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A cubic relationship between air-sea CO_2 exchange and wind speed

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Abstract. Using recent laboratory and field results we explore the possibility of a cubic relationship between gas exchange and instantaneous (or short-term) wind speed, and its impact on global air-sea fluxes. The theoretical foundation for such a dependency is based on retardation of gas transfer at low to intermediate winds by surfactants, which are ubiquitous in the world's oceans, and bubble-enhanced transfer at higher winds. The proposed cubic relationship shows a weaker dependence of gas transfer at low wind speed and a significantly stronger dependence at high wind speed than previous relationships. A long-term relationship derived from such a dependence, combined with the monthly CO_2 climatology of *Takahashi* [1997], leads to an increase in the global annual oceanic CO_2 uptake from 1.4 Gigaton C yr^{-1} to 2.2 Gigaton C yr^{-1}. Although a cubic relationship fits within global bomb-^{14}C oceanic uptake constraints, additional checks are warranted, particularly at high wind speeds where the enhancement is most pronounced.

Introduction

The flux of CO_2 (or other gas), F, across the air-sea interface is often determined from the bulk formula:

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

where k is the gas transfer velocity, s is the solubility, and pCO_{2w} and pCO_{2a} are the partial pressures of CO_2 in water and air, respectively. In order to extrapolate fluxes over longer time and space scales, gas transfer velocities are frequently related to wind speed. Several relationships have been proposed based on laboratory and field studies while taking into account a variety of physical variables such as wind, bubbles, atmospheric boundary layer stability, and drag coefficients [*Monahan and Spillane*, 1984; *Smethie et al.*, 1985; *Liss and Merlivat*, 1986; *Erickson*, 1993; *Woolf*, 1997; *Asher and Wanninkhof*, 1998]. The relationships span a wide range of solutions (Fig. 1). The large differences are attributed to a dearth of data, uncertainty in field results, and often poorly constrained forcing functions. Until better regional multi-parameter algorithms are established, reasonable proxies for k are essential to estimate global and regional fluxes over a variety of time scales. While it is doubtful that a single, simple parameterization with wind speed can cover all spatial scales and environmental conditions, wind is currently the most robust parameter available to estimate global exchange. Wind is the primary forcing of the aqueous boundary layer that controls gas exchange, and it is a remotely-sensed product that can be obtained globally.

The commonly used relationships between gas exchange and wind speed are those of *Liss and Merlivat* [1986] and *Wanninkhof* [1992], henceforth referred to as LM-86 and W-92, respectively. The W-92 relationship is quadratic, and that of LM-86 can be closely approximated by a quadratic over a wind speed range of 0 to 15 m s^{-1}. The physical foundation for a nonlinear increasing relationship is that k is related to friction velocity, $u_w{*}$: $k = \beta^{-1}\, Sc^{-n}\, u_w{*}$, where Sc is the Schmidt number, defined as the kinematic viscosity of the water divided by the molecular diffusivity of the gas in water, and the variable β is dependent on the hydrodynamic regime, decreasing from about 16 to 11 with increasing turbulence as shown in a variety of wind-wave tank studies [*Jähne et al.*, 1984]. The exponent, n, is the Schmidt number dependency that changes from 0.67 for a smooth surface to about 0.4 for a regime with bubbles [*Deacon*, 1977; *Jähne et al.*, 1987; *Keeling*, 1993; *Asher et al.*, 1995].

Several investigators have suggested a stronger dependency of k on wind speed than a quadratic relationship but such relationships have rarely been verified in the field. *Monahan and Spillane* [1984] proposed that gas transfer is proportional to whitecap coverage and that whitecap coverage scales approximately to u^3. Extensive laboratory studies by *Asher et al.* [1995] have shown a linear, gas specific dependence of gas transfer with whitecaps. *Erickson* [1993] incorporated the whitecap parameterization with wind speed accounting for boundary layer stability, thereby creating a series of curves. *Woolf* [1997] established a relationship with wind speed based on a theory of bubble enhanced gas transfer. A summary of the parameterizations, including the effect of breaking waves, is shown in Fig. 1. A seasonal carbon mass balance in the Baltic Sea investigated by *Schneider et al.* [1999] could be best reconciled if cubic wind speed dependence for CO_2 was invoked.

