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Effect of wind waves on air–sea gas exchange: proposal of an overall CO_2 transfer velocity formula as a function of breaking-wave parameter

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ABSTRACT

A new formula for gas transfer velocity as a function of the breaking-wave parameter is proposed based on correlating gas transfer with whitecap coverage. The new formula for gas transfer across an air–sea interface depends not only on wind speed but also on wind-wave state. At the same wind speed, a higher gas transfer velocity will be obtained for a more developed wind-sea, which is represented by a smaller spectral peak frequency of wind waves. We suggest that the large uncertainties in the traditional relationship of gas transfer velocity with wind speed be ascribed to the neglect of the effect of wind waves. The breaking-wave parameter can be regarded as a Reynolds number that characterizes the intensity of turbulence associated with wind waves in the downward-bursting boundary layer (DBBL). DBBL provides an effective way to exchange gas across the air–sea interface, which might be related to the surface renewal.

1. Introduction

Carbon dioxide in the atmosphere is very significant due to its influence on the Earth's heat budget and climate change. The flux of CO_2, F, across the air–sea interface is often estimated from the bulk formula:

$$F = k_L s(pCO_{2w} - pCO_{2a}) \quad (1)$$

where k_L is the gas transfer velocity, s the gas solubility in water, and pCO_{2w} and pCO_{2a} are the partial pressure of CO_2 in water and air, respectively. This paper focuses on the parameterization of the gas transfer velocity.

Gas transfer is thought to be regulated by turbulence associated with wind waves at the air–water interface (Jähne et al., 1987). Therefore, the gas transfer velocity should be a function of parameters which represents the turbulence intensity at the air–sea interface. However, it is very difficult to find a parameter that is robust enough to be used in naturally environmental conditions. Wind is just an indirect factor affecting the near-surface turbulence, but it is currently adopted to parameterize the gas transfer velocity due to its global availability. The gas transfer velocity is traditionally expressed as (Wanninkhof et al., 1985; Wanninkhof, 1992; McGillis et al., 2001):

$$k_L = aSc^{-1/2}U_{10}^b \quad (2)$$

where U_{10} is the wind speed at 10-m height, a and b are the constants determined by observational data, and Sc is the Schmidt number, defined as

$$Sc = \nu/D \quad (3)$$

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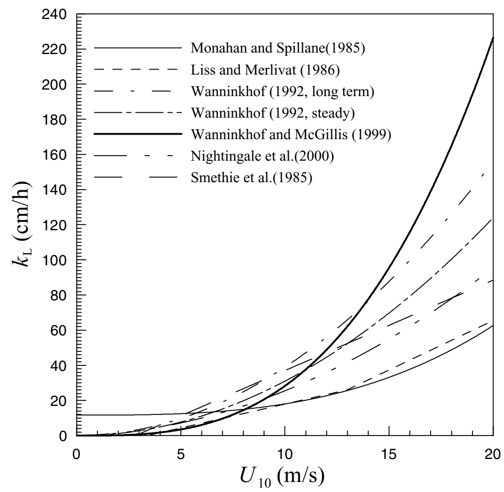

Fig. 1. Empirical relationships between gas transfer velocity and wind speed proposed by different authors.

where ν is the kinematic viscosity of water, and D is the molecular diffusivity of a gas in water.

In spite of intensive efforts in determining wind-speed dependence, the results still show large uncertainties (Fig. 1 and Table 1). The exponents of wind speed thus range from linear to cubic according to various data sets. Recently, combining their field observational data in the North Sea with others' in order to cover a wider range of wind speeds, Nightingale et al. (2000) found that the best fit to the total data was $k_{L600} = 0\ .222\ U_{10}^2 + 0.333U_{10}$. Empirical relationships developed by Monahan and Spillane (1984), Liss and Merlivat (1986), Wanninkhof (1992), Wanninkhof and McGillis (1999) and Tans et al. (1990), in particular, have been used extensively in recent endeavors to determine air–sea fluxes of CO_2. Takahashi et al. (1997) showed that the annual net uptake of CO_2 by the global oceans is from 0.60 to 1.34 Gt yr^{-1} depending on which of three different formulations is used for wind speed dependence on the gas transfer velocity (Liss and Merlivat, 1986; Tans et al., 1990; Wanninkhof, 1992).

