

Gas transfer velocities measured at low wind speed over a lake

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Abstract

The relationship between gas transfer velocity and wind speed was evaluated at low wind speeds by quantifying the rate of evasion of the deliberate tracer, SF₆, from a small oligotrophic lake. Several possible relationships between gas transfer velocity and low wind speed were evaluated by using 1-min-averaged wind speeds as a measure of the instantaneous wind speed values. Gas transfer velocities in this data set can be estimated virtually equally well by assuming any of three widely used relationships between k_{600} and winds referenced to 10-m height, U_{10} : (1) a bilinear dependence with a break in the slope at $\sim 3.7 \text{ m s}^{-1}$, which resulted in the best fit; (2) a power dependence; and (3) a constant transfer velocity for $U_{10} < \sim 3.7 \text{ m s}^{-1}$, with a linear dependence on wind speed at higher wind speeds. The lack of a unique relationship between transfer velocity and wind speed at low wind speeds suggests that other processes, such as convective cooling, contribute significantly to gas exchange when the wind speeds are low. All three proposed relationships clearly show a strong dependence on wind for winds $> 3.7 \text{ m s}^{-1}$ which, coupled with the typical variability in instantaneous wind speeds observed in the field, leads to average transfer velocity estimates that are higher than those predicted for steady wind trends. The transfer velocities predicted by the bilinear steady wind relationship for $U_{10} < \sim 3.7 \text{ m s}^{-1}$ are virtually identical to the theoretical predictions for transfer across a smooth surface.

The gas exchange of slightly soluble gases between surface waters and the atmosphere is driven by near-surface water turbulence (Donelan 1990). Wind is responsible for a significant portion of the turbulence in most surface waters and is quite easy to measure. As a consequence, gas exchange is often parameterized as a function of wind speed. When wind speeds are low, the relative contribution of wind to the overall turbulence in surface waters diminishes, and other factors, such as convective cooling (Crill et al. 1988) and chemical enhancement (for reactive gases) (Wanninkhof and Knox 1996), are thought to become increasingly important. As a consequence, the primary controls on gas transfer velocity are not well understood when wind speeds are low. This problem is exacerbated by the limited number of gas transfer velocity estimates that have been made in the field during periods of low wind. Among the only measurements are those of Emerson et al. (1973), Wanninkhof et al. (1985), Clark et al. (1995), and Cole and Cariaco (1998).

The quantification of gas transfer at low wind speeds is of importance for biogeochemical mass balance studies that involve gaseous species and for estimating volatile pollutant transfer in lakes and inland waters, where low wind speeds are common. In the open ocean, gas transfer at low wind

speeds contributes little to the overall gas transfer. However, the dependence is nonetheless important, because areas with low winds, such as the equatorial regions, have large air-water CO₂ concentration gradients and, thus, significant fluxes (Feely et al. 2002). Furthermore, the trend at lower winds indirectly constrains the trends at higher winds if the average transfer velocity is what is known. For instance, over the global ocean, average gas transfer velocities have been determined from the penetration of bomb ¹⁴C (Broecker et al. 1985). A weak dependence at low wind speeds will have to be compensated for by a stronger dependence at higher winds (and vice versa) to maintain the same global average. Largely because of the dearth of transfer velocity estimates at low wind speeds, a gas exchange experiment that used the deliberate tracer sulfur hexafluoride (SF₆) was carried out on Lake 302N, using an approach similar to that used in other studies (e.g., Wanninkhof et al. 1985; Clark et al. 1995; Cole and Cariaco 1998).

Experimental setting and methods

The experiment was carried out during the summer of 1987 on Lake 302N, a small (12.8 ha; mean depth, 5.7 m) oligotrophic lake within the Experimental Lakes Area in northwestern Ontario. Lake 302N is the northeastern portion of Lake 302, a dimictic lake that, at the time of the experiment, was divided in two at a narrow constriction by a polyethylene curtain, as part of a long-term acidification experiment. During the course of the experiment, the surface water pH remained close to 5.7 (Leavitt et al. 1999) because of intentional additions of HNO₃, whereas surface water temperatures varied from 16°C to 22°C and the thermocline depth increased from 4.5 to 8 m. The residence time of the lake water averages $\sim 5.8 \text{ yr}$ (Kelly et al. 1987). Further

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discussion of the water balance is presented in Rudd et al. (1990). The lake has a steep bathymetry, and there are no extensive shallow regions (Brunskill and Schindler 1971). The area deeper than 4 m spans 60% of the lake surface, and the area deeper than 7 m spans 40% of the lake surface (Brunskill and Schindler 1971).

