

Relationship Between Wind Speed and Gas Exchange Over the Ocean

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Relationships between wind speed and gas transfer, combined with knowledge of the partial pressure difference of CO₂ across the air-sea interface are frequently used to determine the CO₂ flux between the ocean and the atmosphere. Little attention has been paid to the influence of variability in wind speed on the calculated gas transfer velocities and the possibility of chemical enhancement of CO₂ exchange at low wind speeds over the ocean. The effect of these parameters is illustrated using a quadratic dependence of gas exchange on wind speed which is fit through gas transfer velocities over the ocean determined by the natural-¹⁴C disequilibrium and the bomb-¹⁴C inventory methods. Some of the variability between different data sets can be accounted for by the suggested mechanisms, but much of the variation appears due to other causes. Possible causes for the large difference between two frequently used relationships between gas transfer and wind speed are discussed. To determine fluxes of gases other than CO₂ across the air-water interface, the relevant expressions for gas transfer, and the temperature and salinity dependence of the Schmidt number and solubility of several gases of environmental interest are included in an appendix.

INTRODUCTION

Much effort has gone into determining a relationship between gas transfer and wind speed, such that gas fluxes between ocean and air can be determined from air-water concentration differences and wind speed over the ocean [Deacon, 1980; Kromer and Roether, 1983; Liss and Merlivat, 1986; Smethie *et al.*, 1985; Upstill-Goddard *et al.*, 1990; Wanninkhof *et al.*, 1985]. Wind speed is not the only factor influencing the gas transfer velocity. Gas transfer is thought to be regulated by turbulence at the air-water interface [Jähne *et al.*, 1987a]. Boundary layer stability, surfactants, and bubbles are some of the other factors which influence gas transfer [Broecker *et al.*, 1978; Broecker and Siems, 1984; Goldman *et al.*, 1988; Jähne *et al.*, 1984b; Merlivat and Memery, 1983; Memery and Merlivat, 1985]. Several of these parameters are not intimately linked to wind speed, so it is likely that relationships using only wind speed to predict gas transfer velocities will be flawed. Parameters which are more closely related to surface turbulence, such as backscatter of microwave radiation from the water surface, might be better predictors of gas transfer. For this reason, scatterometer-derived winds, such as used by Etcheto and Merlivat [1988], or direct relationships between radar backscatter and gas transfer [Wanninkhof and Bliven, 1991] might be better suited for estimating gas transfer than wind speed records from ships. Only limited data on other parameters influencing surface turbulence are available for the ocean, and experiments in wind-wave tanks and on lakes have shown that wind has a major effect on gas transfer. Thus relationships of gas transfer and wind speed will continue to be used until more comprehensive predictive equations become available.

Several studies have used global or regional wind speeds

to determine gas transfer velocities and gas fluxes based on relationships between wind speed and gas transfer [Erickson, 1989; Tans *et al.*, 1990; Thomas *et al.*, 1988; Feely *et al.*, 1987; Murphy *et al.*, 1991]. Empirical relationships developed by Liss and Merlivat [1986] and one presented by Tans *et al.* [1990], in particular, have been used extensively in recent endeavors to determine air-sea fluxes of CO₂. The relationships have been used without regard for time interval of the CO₂ flux measurement or for possible chemical enhancement effects at low wind speeds.

DISCUSSION

The relationship of Liss and Merlivat [1986], hereinafter referred to as LM, is based on experimental results of a deliberate tracer gas exchange experiment of Wanninkhof *et al.* [1985]. Measurements in the tracer study only extend to wind speeds up to 8 m/s. For higher wind speeds, the experimental results are extrapolated based on the shape of the wind speed–gas transfer curve obtained in wind-wave tank work of Broecker and Siems [1984] and Broecker *et al.* [1978]. The LM relationship consists of three linear segments with breaks at wind speeds measured at 10-m height, u_{10} of 3.6 m/s, at the onset of capillary waves, and of 13 m/s when breaking waves and bubble entrainment enhance gas transfer.

Another relationship which has been used in modeling exercises is that originally proposed by Smethie *et al.* [1985] based on analyses of gas transfer data obtained by the radon deficit method in the Equatorial Atlantic. In this relationship, it is assumed that no gas transfer takes place between zero and 3 m/s wind speed (at 19.5-m height) and that gas transfer is linearly dependent on wind speed above 3 m/s. This relationship was subsequently used by Takahashi [1989] and Tans *et al.* [1990] but revised slightly, such that the line would go through the global average gas transfer velocity obtained from the bomb-¹⁴C inventory in the ocean. The modified relationship is expressed in terms of a CO₂ gas transfer coefficient rather than a transfer velocity (see appendix).

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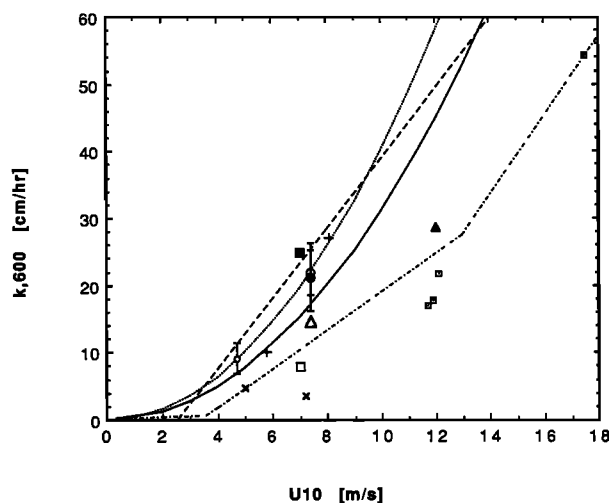


