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Journal of Marine Systems 66 (2007) 195 – 203
JOURNAL OF MARINE SYSTEMS
www.elsevier.com/locate/jmarsys

Application of new parameterizations of gas transfer velocity and their impact on regional and global marine CO_2 budgets

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Received 5 October 2005; accepted 8 January 2006
Available online 12 September 2006

Abstract

One of the dominant sources of uncertainty in the calculation of air–sea flux of carbon dioxide on a global scale originates from the various parameterizations of the gas transfer velocity, *k*, that are in use. Whilst it is undisputed that most of these parameterizations have shortcomings and neglect processes which influence air–sea gas exchange and do not scale with wind speed alone, there is no general agreement about their relative accuracy.

The most widely used parameterizations are based on non-linear functions of wind speed and, to a lesser extent, on sea surface temperature and salinity. Processes such as surface film damping and whitecapping are known to have an effect on air–sea exchange. More recently published parameterizations use friction velocity, sea surface roughness, and significant wave height. These new parameters can account to some extent for processes such as film damping and whitecapping and could potentially explain the spread of wind-speed based transfer velocities published in the literature.

We combine some of the principles of two recently published *k* parameterizations [Glover, D.M., Frew, N.M., McCue, S.J. and Bock, E.J., 2002. A multiyear time series of global gas transfer velocity from the TOPEX dual frequency, normalized radar backscatter algorithm. In: Donelan, M.A., Drennan, W.M., Saltzman, E.S., and Wanninkhof, R. (Eds.), Gas Transfer at Water Surfaces, Geophys. Monograph 127. AGU,Washington, DC, 325–331; Woolf, D.K., 2005. Parameterization of gas transfer velocities and sea-state dependent wave breaking. Tellus, 57B: 87–94] to calculate *k* as the sum of a linear function of total mean square slope of the sea surface and a wave breaking parameter. This separates contributions from direct and bubble-mediated gas transfer as suggested by Woolf [Woolf, D.K., 2005. Parameterization of gas transfer velocities and sea-state dependent wave breaking. Tellus, 57B: 87–94] and allows us to quantify contributions from these two processes independently.

We then apply our parameterization to a monthly TOPEX altimeter gridded $1.5° \times 1.5°$ data set and compare our results to transfer velocities calculated using the popular wind-based *k* parameterizations by Wanninkhof [Wanninkhof, R., 1992. Relationship between wind speed and gas exchange over the ocean. J. Geophys. Res., 97: 7373–7382.] and Wanninkhof and McGillis [Wanninkhof, R. and McGillis, W., 1999. A cubic relationship between air−sea CO2 exchange and wind speed. Geophys. Res. Lett., 26(13): 1889–1892]. We show that despite good agreement of the globally averaged transfer velocities, global and regional fluxes differ by up to 100%. These discrepancies are a result of different spatio-temporal distributions of the processes involved in the parameterizations of *k*, indicating the importance of wave field parameters and a need for further validation.
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Keywords: Air–water exchanges; Gas exchange; Carbon dioxide; Remote sensing; Altimetry

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doi:10.1016/j.jmarsys.2006.01.012

1. Introduction

The air–sea exchange of carbon dioxide (CO_2) can be described as

$$F = k\ s\ \Delta pCO_2 \tag{1}$$

where k is the gas transfer velocity expressed in cm/h, s is the solubility of the gas in water, and ΔpCO_2 is the difference in partial pressure of the gas across the interface. The solubility can be expressed as a well-known function of sea surface temperature (SST) and salinity (Weiss, 1974; Wanninkhof, 1992). Climatological values of ΔpCO_2 have been produced by Takahashi et al. (2002) based on approximately 940,000 measurements of pCO_2 in surface waters excluding any observations in the equatorial Pacific between 10°N and 10°S during El Niño events (Takahashi et al., 1993, 2002). Whilst this data set presents the current state of the art for global calculations of air–sea CO_2 flux there are some uncertainties associated with it that are of particular relevance when studying regional or seasonal subsets.

