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A quantitative evaluation of the factors influencing the air-sea carbon dioxide transfer velocity

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Abstract

The numerous factors influencing the air-sea carbon dioxide (CO_2) transfer velocity have been discussed for many years, yet the contributions of various factors have undergone little quantitative estimation. To better understand the mechanism of air-sea transfer, the effects of different factors are discussed on the air-sea transfer velocity and the various parametric models describing the phenomenon are classified and compared. Then, based on GAS EX-98 and ASGAMAGE data, wind models are evaluated and the effects of some factors are discussed quantitatively, including bubbles, waves, wind and so on by considering their interaction through a piecewise average approach. It is found that the air-sea CO_2 transfer velocity is not only the function of the wind speed, but is also affected by bubbles, wave parameters and other factors. Stepwise and linear regressions are used. When considering the wind speed, bubbles mediated and the significant wave height, the root mean square error is reduced from 34.53 cm/h to 16.96 cm/h. Discussing the various factors quantitatively can be useful in future assessments of a large spatial scale and long-term air-sea CO_2 flux and global change.

Key words: influence factors, transfer velocity, carbon dioxide, quantitatively

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1 Introduction

Carbons in the earth are stored in the hydrosphere, the biosphere, the atmosphere, and the lithosphere. Of these the ocean, which accounts for 71% of the earth's surface, is the largest carbon sink to absorb anthropogenic carbon and slow climate change (Falkowski et al., 2000). The reserve of carbon dioxide in the ocean is roughly equivalent to 50 times the amount in the atmosphere and 20 times the amount in the biosphere (Chen et al., 2004). Carbon dioxide is absorbed via biological, chemical, flow, and deposition processes by the oceans and is then stored in the seabed or converted to other carbonaceous materials (Wang and Wen, 1996).

Many studies have examined the carbon dioxide transfer velocity because it is an important parameter in the accurate calculation of the air-sea carbon dioxide flux. The air-sea carbon dioxide (CO_2) transfer velocity k is defined in terms of the air-sea CO_2 flux (Frankignoulle, 1988):

$$F = kL\left(p_{\mathrm{CO_2,\,w}} - p_{\mathrm{CO_2,\,a}}\right), \tag{1}$$

where F is the air-sea carbon dioxide flux [mmol/(m^2·d)]; L is the solubility [mmol/(dm^3·Pa)] of carbon dioxide; $p_{\mathrm{CO_2,\,w}}$ is the carbon dioxide partial pressure (μPa) of the water; $p_{\mathrm{CO_2,\,a}}$ is the carbon dioxide partial pressure (μPa) of the air. The air-sea transfer velocity is the speed at which CO_2 moves from the air to the sea, or from the sea to the air. The gas transfer is an important process that is dominated by the turbulence near the air-sea interface, which is very difficult to obtain or describe. The wind speed is widely used to calculate the transfer velocity, and until now has been a good proxy (Mørk et al., 2014; Goddijn-Murphy et al.,

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2015). However, numerous factors influence the transfer velocity. The major environmental factors that do so are the diffusion coefficient, the boundary layer stability, the surfactant, microscale wave breaking, the wind speed, the current, the wave mean square slop, the wave age, temperature and humidity gradients, the fetch, wave breaking, the surface disruption, whitecaps and turbulence and boundary layer depths. Among these factors, waves are the most critical because they influence various aspects of the transfer velocity, such as boundary layer, surface disruption, turbulence and whitecaps. Figure 1 shows how these factors affect the CO_2 transfer velocity and the related relationships.

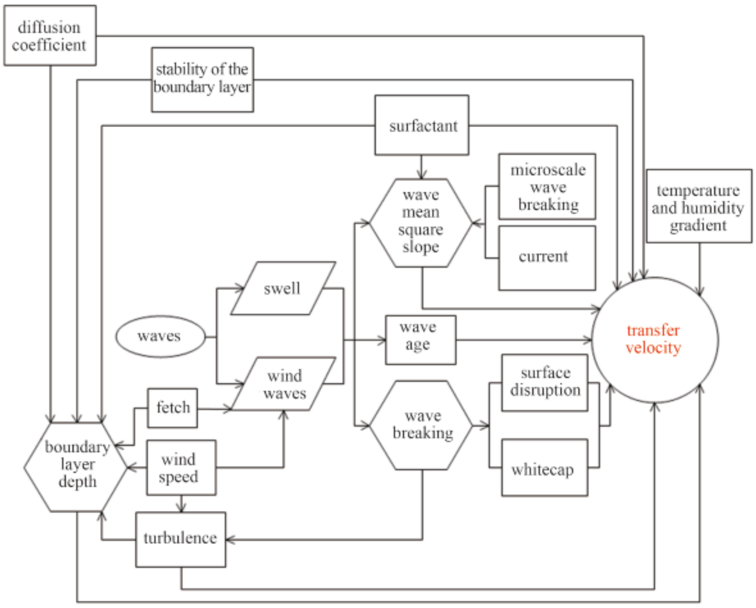

Fig. 1. Sketch map of the factors that affect the carbon dioxide transfer velocity.

Wanninkhof et al. (2009) discussed the fundamental principles of the air-sea gas transfer and recent developments in a gas transfer theory, parameterizations and measurement technologies in the context of CO_2 exchange. However, there has been no quantization of the various factors influencing the transfer velocity. Yu et al. (2014) revealed great uncertainty in the air-sea CO_2 flux due to various transfer velocity formulas. Thus, deep research into the factors influencing the transfer velocity is merited.

To better understand the air-sea transfer mechanism, we evaluated wind models and discussed the quantitative effects of factors such as bubbles, waves, wind and so on. We considered their interactions using a piecewise average method based on GAS EX-98 and ASGAMAGE data. Then, we discussed the effects of different factors on the air-sea transfer velocity, classified and compared the various parametric models describing that phenomenon. Finally, we present the conclusion.

2 Data

2.1 *GAS EX-98*

Data from GAS EX-98 and ASGAMAGE were used in this study. The GAS EX-98 data were obtained from the GAS EX-98 cruise, which was conducted in a North Atlantic carbon sink area and the northeast Pacific Ocean between May 7, 1998 and July 27, 1998. We used data from the North Atlantic area (Fig. 2). The primary focus of the cruise was an open-ocean air-sea exchange experiment conducted within a cold-core eddy during a 1 month process study.

In the GAS EX-98 data, the transfer velocity for CO_2 was normalized to a temperature of 20°C, the wind speed (m/s) was normalized to two heights 10 m and 18 m, the air-sea partial pressure difference was in μPa, and the air-sea CO_2 flux was in mmol/(m^2·d).

