

# Tracers of Air-Sea Gas Exchange [and Discussion]

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## Tracers of air–sea gas exchange

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The flux of gas across the air–sea interface is determined by the product of the interfacial concentration difference driving the exchange and a rate constant, often termed the transfer velocity. The concentration-difference term is generally obtained by direct measurement, whereas more indirect approaches are required to estimate the transfer velocity and its variation as a function of controlling parameters such as wind and sea state.

Radioactive tracers have proved particularly useful in the estimation of air–sea transfer velocities and, recently, stable purposeful tracers have also started to be used. In this paper the use of the following tracers to determine transfer velocities at the sea surface is discussed: natural and bomb-produced  $^{14}\text{C}$ , dissolved oxygen,  $^{222}\text{Rn}$  and sulphur hexafluoride. Other topics covered include the relation between transfer velocity and wind speed as deduced from tracer and wind-tunnel studies, and the discrepancy between transfer velocities determined by using tracers and from eddy correlation measurements in the atmosphere.

### 1. BASIC PRINCIPLES OF AIR–SEA GAS EXCHANGE

The net flux ( $F$ ) of a gas across the sea surface is given by the product of the interfacial concentration (strictly fugacity) difference ( $\Delta C$ ) driving the flux and a factor that quantifies the kinetics of the exchange, often called a transfer velocity ( $K$ ):

$$F = K \cdot \Delta C. \quad (1)$$

The term  $\Delta C$  is generally obtained by direct measurement of near-surface air and water gas concentrations and is not discussed further here. There are many papers on the subject, a convenient up-to-date selection of which are the chapters by Andreae (on sulphur compounds), Atlas & Giam (on high molecular mass synthetic organic compounds), Conrad & Seiler (on  $\text{CO}$  and  $\text{H}_2$ ), Fitzgerald (on mercury), Liss (on low molecular mass halocarbon gases) and Siegenthaler (on  $\text{CO}_2$ ), all in Buat-Ménard (1986).

The transfer velocity in (1) includes contributions from both the air and seawater near to the interface. However, it is possible to split the overall transfer velocity ( $K_w$ , where the subscript indicates that  $\Delta C$  is expressed on a water-phase basis) into its air and water-phase components:

$$\frac{1}{K_w} = \frac{1}{\alpha k_w} + \frac{1}{H k_a}, \quad (2)$$

where  $k_w$  and  $k_a$  are the transfer velocities in the water and air, respectively;  $H$  is the Henry Law constant of the exchanging gas (dimensionless ratio of air:water concentrations at equilibrium); and  $\alpha$  is a factor that accounts for any enhancement of transfer on the water side of the interface from chemical reaction between the exchanging gas and the water. For unreactive gases  $\alpha = 1.0$ , whereas for those like  $\text{SO}_2$  that have rapid aqueous-phase chemistry,

$\alpha$  can have a value of several thousand (Liss 1971). The form of (2) is similar to that for addition of electrical conductances in series and by using the same analogy the equation can be written in terms of resistances to interfacial gas transfer:

$$R_w = r_w + r_a, \quad (3)$$

where

$$R_w = (K_w)^{-1}, \quad r_w = (\alpha k_w)^{-1}, \quad r_a = (Hk_a)^{-1}.$$

By substituting into (2) and (3) reasonable values for the various quantities it can be shown that for most gases either  $r_w$  or  $r_a$  is dominant. Thus, for gases that partition strongly into the water (low  $H$ ) and/or react rapidly in the aqueous phase,  $r_a \gg r_w$ ; gases in this class include  $H_2O$ ,  $HCl$ ,  $SO_2$  and  $HNO_3$ . On the other hand, for gases that have high values of  $H$  and are inactive or only slowly reactive in water,  $r_w \gg r_a$ . This type includes many of the oceanographically important gases including  $O_2$ ,  $N_2$ ,  $CO_2$ , the Group 0 elements,  $SF_6$  and the Freons. Thus, for the purpose of this paper it is permissible to confine attention to  $r_w$  and the factors controlling it, i.e.  $\alpha$  and  $k_w$ . A further simplification is also possible because for all of these gases, with the possible exception of  $CO_2$ , their slow or non-existent reactivity in seawater means that  $\alpha$  is effectively unity. Even for  $CO_2$  the extent of exchange enhancement by chemical reaction is small, with  $\alpha$  estimated to be about 1.02–1.03 under typical oceanic conditions (i.e. only a 2–3% increase in  $k_w$  compared with an inactive gas). Thus, in the present context, for all practical purposes, it is the value of  $k_w$  alone that is important. The discussion of air–sea transfer velocities given here has been kept to a minimum. The interested reader will find a more detailed treatment in, for example, Liss (1983).

