

Atmospheric exchange of carbon dioxide in a low-wind oligotrophic lake measured by the addition of SF₆

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Abstract

Many freshwater lakes are supersaturated in CO₂ with respect to the atmosphere. This concentration gradient implies a net flux of CO₂ from the water to the air. The actual rate of gas exchange is governed by both this concentration gradient and the gas transfer coefficient, *k*. To directly measure *k*, we added the chemically and biologically inert gas, sulfur hexafluoride (SF₆), to the epilimnion of Mirror Lake, New Hampshire, a small (15 ha), low-wind softwater lake. *k* was independent of wind speed over the 50-d summer stratification period and averaged $2.65 \pm 0.12 \text{ cm h}^{-1}$ (95% CI; normalized to a Schmidt number of 600); *k*₈₀₀ was better correlated to precipitation events than it was to wind speed. Our data support the idea that gas exchange across the air–water interface is largely independent of wind at low wind speeds. The surface water of Mirror Lake was persistently supersaturated in CO₂ with respect to the atmosphere. During a 3.5-year period the partial pressure of CO₂ in the surface waters of the lake averaged $726 \pm 39 \text{ } \mu\text{atm}$ (95% CI) and showed substantial seasonal variation (360–2,000 μatm). Diel and day-to-day variation in CO₂ were very small compared to the CO₂ pool. We combined our estimates of *k* with weekly measurements of the partial pressure of CO₂ to estimate CO₂ gas exchange in the lake. Mirror Lake released from 26 to 50 g C m⁻² to the atmosphere each year, depending on the method of calculating *k*. Atmospheric CO₂ exchange is a large term in the C economy of the lake—the most conservative gas flux estimate is about four times as large as outflow plus seepage of total dissolved inorganic carbon and 1.5 times as large as the export of dissolved organic C from the lake.

The exchange of CO₂ across the air–water interface is an important term in the C budget of aquatic ecosystems. The direction of CO₂ gas exchange is dependent simply on the direction of the CO₂ concentration gradient between the air and the surface water; the magnitude of the exchange depends additionally on the gas exchange coefficient, *k*. While the oceans are net sinks for atmospheric CO₂ (e.g. Broecker and Peng 1974, 1984; Watson 1993; and many others), many lakes and rivers are supersaturated in CO₂ and are therefore sources of CO₂ to the atmosphere (Schindler et al. 1975; Bower and McCorkle 1980; Kling et al. 1991; Hesslein et al. 1991; Cole et al. 1994). When there is net evasion of CO₂ to the atmosphere, it must be supported by some input of CO₂. These inputs can come from net heterotrophy within the system (Devol et al. 1987; del Giorgio et al. 1997)—CO₂ inputs in inflowing groundwater (Kling et al. 1991) or carbonate precipitation within the system (McConnaughey et al. 1994).

Knowledge of the actual magnitude of CO₂ flux across the air–water interface of a lake could set useful ecosystem-level constraints on processes occurring in the carbon cycle within the lake. To accurately calculate CO₂ gas flux requires a

detailed knowledge of the concentration of CO₂ in both the air and water. As aqueous CO₂ concentrations can vary both seasonally and in some systems diurnally, accurate assessments of the concentration gradient may require a large number of CO₂ measurements (Sellers et al. 1995). Furthermore, although CO₂ concentrations can be estimated indirectly from pH and dissolved inorganic carbon (DIC) or alkalinity, these estimates can be inaccurate in some freshwaters (Herczeg et al. 1985; Stauffer 1990). Direct measurements of pCO₂ are only rarely made (Sellers et al. 1995).

The estimation of CO₂ gas flux also requires a knowledge of *k*. There have been many experimental determinations of *k* in a variety of freshwater and marine systems. *k* varies both within and across these systems by about two orders of magnitude (Wanninkhof 1992). Most of these studies suggest that *k* increases predictably with increasing wind speed at winds $\geq 3 \text{ m s}^{-1}$ (Wanninkhof 1992; Marino and Howarth 1993; MacIntyre et al. 1995). Thus, if wind speed is known, *k* can be estimated from several empirical relationships. However, both wind tunnel and tracer studies on whole systems show substantial variation around these relationships, especially at low wind; below wind speeds of $\sim 2\text{--}3 \text{ m s}^{-1}$, *k* appears to be largely independent of wind and is not yet predictable from either an empirical or theoretical standpoint (Crill et al. 1988; Clark et al. 1995; MacIntyre et al. 1995; Ho et al. 1997). As many small lakes experience quite low wind speeds, this presents a problem in the estimation of *k* from existing relationships. An option to using modeled values of *k* is to directly measure it using additions of an inert gas tracer such as sulfur hexafluoride (SF₆) to the water body of interest. SF₆ is a human-made gas that is sparingly soluble, easy to measure at extremely low concentrations, and both biologically and chemically inert. Its use as a tracer of gas exchange was pioneered by Wanninkhof et al. (1985)

Acknowledgments

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and has been used in both freshwater (Wanninkhof 1992; Clark et al. 1994, 1995) and in the ocean (Ledwell et al. 1986; Watson et al. 1991; Wanninkhof et al. 1993).

In this study we coupled direct measurements of $p\text{CO}_2$ that covered diel, seasonal, and between-year variation with direct estimates of k in a small, low-wind oligotrophic lake. k was estimated by whole-lake SF_6 addition during a 70-d period. We created two new models to explain the variation in k , one based solely on wind speed and one based on wind speed and precipitation. We then used these models of k in conjunction with our $p\text{CO}_2$ record to calculate gas flux.

Site description

Mirror Lake is a softwater oligotrophic lake located in central New Hampshire (43°56.5'N, 71°41.5'W), and has been the subject of numerous investigations, many of which are summarized in Likens et al. (1985). The lake is dimictic and slightly acidic, with surface-water concentrations of DIC near 100 μM and total phosphorus near 0.15 μM (Caraco et al. 1992). The surface area of the lake is 15 ha and its maximum depth is 10 m. The watershed of the lake (106 ha) consists of several large knobs; the largest of these knobs on the northwest side of the lake directly blocks wind from the predominant northwest direction (Winter 1984). Water inflow is split between groundwater flow and three surface streams; the hydrologic residence time for the lake is ~ 1 year (Winter 1984).