2.2 *ASGAMAGE*

The name "ASGAMAGE" is a contraction of ASGAS-EX (air sea gas exchange, an earlier project with many of the same participants) and MAGE (marine aerosol and gas exchange), in which eddy-correlation measurements are conducted at research platform Meetpost Noordwijk (MPN) in the southern North Sea from March 1, 1996 to March 1, 1999. The "ASGAMAGE" included two parts: ASGAMAGE-A was conducted from May 6, 1996 to June 7, 1999 and ASGAMAGE-B was conducted from October 7, 1996 to November 8, 1996. The area from which our ASGAMAGE data were taken is also shown in Fig. 2.

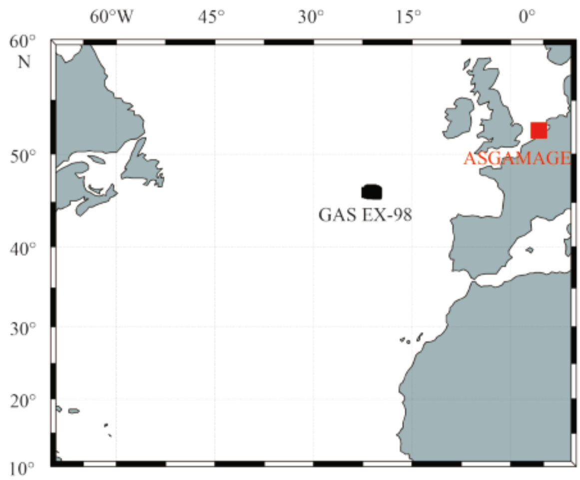

Fig. 2. The location of the study area.

3 Methods

3.1 *Stepwise regression*

A stepwise regression establishes a regression equation that contains all of the variables that significantly contribute to the dependent variable, and none that do not (Chen and Ma, 1991).

The factors influencing the transfer velocity were introduced into the regression equation individually according to their contributions to the transfer velocity. Any previously introduced variables were removed if their contributions were not found to be significant, due to the introduction of other new variables. This continued until no more variables in the regression equation could be removed and or introduced.

First, we selected the factors that might have affected the transfer velocity. The factors we chose were water direction [flow direction (°)], the west–east water current velocity (m/s), because the water current may contribute to the gas transfer velocity and to its variability by generating the turbulence (Zappa et al., 2007; Takahashi et al., 2009). The values of the CO_2 transfer velocity were significantly greater when the water currents and the wind were in opposing directions (Abril et al., 2009). The Webb velocity (mean vertical velocity) (cm/h); the squared Webb velocity; the cubed Webb velocity; wind direction (°); wind speed normalized to a height of 10 m and to neutral conditions; the squared wind speed normalized to a height of 10 m; the cubed wind speed normalized to a height of 10 m; which may generate near the surface turbulence through the direct wind shear and may generate wind waves (Bock et al., 1999). the significant wave height (m); the phase velocity (m/s) of waves at the peak of spectrum; the cubed phase velocity of waves at the peak of spectrum; wave period (s) at the peak of spectrum; and the cubed wave period at the peak of spectrum, which may generate a gas exchange directly due to wave motion, may generate a turbulence by wind waves, may generate bubbles by wave breaking, break up and accumulate the surface films, and increase the surface drag (Bock et al., 1999).

We then calculated the variance and covariance of the dependent and independent variables l_{ij}:

$$l_{ij} = \sum_{k=1}^{n} x_{ki}x_{kj} - \frac{1}{n}\left(\sum_{k=1}^{n} x_{ki}\right)\left(\sum_{k=1}^{n} x_{kj}\right), \tag{2}$$

where x is the independent variable; i, j=1, 2, ..., m, are the factors that may affect the transfer velocity; m is the number of dependent and independent variables (m=15, including the transfer velocity); and k=1, 2, ..., n, in which n is the number of data (n=133).

Then, we calculated the correlation coefficient matrix $r_{ij}^{(0)}$:

$$r_{ij}^{(0)} = \frac{l_{ij}}{\sqrt{l_{ii}l_{jj}}} = r_{ji}^{(0)}. \tag{3}$$

To measure whether the variance contribution of the selection or elimination of the variables is significant, the critical value of an F-test, $F_{0.05}$, should be given. Here, the confidence is 0.05, the numerator degree of a freedom is 1 and the denominator degree of the freedom is n–k_c–1=133–6–1=126, where k_c is the number of factors that may be chosen in the regression equation.

Then, we calculated the sum of the squares of partial regression on the variables $P_i^{(l_s+1)}$:

$$P_i^{(l_s+1)} = \left[r_{iy}^{(l_s)}\right]^2 / r_{ii}^{(l_s)}, \tag{4}$$

where l_s is the step, and y is the column number of independent variables. The maximum of the sum of squares was then chosen for a partial regression of the variables:

$$P_{\max}^{(l_s+1)} = \max\left\{P_i^{(l_s+1)}\right\}, \tag{5}$$

and then the significance test is as follows:

$$F_{P_{\max}}^{(l_s+1)} = \frac{(n-k_n-1)\,P_{\max}^{(l_s+1)}}{Q^{(l_s)} - P_{\max}^{(l_s+1)}}, \tag{6}$$

where $Q^{(l_s)} = r_{yy}^{(l_s)}$, is the residual sum of squares; and k_n is the number of the variables.

If $F_{P_{\max}}^{(l_s+1)} > F_{0.05}$, then $X_{K_{\max}}^{(l_s+1)}$ makes a significant contribution to the variance in the transfer velocity and $X_{K_{\max}}^{(l_s+1)}$ can be introduced into the regression equation, where $X_{K_{\max}}^{(l_s+1)}$ is the variable whose sum of squares for the partial regression is the maximum and $k_{\max}$ is the column number of $X_{K_{\max}}^{(l_s+1)}$.

Then, the correlation coefficient matrix transforms into $r_{ij}^{(l_s+1)}$:

$$r_{ij}^{(l_s+1)} = \begin{cases} 1/r_{k_{\max}k_{\max}}^{(l_s)} \\ i=j=k_{\max} \\ -r_{ik_{\max}}^{(l_s)}/r_{k_lk_{\max}}^{(l_s)} \\ i\neq k_{\max}, j=k_{\max} \\ r_{k_{\max}j}^{(l_s)}/r_{k_{\max}k_{\max}}^{(l_s)} \\ i=k_{\max}, j\neq k_{\max} \\ r_{ij}^{(l_s)} - r_{ik_{\max}}^{(l_s)}r_{kj}^{(l_s)}/r_{k_{\max}k_{\max}}^{(l_s)} \\ i\neq k_{\max}, j\neq k_{\max} \end{cases} \tag{7}$$

Next, we calculated the sum of squares for the partial regression of the chosen variables $P_{X_{k_{\max,i}}}^{(l_s+2)}$ and chose the minimum of the sum of squares for the partial regression of the chosen variables:

$$P_{\min}^{(l_s+2)} = \min\left\{P_{X_{k_{\max,i}}}^{(l_s+2)}\right\}, \tag{8}$$

where $X_{k_{\min}}^{(l_s+2)}$ is the variable whose sum of squares for the partial regression is $P_{\min}^{(l_s+2)}$; and $k_{\min}$ is the column number of $X_{k_{\min}}^{(l_s+2)}$.