Fig. 1. Summary of some gas transfer results over the ocean. The solid square is average of the radon results of Glover in the Bering Sea [Glover and Reeburgh, 1987]. The open square is the Barbados Oceanographic and Meteorological Experiment (BOMEX) radon result from Broecker and Peng [1971] for the North Atlantic near Bermuda. The solid triangle is for radon at station PAPA [Peng et al., 1974] in the North Pacific. The open triangle is the mean value of all the Atlantic and Pacific radon values obtained during the Geosecs cruises [Peng et al., 1979]. JASIN (plus symbols) and First GARP Global Experiment (FGGE) (crosses) are radon results from Kromer and Roether [1983]. The squares with dots are results from a dual-tracer experiment in the North Sea by Watson et al. [1991]. The large open circle is the global bomb- ^{14}C value [Broecker et al., 1985]; the small open circle is the bomb- ^{14}C value for the Red Sea [Cember, 1989]. The solid circle is the global-averaged natural- ^{14}C value. The error bars for the ^{14}C values are an uncertainty estimate based on the uncertainty in the ^{14}C inventories. The long-dashed line is the best fit curve through the Equatorial Atlantic radon values taken during the TTO cruise [Smethie et al., 1985] forced through $u_{10} = 2.7 \text{ m/s}$, $k = 0 \text{ cm/hr}$. The dotted line is the best fit quadratic dependence through the ^{14}C data points and corresponds to the relationship we propose for gas transfer and long-term wind. The solid line is the curve we propose for gas transfer and short-term wind speed based on the ^{14}C values and the wind speed distribution around the mean oceanic wind speed. The dashed-dotted line is the relationship proposed by Liss and Merlivat [1986]. All data are normalized to $Sc = 600$, assuming that k is proportional to $Sc^{-1/2}$. Corrections are significant for many of the values. For instance, the in situ exchange obtained with radon at ocean station PAPA has to be multiplied by a factor of 2 to correct to $Sc = 600$. If a correction of Sc^{-1} is applied to the PAPA value, the gas transfer will be 4 times as high as the in situ value (see appendix).

Figure 1 shows that the relationship of Smethie et al. [1985] has a significantly stronger dependence on wind speed than that of LM. Data obtained using the radon deficit technique and the global ^{14}C gas transfer values are included in the figure. The large discrepancy between the two relationships and the scatter of the experimental values are indications of the large differences in results over the ocean. Differences are caused in part by uncertainties in measurement of gas transfer velocities and in determination of the wind speed; and in part because other factors which influence gas transfer have not been taken into account.

Any perturbation to surface turbulence can have an effect on gas transfer. Broecker et al. [1978] and Jähne et al. [1984a] have shown in wind-wave tank experiments that surfactants can have a large inhibitory effect on gas transfer. Goldman et al. [1988] have suggested that gas transfer is

retarded even at very low surfactant film pressures. Entrained bubble plumes from breaking waves will enhance gas transfer. Gas solubility will influence gas transfer rates if bubbles contribute to the gas transfer process [Jähne et al., 1984b; Merlivat and Memery, 1983; Memery and Merlivat, 1985]. Changes in wind direction can influence the wave field, possibly affecting gas transfer, but this has not been investigated to date.

In light of discrepancies and uncertainties in different wind speed data sets [Pierson, 1990; Boutin and Etcheto, 1990, 1991; Murphy et al., 1991] and in gas transfer velocities measured in the field [Roether and Kromer, 1984], and because other factors influence gas transfer over the ocean, it is not surprising that large differences in field and modeling results of gas transfer have been obtained. I speculate that some of the differences are due to a fetch dependence of gas transfer, and due to the averaging intervals of wind speed measurement.

Fetch Dependence of Gas Transfer

The gas transfer relationships of LM and Hartman and Hammond [1985] shown in Figure 2 might exhibit a weaker dependence on wind speed than proposed in this work because they were developed using data from fetch-limited systems. Work in wind-wave tanks has indicated that fetch has an influence on gas transfer [Jähne et al., 1989; Siems, 1980; Wanninkhof and Bliven, 1991]. Hartman and Hammond [1984] hypothesize that the difference in radon gas transfer velocities on different sides of San Francisco Bay is caused by a fetch dependence. Wave fields over the open ocean "grow" over distances of hundreds of kilometers off

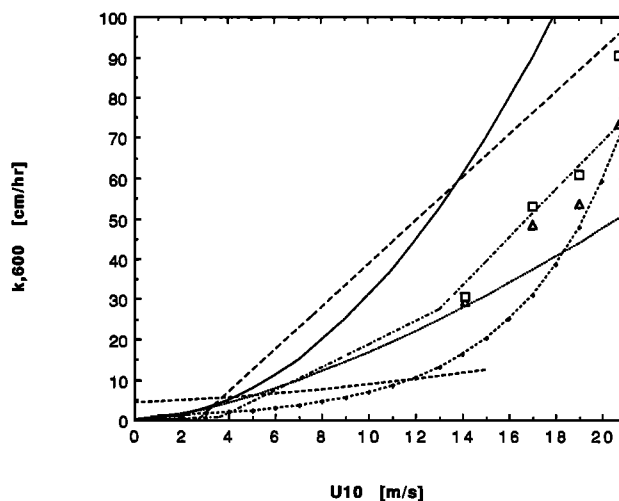


Fig. 2. Empirical gas transfer relationships. The dashed line is the relationship suggested by Smethie et al. [1985]. The solid line is the relationship we propose over the ocean for short-term winds (3). The relationship of Liss and Merlivat [1986] is indicated with a dashed-dotted line. The dotted line is the relationship of Hartman and Hammond [1985]. The lower dashed line is from Deacon [1980], in which he fitted the Geosecs radon values to wind speed after discarding approximately one-half of the values for not fulfilling specified criteria. The dashed line with the plus symbols is a relationship by Smith [1985]. The open triangles are tank-averaged gas transfer velocities from an experiment in a 100-m-long wind-wave tank. The open squares are the corresponding gas transfer velocities at 80 m downwind in the tank, illustrating the fetch effect in the tank [Wanninkhof and Bliven, 1991].

shore [Hasselmann *et al.*, 1975], suggesting that surface turbulence over the ocean influencing gas transfer also might be fetch dependent.

There is evidence of fetch dependence at low wind speeds based on gas transfer work performed using the deliberate tracer sulfur hexafluoride, SF_6 , on lakes with surface areas ranging in size from 0.13 km^2 to 500 km^2 [Crusius and Wanninkhof, 1990; Upstill-Goddard *et al.*, 1990; Wanninkhof *et al.*, 1985, 1987, 1991b]. Figure 3 gives the average gas transfer velocity for each of the experiments. The largest lake, Pyramid Lake, has the highest average gas transfer. The gas transfer velocities on Pyramid Lake also exhibit the strongest dependence on wind speed (Figure 4). There is significant scatter in the individual data points, but a least squares power law fit through all the data in Figure 4 yields a relationship $k_{600} = 0.45u_{10}^{1.64}$, $r^2 = 0.66$, where k_{600} is the gas transfer velocity at a Schmidt number of 600. Gas transfer measurements of Upstill-Goddard *et al.* [1990], which extend up to winds of 12 m/s, show that the increase in gas transfer is not as strong as would be predicted by the LM equation or by Smethie *et al.* The work of Upstill-Goddard *et al.* [1990] and the fetch effect observed in wind-wave tanks at higher wind speeds (see Figure 2) suggest that fetch dependence is particularly pronounced at higher wind speeds.