Although compelling cases for a strong nonlinear dependence of gas transfer at higher wind speeds have been made, lack of clear evidence of enhanced transfer in nature has led to limited acceptance of the work done for estimating CO_2 fluxes. These relationships have also not been reconciled with global constraints of air-sea gas transfer. Based on bomb-^{14}C invasion into the ocean [*Broecker et al.*, 1985], and more recently O_2/N_2 changes in the atmosphere combined with numerical models [*Keeling et al.*, 1998], there are robust, long-term oceanic gas

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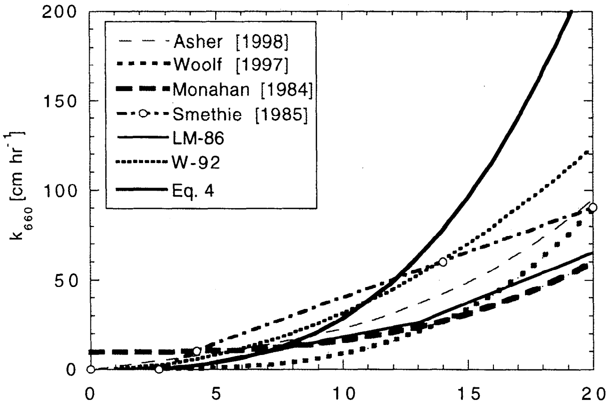

Figure 1. Gas exchange relationships for steady winds reported in the literature. They include the general relationships of *Smethie et al.* [1985], *Liss and Merlivat* [1986], *Wanninkhof* [1992], and the relationships including specific parameterization of bubble mediated processes of *Asher and Wanninkhof* [1998], *Monahan and Spillane* [1984], and *Woolf* [1997]. The thick solid line ($k = 0.0283\ u_{10}^3$) is the deconvolved cubic relationship using the global mean gas transfer rate determined from ^{14}C. Where applicable, a drag coefficient of 1.1×10^{-3} was used and all data were normalized to $Sc = 660$.

transfer constraints that must be fulfilled if relationships are applicable to determine global fluxes.

Here, CO_2 covariance flux and air-water ΔpCO_2 disequilibrium results, recently obtained on a cruise in the North Atlantic (Gas Ex-98), are used to suggest that a cubic dependence of short-term wind and gas transfer is plausible. We then estimate what the coefficient of a cubic dependency would be to reconcile the long-term k based on ^{14}C. The possible impact of such a dependency on global CO_2 fluxes is determined based on the CO_2 climatology of *Takahashi et al.* [1997].

Discussion

During the Gas Ex-98 cruise in June 1998, CO_2 covariance measurements were performed on hourly time scales over a period of several weeks in a strong CO_2 sink region in the North Atlantic (46°N, 20.5°W). The improved techniques used to measure the directional components of the wind, to correct for ship motion [*Edson et al.*, 1998], and to detect CO_2 in the marine boundary layer with a closed path sensor, along with large fluxes, led to the first covariance flux measurements over the ocean that can be reconciled with conventional bulk estimates [*McGillis et al.*, 1999] (W.R. McGillis and J. Edson, Quantifying the ocean CO_2 sink, submitted to *Nature*, 1999). The 1671 data points were bin averaged and plotted against wind speed, and corrected to 10 m height under neutral boundary conditions, u_{10}. Since a covariance measurement takes roughly 30 minutes, episodic high wind events can be captured with the method. In the Gas Ex-98 study, estimates using the dual-deliberate tracers, ^3He and SF_6 in the water (Fig. 2), and air gradient measurements of dimethyl sulfide and CO_2 are in overall agreement with the CO_2 covariance estimates. The entire covariance data set was fit with a quadratic and a cubic relationship. The quadratic dependence yielded $k_{660}\ (\pm 9.1) = 0.312\ (\pm 0.003)\ u_{10}^2$, $r^2 = 0.77$ while the cubic dependence has the form $k_{660}\ (\pm 8.3) = 0.0280\ (\pm 0.00023)\ u_{10}^3$, $r^2 = 0.81$. The numbers in parentheses are the standard errors. The k_{660} is the k normalized to Sc of 660 in cm hr^{-1} (which equals the Sc for CO_2 in seawater at 20°C). The correlation coefficient and uncertainty in k_{660} is slightly better for the cubic dependence and the cubic relationship yields a better fit with the binned data (Fig. 2).

To determine if this is a reasonable fit compared to the global average k obtained from the bomb-^{14}C inventory in the ocean ($u_{10av} = 7.4$ m s^{-1}, $k_{av} = 22$ cm hr^{-1} [*Broecker et al.*, 1985]), a deconvolution of the global wind speed spectrum is performed similarly as in W-92. The global wind distribution closely follows a Weibull probability distribution function $P(u)$:

$$P(u) = u[\exp(-u^2/2\Delta u^2)]/[2\pi\, \Delta u^2] \qquad (2)$$

where $\Delta u = u_{av}\,(\pi/2)^{-1/2}$, u is the steady (or short-term) wind, and u_{av} is the climatological wind speed.