Table 1. *Various wind speed exponents of the relationships between gas transfer velocity and wind speed proposed by different studies*

Wind speed exponent, *b*	Reference
3.0	Monahan and Spillane (1984)
1.0	Liss and Merlivat (1986)
2.0	Wanninkhof (1992)
1.0	Smethie et al. (1985)
1.73	Wanninkhof and Bliven (1991)
3.0	Wanninkhof and McGillis (1999)

Therefore, it is likely that relationships using only wind speed to predict gas transfer velocities will be flawed. The laboratory studies of the LUMINY group (De Leeuw et al., 2001) indicated that a plot of transfer velocity versus the friction velocity in water gave a better correlation than with wind speed. The large differences are attributed to the difficulties in field measurements and factors other than the wind speed influencing gas transfer over the ocean (Broecker et al., 1978; Merlivat and Memery, 1983; Jähne et al., 1987; Komori et al., 1993; Komori and Shimada, 1995). It is doubtful that a simple parameterization with wind speed can cover all spatial scales and environmental conditions (Jähne et al., 1985; Wanninkhof, 1992; Ocampo-Torres and Donelan, 1995; Komori et al., 1999).

We propose a new formula for the gas transfer velocity as a function of the breaking-wave parameter by directly correlating gas transfer with whitecap coverage. The formula agrees well with the observational data if the effect of wind waves is considered. The physical interpretation of this new formula is also provided in this paper.

2. Gas transfer and wave breaking: a new formula

Much evidence has shown that water-controlled mass transfer, such as CO_2, is strongly affected by the turbulence associated with the wave field. As mentioned above, wind is just an external forcing of the aqueous boundary. It does not affect gas exchange directly, since the wind may only influence the surface waves and the near-surface turbulence (Bock et al., 1999). Therefore, we must find an alternative to wind speed for gas transfer through the water-sided boundary layer.

A number of studies (e.g. Merlivat and Memery, 1983; Asher et al., 1996) have reported that whitecapping strongly enhances gas transfer. Two quite distinct mechanisms of gas transfer are associated with large-scale wave breaking and air entrainment. The first is the transfer associated with patches of turbulence in the upper layer generated by breaking waves. Wave breaking can also renew the interface contaminated by surface-active impurities, and it results in a rapid increase of gas transfer in high wind-speed regions (Komori et al., 1999; Komori and Misumi, 2001). The second is transfer mediated by bubbles, where gas is captured in a bubble during a certain interval of its exchange between atmosphere and ocean.

Laboratory and field studies have shown that there is an enhancement in gas exchange with the formation of bubbles. Various modeling and laboratory studies have shown that there is likely to be a solubility effect if bubbles make a significant contribution to gas exchange (e.g., Merlivat and Memery, 1983; Woolf and Thorpe, 1991). So one possible flaw, if the effect of bubbles is neglected, is that we have assumed the index of the Schmidt number in eq. (2) as $-1/2$. Unfortunately, there is no simple way to calculate the bubble contribution to gas transfer for a given wind speed, and the dependence on wind speed varies considerably between the different studies. Most laboratory studies have shown that the transfer velocity for CO_2 is enhanced to a considerably low extent by bubbles because of its relatively high solubility (Jähne et al., 1985; Wanninkhof and Bliven, 1991; Komori and Misumi, 2001). In other words, only those transfer velocities for poorly soluble gases can substantially be enhanced by bubble processes at high wind speeds (Woolf and Thorpe, 1991). In the field measurements, Nightingale et al. (2000) found that there is no evidence of increased gas exchange during periods of rapid changes in wind direction when incidents of breaking waves and bubble formation might be thought to be more likely. In practical applications it is also difficult to distinguish the transfer mediated by turbulence and bubbles because both of them are proportional to wind speed. Therefore, for relatively soluble gases such as CO_2, on which this paper focuses, transfer through the turbulence generated by breaking waves will be the dominant mechanism (De Leeuw et al., 2001). Following Kitaigorodskii (1984), we will assume that the turbulence associated with wind waves or wave breaking dominates the gas exchange through the air–sea interface in the following analysis.

