Ocean Modelling 31 (2010) 28–35

Contents lists available at ScienceDirect

Ocean Modelling

journal homepage: www.elsevier.com/locate/ocemod

Tuning a physically-based model of the air–sea gas transfer velocity

C.D. Jeffery [a,*], I.S. Robinson [b], D.K. Woolf [c]

[a] NOAA National Oceanographic Data Center, Silver Spring, MD, USA
[b] National Oceanography Centre, Southampton, UK
[c] Environmental Research Institute, North Highland College, UHI Millennium Institute, Thurso, UK

ARTICLE INFO

Article history:
Received 31 March 2009
Received in revised form 10 July 2009
Accepted 16 September 2009
Available online 27 September 2009

Keywords:
Gas exchange
Air–water interface
Air–sea interaction
Upper ocean
Diurnal warming
1-D modelling
Transfer velocity
Carbon dioxide
GOTM

ABSTRACT

Air–sea gas transfer velocities are estimated for one year using a 1-D upper-ocean model (GOTM) and a modified version of the NOAA–COARE transfer velocity parameterization. Tuning parameters are evaluated with the aim of bringing the physically based NOAA–COARE parameterization in line with current estimates, based on simple wind-speed dependent models derived from bomb-radiocarbon inventories and deliberate tracer release experiments. We suggest that $A = 1.3$ and $B = 1.0$, for the sub-layer scaling parameter and the bubble mediated exchange, respectively, are consistent with the global average CO_2 transfer velocity k. Using these parameters and a simple 2nd order polynomial approximation, with respect to wind speed, we estimate a global annual average k for CO_2 of 16.4 ± 5.6 cm h^{-1} when using global mean winds of 6.89 m s^{-1} from the NCEP/NCAR Reanalysis 1 1954–2000. The tuned model can be used to predict the transfer velocity of any gas, with appropriate treatment of the dependence on molecular properties including the strong solubility dependence of bubble-mediated transfer. For example, an initial estimate of the global average transfer velocity of DMS (a relatively soluble gas) is only 11.9 cm h^{-1} whilst for less soluble methane the estimate is 18.0 cm h^{-1}.

1. Introduction

The air–sea exchange of CO_2 and other climatically important gases is commonly estimated as a product of the air–sea concentration difference and a transfer velocity (k), which is typically parameterized in terms of wind speed (Liss and Merlivat, 1986; Wanninkhof, 1992; Nightingale et al., 2000a). The thickness of the boundary layer, a function of near surface turbulence and diffusivity, controls the magnitude of the gas transfer velocity.

There are many factors which affect the state of the sea surface, and hence the boundary layer thickness, for example: wave age, fetch, wind speed, the prevalence of bubbles, boundary layer stability and surfactants (Woolf, 1997; Monahan and Spillane, 1984; Liss and Merlivat, 1986; Asher and Wanninkhof, 1998). Therefore it is unlikely that a single such physical variable can completely determine the spatial scales and environmental conditions necessary to predict k. Regardless, many empirical relationships for k in practical use are solely functions of wind speed as it tends to be the dominant mechanism and is comparatively easy to measure. It is widely agreed that a more complete and physically sound model of gas transfer is preferable, however such a model needs to fit observations.

Recently, the discrepancy between estimates of k based on small-scale deliberate tracer measurements and global bomb ^{14}C inventories has been narrowed (Naegler et al., 2006; Sweeney et al., 2007). However, these simple wind-speed dependent models fail to consider the effects of low wind, temperature-related processes and are not suited to describing gases other than CO_2 due to large differences in gas solubility (Blomquist et al., 2006) and bubble-mediated transfer (Woolf, 1997).

The NOAA–COARE (National Oceanic and Atmospheric Administration–Coupled-Ocean Atmospheric Response Experiment) gas transfer parameterization incorporates more physical processes than the simple models and is well suited for high resolution estimates of air–sea CO_2 exchange (Fairall et al., 2000). It can be applied to all gases, irrespective of solubility and Schmidt number. It has since been modified to include enhanced gas transfer due to bubbles via the Woolf (1997) model and a further mechanism of low-wind speed, buoyancy-driven transfer (Jeffery et al., 2007). The parameterization requires a number of empirical coefficients to be specified, which are typically fitted to existing gas transfer field measurements.

The goal of this investigation is to select suitable values for these coefficients, which bring k in-line with models derived from small-scale field measurements and global ocean bomb ^{14}C based estimates, yet retain the variability resulting from changes in temperature/solubility and low wind speed transfer. This is accomplished by using a 1-D upper-ocean model forced by in situ

---

* Corresponding author. Address: NOAA National Oceanographic Data Center, 1315 East-West Highway, Silver Spring, MD 20910, USA. Tel.: +1 301 713 3272x102.
E-mail address: christopher.d.jeffery@noaa.gov (C.D. Jeffery).

1463-5003/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.ocemod.2009.09.001

meteorological observations to generate synthetic data, including hourly near surface temperature profiles. We aim to demonstrate that the suitably tuned model is both consistent with observational constraints and is applicable to a wide range of gases. This is necessary to establish the model as the preferred method of calculating air–sea gas fluxes.

2. Modified NOAA–COARE gas transfer model

Interest in developing a model for gas transfer that can be applied to all gases had led to the application of micrometeorological models based on surface renewal and turbulent-molecular diffusion theory near the air–sea interface. The NOAA–COARE gas transfer parameterization is based on the well-known COARE Bulk Flux Algorithm (Fairall et al., 1996) with the addition of surface renewal concepts from Soloviev and Schlüssel (1994). The original COARE model contains an algorithm for the oceanic cool skin, which has been generalized for gas transfer applications.

The gas transfer parameterization makes use of turbulence scaling theory applied to both fluids, and matches the fluid models at the interface where the suppression of the smallest turbulent eddies is accomplished via viscous dissipation. Other effects, such as bubble mediation and wave breaking were also included in subsequent revisions of the parameterization. The fine details of the parameterization are well documented in Fairall et al. (2000) and Hare et al. (2004) evaluate the model based on field data from the GasEX-1998 and GasEX-2001 experiments.