A major source of uncertainty in calculations of air–sea flux of CO_2 and its role in the global carbon cycle arises from the parameterizations of the transfer velocity k. The transfer velocity of CO_2 critically depends on molecular diffusion and wind-driven turbulence in the upper millimetre of the ocean (Liss and Merlivat, 1986), hence wind speed is an obvious parameter used to describe k. However there has been growing consensus that it is not wind speed alone which determines gas transfer, but that other processes such as organic films, boundary layer instabilities, and wave field parameters have an important impact (Jähne et al., 1987; Frew, 1997; Glover et al., 2002; Frew et al., 2004; Woolf, 2005), none of which scale directly with wind speed. Despite this, the k parameterizations which are still used most widely (Wanninkhof, 1992; Wanninkhof and McGillis, 1999) are of the form

$$k = A\ u_{10}^{B}(Sc/660)^{-1/2} \tag{2}$$

where u_{10} is the wind speed at 10 m height in conditions of neutral atmospheric stability, Sc is the Schmidt number, a known function of SST and salinity (e.g. Wanninkhof, 1992), and $B=2$, 3.

More recently, Glover et al. (2002) and Woolf (2005) have suggested new parameterizations of the gas transfer velocity that depart from the traditional model since they no longer rely on wind speed as a primary proxy for gas transfer. Glover et al. (2002) relate gas transfer velocity directly to the roughness of the sea surface using mean square slope values from the dual-frequency altimeter TOPEX. Using the return signal at two frequencies allows them to isolate wave spectra in the region of 6.3–16.5 cm which is relevant to gas transfer. Their resulting global average transfer velocity is low (13 cm/h) compared to the results of Wanninkhof (1992) (22 cm/h) and a lack of ground truth validation is highlighted.

Woolf (2005) uses a hybrid model which separates direct gas transfer, k_d, from bubble-mediated gas transfer, k_b,

$$k = k_d + k_b \tag{3}$$

The direct transfer is parameterized as a function of friction velocity, u_*. In contrast to u_{10}-based parameterizations the use of u_{20*} incorporates atmospheric boundary layer effects via the drag coefficient. The bubble-mediated transfer is parameterized as a function of whitecapping. It is shown that the hybrid model has the potential to explain the spread observed in current wind-speed dependent parameterizations and that sea state, particularly as it affects whitecapping, is likely to be a major factor influencing gas transfer. However, there are some open questions as to the absolute values of transfer velocity obtained with the hybrid model and the relative scaling of the two contributions to the total transfer velocity Woolf (2005).

In this paper we derive a parameterization of gas transfer velocity based largely on the theories of Glover et al. (2002) and Woolf (2005). Details of this parameterization are presented in Section 2. We then describe in Section 3 the data we use to evaluate our new model and to compare it to results obtained using traditional k parameterizations primarily dependent on wind speed. The results of this comparison are shown and discussed in Section 4 along with some revised values of annual transfer velocities and air–sea CO_2 flux. Finally, we summarize our conclusions in Section 5.

2. Theory

The new parameterization of gas transfer velocity that we use in this work combines the concepts proposed by Glover et al. (2002) and Woolf (2005). One base is a direct measurement of the sea surface roughness, the backscatter measured by the dual-frequency altimeter TOPEX. This measurement is used to estimate the direct, i.e. the non-breaking part of the gas transfer. We adopt the Glover et al. (2002) formulations to calculate mean square slope, $\langle s^2\rangle$, from

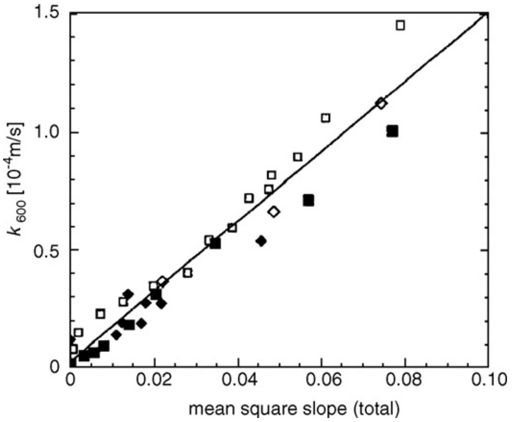

Fig. 1. Gas transfer velocity k_{600} for varying mean square slope integrated over all wavelengths. Adapted from Fig. 9a by Bock et al. (1999).

the altimeter backscatter signal at K_u-band, σ_{Ku} (Barrick, 1974):

$$\langle s^2 \rangle = \frac{\rho_{Ku}}{\sigma K_u} \tag{4}$$

with $\rho_{Ku}=0.38$. We then relate this slope to gas transfer velocity according to results published by Bock et al. (1999) as shown in Fig. 1. This results in

$$k_d = \left(\frac{a\ \rho_{Ku}}{\sigma K_u} + b\right)(Sc/600)^{-1/2} \tag{5}$$

with $\alpha=1.49\times10^{-3}$, $b=10^{-6}$ (as determined from Fig. 1).