Wind speeds were determined using a cup anemometer from Science Associates that was connected to a 10-register wind spectrum analyzer that registered the wind speed in 1 m s^{-1} bins at 1-min intervals. The threshold for startup of the anemometer was 0.75 m s^{-1} . The calibration of the anemometer was assessed by placing it, along with a Young propeller-type anemometer (considered a benchmark in marine weather observations), on top of a car and driving at low speed during periods of negligible wind. The car speed was determined by dividing the distance driven by the time. Wind speeds and car speeds assessed in this manner from 2.8 to 6.6 m s^{-1} differed by $<7\%$.

Wind speeds during the experiment were recorded from the center of lake 302N with the anemometer positioned at 1-m height. One-minute-averaged wind speed estimates were collected for each period during which the gas transfer velocity was estimated. For the purpose of intercomparison with other work, wind speed estimates were converted to a height of 10 m under the assumption of a neutrally stable boundary layer, a logarithmic wind profile, and a drag coefficient at 10-m height, C_{d10} , of 1.3×10^{-3} (Large and Pond 1981). The conversion to a wind speed at 10 m height was carried out according to

$$U_{10} = U_1 \left[1 + \frac{(C_{d10})^{0.5}}{k} \ln \left(\frac{10}{1} \right) \right] \quad (1)$$

(Donelan 1990), where U_{10} is the wind speed at 10 m height (in m s^{-1}), U_1 is the wind speed at 1 m height (in m s^{-1}), C_{d10} is the drag coefficient at a height of 10 m, and k is the Von Karman constant ($=0.4$). Using the constants listed yields the relationship $U_{10} = 1.22 \times U_1$.

SF_6 was introduced into the surface waters of the lake at the end of June 1987. A 4-liter glass bottle was filled with pure gaseous SF_6 and fitted with a rubber stopper that had one open hole and one hole fitted with a small-gauge needle. The bottle was lowered at the center of the lake to a depth of $\sim 2 \text{ m}$ (within the mixed layer or epilimnion). Hydrostatic pressure slowly forced water into the bottle, causing the SF_6 to bubble out slowly. This approach facilitated a slow injection with fine bubbles, which leads to a greater dissolution of SF_6 than other commonly used methods. For example, Clark et al. (1995) injected a pressurized mixture of SF_6 , ^3He , and N_2 through a diffusion stone while canoeing around the center of the pond and varying the release depth. Cole and Cariaco (1998) bubbled pure SF_6 through a plastic diffuser from a depth of 2 m. For our study, $>30\%$ of the injected gas dissolved, with the remainder escaping to the atmosphere. This estimate was derived from the known amount injected and the initial estimate of the amount of SF_6 dissolved in the lake, calculated from the bathymetry and the first measured concentration profiles after the gas was homogeneously distributed throughout the epilimnion.

The gas was observed to be homogeneously distributed

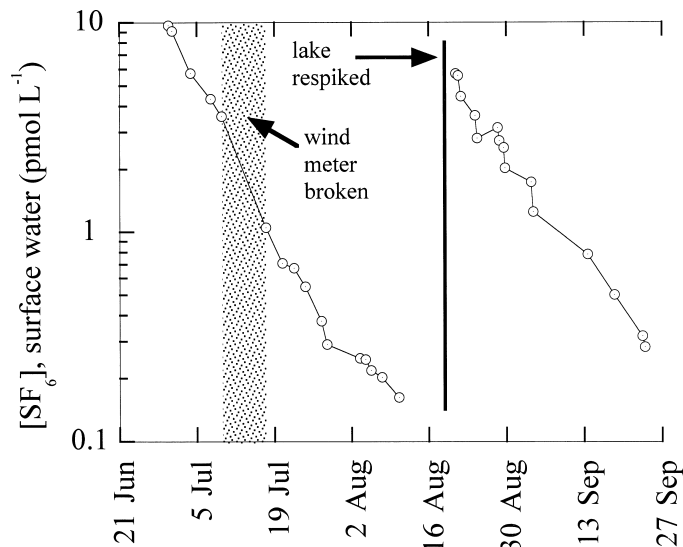


Fig. 1. Surface water SF_6 concentrations during the course of the gas exchange experiment on Lake 302N.

throughout the epilimnion within a few days of injection. This was determined by collecting and analyzing samples at points $\sim 10 \text{ m}$ from the shore in four different quadrants of the lake. The timescale for homogeneous distribution of this tracer was similar to that of other point-source tracer additions on lakes of similar size (Hesslein and Quay 1973). Indeed, spot samples and profiles taken at other locations during the experiment suggested that the spatial variation was less than the analytical error of 2%, such that a single profile in the center of the lake was sufficient for the analysis. The initial concentrations in the lake were $\sim 10 \text{ pmol L}^{-1}$ (see Fig. 1). Because concentrations decreased to near-undetectable levels after 2 months, surface waters were spiked a second time in mid-August, to facilitate the easy measurement of SF_6 , yielding concentrations of $\sim 6 \text{ pmol L}^{-1}$.