The significance test is then as follows:

$$F_{P_{\min}}^{(l_s+2)} = \frac{(n-k_n-1)\left[b_{r,k_{\min}}^{(l_s+1)}\right]^2}{r_{yy}^{(l_s+2)}r_{k_{\min}k_{\min}}^{(l_s+2)}}, \tag{9}$$

where $b_{r,k_{\min}}^{(l_s+1)} = r_{k_{\min}y}^{(l_s+1)}$, is the standard partial regression coefficient.

If $F_{P_{\min}}^{(l_s+2)} < F_{0.05}$, then $X_{k_{\min}}^{(l_s+2)}$ should be removed.

The process continues until no variables in the regression equation can be removed or introduced.

The regression coefficient of the regression equation is as follows:

$$b_{k_{\max,i}} = b_{r,k_{\max,i}}^{(l_s+n)}\sqrt{\frac{l_{yy}}{l_{k_{\max}k_{\max}}}}, \tag{10}$$

where $b_{r,k_{\max,i}}^{(l_s+n)} = r_{k_{\max,i}y}^{(l_s+n)}$.

The constant term is

$$b_0 = \overline{Y} - \sum_{i=1}^{q} b_{k_{\max,i}} \overline{X}_{k_{\max,i}}, \tag{11}$$

where q is the number of selected variables in the regression equation.

The residual sum of square σ is

$$\sigma = \sqrt{\frac{Q}{n-q-1}}, \tag{12}$$

and the multiple correlation coefficient R is

$$R = \sqrt{1 - \frac{Q}{l_{yy}}}, \tag{13}$$

Then, the regression equation becomes

$$Y_R = b_0 + \sum_{i=1}^{q} b_{k_{\max,i}} X_{k_{\max,i}}, \tag{14}$$

and the root mean square error (RMSE, $e_{\rm rms}$) is calculated as

$$e_{\rm rms} = \left(\frac{1}{n}\sum (Y - Y_R)\right)^{\frac{1}{2}}. \tag{15}$$

3.2 *Piecewise average*

The wind speed is one of the most important factors affecting the CO_2 transfer velocity because the energy contained in the ocean's surface is mainly from the wind, and wind data are easy to obtain. However, the plots for the wind speed and the transfer velocity are scattered for both GAS EX-98 and ASGAMAGE data, due to the sheer number of factors influencing the transfer velocity.

To understand the relationship between the wind speed and the CO_2 transfer velocity, piecewise averages were applied to the GAS EX-98 and ASGAMAGE data, which were divided into sections by the wind speed from 0 to the maximum wind speed in 0.5 m/s intervals. The data were then averaged in every section.

To determine how the wind speed and significant wave height influenced the CO_2 transfer velocity, in addition to the aforementioned division based on the wind speed, the data were also divided into sections based on the significant wave height, from 0 to the maximum in 0.5 m/s intervals. The data were then averaged in every section.

3.3 *Linear regression*

Given that the wind speed, the significant wave height and the bubble medium transfer velocity are the most important influential factors, and the relative ease in obtaining such data, to determine their effects on the CO_2 transfer velocity, we used linear regressions for both the GAS EX-98 and ASGAMAGE data after applying the piecewise averages. A quadratic equation exclusively for the wind speed was obtained, along with a multi-factor linear regression model of the wind speed, the significant wave height and the bubble medium transfer velocity. The coefficients were obtained using the least squares method.

The RMSE is used to respect the accuracy of the transfer velocity. The RMSE is calculated as follows:

$$e_{\rm rms} = \left(\frac{1}{n}\sum_{i=1}^{n} (k_{{\rm obs},i} - k_{{\rm cal},i})\right)^{\frac{1}{2}} \tag{16}$$

where $k_{{\rm obs},i}$ is the observed carbon dioxide transfer velocity and $k_{{\rm cal},i}$ is the calculated carbon dioxide transfer velocity.

3.4 *Bubble medium transfer velocity*

Bubbles may generate a gas transfer directly, and may enhance the turbulence. The contribution of the bubble medium to the carbon dioxide transfer velocity (Woolf, 2005) was calculated as follows:

$$k_{\rm b} = c\,\frac{u_* H_{\rm s}}{\nu_{\rm w}}, \tag{17}$$

where $k_{\rm b}$ is the bubble medium transfer velocity; $c=2\times10^{-5}$, is a constant; $\nu_{\rm w} = 1.83 \times 10^{-6} \exp(-T_{\rm ss}/T_0)$, is the kinematic viscosity of water, in which $T_{\rm ss}$ is the sea surface temperature (here we used the water temperature bulk instead of the sea surface temperature) and T_0=36 ; u_* is the friction velocity; and $H_{\rm s}$ is the significant wave height.

4 Results and discussion

4.1 *Factors influencing air-sea CO_2 transfer velocity*

We calculated the correlation coefficient among the transfer velocity, the wind speed, the significant wave height and other influential factors. For the GAS EX-98 data, the correlation coefficient between the transfer velocity and the wind speed normalized to a height of 10 m or 18 m was 0.15, which passed the 95% significance test. However, the correlation coefficient between the cube of the transfer velocity and the wind speed normalized to a height of 10 m or 18 m was 0.25, which also passed the 95% significance test.

For the ASGAMAGE data, the correlation coefficient for the transfer velocity, the water velocity, the water concentration, the water vapor pressure, the specific humidity, the density of dry components of air, the CO_2 concentration, the indication of rain, the air pressure or CO_2 concentration in air did not pass the 95% significance test, so the value is not shown here. The correlation coefficient between the transfer velocity and its influencing factors is shown in Table 1. The relationship between the reciprocal of the transfer velocity and the west-east water velocity was 0.22 and the water direction was 0.20, both of which passed the 95% significance test. The correlation coefficients between the transfer velocity and the Webb velocity (mean vertical velocity) (0.27), squared Webb velocity (0.32), cubed Webb velocity (0.34), wind direction (0.24), wind speed normalized to a height of 10 m and to neutral conditions (0.34), squared wind speed normalized to a height of 10 m (0.25), cubed wind speed normalized to a height of 10 m (0.19), significant wave height in m (0.28), phase velocity of waves at peak of spectrum (0.18), cubed phase velocity of waves at peak of spectrum (0.25), wave period at peak of spectrum (0.17), cubed wave period at peak of spectrum (0.23) and bubble medium transfer velocity (0.25) all passed the 95% significance test.

