Multiple approaches to estimating air-water gas exchange in small lakes

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Abstract

The rate of gas exchange between air and water is an essential quantity in a number of contexts, from mass balances to the calculation of whole-system metabolism. The exchange of a gas between water and the atmosphere is controlled by differential partial pressures of gases in air and in water (both straightforward to measure) and by the amount of turbulent energy exchange between the air-water interface, the measurement of which is neither simple nor direct. This physical exchange is often expressed as a piston velocity (k). We compared four methods for estimating k in a series of small (0.3 to 45 ha), low-wind (mean wind < 3 m s^{-1}) lakes: 1) floating chambers using ambient CH_4; 2) whole-lake SF_6 additions; 3) three wind-based models from the literature; and 4) C mass balances constrained by whole-lake ^{13}C additions. All of the methods, with the exception of one wind-based model, converged on values for k_{600} of between 0.35 and 0.74 m d^{-1} with no biases among methods. The floating chambers, if designed properly, are a cost-effective way of obtaining site-specific values of k for low wind lakes over fairly short time frames (hours).

The flux of gases across the air-water interface is a key process in biogeochemistry affecting both the water body and, depending on system scale, the atmosphere (Wanninkhof 1992). Estimating the magnitude of these gas fluxes is useful in a number of contexts and studies including: measurement of open ocean primary production using oxygen isotopes (Luz and Barkan 2000); the role of oceans in the control of CO_2 (and other greenhouse gasses) in the atmosphere (McGillis et al. 2001; Takahashi et al. 2002); the role of inland waters in regional (Billett and Moore 2008) or global C cycle (e.g., Richey et al. 2002; Cole et al. 2007; Bastviken et al. 2008) air-sea exchange of toxic volatiles such as mercury (Mason et al. 1994); or whole system metabolism estimates for individual lakes or rivers (Hanson et al. 2004; Van de Bogert et al. 2007).

The actual physics of gas exchange is complex (MacIntyre et al. 1995). Nevertheless, the diffusive transfer of gases to or from aquatic surfaces can be adequately described using the equation:

$$F = k(C_{sur} - C_{eq}) \tag{1}$$

where *F* is the flux (e.g., mmol m^{-2} d^{-1}); *k* is the piston velocity (e.g., m d^{-1}) which can be conceptualized as the depth of the water column equilibrating with the atmosphere per unit time; and C_{sur} and C_{eq} are actual surface water and air-equilibrium concentrations, respectively, of the gas in focus (Jähne et al. 1987; MacIntyre et al. 1995). Three components are required to calculate the diffusive flux. While the first two, C_{sur} and C_{eq}, can be obtained by measurements of air and surface water gas concentrations, temperature, and pressure, the third, *k*, is more difficult to assess and is, in theory, a function of turbulent energy exchange between the surface water and the atmosphere (e.g., McKenna and McGillis 2004). However, from studies in which C_{sur}, C_{eq}, and *F* have been simultaneously measured, *k* can be calculated. This work has generated extremely useful, empirically determined estimates of k (e.g., Wanninkhof 1992; Wanninkhof and McGillis 1999). Measured values of *k* vary, as theory predicts, with both the gas in question and the temperature. The variation of *k* values

among gases and temperatures are related via the Schmidt number for each gas (the ratio of kinematic viscosity of water and the gas diffusion coefficient; Jähne et al. 1987). Thus, a *k* value determined for one gas can be used to calculate *k* values for other gases and other temperatures (*see* "Methods" section).

Several approaches have been used to estimate *k* values in lakes as summarized by Matthews et al. (2003), which include additions of inert tracers such as SF_6 (Wanninkhof 1985; Wanninkhof 1992; Clark et al. 1994, 1995; Cole and Caraco 1998); floating chambers (e.g., Marino and Howarth 1993; Engle and Melack 2000; Kremer et al. 2003; Matthews et al. 2003; Bastviken et al. 2004; Borges et al. 2004); and existing empirical relationships between wind speed and *k* from the literature (e.g., Wanninkhof 1992; Clark et al. 1994, 1995; Cole and Caraco 1998; Crusius and Wanninkhof 2003; Jonsson et al. 2008). In these empirical wind relationships, scientists use measured values of *k* (from a variety of approaches) for systems that experience different ranges of wind speeds and attempt to derive a generalized relationship between wind speed and *k*. All these approaches have flaws. For the empirical models between wind and *k*, wind is really a proxy for turbulent energy exchange with the atmosphere. First, there can be other causes of turbulence such as currents or convection. Further, local conditions such as fetch, stratification, roughness, or surrounding vegetation can alter the way in which wind is translated into turbulent energy. For example, Jonsson et al. (2008), using eddy-flux towers on a large lake (3.8 km²) found much higher values of *k* for given wind speeds than is usually reported for small (< 50 ha) lakes. This problem is particularly severe in small, partly wind-sheltered aquatic environments, which are very common globally (Downing et al. 2006) because *k* seems to be more or less independent of wind and difficult to predict below wind speeds of 2 or 3 m s⁻¹ (Crill et al. 1988; Clark et al. 1995; MacIntyre et al. 1995; Ho et al. 1997; Cole and Caraco 1998). Further, these numerous small lakes can be significant to the regional balance of both CO_2 and CH_4 in some lake-rich areas (Billett and Moore 2008). For all these reasons, it would be useful to have site-specific values of *k*.