Whitecap coverage is usually used to quantitatively describe the wave-breaking and air-entrainment processes, and should correlate with gas transfer exchange (Asher et al., 1996). Monahan and Spillane (1984) first related gas transfer velocity with whitecap coverage and proposed that gas transfer velocity is proportional to the cube of wind speed.

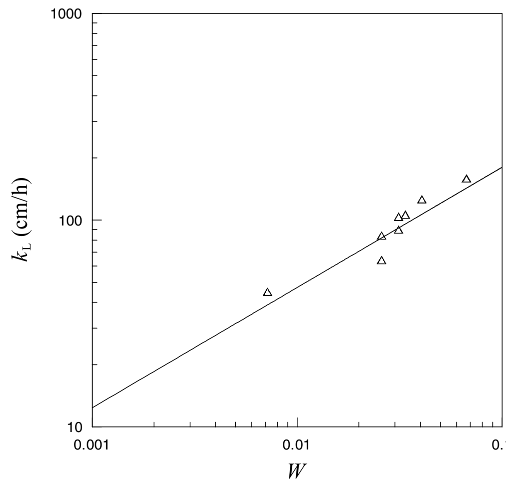

Fig. 2. Gas transfer velocity plotted versus whitecap coverage. The solid line is the regression result based on the observation data of Wanninkhof et al. (1995).

Wanninkhof et al. (1995) measured gas transfer velocity and whitecap coverage simultaneously (Fig. 2). The best fit of their data is

$$k_L = 687.9W^{0.58} \tag{4}$$

where W is the whitecap coverage. Zhao and Toba (2001) demonstrated that whitecap coverage correlates with the breaking-wave parameter R_B proposed by Toba and Koga (1986) better than the wind speed and the friction velocity. From their study, the whitecap coverage can be expressed as

$$W = 3.88 \times 10^{-7} R_B^{1.09} \tag{5}$$

where $R_B = u_*^2/\omega_p\nu$, in which ω_p is the spectral peak angular frequency of wind waves, u_* is the air friction velocity, and ν is the kinematic viscosity of air. The breaking-wave parameter can be regarded as a kind of Reynolds number that describes the turbulence generated by waves (Toba and Koga, 1986; Zhao and Toba, 2001). Substituting eq. (5) into eq. (4), we obtain

$$k_L = 0.13R_B^{0.63} \tag{6}$$

where k_L is in cm h^{-1}. This is the new formula for gas transfer velocity as a function of the breaking-wave parameter. Obviously, in addition to wind speed, this relationship also depends on the spectral peak angular frequency of wind waves, which reflects the development degree of wind waves. It indicates that a larger peak frequency corresponds to a smaller gas transfer velocity at the same wind speed. In other words, gas transfer velocity will increase with fetch.

It should be noted here that ω_p in R_B is the peak angular frequency of wind waves, which is perfectly defined only in the case of pure wind-wave fields or the steady wind conditions. Consequently, when applying it to wave states in which considerable swell components exist, we should adopt the peak angular frequency of the wind-wave part of the frequency spectra, not of the swell components.

In the next section, we will demonstrate that eq. (6) is consistent with observational data available, and the large uncertainties in the traditional approach correlating gas transfer velocity with wind speed are ascribed to the different wave fields they encountered.