Assuming a cubic dependency of the form $k = a\,u^3$, the coefficient "a" can be determined according to:

$$a = \left\{k_{av}/\sum\ [P(u)u^3]\right\} \qquad (3)$$

The resulting equation is:

$$k = 0.0283\ u_{10}^3\ (Sc/660)^{-1/2} \text{ (steady/short-term wind)} \qquad (4)$$

which is in very good agreement with the covariance results obtained during Gas Ex-98 (Fig. 2).

Based on the theoretical and laboratory studies referenced above, we hypothesize that the stronger dependence at high

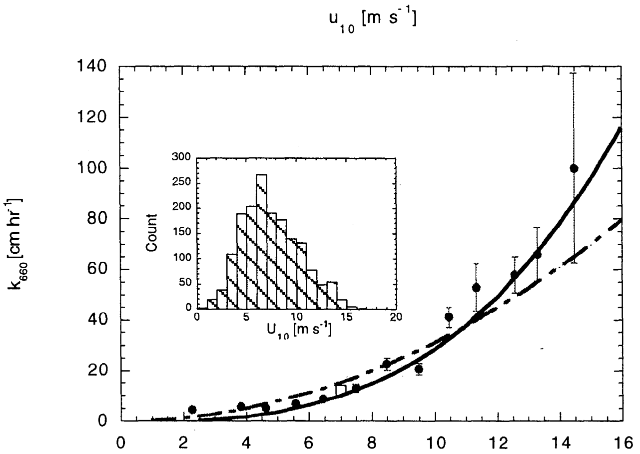

Figure 2. Comparison of fits to field data. The solid circles are the CO_2 covariance flux results from Gas Ex-98 with error bars signifying the 1-sigma uncertainty. The open square is the average k obtained from the dual deliberate tracer study during Gas Ex-98. The dashed line is a least squares quadratic fit through the 1671 covariance data points (not shown) and fortuitously corresponds to the quadratic fit proposed in W-92. The thick solid line is the best cubic fit through all the CO_2 covariance data and corresponds to the deconvolved short-term cubic relationship using the global mean gas transfer rate (eq. 4). The insert shows the distribution of CO_2 covariance datapoints with wind speed.

winds is caused by bubble entrainment while the weaker dependence at lower winds is attributed to retardation by surfactants. *Frew* [1997] showed that surfactants are prevalent in the ocean and that surfactant concentration equaling less than is necessary to form a mono-molecular microlayer can significantly retard gas exchange at low to intermediate winds. Bubbles are thought to enhance gas transfer by exchange into or out of the bubbles and increase turbulence when the bubbles impinge upon the air-water interface [*McGillis et al.,* 1995; *Woolf,* 1997; *Asher and Wanninkhof,* 1998]. Gas transfer into or out of bubbles is a function of gas solubility, thus the proposed relationship is unique for CO_2. The temperature dependency of bubble enhanced CO_2 exchange is small. Based on the formulation of *Asher and Wanninkhof* [1998], the k of CO_2 changes by less than 5% from 0 to 30°C and eq. (4) should be applicable for CO_2 over the ambient temperature range.

The proposed relationship is for short-term (<day) or "steady winds." Frequently, long-term wind products, u_{10av}, are used in CO_2 flux calculations, which will have a different dependency. A relationship for longer time periods (>month) is developed by assuming a Weibull distribution for average wind speeds from 0-20 m s^{-1} and calculating the long-term gas transfer. The results are shown in Fig. 3 and can be fit to a polynomial of the form:

$$k_{av} = [1.09\, u_{10av} - 0.333\, u_{10av}^{2} + 0.078\, u_{10av}^{3}]\ (Sc/660)^{-1/2}\ \text{(long-term av. wind)} \qquad (5)$$

The inferred long-term relationship is strongly dependent on the assumptions of a Weibull wind distribution at high winds and that the cubic gas exchange-wind dependence holds at higher winds than were measured during Gas Ex-98 (15 m s^{-1}). The difference between the short-term (eq. 4) and long-term (eq. 5) relationship is a factor of two, while they differ by 25% for the W-92 relationship.