The modified form of the parameterization used in this study is presented in Jeffery et al. (2007), it considers boundary layers on both sides of the sea surface. The gas transfer velocity (k) is expressed in terms of molecular and turbulent components such that:

$$\frac{1}{k} = \frac{1}{k_w} + \frac{1}{k_a}. \tag{1}$$

It can be applied to any gas providing the solubility and the Schmidt number (the ratio of kinematic viscosity and mass diffusivity) are known. The water-side (subscript w) transfer velocity is defined as

$$k_w = k_b + \frac{u_{*w}}{r_w}, \tag{2}$$

where u_* is the friction velocity and r is the dimensionless resistance to the transfer, defined as

$$r_w = \left[\frac{13.3}{A\phi} S_{cw}^{1/2} + ln(z_w/\delta_w)/\kappa\right], \tag{3}$$

where S_c is the Schmidt number for the gas in the fluid, z is the depth of the measurement, δ is the estimated turbulent surface layer thickness, κ is the Von Karman constant. A is the first tunable parameter we consider, and the empirical function ϕ accounts for buoyancy-driven transfer in the molecular sub-layer. This is simply $\phi = 6/\lambda$, where λ is the Saunders constant (Saunders, 1967). The model also accounts for bubble-mediated gas transfer via the Woolf (1997) parameterization:

$$k_b = BV_0 f \alpha^{-1}[1 + (e\alpha S_{cw}^{-1/2})^{-1/n}]^{-n}, \tag{4}$$

where $V_0 = 6.8 \times 10^{-3}$ m s^{-1}, $e = 14$, $n = 1.2$ for CO_2, α is the gas solubility, B is the second tunable parameter and f is the whitecap fraction; a strong function of wind speed at 10 m. However, Woolf (2005) suggests that f may be sea-state dependent rather than solely a function of wind speed.

Similarly, the air-side (subscript a) transfer velocity is defined as

$$k_a = \frac{u_{*a}\alpha}{r_a}, \tag{5}$$

and the dimensionless air-side resistance term is

$$r_a = \left[13.3 S_{ca}^{1/2} + C_{da}^{-1/2} - 5 + ln(S_{ca})/(2\kappa)\right], \tag{6}$$

where C_d is the drag coefficient. Note that it is the water-side that primarily controls the magnitude of the k for all gases considered in this paper (CO_2, CH_4 and DMS) since for their relatively low solubilities $r_w \gg r_a$.

Literature values for A and B are based on in situ and laboratory experiments (see Table 1). There is a third tunable parameter β, which scales the atmospheric and water-side buoyancy effects. This is accomplished by using an average wind speed, that is modified to include a 'gustiness' parameter, to calculate the friction velocity u_{*x} (where subscript x denotes either the atmospheric or water-side of the equation). Thus, the 'average wind speed' can incorporate buoyancy effects in addition to regular wind-driven forcing (Stull, 1994; Godfrey and Beljaars, 1991; Jeffery et al., 2007):

$$u_{*x} = \sqrt{C_{dx} S_x^2}, \tag{7}$$

where C_{dx} is the drag coefficient and S_x is the average wind speed. This is defined in Jeffery et al. (2007) as

$$S_x^2 = u_x^2 + (\beta(-F_{Bx} Z_x)^{1/3})^2, \tag{8}$$

where u_x is either the wind speed or water-side equivalent, F_{Bx} is the atmospheric or water-side buoyancy term, and Z_x is either the atmospheric inversion height or convective mixed layer depth. Published values for β include 1.25 (Fairall et al., 1996), 1.0 (Miller et al., 1991) and 0.7 (Schumann, 1988). However, we choose not to vary the value of β, instead we select the central value of $\beta = 1.0$.

The tunable constants must be carefully selected otherwise additional uncertainty is introduced into the calculation of k and subsequently CO_2 flux (Hare et al., 2004; Jeffery et al., 2007). In this study, we aim to select values for A and B which bring the physically-based parameterization in line with the current 'best' estimate from a simple, empirical, wind-speed dependent model. The suggested values should enable the use of the NOAA–COARE model in global calculations of k and air–sea CO_2 flux, without the need for additional fitting of the tuning parameters.

Table 1

Characteristics of 2nd order polynomial fits[a] to NOAA–COARE k with respect to wind speed for different tuning parameters (A, B). A GOTM run at a typical site in the tropical Atlantic (10°S10°W) was used to generate the CO_2 transfer velocities for 2002.

Coefficients	Study	Experiment	2nd order fit	R^2	RMSE (cm h^{-1})
$A = 1.3$, $B = 0.82$	McGillis et al. (2004)	GasEx 2001	$k = 0.27u^2 - 0.55u + 6.91$	0.98	0.75
$A = 0.625$, $B = 2.0$	Hare et al. (2004)	GasEx 1998	$k = 0.52u^2 - 3.48u + 10.72$	0.99	0.62
$A = 1.85$, $B = 1.0$	Soloviev and Schlüssel (1994)	Lab	$k = 0.35u^2 - 0.42u + 9.38$	0.98	1.12
$A = 1.3$, $B = 1.0$	Blomquist et al. (2006)	Modified GasEx 2001	$k = 0.31u^2 - 0.91u + 7.76$	0.98	0.78

[a] 3rd order and 4th order polynomial fits were also investigated, but are not shown.

3. Estimated global CO_2 transfer velocity

A one-dimensional, k–ϵ turbulence closure model (GOTM – General Ocean Turbulence Model) (Burchard and Baumert, 1995; Burchard and Bolding, 2001) was used to generate a year of gas transfer velocities (15/01/02–25/12/02) for a typical location in the Tropical Atlantic (10°S10°W). It has been previously used to study buoyancy-driven CO_2 transfer and the effect of the diurnal cycle in calculations of predominantly low wind-speed CO_2 transfer (Jeffery et al., 2007; Jeffery et al., 2008). The model grid is spread over 200 levels with a range of level thicknesses (millimetre to metre) from the surface to 200 m. The uppermost level is located at 1.7×10^{-3} m. This is the same site and model setup used in the previous studies, primarily chosen for its small contribution from advective processes (Foltz et al., 2003), which are neglected by the 1-D model.

PIRATA (Prediction and Research Moored Array in the Tropical Atlantic) surface meteorology, NCEP (National Centers for Environmental Prediction) pressure and Meteosat-7 cloud cover are combined to produce the GOTM forcing, consisting of: solar insolation, wind speed, air temperature, pressure, cloud cover, relative humidity and rain rate. The model was initialized with temperature and salinity profiles from the PIRATA mooring located at 10°S10°W, and was allowed to free-run for the duration of the experiment. The model time-step was 1 h, and the gas transfer velocity k was calculated by the 1-D model at every time-step using the modified NOAA–COARE parameterization.