Floating chambers are easy to deploy at multiple sites but are infrequently used because of drawbacks, particularly the formation of microenvironments within the chambers or altered turbulence at the air-water interface. Matthews et al. (2003) reported results indicating that their flux chambers substantially overestimated *k* compared with other methods, but also carefully analyzed potential causes for this and provided valuable recommendations for future chamber studies.

In this study, we compared *k* estimates for a series of lakes in northern Michigan using several methods: floating flux chamber measurements of methane (CH_4) flux; a whole-lake SF_6 addition; three different wind speed models; and a carbon mass balance model constrained by whole lake ¹³C-bicarbonate additions. We found that by using design modifications suggested by Matthews et al. (2003) the flux chamber approach for CH_4 represents an effective way to determine system specific *k* values without significant bias in these small, sheltered lakes; these chambers are not designed for use in flowing waters. Further, by evaluating *k* using multiple methods, we can provide greater confidence for approximating values of *k* where no measurements are available, especially in numerous small, forested lakes of the temperate environment.

Materials and procedures

Study site—Our measurements of *k* were performed in lakes at the University of Notre Dame Environmental Research Centre (UNDERC) near Land O' Lakes, WI, USA (89°32′W, 46°13′N). These lakes are situated in one of the most lake-rich districts in the United States and the lakes are representative of a large area in the north temperate regions of the world (Marin et al. 1990). The minimal topography consists of rolling hills with extensive bogs and low-lying forests (Webster et al. 1996) resulting in wind-sheltered lake shores. Of the lakes in this study, many of the lakes have been well quantified in terms of hydrology and chemistry (Cole and Pace 1998; Pace and Cole 2002) and lake area varied between 0.3 to 32.9 ha (Table 1), and mean wind speeds are <3 m s⁻¹ (Table 2).

The floating chamber approach—Floating flux chambers (Fig. 1) (0.03 m², 5 L, polyethylene/Plexiglas) were deployed on all the 10 lakes in Table 1 resulting in 256 independent flux estimates covering 52 dates during 3 y. The number of individual chamber measurements in each lake is shown in Table 1. We took the following measures to minimize the risk of biased estimates of *k*, including some recommendations from Matthews et al. (2003):

The chamber walls extended approximately 3 cm into the water. Previous studies using chambers flush with the water surface have uncertainties regarding what area is actually covered by chambers, and these flush chambers may induce a greater disturbance at the air water boundary layer.

The chamber measurements were performed for full 24-h cycles because short-term measurements (e.g., 30 min) during the day can be highly variable due to diurnal variability in fluxes and water turbulence (2 fold difference between day and night fluxes; Bastviken et al. 2004). Further, 24-h measurements allow better comparison with our other methods that integrate over longer time periods.

Chambers were placed in transects from shore to the center of the lakes to capture heterogeneity in turbulence patterns as well as other processes that may influence gas flux (e.g., ebullition).

Unlike Matthews et al. (2003), we did not assume linear increase in chamber gas concentrations over time, but accounted for declining flux due to increasing head space concentrations in our underlying model and calculations.

Gas samples of the air enclosed by the chamber were withdrawn by syringe through a butyl rubber stopper on the top of the chambers immediately after placing them on the lake, and again at the end of the measurement period. Surface water CH_4 concentrations were measured by headspace extraction as

Table 1. Lake area, surface water concentrations of key constituents (dissolved organic carbon (DOC), total phosphorous (TP), pH, and CH_4), and the number of individual flux chamber estimates of k ($n_{chambers}$) in the studied lakes. Note that $n_{chambers}$ denotes the number of chambers receiving diffusive flux only after discounting other chambers receiving bubble flux as well (*see* "Methods"). pH values are from multiple sources: for Brown, Crampton, Hummingbird, Morris, North Gate Bog, Roach and Tuesday, values are annual means for 1995-2003 (*see* Pace and Cole 2002 for methods); for Paul and Peter values are for 2001 in Carpenter et al. 2005; values for East Long are reported in Cole et al. 2002. CH_4 concentrations are means from Bastviken et al. 2004.