Theory of gas exchange

The processes that control the rate of exchange of a gas between surface waters and the atmosphere have been the subject of considerable study and have been recently reviewed by MacIntyre et al. (1995 and references therein). Briefly, the flux depends on two main factors: the concentration gradient between the water and the air, and the gas exchange coefficient for a given gas at a given temperature, k . The concentration gradient is expressed as the difference between the actual concentration of gas in the water and the concentration that water would have if it were in equilibrium with the atmosphere. Thus,

$$\text{Flux} = \alpha k (P_{\text{gas}} K_h - [\text{gas}]_{\text{sat}}), \quad (1)$$

where $[\text{gas}]_{\text{sat}}$ is the concentration of gas the water would have at equilibrium with the overlying atmosphere; K_h is Henry's constant for the gas at a given temperature and salinity; P_{gas} is the partial pressure of the gas in the surface water; and the product, $P_{\text{gas}} \times K_h$, is the concentration of the gas in the water. The concentration gradient term is routinely measured, whereas the gas exchange coefficient is not. k is a piston velocity (cm h^{-1}), and can be thought of as the height of water that is equilibrated with the atmosphere per unit time for a given gas at a given temperature. α is the chemical enhancement factor. Once k is known for any one gas and temperature (k_{gas1}), it can be calculated for any other gas and temperature (k_{gas2}) by the ratio of the Schmidt numbers (Jahne et al. 1987):

$$k_{\text{gas1}}/k_{\text{gas2}} = (\text{Sc}_{\text{gas1}}/\text{Sc}_{\text{gas2}})^n, \quad (2)$$

where Sc is the Schmidt number for the respective gases evaluated for a particular temperature and water density (Wanninkhof et al. 1987; Wanninkhof 1992). The exponent, n , can vary from unity to -0.67 depending on which process dominates diffusion (Ledwell 1984; Jahne et al. 1987).

For a totally nonreactive gas, α equals 1.0. We are interested in CO_2 for which chemical reactions with OH^- can enhance the diffusion rate. The lake in this study is always supersaturated in CO_2 and has soft water that is slightly acid to neutral (pH of 6.3–7; Cole et al. 1994; Likens 1985). Under these conditions, α is effectively ~ 1 and the gas exchange for CO_2 is not affected appreciably by chemical reactions that can enhance CO_2 invasion into undersaturated waters at high pH (Hoover and Berkshire 1969; Emerson 1975; Smith 1985; Wanninkhof and Knox 1996).

Methods

Partial pressure of CO_2 —We made direct measurements of the partial pressure of CO_2 in the surface waters of Mirror Lake for 3.5 years. Samples were taken at weekly intervals between 1000 and 1400 h at the geographic center of the lake. The direct measurement of $p\text{CO}_2$ was accomplished by headspace equilibration (Raymond et al. 1997). Briefly, a thermally insulated, heavy-walled glass bottle (1.2 liters) was filled with water and allowed to flush for several volumes. The bottle was capped with a specially designed stopper with gas-tight valves that allow the introduction and removal of gas or water phases. We immediately introduced a 50-ml headspace of ambient air and shook vigorously for 60 s. Prior tests demonstrated that this shaking was approximately twice the time required to equilibrate the air and water phases for CO_2 . The temperature of the water was unchanged during this procedure. Samples of both the equilibrated gas headspace and ambient air (1 m above the surface) were transported to the laboratory in modified 20-ml nylon syringes. CO_2 was measured by gas chromatography using a Shimadzu model GC-AIT equipped with a thermal conductivity detector. For each sample we made duplicate equilibrations (the C.V. for this procedure averaged 8% of the mean).

During the summer of 1995 we made additional direct measurements of CO_2 at dusk and dawn for 29 d from late June through early August to assess the effect that diel variation in CO_2 could have on gas flux estimates. For these measurements, we followed the same equilibration procedure (above), but collected the equilibrated gas into pre-evacuated 9-ml glass serum vials. These samples were used for the measurement of both CO_2 and SF_6 (*see below*).

Calculated CO_2 —As a check on the direct measurements of $p\text{CO}_2$, we calculated $p\text{CO}_2$ from measurements of DIC and pH, with appropriate corrections for temperature, altitude, and ionic strength (Kling et al. 1992). We calculated $p\text{CO}_2$ for a large subset of the surface-water samples ($n = 152$). DIC was measured using the syringe gas-stripping method of Stainton (1973) and the Shimadzu gas chromatograph (*see above*). When using this procedure, the C.V. was 1.2% of the mean for triplicates. For the large number of dusk-to-dawn samples generated in the summer of 1995, we

measured DIC on a Shimadzu model 5050 TOC analyzer. pH was measured with a Fisher Accumet 1001 meter using a gel-filled combination, temperature-compensating (ATC) electrode. Samples were either collected in gas-tight BOD bottles and transported in a cooler or they were measured directly in the field. Calibration was done by using two buffers (4.00 and 7.00; Fisher). To measure pH accurately, we allowed the electrode to soak in a water sample for 30 min after calibrating and thoroughly rinsing the electrode. After this initial soak we measured pH from the previously unopened BOD bottle (Stauffer 1990). Replicate determinations with this procedure agreed to within 0.03 pH units.

We estimated ionic strength from conductivity (Butler 1992); activity coefficients for carbonate and bicarbonate were estimated using MINEQL vers. 2.1 (Schecher and McAvoy 1991) and complete anion and cation measurements for Mirror Lake (Likens 1985). Henry's constant (K_h) was corrected for temperature and salinity. Aqueous CO₂ in equilibrium with the atmosphere ($[CO_2]_{sat}$) was calculated, as in Kling et al. (1992), from Henry's law and the fugacity-pressure relationship from Weiss (1974).

Temperature and conductivity of the surface water of the lake were measured for every sample taken. Additionally, temperature profiles were taken at several day-to-weekly intervals to determine the thermal structure of the lake using a YSI model 5000 TLC meter.

Sulfur hexafluoride addition—SF₆ at 99.8% purity was obtained from Matheson. On 10 June 1996, we released ~1 kg of SF₆ into the lake by bubbling it slowly through a plastic diffusor that produced a fine stream of bubbles at the bottom of the epilimnion at a 2-m depth. Most of the added SF₆ was immediately re-released into the atmosphere as bubbles rose to the surface. We sampled the lake at multiple locations (10 in a star pattern) 1 and 4 d after the addition to determine the extent of vertical and horizontal mixing. Once complete horizontal mixing occurred, we sampled at a single location in the center of the lake.