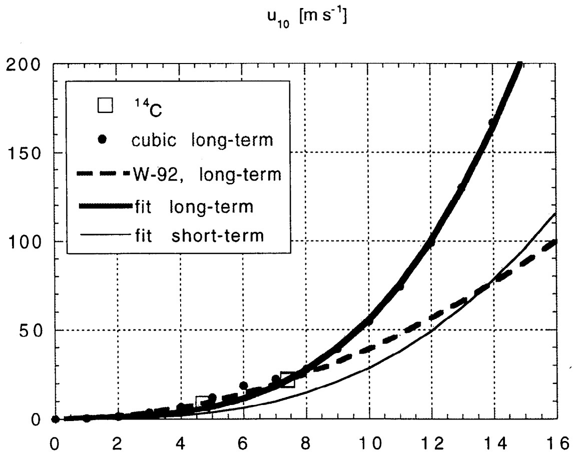

Figure 3. Summary of long-term relationships between k_{av} and u_{10av}. The open squares are the gas transfer velocities derived from bomb-^{14}C invasion. The solid circles are the k_{av} assuming a Weibull wind speed distribution function for a global average wind speed of 7.4 m s^{-1}. The solid line is the proposed long-term relationship (eq. 5). The dashed line is the long-term quadratic relationship in W-92, $k_{av} = 0.39\, u_{10av}^2$ and the thin line is the short-term relationship (eq. 4).

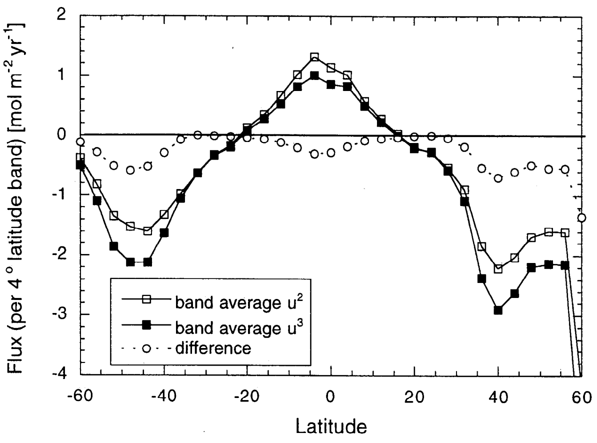

Figure 4. Comparison of the difference in global oceanic CO_2 uptake using the long-term W-92 relationship and (eq. 5) depicted in 4° latitude bands.

The implications of the revised dependency are far reaching for global CO_2 uptake. Using the monthly ΔpCO_2 climatology of *Takahashi et al.* [1997], the global CO_2 uptake increases from 1.4 Gigaton C yr^{-1} using the long-term W-92 relationship to 2.2 Gigaton C yr^{-1} using the proposed long-term relationship (eq. 5). The lower k_{av} compared to the W-92 relationship is in low wind speed regions with predominantly CO_2 outgassing while the higher k_{av} are in regions of high wind speeds with CO_2 uptake, thereby amplifying the influence of k_{av} on global CO_2 fluxes (Fig. 4). Although similar differences in annual CO_2 uptake have been observed using other relationships, the important difference with previous comparisons is that both the W-92 and (eq. 5) satisfy the same global ^{14}C constraint.

To validate this cubic dependency, more covariance studies are necessary, and the influence of the proposed parameterization on penetration of tracers with long air-sea equilibration times, such as ^{14}C and ^{13}C, should be studied in numerical ocean circulation models and compared to observations. Gas transfer becomes more of a rate-limiting step for these isotopes, and adjustments in the gas transfer velocities will show up in the penetration patterns and regional inventories of ^{14}C and ^{13}C. A caveat in our hypothesis is that results of dual deliberate tracer experiments using $^3He/SF_6$ [*Watson et al.,* 1991; Nightingale, pers. com.] yield significantly lower k at high winds than observed from the CO_2 covariance measurements. Because of the low solubility of these gases, their gas transfer should actually be enhanced over CO_2.

Conclusions

Based on recent results from a covariance flux study in the North Atlantic (Gas Ex-98), the gas transfer velocities can be well quantified with a cubic relationship $k = 0.0280\ u_{10}^3\ (Sc/660)^{-1/2}$. A cubic relationship can be reconciled with global constraints using the bomb-^{14}C inventory, assuming that the global wind distribution follows a Weibull relationship with a relationship $k = 0.0283\ u_{10}^3\ (Sc/660)^{-1/2}$. The relationship will increase the global annual uptake of CO_2 by 50% compared to the quadratic relationship of gas exchange with wind speed that was used in the global CO_2 flux estimate of *Takahashi et al.* [1997].

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