The gas transfer velocity parameterization requires a number of inputs, not all of which are available from the PIRATA mooring. Use of 1-D ocean model allows better representation of the diurnal cycle of SST and the near surface temperature structure. Since the mooring's uppermost sensor is at 1 m depth, GOTM is used to generate the inputs for the gas transfer parameterization using the meteorological observations as forcing. The uppermost SST in GOTM is at 1.7×10^{-3} m and the cool-skin layer is explicitly included via the (Fairall et al., 1996) parameterization. The hourly transfer velocities incorporate the range of wind speed and model-based SST present at the PIRATA mooring site during the course of 2002. In this way, we account for both diurnal variability and the low wind, buoyancy-related effects on k (Jeffery et al., 2007, 2008), which are overlooked by simple wind speed-only dependent models.

Fig. 1 shows the hourly PIRATA wind speed and SST, as well as the model SST and gas transfer velocity during 2002. The hourly CO_2 flux is estimated by using climatological air–sea pCO_2 differences from Takahashi et al. (2002), although that flux is not the focus of this study. Additionally, the presence of surfactants (Frew et al., 1990; McKenna and McGillis, 2004) and chemical enhancement of CO_2 (Wanninkhof and Knox, 1996) have the potential to significantly affect air–sea gas exchange; however, neither is included in this study.

Fig. 2 shows surface plots of the CO_2 transfer velocity in cm h^{-1} against tuning parameters A and B, ranging from 0 to 2 in increments of 0.1. Fig. 2A–C shows that increasing wind speed, with constant temperature, results in an increase in k. At low winds the sub-layer parameter A has a larger effect on k than the bubble mediated parameter B, which becomes dominant at higher winds. Similarly, Fig. 2D–F shows that the effect of increasing sea surface temperature, with constant wind speed, is also to increase k. The filled red circles show the transfer velocities resulting from the use of previously published A and B coefficients, which have been tuned to specific in situ or laboratory gas transfer measurements (see Table 1).

Fig. 3 shows k versus u_{10}, predicted by four versions of the NOAA–COARE model with different A and B parameters taken from the literature (see Table 1). In addition the wind-speed dependent model of Sweeney et al. (2007) is shown for comparison. ϕ, the sub-layer buoyancy term in (3) maintained significant values day and night.

The discrete points from the individual instances of the NOAA–COARE model in Fig. 3 reflect the variability in k resulting from hourly wind and temperature changes. The variation between the four instances of the parameterizations themselves is a direct result of differing tuning parameters. Overlaid on the discrete points in Fig. 3 are 2nd order polynomial fits, with respect to wind speed, for each of the NOAA–COARE predicted transfer velocities. The coefficients, R^2 and RMSE can be seen in Table 1. In addition, 3rd and 4th order polynomials fits were also investigated, but are not shown.

The four literature coefficients were selected as a starting point with the intention of testing other values within the A/B parameter space (see Fig. 2). However, it was found that one set of coefficients provided a good representation of the k versus u_{10} curve, when compared with other popular parameterizations and in situ measurements (see Fig. 4). Thus it was decided to use only these four, previously published, coefficients that are commonly implemented by the gas exchange community. Given the accuracy of all validation data (10% at best) it seems unrealistic to refine the coefficients further and thus we simply adopt one set of coefficients that performs adequately.

Using an updated oceanic inventory of bomb-produced ^{14}C, the Sweeney et al. (2007) model agrees with short-term field experiments, such as Nightingale et al. (2000a). The Sweeney et al. (2007) model, which is based on Wanninkhof (1992), is currently a favored method for calculating the global gas transfer velocity. However, it relies on a single point for validation; the global mean CO_2 transfer velocity, determined from the bomb ^{14}C budget. Whilst such agreement is important, simple models tend toward zero at low winds. As a result potentially important means of exchange, which can affect the shape of the k versus u_{10} dependence, are overlooked e.g. diurnal variability and buoyancy-driven transfer.

For simplicity, we assume that the 2nd order polynomial fits are universally characteristic of global average k predicted by the modified NOAA–COARE parameterization. This is convenient rather than precise, especially at very low and very high winds. The large non-zero intercept shown here is likely confined to Tropical regions where diurnal warming is prevalent. This assumption allows us to compare the average NOAA–COARE k using a global average wind speed, such as the comparison made in Sweeney et al. (2007). It is important to note, that such a comparison ignores the variability of the wind field throughout the period in which the flux is derived. The R^2 for each of the polynomial fits in Fig. 3 is at least 0.98 and the greatest RMSE is 1.12 cm h^{-1} (see Table 1).

The sensitivity of k resulting from differences in wind speed and temperature is well summarized in Kettle et al. (2009); Fig. 3. Here, the authors show the modified NOAA–COARE k for 0–20 m s^{-1} and for SST = 5, 10, 15, 20, 25 and 30 °C. Increasing SST results in larger k values and in an increase in the curvature, whereas reducing SST results in the opposite effect. We would expect similar variability even at locations significantly different from the tropical Atlantic e.g. polar regions, although without the large non-zero intercept. However, this should not be a huge effect relative to the variations in the coefficients given the scatter of the individual model points in Fig. 3.

Given that we are only trying to show that the modified NOAA–COARE model can perform as well as a simple model e.g. Sweeney et al. (2007), the GOTM derived results from the Tropical Atlantic contain an adequate range of wind speeds and temperatures, between 0 and 14 m s^{-1} and 23–29 °C, respectively (see Fig. 1). However, a more detailed study would use multiple model locations

