Provisional chapter

Near Surface Turbulence and Gas Exchange Across the Air-Sea Interface

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Additional information is available at the end of the chapter

1. Introduction

Oceans and the atmosphere are tightly coupled to influence the energy budget, gas exchange and the global climate. For example, 20%~30% anthropogenic emitted CO_2 was sequestered by oceans. The ocean surface boundary layer plays an intermediate role on the exchange of mass, momentum and energy between air and ocean. Quantifying transport terms (such as temperature, gas fluxes) across the air-water interface has been an important subject of physical oceanography for several decades.

The physical mechanism of interfacial gas exchange is essentially natural and complex for several reasons. (1) Fluid motions on both sides of the interface are typically turbulent, which demonstrate a stochastic feature with a wide range of scales; (2) The interface can be disturbed and hence deformed into irregular shapes, interacts with the turbulence structure in both boundary layers.

Gas transfer velocity k is the key parameter that regulates the interfacial gas exchange, which is usually determined through experimental methods. The gas transfer velocity can be defined as

$$k = \frac{F}{C_w - \alpha C_a} \tag{1}$$

where, F is gas flux across the air water interface, C_w and C_a are bulk gas concentration at water and air phase, α is the Ostwald solubility coefficient.

Although the definition is simple, quantification of gas transfer velocity is indirect and difficult since it is affected by a wide range of environmental variables, including wind, rainfall, surfactants, surface waves, etc. Most of these variables are strongly coupled to affect the gas transfer process.

2. Theoretical models

It is well accepted that the gas flux of slightly soluble (such as CO_2) across the air-water interface without wave breaking is largely controlled by the transport mechanism through a very thin aqueous diffusive boundary layer. The gas transfer velocity is determined by molecular transport though this thin layer, whose thickness is usually related to the level of turbulence very close to the interface.

2.1. Film theory

The simplest model to quantify the interfacial gas exchange is the film theory [1]. In this model, gas transfer occurs through a thin "stagnant" film of laminar fluid adjacent to the air-water interface, and its thickness can be denoted as δ. According to the Fick's diffusion law, the gas transfer velocity can be determined as,

$$k = \frac{D}{\delta} \tag{2}$$

where D is molecular diffusivity of the dissolved gas.

In reality, a "stagnant" diffusivity boundary layer (DBL) with a constant thickness is a poorly modeled concept, actual DBL is disrupted by sporadic "bursts" of turbulent "eddies", which are large scale turbulent motions that lift "fresh" fluids to the surface and create a renewed exposure to the air phase [2, 3]. The gas transfer is still driven by molecular diffusion during these exposures. Therefore, the exposure time θ_s becomes a key parameter to control the flux across the interface. And the thickness of near surface DBL is a dynamic value, which is related to properties of impinging turbulent eddies.

2.2. Penetration model and surface renewal model

In the penetration model [2], near surface DBL is periodically disrupted by penetrating eddies from the bulk water body with a constant exposure time. In contrast, the surface renewal model [3] considered the renewal time as a random variable with an exponential probability distribution. Accordingly, the averaged gas transfer velocity can be modelled as

$$k = \sqrt{\frac{4D}{\pi\theta_s}} \quad (\text{Penetration model}) \tag{3}$$

$$k = \sqrt{\frac{D}{\theta_s}} \text{ or } k = \sqrt{Df} \qquad (\text{Surface renewal model}) \tag{4}$$

where *f* is the surface renewal frequency. In these two models, gas transfer velocity is related to the diffusivity as

$$k \sim D^{1/2} \tag{5}$$

Both laboratory and fields studies have shown that *k* is better modeled by the surface renewal model than by the "stagnant film" model [4, 5]. And *k* is observed to be $k \sim D^n$, where *n* varies between 1/2 and 2/3, depending on free surface roughness and near surface hydrodynamics [6].

2.3. Random eddy model

Differed slightly from the concept of surface renewal, Harriott [7] proposed that near surface random eddies would also enhance the gas flux while approaching air-water interface even without completely renewing the interfacial layer. Laboratory study of renewal events of a thermal boundary layer (TBL) has proven that significant fraction of renewal events do not renew the TBL completely [8]. Gas transfer is therefore controlled by the eddy penetration depth and the lifetime of those random eddies [9].

Many efforts have been made to parameterize the average time interval between surface renewals through the properties of near surface random eddies. The "large eddy model" [10] argued that the renewal time scale is scaled with the largest turbulent eddies, which suggested,

$$\theta_s \sim L / u' \tag{6}$$

where L is the integral length scale and u' is the root-mean-square of fluctuating turbulent velocities.

On the other hand, the "small eddy model" [11, 12] suggested that the smallest eddies are the controlling mechanism of interfacial gas exchange. Thus the renewal time scale is determined by the Kolmogorov time scale,

$$\theta_s \sim (\nu / \varepsilon)^{1/2} \tag{7}$$

where ν is kinematic viscosity and ε is turbulent dissipation rate at the interface.

If we substitute the renewal time scale into the surface renewal model (e.g. equation (4)), *k* can be written as,

$$k \sim Sc^{-1/2} u' \mathrm{Re}_t^{-1/2} \;(\text{large eddy model}) \tag{8}$$

$$k \sim Sc^{-1/2} u' \mathrm{Re}_t^{-1/4} \;(\text{small eddy model}) \tag{9}$$

where Sc is Schmidt number defined as $Sc = \nu / D$, Re_t is turbulent Reynolds number, which is defined as,

$$\mathrm{Re}_t = u' L / \nu. \tag{10}$$

In the "small scale eddy" model, dissipation rate has been scaled with the large scale eddies as,

$$\varepsilon \sim u'^3 / L, \tag{11}$$

following the concept of turbulent energy cascade. These hydrodynamic models agreed well with both laboratory and field measurements on the interfacial gas transfer velocity. Chu and Jirka [13] conducted simultaneous measurements on turbulence and gas concentration in a grid-stirred tank to reveal the relation between large eddy motions and gas transfer process with the turbulent Reynolds number varying from 80 to 660. Small scale eddy motions have also been shown to be correlated with gas flux in a variety of experiments [14-16]. In the "small scale eddy" model, gas transfer velocity is generally expressed explicitly as related with the near surface turbulence dissipation rate,

$$k \sim Sc^{-1/2} (\nu\varepsilon)^{1/4} \tag{12}$$

The "two regime model" proposed by Thoefanus et al. [17] combined the "large eddy model" and the "small eddy model" by arguing that different size of the near surface turbulent eddies dominate interfacial gas flux mechanism depending on the turbulent Reynolds number. That is, the "large eddy model" is more appropriate at low turbulent Reynolds numbers ($\mathrm{Re}_t < 500$), and small scale eddies are more relevant to high turbulent Reynolds number flows ($\mathrm{Re}_t > 500$),

$$k = 0.73 Sc^{-1/2} u' \mathrm{Re}_t^{-1/2} \text{ at } \mathrm{Re}_t < 500 \tag{13}$$

$$k = 0.25 Sc^{-1/2} u' \mathrm{Re}_t^{-1/4} \text{ at } \mathrm{Re}_t > 500 \tag{14}$$

2.4. Surface divergence model

Based on the source layer theory (or blocking theory) and considering the transport of homogeneous and isotropic turbulence in the far field away from the free surface without tangential shear [18], Banerjee [19] provided a “surface divergence model” that relates the gas transfer velocity to the divergence of horizontal velocities on the air-water interface,

$$k \sim Sc^{-1/2} u' \mathrm{Re}_t^{-1/2} \left[\left\langle \frac{\partial u'}{\partial x} + \frac{\partial v'}{\partial y} \right\rangle^2 \right]_{\mathrm{int}}^{1/4} \tag{15}$$

where u' and v' are fluctuating horizontal velocities, and subscript “*int*” denotes the air-water interface.

Banerjee, Lakehal [20] pointed out that the “surface divergence” physically is the signature of turbulent “sweep” events representing local “upwelling” motions at the surface from the bulk fluid. On the other hand, it is an alternative expression of the surface renewal and more specifically modeled by tangential components of velocities at the interface. Csanady [21] emphasized the role of breaking wavelet at the interface with high surface divergence that squeezes the DBL by “upwelling” motions, i.e., the disruption of DBL by turbulent eddies is enhanced during micro-wave breaking events. Recently, surface divergence has been shown to correlate with interfacial gas transfer process in laboratory studies [22, 23].