## 2. THE USE OF TRACERS IN THE MEASUREMENT OF $k_w$ AT THE SEA SURFACE

A variety of gases have been used as tracers in the estimation of the liquid-phase transfer velocity,  $k_w$ , at the air–sea interface. In this section the various methods and the results of their application are reviewed.

### (a) *Natural and bomb-produced $^{14}C$*

Natural  $^{14}CO_2$  in the atmosphere is produced by the bombardment of nitrogen molecules by cosmic rays. Assuming this production is time invariant and that steady state exists in the atmosphere–ocean system, the rate at which  $^{14}CO_2$  enters the oceans across the sea surface must balance the rate at which the  $^{14}C$  activity decays in the oceans. As Broecker & Peng (1974) have shown, by substituting measured values for the  $^{14}C$  activity in the atmospheric and oceanic reservoirs into the steady-state equation a global estimate of  $k_w$  may be obtained.

Another way radiocarbon enters the atmosphere–ocean system is from the detonation of nuclear bombs. The temporal and spatial variations in bomb  $^{14}C$  in the atmosphere since nuclear-weapons testing started in 1954 are well documented. By integrating the excess  $^{14}C$  (i.e. from bomb detonation) in oceanic depth profiles, the rate of uptake of this radiocarbon and hence its air–sea transfer velocity may be calculated (Broecker & Peng 1974).

Values of  $k_w$ , whether obtained from natural or bomb  $^{14}C$ , average about  $20 \text{ cm h}^{-1}$ , with a probable error of less than 25%. It should be stressed that this is very much a large-scale or global estimate and says nothing about the variability of  $k_w$  in space and time, or with possible controlling parameters such as wind speed or wave field. Although lacking in sensitivity, the use of  $^{14}C$  in this context sets important constraints on other methods that may produce values

of  $k_w$  with greater resolution. For example, a technique that consistently predicts  $k_w$  as very different from  $20 \text{ cm h}^{-1}$  must be suspect (see § 2e); unless our understanding of the partitioning of  $^{14}\text{CO}_2$  in the atmosphere-ocean system is grossly in error, which seems unlikely.

(b) *Dissolved-oxygen-balance method*

In this approach a time series of dissolved-oxygen measurements is made at some location. The total change in oxygen concentration between observation times ( $\delta\text{O}_2^t$ ) is then attributed to a combination of biological production-consumption due to photosynthesis-respiration and decomposition ( $\delta\text{O}_2^b$ ), and exchange across the sea surface ( $\delta\text{O}_2^e$ ). Then,

$$\delta\text{O}_2^t = \delta\text{O}_2^e + \delta\text{O}_2^b. \quad (4)$$

The method was first described by Redfield (1984) and he used the so called 'Redfield ratios' to obtain the term  $\delta\text{O}_2^b$ , as have all subsequent workers. The Redfield ratio links the change in oxygen to the concomitant change in dissolved phosphate (or other nutrient). Thus, by making measurement of changes in phosphate at the same time as those for dissolved oxygen, it is possible to correct the measured changes in oxygen concentration for biological addition or subtraction in the water column. The residual signal is then attributable to the exchange flux across the sea surface, and knowing the concentration gradient, the transfer velocity for oxygen can be calculated.

Although simple in concept, there are several important assumptions involved in this approach; for example, that the single value of the Redfield ratio ( $1\text{PO}_4^{3-} = 138 \text{ O}_2$ ) applies in every area, and that horizontal and vertical advection of water into or out of the study area brings about no change in oxygen concentration. The method and its associated assumptions are discussed in greater detail in Liss (1983), where the main results of its application in a number of areas are summarized. Values of  $k_{\text{O}_2}$  measured with this technique in summer range between  $5$  and  $15 \text{ cm h}^{-1}$ , with winter values from  $40$  to  $50 \text{ cm h}^{-1}$ . The increased values in winter may be because of generally higher wind speeds in that season (see § 3). There would not seem to be any significant discrepancy between the results from this approach and the globally averaged values given by the  $^{14}\text{C}$  methods. Some results obtained by Tsunogai & Tanaka (1980) from applying the oxygen-balance method in Funka Bay, Japan, are shown in figure 1. A clear increase in  $k_{\text{O}_2}$  from summer to winter is apparent, and there is evidence that the transfer velocity increases by more than the single power of the measured wind speed.