In agreement with the results by Jähne et al. (1987) and Bock et al. (1999) we obtain best results by using a relationship based on the total mean square slope (measured in the absence of large-scale wave breaking), taking into account surface steepness from all wavenumbers rather than restricting our relationship to a narrower wave range. The latter is often given preference over using the entire wave spectrum since theoretically there is no link between long waves and gas transfer velocity (as shown, e.g., in Bock et al. (1999), Fig. 9b).

Towards the high-wavenumber end of the spectrum, geometrical optics would suggest that K_u-band altimeters can only take into account surfaces waves up to about 100 rad/m (Brown, 1990), limiting the applicability of the results by Bock et al. (1999) since these also account for shorter waves. However, Chapron et al. (1995) have demonstrated that physical optics allow for an influence of shorter waves on K_u-band scattering. Whilst there is still a lack of quantitative information on this effect these findings encourage us to apply the relationship found by Bock et al. (1999).

As proposed by Woolf (2005), bubble-mediated gas transfer is parameterized as

$$k_b = c\frac{u_* H_s}{v_w} \tag{6}$$

with $c=2\times10^{-5}$, u_* is the friction velocity, H_s is significant wave height, and v_w is the kinematic viscosity in sea water parameterized as $v_w=1.83\times10^{-6}$ exp $(-SST/T_0)$, with $T_0=36°C$.

Combining the two parts of the total transfer velocity (Eqs. (5) and (6)) according to Eq. (3) yields a ratio of about 3:1 for the non-breaking and breaking contributions of the total transfer velocity averaged over the global oceans. We refer to this parameterization as ALT1. However, since there is some uncertainty as to the absolute scaling of Eq. (6) (i.e. the magnitude of c) we also consider a second version in which we assign more emphasis to the contribution of wave breaking. This procedure allows us to quantify the impact that an explicit parameterization of breaking wave contribution has on the overall transfer velocity and gas flux and to study the sensitivity of these parameters to the relative weighting of the two contributing parts of the transfer velocity, k_d and k_b. Accordingly, we keep the annual mean value obtained from ALT1 for k constant but swap the contributions of the non-breaking and breaking parts so that they have a global ratio of 1:3. We refer to this second parameterization in which the breaking contribution to transfer velocity exceeds the non-breaking contribution as ALT2.

3. Data

In order to compare transfer velocities on a regional or even a global scale, remote sensing data are ideally suited to provide the spatio-temporal coverage required. Measurements of backscatter, friction velocity and significant wave height can all be obtained from a satellite altimeter. We use TOPEX data interpolated to monthly means on a 1.5°×1.5° geographical grid following a gridding scheme described by Woolf et al. (2002). A 5×5 square Gaussian filter is employed to interpolate and smooth the data. The filter is configured to use interpolated values in data fields without any TOPEX measurements. In addition to that, sea surface temperature (SST) obtained by the Advanced Microwave Scanning Radiometer (AMSR-E) are used to calculate Schmidt numbers as well as the kinematic viscosity of water.

The TOPographic EXperiment (TOPEX) altimeter has been operational since summer 1992. It operates at two frequencies, 13.6 GHz (K_u-band) and 5.3 GHz (C-band) obtaining measurements up to latitudes of 66°. TOPEX has a repeat cycle of 10 days and takes measurements of the sea surface roughness at a frequency of about 1 Hz, giving a ground spacing of about 5.8 km between data points. Ground tracks are separated by about 315 km at the equator (Fu et al., 1994). Backscatter is reported with a precision of 0.25 dB which translates to about 0.5 m/s for typical wind speeds; comparisons to buoys show a variance of about 1.5 m/s (Callahan et al., 1994; Quartly, 2000). The backscatter calibration is maintained to about 0.1 dB. TOPEX data have been obtained from the Radar Altimeter Database System (RADS) (Scharroo, 2003). We use the algorithm by Witter and Chelton (1991) to calculate u_{10} and use the drag coefficient to derive friction velocity.

The AMSR-E passive microwave instrument aboard NASA's Aqua satellite was launched in 2002. It operates 12 channels at 6 frequencies and covers a swath of 1445 km. The AMSR-E ocean products used in this study were produced using a modified version of the ASMR-E Direct Broadcast algorithm developed for NASA, using an on-orbit calibration method developed at Remote Sensing Systems (RSS) to convert counts to brightness temperatures (Wentz et al., 2003). We use RSS version 4 data which are gridded onto a global $0.25° \times 0.25°$ grid. The target accuracy of measurements of sea surface temperature is 0.5 K in the range of −2 to 35°C (EORAC, 2004).