Lake	Area (ha)	Z_{max} (m)	pH	CH_4 (μmol L^{-1})	DOC (mg L^{-1})	TP (μmol L^{-1})	$n_{chambers}$	Chamber k_{600} (m d^{-1})
Brown	32.9	5.5	8.2	0.8	7.9	1.13	5	0.49 ± 0.10
Crampton	25.8	15.2	6.2	0.4	3.7	0.24	18	0.41 ± 0.09
East Long	2.3	13.2	5.2	0.7	12.1	1.22	15	0.51 ± 0.10
Hummingbird	0.8	7.6	4.9	0.7	22.0	1.09	16	0.32 ± 0.05
Morris	5.9	6.7	7.4	1.2	12.7	0.62	15	0.50 ± 0.03
North Gate	0.3	8.0	4.3	0.3	21.3	0.46	10	0.53 ± 0.09
Paul	1.7	15.0	6.4	2.2	3.1	0.38	32	0.39 ± 0.07
Peter	2.7	19.6	6.9	1.3	4.5	0.25	105	0.41 ± 0.09
Roach	45.0	9.1	5.8	0.3	2.7	0.19	15	0.51 ± 0.12
Tuesday	0.9	15.0	6.1	0.3	7.6	0.29	25	0.40 ± 0.11

Table 2. Summary of wind measurements at 5-min intervals for Peter Lake 2002 (43 d during the SF$_6$) addition and 71 d Crampton Lake 2005 (for the ^{13}C addition). Values are expressed as ms^{-1} corrected to a height of 10 m.

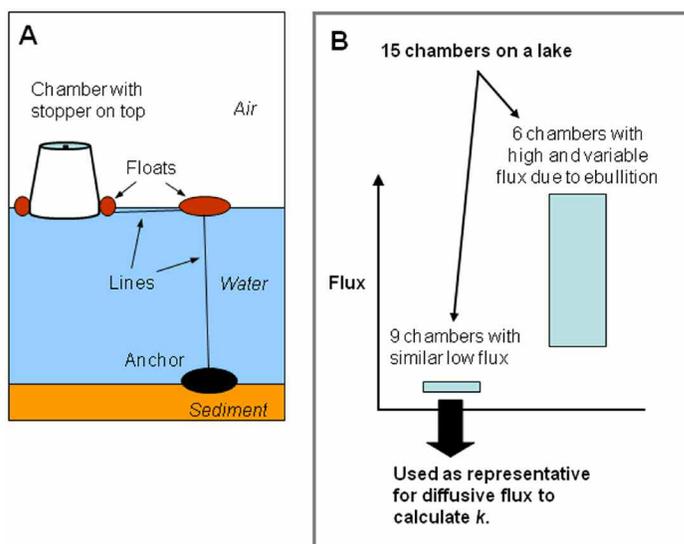| Wind statistic (m s^{-1})	Peter Lake 2002	Crampton Lake 2005
Mean	1.28	1.63
Median	1.23	1.52
Standard deviation	0.89	0.96
Minimum	0	0
Maximum	4.72	8.18
Number of observations	12,414	20,418

Fig. 1. A: Diagram of the floating chambers used in this study made from 5-L plastic buckets. The chambers had an inner radius of 0.2 m at the end sitting in the water and walls extended 3 cm below the water surface. The anchor was attached to a separate float connected to the chamber to avoid the gases released near the anchor reaching the chamber. B: Conceptual diagram of how the flux rates and variability among chambers can be used to assess if the flux was only diffusive. The bars in the graph represent the whole range of the flux measurements for the 2 groups of chambers.

described in detail in Bastviken et al. (2004). Gas samples were stored in evacuated vials and analyzed within 24 h by gas chromatography using a flame ionization detector (Shimadzu GC-8, Poropack N column). Temperature, measured using a calibrated mercury thermometer, and surface water CH_4 concentrations were measured at the location of each chamber.

The diffusive flux of gas into the chamber is not linear with time because of the dependence on the concentration difference, which will decrease with time, as the partial pressure in the head-space begins to approach the partial pressure in the water. However, assuming that the all other terms in the equation remain constant over time, it is possible to derive an analytical solution to determine k. Therefore, we solved for k as follows. Flux into the chamber is represented as the mass of gas moving across the area of the chamber (A, m^2) intersecting the water surface, over time:

$$F = \frac{dM}{dt \cdot A}. \tag{2}$$

By substituting into Eq. 1 (and converting to mass and concentration to partial pressures),

$$\frac{dP}{dt} = k \cdot \frac{K_h \cdot R \cdot T \cdot A}{V} \cdot (P_w - P), \tag{3}$$

where P_w and P are the partial pressures (Pa) of methane in the water and chamber, respectively. V is the chamber volume (m^{-3}), R is the gas constant (8.314 m^3 Pa K^{-1} mol^{-1}), T is the temperature (K), and K_h is the Henry law constant for methane (moles m^{-3} Pa^{-1}). Integrating Eq. 3 results in

$$k = \frac{V}{K_h \cdot R \cdot T \cdot A} \ln\left(\frac{P_w - P_i}{P_w - P_f}\right) \Big/ (t_f - t_i), \qquad (4)$$

where subscripts *i* and *f* refer to initial and final times and partial pressures. The temperature dependence of K_h was calculated from the Bunsen coefficients (Wiesenburg and Guinass 1979). The calculated *k* values for each chamber were normalized for comparison to k_{600} values. k_{600} is *k* for a CO_2 at 20°C, which corresponds to a Schmidt number of 600 and allows *k* values to be compared for any gas and temperature according to Eqs. 5 and 6 (Jähne et al. 1987; Wanninkhof, 1992).