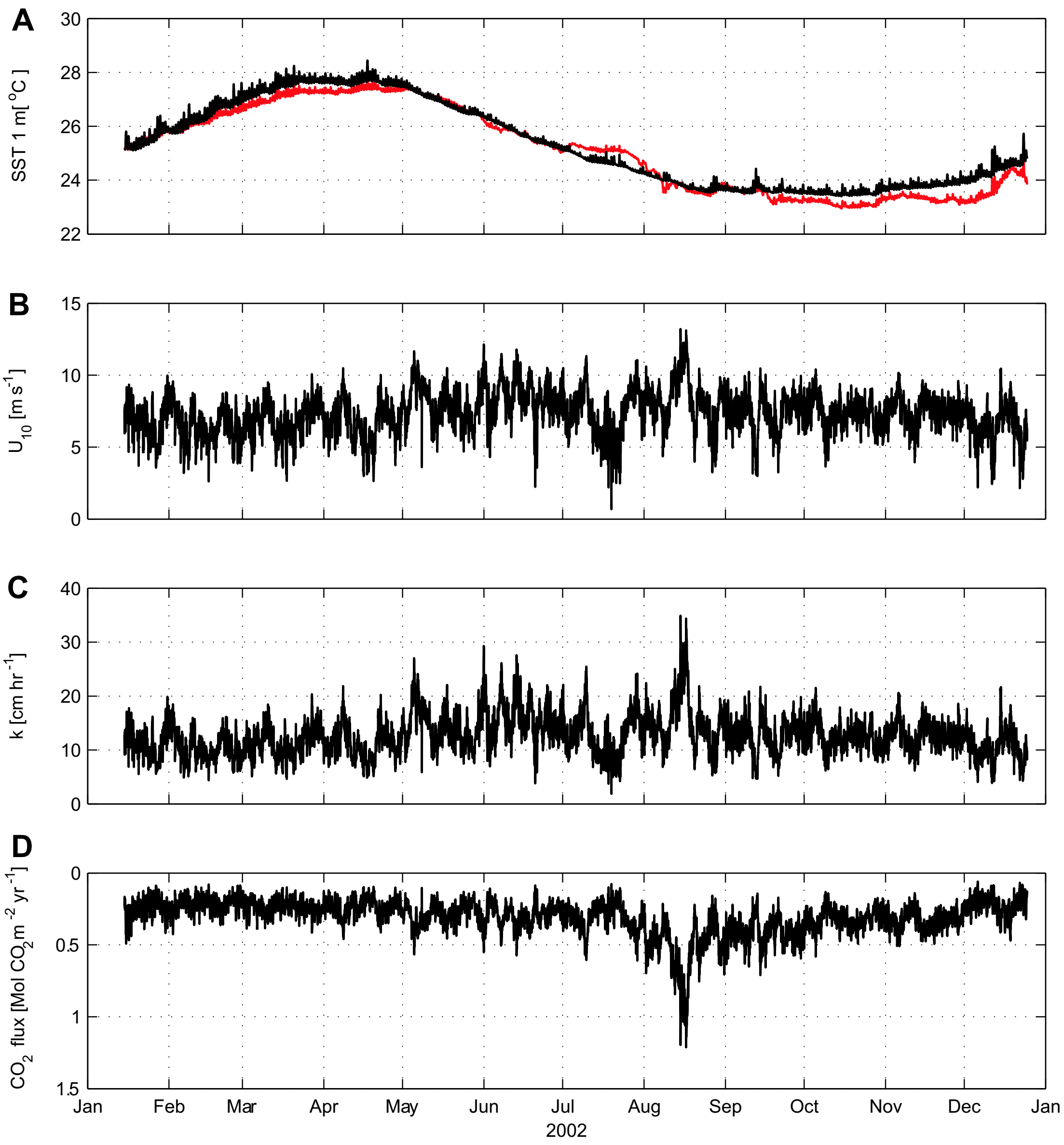

Fig. 1. Hourly: (A) GOTM 1 m SST (°C) (black), PIRATA mooring 1 m SST (°C) (red), (B) wind speed (m s^{-1}), (C) example NOAA–COARE gas transfer velocity ($A = 1.3$, $B = 1.0$) (cm h^{-1}), (D) CO$_2$ flux (mol CO$_2$ m^{-2} y^{-1}) at 10°S10°W for 2002. (For interpretation of color mentioned in this figure the reader is referred to the web version of the article.)

and multiple years to capture a larger amount of variability in the underlying meteorological observations.

Using the 2nd order polynomial and coefficients, $A = 1.3$ and $B = 1.0$, from Blomquist et al. (2006) results in a curve that is very similar to that described in Sweeney et al. (2007). The main difference is that the new model predicts significant k at low wind speeds, leading to enhanced gas exchange between 0 and 6 m s^{-1}. This set of A and B coefficients is based on minimal adjustment to the parameters from the GasEx 2001 field experiment, and it is these that we will use to calculate the global average k.

Using the 3rd and 4th order polynomial fits results in the coefficients $A = 0.625$ and $B = 2.0$ producing the closest match to the Sweeney et al. (2007) curve, at wind speeds less than 10 m s^{-1}. For wind speeds greater than 10 m s^{-1}; $A = 1.3$ and $B = 0.82$ for the 3rd order fit; and $A = 1.3$ and $B = 1$ for the 4th order fit are the most similar. In both cases, for wind speeds in excess of 16 m s^{-1} these higher order polynomial fits diverge significantly from the Sweeney et al. (2007) result.

The global $\overline{k_{\mathrm{CO_2}}}$ estimated from the 2nd order fit to NOAA–COARE ($A = 1.3$ and $B = 1.0$) is 16.4 ± 5.6 cm h^{-1} (see Fig. 4). This was simply estimated by applying the polynomial fit to the global mean wind speed from the NCEP/NCAR Reanalysis 1 1954–2000 as used by Sweeney et al. (2007). Fig. 4 also shows a number of popular gas transfer models versus wind speed, in situ gas exchange data based on tracer release experiments (Nightingale et al., 2000a,b), and previous calculations of global $\overline{k_{\mathrm{CO_2}}}$.

Sweeney et al. (2007) also state that there will be some variability in the global average k due to differences in regional variability of the wind speed between wind reanalysis products. The original formulation for k used in Wanninkhof (1992) assumed that a Rayleigh distribution of wind speeds best described how short-term winds were distributed about the mean. Although practical this can introduce regionally and globally significant errors in k which require correction factors to account for non-Rayleigh distribution of winds (Wanninkhof et al., 2002). Whilst not explored in this study, a more thorough approach that could be applied is described in Fangohr et al. (2008).