In order to compare the transfer velocity obtained by applying ALT1 and ALT2 with the traditional, wind-speed based parameterizations of gas transfer velocity, we use u_{10} wind speed data acquired by the SeaWinds scatterometer for the latter. The SeaWinds scatterometer on QuikSCAT was launched in June 1999. It operates at 13.4 GHz (K_u-band) with a swath of 1800 km. At 12 h temporal resolution, daily coverage is about 92% of the global icefree oceans. Measurements of wind speed and direction have an accuracy of 1 m/s and 20°, its highest spatial resolution is 25 km (Ebuchi et al., 2002), gridded into a $1° \times 1°$ geographical grid. We use data processed by RSS as version 3, using their K_u-2001 algorithm (Wentz et al., 2001). Compared to previous versions which exhibited an overestimation at high wind speeds (Ebuchi et al., 2002) K_u-2001 has a flatter σ_0 vs wind speed response at high winds. The measurements obtained by the sensor equal a time average over approximately 8–10 min.

As an alternative source of wind data with improved temporal coverage we use data from the European Centre for Medium-Range Weather Forecasts (ECMWF) ERA-40 project. These consist of a comprehensive set of global analyses describing the state of the atmosphere, land and ocean-wave conditions from mid 1957 to August 2002. Data sets are available at 6 h temporal resolution on a $2.5° \times 2.5°$ geographical grid (Uppala, 2001; Kållberg et al., 2004). This high temporal resolution does not always represent the true resolution of the underlying input data but can be a simple interpolation between two points spaced further apart. For the purpose of this study only monthly mean fields of ERA-40 wind data are used.

4. Results and discussion

Comparisons of gas fluxes derived from various sources of wind data have yielded differing results by up to 30% in the past making a baseline choice for the evaluation of our new algorithms difficult. For reasons of temporal coverage, ERA-40 wind data are well suited for our comparison since they allow the calculation of long-term averages. However, there are two issues with this choice we would like to point out. Firstly, ERA-40 wind speed data are known to have a bias towards lower winds when compared to, e.g., QuikSCAT wind data. Secondly, we use only monthly mean values of ERA-40 wind speeds. To account for sub-monthly variability of wind speeds we then apply a climatological correction factor derived from five years (2000–2004) of 12-hourly QuikSCAT data on a $1° \times 1°$ longitude/latitude grid. This is a more satisfactory procedure than simply assuming a Rayleigh distribution of winds, as shown by Wanninkhof et al. (2002):

$$R_{\mathrm{QS}} = \overline{k(u_{\mathrm{QS}})}/k(\overline{u_{\mathrm{QS}}}) \tag{7}$$

$$\overline{k(u_{\mathrm{ERA}})} = R_{\mathrm{QS}}\ k(\overline{u_{\mathrm{ERA}}}) \tag{8}$$

with subscripts QS and ERA denoting quantities based on QuikSCAT and ERA-40 data, respectively. Whilst this method will introduce some error due to the use of data from two different sources, it allows us to calculate 20-year averages of transfer velocity and gas flux based on ERA-40 wind speeds whilst relying on the more accurate distributions sampled by QuikSCAT.

We use these wind speed data to calculate 20-year (1982–2001) averages of transfer velocity and carbon flux using the parameterizations by Wanninkhof (1992) (W92) and Wanninkhof and McGillis (1999) (WG99). Altimeter-based fluxes are calculated and averaged over the period of TOPEX data availability overlapping with the time frame of ERA-40 (1993–2001). Results are shown in Table 1. Numbers given in brackets for W92 and WG99 refer to values for up to 66° latitude to allow a direct comparison with values for ALT1 and ALT2.