Surface-water samples were taken at both dusk and dawn several days per week, and complete vertical profiles were taken once per week. Samples were pumped to the surface in thick-walled tygon tubing using a peristaltic pump. To sample SF₆, we used the same approach as for the pCO₂ equilibration. Two 20-ml aliquots of gas were removed by nylon syringe and 9 ml of gas was immediately injected into preevacuated 9-ml glass vials with butyl rubber septa and aluminum sealing rings.

During the period of the SF₆ addition, both SF₆ and CO₂ were detected by gas chromatography on the same sample that passed through both the electron capture detector (350°C) and the thermal conductivity detector of a Tracor model 540 gas chromatograph attached to a Tekmar 7000 autosampler. The gases were separated on a Poropak Q column at a flow rate of 25 ml min⁻¹ with N₂ as carrier gas and a column temperature of 40°C. By using this method, our detection limit for SF₆ was 0.05 ppbv directly as gas or ~10⁻¹³ M in water (or 2.5 × 10⁻¹² ml STP g⁻¹). The method we used is about one order of magnitude less sensitive than that of Wanninkhof et al. (1987), who used a different column (molecular sieve) and different flow and temperature

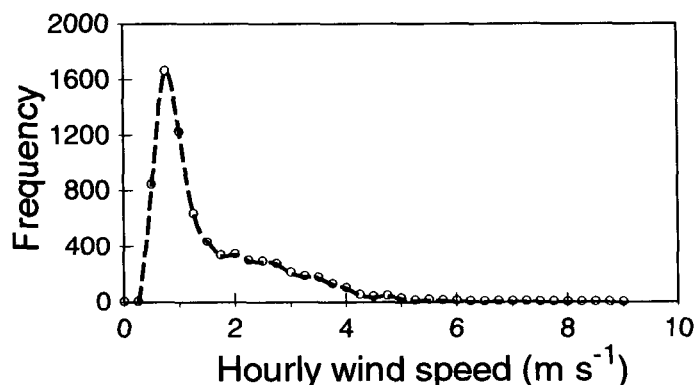


Fig. 1. Frequency of hourly average wind speed measurements (corrected to a height of 10 m, *see text*) made in the center of Mirror Lake. These lake data are for the ice-free periods from May 1992 through November 1995 (source: T. Winter unpubl.).

conditions, but had the advantage that SF₆, CO₂, and N₂O can all be run on a single sample with a dual detector GC. For SF₆, reproducibility was ±3.2% and the GC response was nearly linear over wide ranges of concentration.

Wind and rain data—During the SF₆ addition, wind speed was measured continuously by anemometers at 2 and 3 m above the surface of the lake on a floating raft at the center of the lake (Winter 1984, 1991; Sturrock et al. 1988). The lake-based meteorological station also includes continuous measures of air and surface-water temperatures and relative humidity, which were used in the calculation of the water friction velocity (*see below*). An additional record of wind comes from the U.S. Forest Service Station, ~0.3 km from the lake. Wind data for the raft are available for the ice-free seasons from 1978 through the present. Wind data have been measured since 1965 at the station and are described in Federer (1990). For comparison with other data, we normalized our measured wind speeds to wind speed at a height of 10 m above the lake. We assumed a neutrally stable boundary layer and a logarithmic wind profile with a drag coefficient of 1.3 × 10⁻³ (Liu and Schwab 1987; Clark et al. 1995).

Rain amounts have been measured at Hubbard Brook since 1965 (Federer 1990), and methods are described in Likens (1985). During the period of interest, the closest rain gauges to Mirror Lake were at the U.S. Forest Service Station and at the Henrietta K. Towers Laboratory, ~0.4 km southeast of the lake. We used averaged values from the two sites.

Results

Wind speed—Mirror Lake is a low-wind environment. For the ice-free periods from May 1991 through December 1995, daily wind speed (normalized to 10-m height) on the raft averaged 1.39 ± 0.06 m s⁻¹ (95% CI). During the same time, but including periods of ice cover, wind speed at the Forest Service Station averaged 1.64 ± 0.05 m s⁻¹ (Fig. 1). On an hourly basis, wind exceeded 4 m s⁻¹ only 4.3% of the time and 5 m s⁻¹ only 1.1% of the time (Fig. 1). The water friction velocity (u_{*}^*), calculated according to Watson (1993),

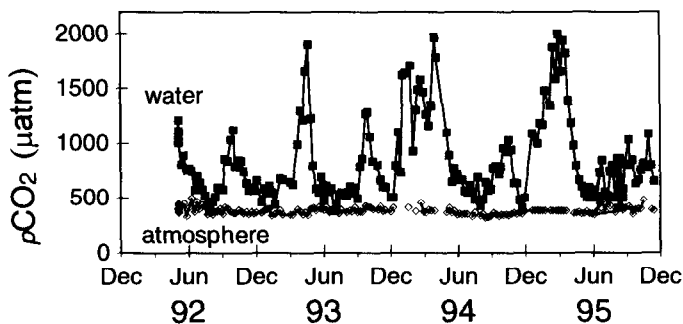


Fig. 2. Direct measurements of the partial pressure of CO_2 in the surface water (■) and atmosphere (◇) at Mirror Lake for a 3.5-year period. The water samples come from $\sim 0.05\text{--}0.1\text{-m}$ depth at the central part of the lake; the air samples were taken 1 m above the surface.

ranged from 0.06 to 0.48 cm s^{-1} and averaged $0.19 \pm 0.06\text{ cm s}^{-1}$. u^* was well correlated ($r^2 = 0.92$, $P < 0.001$) to U_{10} since the densities of air and water did not vary dramatically during the period.

Partial pressure of CO_2 —Mirror Lake is persistently supersaturated in CO_2 , with respect to the overlying atmosphere (Fig. 2). From the weekly measurements for the 4-year period, the mean directly measured surface water $p\text{CO}_2$ was $726 \pm 39\ \mu\text{atm}$ (95% CI; $n = 149$). Highest values ($1,800\text{--}2,000\ \mu\text{atm}$) were observed just after ice-out; minimum values ($380\text{--}480\ \mu\text{atm}$) were observed in early July. For the same period, the average $p\text{CO}_2$ in the atmosphere was $380 \pm 57\ \mu\text{atm}$ (Fig. 2). Although the atmospheric value is relatively constant, $p\text{CO}_2$ in the water showed pronounced and reproducible seasonal cycles. Calculated $p\text{CO}_2$ in the surface water tracked measured $p\text{CO}_2$, but consistently overestimated it in agreement with some other studies (Herczeg et al. 1985). Mean calculated $p\text{CO}_2$ was $1,018 \pm 69\ \mu\text{atm}$ ($n = 152$).