The trend of increasing gas transfer with increasing lake size could be caused by other factors. The experiments on two of the smaller lakes, Rockland Lake and Siblyback, were performed at water temperatures of 5°–10°C, while the experiments on the larger lakes were done at 18°–25°C. The correction to a common Schmidt number was performed

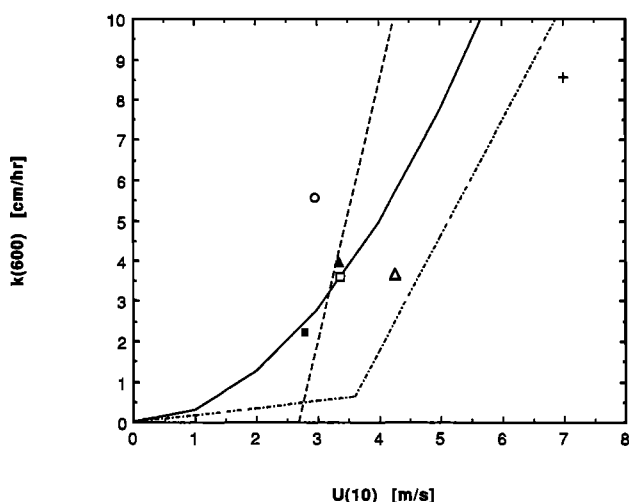


Fig. 3. One- to 3-month averaged SF_6 gas transfer velocities from experiments on lakes. The plus is for Siblyback Lake (surface area 0.5 km^2) [Upstill-Goddard *et al.*, 1990]. The solid square is for ELA lake 302N (surface area 0.13 km^2) [Crusius and Wanninkhof, 1990]. The open triangle is for Rockland Lake (surface area 1 km^2) [Wanninkhof *et al.*, 1985]. The open square is for Mono Lake (surface area 200 km^2) [Wanninkhof *et al.*, 1987]. The solid triangle is for Crowley Lake (surface area 20 km^2) [Wanninkhof *et al.*, 1987]. The open circle is for Pyramid Lake (surface area 500 km^2) [Wanninkhof *et al.*, 1991b]. The larger lakes show higher average gas transfer values at a particular wind speed. The relationship of LM is the dashed-dotted line. Equation (3) in the text is the solid line, and the dashed line is the relationship of Smethie *et al.* [1985]. All points are normalized to a wind speed at 10-m height and a Schmidt number of 600.

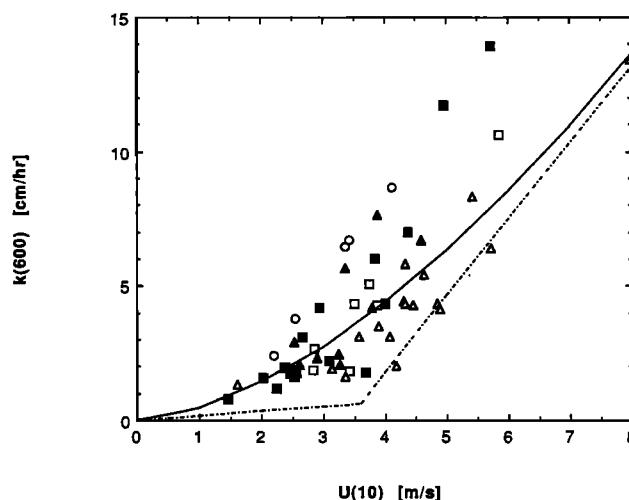


Fig. 4. Compilation of all the data points obtained by deliberate tracer experiments on lakes by Lamont Observatory. The data only cover a limited wind speed range. The different symbols refer to the data from individual lakes (see Figure 3). The scatter suggests that factors other than wind speed influence gas transfer. The solid line is a least squares power law fit of the form $k_{600} = 0.45u_{10}^{1.64}$ through all the data. The dashed-dotted line is the relationship suggested by LM.

using an estimated Schmidt number and a $\text{Sc}^{-0.5}$ dependence (see appendix). A large systematic error in the temperature dependence of the gas transfer velocity of SF_6 could cause the observed difference. However, the experiment on the smallest lake, ELA Lake 302N, was performed at water temperatures of 18°–22°C. Wind speeds were only measured at one location at the lakes, except for Pyramid Lake, where five anemometers were spread along the lake shore, and one on the lake. On this large lake, wind speed varied significantly with location. Even 6-week wind speed averages varied with location, ranging from 3.6 m/s at a land station to 1.9 m/s at the raft. This clearly indicates the importance of adequate wind speed measurements for gas transfer experiments, and that relationships between gas transfer and wind speed obtained on lakes can be biased by the location of the wind meters.

Wind Speed Variance

The variance of wind speed during the measurement interval can have a significant influence on the gas transfer velocity calculated from a relationship between gas transfer and wind speed. Gas transfer–wind speed relationships presented in the literature have been used without regard to the averaging period of the wind speed measurement. Some of the difference in calculated gas fluxes over the ocean could be caused by this effect. If the relationship between gas exchange and wind speed is nonlinear or has a nonzero intercept, the calculated gas transfer velocities at a particular mean wind speed will depend on the wind speed distribution. Most experimental results suggest that the relationship has a positive curvature, so gas transfer velocities measured over long time periods with variable winds will be higher than if gas transfer velocities are measured instantaneously or under steady wind conditions for the same average wind speed. Gas transfer velocities obtained with ^{14}C correspond to average long-term winds, while gas transfer measurements