During the study, samples were taken from the center of the lake, using a Niskin bottle, by filling BOD bottles from the bottom and overflowing three times. Profiles were taken at 0.5–1 m depth intervals from the surface into the thermocline, below the level of measurable SF_6 , to estimate the integrated mass of SF_6 in the water column. Profiles were collected every 3–4 d, on average, during the course of the experiment, and surface water concentrations (obtained by submerging an open bottle at a depth of $\sim 15 \text{ cm}$, also at the lake center) were determined every 2–3 d, on average. Bottles were stored underwater and kept below ambient lake-water temperatures with the aid of coolers and a refrigerator, to avoid bubble formation until they could be analyzed by electron-capture gas chromatography.

The analytical method for determination of SF_6 is described by Wanninkhof et al. (1991). In brief, a predetermined amount of water was drawn into a syringe, and a known head-space volume of nitrogen gas was added. The syringe was shaken for 3 min, which transferred virtually all of the insoluble SF_6 into the gas phase. The head space of the syringe was then injected into an electron-capture gas

chromatograph. Concentrations were determined by comparing samples to a known standard. The detector response varies linearly with concentration over two orders of magnitude, from ~ 2 to 200 parts per trillion (Wanninkhof et al. 1991). Precision is on the order of 1%–2%, as determined from replicate analyses.

Average gas transfer velocities were determined for each interval between SF₆ profiles from the change in the integrated concentration of SF₆ in the water column using the method presented in Ledwell (1982), according to

$$k = \frac{\text{moles SF}_{6,i} - \text{moles SF}_{6,f}}{(t_f - t_i) \cdot A \cdot C_{\text{surf}}} \quad (2)$$

where k is the transfer velocity (in cm h⁻¹), t_i is the time of sample collection at the beginning of the interval, t_f is the time of sample collection at the end of the interval, moles SF_{6,i} is the total moles of SF₆ in the water at t_i (all in the mixed layer), moles SF_{6,f} is the total moles of SF₆ in the water at t_f (all in the mixed layer), A is the surface area of the lake (in cm²), and C_{surf} is the mean SF₆ concentration difference between surface waters and surface water in equilibrium with ambient SF₆ concentrations in air (in moles cm⁻³) during the time interval. The concentrations of SF₆ in equilibrium with air are three to four orders of magnitude smaller than the spiked water levels, such that the measured surface water concentrations can be used for C_{surf} without the need for an ambient air level correction. During the study, the mixed layer remained well mixed with respect to SF₆; hence, this approach was appropriate throughout the experiment. SF₆ loss from the lake outflow was negligible—the residence time of the lake water was ~ 5.8 yr, as estimated from the lake volume divided by the mean annual discharge (Kelly et al. 1987).

The overall uncertainties in the transfer velocity measurements were estimated by the propagation of cumulative uncertainties. These included the analytical uncertainty ($\pm 2\%$), the uncertainty in the mixed layer depth (up to $\pm 13\%$), and the uncertainty in the surface water SF₆ concentration change, which varied from plus or minus a few percent to $\pm 55\%$, depending on the measurement interval.

To facilitate comparison of these data with data from other experiments, transfer velocities were adjusted to a Schmidt number (Sc) of 600, where Sc is defined as the kinematic viscosity of water divided by the diffusion coefficient of SF₆. The value of $Sc = 600$ is the value for CO₂ at 20°C. For the normalization of Sc , which ranged from 850 to 1200 for the present study, a $-2/3$ power dependence of Sc was assumed below a wind speed of 3 m s⁻¹ (measured at 1-m height) under the assumption that the surface was smooth (Deacon 1977; Jähne et al. 1987), and a $-1/2$ power dependence of Sc was assumed above 3 m s⁻¹ for a surface with waves (Ledwell 1982, 1984; Jähne et al. 1984). These conversions were carried out according to

$$k_{600} = k_x \left(\frac{600}{Sc_x} \right)^{-2/3 \text{ or } -1/2} \quad (3)$$

where k_{600} is the transfer velocity adjusted to $Sc = 600$, k_x is the transfer velocity for Sc_x prior to the conversion, 600 is the value of Sc to which the data are to be adjusted, and

Sc_x is the value of Sc prior to conversion. The diffusion coefficients for SF₆ were estimated from the work of King and Saltzman (1995), and the kinematic viscosity values were from the CRC handbook (Weast 1981–1982).