The diel variation in surface-water CO_2 was small in comparison to the CO_2 supersaturation. In May, for example, a series of measurements over a 24-h period failed to resolve any significant diel variation in CO_2 (Fig. 3). In midsummer, during peak photosynthetic activity, we were able to detect some diel differences by pooling dusk and dawn measurements. For the 57 dawns and 47 dusks, mean dawn $p\text{CO}_2$ was higher than mean dusk $p\text{CO}_2$. Although not statistically different with a t -test, this difference is significant ($P = 0.004$) with a Mann-Whitney rank sum test. A paired t -test for the days on which we have both dusk and dawn measurements ($n = 43$) shows a significant ($P = 0.01$) decline of CO_2 from dawn to dusk of $\sim 2\ \mu\text{M}$.

SF_6 concentrations and losses—Spatial sampling showed that by only 24 h after the addition of the tracer, SF_6 had covered a large area of the lake but was not yet uniformly distributed; by 96 h it was. At this time the concentration of SF_6 was nearly uniform through the upper mixed layer (Fig. 4). Below that it decreased sharply to trace levels at 4 m and was undetectable in the hypolimnion (Fig. 4). Over the course of the 50-d observation period, SF_6 was advected

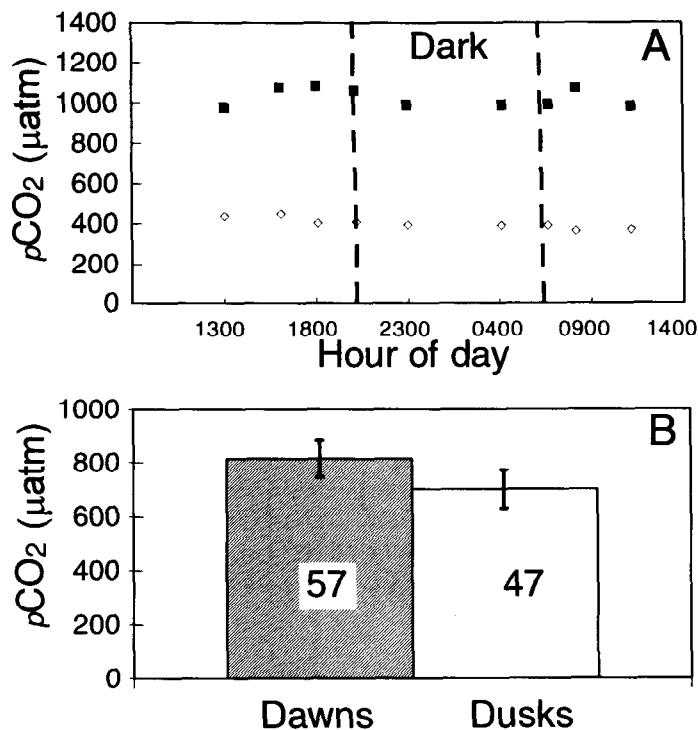


Fig. 3. A. Diel variation in $p\text{CO}_2$ on a single date (in May 1992) in the water (■) and air (◇). B. Mean dusk and mean dawn $p\text{CO}_2$ for the surface waters of Mirror Lake for 57 dawns and 47 dusks during the summer of 1995. The error bars represent 95% CI. In both A and B, values are direct measurements of $p\text{CO}_2$.

downward with the deepening of the thermocline, but at no time did we detect it below the thermocline (Fig. 4).

Both the concentration of SF_6 in the surface water as well as the total mass of SF_6 in the lake declined rapidly after addition. By 12 d the concentration had been reduced to $\sim 20\%$ of its initial value, and by 54 d to $< 1\%$ (Fig. 5).

In theory, SF_6 could be lost from the system by three processes: gas exchange, export in outflowing water, and export in methane bubbles that exit the surface of the lake. If SF_6 experienced losses other than through gas exchange, it would complicate the estimation of k . The loss of SF_6 in outflowing water is extremely small in comparison to the total loss of SF_6 . The averaged hydrologic residence time of Mirror Lake is ~ 1 year. The theoretical residence time of the epilimnion during summer (the time of the SF_6 addition) is actually even longer (~ 880 d) when hydrologic inputs have slowed down (Winter et al. 1989). Even if the hydrologic loss were constant at 1 year, it would remove the tracer at a half-life of 252 d. The measured half-life of SF_6 in our experiment was 6–9 d, more than 30 times faster than hydrologic losses could have caused (see below).

A factor that is more difficult to estimate is the loss of SF_6 caused by methane ebullition. SF_6 is much more soluble in gas than in water and could be concentrated in methane bubbles. We do not know how much methane in bubble form exits the surface water of Mirror Lake, but we do know the amount that reaches the epilimnion from epilimnetic sediments and the hypolimnion. Based on a direct bubble-trap-

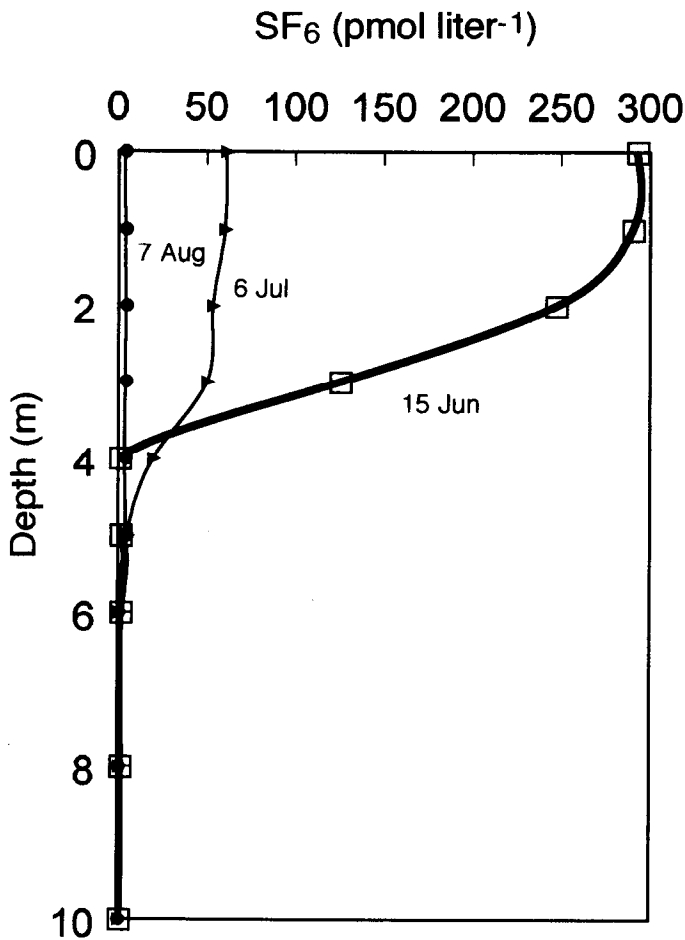


Fig. 4. Representative depth profiles of SF₆ on several dates. Samples were taken at 1–2-m intervals. The line is a spline fit through the data.