Table 1
Mean transfer velocities and net carbon fluxes calculated using transfer velocity parameterizations by Wanninkhof (1992) (W92), Wanninkhof and McGillis (1999) (WG99), ALT1 and ALT2

	Zonal coverage	Mean transfer velocity [cm/h]	Net sink [Gt C/yr]
W92	±90° (±66°)	17.8 (17.9)	1.63 (1.53)
WG99	±90° (±66°)	16.4 (16.4)	2.15 (2.05)
ALT1	±66°	18.4	1.00
ALT2	±66°	18.4	1.72

The numbers illustrate that without further tuning of the new parameterizations ALT1 and ALT2, there is reasonable agreement between global mean transfer velocities (Table 1, first column) calculated using the traditional or new parameterizations. Transfer velocities obtained using ALT1 and ALT2 are identical since the coefficients of k_d and k_b were adjusted in such a way that the global mean transfer velocity was kept constant. Nonetheless, the fact that the transfer velocities obtained from our new parameterizations are in the same range as those from traditional formulae shows that both sets of coefficients give reasonable results for k.

Comparing the global net flux values (Table 1, second column), results obtained from W92 and ALT2 are of comparable magnitude (1.53 and 1.72 Gt C/yr for ±66°), WG99 predicts a 34% increase from W92 (2.05 Gt C/yr) whilst ALT1 lies 53% below that value. These discrepancies indicate that despite the similar mean transfer velocities there are substantial differences in the spatial and temporal distribution of k resulting in fluxes that differ by 100%. Whilst the carbon flux value for ALT1 may appear unrealistically low it should be noted that this value does not contain any corrections for a flux increase due to a lower sea surface temperature in the thin thermal layer at the surface of the ocean (thermal skin effect) or shelf sea fluxes. Considering that these factors could contribute on the order of −1.4 Gt C/yr (Van Scoy et al., 1995; Borges and Frankignoulle, 2002) indicates that the values obtained are not unrealistic after all when compared to studies based on O_2/N_2 ratios (Keeling et al., 1996).

To highlight regional differences in fluxes calculated with the four k parameterizations, Table 2 shows Atlantic, Pacific, Indian, and Southern Ocean fluxes subdivided into five zonal bands. In order to be able to compare bands of equivalent size despite the different spatial coverage of TOPEX and ERA-40 data sets, W92 and WG99 fluxes are given for up to 66° latitude in brackets as well as for full global coverage.

As can be seen from Table 2, regional results for the four parameterizations are within a similar range in most areas. The single most striking discrepancy occurs in the tropical Pacific where ALT1 and ALT2 give significantly greater values than W92 andWG99. Fluxes vary by up to 0.49 Gt C/yr between WG99 and ALT1 explaining almost half of the observed global flux discrepancies. A further discrepancy of 0.13 Gt C/yr originates from the tropical Atlantic and Indian Ocean. In the tropics, wind speeds are low on average compared to higher latitudes. In these conditions ($u_{10} \leq 10$ m/s), WG99 gives lower transfer velocities than other wind-speed based parameterizations such as W92 and in many instances wind speeds and transfer velocities will be close to zero. By contrast, even in no-wind conditions the sea surface is hardly ever completely flat as a result of swell. Thus the mean square slope used to parameterize gas transfer velocity in ALT1 and ALT2 has a non-zero value giving a higher k than would be obtained from a wind-speed based parameterization. This contribution to the total transfer velocity originates from the non-breaking part of k (k_d), resulting in higher fluxes for ALT1 than for ALT2.

In order to convey an impression of the spatial distribution of transfer velocities obtained from the new parameterizations, Fig. 2 compares the two contributions, k_d and k_b, averaged over a 9-year period (1993–2001). The absolute magnitudes of the two parameters are unmodified, i.e. representing ALT1 conditions. The spatial distributions of the two contributions to the total transfer velocity show striking differences in that they exhibit contrasting zonal variations. Whilst transfer

Table 2
Average net carbon fluxes in Gt C/yr calculated using transfer velocity parameterizations by Wanninkhof (1992) (W92), Wanninkhof and McGillis (1999) (WG99), ALT1 and ALT2

Latitude	Region	1982–2001		1993–2001	
		W92	WG99	ALT1	ALT2
50°N–90°N	Atlantic	−0.29	−0.32		
50°N–66°N	Atlantic	(−0.20)	(−0.22)	−0.28	−0.30
50°N–90°N	Pacific	−0.01	0.0		
50°N–66°N	Pacific	(−0.01)	(0.0)	0.0	−0.01
14°N–50°N	Atlantic	−0.25	−0.27	−0.27	−0.31
	Pacific	−0.47	−0.53	−0.49	−0.58
	Indian	0.04	0.04	0.07	0.06
14°N–14°S	Atlantic	0.11	0.07	0.17	0.13
	Pacific	0.57	0.37	0.86	0.69
	Indian	0.13	0.09	0.21	0.16
14°S–50°S	Atlantic	−0.23	−0.27	−0.17	−0.22
	Pacific	−0.31	−0.32	−0.30	−0.36
	Indian	−0.54	−0.56	−0.49	−0.61
50°S–66°S	Southern	(−0.38)	(−0.45)	−0.30	−0.39
50°S–90°S	Southern	−0.38	−0.45		
Total	Global	−1.63	−2.15		
Total	±66°	(−1.53)	(−2.05)	−1.00	−1.72