3. Confirmation of new formula for gas transfer velocity

Gas transfer processes across the air–sea interface is involved both the wind and the wave field. It is impossible, as is traditionally done, to accurately describe gas transfer velocity by wind speed only. Therefore, we have suggested that the breaking-wave parameter R_B is a good candidate to describe properties of gas exchange across the air–sea interface in place of wind speed [eq. (6)]. If we use R_B, gas exchange depends on wind-wave state in addition to wind speed. It shows that the larger the wind-wave peak angular frequency ω_p, the smaller the gas transfer velocity k_L. Gas transfer becomes effective with increasing fetch, and the effect of wind waves should be considered in order to operate with different wave fields. In the following analysis, we can see that the large uncertainties in the traditional approach to parameterizing gas transfer velocity with wind speed can be ascribed to their neglect of the wind-wave effect.

3.1. Quantitative evidence

First, the observational data including wave information measured by Jähne et al. (1985) can be used to directly confirm eq. (6). Jähne et al. (1985) measured gas transfer rates, mean-square slopes and peak angular frequency ω_p of wind waves at four fetches in a linear wind-wave tunnel. A general problem arising for gas exchange measurements in a linear wind-wave tunnel is that the state of the air–water interface is not locally homogeneous. The fetch-dependent locally measured parameters such as u_* and ω_p should be averaged in order to be compared with the gas transfer velocity, which is measured as an integral over the whole water surface. Since we have no idea about how to average these local parameters, for simplicity, local parameters at fetch 21 m are used in this analysis.

From the data of Jähne et al. (1985), by using the method of least squares, the gas transfer velocity, as functions of the peak angular frequency only, the friction velocity of air only and the breaking-wave parameter, can be expressed tentatively as

$$k_L = 1.42 \times 10^4 \omega_P^{-2.34} \quad (7)$$

$$k_L = 101.4 u_*^{1.88} \quad (8)$$

$$k_L = 0.25 R_B^{0.67} \quad (9)$$

as shown in Figs. 3–5. We also note that eq. (6) can be rewritten as

$$k_L = 0.13(\nu\omega_p)^{-0.63} u_*^{1.26}. \quad (10)$$

Comparing eq. (10) with eq. (7) or (8), we can see that the exponents of ω_p or u_* are significantly different from each other due to their different backgrounds. In fact, in a wind-sea tank experiment, wind-sea frequency in the tank changes systematically with the controlling wind, and it is impossible to separate the effects of wind and waves using one tank experiment

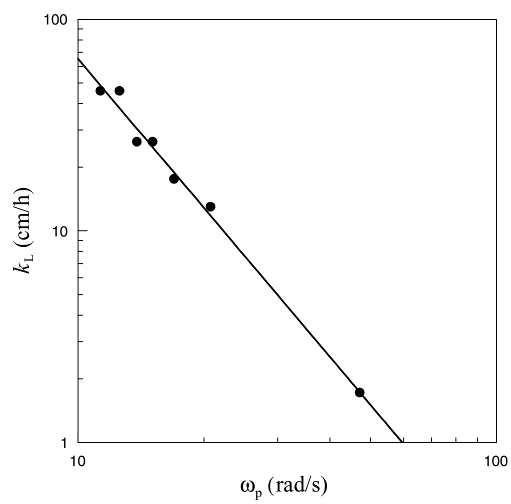

Fig. 3. Gas transfer velocity plotted versus peak angular frequency of wind waves based on the laboratory observation of Jähne et al. (1985). Peak angular frequencies corresponding to a fetch of 21 m have been adopted in the figure.