One advantage of the “surface divergence” model is that it can be easily implemented: (1) concept of “surface divergence” replaces the renewal time scale by velocity fluctuating motions, while the renewal time varies due to different environmental flow conditions (2) “surface divergence” is easier to be measured than the renewal time (e.g. through the surface PIV measurement using infrared imaging techniques at the water surface [23]).

3. Measurement techniques on interfacial gas transfer

Considering the fact that the interfacial gas transfer is ultimately limited by the very thin layer of the DBL (on the order of micrometers), the existent measurement technologies are hardly directly measuring the gas transfer velocity across the air-water interface. Most applied measurement techniques are indirect methods, e.g., measuring a designed tracer flux across the air-water interface then convert it to the gas of interest assuming that both are controlled by the same near surface turbulence then the transfer velocity is scaled by the molecular diffusivity (i.e. equation (5) in the surface renewal model).

3.1. Deliberate volatile trace experiments

Inert volatile tracers have been widely used in determining gas transfer velocities in field studies through a mass balance approach. For example, sulfur hexafluoride (SF_6) was deliberately added to water bodies to quantify the gas transfer velocity as a function of wind speed [5, 24-27], since it can be detected at a very low level in water with an excellent signal-to-noise ratio. Based on mass balance approach, gas transfer velocity can be determined,

$$k \approx \frac{h}{t_2 - t_1} \ln \frac{C_{wt_1}}{C_{wt_2}} \tag{16}$$

where C_{wt} is the concentration of released tracer in water at time t. h is the mean depth of the mixed layer. Originally, the tracer experiment is designed for closed lake with relatively small size [27]. The experiment time scale is on the order of days to weeks depending on the size of lakes. However, for a large lake or ocean, the concentration of tracer decreases quickly due to horizontal transport and dispersion. Meanwhile, the mixing layer depth may vary significantly in space as the surface area and volume exposed to the atmosphere increases due to dispersion effect.

The tracer method can be improved by co-releasing a second inert tracer with a different diffusion coefficient (e.g. ^{3}He). By releasing two tracers with a constant ratio, the decreases of concentration due to dispersion are the same for the two gases, but different due to interfacial exchange. Since we know the transfer velocity should differ by a factor of 3, as $Sc(^3\text{He})$ is about eight times smaller than $Sc(\text{SF}_6)$, the effect of horizontal dispersion can be separated out. The dual tracer technique has been used to measure gas exchange in different water bodies [28-31]. Besides the dual tracer technique, a third nonvolatile tracer (e.g. bacterial spores and rhodamines) can also be introduced to determine the gas transfer velocity independently based on an arbitrary tracer pair [32].

3.2. Active controlled flux technique (proxy technique)

The active controlled flux technique (ACFT) is a method to quantify the gas transfer velocity through the analogy with the heat transfer across the air-water interface [33, 34]. One example is to use an infrared laser to heat a certain area of water surface. A sensitive infrared imager is used to capture the time series of images of the heated patch on water surface. In order to determine the renewal frequency f, the "surface renewal model" is employed to fit the observed average surface temperature decay curve. The transfer rate of heat can be calculated as,

$$k_H = \sqrt{D_H f} \tag{17}$$

where D_H is thermal conductivity of water. Thus, gas transfer velocity can be estimated as,

$$k_G = k_H \left(\frac{Sc}{\text{Pr}} \right)^{-n} \tag{18}$$

where Sc is Schmidt number of gas of interest and Pr is Prandtl number defined as $\text{Pr} = \nu / D_H$, the exponent n varies in the range between 1/2 and 2/3 depending on the roughness of water surface [6, 35]. Using this technique, Garbe, Schimpf [36] have experimentally demonstrated the probability density function of the surface renewal time can be described with a lognormal distribution.

However, several experiments found that discrepancies exist between estimates of transfer velocity based on ACFT and that from dual tracers measurements [9] or direct covariance method [37, 38]. Atmane, Asher [9] found gas transfer velocity (as referenced to $Sc = 600$) determined by ACFT (using heat as proxy) was overestimated by a factor of 2, approximately.

The discrepancy can be attributed to the fact that the random eddies might not take effect on heat and gas exchange equally through renewal events. The Sc number is typically much greater (e.g. Sc(CO_2) is 600 at 25°C in fresh water) than the Pr (e.g. Pr is around 7 at 20°C in water) number, hence the thickness of the gas DBL is significantly smaller than that of the TBL. Some of the "upwelling" eddies might not approach the gas DBL but they can disturb the TBL effectively. Asher, Jessup [39] proposed a different scaling with Sc number and provided a solution using the surface penetration model. Atmane, Asher [9] argued that the eddy approaching distance needs to be included as an extension to the surface renewal model.

3.3. Eddy covariance (correlation) method

The vertical flux of a scalar of interest (e.g. temperature, moisture, CO_2 concentration) can be estimated by evaluating the covariance between the fluctuating vertical velocity component and the fluctuating scalar concentration measured simultaneously at a certain height above the air-water interface. With the method, horizontal homogeneity is assumed and Reynolds decomposition is applied. The "eddy flux" is written as,

$$F = \overline{w'c'} \tag{19}$$

In order to apply the eddy covariance method, fast response instrumentations are required to capture the high frequency fluctuations of the gas concentration and the turbulent velocity, if we intent to measure gas transfer across the air-water interface. The eddy covariance method has been applied to measure the air-sea CO_2 flux from the air side [37, 40] and DO (Dissolved Oxygen) flux from the aqueous side [13]. Applying eddy covariance method from the air side on the open ocean can be challenging due to the contamination of flow induced by the movement of ship-based platform and the uncertainty of gas concentration due to changes in air density caused by variations of temperature and water vapor known as the Webb effect [41].

Alternative to the eddy covariance method, a relaxed eddy accumulation (EA) method [42-44] was developed and employed to estimate the gas flux by separating measurement of gas concentration from updrafts and downdrafts. This method avoids the requirement of high frequency measurement on the fluctuating gas concentration.

Recently, measurements of turbulent flux with particle image velocimetry (PIV) and laser induced fluorescence (LIF) techniques [45] were conducted in a grid stirred tank. Herlina and Jirka [46] suggested that the gas transfer at different turbulent levels can be associated with different dominant eddy sizes according to the spectra of covariance terms, which agreed with the "two regime" theory [17].

In the field, eddy covariance method has been widely applied to measure DO flux across the water-sediment interface [47, 48]. Recently, a waterside direct covariance measurement [49] has also been conducted in the field to investigate the air-sea gas exchange under extreme wind speed conditions. Although the requirement of high sampling rate can be relaxed due to longer time and length scales of turbulence on the waterside than the air side, the isotropic turbulence assumption still needs to be invoked and justified.

3.4. Floating chamber measurements

Gas flux across the air-water interface can also be estimated by monitoring the change of gas concentration in the floating chamber (FC) [50] due to interface gas exchange over a certain period of time. Kremer, Nixon [51] suggested that FC method would be applicable for low to moderate wind conditions (less than 8-10 m/s) and with a limited fetch such that waves are young and nonbreaking. An ideal chamber should have a large ratio of water surface area to chamber volume. Matthews, St Louis [52] compared the CO_2 and CH_4 fluxes based on the FC method, tracer technique and wind dependence estimation. The result showed that the FC method overestimate the transfer velocity in low wind shear condition. Guerin, Abril [53] conducted FC measurements in reservoirs and rivers, which gave similar results with the eddy covariance technique. FC method was also applied in coastal regions [54] under low to moderate wind (<10 m/s) and weak current condition (<20 cm/s). The results showed overestimation on transfer velocity compared with wind dependent relationship. Vachon, Prairie [55] tested the FC method with dissipation rate measurement. The results showed that the artificial effect of FC on near surface turbulence depends strongly on the background turbulence level, that is, overestimation by FC method is relatively large in a low turbulence environment.

4. Driving forces and parameterizations

4.1. wind speed

Most experimental work and modeling on gas transfer velocity are based on wind speed measurements and parameterization. Although it is not a direct driving force on interfacial gas transfer, wind stress has been considered as the primary source of near surface turbulence. Overall, wind speed is a reliable parameterization variable and is found to agree well with experimental data on gas transfer velocity. The advantage of wind speed models is that wind speed can be easily measured or obtained through meteorological modeling or remote sensing thus it can be easily implemented into regional and global gas flux estimations.