The effect of each factor on the CO_2 transfer velocity was quantitatively explained and the results are consistent with previous findings (Woolf, 2005; Wanninkhof et al., 2009; Zhao and Xie, 2010). All of the above factors were used for the stepwise regression.

Table 1. Correlation coefficients between the transfer velocity and its influencing factors

Independent variables X			Correlation coefficient	
			k_{660}	$-k_{660}^{-1}$
1	u_w	west-east water velocity (m/s)		−0.22
2	D_w	water direction (°)		−0.20
3	w	Webb velocity (mean vertical velocity) (cm/h)	0.27	
4	w^2		0.32	
5	w^3		0.34	
6	D_a	wind direction (°)	0.24	
7	u_{10}	wind speed (m/s) normalized to a height of 10 m and to neutral conditions	0.34	
8	u_{10}^2		0.25	
9	u_{10}^3		0.19	
10	H_s	significant wave height (m)	0.28	
11	c_p	phase velocity (m/s) of waves at peak of spectrum	0.18	
12	$-c_p^{-3}$		0.25	
13	T_s	wave period (s) at peak of spectrum	0.17	
14	$-T_s^{-3}$		0.23	
15	k_b	bubble medium transfer velocity (cm/h)	0.25	

4.2 *Significant factors influencing air-sea CO_2 transfer velocity*

The result of the stepwise regression was

$$k_{SRM} = -59.54 + 7.62u_{10} - 6.65k_b + 0.1w^2 - 0.0009w^3 - 1.03w. \tag{18}$$

The most significant factors influencing the air-sea CO_2 transfer velocity were the wind speed normalized to a height of 10 m and to neutral conditions, the bubble medium transfer velocity and the Webb velocity (mean vertical velocity). Among all of the factors studied, the Webb velocity was the most difficult to obtain.

The RMSE was 30.05, the multiple correlation coefficient R was 1.0, and the residual sum of square σ was 0.068.

A comparison of k between the measurements and those calculated using the stepwise regression is shown in Fig. 3. The stepwise regression was suitable as long as the transfer velocity was less than 100 cm/h. However, when the transfer velocity was higher than 100 cm/h, the stepwise regression equation was underestimated.

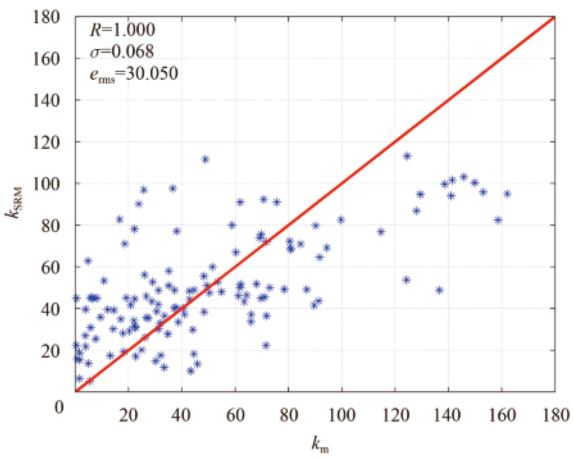

Fig. 3. Scatter diagrams of the measured transfer velocity (k_m) versus those calculated using the stepwise regression (k_{SRM}).

4.3 *Influence of wind speed*

Among the most significant factors, the wind speed was the most important and was easiestly obtained. We divided the data into many sections by the wind speed from 0 to the maximum in 0.5 m/s intervals, as the data were scattered. Then, the linear regression was conducted.

The fitting results are shown in Table 2. The fitting result is compared with the formula of Wanninkhof (1992) in Fig. 4. The fitting result of GAS EX-98 is shown in Fig. 4a, and the result of ASGAMAGE is shown in Fig. 4b. A comparison of k between the measurements and those calculated using the linear regression of the GAS EX-98 and ASGAMAGE data is shown in Figs 4c and d. The RMSE of the linear regression formula for the wind speed in the GAS EX-98 and ASGAMAGE data were 10.92 and 18.28, re-

Table 2. Fitted formulas and their error using linear regression method

Fitting			e_{rms}/cm·h^{-1}	
			GAS EX98	ASGAMAGE
		Average (cm/h)	33.05	53.17
Formulas of wind	Formula of Wanninkhof (1992)	$k = 0.3\,1u_{10}^2$	22.01	34.53
	relationship of constant, first order and second order	$k = 0.42u_{10}^2 - 5.68u_{10} + 41.71$	10.92	
		$k = -0.95u_{10}^2 + 23.34u_{10} - 68.3$		18.28
Addition of bubbles	formula of Wanninkhof (1992) added the bubbles	$k = 0.3\,1u_{10}^2 + 1.23k_b$		28.73
	linear fitting	$k = -0.39u_{10}^2 + 18.61u_{10} - 55.81 - 1.61k_b$		18.03
Addition of waves	with bubbles	$k = 0.01u_{10}^2 + 21.81u_{10} - 98.22 + 70.19H_s + 9.08k_b - 15.03u_{10}H_s$		16.96
	without bubbles	$k = 0.27u_{10}^2 + 12.81u_{10} - 56.22 + 34.52H_s - 4.8u_{10}H_s$		17.59