Results and discussion

Surface water concentrations decreased monotonically from a value of ~ 10 pmol L⁻¹ ($p = 10^{-12}$) at the start of the experiment to ~ 0.1 pmol L⁻¹ by mid-August (Fig. 1, Table 1). A second addition of SF₆ to the lake increased surface water concentrations to ~ 6 pmol L⁻¹, after which they decreased to values of ~ 0.3 pmol L⁻¹ by mid-September. Profiles of SF₆ concentrations and 1-min-averaged wind speeds are provided in Web Appendix 1 at http://www.aslo.org/lo/toc/vol_48/issue_3/1010a1.pdf.

Average gas transfer velocities ranged from ~ 0.7 to ~ 5 cm h⁻¹ for average wind speeds between 0 and 3.7 m s⁻¹ (10 m height) and showed a generally increasing trend with wind speed (Fig. 2, Table 1). At the highest average wind speeds over a particular sampling interval of ~ 5.4 m s⁻¹, average transfer velocities reached values as high as 12 cm h⁻¹ (Fig. 2, Table 1). The average transfer velocity estimates at a given wind speed from this work are similar to those obtained from other lake experiments (Fig. 2), but this data set is unique in that it has a larger number of determinations at low wind speed (< 3.7 m s⁻¹) to characterize this interval. In all the studies shown in Fig. 2 the same anemometer was used, which facilitates comparison, but environmental conditions differed. The water temperatures during the Rockland Lake experiment (Wanninkhof et al. 1985) were 10°C colder, and the lake was eutrophic, with very high algal densities. The work of Clark et al. (1995) was carried out in an oligotrophic lake with water temperatures similar to those in the present study.

To determine a relationship between gas transfer and wind speed, the variability of the wind over the sampling interval must be accounted for. This was accomplished by deconvolving the wind speed distributions into “instantaneous” winds. Various relationships between the transfer velocity and instantaneous wind speed, which have appeared elsewhere in the literature (cited below), were explored using the binned 1-min wind speed averages as estimates of the instantaneous wind speed. For each function used, the fitting parameters were applied to each 1-min-averaged wind speed and the 1-min-averaged transfer velocity predictions were summed to generate an average transfer velocity prediction for the entire time interval between SF₆ measurements. The values of the fitting parameters were iteratively changed until the best estimates for each function were obtained by minimizing the sum of the squares of the differences between the predicted and the measured average transfer velocities. The best fit thus generated was assumed to be the steady-wind trend. One function chosen to fit the data was a bilinear trend with a weak dependence of transfer velocity on wind speed < 3.7 m s⁻¹ and a stronger dependence at > 3.7 m s⁻¹. The weak wind speed dependence at low wind speeds follows the theoretical prediction of gas transfer across a smooth surface (Deacon 1977), whereas the stronger depen-

Table 1. Data from the gas exchange experiment on Lake 302N. Data in the six right-most columns are average values over each measurement period. The vertical position of these six columns is thus offset from the vertical position of the two left-most columns, to reflect this. Profiles of SF₆ concentrations and 1-min-averaged wind speeds are provided in Web Appendix 1, at http://www.aslo.org/lo/toc/vol_48/issue_3/1010a1.pdf.

Date, time	$\mu\text{moles SF}_6$	Surface concentration (pmol L ⁻¹)	Surface temperature (°C)	U_{10} (m s ⁻¹)	k_{measured} (cm h ⁻¹)	k_{600} (cm h ⁻¹)	Error bar ₆₀₀ (cm h ⁻¹)
Jun 29, 0800 h	4,080	9.3	20	0.95	0.64	0.86	0.90
Jun 30, 1030 h	3,970	7.0	20	1.78	1.38	1.88	0.33
Jul 03, 2000 h	2,960	4.8	21	1.78	0.96	1.26	0.23
Jul 07, 1030 h	2,450	3.6	22	1.84	2.23	2.83	0.49
Jul 09, 1030 h	1,870	1.8	22		2.9	3.68	2.05
Jul 17, 1045 h	633	0.8	20		2.44	3.33	0.88
Jul 20, 1000 h	453	0.67			1.99	2.62	0.26
Jul 24, 1400 h	282	0.28	22	1.88	1.36	1.48	0.27
Aug 07, 1100 h	143						
Aug 20, 2030 h	3,230	5.7	21	1.64	3.36	4.41	1.59
Aug 21, 0630 h	2,980	4.85	21	5.0	7.38	9.06	1.21
Aug 21, 2020 h	2,340	3.8	20.5	1.50	0.8	1.07	0.14
Aug 28, 1000 h	1,740	2.8	19	4.52	5.16	6.67	2.44
Aug 28, 0430 h	1,620	2.6	19.5	2.83	3.42	4.74	0.91
Aug 29, 1230 h	1,400	2.2	19.3	5.43	9.03	11.4	3.0
Aug 29, 1830 h	1,240	1.85	19.5	2.40	1.43	1.97	0.26
Sep 03, 1200 h	880	1.4	17.7	5.11	8.24	11.0	2.4
Sep 03, 1900 h	750	0.93	17.8	1.71	1.17	1.71	0.38
Sep 13, 1400 h	421	0.6	16.6	1.56	1.42	2.18	0.40
Sep 18, 1000 h	293	0.38	16.6	2.62	1.62	2.48	0.68
Sep 23, 1000 h	200	0.29	15.6	3.47	3.73	5.27	2.08
Sep 23, 2000 h	184						