Although it is difficult to measure the wind speed with the accuracy that is required for modelling the gas transfer velocity, [32, 56-58], a large amount laboratory and field experiments [26, 32, 56, 59-64] have been conducted to estimate the empirical relationship between wind speed and gas transfer velocity and they are summarized in the following.

The first wind speed model was presented by Liss and Merlivat [61]. A "three linear segments" relationship between the gas transfer velocity and the wind speed was proposed based on wind tunnel experiments. The three segments were categorized according to the surface roughness (smooth surface, $U_{10} < 3.6$ m/s; rough surface, 3.6 m/s $< U_{10} <$ 13 m/s; breaking wave region, $U_{10} > 13$ m/s).

Up to the present day, the most popular wind speed based gas transfer model is a quadratic relation. Wanninkhof [62] suggested that gas transfer velocity scales with U_{10}^2 [26] based on the global bomb ^{14}C constraint [65] and wind wave tank results. The quadratic relation indicates that the gas transfer scales with wind stress as $\tau \sim C_D U_{10}^2$. The quadratic relationship [62] for gas transfer velocity of CO_2 at 20°C for seawater ($Sc = 660$) is written as

$$k_{660} = 0.39 \langle U_{10} \rangle^2 \tag{20}$$

where the transfer velocity is expressed in "cm/hour" and wind speed is in "m/s". Furthermore, Wanninkhof [62] modified the scaling factor for the cases of short-term or steady wind conditions,

$$k_{660} = 0.31 \langle U_{10} \rangle^2 \tag{21}$$

Similar quadratic relationship was derived by Nightingale, et al. [32] from deliberate tracer experiments in the coastal ocean:

$$k_{660} = 0.222 U_{10}^2 + 0.333 U_{10} \tag{22}$$

This result is in between the model of Liss and Merlivat [61] and that of Wanninkhof [62]. Recently, the SOLAS Air-Sea Gas Exchange (SAGE) experiment was conducted in the Southern Ocean [66]. The new quadratic relationship is given from dual tracer injection experiments as

$$k_{660} = (0.266 \pm 0.019) U_{10}^2 \tag{23}$$

More recently, additional dual tracer experiments were conducted in Southern Ocean [67]. From the new data, the relationship [31] was updated to,

$$k_{660} = (0.262 \pm 0.022) U_{10}^2 \tag{24}$$

Alternatively, a cubic relation was proposed by Wanninkhof and McGillis [64] for steady or short term wind conditions,

$$k_{660} = 0.0283U_{10}^{3} \tag{25}$$

This relation is in good agreement with direct covariance results of air-sea Gas Exchange Experiment conducted in 1998 (GasEx-98). The cubic relation is supported by GasEx-98 data [37] and GasEx-2001 data [38] in the following expressions,

$$k_{660} = 0.026U_{10}^{3} + 3.3 \tag{26}$$

$$k_{660} = 0.014U_{10}^{3} + 8.2 \tag{27}$$

Although wind speed parameterization is probably the most convenient and a successful model [68] for estimating interfacial gas transfer velocity, the method is largely empirical. Most supporting data came from local experiments, which could be affected by many factors (such as the experiment location, measurement techniques, instrumentation errors and experimental uncertainties). Ho, Law [66] argued that the experiments of Nightingal, et al. [32] might be affected by an underdeveloped wind field and higher concentration of surfactants in coastal area. And the result of Wanninkhof [62] is most likely an overestimate because of an excessive ^{14}C inventory of the global ocean.

If the wind speed model were to apply to estimate the global CO_2 uptake by oceans, the global wind speed estimate would be a very critical issue. The total fluxes estimation is very sensitive to the accuracy of global wind speed estimation [69, 70]. Wanninkhof, Asher [71] pointed out since the long term averaged transfer velocity essentially scales with the second or third order of moment of the wind speed, the quadratic relationship gives a 27% higher result compared with the short term estimation while the cubic relationship gives a 91% higher result. It should be noted that the global wind speed distribution can be approximately represented by a Rayleigh distribution [62, 72].

4.2. Wind stress

In general, the relation between gas transfer velocity and wind speed can be summarized as,

$$k \sim Sc^{-n}U_{10}^{b} \tag{28}$$

where $b = 1, 2, 3$, representing linear, quadratic, cubic relations with respect to the wind speed. According to Charnock's Law [73],

$$\frac{U(z)}{u_{*a}} = \kappa^{-1} \ln\left(\frac{gz}{u_{*a}^2}\right) + C \tag{29}$$

where κ is von Kármán's constant. Meanwhile the surface shear stress caused by wind can be related to the wind speed as,

$$\tau = \rho_a C_D U_{10}^2 \tag{30}$$

where C_D is the wind drag coefficient, which is also a function of U_{10} [74, 75]. If we apply the continuity of shearing stress at the interface,

$$\tau = \rho_a u_{*a}^2 = \rho_w u_{*w}^2 \tag{31}$$

So the relation among the wind speed and friction velocities of the air and water sides can be,

$$U_{10} \sim u_{*a}^{\alpha} \sim u_{*w}^{\alpha} \tag{32}$$

where α depends on the scaling of the drag coefficient with the wind speed. Many experimental results suggested that the drag coefficient increases linearly with wind speed except for the case of low wind speed, so α= 1/2 can be derived [74-78]. Also since the quadratic law is the most widely accepted wind speed model for gas transfer velocity, i.e., $b = 2$ in equation (28), the gas transfer velocity is linearly scaled with the water side shear velocity,

$$k \sim Sc^{-n} u_* \tag{33}$$

It's noting that for most wind speed models, the power of Schmidt number $-n$ is set to be -1/2, we have,

$$k \sim \sqrt{D} \tag{34}$$

which is consistent with the surface renewal model (equation (4)).

On the other hand, Jähne and Haußecker [35] shows that the gas transfer velocity can be expressed explicitly by interfacial shear velocity though turbulent diffusive boundary layer theory:

$$k \sim u_* Sc_t \tag{35}$$

where Sc_t is the turbulent Schmidt number, defined as the ratio of turbulent diffusion coefficient of momentum and gas concentration:

$$Sc_t = \frac{K_m}{K_c} \tag{36}$$

Using the concept of diffusive boundary layer Deacon [79] proposed that,

$$k = 0.082 Sc^{-2/3} u_{*_w} \tag{37}$$

which shows that gas transfer velocity is proportional to interfacial shear velocity.

The relation derived from the diffusive boundary layer theory is also similar to equation (33), which is derived from the empirical wind speed model (quadratic relation). The difference is the exponent of the Schmidt number. In Deacon [79]'s model, the -2/3 power scaling is suitable for smooth surface, as it is pointed out by Jähne and Haußecker [35]. The -1/2 power scaling is more appropriate for a wave-covered water surface [6]. Fairaill et al. [80] conducted a comprehensive analysis on a number of parameters including effects of shear forcing, roughness Reynolds number and buoyancy effects on the gas transfer. Their results have been applied by Hare et al. [81] to evaluate the GasEx data. And they found significant gas flux occurs due to wave breaking and air bubble entrainment, which will be discussed in the next section.

4.3. The effect of sea surface roughness, wave breaking and entranced air bubbles

Experiments confirmed that gas transfer is enhanced by the presence of wind induced ripples. From the perspective of momentum transport, turbulence can be enhanced by the increase of surface roughness. The exponent of the Schmidt number in wind speed models or wind shear models varies from about -2/3 to -1/2, which was found to be dependent on the surface roughness. For CO_2, that implies a variation in the transfer velocity by a factor of 3. Jähne et al. [6] demonstrated a good correlation between the gas transfer velocity and the mean square slope of surface waves in a wind/wave facility. Frew et al. [82]'s field experiments showed stronger correlation between the transfer velocity and the mean square slope compared to wind speed relation. Since the wave slope can be obtained through satellite-base remote sensing, this relation provides a method that can be easily implemented to estimate the global gas flux [83].