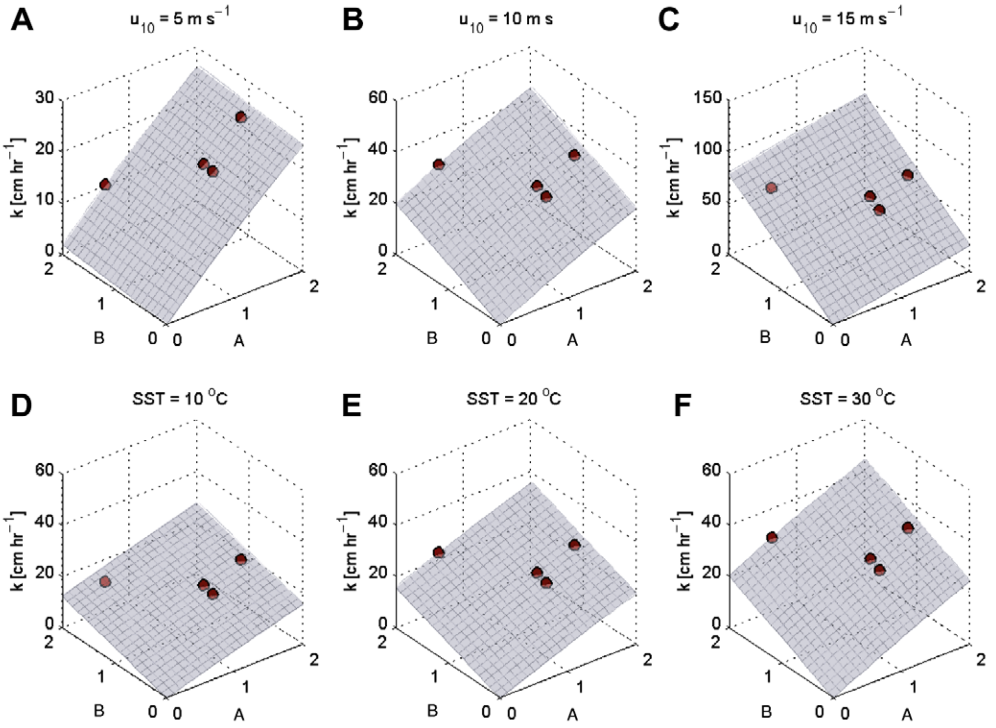

Fig. 2. Surface plots of the CO_2 transfer velocity, *k* (cm h^{-1}) against a range of NOAA–COARE *A* and *B* tuning parameters: For u_{10} = 5, 10, 15 m s^{-1}, with a constant SST = 30 °C (A–C), and for SST = 10, 20, 30 °C, with a constant u_{10} = 10 m s^{-1} (D–F). The red filled circles are the CO_2 transfer velocities resulting from the literature values of the *A* and *B* coefficients in Table 1. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this paper.)

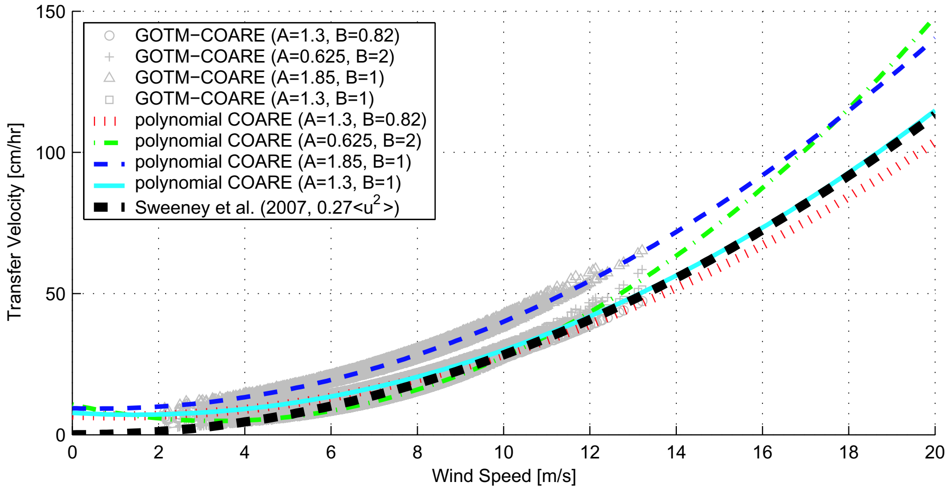

Fig. 3. $\overline{k_{CO_2}}$ (cm h^{-1}) as a function of wind speed (m s^{-1}). Four different NOAA–COARE experiments based on the previously published coefficients are shown, overlaid with 2nd order polynomial fits. The Sweeney et al. (2007) model is also shown for comparison (thick black dashed line) (S_c = 660).

If the original Blomquist et al. (2006) values of $A = 1.3$ and $B = 0.82$ are used then the global $\overline{k_{CO_2}}$ is reduced to 15.9 cm h^{-1}. This is slightly closer to the Sweeney et al. (2007) result, however, the overall agreement with the shape of wind speed dependence deteriorates especially at higher wind speeds. Note that whilst Sweeney et al. (2007) simply assume a 'square law' the general shape is supported by tracer experiments e.g. Nightingale et al. (2000a,b). Use of the other sets of COARE coefficients results in values for the global $\overline{k_{CO_2}}$ which are either significantly higher (using $A = 1.85$, $B = 1.0$) or significantly lower (using $A = 0.625$, $B = 2.0$).

Whilst there remains considerable spread between the older models e.g. Liss and Merlivat (1986), Wanninkhof (1992), Wanninkhof and McGillis (1999), and in situ measurements, the gap between recent global inventory studies and small scale tracer experiments has been narrowed by Naegler et al. (2006) and Sweeney et al. (2007). Previous estimates of the global annual *k*, based on bomb ^{14}C and implied wind-speed dependent models are shown in Table 2. It is important to remember that the wind field used by Wanninkhof (1992) and Naegler et al. (2006) is considerably different to that used here. Regardless, $\overline{k_{CO_2}}$ calculated using the 2nd order polynomial fit to the modified NOAA–COARE model

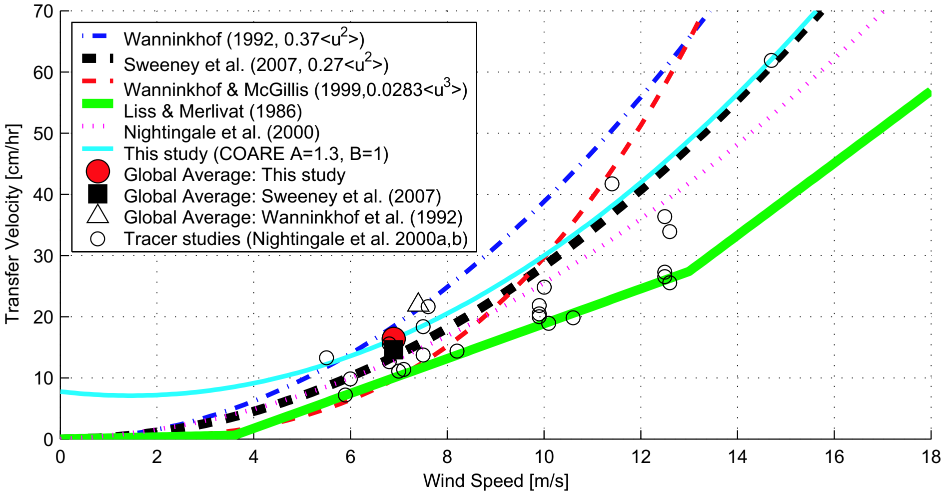

Fig. 4. A comparison of popular k parameterizations ($S_c = 660$) versus wind speed. Small open circles represent in situ deliberate tracer measurements. Global average k is shown for; this study (filled red circle); Sweeney et al. (2007) (filled black square); and Wanninkhof (1992) (open triangle). Note the original Wanninkhof (1992) coefficient (0.31) is adjusted for NCEP/NCAR reanalysis 1 average wind speed. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this paper.)