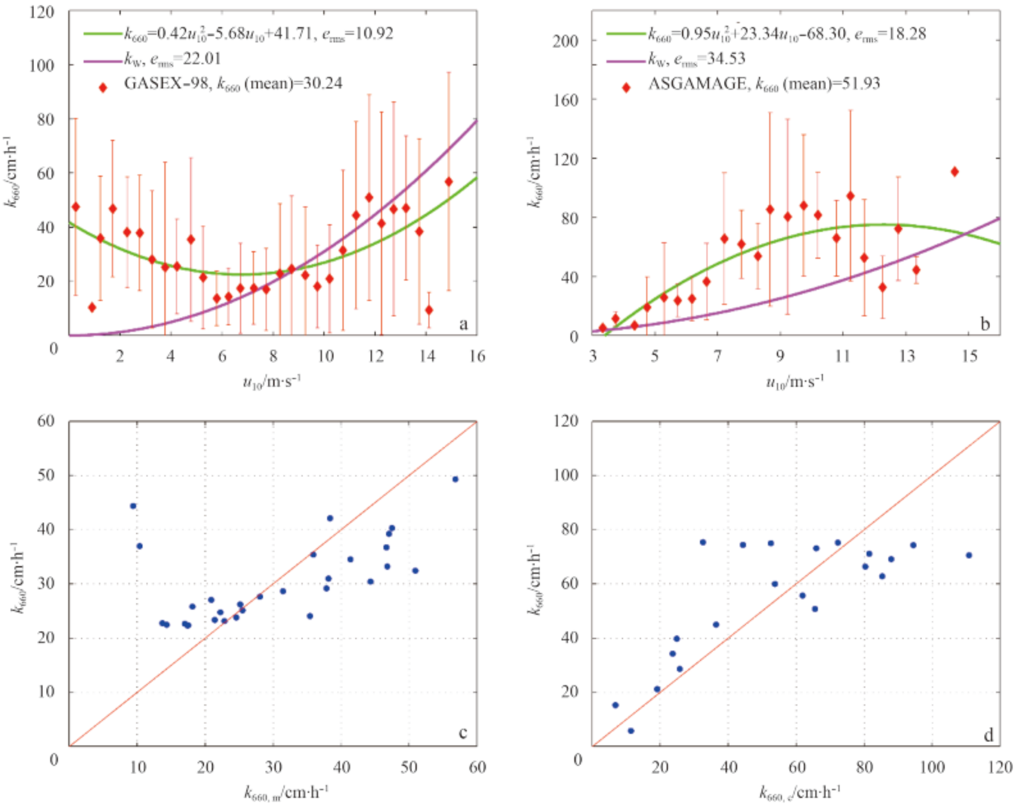

Fig. 4. Scatter diagrams of the transfer velocity versus the wind speed. a. Fitting result of GAS EX-98 and b. fitting result of ASGAMAGE, c. comparison of k between the measurements and those calculated from the linear regression method of GAS EX-98 data and d. Comparison of k between the measurements ($k_{660,\ m}$) and those ($k_{660,\ c}$) calculated from the linear regression method of ASGAMAGE data. The subscript W of k_W is abbreviated from Wanninkhof.

spectively much smaller than those (22.01 and 34.53) in Wanninkhof (1992).

For the GAS EX-98 data, the carbon dioxide transfer velocity is high at both low and high wind speeds and lower at the medium wind speeds. The high value at low wind speeds proves that the transfer velocity is not 0, which may be a result of buoyancy, microwave breaking, chemical enhancement, or other factors. Further data are needed to confirm the reasons. The high value at the high wind speeds may be a result of wave breaking and foam entrainment. The linear regression formula of the wind speed is overestimated when the transfer velocity is less than 20 cm/h, and underestimated when greater than 40 cm/h.

In the contrast, the ASGAMAGE carbon dioxide transfer velocity is not as high at the low wind speeds as indicated by the GAS EX-98 data, but it is high at the medium and high wind speeds, which may be a result of the relative stability of the water surface in this area at the low wind speeds. The ASGAMAGE data had a relatively low value when the wind speed was about 12 m/s, but returned to a higher value when it increased to about 15 m/s. The reasons for this require additional data to confirm. The linear regression exceeded the wind speed estimate when the transfer velocity was between 30 cm/h and 50 cm/h and underestimated it when the transfer velocity was greater than 80 cm/h.

The differences between the GAS EX-98 and ASGAMAGE data may have been caused by different sea states. It is difficult to estimate the transfer velocity at both ends, perhaps because the wind speed stops being the control factor once the transfer velocity becomes too small or too large.

We put the GAS EX-98 and ASGAMAGE data together and divided them into sections based on the wind speed, from 0 to the maximum in 0.5 m/s intervals. The RMSE of the linear regression formula for the wind speed in the GAS EX-98 data was 15.19 (Fig. 5), which was much smaller than that (23.28) in Wanninkhof (1992). The CO_2 transfer velocity was high at both low and high wind speeds, but lower at the medium wind speeds, similar to the GAS EX-98 data alone far more than the ASGAMAGE data. The linear regression exceeded the wind speed estimate when the transfer velocity was less than 20 cm/h and underestimated it when the transfer velocity was greater than 80 cm/h.

We only compared our linear regression with the results obtained by Wanninkhof (1992). In fact, much research has been conducted on the wind speed and the transfer velocity and the results support the work of our predecessors as follows.

The relationships between the CO_2 ancentration and the wind speed are the simplest and most popular. The parameterized functions of the carbon dioxide ancentration and the wind speed include linear equations, quadratic dependence, third-degree equations and equations with one variable and a second-degree. Long-term winds, steady or short-term winds, and mean winds are all included. The data are obtained from laboratory wind-wave tanks, tracer experiments in lakes and the open ocean, wind-wave field experiments, local coastal experiments, scatterometry, passive microwave radar radiometry, and reanalysis of data.

Deacon (1977) carried out a treatment over a smooth plane surface with low winds to obtain the linear relationship between the transfer velocity and the friction velocity. The transfer velocity is greater than the value calculated with this relationship and

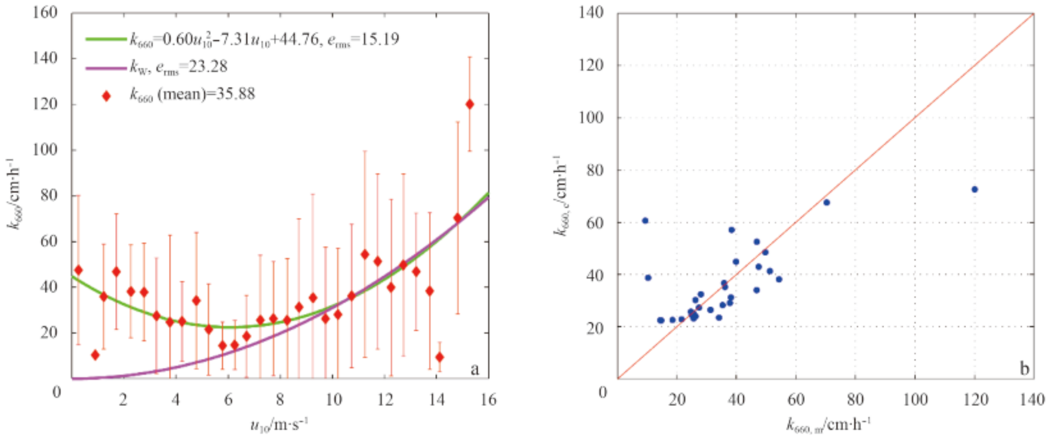

Fig. 5. Scatter diagrams of the transfer velocity versus the wind speed for the GAS EX-98 and ASGAMAGE data when divided into sections by the wind speed in 0.5 m/s intervals. a. Fitting result for the GAS EX-98 and ASGAMAGE data and b. the comparison of k between the measurements and those calculated from the linear regressions of the GAS EX-98 and ASGAMAGE data.