The majority of laboratory and field experiments on gas transfer were conducted under weak to moderate wind conditions. Extremely high wind speed makes the measurement very difficult. From the few existing data, the transfer velocity is significantly enhanced in high wind fields. The accepted theory is that the gas flux across the interface is dominated by wave breaking and entrained air bubbles [60, 84-88]. Woolf and Thorpe [89] argued that the transfer velocity is only enhanced by bubbles for very low soluble gases. Woolf [90] introduced a transfer velocity term which is specifically due to bubbles. Thus the transfer velocity can be expressed by a hybrid model [91],

$$k = k_0 + k_b \tag{38}$$

where k_b is approximately proportional to the whitecap coverage [92]. Factors that influence bubble mediated transfer were reviewed by Woolf [92] and Woolf et al. [93]. Alternatively, other parameterizations and analyses on gas transfer velocity through the whitecap coverage exist [94, 95].

4.4. The effect of surfactants

The presence of surfactants is believed to have an attenuation effect on interfacial gas exchange. Early laboratory experiments observed a large amount of reduction of transfer velocity due to the presence of surfactants [96]. Asher [97] reported a linear relationship between the transfer velocity and wind speed at the presence of surfactant when wind speed is smaller than 12.5 m/s.

Numerous studies of the effects of surfactants on air-sea gas transfer have been conducted in laboratory settings and *in situ* [14, 22, 98-102]. It's noting that some of surfactants are soluble, while others are not. The insoluble surfactant acts as a barrier film. However, this effect can be easily dispersed by wind and waves. For high wind condition, the soluble surfactants are believed to have a prevailing effect on gas transfer even at the presence of breaking waves, while insoluble surfactants do not [103-105].

4.5. The effect of rainfall

Air-sea gas exchange during rainfall events has been brought into attention recently. It has been shown that rainfall will enhance the transfer velocity across the interface [56, 106-109]. Existing evidence shows that the enhancement is due to rainfall generated turbulence and bubble entrainments. The kinetic energy flux (KEF) caused by raindrops has been introduced to scale with the gas transfer velocity [106, 110]. However, Takagaki and Komori [111] argued that transfer velocity is more correlated with the momentum flux of rainfall (MF).

The effect of raindrops on the enhancement of surface mixing, damping waves and changing the air-sea momentum flux has been investigated through the surface renewal model [112]. Rainfall could also induce surface density stratification and additional surface heat flux because of temperature difference between raindrops and the sea surface. The combined effect of rainfall and high wind speed is believed to have a significant impact on air-water gas exchange, however, this effect is complex and yet to be investigated comprehensively.

4.6. Near surface turbulence

The parameterizations of interfacial gas exchange discussed above are generally empirical or semi-empirical. For most empirical models, gas transfer velocities are scaled with meteorological parameters such as wind speed, wind shear, momentum flux or kinetic energy flux induced by rainfalls (rainfall dominant environment), etc. In comparison, models based on near surface turbulence structures, such as the surface renewal model and the surface divergence model, are more mechanistic. For gases with low solubility, the resistance of gas transfer is dominated by the water side, which is in turn controlled by the near surface turbulence.

A large amount experiments were conducted to investigate the near surface turbulence and its relation to air-sea gas transfer process. Lamont and Scott [11] presented an eddy cell model to quantify the mass transfer from the hydrodynamic parameters (equation (12)). Some recent studies show the gas transfer velocity is better scaled with the surface turbulence [14, 16, 109]. Zappa, McGillis [15] has shown that gas transfer velocity is well correlated with the dissipation rate rather than wind speed under a variety of environmental forcing, regardless the how the near surface turbulence was produced. Vachon et al. [55] performed a number of measurements to demonstrate the direct relationship between gas transfer velocity (measured by a floating chamber) and near surface turbulent dissipation rate (measured by an ADV). Lorke and Peeters [113] demonstrated that equation (12) can be derived by assuming the thickness of diffusive sub-layer to be scaled with the Batchelor's micro-scale,

$$\delta_D = L_B = 2\pi \left(\frac{\nu D^2}{\varepsilon} \right)^{1/4} \tag{39}$$

It is worth noting that the dissipation rate scaling is based on the assumption of homogenous and isotropic turbulence near the water surface. Correspondingly, the small eddy model is applicable for a high Reynolds number condition, which is the prerequisite of Kolmogorov's similarity hypothesis.

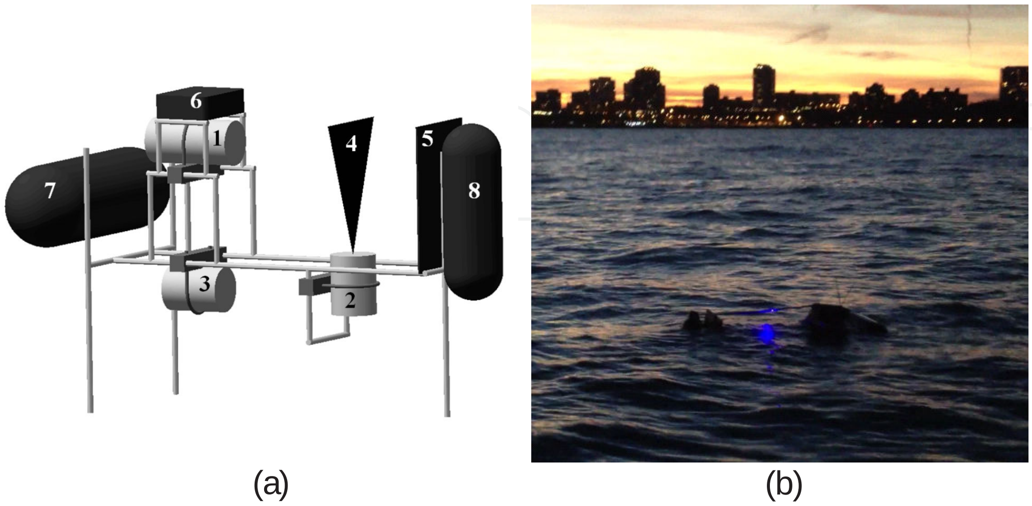


Figure 1. (a) The free floating UWMPIV. Components: (1) camera housing (2) laser housing (3) battery housing (4) laser sheet (5) guide plate (6) wireless router (7)(8) floating buoys (b) Deployment of UWMPIV on Lake Michigan

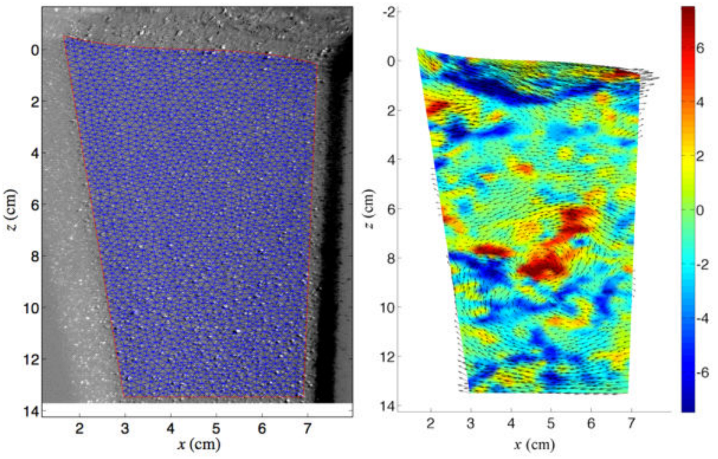
Despite the promising results from small scale eddy models, the scaling coefficient has not been clearly determined yet. In most of these studies, the coefficient is usually obtained empirically from fitting modeled transfer velocities with measured ones. Another uncertainty is associated with the depth at which the dissipation rate should be applied in the model. In theory the dissipation rate should be measured immediately below the air-water interface, but this cannot be easily achieved during field measurements. While there is very few *in situ* data available for the near surface turbulence, existing field data was obtained at a short distance (tenth of centimeters) away from the wavy surface. Zappa et al. [15]argued that this might not be a serious issue, as the gas transfer velocity should scale with $\varepsilon^{1/4}$. However, if a strong gradient of dissipation rate exists near the surface, this assumption has to be examined carefully.