(c) *Radon-deficiency method*

This technique was first described by Broecker (1965) and relies on measuring the radioactive disequilibrium between the nuclides  $^{222}\text{Rn}$  and  $^{226}\text{Ra}$  in near-surface seawater. In the deep oceans the two isotopes are found to be generally in radioactive equilibrium. However, near the sea surface the gas  $^{222}\text{Rn}$  is lost to the atmosphere because its activity in air is much less than that in seawater. By assuming steady state, for any measured vertical profile the rate of loss of  $^{222}\text{Rn}$  to the atmosphere must equal the depth integrated deficiency in  $^{222}\text{Rn}$  activity. The following equation shows this equality.

$$k_{\text{Rn}}(A_I - A_A) = \lambda \int_0^\infty (A_E - A_z) dz, \quad (5)$$

where  $k_{\text{Rn}}$  is the transfer velocity obtained from the method,  $A_I$  is the measured activity of

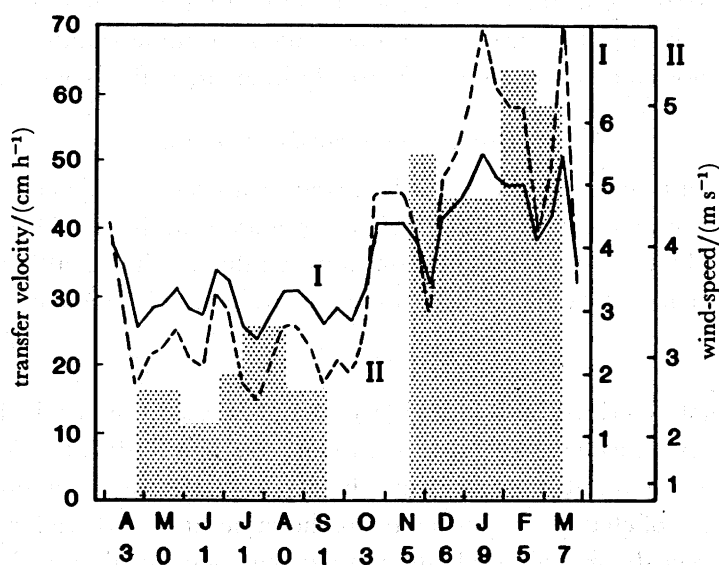


FIGURE 1. Transfer velocity for  $O_2$  (shaded bars) and wind speed (line I) in Funka Bay, Japan, for the period 1979–1980. Curve II is proportional to the square of the wind speed averaged for each period of 10 days. Numbers below the letter for each month indicate the number of days that month when the wind velocity exceeded  $10 \text{ m s}^{-1}$ . In this study, the meteorological observations were made about 30 km from the water sampling point. (After Tsunogai & Tanaka 1980.)

$^{222}\text{Rn}$  in the surface-most seawater,  $A_A$  is the activity to be expected in this water if at equilibrium with the amount in air (generally taken as zero in view of the small atmospheric activity and the low solubility of the gas in water),  $A_E$  is the activity of  $^{222}\text{Rn}$  expected in the water column if equilibrium is achieved with dissolved  $^{226}\text{Ra}$ ,  $A_z$  is the measured activity of  $^{222}\text{Rn}$  at depth  $z$ , and  $\lambda$  is the decay constant of  $^{222}\text{Rn}$  ( $0.18 \text{ d}^{-1}$ ). A vertical profile of  $^{222}\text{Rn}$  in the surface oceans is shown in figure 2. An important assumption of the method is that the  $^{222}\text{Rn}$  profile is not affected by horizontal or vertical water movements.