Table 2
Global annual mean wind speeds over the ice-free ocean $(\overline{u})$ and $(\overline{u^2})$, and the global annual mean CO_2 transfer velocity $(\overline{k_{CO_2}})$ for a number of recent studies.

Study	$\overline{u_{10}}$ (m s^{-1})	$\overline{u_{10}^2}$ (m s^{-1})	$\overline{k_{CO_2}}$ (cm h^{-1})
Wanninkhof (1992)	7.4[a]	54.8	21.9 ± 3.3
Naegler et al. (2006)	7.3[b]	53.3	16.7 ± 2.9
Sweeney et al. (2007)	6.89[c]	47.5	14.6 ± 4.7
This study ($A = 1.3$, $B = 1.0$)	6.89[c]	47.5	16.4 ± 5.6

[a] Average global wind speed with a Rayleigh distribution.
[b] Average of five climatologies: NCEP, ECMWF, SSMI, QSCAT, ERS12.
[c] NCEP/NCAR Reanalysis 1 1954–2000.

Table 3
Molecular mass, gas coefficient, activation energy used in Eq. (9), and global average gas transfer velocity for DMS, CH_4 and CO_2.

Compound	Molecular mass	a (cm^2 s^{-1})	E_a (kJ mol^{-1})	Reference	$\overline{k}$ (cm h^{-1})
CH_4	16.04	0.031	18.3	Saltzman et al. (1993)	18.0
CO_2	44.01	0.050	19.5	Jähne et al. (1987)	16.4
DMS	62.13	0.020	18.1	Saltzman et al. (1993)	11.9

is in-line with recent bomb ^{14}C derived models when using $A = 1.3$ and $B = 1.0$.

4. DMS and CH_4 transfer velocity

Having settled on tuning parameters $A = 1.3$ and $B = 1.0$, we use them to calculate transfer velocities for two additional gases; DMS and CH_4. To do this we need to know the Schmidt number ($S_c = v/D$), which is dependent on the kinematic viscosity (v) and the molecular diffusivity (D) of the gas. The approximate viscosity (v) of seawater = $1.83 \times 10^{-6}\exp(-T/36)$ where T is temperature in °C. The diffusivity of a gas can be determined from the following formula, described by King et al. (1995):

$$D = ae^{-E_a/RT}, \tag{9}$$

where D is the diffusivity (m^2 s^{-1}), a is a gas dependent coefficient (cm^2 s^{-1}), E_a is the activation energy for diffusion in water (kJ mol^{-1}), R is the gas constant (8.31×10^{-3} kJ mol^{-1} K^{-1}) and T is the temperature in Kelvin. The constants for Eq. (9) can be found in Table 3. In addition to the Schmidt number, the Ostwald solubility (α) (1/Henry's law constant) is also required. For this preliminary demonstration, we fix these as 14, 0.9 and 0.033 for DMS, CO_2 and CH_4, respectively (for Henry's law constants; see Wiesenburg and Guinasso (1979) and Dacey et al. (1984)). It is assumed that the curvature caused by solubility remains constant from the equator to very cold water, this is justified by the fact that the change in solubility is small compared to the difference between gases, however this should be checked in a more thorough study.

Blomquist et al. (2006) showed that adjustments to S_c for simple wind-speed dependent models such as Wanninkhof (1992) and Nightingale et al. (2000b) merely result in moving the k versus u_{10} curve up or down, but does not change the curvature. Those models are unlikely to accurately describe the wind speed dependence for gases such as DMS and CH_4. Conversely, the NOAA–COARE model's dependence on gas solubility, inclusion of low wind transfer and bubble mediated exchange correctly reproduces the differences between observed values of k_{CO_2} and k_{DMS}.

Fig. 5 shows k_{DMS}, k_{CO_2} and k_{CH_4} against wind speed using the NOAA–COARE parameterization, 2nd order polynomial fits for each of the gases are also shown. The difference in curvature between the trace gases is due to solubility. DMS has the largest solubility, hence the dependence on wind speed is weaker, resulting in the flattest curve. CH_4 on the other hand has a very low solubility, resulting in a strong dependence on u_{10} at higher winds, due to strong bubble-mediated transfer.

The global $\overline{k}$ for DMS, CO_2 and CH_4 are 11.9, 16.4 and 18.0 cm h^{-1}, respectively (see Table 3). As in the previous section $\overline{k}$ was estimated by applying the global mean wind speed, $u_{10} = 6.89$ m s^{-1} from the NCEP/NCAR Reanalysis 1, to the polynomial fit for each gas e.g. $k = [a + bu_{10} + cu_{10}^2](660/S_c)^{1/2}$ where a, b and c are the polynomial coefficients and k is normalised with respect to CO_2 dissolved in seawater at 20 °C ($S_c = 660$). Following Blomquist et al. (2006), it is clear that the NOAA–COARE model will enable better agreement with observations (for gases other than CO_2) than parameterizations based solely on Schmidt number and a power of u_{10} alone.

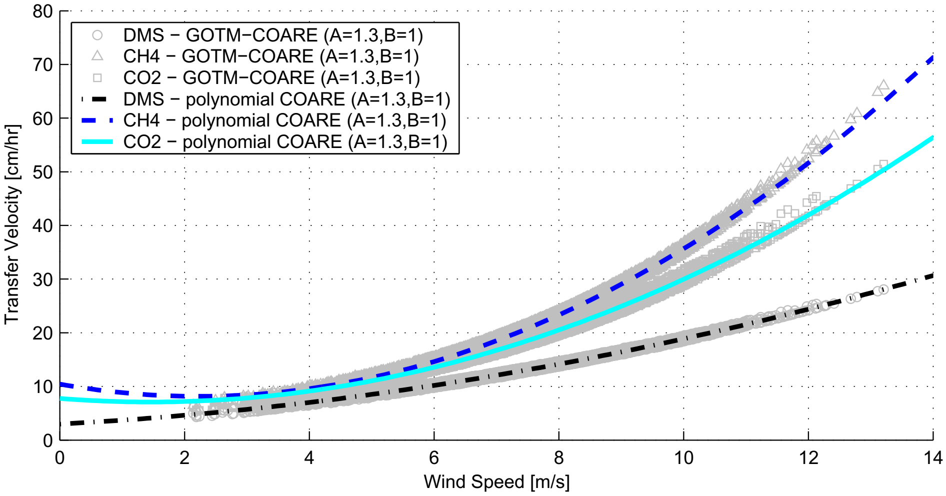

Fig. 5. k_{DMS} (circles), k_{CO_2} (squares) and k_{CH_4} (triangles) versus wind speed using the NOAA–COARE parameterization ($A = 1.3$, $B = 1.0$). Individual points are from the 1-D model and the curves represent 2nd order polynomial fits: DMS (black dot-dashed line), CO_2 (solid cyan line), CH_4 (blue dashed line). (For interpretation of color mentioned in this figure the reader is referred to the web version of the article.)