Wang et al. [114] have recently developed a free floating Under Water Miniature Particle Velocimetry system (UWMPIV) (Figure 1) to measure vertical profiles of the turbulence dissipation rate immediately below the water surface, and has successfully deployed it on Lake Michigan. Figure 2 shows a sample of measured near surface turbulence structure. In order to calculate the vertical dissipation rate profile, velocity maps were evaluated on a dynamic triangular mesh with the moving air-water interface as the top boundary (see figure 2(a)). Statistics were obtained with the vertical coordinates attached to the local water surface where $z = 0$ and z increases with water depth. Figure 3 shows measured dissipation rate profiles under varying wind speed (U_{10} ranged from 2 to 15 m s^{-1}) and wave conditions. Runs 1~5 were measured in a harbor with essentially zero wind fetch and very short waves, whereas run 6 was measured on the open lake with weak wind ($U_{10} \approx 2$ m s^{-1}) and developed wave field (significant wave height ≈ 0.35 m). The detailed description of each runs can be found in Wang et al. [114].

A wide range of dissipation rate (from 10^{-6} to 10^{-3} m^{2}s^{-3}) was covered in the data series. From the case of run 6, it shows that surface waves might also be a significant source of surface turbulence since the wind speed is rather small in this case while the dissipation rate is comparable to that from the cases where wind speed was in the range of 10~15 m s^{-1} and a nearly zero fetch (run1-5. For all cases, a strong vertical gradient of dissipation rate was found, with peak dissipation immediately below the water surface, and then it decays rapidly with depth, usually by one order of magnitude within several centimeters. Profiles of dissipation rates can be described by a power law with the exponent ranging between 1 and 2. These new findings suggest that measurements of turbulence at some distance away from the surface may not be directly applied to estimate the gas transfer velocity at the surface. It also suggests that more efforts are needed to reveal the exact structure of small scale turbulence within several centimeters of the surface water.

Figure 4 compares estimated transfer velocity of CO_2 across the air-sea interface at 20^{o}C seawater (Sc = 660) from three wind speed models and the small scale eddy model based on the UWMPIV measurement, i.e., equation (12) with the scaling factor = 0.419 following [15]. The dissipation rate in the small scale eddy model was measured at z = 1 cm below the air-water interface for all runs. For three wind speed models, W92 represents the short term or steady wind speed condition estimation [62]; N00 represents the coastal area measurement in fetch limited environments [32]; H06 relationship is obtained from SOLAS Air-Sea Gas Exchange (SAGE) experiment in Southern Ocean [66]. Since runs 1~5 were conducted in the Milwaukee Harbor with an almost "zero-fetch" condition, the dissipation rate can be considered as a representative of wind shear without any significant wave effects. Transfer velocity estimation based on dissipation rate match all wind speed models very well under conditions of moderate wind speed (5-10 m s^{-1}). For the case when the wind speed was about 15 m s^{-1}. The small scale eddy model might underestimate the actual gas transfer rate as significant bubble entrainments were observed for that case.

For run 6 under a low wind condition, wind speed modeled transfer velocity decreases, however the near surface turbulent dissipation is enhanced possibly due to the interaction among non-breaking waves or the micro-breaking events. The transfer velocity estimated by the small scale eddy model was almost 10 times larger than that of wind speed models. This observation suggested surface waves themselves might contribute to produce the near surface turbulence. Therefore the wind speed model may have significantly underestimated the global air-sea gas transfer, since the sea surface is subject to low to moderate wind speed for most of the time [115], while surface waves are present almost all the time.



(a) (b)

Figure 2. (a) A sample image pair with triangular PIV mesh (b) the instantaneous velocity vector map superimposed on the calculated vorticity map, the unit of the color bar is (s^{-1}) [114]

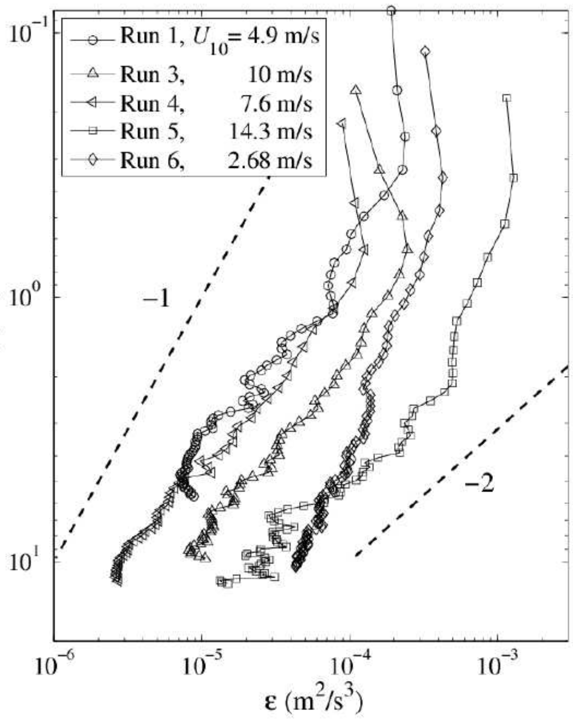


Figure 3. The dissipation rate profiles at different wind shear and wave conditions (log-log scale) [114]

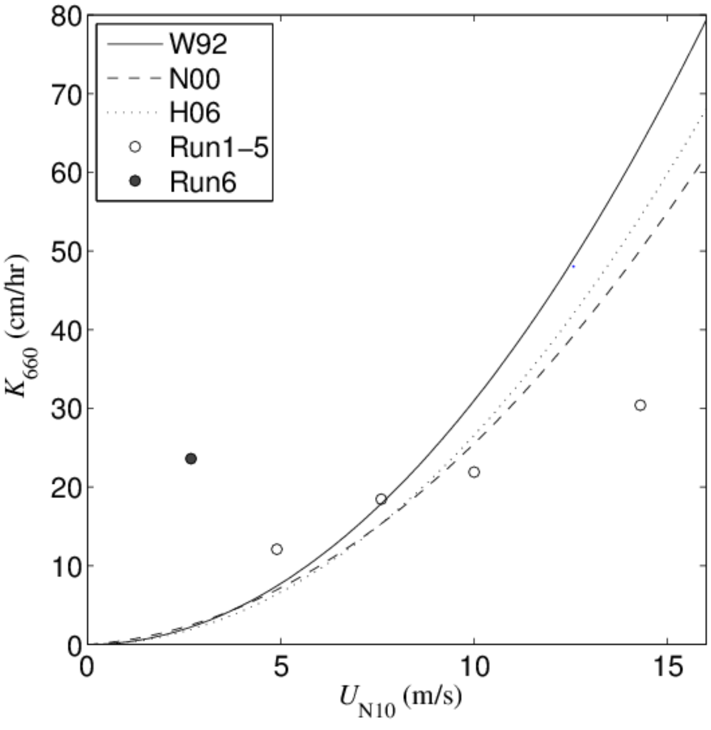


Figure 4. Comparison of CO_2 transfer velocity models based on wind speed and the surface turbulence dissipation rate.

5. Conclusion

Gas transfer across the atmosphere/ocean interface is a very important physical process that regulates the global climate, considering the fact that this process occurs over an area that is about 70% of the Earth surface. This chapter provides a review on the current technologies of measuring the gas flux across the air/ocean surface and existing models for the gas transfer velocity. Many environmentally important gases, such as O_2 or CO_2, have a low solubility, so the major resistance of gas exchange is from the water side. Near surface turbulence might be the key physical parameter that determines the gas transfer velocity as it controls the thickness of the diffusive boundary layer, e.g., "eddy" upwelling induced surface renewal. Global gas flux estimates still use the wind speed, or wind shear stress as the primary modeling parameter, as wind is the major source of near surface turbulence. For example W92 model is commonly applied to estimate the global air-sea CO_2 flux. Additionally, breaking wave parameters such as the whitecap coverage, are also included to account for gas exchange through bubbles induced by breaking waves. Other environmental forcing may also be significant sources of near surface turbulence that can affect the gas flux. Turbulence can be generated by bottom mixing then diffuses to the surface in a coastal area; turbulent buoyant convection, surface currents, precipitation and microbreaking of short surface waves can also contribute to near surface turbulence production. These parameters are usually not directly related to the wind stress.

Recent studies indicated that small scale eddy models parameterized with the surface dissipation rate or divergence are more mechanistic thus a more universal approach to estimate the gas transfer velocity under a wide range of environmental forcing conditions, except for the case of breaking waves. Advances in measurement technologies, such as the floating UWMPIV [114], provide encouraging opportunities to quantify the structure of turbulence in the upmost layer below the air-sea interface. Preliminary results showed that surface wave itself might be a source of near surface turbulence and it can significantly enhance the gas transfer velocity under low wind conditions. Future research on this subject should focus on the scaling of the surface turbulence structure with properties of large scale environmental forcing. Simultaneous field measurements of the flow field and the gas transfer velocity are also needed to provide further insights into air-sea gas exchange processes.