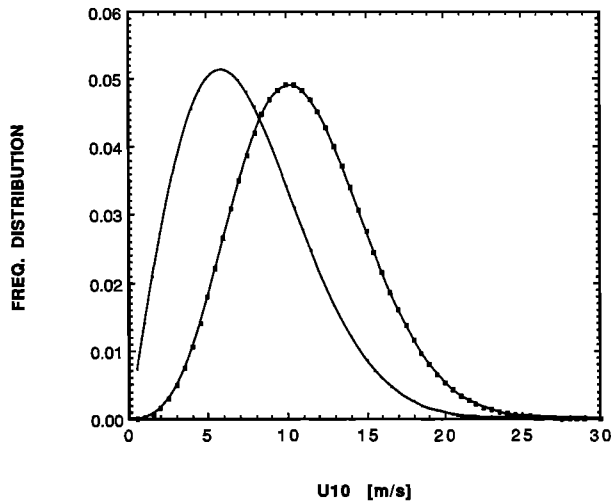


Fig. 5. Wind speed distribution used to determine the relationship between gas transfer velocity and steady wind speed (solid line). The fit is a normalized Rayleigh distribution function [Wentz, 1984]. The line with solid squares is the product of the wind speed distribution and the proposed gas transfer-wind speed relationship (3), indicating the importance of a particular wind speed on the oceanic gas transfer.

in wind tunnels are performed under steady wind conditions. The relationship of Liss and Merlivat is based on gas transfer velocities measured over 1–2 days on a small lake. Thus, because of the short time interval of measurement, the gas transfer-wind speed relationship of LM will yield low gas transfer values if long-term averaged winds over the ocean are used. The relationship used by Tans *et al.* [1990], to the contrary, has been fit through the long-term bomb- ^{14}C invasion rates over the ocean. This relationship will yield anomalously high values if used for short-term or steady winds.

To further illustrate this point and to quantify this effect, a quadratic dependence between gas transfer and wind speed is assumed, and the difference in proportionality in the case of steady (short-term) winds and long-term averaged winds is compared. Since a quadratic dependence is strongly nonlinear, the difference between short-term and long-term relationships will be larger than for a relationship with less curvature. A quadratic dependence of gas transfer and wind speed does not have any physical significance, but is a reasonable fit to experimental results. Wind tunnel results can be adequately modeled with a quadratic [Kanwisher, 1963; Wanninkhof and Bliven, 1991]. Gas exchange data obtained in the field have been related to wind speed with power laws using factors ranging from 1.5 [Hartman and Hammond, 1985] to 2.2 [Broecker *et al.*, 1985]. The LM relationship can also be closely approximated by a quadratic dependence in the range from zero to 15 m/s, of the form $k = 0.177u^2$.

The proportionality factor f in the relationship between the gas transfer velocity, k_{av} and long-term averaged wind speed squared ($k_{av} = fu_{av10}^2$) is determined using the bomb- and natural- ^{14}C gas exchange data from Broecker *et al.* [1986, 1985], and the Red Sea bomb- ^{14}C data from Cember [1989]. Bomb- and natural- ^{14}C invasion rates are related to gas transfer velocities (see appendix) using a pre-anthropogenic atmospheric pressure of CO_2 for water-

saturated air of 275 μatm for natural ^{14}C and an atmospheric partial pressure of 314 μatm for bomb- ^{14}C invasion, combined with a CO_2 solubility of 0.0324 mol/L atm at 20°C. The resulting CO_2 gas exchange values are 21.9 ± 3.3 cm/hr (wind speed 7.4 m/s) for the average ^{14}C gas transfer over the ocean determined with bomb ^{14}C , 21.2 ± 5.0 cm/hr (wind speed 7.4 m/s) for gas transfer determined from natural ^{14}C , and 9.11 ± 2.3 cm/hr for gas transfer on the Red Sea at an average wind of 4.7 m/s. The resulting equation is $k = 0.39u_{av}^2$. If the Schmidt number (Sc) dependency of gas transfer is included (see appendix),

$$k_{av} = 0.39u_{av}^2(Sc/660)^{-0.5} \quad (1)$$

where 660 is the Schmidt number of CO_2 in seawater at 20°C, as opposed to a Schmidt number of CO_2 of 600 at 20°C in fresh water (see appendix).

To obtain a relationship between steady wind speed and gas transfer, which would be more applicable for determination of gas transfer velocities using instantaneous or short-term wind speed measurements, a quadratic dependence is again assumed, and a global wind speed distribution is used. Wind speed distributions over the ocean are frequently expressed as Weibull distribution functions [Erickson and Taylor, 1989; Pavia and O'Brien, 1986]. A solution to the Weibull distribution for isotropic winds is the Rayleigh probability distribution function [Hennessey, 1977]. The Rayleigh distribution function can be defined in terms the average wind speed. It is a reasonable approximation for a global ocean wind speed frequency distribution [Wentz *et al.*, 1984]. The Rayleigh distribution function can be expressed as

$$P(u) = \frac{u[\exp(-u^2/2\Delta u^2)]}{2\pi\Delta u^2} \quad (2)$$

$$\Delta u = u_{av}(\pi/2)^{1/2}$$

where $P(u)$ is the probability distribution function, u is the steady wind speed, and u_{av} is the average climatological wind speed.

The normalized fraction of time the wind blows at a certain speed is determined at 0.5 m/s intervals from zero to 30 m/s from the Rayleigh probability distribution function (Figure 5). The proportionality constant, a , in the relationship $k = au^2$ is determined according to $a = \{k_{av}/\Sigma[P(u)u^2]\}$, where k_{av} is the long-term transfer velocity. This exercise is performed for the global bomb- ^{14}C and natural- ^{14}C transfer velocities using an average wind speed of 7.4 m/s, which yields values of $a = 0.31$ and 0.30, respectively. For the bomb- ^{14}C invasion rate in the Red Sea from Cember [1989] using a long-term climatological wind speed of 4.7 m/s, a value of 0.32 is obtained. Thus for steady winds, the relationship between gas transfer and wind speed is taken to be

$$k = 0.31u^2(Sc/660)^{-1/2} \quad (3)$$

The relationship (3) should be applicable to deduce gas transfer velocities at steady winds, from spot measurements using shipboard anemometers, and from wind speeds derived from scatterometers or radiometers.

Data points from field experiments at wind speeds of 12–17 m/s fall well below the curve which is proposed (see Figure 1). This could be an indication that a quadratic dependence

is too strong or that the experimental data at high wind speeds are systematically low. Radon gas transfer values at station PAPA could be low due to entrainment of water with high radon concentrations from below the mixed layer during stormy conditions. Gas transfer results at 17 m/s are from a dual gaseous tracer technique using ^3He and SF_6 [Watson *et al.*, 1991]. This method will yield low gas transfer velocities for He and SF_6 if gas transfer through bubbles is an important mechanism [Asher *et al.*, 1991].