is approximately proportional to the square of the wind speed. Liss and Merlivat (1986) provided three linear segments of the transfer velocity with the wind speed according to the intensity of the wind: a smooth surface regime, a rough surface regime, and a breaking wave (bubble) regime. Its disadvantages are oversimplified. The relationship for a medium wind speed was consistent with the deliberate tracer results obtained in lakes (Wanninkhof, 1985). Wanninkhof (1992) used the global bomb carbon-14 constraint (Broecker et al., 1985) and wind-wave tank results to provide two relationships between the transfer velocity and the long-term wind speed, and the steady and the short-term wind. The long-term relationship was consistent with the Red Sea bomb carbon-14 estimates (Cember, 1989). The steady or short-term relationship has been widely used because it fitted well when applied to numerical global ocean biogeochemistry models that used the same global bomb carbon-14 constraint (Sarmiento and Le Quere, 1996). However, in the global flux estimation, the relationship of Liss and Merlivat (1986) was approximately 50% lower than the steady or short-term relationship of Wanninkhof (1992). Wanninkhof and McGillis (1999) proposed a cubic relationship of the transfer velocity and the wind speed that yields global fluxes approximately 70% higher than the steady relationship proposed by Wanninkhof (1992) or the short-term relationship proposed by Takahashi et al. (2009) and Rutgersson and Smedman (2010).

Neither the relationship of Wanninkhof (1992) nor that of Wanninkhof and McGillis (1999) has good fit with high wind speeds. Ho et al. (2006) gave a quadratic relationship of the transfer velocity and the wind speed at the higher wind speeds (16.0 m/s) based on the SOLAS air-sea gas exchange (SAGE) experiment conducted in the western Pacific sector of the Southern Ocean using the $^3He/SF_6$ dual gas tracer technology. The relationship improved the relationships of Wanninkhof (1992) and Wanninkhof and McGillis (1999) at the high wind speeds and were consistent with the results of Sweeney et al. (2007) and Nightingale et al. (2000). Nightingale et al. (2000) proposed a global transfer velocity based on a local reach of a limited wind field in coastal areas.

McGillis et al. (2001, 2004) suggested a cubic relationship between the transfer velocity and the wind speed with a low wind speed and a low whitecap coverage using a direct covariance technology. Weiss et al. (2007) assumed a linear, quadratic dependency of the transfer velocity and wind speed using a long-term series of direct eddy correlation carbon dioxide flux measurements. Wanninkhof et al. (2009) provided the relationships of the transfer velocity and an average wind speed, and the second moment and the third moment. Fangohr et al. (2008) calculated the long-term global air-sea flux of carbon dioxide using scatterometer QuikSCAT, passive microwave AMSR-E, and model reanalysis ERA-40 wind data.

Most of the global air-sea transfer velocity relationships are quadratic dependencies with 0 intercepts, which are applicable to any sparing, non-reactive gas. However, much of the evidence shows that the transfer velocity is not 0 when the wind speed is very low because factors such as buoyancy flux, microscale wave breaking, and chemical enhancement, conflict with the zero intercepts of the quadratic parameterizations (Wanninkhof et al., 2009).

In addition to the wind speed, wind and water directions also influence the transfer velocity.

4.4 *Influence of wind and water directions*

The distribution of wind and water directions is shown in Fig. 6. The main wind direction is 225°–235° and the main water directions is 25°–35° and 205°–215°.

We divided the data into up-or downwind based on whether the flow direction was similar or opposite to the wind direction. The downwind direction was 205°–235° and the upwind direction was 25°–55°. The up-and downwind data are shown in Fig. 7. The downwind transfer velocity was a little less than the upwind data, possibly because the mixing is enhanced when the upwind.

To improve the inversion precision, we also considered the roles played by bubbles and the significant wave height. Only the ASGAMAGE data were used in our calculation due to the absence of significant wave height data values in the GAS EX-98 data.

4.5 *Influence of bubble medium*

Figure 8 demonstrated the contributions of the wind speed and the bubble medium to the carbon dioxide transfer velocity. When bubbles are considered, the RMSE is reduced to 18.03 cm/h compared with the Wanninkhof (1992) formula which is 28.73. The precision is also improved compared with the fitting relationship of the wind speed and the transfer velocity. The in-

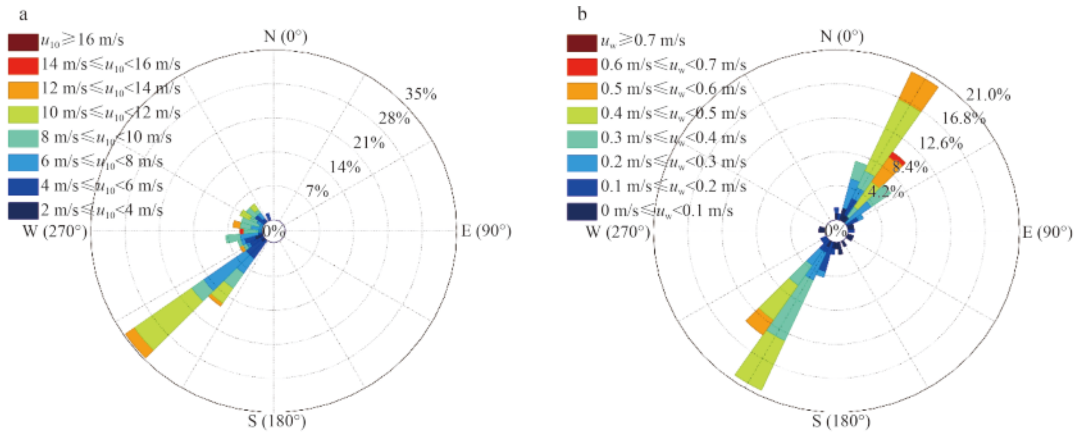

Fig. 6. Wind (a) and flow (b) roses figures.

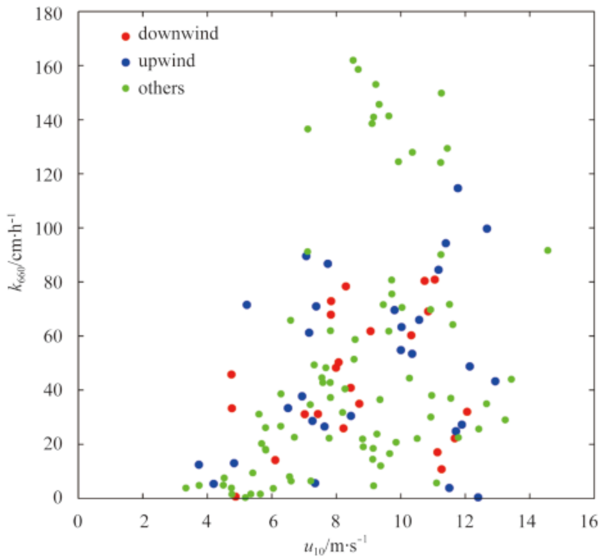

Fig. 7. Scatter diagrams of the upwind versus downwind.

fluence of the bubbles on the transfer velocity is proven; however, the contribution of the bubbles is affected by the friction velocity and the significant wave height, as detailed in Eq. (17). The bubble coefficient may be negative because of the combined effects of the wind speed and the bubbles.