$$\frac{k_{gas1}}{k_{gas2}} = \left(\frac{Sc_{gas1}}{Sc_{gas2}}\right)^n \qquad (5)$$

$$k_{600} = \left(\frac{600}{Sc_{gas2}}\right)^n \cdot k_{gas2} \qquad (6)$$

Sc denotes Schmidt number for the respective gases evaluated for a particular temperature and water density (Wanninkhof et al. 1987; Wanninkhof 1992; we calculated Sc_{CH4} from $Sc_{CH4} = 1897.8 - 114.28t + 32902t^2 + 0.039061t^3$ as used by Matthews et al. 2003, and where *t* is temperature in °C). The exponent, *n*, can vary from unity to –0.67 depending on which process dominates diffusion (Ledwell et al. 1984; Jähne et al. 1987). We used the value –0.5 for *n*, which should be appropriate for low-wind systems (Jähne et al. 1987). Using $n = -0.67$ had only minor impacts on *k* (a 5% increase, on average).

Floating chambers can potentially receive methane by both diffusive flux and ebullition. Our approach to ensure that *k* estimates were not made from chambers receiving ebullition was to always deploy many chambers simultaneously along transects from shallow to deep water. In this way, we could distinguish 2 groups of chambers: 1 group receiving diffusive flux only resulting in low flux rates and low between chamber variability, and another group receiving both diffusion and ebullition resulting in substantially higher and more variable flux rates between chambers. The separation between these groups is described in detail in Bastviken et al. (2004), and only chambers to which diffusive flux dominated were used for calculating *k* values reported here. Briefly, we used the distribution and variance in the apparent piston velocities to determine which chambers received ebullition flux. Where ebullition into a chamber is significant k_{600} values are biased because ebullition makes apparent k_{600} values substantially higher than for chambers receiving methane only by diffusive flux. For each chamber from the same lake and sampling period, each k_{600} was divided by the minimum k_{600} (the minimum value was attributed solely to diffusive flux). The frequency distribution of this ratio for all chambers clearly indicated that there were two distinct groups of chambers having ratios of 1–1.8 and >2, respectively (*see* Fig. 2 in Bastviken et al. 2004). Hence a ratio of 2 was chosen as a threshold below

which we inferred that methane flux into the chamber had occurred by diffusive flux only. For this study, we had 256 deployments below the threshold and 66 above the threshold. Thus, of 322 deployments, we had to reject 20%. Had we deployed all chambers at depths greater than 4 m, <5% would have been rejected.

The SF_6 approach—SF_6 was added by slowly bubbling about 34.2 moles, of 99.99% pure SF_6 (Concorde Specialty Gases) into Peter Lake via 8 air stones at 4–5 psi at the bottom of the epilimnion (3 m) over a 3-d period (16 to 19 July). This is similar to the methods of Matthews et al. (2003) and Cole and Caraco (1998). Two days after bubbling was terminated we began sampling. On this date (21 July) and again on 24 July, we sampled every 20 m from the shore to the center of lake along 4 cardinal transects to assure that horizontal mixing had occurred. On 25 July, we took samples over depth (1, 2, 2.5, 3, 3.5, 4, 4.5, and 5 m) to determine the penetration of SF_6 into the water column. Beginning at 96 h after bubbling was terminated, we also sampled daily at the central location over time. At the start of the experiment the concentration of SF_6 was about 20 nM evenly mixed throughout the surface layer, with no detectible SF_6 below the thermocline. During the subsequent 35 d, the depth of the mixed layer of Peter Lake remained constant at 3.25 m. Thus, the loss of the concentration of SF_6 could be adequately modeled as a negative exponential function, the slope of which is k/zmix.

$$[SF_6]_t = [SF_6]_{t0} \times e^{-k/zmix} \qquad (7)$$

where the subscripts t and t_0 denote the concentration of SF_6 at the time of sampling and at the start of the experiment (after complete mixing), respectively.

Samples for SF_6 were taken by peristaltic pump using thick-walled Tygon tubing, and pumped into 1-L gas tight bottles with thermally insulated jackets. In the field, a head-space equilibration was performed to concentrate the gas from the liter of water into 50 mL of head-space air. Air samples were then injected into pre-evacuated 9-mL Tekmar vials and SF_6 analyzed using a Shimadzu GC with ECD detector against appropriate SF_6 gas standards. Details are the same as Cole and Caraco (1998).