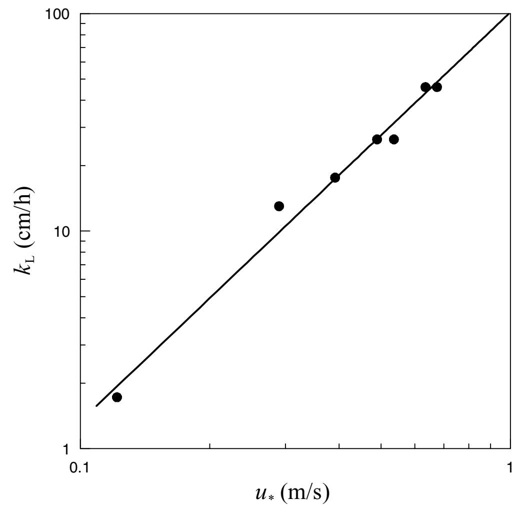

Fig. 4. Gas transfer velocity plotted versus friction velocity of air based on the laboratory observation of Jähne et al. (1985). Friction velocities of air corresponding to a fetch of 21 m have been adopted in the figure.

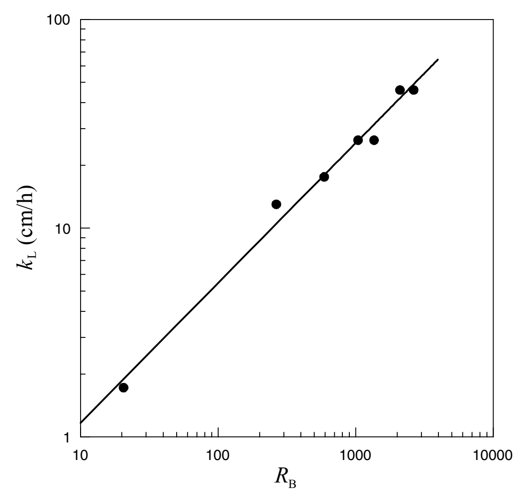

Fig. 5. Gas transfer velocity plotted versus breaking wave parameter based on the laboratory observation of Jähne et al. (1985). As in Fig. 4, the peak angular frequencies and friction velocities in R_B correspond to a fetch of 21 m.

like eqs. (7) and (8). A parameter which takes into account both of them should be used to describe gas transfer velocity, such as eq. (6). Comparing eq. (6) with eq. (9), we can see that the exponents of R_B are very close to each other. Therefore, R_B is a robust parameter for application in reconciling various observational data.

Second, eq. (6) can be confirmed directly from a composite data set of the observational data. Although almost none of the measurements of gas exchange provided wave information such as wave height or peak frequency of wind waves, a composite data set including field, lake and laboratory, at least to some extent will reduce the effect of wind waves, which influences the wind-speed dependence. In other words, we expect that a wind-speed dependence of gas transfer velocity from a composite data set will give a comparable result to eq. (6).

We collected observational data from the field (Smethie et al., 1985; Watson et al., 1991; Wanninkhof et al., 1993; Clark et al., 1995), lakes (Upstill-Goddard et al., 1990), linear wind tunnels (Merlivat and Memery, 1983; Jähne et al., 1985; Wanninkhof and Bliven, 1991; Ocampo-Torres et al., 1994) and a circular wind tunnel (Bock et al., 1999). In our analysis, all gas transfer velocities k_L are corrected to a Schmidt number Sc of 666 (CO_2 in seawater at 20 °C) by using the flowing relationship (Wanninkhof, 1992):

$$k_{L1}/k_{L2} = (Sc_1/Sc_2)^{-1/2} \quad (11)$$

where k_{L1} and k_{L2} are the gas transfer velocities corresponding to different gases, and Sc_1 and Sc_2 are their respective Schmidt numbers. Here we assume that the effects of surface-active impurities in the low-wind speed region (Komori et al., 1999) are negligible small. The Schmidt number depending on temperature for various trace gases are adjusted according to the study of Wanninkhof (1992).