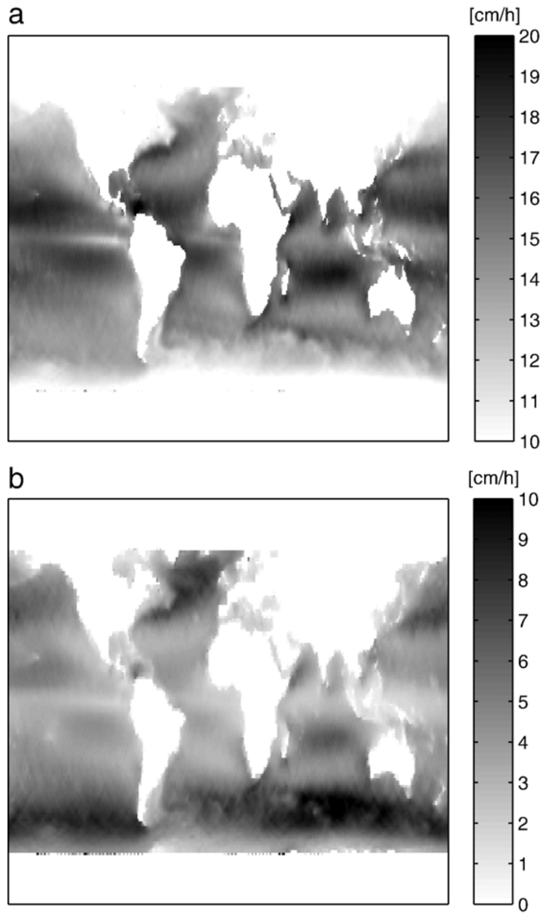

Fig. 2. Gas transfer velocities calculated using the new parameterization ALT1, averaged over 1993−2001. a) Shows the velocity of direct gas transfer, b) the velocity of bubble-mediated gas transfer. Note the difference in gray scale between plots a) and b).

velocities for direct gas transfer are greatest in the tropics, velocities of bubble-mediated gas transfer peak in the higher latitude oceans and follow the northern and southern hemisphere storm tracks. The former result may not seem surprising given that wind speed (and mean square slope) is generally higher at high latitudes but the Schmidt number dependence of k_d and thus the influence of water temperature is also significant. A combination of fairly high winds and warm waters leads to high direct transfer velocities in trade wind regions.

The spatial distribution of surfactants as published, e.g., by Tsai and Liu (2003) exhibits similar patterns to that of the direct transfer velocity (high surfactant coverage in regions of low transfer velocity) which may indicate an additional contribution from this process. However, the similarities between the seasonal and spatial patterns of SST and surfactants as identified by Tsai and Liu (2003) make it difficult to distinguish between the effects of these two factors. However, some preliminary studies have shown that dual-frequency altimeters such as TOPEX may offer a solution to this problem in the future (Woolf and Ufermann, 2005).

Investigating these results at higher temporal resolution illustrates the seasonal variability of these patterns. Fig. 3 shows box plots for both contributions to the total gas transfer velocity, k_d (Fig. 3a, c, e) and k_b (Fig. 3b, d, f) plotted against time for ALT1. Values on the *x*-axes correspond to 9-year averages of monthly values ranging from January to December for the period 1993–2001. Averaging has been carried out in such a way that contributions from grid cells of different size resulting from the regular longitude–latitude grid are weighted according to their area coverage. Regionally, we have divided the global oceans into a tropical region ranging from 30°N to 30°S (Fig. 3c and d), and a higher latitude northern (a and b) and southern section (e and f), ranging from 30° to 66° in either hemisphere, respectively. Whilst this reduces spatial resolution significantly it captures the main regional zones of variability and allows a comparison of seasonal and inter-annual variability.

The values for each month reflected in the box plot correspond to the median of the 9-year spatial mean values and the upper and lower quartile of the data for the respective region and month. The range of remaining values is covered by the whiskers of each individual box, outliers are marked by dots above or below the respective box. Accordingly, seasonal variability is indicated by the location of centre lines through the boxes throughout the year, whilst inter-annual variability is indicated by the size of the boxes for each month, with larger boxes representing a wider spread of the data.