The method is relatively easy to apply and it has been used quite extensively. Probably the biggest data set is that for the Atlantic and Pacific Oceans obtained as part of the GEOSECS cruises (Peng *et al.* 1979). These results are shown in figure 3: two important conclusions can be drawn. Firstly, the mean value of  $k_{\text{Rn}}$  for all the data is about  $12 \text{ cm h}^{-1}$ , which corresponds to an equivalent value for  $k_{\text{CO}_2}$  between 14 and  $16 \text{ cm h}^{-1}$ , the range arising from uncertainty over how the conversion from  $k_{\text{Rn}}$  to  $k_{\text{CO}_2}$  should be made (for further details see Liss & Merlivat 1986). A more recent set of results obtained by Smethie *et al.* (1985) in the tropical Atlantic gives a mean  $k_{\text{Rn}}$  of  $15.0 \text{ cm h}^{-1}$ , corresponding to a  $k_{\text{CO}_2}$  of approximately  $18 \text{ cm h}^{-1}$ . Thus, it is reasonable to conclude that there is quite close agreement between transfer-velocity values from the radon-deficiency method and those from radiocarbon.

The second conclusion to be made from the results in figure 3 is a negative one, i.e. that if there is a relation between transfer velocity and wind speed, as might be expected, it is not apparent in this substantial data set. The more recent results from the tropical Atlantic (Smethie *et al.* 1985) do show a better relation but even here the correlation coefficient is only about 0.5 and the data set is much smaller (less than 30 data points compared with about 100 for the GEOSECS results). The reasons for the apparent inability of the method to demonstrate



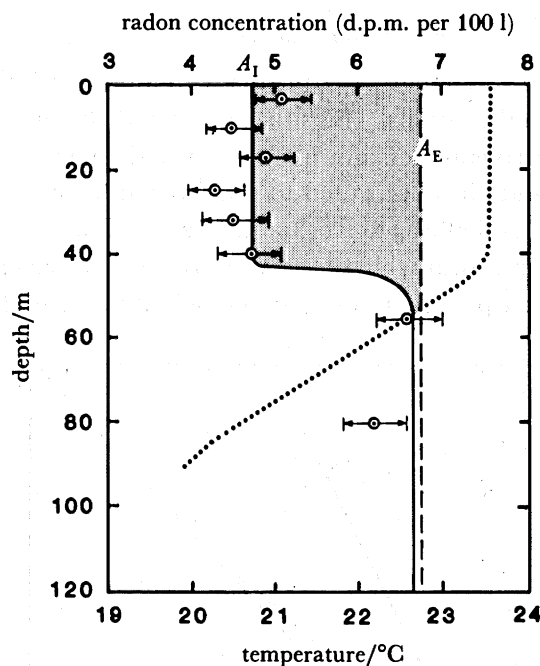


FIGURE 2. Activity of  $^{222}\text{Rn}$  as a function of depth at GEOSECS station 57 in the Atlantic ( $24^\circ\text{S}$ ,  $35^\circ\text{W}$ ). The broken line is the  $^{222}\text{Rn}$  activity to be expected if the isotope is in equilibrium with its parent  $^{226}\text{Ra}$ . The shaded area represents the amount of  $^{222}\text{Rn}$  lost to the air. The dotted line is the temperature profile. (Radon concentration in disintegrations per minute per 100 l.) (After Broecker 1974.)

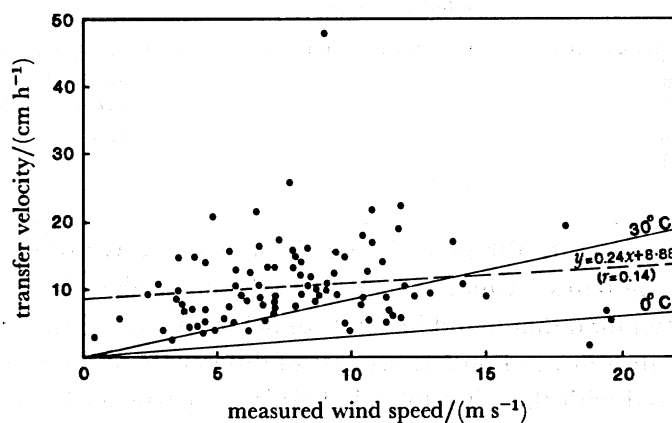


FIGURE 3. Transfer velocity determined on GEOSECS Atlantic and Pacific cruises by Radon Deficiency Method plotted against wind speed measured 0–24 h before sample collection (Peng *et al.* 1979). Wind speeds are at a nominal height of 10 m reduced to 10 cm height by assuming a logarithmic wind profile. Full lines are predictions based on the theoretical approaches of Deacon (1977) and Hasse (1971); broken line is the least squares fit through the data points. (After Hasse & Liss 1980.)

a clear wind-speed dependence are discussed in Liss (1983) and in Roether & Kromer (1984). Basically the vertical radon profile has a response time of a few days to any perturbation, which makes it problematical what value of the wind speed should be used in trying to correlate it to the derived transfer velocity. Further, during the response period the assumption of zero vertical water movement may be invalid because of changes in mixed-layer depth and dynamics.