Note that the anemometer malfunctioned from 09 to 24 July. We did not use the transfer velocities measured during that period.

dence at higher wind speeds is due to the onset of capillary waves (Jähne et al. 1984). This form was also assumed in the often-used relationship of Liss and Merlivat (1986). The equations used to define the bilinear steady wind trend can be expressed as follows:

$$k_{\text{predicted, average}} = \frac{\left\{ \sum_{u=0}^3 (a \cdot u \cdot t_u) + \sum_{u=3}^{\infty} [b(u-3) + 3a] \cdot t_u \right\}}{t_{\text{total}}} \quad (4)$$

where a is the slope of the steady wind trend for wind speeds $< 3.7 \text{ m s}^{-1}$ (in $\text{cm h}^{-1}/\text{m s}^{-1}$); b is the slope for wind speeds $> 3.7 \text{ m s}^{-1}$ (in $\text{cm h}^{-1}/\text{m s}^{-1}$); u is the 1-min-averaged wind speed (in m s^{-1}), defined as the midpoint of the 1 m s^{-1} anemometer bin interval; t_u is the time at a given wind speed during the measurement interval (in min); and t_{total} is the total time of the measurement interval (in min). As discussed earlier, the slopes a and b were altered iteratively until the sum of the squares of the differences between the predicted and the measured average transfer velocities was minimized.

The best fit for this bilinear relationship shows good correspondence between measured and predicted values (Fig. 3A; $r^2 = 0.94$). The trends can be expressed as

$$\text{for } U_{10} < 3.7 \text{ m s}^{-1} \quad k_{600} = 0.72U_{10} \text{ cm h}^{-1} \quad (5)$$

$$\text{for } U_{10} \geq 3.7 \text{ m s}^{-1} \quad k_{600} = 4.33U_{10} - 13.3 \text{ cm h}^{-1} \quad (6)$$

Note that the break in slope occurs at a wind speed (U_{10}) of 3.7 m s^{-1} , which is similar to the value of 3.6 m s^{-1} suggested by Liss and Merlivat (1986). However, the slopes of the two line segments proposed by Liss and Merlivat, 0.17 and 2.85, respectively, are quite different from those in our relationship.

Another relationship between wind speed and transfer velocity that was explored was a power-law dependence similar to those proposed by Wanninkhof et al. (1991) and Nightingale et al. (2000). Such a relationship is a modification of the bilinear relationship that recognizes that the break from weak to strong wind speed dependence is believed to occur at the onset of capillary waves, which can vary with wind speed because of variations in fetch, the presence or absence of organic surface films, etc. The power-law dependence also yielded good agreement between measured and predicted results (Fig. 3B; $r^2 = 0.93$), although the sum of the square of the differences between measured and predicted results was $\sim 10\%$ higher than that for the bilinear trend, with a change in slope at $\sim 3.7 \text{ m s}^{-1}$. The power function that best fits the data is

$$k_{600} = 0.228U_{10}^{2.2} + 0.168 \quad (7)$$

A third relationship suggests that the transfer velocity is constant at low wind speeds (McGillis et al. 2001); hence, a relationship that assumed that k is constant for $U_{10} < 3.7$

