage of this system is that spatial surveys of bubble concentrations can be made much more quickly and with much finer spatial resolution than was previously possible with high-frequency acoustic systems mounted on a mooring or on a submarine.

R. Hill (NOAA), J. Churnside, and I have looked into the possibility of using the absorption of electromagnetic waves by CO_2 to measure CO_2 flux just

above the ocean surface. In particular, there exists a strong CO₂ absorption line at a wavelength of about 4.3 μm. At this wavelength there is little absorption due to water vapor. One technique is based on the scintillation pattern generated by CO₂ absorption fluctuations along a long propagation path. The technique involves measuring extremely small phase fluctuations (on the order of 10⁻²¹ radians) in the received signal, far beyond our present capabilities (R. Hill; WPL, Boulder, Colorado; personal communication, 1987). Another involves measuring the mean CO₂ concentration (using differential absorption) at two different heights to get the mean concentration gradient, measuring a turbulent diffusion coefficient using some wind sensor apparatus, and then calculating the flux. Under typical conditions, the concentration gradient is very much smaller than the mean concentration and would probably be below the noise level of the system. In addition, the absorption line widths are temperature dependent, so the transmission wavelengths would probably have to be adjusted frequently in order to use the differential absorption technique (J. Churnside; WPL, Boulder, Colorado; personal communication, 1987).

8. REFERENCES

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