*(d) Sulphur hexafluoride*

At the time of writing, no gas-exchange experiments with a purposefully added tracer, such as  $\text{SF}_6$ , have been attempted in the oceans. This situation should change because several ocean releases of  $\text{SF}_6$  and similar gaseous tracers are planned over the next few years.

However, sulphur hexafluoride has been used to obtain transfer velocities for a freshwater lake. Wanninkhof *et al.* (1985) added  $\text{SF}_6$  to Rockland Lake in New York State and measured its rate of loss to the atmosphere, from which observations transfer velocities were calculated. The results are shown in figure 4 plotted as a function of wind speed. A clear relation between

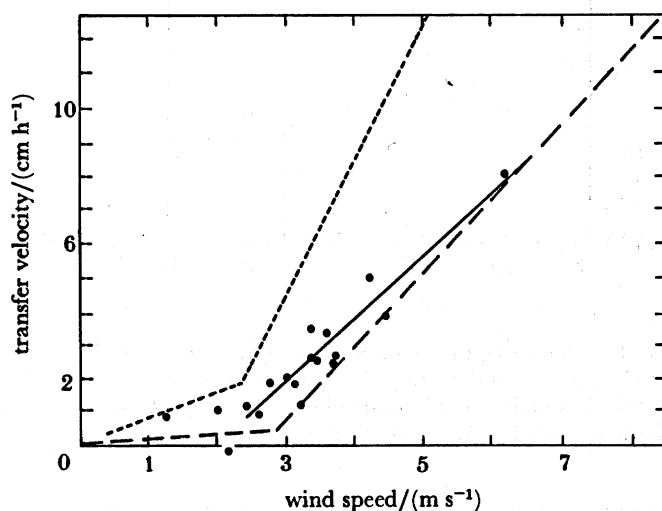


FIGURE 4. Transfer velocity for  $\text{SF}_6$  determined on Rockland Lake (New York State, U.S.A.) as a function of wind speed measured 1 m above the lake. The solid line is the least squares fit to the data above a wind speed of  $2.4 \text{ m s}^{-1}$ . The short-dashed curve is from the wind tunnel study of Broecker *et al.* (1978). The long-dashed curve is an estimate of the relation between the transfer velocity and wind speed if the wind was steady. (After Wanninkhof *et al.* 1985.)

$k_{\text{SF}_6}$  and wind speed is apparent, although the wind-speed range is rather limited with no measurements much above  $6 \text{ m s}^{-1}$  wind. It should also be noted that the slope of the graph is about a factor of two less than that found in wind-tunnel studies (see §3). It seems likely that the apparently smaller effect of wind on  $k$  is because of differences in the wind-induced wave field for the lake compared with the wind tunnel. This is not particularly surprising but does indicate that caution is required in extrapolating laboratory results to field situations where, among other differences, much larger wind fetches are the norm.

*(e) Micrometeorological techniques*

The methods so far discussed for determining  $k_w$  all rely on measurements on the seawater side of the air-sea interface. In contrast, micrometeorological techniques require measurements in the atmosphere. They have more usually been used for the determination of 'physical' fluxes of momentum, heat and water vapour, where the controlling resistance is generally on the atmospheric side of the interface. This highlights a basic problem in using micrometeorological methods for measuring  $k_w$ . For a gas for which  $r_w \gg r_a$  (i.e.  $k_w$  is the effective transfer velocity) the fraction of the total concentration gradient in the air phase will be very small. This will

inevitably lead to difficulties in measuring the gradient, and high instrumental signal:noise ratios will be important constraints. As an example of the problem, Deacon (1977) has calculated that for air-sea transfer of  $\text{CO}_2$  the vertical gradient of the gas in the air between 1 and 10 m height would typically be 0.05 p.p.m. (by volume). This is less than 0.02 % of the atmospheric concentration and hence difficult to measure accurately. For this reason the straightforward gradient-measurement approach does not appear to have been used for measuring  $k_w$  in the marine environment.