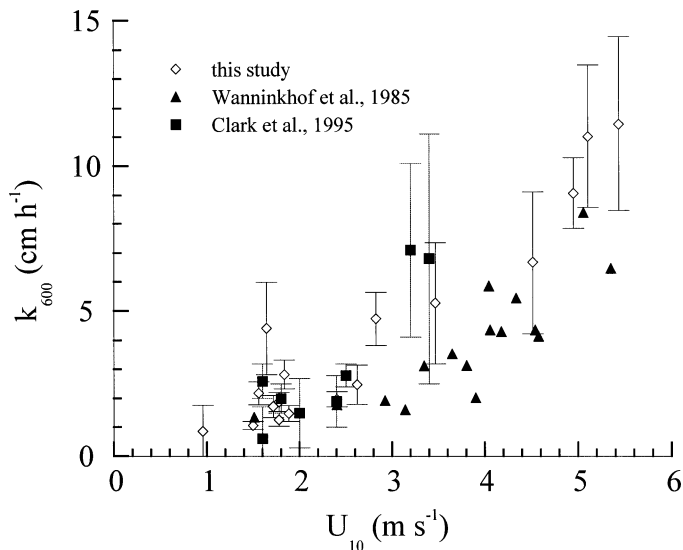


Fig. 2. Gas transfer velocities from the present work and two other lake experiments with significant data at low wind speeds, plotted vs. wind speed. Data are from the present work, Clark et al. (1995) from Sutherland Pond (New York), and Wanninkhof et al. (1985) for Rockland Lake (New York). Note that no error bars were provided by Wanninkhof et al.; hence, they are not plotted. Data from the study by of Upstill-Goddard et al. (1990) are not included because of questions regarding the wind speed conversions in their work (Kwan and Taylor 1993; Upstill-Goddard et al. 1993).

m s^{-1} and is linearly dependent on k at higher wind speeds was also explored. Such a relationship might result if a steady, non-wind speed-driven turbulence was primarily driving gas exchange when wind speeds are low. This relationship also yielded good agreement between measured and predicted results (Fig. 3C; $r^2 = 0.93$), although the sum of the square of the differences was $\sim 7\%$ higher than that for the bilinear trend, with a change in slope at $\sim 3.7 \text{ m s}^{-1}$. The best fit for the trend was

$$\text{for } U_{10} < 3.7 \text{ m s}^{-1} \quad k_{600} = 1.0 \text{ cm h}^{-1} \quad (8)$$

$$\text{for } U_{10} \geq 3.7 \text{ m s}^{-1} \quad k = 5.14U_{10} - 17.9 \text{ cm h}^{-1} \quad (9)$$

Other functions did not fit the data as well, including a linear trend through all the data forced through the origin and a linear trend not forced through the origin ($r^2 = 0.89$ for each; Fig. 3D). Moreover, the linear fit through the origin significantly overestimated the transfer velocity at low wind speeds (Fig. 3D). The linear trend that does not pass through the origin yielded a transfer velocity estimate of zero at a wind speed of $\sim 0.8 \text{ m s}^{-1}$, which is inconsistent with previous work. Also, a bilinear trend with a slope change at 3.7 m s^{-1} provided a better fit than bilinear relationships with a slope change at higher or lower wind speeds. For instance, for the trend with the slope change at a wind speed of 2.4 m s^{-1} , the sum of the square of the differences was 25% higher than that for the trend with a slope change at 3.7 m s^{-1} .

For the bilinear trend with a change in slope at 3.7 m s^{-1} , the slope of the portion below $\sim 3.7 \text{ m s}^{-1}$ was higher than has been suggested by previous field studies (Wanninkhof et

al. 1985) but showed excellent agreement with the theoretical prediction by Deacon (1977) for gas transfer over a smooth surface (Fig. 4). The trend from the present work may be closer to the theoretical prediction than that of other studies because of the lack of any significant organic film on the Lake 302N water surface. Depression of gas transfer velocities by organic films has been observed elsewhere (Frew et al. 2002) and may have led to lower transfer velocities during the study by Wanninkhof et al. (1985). Moreover, the relationship at low wind speed was not well constrained by many data in the work of Wanninkhof et al. It is also worth noting that the trend below $\sim 3.7 \text{ m s}^{-1}$ from the present work on Lake 302N lies in the middle of the observed range of wind tunnel data (Fig. 4). However, the parameterizations derived from the present work for wind speeds in the range of $0\text{--}1 \text{ m s}^{-1}$ yielded transfer velocities lower than those observed by Liss et al. (1981).

The relationships described above (Fig. 3A–C) each resulted from different assumptions about the mechanisms controlling k at low wind speeds (as discussed earlier). However, we were unable to discern which one is most applicable from the data at hand. Future studies should include near-surface turbulence measurements and/or more rapid response measurements of k , such as eddy correlation techniques (McGillis et al. 2001).