The wind speed model approach—A number of regressions between average wind speed and average k_{600} have been published. We estimated k_{600} from measured wind speed (corrected to a height of 10 m) on Peter Lake and three commonly used regressions: Liss and Merlivat (1986), Wanninkhof (1992), and Cole and Caraco (1998). For all three cases, we estimated k from both mean daily wind speeds and from wind for each 5 min interval. Because the relationship between k_{600} and wind speed is highly nonlinear, mean daily wind speed tends to underestimate the importance of short-term changes in wind speed. On the other hand, the regressions are derived from data generally over longer periods of time. Many of the data points used by both Wanninkhof (1992) and Cole and Caraco (1998) are derived from SF_6 additions in various systems. To

obtain significant differences in SF_6 concentrations generally takes more than 24 h. Wind speed was measured at 2 m above the water surface along the shore between Peter and Paul Lakes using an R.M. Young model 5103 anemometer. Minimum, maximum, and average values were recorded for every 5-min interval using a Campbell Scientific 6350 data logger. We estimated wind speed at 10-m height using the equations in Smith (1985).

The carbon mass balance approach—As part of another project, we enriched several lakes with inorganic ^{13}C by daily addition of $NaH^{13}CO_3$ (Pace et al. 2004, 2007; Cole et al. 2006; Carpenter et al. 2005). These whole-lake ^{13}C additions allowed us an additional way to assess k. Briefly, we made a simplified mass balance calculation for both C and ^{13}C each day during the 45-day addition period on each of three lakes. We solved this mass balance under steady state conditions and varied k until measured and modeled ^{13}C for DIC were in good agreement. The inputs of ^{12}C and ^{13}C include the daily ^{13}C addition (done each day at ~0700), mean inputs in ground water, inputs from the difference between total mean system respiration (R) and mean Gross Primary Production (GPP). The approach here is a simplification of the C mass balance in Cole et al. (2006) and Pace et al. (2007). Here we used mean values of GPP and R and imposed steady state so that we could look at the effect of varying k without other influences. GPP and R were measured continuously using YSI UPG-6000 sondes that measured oxygen and temperature. We assumed a $CO_2:O_2$ quotient of 1 (Cole et al. 2006; Coloso et al. 2008). For the calculation of GPP and R, we used the wind-based approach of Cole and Caraco (1998) to estimate k for an initial guess and to complete the mass balance. We then updated this estimate with the one from the isotope mass balance. We performed this steady state analysis on three lakes (Paul, Peter, and Tuesday) for which we had appropriate data. On a fourth lake, Crampton, where we had better data, we used a dynamic mass balance. Wind was measured continuously on a raft in the center of this lake, and we made daily measurements of ^{13}C-DIC. GPP and R estimates were based on multiple sondes deployed horizontally and vertically as well as frequent temperature profiles to assess Z_{mix} (Coloso et al. 2008). Thus, for Crampton Lake, we did a similar analysis but without imposing steady state and solved the mass balance at 100 time steps per day. We used the wind-based power relationship of Cole and Caraco (1998) as the basis for the k_{600} prediction, but altered the coefficients until we could best match predicted and observed values of ^{13}C of DIC (at 07:00, just prior to the daily ^{13}C addition. Further details are in Pace et al. 2007).

Assessment and discussion

The floating chamber approach yielded 256 separate k_{600} values ranging from 0.21 to 0.71 m d^{-1} combining all 256 diffusive measurements in all lakes. Since measurements on each lake were made during different dates, results from individual lakes are not directly comparable due to different wind condi-

tions. Therefore we choose to evaluate k_{600} values obtained from all lakes together, resulting in an average daily k_{600} value of 0.42 ± 0.006 (SD) m d^{-1} for lakes in this region with surface areas of from 0.3 to 32.9 ha (Table 1). Average k_{600} values from individual lakes did not vary greatly and were not related to lake area (Table 1). An average value also integrates over time during the sampling periods, which is necessary for comparison with other approaches.

The SF_6 added to Peter Lake was rapidly mixed homogenously throughout the surface mixed layer. The decline over time of SF_6 in this mixed layer resulted in an average k_{600} estimate of 0.49 ± 0.004 m d^{-1} over a 30-d period (Fig. 2).