The normalized gas transfer velocities with respect to wind speeds are shown in Fig. 6. We can see that all of the data reconcile with each other very well considering the fact that the data sources are so different. With the method of least squares, the gas transfer velocity can be described as

$$k_L = 0.86U_{10}^{1.35} \quad (12)$$

where k_L is in cm h^{-1}, and U_{10} is in m s^{-1}. The correlation coefficient is 0.88. The relationship of gas transfer velocity to friction velocity is presented in Fig. 7. The best fit to these data can be expressed as

$$k_L = 61.79u_*^{1.22} \quad (13)$$

where u_* is the friction velocity in m s^{-1}. Gas transfer velocities correlate little better with the friction velocity than wind speed, with a correlation coefficient of 0.89. Comparing eq. (13) with eq. (10), we can see that the exponents for friction velocity agree well with

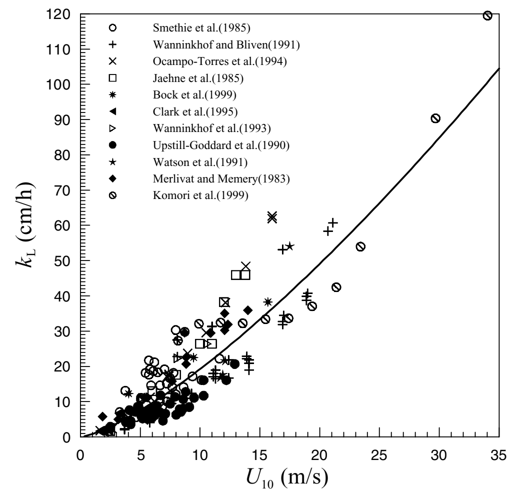

Fig. 6. Gas transfer velocity plotted versus wind speed. The solid line is the regression result.

each other, though they are obtained from different backgrounds.

Third, a theoretical model for gas transfer proposed by Kitaigorodskii (1984) seems to agree with eq. (6). Kitaigorodskii (1984) suggested that the turbulence

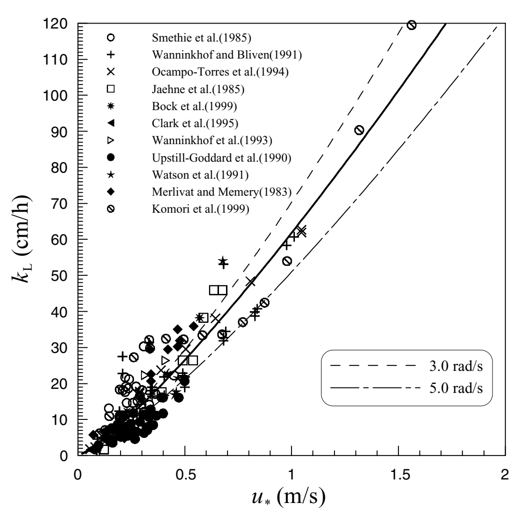

Fig. 7. Gas transfer velocity normalized by $Sc = 666$ plotted versus friction velocity in the air. The dashed lines from the upper to lower obtained from eq. (6) correspond to peak angular frequencies from 5 to 20 rad s^{-1} in steps of 5 rad s^{-1}. The solid line is the best fit to the data. The data source is the same as for Fig. 6.

associated wind wave breaking is responsible for the enhancement of air–sea gas exchange and showed

$$k_L = \alpha Sc^{-1/2} \varepsilon_0^{5/12} \tag{14}$$

where ε_0 is the total rate of energy dissipation due to wave breaking, and α is a constant. Zhao and Toba (2001) estimated the total rate of wave energy dissipation

$$\varepsilon_0 \approx 2.21 \times 10^{-3} \rho_w u_*^3 \tag{15}$$

where ρ_w is the water density. Substituting eq. (14) into eq. (13), we find

$$k_L \propto u_*^{1.25}. \tag{16}$$

The exponent of friction velocity in eq. (16) is almost the same as in eq. (10).