5. Conclusions

A 1-D k–ϵ turbulence closure model (GOTM), forced using meteorological observations from a PIRATA buoy in the tropical Atlantic and cloud cover from Meteosat-7, was run for 2002. A year of hourly values of gas transfer velocities were estimated using the modified NOAA–COARE gas transfer velocity parameterization (Jeffery et al., 2007). Use of the 1-D ocean model allowed better representation of the diurnal cycle of SST and near surface temperature structure, which can be important for gas transfer at low winds. Assuming the results are universally typical, a simple 2nd order polynomial equation with respect to wind speed was fitted to the data. The fitted curve is in agreement with a recent gas transfer velocity model based on global ocean inventory of radiocarbon (Sweeney et al., 2007) and also that of a model based on small-scale dual-tracer studies (Nightingale et al., 2000b).

Accurate determination of k is required for good estimates of air–sea gas exchange. Gas flux estimates have important implications for climate modelling and biogeochemical budgets. Since the NOAA–COARE model incorporates more physical processes then any other model and can be applied to all gases, regardless of solubility and Schmidt number, its greater use would improve estimates of air–sea gas transfer. Synthetic GOTM data can be used as input parameters for the gas transfer parameterization where in situ meteorological observations are limited. This allows buoyancy-driven and bubble-mediated gas transfer to be included.

The global CO_2 transfer velocity was estimated using wind speed from NCEP/NCAR reanalysis 1 1954–2000. Our estimate of the global annual average k is 16.4 ± 5.6 cm h^{-1} which is consistent with other estimates. The simple polynomial fit to a single typical location in the tropical Atlantic is sufficient to highlight that the modified NOAA–COARE model performs similarly to the current ‘state-of-the-art’ wind-speed dependent model. Hence, it can be used for global calculations of CO_2 transfer velocities with suitable tuning parameters. In addition, gas transfer velocities are also shown for DMS and CH_4, demonstrating the ability of the model to incorporate the dependence on gas solubility not present in simple models based on wind speed only.

Obviously, a more robust method would be to run the 1-D model globally and compile a large dataset of predicted transfer velocities, incorporating a greater range of wind and temperature regimes. This should be the focus of future studies along with using climatologies of the surface concentration of gases (e.g. CO_2 and DMS) to calculate the gas fluxes. We suggest that the tuning parameters $A = 1.3$ and $B = 1.0$ will not only provide an adequate estimate for k_{CO_2} and allow the inclusion of both low wind speed temperature related effects, but also the ability to calculate k for trace gases (e.g. DMS and CH_4) with varying solubilities.

Acknowledgments

This work was supported by NERC through a CASE studentship (NER/S/A/2004/12992) in partnership with the UK Met Office, the Centre for observation of Air–Sea Interaction and fluXes (CASIX) and the National Centre for Earth Observation (NCEO).

References

Asher, W.E., Wanninkhof, R., 1998. The effect of bubble-mediated gas transfer on purposeful dual-gaseous tracer experiments. Journal of Geophysical Research 103 (C5), 10555–10560.

Blomquist, B.W., Fairall, C.W., Huebert, B.J., Kieber, D.J., Westby, G.R., 2006. DMS sea–air transfer velocity: Direct measurements by eddy covariance and parameterization based on the NOAA/COARE gas transfer model. Geophysical Research Letters 33 (L07601). doi:10.1029/2006GL025735.

Burchard, H., Baumert, H., 1995. On the performance of a mixed layer model based on the k-turbulence closure. Journal of Geophysical Research 100, 8523–8540.

Burchard, H., Bolding, K., 2001. Comparative analysis of four second-moment turbulence closure models for the oceanic mixed layer. Journal of Physical Oceanography 31, 1943–1968.

Dacey, J.W.H., Wakeham, S.G., Howes, B.L., 1984. Henry's law constants for dimethylsulfide in freshwater and seawater. Geophysical Research Letters 11 (10), 991–994.

Fairall, C.W., Bradley, E., Rogers, D., Edson, J.B., Young, G., 1996. Bulk parameterization of air–sea fluxes for tropical ocean-global atmosphere coupled-ocean atmosphere response experiment. Journal of Geophysical Research 101 (C2), 3747–3764.

Fairall, C.W., Hare, J.E., Edson, J.B., McGillis, W.R., 2000. Parameterization and micrometerological measurement of air–sea gas transfer. Boundary-Layer Meteorology 96, 63–105.

Fangohr, S., Woolf, D.K., Jeffery, C.D., Robinson, I.S., 2008. Calculating long-term global air–sea flux of carbon dioxide using scatterometer, passive microwave, and model re-analysis wind data. Journal of Geophysical Research 113 (C09032). doi:10.1029/2005JC003376.

Foltz, G.R., Grodsky, S.A., Carton, J.A., 2003. Seasonal mixed layer heat budget of the tropical Atlantic Ocean. Journal of Geophysical Research 108 (C5). doi:10.1029/2002JC001584.

Frew, N.M., Goldman, J.C., Dennett, M.R., Johnson, A.S., 1990. Impact of phytoplankton-generated surfactants on air–sea gas exchange. Journal of Geophysical Research 95, 3337–3352.

Godfrey, J.S., Beljaars, A.C.M., 1991. On the turbulent fluxes of buoyancy, heat and moisture at the air–sea interface at low wind speeds. Journal of Geophysical Research 96 (C12), 22043–22048.

Hare, J.E., Fairall, C.W., McGillis, W.R., Edson, J.B., Ward, B., Wanninkhof, R., 2004. Evaluation of the national oceanic and atmospheric administration/coupled-ocean atmosphere response experiment (NOAA/COARE) air–sea gas transfer parameterization using GasEx data. Journal of Geophysical Research 109 (C08S11). doi:10.1029/2003JC001831.

Jähne, B., Heinz, G., Dietrich, W., 1987. Measurement of the diffusion coefficient of sparingly soluble gases in water. Journal of Geophysical Research 92, 10767–10776.