Summary wind data for the two lakes for which we have continuous data are shown in Table 2. We used both the individual 5-min mean, and the mean daily wind speeds to compute k_{600}. The k_{600} values based on wind speed models differed depending on which model was used and the time frame for averaging the wind speed (Fig. 3A,B). Based on the 5-min wind speeds, the model of Liss and Merlivat (1986) grossly underestimated k_{600}, by about 6.1-fold (or 0.41 md^{-1}), relative to the SF_6 addition. The discrepancy is consistent with prior underestimates by the Liss and Merlivat model observed for systems with low wind speeds (*see* Cole and Caraco 1998). The Wanninkhof (1992) model slightly underestimated (by about 1.3 fold; or 0.12 md^{-1}) and the Cole and Caraco (1998) model slightly overestimated (by about 1.4 fold; or 0.19 md^{-1}) the mean k_{600} from the SF_6 addition (Fig. 3). The relative performance of the three wind-based models was about the same whether mean daily or 5-min wind speeds were used (Fig. 3B). The mean of Wanninkhof (1992) model using the 5-min wind
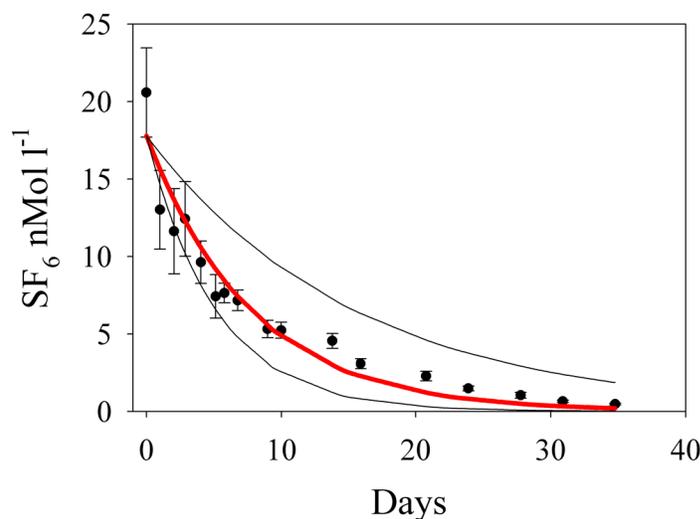

Fig. 2. Time series of the concentration of SF_6 in the upper-mixed layer of Peter Lake. Each point represents the mean (with SD) of all samples taken on a given date. The solid red line shows the best fit to these data using the equation: $[SF_6]_t = [SF_6]_{t0} \times e^{-k/zmix}$. The regression is significant ($P < 0.001$; $r^2 = 0.94$). k_{600} for this fit is 0.49 ± 0.004 m d^{-1}. The two lines that bracket the regression line illustrate the predicted concentration of SF_6 with k_{600} of 0.25 m d^{-1} (upper line) and 0.75 m d^{-1} (lower line).
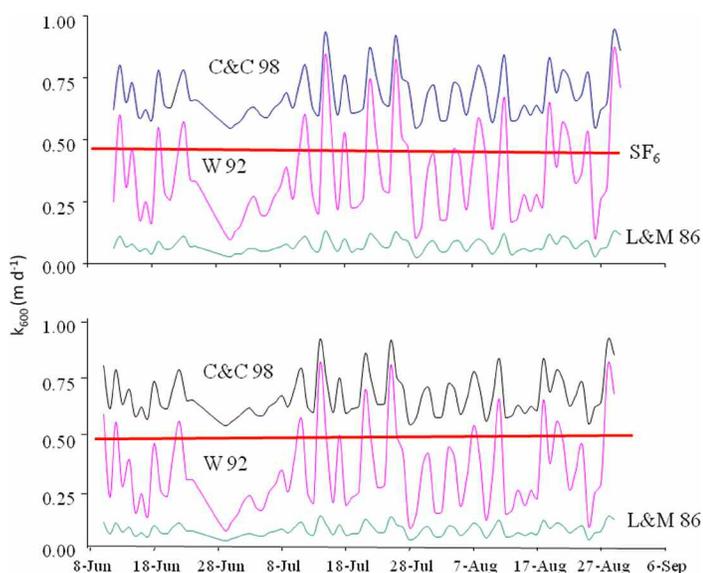
Fig. 3. Results of wind-based estimates of k_{600}. The upper panel shows k_{600} calculated from 5-min wind intervals and then averaged for each day. The lower panel shows mean daily k_{600} calculated from mean daily wind speed. In both cases, the lines are cubic spline fits of the data. The heavy red line (labeled "SF$_6$") is the mean result for the SF$_6$ experiment (*see* text). The wind-based calculations of k_{600} are C&C 98 (Cole and Caraco 1998); W 92 (Wanninkhof 1992); L&M 86 (Liss and Merlivat 1986).

speeds came closest to hitting the SF$_6$-based estimate. Evaluated at only the mean wind speed (for the 91-d period) for Peter Lake (1.23 ms^{-1}), the Cole and Caraco (1998) comes much closer to the SF$_6$ estimate than does Wanninkhof (1992); 0.57 md^{-1} versus 0.15 md^{-1}, respectively.

The steady state carbon mass balance approach constrained the possible range of k_{600} to between 0.35 and 0.65 m d^{-1} among the three small lakes (Fig. 4). Because the results come from mass balance models with many sources of uncertainty, we cannot put meaningful error estimates on the values from the individual lakes. However, for each lake, we can bracket the mean values of k and show k values, which would either be too high or too low (Fig. 4).