3.2. *Qualitative evidence*

Observations also provide qualitative evidence to support our viewpoint that the gas transfer velocity increases with the development degree of wind waves. Nightingale et al. (2000) measured air–sea gas transfer velocities by two deliberate tracer experiments in the southern North Sea. Their Fig. 13 clearly shows that gas transfer velocity increases with significant wave height or fetch. Hartman and Hammond (1984) hypothesize that the difference in radon gas transfer velocities on different sides of San Francisco Bay is caused by fetch dependence. Wanninkhof (1992) pointed out that there is evidence of fetch dependence of gas transfer velocity based on a study performed using the deliberate tracer sulfur hexafluoride, SF_6, on lakes with surface areas ranging in size from 0.13 to 500 km^2 (Wanninkhof et al., 1987). Gas transfer velocities increase as the area of the lake increases, which is pronounced at higher wind speeds. Deacon (1981) also indicated that a larger transfer velocity would be obtained in the field than those in the laboratory. We must emphasize that the gas transfer velocity in the field is larger than that in the laboratory at the same wind speed simply due to the fact that the peak angular frequency of wind waves for the former is generally smaller than the latter.

Slinn et al. (1978) postulated that the discrepancy between various methods of observation might be related to a greatly different wave age and development situation, which exists between wind-wave tanks and the natural atmosphere–ocean environment. Works in wind-wave tanks has indicated that fetch has an influence on gas transfer (Jähne et al., 1989; Wanninkhof and Bliven, 1991). Influence of fetch on the gas transfer velocity was probably first reported when comparing results for N_2O from an 8 m tank (Merlivat and Memery, 1983) with those obtained for CO_2 from an 18 m tank (Broecker et al., 1978). Transfer velocities were about 30% higher for the larger fetch flume. By using the same flume, Ocampo-Torres and Donelan (1995) observed an increase of about 20% in transfer velocity for the 10 m s^{-1} reference wind speed from the full length (32 m) tank experiments when compared to the case of 16 m fetch (Ocampo-Torres et al., 1994).

The effect of wind waves on the gas transfer velocity can be confirmed from the following facts. In contrast to the spectacular increase of gas exchange with wind speed observed in wind tunnels, the earlier field data come mainly from radon evasion measurements (Peng et al., 1979) that show no increase of gas transfer rate with wind speed. As pointed out by Hasse and Liss (1980), it seems physically unrealistic to find little or no effect of wind speed on the rate of gas transfer when all the wind tunnel studies show clear positive relationships. Deacon (1981) attempted to reconcile the two data sets by filtering the field data on the basis of wind dependence. He concluded that the field data, judged to originate from steady wind conditions, do not conflict with the laboratory data up to 14 m s^{-1} wind speed. This may be true as far as it goes, but it does not explain some very low observed transfer velocities in winds up to 19 m s^{-1} (Csanady, 1990).

We will try to explain this discrepancy. Under precisely controlled conditions, the waves will monotonically grow with increasing wind speed in a wind tunnel. Either increasing wind speed or decreasing peak frequency with fetch will increase the breaking-wave parameter and enhance of gas transfer. In the field, however, there is a wide scope for the variation of gas transfer with wind–wave states. High wind speed does not have to correspond to long waves. If a high wind speed coexists with very young field waves, i.e., very large peak frequencies, the breaking-wave parameter will be small, which tends to reduce the transfer velocity.

4. Physical interpretation of our new formula

For a smooth surface, the turbulent motions cannot penetrate the interface. They can only approach it attenuated by viscous forces, even though the turbulent transport exceeds the molecular diffusion by several orders of magnitude in the bulk. Thus, the turbulent transport gradually decreases toward the surface. Finally, a boundary layer at the surface called the surface diffusion boundary layer (DBL) exists in which molecular diffusion is dominant. The DBL thickness depends on the molecular diffusivity of the tracer and the intensity of the turbulent motions at the very surface. Due to the low gas diffusivity in water, resistance to gas transfer in air is negligible compared to that in water. DBL has a characteristic thickness on the order of 10 μm (Csanady, 1990), and its resistance to gas exchange is described by the Schmidt number [eq. (3)].