A micrometeorological technique that has been used in this context is eddy correlation. Here gas fluxes, and hence transfer velocities, are obtained from the time-average product of measured gas concentrations in air and the vertical component of the wind. The technique and some of the problems associated with it in estimating gas fluxes are discussed in Liss (1983).

The method has been used to estimate air-sea  $\text{CO}_2$  fluxes by two groups (Jones & Smith 1977; Smith & Jones 1985; Wesely *et al.* 1982). The fluxes obtained, and the corresponding values of  $k_{\text{CO}_2}$ , are up to 100 times greater than those derived from the methods described earlier. This discrepancy, between results from eddy correlation and those from isotopic tracers, is critically discussed by Broecker *et al.* (1986), with replies to the criticisms from Smith & Jones (1986) and Wesely (1986). There are clearly problems with the eddy-correlation method as applied to gas exchange that have yet to be resolved. Fundamentally, as already mentioned, the problem is the poor instrumental signal:noise ratio; for  $\text{CO}_2$  exchange,  $r_a$  is typically only about 0.6 % of the total resistance ( $R_w$ ).

The eddy-correlation method does appear to give reasonable results for ozone uptake by seawater (data of Lenschow *et al.* 1982, discussed in Liss & Merlivat 1986). The reason why it works for  $\text{O}_3$ , for which  $r_w$  is still the dominant resistance, is probably because the relatively rapid kinetics of the reaction of  $\text{O}_3$  with seawater components ( $\alpha$  of order  $10^4$ ) means that in this case  $r_a$  is about 4 % of  $R_w$ . However, this is not a method for estimating  $k_w$  because  $\alpha_{\text{O}_3}$  is not sufficiently well known.

### 3. RELATION BETWEEN AIR-SEA TRANSFER VELOCITY AND WIND SPEED

In view of the difficulties, discussed in the previous section, of measuring  $k_w$  at sea, it would clearly be very useful if it could be related to some easily measured meteorological or oceanographic parameter. Several times already the presence (or absence) of a relation between  $k_w$  and wind speed has been mentioned.

Certainly, experiments conducted in laboratory wind tunnels all show clear increase(s) in  $k_w$  with wind speed (or, more appropriately, friction velocity). These results are described in Liss (1983), and Liss & Merlivat (1986) give an idealized plot of the wind-tunnel data, which is reproduced here as figure 5.

Liss & Merlivat (1986) identify three régimes each having different  $k_w$  against wind-speed relations. In the 'smooth-surface' régime (up to about  $5 \text{ m s}^{-1}$  wind) the water is largely smooth and undisturbed by capillary waves. At wind speeds between 5 and  $10\text{--}12 \text{ m s}^{-1}$  the surface becomes covered with capillary and larger waves ('rough-surface' régime) and  $k_w$  increases with wind speed at a faster rate than for the smooth surface. At higher wind speeds still, bubbles become common because of wave breaking ('breaking-wave (bubble)' régime) and the slope of the  $k_w$  against wind-speed relation becomes even greater. As indicated in figure 5, the effect of bubbles depends on the solubility of the exchanging gas in water. This is