Jeffery, C.D., Robinson, I.S., Woolf, D.K., Donlon, C.J., 2008. The response to phase-dependent wind stress and cloud fraction of the diurnal cycle of SST and air–sea CO_2 exchange. Ocean Modelling 23, 33–48. doi:10.1016/j.ocemod.2008.03.003.

Jeffery, C.D., Woolf, D.K., Robinson, I.S., Donlon, C.J., 2007. 1-D modelling of convective CO_2 exchange in the Tropical Atlantic. Ocean Modelling 19, 161–182. doi:10.1016/j.ocemod.2007.07.003.

Kettle, H., Merchant, C.J., Jeffery, C.D., Filipiak, M.J., Gentemann, C.L., 2009. The impact of diurnal variability in sea surface temperature on the central Atlantic air–sea CO_2 flux. Atmospheric Chemistry and Physics 9, 529–541.

King, D.B., DeBryun, W.J., Zheng, M., Saltzman, E.S., 1995. Uncertainties in the molecular diffusion coefficient of gases in water for use in the estimation of air–sea gas exchange. In: Jähne, B., Monahan, E.C. (Eds.), Air–Water Gas Transfer: Selected Papers from the Third International Symposium on Air–Water Gas Transfer, Heidelberg Univerisity, AEON Verlag & Studio, 24–27 July, 1995, pp. 13–22.

Liss, P.S., Merlivat, L., 1986. Air–sea gas exchange rates: Introduction and synthesis. In: Buat-Menard, P. (Ed.), The Role of Air–Sea Exchange in Geochemical Cycling. Kluwer Academic Publishers, Dordrecht, Holland, pp. 113–127.

McGillis, W.R., Edson, J.B., Zappa, C.J., Ware, J.W., McKenna, S.P., Terray, E.A., Hare, J.E., Fairall, C.W., Drennan, W., Donelan, M., DeGrandpre, M.D., Wanninkhof, R., Feely, R.A., 2004. Air–sea CO_2 exchange in the Equatorial Pacific. Journal of Geophysical Research 109 (C08S02). doi:10.1029/2003JC002256.

McKenna, S.P., McGillis, W.R., 2004. The role of free-surface turbulence and surfactants in air–water gas transfer. Journal of Marine Research 53, 151–169.

Miller, M.J., Beljaars, A.C.M., Palmer, T.N., 1991. The sensitivity of the ECMWF model to the parameterization of the evaporation from the tropical ocean. Journal of Climate 5 (5), 414–434.

Monahan, E.C., Spillane, M.C., 1984. The role of oceanic whitecaps in air–sea gas exchange. In: Brusaert, W., Jirka, G.H. (Eds.), Gas Transfer at Water Surfaces. D. Reidel Pub. Co., pp. 495–503.

Naegler, T., Ciais, P., Rodgers, K., Levin, I., 2006. Excess radiocarbon constraints on air–sea gas exchange and the uptake of CO_2 by the oceans. Geophysical Research Letters 33 (L11802). doi:10.1029/2005GL025408.

Nightingale, P.D., Liss, P.S., Schlosser, P., 2000a. Measurements of air–sea gas transfer during an open ocean algal bloom. Geophysical Research Letters 27 (14), 2117–2120.

Nightingale, P.D., Marlin, G., Law, C.S., Watson, A.J., Liss, P.S., Liddicoat, M.I., Boutin, J., Upstill-Goddard, R.C., 2000b. In situ evaluation of air–sea gas exchange parameterizations using novel conservative and volatile tracers. Global Biogeochemical Cycles 14 (1), 373–387.

Saltzman, E.S., King, D.B., Holmen, K., Leck, C., 1993. Experimental determination of the diffusion coefficient of dimethylsulfide in water. Journal of Geophysical Research 98, 16481–16486.

Saunders, P.M., 1967. The temperature at the ocean–air interface. Journal of the Atmospheric Sciences 24, 269–273.

Schumann, U., 1988. Minimum friction velocity and heat transfer in the rough surface layer of a convective boundary layer. Boundary-Layer Meteorology 44, 311–326.

Soloviev, A.V., Schlüssel, P., 1994. Parameterization of the cool skin of the ocean and of the air–ocean gas transfer on the basis of modeling surface renewal. Journal of Physical Oceanography 24, 1339–1346.

Stull, R.B., 1994. A convective transport theory for surface fluxes. Journal of the Atmospheric Sciences 51 (1), 3–22.

Sweeney, C., Gloor, E., Jacobson, A.R., Key, R.M., McKinley, G., Sarmiento, J.L., Wanninkhof, R., 2007. Constraining global air–sea gas exchange for CO_2 with recent bomb ^{14}C measurements. Global Biogeochemical Cycles 21. doi:10.1029/2006GB002784.

Takahashi, T., Sutherland, S.C., Sweeny, C., Poisson, A., Metzl, N., Tilbrook, B., Bates, N., Wanninkhof, R., Feely, R.A., Sabine, C., Olafsson, J., Nojiri, Y., 2002. Global sea–air CO_2 flux based on climatological surface ocean pCO_2 and seasonal biological and temperature effects. Deep-Sea Research II 49, 1601–1622.

Wanninkhof, R., 1992. Relationship between wind speed and gas exchange over the ocean. Journal of Geophysical Research 97 (C5), 7373–7382.

Wanninkhof, R., Doney, S.C., Takahashi, T., McGillis, W.R., 2002. The effect of using time-averaged winds on regional air–sea CO_2 fluxes. In: Gas Transfer at Water Surfaces. Geophysical Monograph, vol. 127. American Geophysical Union, pp. 351–356.

Wanninkhof, R., Knox, M., 1996. Chemical enhancement of CO_2 exchange in natural waters. Limnological Oceanography 41 (4), 689–697.

Wanninkhof, R., McGillis, W.R., 1999. A cubic relationship between air–sea CO_2 exchange and wind speed. Geophysical Research Letters 26 (13), 1889–1892.

Wiesenburg, D.A., Guinasso Jr., N.L., 1979. Equilibrium solubilities of methane, carbon monoxide, and hydrogen in water and sea water. Journal of Chemical Engineering Data 24 (4), 356–360.

Woolf, D.K., 1997. Bubbles and their role in gas exchange. In: Liss, P.S., Duce, R.A. (Eds.), The Sea Surface and Global Change. Cambridge University Press, Cambridge, UK, pp. 173–206.

Woolf, D.K., 2005. Parameterization of gas transfer velocities and sea-state-dependent wave breaking. Tellus 57B, 87–94.