If waves occur, the turbulent wind field transfers energy not only into the mean shear current but also into the waves. Energy transferred by the wind field to the waves is carried away with the group velocity of the waves; it is then transferred by nonlinear wave–wave interaction to other waves and is finally dissipated by steep waves into near surface turbulence. Many studies have focused on the relationship between gas transfer and the near surface turbulence (e.g. Kitaigorodskii, 1984). The turbulent intensity is proportional to u_*^2, and the wind-drift velocity on the air–water interface is proportional to u_* (Toba, 1988). u_*/ω_p can thus be regarded as the wind-driven distance on the air–water interface in a period of wind wave. Therefore, the breaking-wave parameter can be thought as a kind of Reynolds number, which describes the intensity of turbulence induced by wind waves (Toba and Koga, 1986; Zhao and Toba, 2001).

In the wave-induced turbulent layer, the logarithmic velocity profile seems to hold, but the downward momentum flux, or turbulent dissipation, is larger than the values reduced by the wall law with a conventional value of the von Kármán constant (e.g., Agrawal et al., 1992). Yoshikawa et al. (1988) demonstrated that turbulence in this layer was produced primarily by downward bursting of water near the wind–wave surface, even though there was no visible wave breaking with air entrainment. This downward bursting was considered the principal mechanism for the downward momentum, masses and heat fluxes within this layer. Toba and Kawamura (1996) called this layer the downward-bursting boundary layer (DBBL), and suggested the depth of DBBL is about five times the significant wave height of wind waves. According to their study, the depth of DBBL holds equally for laboratory wind waves to wind-sea in the field. Measurements show that, compared with a rigid smooth wall, gas transfer through a free wavy surface is 2.5–10 times faster (Jähne et al., 1987). We suggest that this enhancement is linked to the occurrence of DBBL, which should also be linked to surface renewal as studied by Komori et al. (1993). In contrast to the resistance of DBL, DBBL will accelerate the gas transfer from the water surface to its interior. This idea seems to agree with the observation by Komori et al. (1993). In other words, DBBL might effectively influence the surface renewal.

The DBBL depth should reflect the magnitude of the transfer velocity. A reasonable hypothesis is that the transfer velocity should be proportional to the DBBL depth, or the significant wave height of wind waves, which increases with decreasing ω_p. This hypothesis is in agreement with the field observation by Wallace and Wirick (1992), in which they found that the sudden increases in dissolved O_2 corresponded closely with the significant wave height. Figure 13 of Nightingale et al. (2000) clearly confirmed this point. Thus, gas transfer velocity becomes greater with the development of wind waves, which is consistent with eq. (6).

Finally, we emphasize that the breaking-wave parameter R_B represents the turbulence intensity in water, and is not a parameter simply representing whitecapping as the large-scale wave breaking. R_B is regarded as a Reynolds number, which is constructed by using external parameters of the wind (u_*) and the present state of wind waves (ω_p). As shown by Zhao and Toba (2001), the visible breaking occurs when $R_B > 1000$. Lower than this critical value, R_B is expected to represent microscale wave breaking, which is invisible. We also note that the wind stress is not wholly applied to generate wind waves but also directly to drive drift currents. The existence of a drift current will affect the development of wind waves, and is expected to enhance the probability of whitecapping, which finally intensifies the turbulence in water. Thus, the effect of drift current, to some extent, can also be parameterized by R_B.

5. Conclusion

In the light of the turbulence generated by wave breaking dominating the sparingly soluble gas transfer process, we proposed a relationship for gas transfer velocity with respect to the breaking-wave parameter [eq. (6)] which is in agreement with the available observational data. It shows that the gas transfer velocity will increase with the development of wind waves. The effect of wind waves should be considered if a robust formula for gas transfer velocity is expected. The large uncertainties in gas transfer velocities that arise in the traditional approach correlating with wind speed are ascribed to the neglect of the effect of wind waves. The breaking-wave parameter represents the intensity of turbulence associated with wind waves in DBBL. The existence of DBBL effectively accelerates the gas exchange processes.

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