No error estimates have been included for relationships (1) and (3). If we use the rough error estimates of ^{14}C invasion rates, the uncertainty in the proportionality factor in (1) is $\pm 25\%$. However, uncertainties in the global average wind speed are not quantified. Error estimates for (3) are even more nebulous, since there are large regional variances of wind speed distributions from the Raleigh distribution.

The relationships for long-term averaged wind speed and steady wind speed yield gas transfer velocities that differ by 30%, for the same average wind speed (Figure 1). This indicates that the time interval over which the wind speed is determined is important in models. This can, in part explain the puzzling discrepancy between the average gas transfer velocity obtained with radon during Geosecs [Peng *et al.*, 1979] and the average gas transfer velocity measured with ^{14}C (Figure 1). The gas transfer velocity measured with radon falls close to the line of gas transfer with steady winds. Winds used with the Geosecs radon gas exchange values are instantaneous or 24-hour averaged wind speeds and should be more closely related to steady winds. Other radon data at similar wind speeds vary by as much as a factor of 3, which indicates that other factors influence gas exchange and/or that experimental errors in measuring gas transfer with radon are significant.

Using the wind speed distribution and gas exchange relationship for steady wind suggested above, the relative contribution of gas transfer at particular winds to the total gas transfer velocity can be determined. Figure 5 shows that for a Raleigh distribution around an average wind speed of 7.4 m/s, the gas transfer distribution peaks at wind speeds of 10–11 m/s due to the nonlinear nature of the gas transfer–wind speed relationship proposed. Although wind speeds above 15 m/s do not occur frequently over the ocean, they do contribute significantly to the global gas transfer in the proposed relationship.

Chemical Enhancement of CO_2 Gas Transfer

Chemical enhancement of CO_2 exchange at low wind speeds over the ocean has been ignored in all relationships between gas transfer and wind speed. Chemical enhancement of CO_2 exchange occurs by reaction of CO_2 with water or hydroxide ions in the surface boundary. This increases the concentration gradient of the diffusing species in the water boundary layer and, thereby, the gas transfer. The contribution of chemical enhancement to CO_2 gas transfer has been determined by Bolin [1960], Emerson [1975], Hoover and Berkshire [1969], and Quinn and Otto [1971]. All the models are based on the stagnant film model of gas transfer and, except for the numerical model of Emerson, have certain simplifications regarding the hydroxide ion profiles and hydroxide ion concentrations in the boundary layer.

There has been some experimental verification of chemical enhancement in seawater. Peng [1973] [see also Broecker and Peng, 1974] performed laboratory experiments with a

stirred tank of seawater and observed significant enhancement of CO_2 exchange at low exchange rates compared to CO_2 exchange using acidified seawater. Hoover and Berkshire [1969] observed chemical enhancement in wind tunnel studies with distilled water using different buffer solutions. The magnitude of enhancement of exchange for solutions with $\text{pH} \approx 6.5$ compared to solution with $\text{pH} \approx 3$ was in agreement with their model. Liss [1973] did similar experiments and compared O_2 and CO_2 exchange. He also observed enhancement at low wind speed. Berger and Libby [1969] suggested that the enzyme carbonic anhydrase might be present in sufficiently high concentrations in surface seawater to enhance CO_2 exchange. Several experiments were since performed [Goldman and Dennet, 1983; Williams, 1983] which refute the large chemical enhancements observed by Berger and Libby [1969].

All experimental and theoretical evidence points to negligible enhancement at gas transfer velocities corresponding to steady winds above 5–7 m/s. To estimate the influence of chemical enhancement at low winds, we use the formulation of Hoover and Berkshire [1969] and consider two relationships between gas exchange and wind speed: the one suggested by Liss and Merlivat, and the relationship expressed in (3). The derivation of Hoover and Berkshire [1969] assumes constant pH in the surface boundary layer, which is a violation of electroneutrality conditions. The analytical solution of Hoover and Berkshire [1969] is similar to numerical solutions of Quinn and Otto [1971] and Emerson [1975], using electroneutrality constraints for unenhanced gas transfer velocities greater than 1 cm/hr.

The enhancement factor, $E(t, \text{pH}, k)$, due to chemical enhancement can be expressed in the form

$$E(t, \text{pH}, k) = \frac{F_{\text{en}}}{k_{\text{un}}(C_w - \alpha C_a)} \quad (4)$$

where F_{en} is the flux, k_{un} is the gas transfer velocity without chemical enhancement, C_w and C_a are the $\text{CO}_2(\text{gas})$ concentrations in water and air, respectively, and α is the Ostwald solubility coefficient. Thus $k_{\text{en}} = E(t, \text{pH}, k)k_{\text{un}}$, where k_{en} is the gas transfer velocity including chemical enhancement and $E(t, \text{pH}, k)$ is a function of pH , temperature, and k_{un} .

For the LM formulation, which is assumed to express k_{un} as a function of steady wind, k_{en} and wind can be related by $k_{\text{en}} = E(t, \text{pH}, k)[au_{10} - b]$. $E(t, \text{pH}, k)$ is determined according to Hoover and Berkshire [1969] using k_{un} obtained from the wind speed and the LM relationship. The result of this exercise at 20°C is shown in Figure 6. Significant enhancement at wind speeds up to 4 m/s are predicted.