Regionally, Fig. 3 still reflects the different regional patterns of k_d and k_b with higher latitude velocities exceeding those in the tropics for bubble-mediated transfer. In contrast, direct transfer velocities are greatest in the tropics all year round.

Comparing seasonal patterns, k_d and k_b show a similar behaviour as would be expected given the fact that both wind speeds and wave heights follow a similar seasonal pattern. There is little seasonal variability in the tropical region for both parameters, and at higher latitudes greater values are found in the winter months of the respective hemisphere whilst values are comparatively low during the summer months.

It is also clear from Fig. 3 that at higher latitudes, k_b, the velocity of bubble-mediated gas transfer, has a higher seasonal and inter-annual variability than k_d. In both hemispheres, seasonal variability of k_b exceeds that of k_d, by approximately 1.5−2.0 cm/h whereas

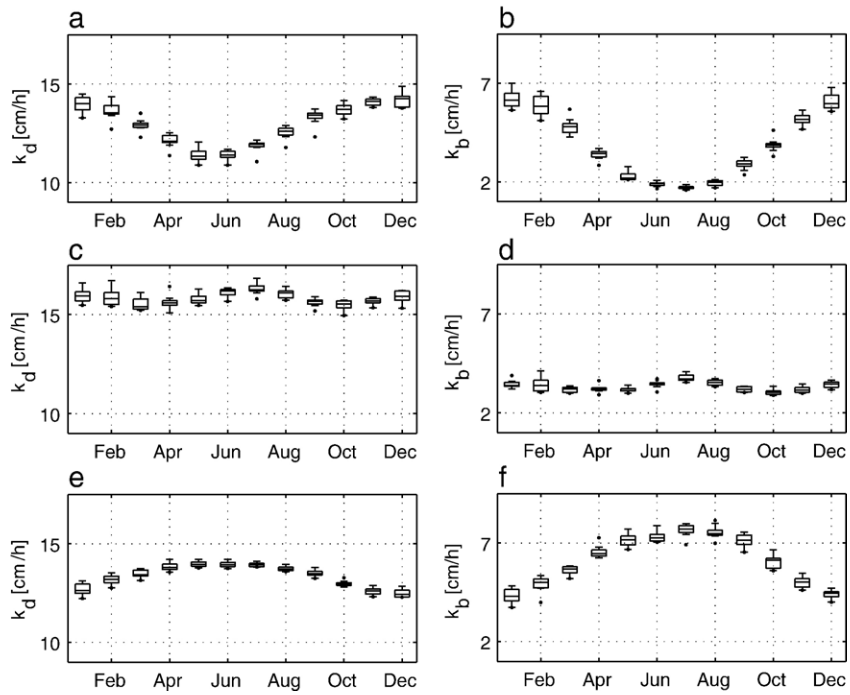

Fig. 3. Seasonal variation of area-weighted, averaged transfer velocities for the period 1993−2001 for velocity of direct gas transfer (a, c, e) and velocity of bubble-mediated transfer (b, d, f). Note the different scaling of *y*-axes in plots a) and b), the range of values is identical. a) and b): 30°N−66°N, c) and d): 30°N−30°S, e) and f): 30°S−66°S.

variability in the tropics is small and of comparable magnitude between the two parameters.

Fig. 4 shows that in the North Atlantic k_b is sensitive to the North Atlantic Oscillation Index (NAO). This results from a sensitivity of both wind speeds and particularly wave heights to the NAO. The response of wave heights to the NAO has been well studied (e.g. Woolf et al., 2002) and is known to be a robust feature. In large parts of the northeastern Atlantic, the NAO is responsible for a majority of winter time inter-annual variability in wave heights. The response of k_b to the NAO has not yet been studied in similar detail but it is clearly of interest. This is an example of a dependency of CO_2 uptake on large-scale weather patterns and large-scale climate variability.