ping technique, Mattson and Likens (1990) measured a mean rate of methane ebullition of 0.76 mmol m⁻² d⁻¹ during summer, with a mean bubble composition of 70% methane. This equates to a gas bubble volume flux of 0.026 liters gas m⁻² d⁻¹. If we assume that all of this methane exits to the atmosphere and that all the bubbles are fully equilibrated with SF₆ (both assumptions are clear overestimates), the stripping of SF₆ by these bubbles would occur with a k of 0.009 cm h⁻¹, about 200-fold more slowly than the measured loss of SF₆. We conclude that the SF₆ loss that we measure must be due almost entirely to gas evasion and we can use the loss of SF₆ to calculate k .

Because the concentration of added SF₆ was orders of magnitude above the concentration that the water would have were it in equilibrium with the atmosphere (C_{eq}), we can treat C_{eq} as if it were 0; this simplifies the calculations (Wanninkhof et al. 1987). Based on the weekly depth profiles and the hypsometry of the lake, we computed the total mass of SF₆ remaining in the lake over time (Fig. 5A). A single exponential function fits this curve reasonably well ($r^2 = 0.91$), suggesting that the gas evasion rate was relatively constant when looked at as a weekly average rate. The concentration of SF₆ in the surface water also decreased ex-

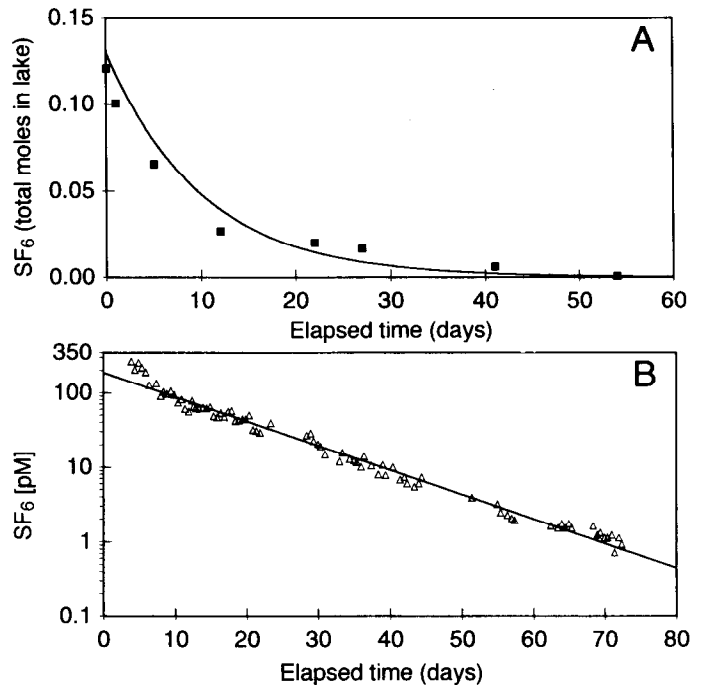


Fig. 5. Time-series of SF₆ concentration as (A) the total mass of SF₆ in the entire lake calculated from the depth profiles and hypsometry, and (B) the concentration of SF₆ remaining in the surface water. Elapsed time is in days after 18 June, the first day complete horizontal mixing had been observed.

ponentially with time (Fig. 5B). A single exponential function fit these data quite well ($r^2 = 0.98$). These two curves can give us a first approximation of the average gas evasion coefficient for the period. Because

$$k = z/t \times [\ln(\text{concn})_{t-1} - \ln(\text{concn}_t)], \quad (3)$$

the slope of a ln-linear plot of surface-water concentration is k/z , where z is the average depth of water above the thermocline (determined from the temperature profiles). The slope of a ln-linear plot of the total mass of SF₆ in the lake also provides an estimate of mean k . By using these approaches, the profiles yield a mean k value of 1.9 cm h⁻¹ and the surface water series, a value of 1.6 cm h⁻¹ normalized to a Schmidt number of 600.

k can also be estimated from the individual surface-water measurements and profiles. For the profiles, we calculated the total mass loss of SF₆ per unit area of lake between each time point and calculated k directly as

$$k = \text{Flux}/(C_{\text{surface}}), \quad (4)$$

where C_{surface} is the average SF₆ concentration between two time points and the flux is the loss of SF₆ (mass per area per time). We normalized k to a Schmidt number of 600 using Eq. 2 and assuming a value of -0.67 for n (Jahne et al. 1987). Based on the masses from the profiles, k_{600} ranged from 1.4 to 4.8 cm h⁻¹ and averaged 2.69 ± 0.9 cm h⁻¹ (95% CI). Based on the surface-waters series ($n = 88$ half-day to several-day periods), we estimated mean k_{600} (using Eq. 1 and a thermally based estimate of the average depth

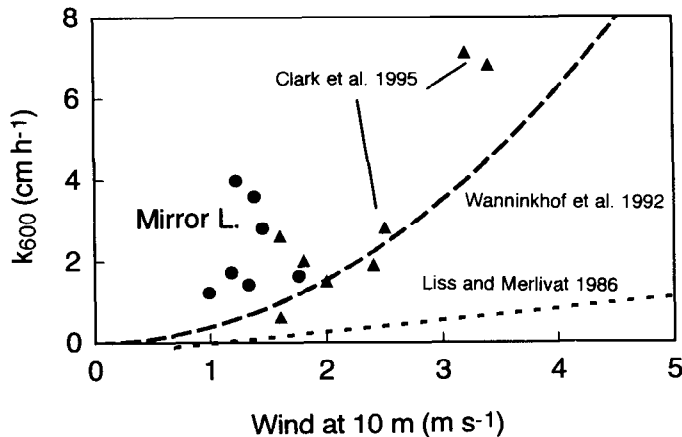


Fig. 6. Relationship between k_{600} and wind speed at 10-m height for Mirror Lake (●) and Sutherland Pond (Clark et al. 1995). The values for Mirror Lake are derived from the total mass of SF_6 in the lake from the weekly profiles. The heavy dashed curve is the power relationship from Wanninkhof (1992; $k_{600} = 0.45U_{10}^{1.64}$). The light dashed line is the low-wind segment of the tri-linear relationship of Liss and Merlivat (1986).

of the mixed layer from the temperature profiles) to be $2.65 \pm 0.12 \text{ cm h}^{-1}$ (95% CI).