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References

[1] Lewis, W. K, & Whitman, W. G. Principles of Gas Absorption. Ind Eng Chem. (1924). , 16(12), 1215-20.

[2] Higbie, R. The rate of absorption of a pure gas into a still liquid during short periods of exposure. AIChE Transactions. (1935). , 31, 365-90.

[3] Danckwerts, P. V. Sinificance of liquid-film coefficients in gas absorption. Ind Eng Chem. (1951). , 43, 1460-7.

[4] Jähne, B, Huber, W, Dutzi, A, Wais, T, & Ilmberger, J. Wind/wave-tunnel experiments on the Schmidt number and wave field dependence of air-water gas exchange. In: Brutsaert W, Jirka GH, editors. Gas transfer at water surfaces(1984). , 303-309.

[5] Upstill-goddard, R. C, Watson, A. J, Liss, P. S, & Liddicoat, M. I. Gas transfer velocities in lakes measured with SF_6. Tellus B. (1990). , 42, 364-77.

[6] Jähne, B, Munnich, K. O, Bosinger, R, Dutzi, A, Huber, W, & Libner, P. On the Parameters Influencing Air-Water Gas-Exchange. J Geophys Res-Oceans. (1987). C2): 1937-49.

[7] Harriott, P. A random eddy modification of the penetration theory. Chem Eng Sci. (1962). , 17, 149-54.

[8] Jessup, A. T, Asher, W. E, Atmane, M, Phadnis, K, Zappa, C. J, & Loewen, M. R. Evidence for complete and partial surface renewal at an air-water interface. Geophys Res Lett. (2009).

[9] Atmane, M. A, Asher, W. E, & Jessup, A. T. On the use of the active infrared technique to infer heat and gas transfer velocities at the air-water free surface. J Geophys Res-Oceans. (2004). C8).

[10] Fortescue, G. E. Pearson JRA. On gas absorption into a turbulent liquid. Chem Eng Sci. (1967). , 22, 1163-76.

[11] Lamont, J. C, & Scott, D. S. An eddy cell model of mass transfer into the surface of a turbulent liquid. Aiche J. (1970). , 16, 513-9.

[12] Banerjee, S, Rhodes, E, & Scott, D. S. Mass transfer through falling wavy liquid films in turbulent flow. Industrial and Engineering Chemicals Fundamentals. (1968). , 7, 22-7.

[13] Chu, C. R, & Jirka, G. H. Turbulent Gas Flux Measurements Below the Air-Water-Interface of a Grid-Stirred Tank. Int J Heat Mass Tran. (1992). , 35(8), 1957-68.

[14] Asher, W. E, & Pankow, J. F. The interaction of mechanically generated turbulence and interfacial films with a liquid phase controlled gas/liquid transport process. Tellus B. (1986). , 38, 305-18.

[15] Zappa, C. J, Mcgillis, W. R, Raymond, P. A, Edson, J. B, Hintsa, E. J, Zemmelink, H. J, et al. Environmental turbulent mixing controls on air-water gas exchange in marine and aquatic systems. Geophys Res Lett. (2007).

[16] Zappa, C. J, Raymond, P. A, Terray, E. A, & Mcgillis, W. R. Variation in surface turbulence and the gas transfer velocity over a tidal cycle in a macro-tidal estuary. Estuaries. (2003). , 26(6), 1401-15.

[17] Theofanus, T. G, Houze, R. N, & Brumfield, L. K. Turbulent mass transfer at free, gas liquid interfaces with applications to open channel, bubble and jet flows. Int J Heat Mass Tran. (1976). , 19(6), 613-24.

[18] Hunt JCRGraham JMR. Free stream turbulence near plane boundaries. J Fluid Mech. (1978). , 84, 209-35.

[19] Banerjee, S. Turbulence structure and transport mechanisms at interfaces. Proc 9th International Heat Transfer Conference(1990). , 395-418.

[20] Banerjee, S, Lakehal, D, & Fulgosi, M. Surface divergence models for scalar exchange between turbulent streams. Int J Multiphas Flow. (2004).

[21] Csanady, G. T. The Role of Breaking Wavelets in Air-Sea Gas Transfer. J Geophys Res-Oceans. (1990). C1):749-59.

[22] Mckenna, S. P, & Mcgillis, W. R. The role of free-surface turbulence and surfactants in air-water gas transfer. Int J Heat Mass Tran. (2004). , 47(3), 539-53.

[23] Asher, W. E, Liang, H, Zappa, C. J, Loewen, M. R, Mukto, M. A, Litchendorf, T. M, et al. Statistics of surface divergence and their relation to air-water gas transfer velocity. J Geophys Res-Oceans. (2012). C05035).

[24] Wanninkhof, R, Ledwell, J. R, & Broecker, W. S. Gas exchange-wind speed relation measured with sulfur hexafluoride on a lake. Science. (1985). Epub 1985/03/08., 227(4691), 1224-6.

[25] Wanninkhof, R, Ledwell, J. R, Broecker, W. S, & Hamilton, M. Gas-Exchange on Mono Lake and Crowley Lake, California. J Geophys Res-Oceans. (1987). C13): 14567-80.

[26] Wanninkhof, R. H, & Bliven, L. F. Relationship between Gas-Exchange, Wind-Speed, and Radar Backscatter in a Large Wind-Wave Tank. J Geophys Res-Oceans. (1991). C2):2785-96.

[27] Clark, J. F, Schlosser, P, Wanninkhof, R, & Simpson, H. J. Schuster WSF, Ho DT. Gas Transfer Velocities for Sf6 and He-3 in a Small Pond at Low Wind Speeds. Geophys Res Lett. (1995). , 22(2), 93-6.

[28] Watson, A. J, Upstillgoddard, R. C, & Liss, P. S. Air Sea Gas-Exchange in Rough and Stormy Seas Measured by a Dual-Tracer Technique. Nature. (1991). , 349(6305), 145-7.

[29] Wanninkhof, R, Sullivan, K. F, & Top, Z. Air-sea gas transfer in the Southern Ocean. J Geophys Res-Oceans. (2004). C8).

[30] Ho, D. T, Law, C. S, Smith, M. J, Schlosser, P, Harvey, M, & Hill, P. Measurements of air-sea gas exchange at high wind speeds in the Southern Ocean: Implications for global parameterizations. Geophys Res Lett. (2006).

[31] Ho, D. T, Wanninkhof, R, Schlosser, P, Ullman, D. S, Hebert, D, & Sullivan, K. F. Toward a universal relationship between wind speed and gas exchange: Gas transfer velocities measured with (3)He/SF(6) during the Southern Ocean Gas Exchange Experiment. J Geophys Res-Oceans. (2011).

[32] Nightingale, P. D, Malin, G, Law, C. S, Watson, A. J, Liss, P. S, Liddicoat, M. I, et al. In situ evaluation of air-sea gas exchange parameterizations using novel conservative and volatile tracers. Global Biogeochem Cy. (2000). , 14(1), 373-87.

[33] Haußecker HJähne B. In situ measurements of the air-sea gas transfer rate during the MBL/CoOP west coast experiment. In: Jähne B, Monahan EC, editors. Air Water Gas Transfer(1995). , 775-784.

[34] Haußecker HJähne B, Reinelt S. Heat as a proxy tracer for gas exchange measurements in the field: principles and technical realization. In: Jähne B, Monahan EC, editors. Air Water Gas Transfer(1995). , 405-413.

[35] Jähne, B. Haußecker H. Air-water gas exchange. Annu Rev Fluid Mech. (1998). , 30, 443-68.

[36] Garbe, C. S, Schimpf, U, & Jähne, B. A surface renewal model to analyze infrared image sequences of the ocean surface for the study of air-sea heat and gas exchange. J Geophys Res-Oceans. (2004). C8).

[37] Mcgillis, W. R, Edson, J. B, Hare, J. E, & Fairall, C. W. Direct covariance air-sea CO2 fluxes. J Geophys Res-Oceans. (2001). C8):16729-45.