The good agreement between measured and predicted k using all three relationships implies that average transfer velocities are related to wind speed even in areas of low wind. This conclusion differs from the recent work of Cole and Cariaco (1998), who did not see a dependence between transfer velocity and wind speed at wind speeds $< 3 \text{ m s}^{-1}$ (U_1). The difference in interpretation stems largely from the assumed nonlinearity in all of the relationships examined between transfer velocity and wind speed and the different timescales of the wind speed estimates used in the two studies. The present study relied on 1-min-averaged wind speeds, whereas the work of Cole and Cariaco used weekly averaged wind speeds (although the data were measured hourly). For any nonlinear relationship between k and wind speed in which k increases more strongly with increasing winds, points on the trend of average k versus average wind speed will be higher than those for steady wind, particularly in the wind speed region of the slope change. This can be conceptualized from Fig. 3A–C, under the assumption of an extreme situation in which there is no wind for half the sampling period and a 6 m s^{-1} wind for the other half. The gas transfer velocity for the average wind of the period of 3 m s^{-1} will lie on a line halfway between the gas transfer values at 0 and 6 m s^{-1} , well above the suggested steady wind parameterizations. Thus, at the typical low average wind speeds encountered on most lakes, the variability of instantaneous wind speeds that contribute to the average will lead to varying, and higher, average estimates of k and may obscure any dependence of k upon U (Livingstone and Imboden 1993). Indeed, this effect is readily observed in the data set presented in the present work, in that all measured average values of k fall above those predicted for steady wind due to this effect (Fig. 3A–C), regardless of the form of the relationship for low wind speeds. Despite this, the predicted values of k generated using the 1-min-averaged wind speeds