At the low wind speeds encountered on Mirror Lake during the SF_6 addition, k did not vary predictably with wind speed (Fig. 6). At the scale of the weekly profiles, the wind velocity was relatively invariant, so wind dependence was not expected. However, our weekly values of k fell well above those that would have been predicted from wind speed based on the tri-linear model of Liss and Merlivat (1986) or the power relationship of Wanninkhof (1992; Fig. 6). At the scale of the half- to several-day periods, however, wind velocity varied substantially (from 0.09 to 4.2 m s^{-1}), yet k still did not track wind speeds. We were unable to obtain a significant ($P < 0.05$) relationship of any form (linear, exponential, or power) to short-term k and wind speed with our dataset (Table 1). None of these models explained more than a small percentage of the variance in k_{600} .

k_{600} was positively related to rainfall. Because the rainfall data available to us were averaged on a daily basis, we compared daily k_{600} to daily rainfall. When including all dates, rainfall explained only a small fraction of the variance in

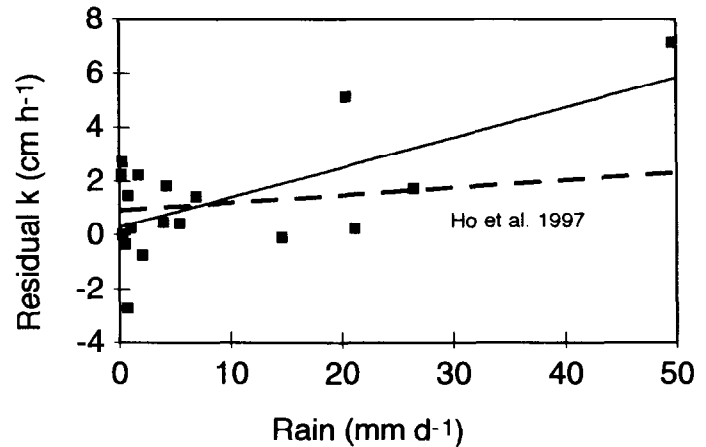


Fig. 7. The relationship between k_{600} and rain on Mirror Lake. Values of residual k against the rate of rain for those periods with non-zero rainfall are plotted. Residual k is the difference between our measured k and that predicted from wind from the relationship of Wanninkhof (1992). The solid line is the regression (residual $k = 0.11 \times \text{Precipitation}$; $r^2 = 0.49$, $P < 0.01$); the dashed line is the prediction of k (at zero wind) from precipitation from Ho et al. (1997).

k_{600} ($r = 0.11$), but the two variables were significantly and positively related ($P < 0.05$). To remove a possible effect of wind on this relationship, we calculated k_{600} according to Wanninkhof's (1992) power relationship and plotted (Fig. 7) the relationship between the residual k (our measured value minus that predicted by the Wanninkhof 1992 wind relationship) vs. the daily rate of rain for the days that had rain. The relationship is highly significant ($P = 0.003$) and explains about 40% of the variance in residual k (adjusted $r^2 = 0.39$). The highest k values, corrected for a possible effect of wind, appear to occur at the highest rates of rain; there is still a great deal of unexplained variation in k when rain is absent or low. Neither k_{600} (Fig. 6) nor residual k values (Fig. 7) were related to the friction velocity, the mean daily relative humidity, or the mean or maximum daily differences between water and air temperature ($P > 0.25$ in all cases; Pearson product-moment correlation).

To put the data from Mirror Lake and several other low-wind sites in the context of existing relationships between wind speed and k_{600} , we combined our data with published

Table 1. Lack of correlation between wind and k_{600} for the Mirror Lake dataset at low wind. P values and r^2 for three types of regressions and three parsings of the dataset are shown. The weekly profile set uses the mass of SF_6 in the lake as a basis for calculating loss; the two surface-water sets use the concentration in the surface water and a thermally based estimate of the mixing depth (see text). The surface values were analyzed as an entire dataset and from winds $>2.5 \text{ m s}^{-1}$. None of the regressions are significant at $P < 0.05$, and none explain $>1\%$ of the variability in k_{600} .

Dataset	Linear		Exponential		Power	
	P	r^2	P	r^2	P	r^2
Weekly profiles						
Weekly averaged wind	0.92	0.002	0.93	0.002	0.97	0.0001
Surface values						
Daily to subdaily and matching wind	0.65	0.002	0.67	0.003	0.69	0.002
Daily to subdaily for winds $>2.5 \text{ m s}^{-1}$	0.78	0.02	0.80	0.01	0.68	0.04