[38] Mcgillis, W. R, Edson, J. B, Zappa, C. J, Ware, J. D, Mckenna, S. P, Terray, E. A, et al. Air-sea CO2 exchange in the equatorial Pacific. J Geophys Res-Oceans. (2004). C8).

[39] Asher, W. E, Jessup, A. T, & Atmane, M. A. Oceanic application of the active controlled flux technique for measuring air-sea transfer velocities of heat and gases. J Geophys Res-Oceans. (2004). C8).

[40] Edson, J. B, Hinton, A. A, Prada, K. E, Hare, J. E, & Fairall, C. W. Direct covariance flux estimates from mobile platforms at sea. J Atmos Ocean Tech. (1998). , 15(2), 547-62.

[41] Webb, E. K, Pearman, G. I, & Leuning, R. Correction of flux measurements for density effects due to heat and water vapour transfer. Q J Roy Meteor Soc. (1980). , 106, 85-100.

[42] Businger, J. A, & Oncley, S. P. Flux Measurement with Conditional Sampling. J Atmos Ocean Tech. (1990). , 7(2), 349-52.

[43] Zemmelink, H. J. Gieskes WWC, Klaassen W, de Groot HW, de Baar HJW, Dacey JWH, et al. Simultaneous use of relaxed eddy accumulation and gradient flux techniques for the measurement of sea-to-air exchange of dimethyl sulphide. Atmos Environ. (2002).

[44] Zemmelink, H. J. Dacey JWH, Hintsa EJ. Direct measurements of biogenic dimethylsulphide fluxes from the oceans: a synthesis. Can J Fish Aquat Sci. (2004). , 61(5), 836-44.

[45] HerlinaJirka GH. Application of LIF to investigate gas transfer near the air-water interface in a grid-stirred tank. Exp Fluids. (2004). , 37(3), 341-9.

[46] HerlinaJirka GH. Experiments on gas transfer at the air-water interface induced by oscillating grid turbulence. J Fluid Mech. (2008). , 594, 183-208.

[47] Berg, P, Roy, H, Janssen, F, Meyer, V, Jorgensen, B. B, Huettel, M, et al. Oxygen uptake by aquatic sediments measured with a novel non-invasive eddy-correlation technique. Mar Ecol-Prog Ser. (2003). , 261, 75-83.

[48] Berg, P, Glud, R. N, Hume, A, Stahl, H, Oguri, K, Meyer, V, et al. Eddy correlation measurements of oxygen uptake in deep ocean sediments. Limnol Oceanogr-Meth. (2009). , 7, 576-84.

[49] Asaro, D, Mcneil, E, & Air-sea, C. gas exchange at extreme wind speeds measured by autonomous oceanographic floats. J Marine Syst. (2007).

[50] Frankignoulle, M. Field measurements of air-sea CO_2 exchange. Limnol Oceanogr. (1988). , 33(3), 313-22.

[51] Kremer, J. N, Nixon, S. W, Buckley, B, & Roques, P. Technical note: Conditions for using the floating chamber method to estimate air-water gas exchange. Estuaries. (2003). A):, 985-90.

[52] Matthews CJDSt Louis VL, Hesslein RH. Comparison of three techniques used to measure diffusive gas exchange from sheltered aquatic surfaces. Environ Sci Technol. (2003). , 37(4), 772-80.

[53] Guerin, F, Abril, G, Serca, D, Delon, C, Richard, S, Delmas, R, et al. Gas transfer velocities of CO(2) and CH(4) in a tropical reservoir and its river downstream. J Marine Syst. (2007).

[54] Tokoro, T, Watanabe, A, Kayanne, H, Nadaoka, K, Tamura, H, Nozakid, K, et al. Measurement of air-water CO2 transfer at four coastal sites using a chamber method. J Marine Syst. (2007).

[55] Vachon, D, Prairie, Y. T, & Cole, J. J. The relationship between near-surface turbulence and gas transfer velocity in freshwater systems and its implications for floating chamber measurements of gas exchange. Limnol Oceanogr. (2010). , 55(4), 1723-32.

[56] Frost, T, & Upstill-goddard, R. C. Meteorological controls of gas exchange at a small English lake. Limnol Oceanogr. (2002). , 47(4), 1165-74.

[57] Upstill-goddard, R. C. Air-sea gas exchange in the coastal zone. Estuar Coast Shelf S. (2006). , 70(3), 388-404.

[58] Yelland, M. J, Moat, B. I, Taylor, P. K, Pascal, R. W, Hutchings, J, & Cornell, V. C. Wind stress measurements from the open ocean corrected for airflow distortion by the ship. J Phys Oceanogr. (1998). , 28(7), 1511-26.

[59] Liss, P. S. Gas transfer: experiments and geochemical implications. In: Liss PS, Slinn WG, editors. Air-sea exchange of gases and partilces(1983). , 241-298.

[60] Merlivat, L, & Memery, L. Gas exchange across an air-water interface: experimental results and modelling of bubble contribution to transfer. J Geophys Res-Oceans. (1983). , 88, 707-24.

[61] Liss, P. S, & Merlivat, L. Air-sea gas exchange rates: introduction and synthesis. In: Buat-Menard P, editor. The role of air-sea exchange in geochemical cycling(1986). , 113-129.

[62] Wanninkhof, R. Relationship between Wind-Speed and Gas-Exchange over the Ocean. J Geophys Res-Oceans. (1992). C5):7373-82.

[63] Wanninkhof, R, Asher, W, Weppernig, R, Chen, H, Schlosser, P, Langdon, C, et al. Gas Transfer Experiment on Georges Bank Using 2 Volatile Deliberate Tracers. J Geophys Res-Oceans. (1993). C11):20237-48.

[64] Wanninkhof, R, & Mcgillis, W. R. A cubic relationship between air-sea CO2 exchange and wind speed. Geophys Res Lett. (1999). , 26(13), 1889-92.

[65] Broecker, W. S, Peng, T. H, Östlund, G, & Stuiver, M. The distribution of bomb radiocarbon in the ocean. J Geophys Res-Oceans. (1985). , 99, 6953-70.

[66] Ho, D. T, Law, C. S, Smith, M. J, Schlosser, P, Harvey, M, & Hill, P. Measurements of air-sea gas exchange at high wind speeds in the Southern Ocean: Implications for global parameterizations (art Geophys Res Lett. (2006). , 33(L16611)

[67] Ho, D. T, Sabine, C. L, Hebert, D, Ullman, D. S, Wanninkhof, R, Hamme, R. C, et al. Southern Ocean Gas Exchange Experiment: Setting the stage. J Geophys Res-Oceans. (2011).

[68] Takahashi, T, Sutherland, S. C, Sweeney, C, Poisson, A, Metzl, N, Tilbrook, B, et al. Global sea-air CO2 flux based on climatological surface ocean pCO(2), and seasonal biological and temperature effects. Deep-Sea Res Pt Ii. (2002).

[69] Boutin, J, Etcheto, J, Merlivat, L, & Rangama, Y. Influence of gas exchange coefficient parameterisation on seasonal and regional variability of CO(2) air-sea fluxes. Geophys Res Lett. (2002).

[70] Naegler, T, Ciais, P, Rodgers, K, & Levin, I. Excess radiocarbon constraints on air-sea gas exchange and the uptake of CO2 by the oceans. Geophys Res Lett. (2006).

[71] Wanninkhof, R, Asher, W. E, Ho, D. T, Sweeney, C, & Mcgillis, W. R. Advances in Quantifying Air-Sea Gas Exchange and Environmental Forcing. Annu Rev Mar Sci. (2009). , 1, 213-44.

[72] Wentz, F. J, Peteherych, S, & Thomas, L. A. A model function for ocean radar cross section at 14.6 GHz. J Geophys Res-Oceans. (1984). , 83, 3689-704.

[73] Charnock, H. Wind stress on a water surface. Q J Roy Meteor Soc. (1955). , 81, 639-40.

[74] Yelland, M, & Taylor, P. K. Wind stress measurements from the open ocean. J Phys Oceanogr. (1996). , 26(4), 541-58.

[75] Large, W. G, & Pand, S. Open ocean momentum flux measurements in moderate to strong winds. J Phys Oceanogr. (1981). , 11, 324-36.

[76] Geernaert, G. L, Davidson, K. L, Larsen, S. E, & Mikkelsen, T. Wind Stress Measurements during the Tower Ocean Wave and Radar Dependence Experiment. J Geophys Res-Oceans. (1988). C11):13913-23.