Determination of the effect of chemical enhancement on (3) between steady wind and gas transfer is less straightforward because $^{14}\text{CO}_2$ exchange, which is influenced to the same extent by chemical enhancement as CO_2 , is used to derive the relationship between long-term averaged winds and gas transfer. A functional dependence between gas transfer and wind speed must be assumed, and the average gas transfer must be deconvolved in a similar manner as was done to derive (3). The functional dependence

$$k = [b(t) + du_{10}^2](\text{Sc}/660)^{-1/2} \quad (5)$$

is used, where $b(t)$ accounts for the chemical enhancement effect and d is the proportionality constant between wind

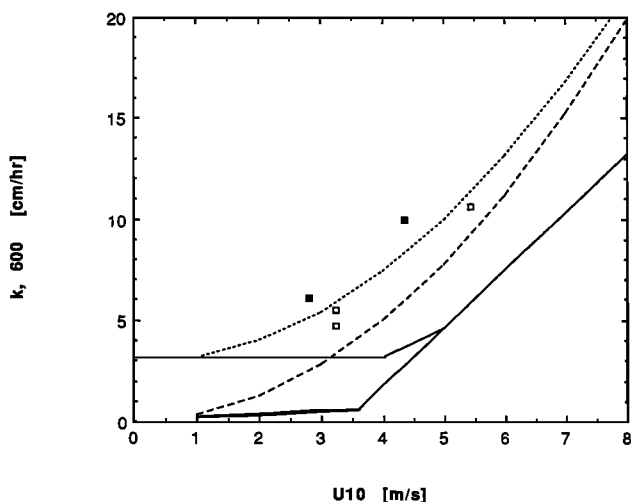


Fig. 6. Influence of chemical enhancement on gas transfer. The solid lines are the relationship of Liss and Merlivat [1986] (bottom solid line), and the enhanced exchange obtained by multiplying the gas transfer velocity by the chemical enhancement factor according to the formulation of Hoover and Berkshire [1969] (top solid line). The dashed lines are the relationship between gas transfer and wind proposed in the text (3) (bottom dashed line) and the relationship including chemical enhancement assuming that it has a functional form $k = b + du^2$ (see (8)) (top dashed line). The squares are the experimental results of Peng [1973] using seawater (solid squares) and artificial seawater (open squares). The measured unenhanced gas transfer value is converted to wind speed using the relationship $k = 0.31u^2$.

speed and gas transfer. Equation (5) implicitly assumes that chemical enhancement can be simply added to physical exchange. Theoretical work suggests that chemically enhanced gas transfer velocities reach a constant value at low exchange rates and that chemical enhancement becomes negligible at higher exchange, so the functional dependence suggested in (5) will slightly overestimate the effect of chemical enhancement at higher winds.

Using the analytical solution of Hoover and Berkshire [1969], rate constants from Johnson [1982], dissociation constants for carbonic acid and bicarbonate from Stumm and Morgan [1981], dissociation constant for water from Culberson and Pytkowicz [1973], a k_{un} of 1 cm/hr, and a pH of 8, the enhanced exchange is determined as a function of temperature. The values are fit to a second-order polynomial in temperature (in degrees Celsius).

$$b(t) = [2.5(0.5246 + 1.6256 \times 10^{-2}t + 4.9946 \times 10^{-4}t^2)] \quad (6)$$

Using this term and the Rayleigh distribution function for the average ocean wind speed, we can obtain factor d :

$$d = k_{av}/\{b(t) + \sum [P(u)u^2]\} \quad (7)$$

For the ^{14}C data point from the Red Sea, normalized to $\text{Sc} = 660$, (7) yields a value for d of 0.285. For the average ocean ^{14}C , $d = 0.304$. The latter value is only slightly different from the coefficient without enhancement, suggesting that for the whole ocean, chemical enhancement has little effect on the gas transfer velocities. Thus the relationship between gas transfer of CO_2 and steady wind speed is

$$k = [2.5(0.5246 + 1.6256 \times 10^{-2}t + 4.9946 \times 10^{-4}t^2) + 0.3u^2](\text{Sc}/660)^{-1/2} \quad (8)$$

The relationship is in agreement with the experimental work of Peng [1973] at lower wind speeds when chemical enhancement is most pronounced (see Figure 6). This could be fortuitous, since processes influencing gas exchange in the laboratory vessels and wind-wave tanks might be different from those in the field [Hasse, 1990].

Although chemical enhancement appears of little importance for gas transfer velocities over the ocean at winds greater than 5 m/s, large regions of the ocean have wind speeds less than this for a significant fraction of time. Chemical enhancement could have a pronounced effect in equatorial regions. These areas have large $p\text{CO}_2$ excesses in the mixed layer [Andrie et al., 1986; Feely et al., 1987; Keeling, 1965; Smethie et al., 1985]. The regions have low winds but large $p\text{CO}_2$ excesses, which results in large water-to-air CO_2 fluxes [Tans et al., 1990; Murphy et al., 1991]. Small changes in transfer velocity due to chemical enhancement have a large effect on the flux in these regions. Using an average wind speed of 4.7 m/s, which is representative for the Equatorial regions of the oceans, a surface water temperature of 25°C and a Rayleigh distribution probability function for the distribution of wind speed, 20% higher gas transfer velocities, and thus gas fluxes, are obtained at the equator for the enhanced case (8) compared to the unenhanced case (3). The effect of chemical enhancement using the LM relationship for the same scenario shows a 6% enhancement.

CONCLUSION

Many uncertainties regarding the relationship between gas transfer and wind speed remain. It is not clear whether wind speed can be used by itself to estimate gas transfer velocities. Extensive wind speed records are available for most of the ocean, and reasonable estimates of wind speed can be made for locations where wind records from ships are unavailable. Therefore it is tempting to use relationships between gas transfer and wind speed to determine global gas fluxes. The relationship between gas transfer and wind speed that is suggested in this work has much in common with others. It uses the trend of gas transfer with wind speed obtained from wind-wave tanks to determine the general shape of the curve, and uses field data for calibration. Relationships between gas transfer in wind tunnels can be well fitted to a quadratic dependence. The ocean ^{14}C gas transfer data of Broecker et al. [1985] and Cember [1989] are used in the proposed relationship along with long-term climatological winds to relate the dependence to the ocean. These winds are deconvolved to a wind speed distribution. The resulting equations suggest that for steady winds, a weaker dependence of gas transfer on wind should be used than if long-term averaged winds are used to estimate gas transfer velocities. When empirical relationships between gas exchange and wind speed are utilized that are not linear or do not intercept the origin, the appropriate relationship should be used, taking the averaging time scale for wind speed into account. This may in part explain why average gas transfer velocities determined from radon mixed layer profiles often fall below ^{14}C gas transfer velocities at similar wind speeds.

Another factor frequently overlooked in relationships between gas transfer and wind speed is that the chemical enhancement of CO₂ exchange will increase CO₂ fluxes at low wind speeds. The chemical enhancement effect is estimated based on theoretical work, but more work is necessary to determine the exact magnitude of this enhancement over the ocean.