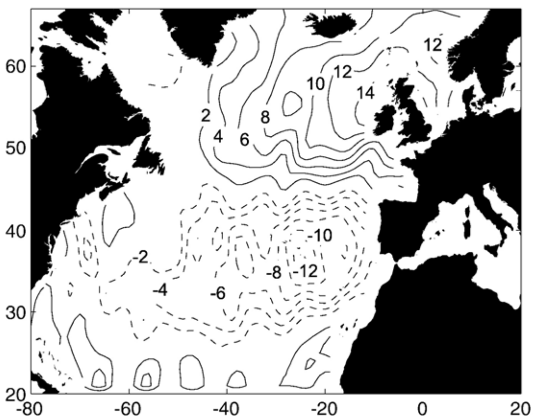

Fig. 4. Sensitivity of the velocity of bubble-mediated transfer of CO_2 to the North Atlantic Oscillation Index (NAO) in percentage change per unit index. Contour lines indicate percentage sensitivities of k_b to NAO changes, solid lines show a positive correlation, dashed lines a negative correlation of NAO and transfer velocity.

These results illustrate the impact of integrating wave field parameters into parameterizations of gas transfer velocity. Higher transfer velocities in the northeastern part of the North Atlantic and the Southern Ocean illustrated in Fig. 2b demonstrate that bubble-mediated gas transfer is likely to play a major part in some of the main global sink regions for CO_2. This is also confirmed by the increase in global CO_2 flux when the contribution by bubble-mediated gas transfer is increased (ALT2, Table 1, column 2). Whilst our current knowledge favours the parameters as used in parameterization ALT1 (i.e. a greater contribution by the direct transfer), the magnitude of the contributions of bubble-mediated gas transfer is still somewhat unclear and a lack of dedicated measurements hinders further validation of this method. Furthermore it appears that the temperature dependence of the velocity of direct gas transfer has a dominant effect on its global spatial structure. This reduces direct gas transfer at high latitudes and promotes tropical outgassing to a degree that may require further analysis. Note also that this result is dependent on the retrieval of mean square slope and the assumed relationship of transfer velocity to slope described by Eqs. (4) and (5), and therefore is subject to revision as we learn more about these relations.

5. Conclusions

In order to improve estimates of regional and global velocities of CO_2 transfer we have introduced a new parameterization of gas transfer velocity that combines two concepts introduced by Glover et al. (2002) and Woolf (2005). We use total mean square slope to incorporate effects of surface films and individually parameterize direct and bubble-mediated gas transfer to allow for effects of breaking waves explicitly.

When applied to a gridded 9-year TOPEX data set, the globally averaged transfer velocities (18 cm/h) fall within the range of previously published results. However, regional differences of the processes involved create significant differences in the globally averaged carbon flux values, resulting in a 9-year average of only 1.0 Gt C/yr. This relatively low net flux is largely a result of intensified outgassing in the tropical Pacific. Given that shelf sea contributions are not included in this estimate and that no cool skin correction has been applied, this value is not unrealistically low when compared to results based on O_2/N_2 ratios (Keeling et al., 1996).

Whilst a lack of dedicated ground truth data makes an absolute validation of the algorithm difficult, we have illustrated the importance of incorporating wave field parameters into the parameterizations of gas transfer velocity and presented a physically sound parameterization of k. The spatial distributions of the results obtained by applying this parameterization globally show significant differences from those obtained using traditional wind-speed based parameterizations of gas transfer velocity.

Future developments should address the relative importance of direct and bubble-mediated transfer (i.e. the value of the coefficients) and refine the dependence of each on remotely retrieved parameters. For example, the current formulation for direct transfer predicts substantial transfer at very low winds which may result from an unreasonable sensitivity to swell. At the same time, the sensitivity of K_u-band backscatter to wavelengths shorter than 0.06 m requires further attention since their role may be underestimated by our current parameterization.

Acknowledgements

QuikSCAT data are produced by Remote Sensing Systems and sponsored by the NASA Ocean Vector Winds Science Team. AMSR-E data are produced by Remote Sensing Systems and sponsored by the NASA Earth Science REASoN DISCOVER Project and the AMSR-E Science Team. Both data sets are available at http://www.remss.com. ERA-40 data are produced by the European Centre for Medium-Range Weather Forecast (ECMWF) and are available at http://www.ecmwf.int. TOPEX data were obtained from the Radar Altimeter Database System (RADS) and are available at http://rads.tudelft.nl. The authors would like to thank Sofia Caires for providing significant wave height data, Taro Takahashi for ΔpCO_2 data, Christine Gommenginger for gridded TOPEX data, and David Glover and an anonymous reviewer for their constructive criticism and comments. This research is supported by the United Kingdom Natural Environment Research Council through the Centre for observation of Air–Sea Interactions and fluXes (CASIX). This is CASIX publication no. 39.

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