The dynamic carbon mass balance approach on Crampton Lake returned a mean value of k_{600} of 0.74 ± + 0.17(SD) m d^{-1} and fit the observed data reasonably well ($r^2 = 0.82$; $P < 0.0001$). The daily highs and lows in the modeled ^{13}C are driven by the daily additions which were done at ~ 07:30; just after the daily sample was taken. The model attempted to fit the observed values at the morning ^{13}C-low by minimizing the SSE of the linear regression of measured versus modeled ^{13}C of DIC at 07:00 each day (Fig. 5). The best fit is imperfect in that the slope of the regression is lower than unity (0.86) but the 95% confidence interval of the slope overlaps 1.0 (0.68 to 1.05). The 95% confidence range on the intercept (–0.37 to 2.9) overlaps 0. The wind versus k_{600} equation that created the best fit was:

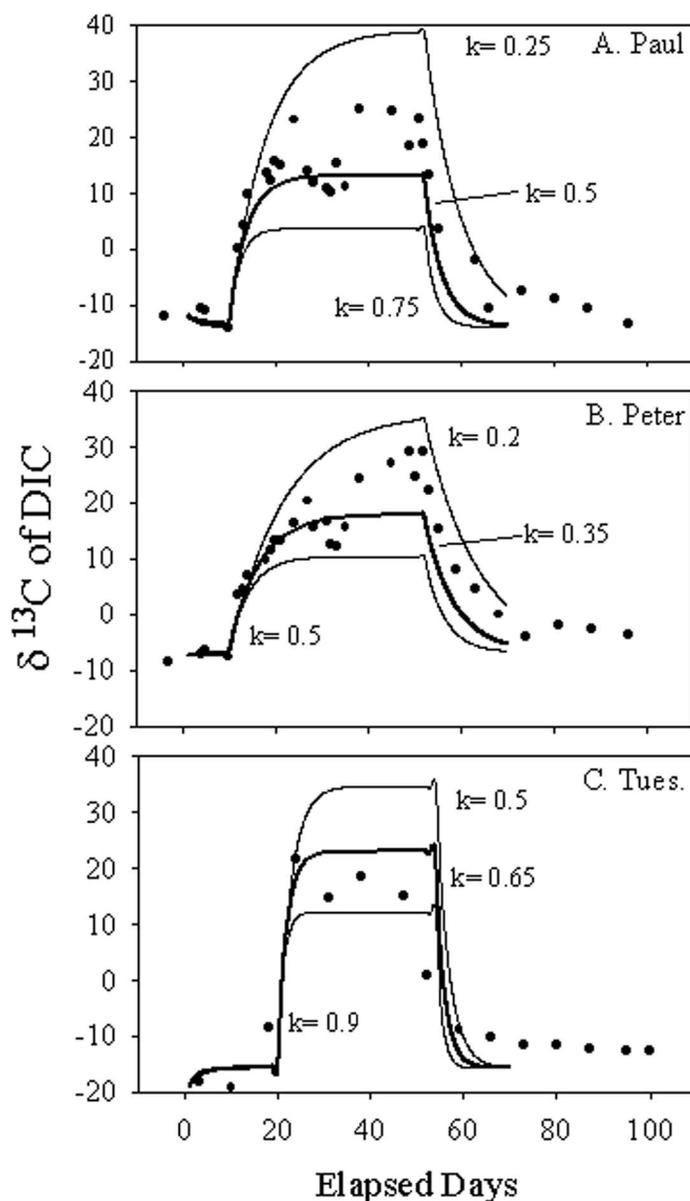$$k_{600} \text{ (m d}^{-1}\text{)} = (0.497 + 0.0064 \times U_{10}^{1.8}) \qquad (8)$$

Fig. 4. Steady state ^{13}C mass balance for the three lakes (Paul, Peter, and Tuesday). Shown are mean values for k_{600} for the best fit to the data (heavy line) and what the resulting ^{13}C of DIC would be with an upper and lower scenario for k_{600} for each lake.

where U_{10} is the wind normalized to a height of 10 m according to Smith (1985). This relationship has the same form as that of Cole and Caraco (1998) but with a faster increase in k_{600} as the wind rises.