[77] Smith, S. D, Anderson, R. J, Oost, W. A, Kraan, C, Maat, N, Decosmo, J, et al. Sea-Surface Wind Stress and Drag Coefficients- the Hexos Results. Bound-Lay Meteorol. (1992).

[78] Anderson, R. J. A Study of Wind Stress and Heat-Flux over the Open-Ocean by the Inertial-Dissipation Method. J Phys Oceanogr. (1993). , 23(10), 2153-61.

[79] Deacon, E. L. Gas transfer to and across an air-water interface. Tellus. (1977). , 29, 363-74.

[80] Fairaill, C. W, Hare, J. E, Edson, J. B, & Mcgillis, W. Parameterization and micrometeorological measurement of air-sea gas transfer. Bound-Lay Meteorol. (2000).

[81] Hare, J. E, Fairall, C. W, Mcgillis, W. R, Edson, J. B, Ward, B, & Wanninkhof, R. Evaluation of the National Oceanic and Atmospheric Administration/Coupled-Ocean Atmospheric Response Experiment (NOAA/COARE) air-sea gas transfer parameterization using GasEx data. J Geophys Res-Oceans. (2004). C8).

[82] Frew, N. M, Bock, E. J, Schimpf, U, Hara, T, Haussecker, H, Edson, J. B, et al. Air-sea gas transfer: Its dependence on wind stress, small-scale roughness, and surface films. J Geophys Res-Oceans. (2004). C8).

[83] Frew, N. M, Glover, D. M, Bock, E. J, & Mccue, S. J. A new approach to estimation of global air-sea gas transfer velocity fields using dual-frequency altimeter backscatter. J Geophys Res-Oceans. (2007). C11).

[84] Asher, W. E, Karle, L. M, Higgins, B. J, Farley, P. J, Monahan, E. C, & Leifer, I. S. The influence of bubble plumes on air-seawater gas transfer velocities. J Geophys Res-Oceans. (1996). C5):12027-41.

[85] Kitaigorodskii, S. A. On the field dynamical theory of turbulent gas transfer across an air-sea interface in the presence of breaking waves. J Phys Oceanogr. (1984). , 14, 960-72.

[86] Farmer, D. M, Mcneil, C. L, & Johnson, B. D. Evidence for the Importance of Bubbles in Increasing Air Sea Gas Flux. Nature. (1993). , 361(6413), 620-3.

[87] Zhang, W. Q, Perrie, W, & Vagle, S. Impacts of winter storms on air-sea gas exchange. Geophys Res Lett. (2006).

[88] Mcneil, C, & Asaro, D. E. Parameterization of air-sea gas fluxes at extreme wind speeds. J Marine Syst. (2007).

[89] Woolf, D. K, & Thorpe, S. A. Bubbles and the Air-Sea Exchange of Gases in near-Saturation Conditions. J Mar Res. (1991). , 49(3), 435-66.

[90] Woolf, D. K. Bubbles and the Air-Sea Transfer Velocity of Gases. Atmos Ocean. (1993). , 31(4), 517-40.

[91] Woolf, D. K. Parametrization of gas transfer velocities and sea-state-dependent wave breaking. Tellus B. (2005). , 57(2), 87-94.

[92] Woolf, D. K. Bubbles and their role in gas exchange. In: Liss PS, Duce RA, editors. The sea surface and global changes: Cambridge University Press, Cambridge; (1997). , 173-205.

[93] Woolf, D. K, Leifer, I. S, Nightingale, P. D, Rhee, T. S, Bowyer, P, Caulliez, G, et al. Modelling of bubble-mediated gas transfer: Fundamental principles and a laboratory test. J Marine Syst. (2007).

[94] Wanninkhof, R, Asher, W, & Monahan, E. C. The influence of bubbles on air-water gas exchange results from gas transfer experiments during WABEX-93. In: Jähne B, Monahan EC, editors. Air-water gas transfer: AEON Verlag & Studio, Hanau; (1995). , 239-254.

[95] Zhao, D, Toba, Y, Suzuki, Y, & Komori, S. Effect of wind waves on air-sea gas exchange: proposal of an overall CO2 transfer velocity formula as a function of breaking-wave parameter. Tellus B. (2003). , 55(2), 478-87.

[96] Broecker, H. C, Petermann, J, & Siems, W. The influence of wind on CO_2 exchange in a wind wave tunnel, including the effects of monolayers. J Mar Res. (1978). , 36, 595-610.

[97] Asher, W. E. The sea-surface microlayer and its effects on global air-sea gas transfer. In: Liss PS, Duce RA, editors. The sea surface microlayer and global change: Cambridge University Press; (1997). , 251-286.

[98] Tsai, W. T. Impact of a surfactant on a turbulent shear layer under the air-sea interface. J Geophys Res-Oceans. (1996). C12):28557-68.

[99] Tsai, W. T. Effects of surfactant on free-surface turbulent shear flow. Int Commun Heat Mass. (1996). , 23(8), 1087-95.

[100] Tsai, W. T. Yue DKP. Effects of Soluble and Insoluble Surfactant on Laminar Interactions of Vortical Flows with a Free-Surface. J Fluid Mech. (1995). , 289, 315-49.

[101] Tsai, W. T, & Liu, K. K. An assessment of the effect of sea surface surfactant on global atmosphere-ocean CO2 flux. J Geophys Res-Oceans. (2003). C4).

[102] Saylor, J. R, Smith, G. B, & Flack, K. A. The effect of a surfactant monolayer on the temperature field of a water surface undergoing evaporation. Int J Heat Mass Tran. (2000). , 43(17), 3073-86.

[103] Goldman, J. C, Dennett, M. R, & Frew, N. M. Surfactant Effects on Air Sea Gas-Exchange under Turbulent Conditions. Deep-Sea Res. (1988). , 35(12), 1953-70.

[104] Frew, N. M, Goldman, J. C, Dennett, M. R, & Johnson, A. S. Impact of Phytoplankton-Generated Surfactants on Air-Sea Gas-Exchange. J Geophys Res-Oceans. (1990). C3):3337-52.

[105] Bock, E. J, Hara, T, Frew, N. M, & Mcgillis, W. R. Relationship between air-sea gas transfer and short wind waves. J Geophys Res-Oceans. (1999). C11):25821-31.

[106] Ho, D. T, Bliven, L. F, Wanninkhof, R, & Schlosser, P. The effect of rain on air-water gas exchange. Tellus B. (1997). , 49(2), 149-58.

[107] Ho, D. T, Veron, F, Harrison, E, Bliven, L. F, Scott, N, & Mcgillis, W. R. The combined effect of rain and wind on air-water gas exchange: A feasibility study. J Marine Syst. (2007).

[108] Ho, D. T, Zappa, C. J, Mcgillis, W. R, Bliven, L. F, Ward, B, et al. Influence of rain on air-sea gas exchange: Lessons from a model ocean. J Geophys Res-Oceans. (2004). C8).

[109] Zappa, C. J, Ho, D. T, Mcgillis, W. R, & Banner, M. L. Dacey JWH, Bliven LF, et al. Rain-induced turbulence and air-sea gas transfer. J Geophys Res-Oceans. (2009).

[110] Ho, D. T, Asher, W. E, Bliven, L. F, Schlosser, P, & Gordan, E. L. On mechanisms of rain-induced air-water gas exchange. J Geophys Res-Oceans. (2000). C10):24045-57.

[111] Takagaki, N, & Komori, S. Effects of rainfall on mass transfer across the air-water interface. J Geophys Res-Oceans. (2007). C6).

[112] Schlussel, P, Soloviev, A. V, & Emery, W. J. Cool and freshwater skin of the ocean during rainfall. Bound-Lay Meteorol. (1997). , 82(3), 437-72.

[113] Lorke, A, & Peeters, F. Toward a unified scaling relation for interfacial fluxes. J Phys Oceanogr. (2006). , 36(5), 955-61.

[114] Wang, B, Liao, Q, Xiao, J, & Bootsma, H. A. A free-floating PIV system: measurements of small-scale turbulence under the wind wave surface. J Atmos Ocean Tech. (2013). in print

[115] Monahan, A. H. The probability distribution of sea surface wind speeds. Part 1: Theory and SeaWinds observations. J Climate. (2006). , 19(4), 497-520.

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