APPENDIX

Expressions for Gas Transfer

The flux of a slightly soluble gas across the air-water interface can be expressed as

$$F = k(C_w - \alpha C_a) \quad (A1)$$

where k is the gas transfer velocity, C_w is the gas concentration in the bulk of the water near the interface, α is the Ostwald solubility coefficient, and C_a is the concentration of gas in the air phase near the interface; k is a function of the interfacial turbulence, the kinematic viscosity of the water μ , and the diffusion coefficient of the gas in question, D . The dependence of k on the last two terms is expressed as the Schmidt number ($Sc = \mu/D$). For a smooth liquid interface, k is proportional to $Sc^{-2/3}$ [Deacon, 1977], while for an interface with waves, most models predict that k is proportional to $Sc^{-1/2}$ [Coantic, 1986; Ledwell, 1984].

Several other terms are used to express gas transfer. In the stagnant film model of gas transfer [Higbie, 1935] the resistance to gas transfer is expressed in terms of a stagnant film z , which is independent of gas. The gas transfer velocity in this model is related to z by $k = D/z$. The stagnant film model implies that k is proportional to Sc^{-1} contrary to experimental evidence.

Gas transfer of CO₂ is sometimes expressed as a gas transfer coefficient K [Etcheto and Merlivat, 1988; Tans et al., 1990; Thomas et al., 1988]. The flux equals the gas transfer coefficient multiplied by the partial pressure difference between air and water:

$$F = K(p\text{CO}_{2w} - p\text{CO}_{2a}) \quad (A2)$$

where $K = kL$ and L is the solubility expressed in units of (concentration/pressure). For CO₂ the increase in $Sc^{-1/2}$ (and thus k) with temperature is nearly compensated by a decrease in L such that K is nearly temperature independent. For example, $(Sc^{-1/2}L)_{5C} = 1.07 (Sc^{-1/2}L)_{25C}$, while the Schmidt number changes by a factor of 3 over this range. In most recent estimates of CO₂ fluxes between the ocean and the atmosphere, K is assumed to be independent of temperature. Although the approximation will not introduce large errors, especially in light of other uncertainties determining K , it is preferable to use the exact form, since the approximation will cause systematic bias with temperature. This bias will be pronounced because the warmer ocean waters are frequently CO₂ sources, while the colder waters are CO₂ sinks.

The ¹⁴C gas transfer velocities referred to in the text were obtained from an inventory of bomb-produced ¹⁴C in the ocean (bomb ¹⁴C), or from the disequilibrium of ¹⁴C between the ocean and atmosphere corrected for bomb-produced ¹⁴C (natural ¹⁴C). These inventories yield a net ¹⁴C invasion rate I , which is sometimes referred to as the CO₂ exchange rate [Broecker et al., 1986, 1984]:

$$I = kLp\text{CO}_{2a} \quad (A3)$$

The invasion rate has the same units as flux and can be envisioned as a one-way flux from air to water. The net flux can be described in terms of I by

$$F = I \left[1 - \left(\frac{Lp\text{CO}_{2a}}{\text{CO}_{2w}} \right) \right] \quad (A4)$$

Temperature Dependence of Schmidt Number and Solubility

The gas transfer velocity can be estimated from wind speeds using (3) for steady or short-term winds, from (1) for long-term climatological winds, or from other relationships presented in the literature [Broecker et al., 1985; Hartman and Hammond, 1985; Liss and Merlivat, 1986; Smethie et al., 1985; Smith, 1985]. In most relationships it is assumed that k is proportional to $Sc^{-1/2}$. Experimental and theoretical work has shown that this is a reasonable assumption at intermediate wind speeds. Table A1 gives the constants to a third-order polynomial fit for the temperature dependence of

TABLE A1. Coefficients for Least Squares Third-Order Polynomial Fits of Schmidt Number Versus Temperature for Seawater (35‰) and Fresh Water for Temperatures Ranging From Zero to 30°C

Gas	A	B	C	D
<i>Seawater</i>				
He*	410.14	20.503	0.53175	0.0060111
Ne*	855.1	46.299	1.254	0.01449
Ar	1909.1	125.09	3.9012	0.048953
O ₂	1953.4	128.00	3.9918	0.050091
CH ₄ *	2039.2	120.31	3.4209	0.040437
CO ₂ *	2073.1	125.62	3.6276	0.043219
N ₂	2206.1	144.86	4.5413	0.056988
Kr*	2205.0	135.71	3.9549	0.047339
N ₂ O	2301.1	151.1	4.7364	0.059431
Rn*	3412.8	224.30	6.7954	0.08300
SF ₆	3531.6	231.40	7.2168	0.090558
CCl ₂ F ₂ (F-12)	3713.2	243.30	7.5879	0.095215
CCl ₃ F (F-11)	4039.8	264.70	8.2552	0.10359
<i>Fresh Water</i>				
He*	377.09	19.154	0.50137	0.005669
Ne*	764	42.234	1.1581	0.013405
Ar	1759.7	117.37	3.6959	0.046527
O ₂	1800.6	120.10	3.7818	0.047608
CH ₄	1897.8	114.28	3.2902	0.039061
CO ₂	1911.1	118.11	3.4527	0.041320
N ₂ *	1970.7	131.45	4.1390	0.052106
Kf	2032.7	127.55	3.7621	0.045236
N ₂ O*	2055.6	137.11	4.3173	0.054350
Rn*	3146.1	210.48	6.4486	0.079135
SF ₆	3255.3	217.13	6.8370	0.086070
CCl ₂ F ₂ (F-12)	3422.7	228.30	7.1886	0.090496
CCl ₃ F (F-11)	3723.7	248.37	7.8208	0.098455

$Sc = A - Bt + Ct^2 - Dt^3$ (t in degrees Celsius). The Schmidt number is defined as the kinematic viscosity of water divided by diffusion coefficient of the gas.

*These diffusion coefficients were determined experimentally by Jähne et al. [1987b] and fitted to a temperature relationship of $D = e^{-(Ea/RT)}$. For the other gases the relationship of Wilke and Chang [1955] was used: $D = (7.4 \times 10^{-8} (qM_b)^{0.5} T) / (n_b V_a^{0.6})$, where q is the association factor of water (=2.26), n_b is the dynamic viscosity of water, M_b is the molar weight of water, and V_a is the molar volume at boiling point. The empirical fit should not be used outside the zero to 30°C temperature range, as the fit deviates rapidly from the calculated values outside this range. The reader is urged to consult and cite the original publications from which these data are derived.