Here, we only compared our linear regression with the results reported by Wanninkhof (1992). In fact, there have been numerous studies on the bubble medium and the transfer velocity, and the results support the work of our predecessors as follows.

Jeffery et al. (2010) believed that a simple transfer velocity and wind speed relationship is not suitable for low wind speeds and temperatures. In addition, the relationship is not applicable to other gases except carbon dioxide because of their considerable solubility differences. Wanninkhof et al. (2009) suggested that the kinetic energy of the wave and wave breaking enter the sea water along with the nonlinear increases of the wind. The influence of the wave breaking includes microscale wave breaking at low wind speeds, wave breaking and bubble entrainment at intermediate wind speeds, and foam injection at high wind speeds. Wave breaking is controlled by the wind speed, fetch, and the wave age, which have significantly different effects on gases of different solubilities. The following is the main status of the effects of wave breaking.

Woolf (1993, 1997) believed that the bubbles associated with wave breaking can greatly enhance the air-sea exchange of gases. Woolf (2005) provided a parameterization in which both wave breaking parts were associated with the whitecap and non-break-

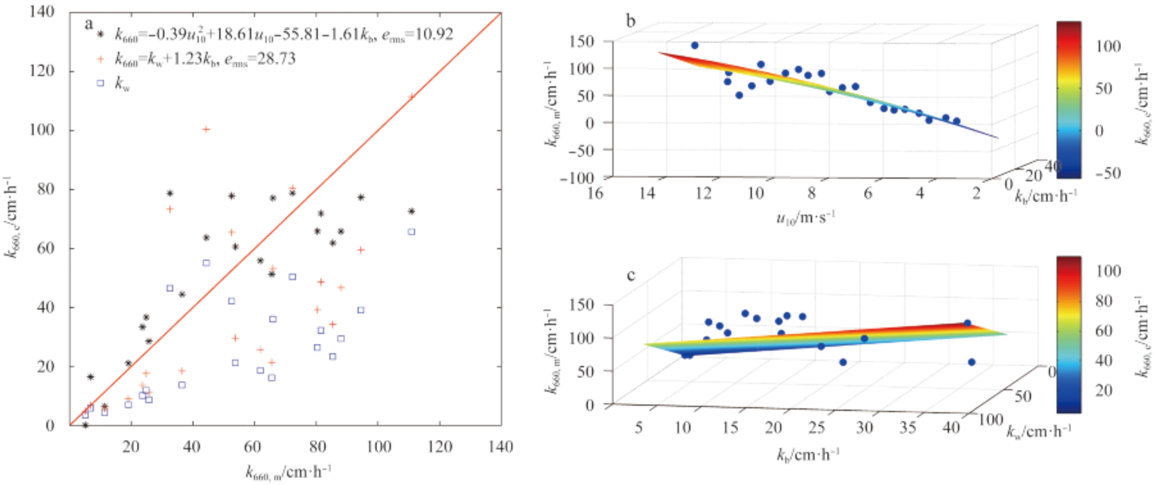

Fig. 8. Scatter diagrams of the contribution of the wind speed and the bubble medium.

ing wave parts. Yu et al. (2013) also considered both the wave breaking part and non-breaking wave part and described the distinct contributions by the whitecap coverage. Hare et al. (2004) obtained direct covariance measurements of air-sea carbon dioxide fluxes over the open ocean during the two recent Gas Ex field experiments. Concurrently, the National Oceanic and Atmospheric Administration/coupled-ocean atmospheric response experiment air-sea gas transfer parameterization, which contained the most variations, was developed to predict gas transfer velocities. The results of these studies show that the gas transfer with breaking wave processes at a moderate (approximately 15 m/s) wind speed accounts for a fourfold increase in the flux over the modeled interfacial processes. Wang (2006) believes that the gas transfer velocity is enhanced with an increase in the wind speed and is reduced with an increase in the wave age. As the waves grow, the increase in the gas transfer velocity with the increase in the wind speed weakens. Fairaill et al. (2000) added the surface renewal content (Soloviev and Schlüssel, 1994) to the CoARE bulk flux algorithm. Fangohr and Woolf (2007) calculated the transfer velocity as the sum of a linear function of the total mean square slope of the sea surface and a wave breaking parameter. Zappa et al. (2001) and Csanady (1990) believes that microscale wave breaking is very important to air-sea gas transfer at the wind speeds between 4.6 m/s and 10.7 m/s. McNeil and D'Asaro (2007) suggested that bubble injection dominated the transfer at extreme wind speeds. Zhao and Xie (2010) provided a function with both wind speed and significant wave height, and the parameterization was consistent with wind speed-transfer velocity parameterizations at a given wave age. Yu et al. (2013) suggested that the transfer velocity was a product of a wave steepness and the wind speed, and the model agrees well with the formulations based on the wind speed; the variation in the wind speed-dependent relationships presented in many previous studies can be explained by this proposed relationship with variations in the wave steepness effect.

Consideration of the influence of wave breaking improved the accuracy of the carbon dioxide transfer velocity. In further studies, the correlation between the wind speed and the wave breaking should be considered carefully to obtain a better inversion of the carbon dioxide transfer velocity.

4.6 *Influence of significant wave height*

Figure 9 shows how the significant wave height and wind speed contribute to the transfer velocity considering (Fig. 9a) and not considering (Fig. 9b) the influence of bubbles. The root mean square error is reduced when the significant wave height is considered. In addition, the root mean square error is lowest when the wind speed, the significant wave height, and the bubbles are considered at the same time, with a value of 16.96 cm/h. This finding proved that consideration of the wind speed, the significant wave height, and the bubbles is the main parameters that describe the carbon dioxide transfer.