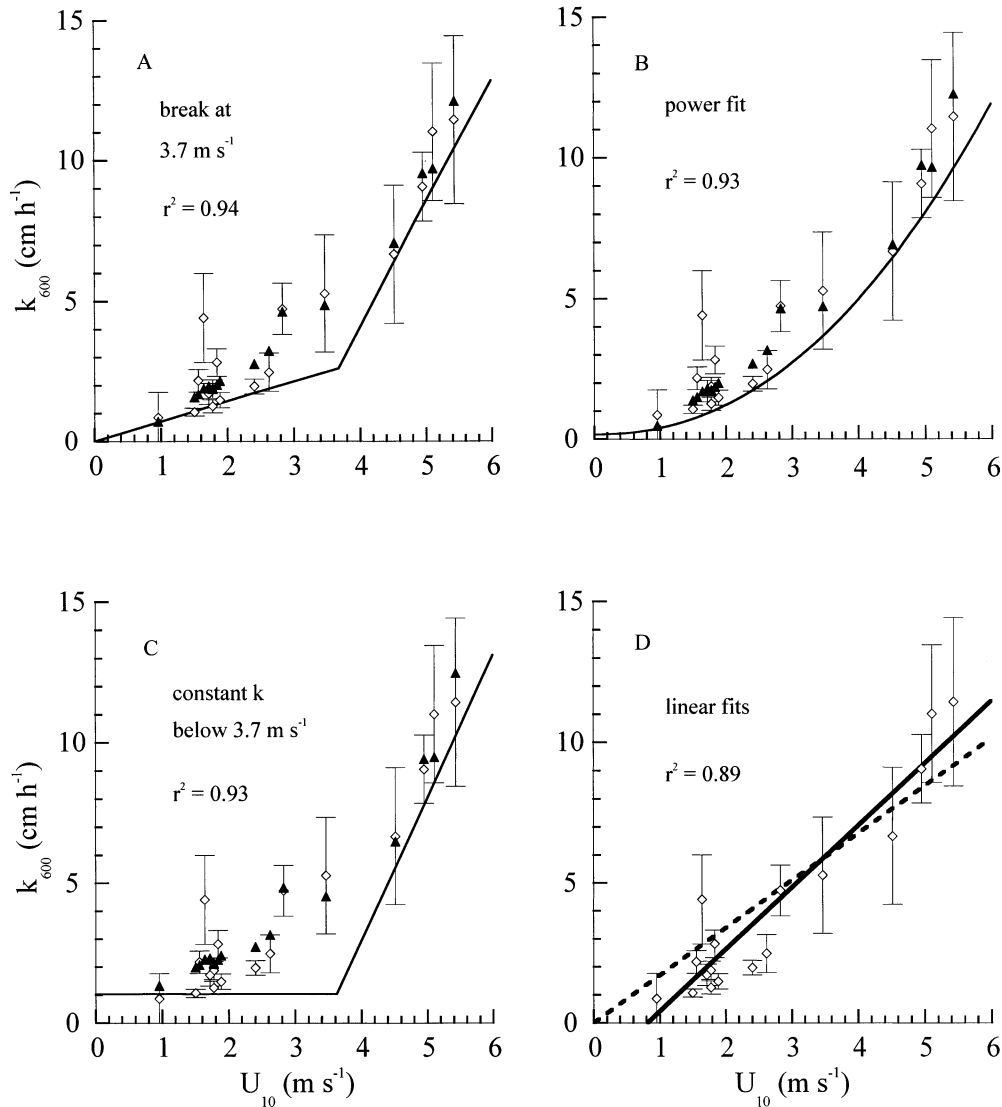


Fig. 3. Best-fit “steady wind trends” (solid lines) estimated from 1-min-averaged wind speeds (under the assumption of a 10-m height), measured average transfer velocities (white diamonds), and average transfer velocities predicted from 1-min-averaged wind speeds (black triangles). Error bars are estimated as discussed in the Experimental setting and methods section. Trends include (A) a bilinear trend with a slope break at 3.7 m s^{-1} , (B) a power fit, (C) constant k below 3.7 m s^{-1} with a linear trend at higher wind speeds, and (D) linear fits through the origin (dashed line) and not forced through the origin (solid line). Note that, for the linear fits, the predicted averages fall on the line; hence, they are not highlighted by symbols.

agreed well with the measured average k values, which suggests that, in an environment with low average wind speeds, occasional periods of elevated winds can increase the average transfer velocity significantly.

However, it is worth pointing out that some of the measured transfer velocity estimates exceeded the prediction by more than our estimate of the uncertainty (Fig. 3A–C). This may well imply that processes other than wind speed, such as convective cooling and rain, also affected the gas transfer velocity during these periods, as has been suggested by other workers (Crill et al. 1988; Ho et al. 1997; Cole and Cariaco 1998).

In conclusion, no strong dependence of gas transfer ve-

locity on wind speed was apparent for low wind speeds ($U_{10} < 3.7 \text{ m s}^{-1}$). The variability of the observed transfer velocities in this range is assumed to be a function of the stronger dependence of gas transfer on winds for the (short) periods of higher winds contributing to the average over the intervals. Gas transfer velocities in this data set can be estimated comparably by assuming any of three relationships between k_{600} and U_{10} : (1) a bilinear dependence with a break in the slope at $\sim 3.7 \text{ m s}^{-1}$, (2) a power dependence, and (3) a constant transfer velocity when $U_{10} < 3.7 \text{ m s}^{-1}$ and a linear relationship when $U_{10} \geq 3.7 \text{ m s}^{-1}$. The lack of a unique relationship between transfer velocity and wind speed at these low wind speeds may mean that other processes,

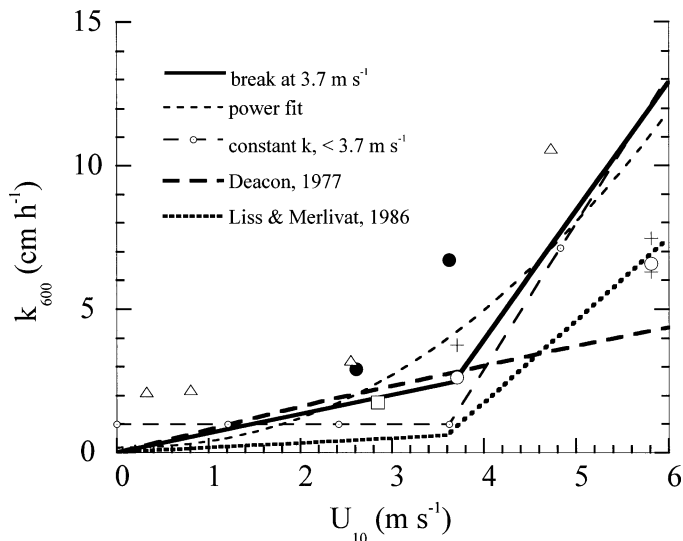


Fig. 4. Comparison of the relationships between transfer velocity and steady wind speed explored in the present work, with the theoretical prediction for gas transfer over a smooth surface of Deacon (1977) and the trend of Liss and Merlivat (1986). Also shown are wind tunnel data, including those of Liss (1981; white triangles), Broecker et al. (1978; black circles), Jähne et al. (1985; white squares), and Wanninkhof and Bliven (1991; crosses are SF₆ and white circles are N₂O). All data were converted to k_{600} and U_{10} (see Experimental setting and methods section), to facilitate comparison.

such as convective cooling, contribute to gas exchange when wind speeds are low. However, the nonlinearity in each relationship tested, coupled with the typical variability in instantaneous wind speeds observed in the field, leads to average transfer velocity estimates that are higher than those predicted for the steady wind trends. The average transfer velocities can be predicted well from the 1-min-averaged wind speeds, largely because of occasional brief intervals of strong wind that drive the elevated transfer velocities. For this reason, it is critical to consider the distribution of instantaneous wind speeds when estimating transfer velocity during periods of low wind.

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