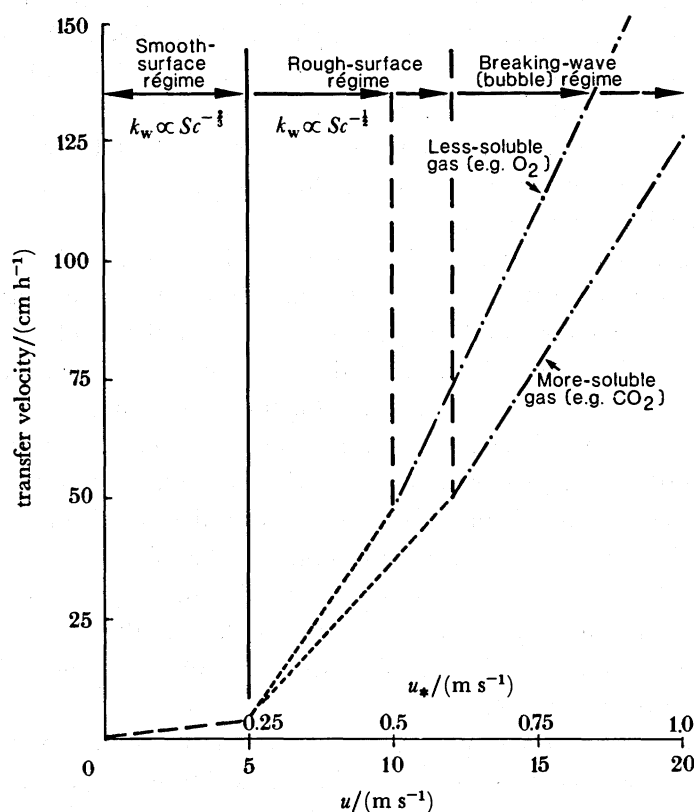


FIGURE 5. Idealized plot of water-phase transfer velocity ( $k_w$ ) against wind speed ( $u$ ) and friction velocity ( $u_*$ ). Based on laboratory results, mainly from the Hamburg wind tunnel (Broecker & Siems 1984). Also shown is the likely dependency of  $k_w$  on Schmidt Number ( $Sc$ , the ratio of the water viscosity to the molecular diffusivity of the gas in water). (From Liss & Merlivat 1986.)

clearly shown in the wind-tunnel results for  $O_2$  and  $CO_2$  of Broecker & Siems (1984); a theoretical treatment of the effect is given in Merlivat & Memery (1983).

As mentioned earlier, the applicability of such necessarily small-scale laboratory studies to the oceans is open to question. To try to overcome this problem, Liss & Merlivat (1986) have used the lake results with purposefully added  $SF_6$  of Wanninkhof *et al.* 1985 (shown in figure 4) to scale up the general relations illustrated in figure 5 to the field situation. Plainly, Rockland Lake is not the open oceans, but it is the most suitable field data available at present. Using this approach, Liss & Merlivat derive the following equations corresponding to the three régimes shown in figure 5.

$$k_w = 0.17 u, \text{ for } u \leq 3.6, \quad (6)$$

$$k_w = 2.85 u - 9.65, \text{ for } 3.6 < u \leq 13, \quad (7)$$

$$k_w = 5.9 u - 49.3, \text{ for } u > 13, \quad (8)$$

where  $k_w$  is in units of centimetres per hour and the wind speed ( $u$ ) is in units of metres per second at a height of 10 m.

Equations (6)–(8) are plotted out in figure 6. Also shown are averaged values for  $k_w$  as determined by the  $^{14}C$  and  $^{222}Rn$  techniques. The broad agreement between the predictions of (6)–(8) and the field data is reassuring. However, it must be noted that several of the field