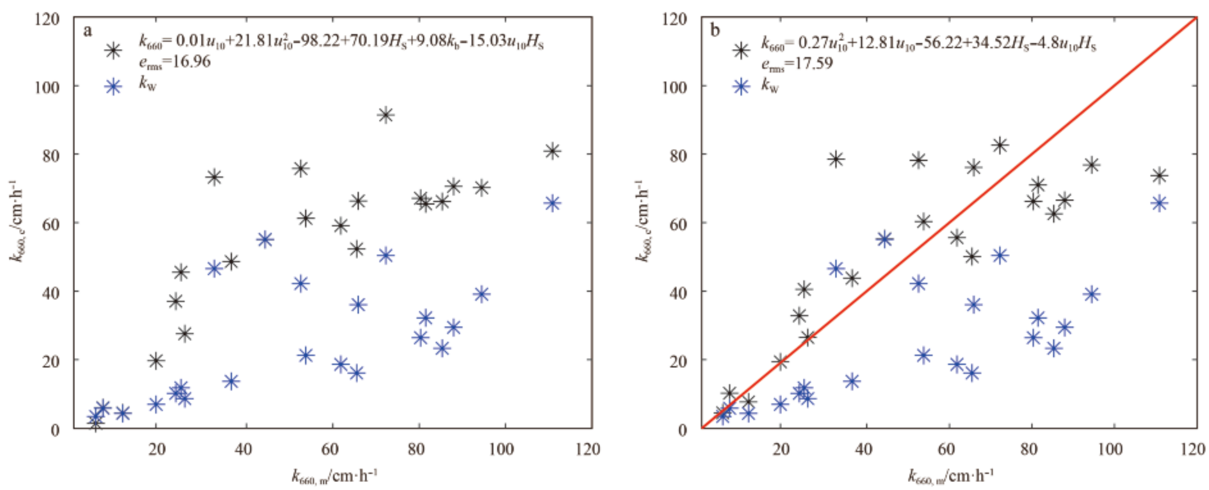

Fig. 9. Scatter diagrams of the contribution of the significant wave height to the transfer velocity.

To remove the interaction between the wind speed and the significant wave height, we added the term $u_{10}H_s$. In fact, the wind speed, the significant wave height, and the bubbles interacted with each other. A means by which to remove the interaction among them is one of the key issues to be considered in the future studies. The root mean square errors of the fitting formula are given in Eq. (16).

We divided the GAS EX-98 and ASGAMAGE data into sections by the wind speed (from 0 to the maximum in 0.5 m/s intervals) and the significant wave height (from 0 to the maximum in 0.5 m intervals). The data were then averaged for each section.

The relationship between the wind speed and the transfer velocity under different significant wave heights is shown in Fig. 10. When the significant wave height was less than 0.5 m and the wind was small, the transfer velocity was minimal, but it increased along with the significant wave height between 0.5 and 1.0, 1.5 and 2.0, 2.0 and 2.5 and 3.0 and 3.5 m. The transfer velocity at a significant wave height between 1.0 and 1.5 m was less than that at the significant wave height between 0.5 and 1.0, and small between 2.5 and 3.0 and 3.5 and 4.0 m. This was abnormal, and an explanation will require additional data and deeper research.

Significant research has been done on the waves and transfer velocity, and the findings support the work of our predecessors as follows.

Jähne et al. (1987) found that the total mean square slope of the capillary gravity wave and the carbon dioxide transfer velocity has a linear relationship. Bock et al. (1999) supported the result of Jähne et al. (1987) by means of laboratory research and found that the relationship between the transfer velocity and the

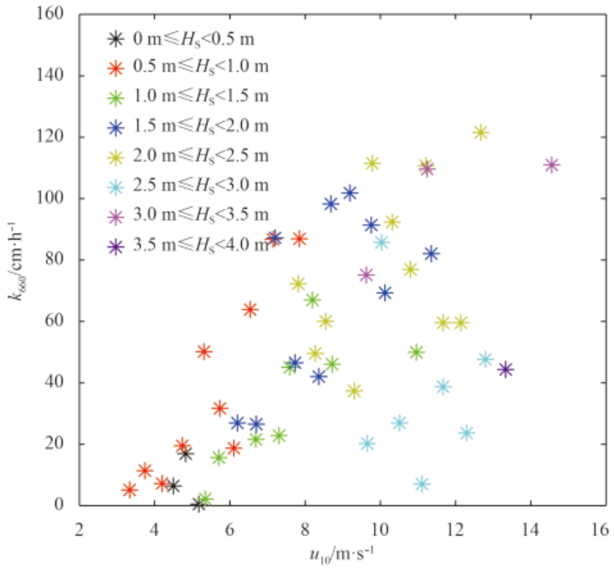

Fig. 10. Scatter diagrams of the wind speed versus the transfer velocity under different significant wave heights.

mean square slope of the short wave is better than that of the long wave. Frew et al. (2004) suggested that the air-sea gas transfer was dependent on a wind stress, a small-scale roughness, and surface films and obtained a result similar to that of Bock et al. (1999).

Frew et al. (2007) provided an approach to estimate the global air-sea gas transfer velocity fields using a dual-frequency altimeter backscatter based on the relationship of the transfer velocity with the mean square slope. Glover et al. (2007) estimated the long-term global air-sea gas transfer velocity from the Jason-1 and TOPEX altimeters using a similar method. Bogucki et al. (2010) estimated the logarithmic gas transfer velocity as a linear function of the logarithmic upwind normalized radar cross-section (NRCS) as measured directly by the scatterometer QuikSCAT, but did not consider the dependence of the wind speed and the transfer velocity, based on the linear relationship of the mean square slope and the carbon dioxide transfer velocity. The relationship between the wind speed and the carbon dioxide transfer velocity expresses the indirect effects of the roughness of the sea surface on the carbon dioxide transfer velocity, which is suitable for a wind wave field but is not adaptable to a swell field or mixed field.

The relationship between the sea's surface mean square slope and the air-sea CO_2 transfer velocity reflects the direct effects of the sea surface roughness on the CO_2 transfer velocity, suitable for both wind-wave and swell fields. The use of satellites can facilitate the study of large areas over long time series inversions, which can be difficult. The relationship between the NRCS and the CO_2 transfer velocity provides higher precision than using the relationship between the transfer velocity and the wind speed inverted from satellites.

5 Conclusions

Many factors influence the air-sea carbon dioxide transfer velocity, and the wind speed is the simplest and commonest of these factors. The relationship between the wind speed and the transfer velocity is useful, especially when only wind speed data are available. However, the waves, especially the significant wave height and the bubbles after the waves break, greatly affect the transfer and should be considered. The transfer velocity is not 0 at very low wind speeds, possibly because of buoyancy, microwave breaking, chemical enhancement, or other factors. The Webb velocity (mean vertical velocity) measured in cm/h, which is one of the most significant factors in the air-sea carbon dioxide transfer velocity, is difficult to obtain.

Our fitting results have greater precision than those of Wanninkhof (1992). For the GAS EX-98 data, the fitting results that take into account the terms of constant, the first-order and second-order have the minimum RMSE of 10.92 cm/h. For the ASGAMAGE data, the fitting results when the wind speed, the significant wave height, and the bubbles are considered at the same time have a minimum RMSE of 16.96 cm/h.

More factors influenced the transfer velocity, and their interactions should be considered with more data in the future studies.

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