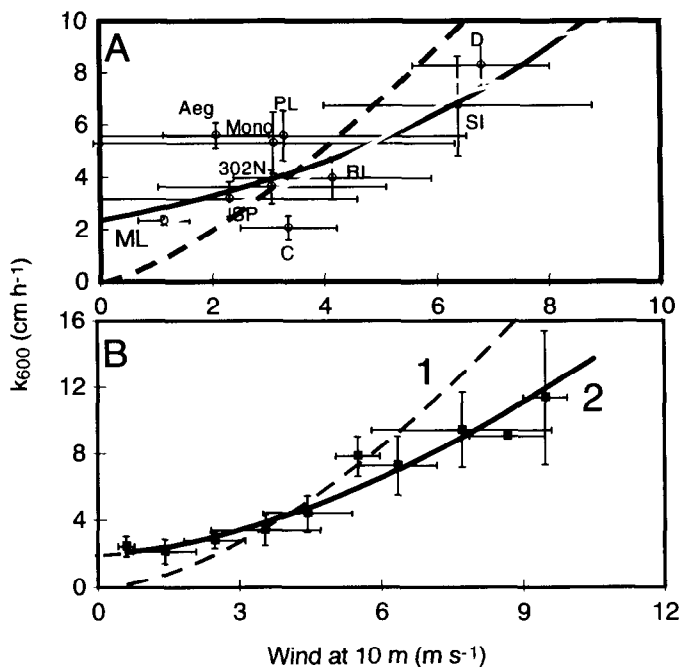


Fig. 8. The relationship between mean wind and mean k_{600} for lakes for which whole-system estimates are available. A. Plot of the mean and 95% CI interval for k and the mean and 95% CI for wind for each lake. B. Combined individual points for the studies shown in panel A that are grouped into wind classes by each 1.0 m s⁻¹ wind interval. We plot the mean wind (with 95% CI) and measured value of k (with 95% CI) for each of these wind intervals. The lowest point is for winds from 0 to <1 m s⁻¹, the next lowest point for winds from 1 to <2 m s⁻¹, and so on. Data come from Mirror Lake (ML, this study), Sutherland Pond (SP, Clark et al. 1995), Dozmary Pond (D) and Siblyback Lakes (SI, Upstill-Goddard et al. 1990), five lakes reviewed by Wanninkhof 1992 and MacIntyre et al. 1995 (Lake 302 N; Crowley, Mono, Pyramid, and Rockland Lakes and Aegirisee (AEG, Livingstone and Imboden 1993). Solid line is the equation $k_{600} = 2.07 + 0.215 U_{10}^{1.7}$; the dashed line is the power relationship from Wanninkhof (1992).

estimates of k (based on whole-lake measurement) and wind speed from nine other lakes to derive a general relationship between k and wind speed (Fig. 8). This relationship adds four lakes to the regression based on five lakes in MacIntyre et al. (1995) and adds three to the six lakes in Wanninkhof (1992), which extends the wind range downward for both. The best fit for the individual points ($n = 192$) was a power function with a constant offset such that at zero wind, k would be ~ 2 cm h⁻¹:

$$k_{600} = 2.07 + 0.215 U_{10}^{1.7} \quad (r^2 = 0.61; P < 0.001; n = 193). \quad (5)$$

Based on the available data Wanninkhof (1992) and MacIntyre et al. (1995) obtained an identical power relationship between k and U :

$$k_{600} = 0.45 U_{10}^{1.64} \quad (6)$$

At winds between 3 and 5 m s⁻¹, k values predicted from Eq. 5 and 6 are nearly identical; the predictions diverge substantially at the low-wind end (Fig. 8) and again at very high

winds. The relationship in Eq. 6 predicts that k will be zero at zero wind; the positive intercept at zero wind in Eq. 5 presumably includes the average effects of processes other than wind that contribute to k . There is, of course, a great deal of scatter in our relationship. We can improve the relationship somewhat by considering the mean k and mean wind speed for the individual lakes (Fig. 8A), or, more substantially, by using the mean k and mean wind speed, grouped by classes of wind speeds (Fig. 8B). In both cases, the modified power relationship (Eq. 5) fits the observations well, including the low-wind end.

Discussion

Gas exchange at low wind speed—Our dataset agrees with other studies that have shown a lack of correspondence between k and wind speed at low wind (Liss et al. 1981; Wanninkhof et al. 1987; Crill et al. 1988; Livingstone and Imboden 1993; Occampo-Torres and Donnelan 1994; Clark et al. 1995). A striking feature of some of these studies is the relatively high and relatively wind-invariant value for k at low winds. A relative constancy of k at winds ≤ 3 m s⁻¹ is partially consistent with the tri-linear model of Liss and Merlivat (1986), which predicts only a 0.7 cm h⁻¹ increase in k_{600} over the first 3.5 m s⁻¹ of wind. The field data from these new low-wind studies differs from the relationship of Liss and Merlivat (1986) in that k_{600} is not zero at zero measurable wind and k_{600} is much higher in the 0–3 m s⁻¹ wind range than this relationship predicts (Fig. 7). The low-wind data collected after the reviews of Wanninkhof (1992) and MacIntyre et al. (1995) also tend to fall well above the wind power relationship used in those reviews (Figs. 7, 8). It is not yet clear which processes generate the turbulence that sustains k at low winds, but the two most likely are penetrative convection and rainfall events. Crill et al. (1988) demonstrated that at the low winds on Lago Calado, the turbulence generated by penetrative convection was 3–200 times greater than that generated by wind, and was the predominant factor influencing methane gas flux (MacIntyre et al. 1995). Ho et al. (1997) showed both in the field and in the laboratory that heavy rainfall could greatly enhance the rate of gas exchange. We do not have a complete energy budget of the surface layer and therefore can not calculate k due to penetrative convection (MacIntyre et al. 1995; Soloviev and Schuessel 1994). The potential for penetrative convection is present in Mirror Lake during this period since the air temperature is often cooler than the water. However, our values of k are related neither to the mean or maximum water–air temperature differences nor to the hours per day that the water is warmer than the air ($P > 0.3$ for both; Pearson product-moment correlation). Thus, we cannot really ascertain the role of convection. Although the rain rate on Mirror Lake was far lower than the tropical downpours (rain rate up to 155 mm h⁻¹) simulated by Ho et al. (1997), the rain rate was better correlated to k_{600} in the lake than any other variable we tested. While our relationship is steeper than that of Ho et al. (1997), it does suggest that some of the variance in k may be caused by the turbulence (or cooling) during rain events. This still leaves much of the variance in k unaccounted for.

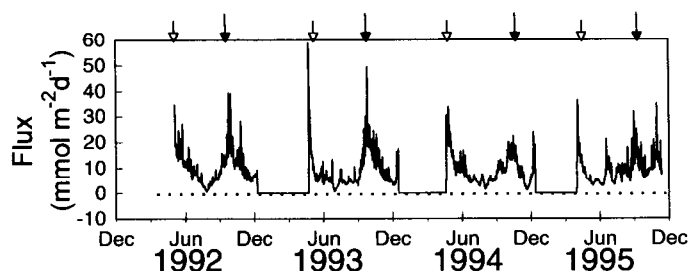


Fig. 9. Estimated CO_2 flux for Mirror Lake for May 1992–November 1995. The calculated CO_2 gas flux according to the relationship between k_{600} and wind speed is shown. Other scenarios are discussed in the text (also see Table 2). We assume that the gas flux is zero under the ice. The times of autumnal and vernal mixing are indicated by the filled and open arrows, respectively.

Estimating CO_2 efflux in Mirror Lake—Although we cannot yet account fully for a mechanistic explanation of the variance in k , we can nevertheless use our measurements of k to calculate gas flux. We provide two types of estimates: (1) We used the empirical relationship between wind and k for lakes that includes the low-wind lakes (e.g. Fig. 8, Eq. 5); the asymptote on this curve is assumed to combine the average effects of both rain and convection on k . (2) Because precipitation may contribute to k , we have also attempted a precipitation-based estimate. To do this, we assume that there is a wind effect and a precipitation effect and that these are additive (see Ho et al. 1997). We used the power relationship of Wanninkhof (1992) and MacIntyre et al. (1995) to estimate the wind effect (since these have a k of zero at zero wind), and then used our empirical relationship between rain and residual k (Fig. 6).