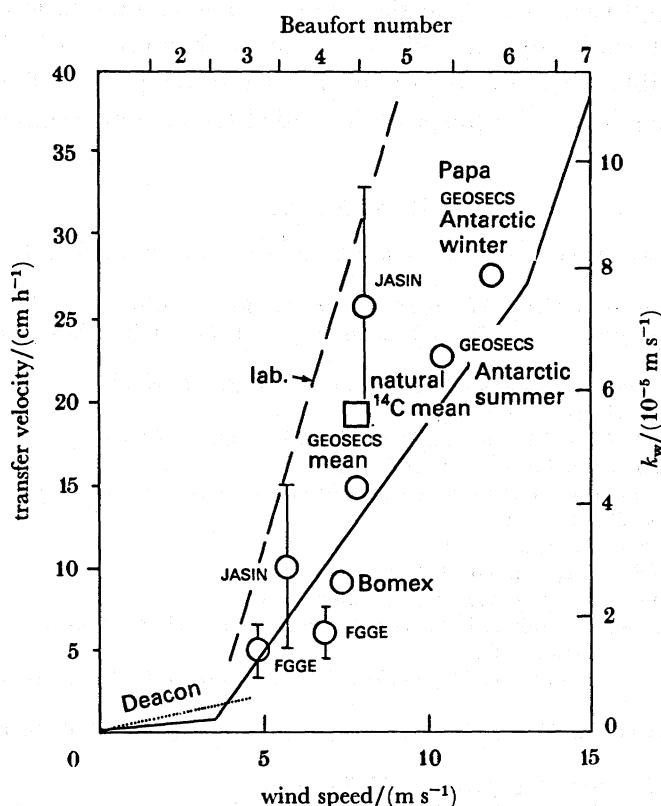


FIGURE 6. Predicted relation between transfer velocity and wind speed according to equations (6)–(8), solid lines. Also shown are oceanic measurements of  $k_w$  plotted as a function of wind speed measured at a height of 10 m and the corresponding Beaufort scale number. The dotted line shows predictions based on the Deacon (1977) smooth surface model. The broken line represents the results for intermediate wind speeds from laboratory wind-tunnel studies. All data have been converted to  $Sc = 600$ , which corresponds to  $CO_2$  at  $20^\circ C$ , by assuming that  $k_w \propto Sc^{-1/2}$  (see caption to figure 5). (After Roether 1986 and Liss & Merlivat 1986.)

results are averages of quite large data sets (for example, from GEOSecs) and in reality show large dispersion in both  $k_w$  and wind speed. Also, there is an absence of field results for wind speeds much above  $10 \text{ m s}^{-1}$ . This, coupled with the fact that the Rockland Lake measurements were limited to wind speeds less than  $7 \text{ m s}^{-1}$ , means that predictions of  $k_w$  from (8) are considerably more uncertain than those from (6) and (7).

#### 4. CONCLUSIONS

From this discussion of the use of tracers to estimate  $k_w$  for the oceans we can conclude that the globally averaged value of the transfer velocity for a gas like  $CO_2$  is about  $20 \text{ cm h}^{-1}$ , with a likely error of  $\pm 25\%$ . The only contradictory indications are the estimates from the eddy correlation method, which yields much higher values, but there is considerable uncertainty over the reliability of this technique.

When it comes to estimating the transfer velocity for a particular part of the oceans at a certain time or season then the situation is much less satisfactory. Instantaneous field measurements of  $k_w$  are very difficult to make with presently available techniques. Extrapolation from wind-tunnel and lake results has yielded predictive equations for  $k_w$ , which

is possibly the best approach we have at the moment. The real limitation here is the absence of field data, against which to test and verify the predictions, particularly for high-wind situations. Two possible ways ahead are the further development of micrometeorological techniques and the deployment of purposefully added tracers in coastal and oceanic waters.

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## Discussion

M. HEIMANN (*Max-Planck-Institut für Meteorologie, Hamburg, F.R.G.*). Is the 10 m wind speed the ideal variable in terms of which to parametrize the gas-transfer velocity? For example, the work of Jähne and co-workers at Heidelberg has shown that the mean square slope of the waves characterizes very well the gas-transfer velocity, opening up interesting possibilities for remote sensing of the latter.

P. S. LISS. Wind speed may not ultimately be the best variable for parametrizing the water-phase transfer velocity. However, it appears to be the best we have for the present. The experiments referred to, that relate gas-transfer velocity to the mean square wave slope, have only been conducted under laboratory conditions; it remains to be seen how well the relation holds at sea. Remote sensing may well become an important technique for air–sea gas-

exchange studies, particularly for giving instantaneous wind speed and wave data over a wide area. However, the relations between these parameters and transfer velocity at sea will still have to be established before usable information can be obtained.

W. ROETHER (*University of Bremen, F.R.G.*). I disagree with Professor Liss's view that the eddy-correlation method for  $\text{CO}_2$  has problems because the air–sea transfer resistance is only a small part of the total. I believe the problems to be related to the high atmospheric  $\text{CO}_2$  concentrations, the effect of any net interfacial transfer being largely masked. However, there are other gases for which destruction in the atmosphere prevents an atmospheric background building up. Then it is attractive to determine their interfacial flux micrometeorologically; in my view such gases show great promise for obtaining a parametrization of the gas-transfer coefficient.

P. S. LISS. I agree to the extent that the relatively high atmospheric concentration of  $\text{CO}_2$  does not help, but there are still fundamental signal : noise ratio problems with approaches involving air measurements. The eddy-correlation method suffers from the difficulties of having to correct for the interfering effects of heat and water-vapour fluxes. To apply the technique to other gases a sensor with a response time of better than 1 s is required; it is not clear that these exist for more than a very few gases. My feeling is that to obtain useful results at sea from either the gradient or eddy-correlation techniques there will have to be considerable improvements in the presently available instrumentation.