TABLE A2. Temperature and Salinity Dependence of Solubilities Using the Fit $\ln \beta = A_1 + A_2(100/T) + A_3 \ln(T/100) + S[B_1 + B_2(T/100) + B_3(T/100)^2]$, where β is the Bunsen Solubility Coefficient, Unless Noted Otherwise, T is Temperature in Degrees Kelvin, and S is the Salinity in Per Mille

Gas	A_1	A_2	A_3	B_1	B_2	B_3
He	-34.6261	43.0285	14.1391	-0.042340	0.022624	-0.0033120
Ne	-39.1971	51.8013	15.7699	-0.124695	0.078374	-0.0127972
Ar	-55.6578	82.0262	22.5929	-0.036267	0.016241	-0.0020114
O ₂	-58.3877	85.8079	23.8439	-0.034892	0.015568	-0.0019387
CH ₄	-68.8862	101.4956	28.7314	-0.076146	0.043970	-0.0068672
CO ₂ *	-60.2409	93.4517	23.3585	0.023517	-0.023656	0.0047036
N ₂	-59.6274	85.7661	24.3696	-0.051580	0.026329	-0.0037252
Kr	-57.2596	87.4242	22.9332	-0.008723	-0.002793	0.0012398
N ₂ O*	-64.8539	100.2520	25.2049	-0.062544	0.035337	-0.0054699
Rn	-11.95	31.66				
SF ₆	-520.606	250.60	(75.701)‡	-0.0117		
F-11†	-136.2685	206.1150	57.2805	-0.148598	0.095114	-0.0163396
F-12†	-124.4395	185.4299	51.6383	-0.149779	0.094668	-0.0160043

The Bunsen coefficient β is defined as the volume of gas at STP dissolved in a unit volume of solution at temperature T when the total pressure and fugacity are 1 atm. K_0 is related to β by $K_0 = \beta/\rho v^+$, where ρ is the density of the solution and V^+ is the molar volume of the gas at STP. The Ostwald solubility coefficient α (see (A1)) is related to β by $\alpha = \beta/T$ (T in degrees Kelvin).

*The solubility is expressed as K_0 (mol/(kg atm)) instead of a Bunsen solubility coefficient.

†The solubility is expressed as K' (mol/(kg atm)). $K' \approx K_0 f/[x(P - P_{H_2O})]$ where f is the fugacity, x is the mole fraction, and P and P_{H_2O} are the total pressure and vapor pressure of water, respectively. This relationship only holds for $x \ll 1$ and $P \approx 1$ atm.

‡For SF₆ the coefficient A_3 relates to $A_3 \ln T$, rather than $A_3 \ln (T/100)$. The solubilities were obtained from the following authors (with the estimated accuracy in parentheses): Ar, N₂ and O₂ [Weiss, 1970] (0.4%); N₂O [Weiss and Price, 1980] (0.3%); Kr [Weiss and Kyser, 1978] (0.4%); CH₄ [Weisenburg and Guinasso, 1979] (1%); chlorofluorocarbons 11 and 12, F-11, F-12 [Warner and Weiss, 1985] (1.5%); CO₂ [Weiss, 1974] (0.3%); SF₆ [Wanninkhof et al., 1991a] (5%); He, Ne [Weiss, 1971] (0.5%); Rn [Hackbusch, 1979]. The reader is urged to consult and cite the original publications from which these data are derived.

the Schmidt number for several gases of environmental interest for seawater and fresh water. These constants were derived by fitting a third-order polynomial through estimates of the Schmidt number. The functional dependence is a curve fitting with no physical significance. The uncertainty in the Schmidt number ranges from 3% to 10%, depending on the gas (mainly due to uncertainties in the diffusion coefficients).

Diffusion coefficients and their temperature dependence were obtained from experimental work by Jähne et al. [1987b]. They fit their data to an exponential function with temperature. The root mean square (rms) deviation of the data points from the best fit is 5% or less. The empirical equation of Wilke and Chang [1955], adjusted for the revised association factor of water [Hayduk and Laudie, 1974], was used for the gases that were not measured by Jähne et al. [1987b]. This equation was compared by Hayduk and Laudie [1974] to available published data and was found to have an average absolute error of 5.8% for gases other than helium and hydrogen. This error is comparable to the error of measurement of the diffusion coefficients.

To derive the Schmidt numbers for seawater, the diffusion coefficients measured in fresh water were decreased by 6% to account for the difference of diffusion of helium in distilled water and seawater as determined by Jähne et al. [1987b]. The kinematic viscosity of distilled water was multiplied by $1.052 + 1.300 \times 10^{-3}t + 5.000 \times 10^{-6}t^2 - 5.000 \times 10^{-7}t^3$ (t in degrees Celsius) to obtain seawater (35‰ salinity) viscosities. This fit is based on experimental work of Rupp and Krummel [Krummel, 1907]. The difference in diffusion coefficient and viscosity between fresh water and

salt water increases the Schmidt number for gases in seawater by approximately 10% compared to freshwater values at the same temperature.

If bubbles contribute significantly to gas transfer, the parameterization of gas transfer velocity will include solubility. Equations (1) and (3) and the equations of Liss and Merlivat [1986] and Tans et al. [1990] were developed specifically for CO₂ exchange. Although the influence of bubbles on gas transfer is poorly understood and not extensively studied, it is clear that if transfer through bubbles is a significant mechanism, gases with low solubility will experience a greater enhancement than gases with higher solubility, such as CO₂ [Broecker and Siems, 1984; Jähne et al., 1984b; Merlivat and Memery, 1983; Memery and Merlivat, 1985].

In order to determine the flux of a gas, the solubility has to be known in addition to the gas transfer velocity. Solubilities have been measured for most gases of geochemical interest. Table A2 gives the equations for the temperature and salinity dependence for solubilities of several gases expressed in the units most often used for the gas in question. Approximate conversions between units are also included. The functional form is derived from an expansion of the "Van t'Hoff" equation including terms for the salting out effect (the Setschenow relationship). The reader is referred to several papers by Weiss and co-workers [Warner and Weiss, 1985; Weiss, 1970, 1971, 1974; Weiss and Kyser, 1978; Weiss and Price, 1980], and a summary paper of Wilhelm et al. [1977] for discussion of methods and the accuracy of the solubility measurements.

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