By combining our dataset on the partial pressure of CO_2 in Mirror Lake, along with our attempts to estimate k_{600} , we can calculate the gas exchange for CO_2 . In both cases we assumed that gas flux would be zero during ice cover. For both calculations above, the seasonal pattern was similar since it is driven more by changes in $p\text{CO}_2$ than by wind speed or precipitation. Peak fluxes (up to 30–50 $\text{mmol m}^{-2} \text{d}^{-1}$) occurred during May after ice-out and reached a brief, temporary minimum ($\sim 1 \text{ mmol m}^{-2} \text{d}^{-1}$) in early July (Fig. 9). This minimum was followed by an increase to a secondary peak in late fall associated with autumnal mixing (Fig. 9). The absolute value of the flux depended, in part, on how we modeled k (Table 2). Had we based these flux estimates on the calculated values of CO_2 , which give higher values than the directly measured values, the fluxes would be

$\sim 25\%$ higher for each model. Had we used the tri-linear wind model of Liss and Merlivat (1986) to estimate k , our annual gas efflux would have been only $4.8 \text{ g C m}^{-2} \text{ yr}^{-1}$, which is from 10 to 16% of the estimates in Table 2. Had we used the wind power relationship of Wanninkhof (1992) and MacIntyre et al. (1995; e.g. Eq. 6), gas flux would have been $17.5 \text{ g C m}^{-2} \text{ yr}^{-1}$, or from 35 to 60% of the two estimates in Table 2.

In this analysis we have not included the effects of diel variation in $p\text{CO}_2$, which can be significant in some systems (Sellers et al. 1995). The samples we base the gas flux analysis on were taken between 1000 and 1400 h; the extremes of CO_2 occur at dawn and dusk. These extremes, even at the time of maximum phytoplankton production in the lake, account for only a $2 \mu\text{M}$ ($57 \mu\text{atm}$) excursion in CO_2 . If we assume that this diel excursion occurs at the same rate year-round (an overestimate), we would have an uncertainty of $\sim 13\%$ in the CO_2 flux estimates for the summer months (when $p\text{CO}_2$ is lowest) and an uncertainty of $< 6\%$ in the other seasons when $p\text{CO}_2$ is higher.

CO_2 efflux in Mirror Lake—The efflux of CO_2 to the atmosphere is an important term in the carbon economy of Mirror Lake. For example, the annual loss of DIC in outflow plus outseepage is $\sim 8.62 \times 10^7 \text{ mmol}$ for the whole lake ($6.9 \text{ g C m}^{-2} \text{ yr}^{-1}$) or $1.6 \text{ mmol m}^{-2} \text{ d}^{-1}$, which is about one-fourth as large as our lower estimate of gas evasion. The export of dissolved organic carbon in outflowing and outseeping water has been estimated at $16 \text{ g C m}^{-2} \text{ yr}^{-1}$ (Cole et al. 1984), which is about one-half of our more conservative gas flux estimate. Similarly, the export of photosynthetically assimilated CO_2 to the hypolimnion by particle settling (export production, $\sim 4 \text{ mmol C m}^{-2} \text{ d}^{-1}$; Caraco et al. 1992) is a slightly smaller sink for CO_2 than is gas evasion. Devol et al. (1987) calculated that for the Amazon River, CO_2 efflux was slightly larger than DIC export in flowing water. From studies in Canadian lakes, Dillon and Molot (1997) suggested that CO_2 gas evasion ranged from co-equal to several times as large as carbon burial in sediments.

The CO_2 lost to the atmosphere must be made up by some input or change in standing stock. Clearly, over an annual-cycle (which is about the hydrologic residence time of Mirror Lake) we cannot explain the CO_2 export from changes in standing stock since the annual average DIC mass does not change. Even over shorter periods changes in standing stock of DIC are insufficient to support the CO_2 gas evasion. Mirror Lake has its largest loss in epilimnetic DIC in May and June, averaging $1.1 \pm 0.8 \text{ mmol C m}^{-2} \text{ d}^{-1}$ for 1992–

Table 2. Estimates of CO_2 gas flux in Mirror Lake under different assumptions about the gas-exchange coefficient, k_{600} . For empirical wind-based calculations, we used the empirical relationship between k_{600} and wind, including the low-wind lakes (e.g. Eq. 5, Fig. 8). For wind and precipitation-based calculations, we modeled k_{600} as a function of both wind speed and precipitation using the wind-based relationship of Wanninkhof (1992) and MacIntyre et al. (1995) and our relationship between residual k and precipitation (Fig. 7; see text).

Calculation	k_{600}^* (cm h^{-1})	Mean daily flux* ($\text{mmol C m}^{-2} \text{ d}^{-1}$)	Annual flux ($\text{g C m}^{-2} \text{ yr}^{-1}$)
Empirical wind based	2.8 ± 0.8	6.7 ± 7.0	29.4
Wind and precipitation based	4.3 ± 4.6	11.5 ± 18.0	50.4

* Values are means \pm SD.

1995. This maximal change in standing stock is smaller than gas efflux during the same period by more than 10-fold, implying a large CO₂ input (*see* Fig. 2). During July–September, epilimnetic DIC concentrations are stable, yet gas efflux continues at a rate of at least 1–2 mmol C m⁻² d⁻¹. These balances argue that the CO₂ efflux must be supported by a net input rather than a loss of DIC mass in the system. We do not yet know the nature of the input of CO₂ but its annual magnitude must support a flux of CO₂ of from 26 to 50 g C m⁻² yr⁻¹. We suggest three ways in which this CO₂ input occurs: (1) net heterotrophy model—respiration (supported by allochthonous inputs) within the lake exceeds the net photosynthetic sink of CO₂; (2) CO₂ injection model—flowing ground water carries in excess CO₂ that is sufficient to support the efflux; (3) alkalinity consumption model—flowing ground water and surface water carry in bicarbonate, which meets a source of acidity within the lake, thereby generating the excess CO₂. For Mirror Lake all three processes are possible. We will not know which process alone or in combination supports the efflux until we can construct complete CO₂ and alkalinity budgets for the system.

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