Altogether, results from floating chambers, SF$_6$ additions, and carbon mass balance modeling corresponded well with each other, and with values reported for other systems of comparable size and comparable wind speeds (Table 3). For comparison, the average k_{600} values using the SF$_6$ approach in the literature on small lakes range from 0.1 to 1.6 m d^{-1} (Wanninkhof 1985; Upstill-Goddard et al. 1990; Wanninkhof et al.
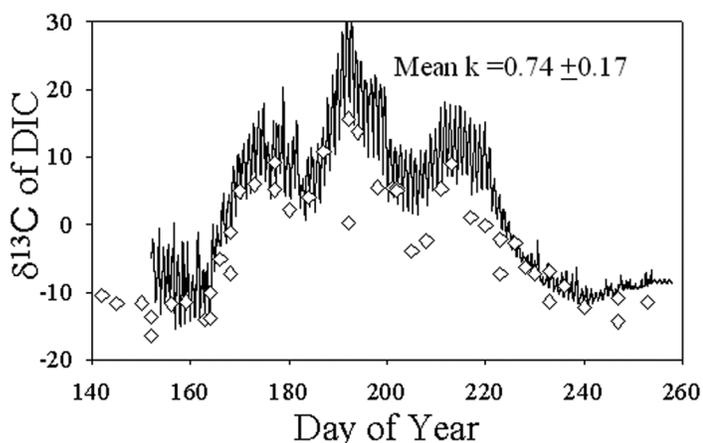
Fig. 5. Dynamic ^{13}C mass balance for Crampton Lake. A: Predicted and observed ^{13}C-DIC in Crampton Lake in which the mass balance was solved at 100 time steps per day (*see* text). B: Regression of the predicted versus observed values at the time of measurement.

Table 3. Comparison of piston velocities normalized to the Schmidt number 600 (k_{600}; can be used to calculate gas exchange for any gas and temperature) obtained with different methods from small wind-sheltered lakes in Northern Michigan, USA. The Domain column denotes the number of lakes studied and whether measurements were performed for several years (e.g., for the floating chamber approach 8 lakes were studied for 1 y, 1 lake for 2 y, and 1 lake for 3 y, yielding 13 lake-year). Average k_{600} values ± 1 SD, or the k_{600} range are given.

Method	Domain	k_{600} (m d^{-1})
SF6	1 lake-year	0.49 ± 0.004
Floating chambers	13 lake-year	0.44 ± 0.08
(CH$_4$ exchange)		
Wind speed models:		
a) Cole and Caraco 1998	4 lake-year	0.68 ± 0.17
b) Wanninkhof 1992	4 lake-year	0.37 ± 0.32
c) Liss and Merlivat 1986	4 lake-year	0.08 ± 0.04
^{13}C mass balance	4 lake-year	0.35–0.74 (range)

1991; Clark et al. 1995; Cole and Caraco 1998; Matthews et al. 2003). The reasonable agreement between chamber values and other approaches in our study contrasts to results of Matthews et al. (2003) and Billett and Moore (2008) who found that chambers yielded substantially higher values than other approaches. We think that the chamber modifications that we used were based on recommendations by Matthews et al. (2003) and described above explain this difference. We suggest that the floating chamber method is most appropriate for systems with minimal ebullition (deeper than about 4 m) and where surface water is not moving rapidly. In environments with high CH$_4$ production and shallow water would promote ebullition, perhaps incorporating bubble shields below the floating chambers would provide a more robust approach to minimize the risk of overestimating *k*.

Wind speed modeled k_{600} values were in the same order of magnitude as values from the other approaches, but were sensitive to which model was used. For example, the wind speed model by Liss and Merlivat (1986) resulted in 6-fold lower k_{600} values than the empirical approaches, and did not come close to the SF$_6$ addition or other approaches. Cole and Caraco (1998) previously showed that several commonly used wind speed–based models underestimate k_{600} at low wind speeds. Possible reasons for this underestimation include penetrative convection, induced when air temperatures are lower than water temperatures, and other water movement and turbulence that is not caused by the immediate wind environment (e.g., currents and internal hydrodynamics).

Comments and recommendations

Based on these results, we recommend that direct measurements of *k* rather than estimates derived from wind-speed models be attempted when gas flux is an important component in the study. Fortunately, direct measurement is easily done using the floating chamber approach and ambient CH$_4$ and fluxes as described here. Using CH$_4$ as the gas of choice has several advantages: it is easy to measure; it is often supersaturated in the surface waters of small lakes; and as a nonreactive gas, avoids problems like chemically enhanced diffusion that occur for CO$_2$ at high pH (Bade and Cole 2006). If such measurements cannot be performed over the time period of interest, they can at least guide the choice of wind speed model to be used for more extended periods (e.g., extrapolating a few daily estimates over an annual cycle). In the near future, values of k may be more easily derived from direct measurements of turbulence (using Acoustic Doppler Velocimeters; ADV) and generalized relationships between turbulence and *k* (McKenna and McGillis 2004; Vauchon et al. in press), or statistical process models (Holtgreive et al. 2002). We look forward to this advance but the development of this approach is still in an early stage and the method may or may not become a standard technique. Our data, using multiple approaches, further suggests that k_{600} on small (<50 ha) wind-sheltered (mean wind < 3 md^{-1}) lakes is likely close to 0.50 m d^{-1}. The mean value of our approaches (excluding the Liss and Merlivat [1986] wind equation) is 0.51 ± 0.16 m d^{-1}.

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