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Meteorological controls of gas exchange at a small English lake

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Abstract

The relationships between gas transfer velocity, k_{600}, wind speed, wind direction, rainfall, and relative humidity were examined using measurements of SF_6 evasion from Coatenhill Reservoir, a small (0.017 km^2), shallow (1.9 $\pm$ 0.1 m), man-made lake in northeast England characterized by predominantly low to intermediate wind speeds ~1–10 m s^{-1}. A graphical method was used to estimate the wind speed at a standard height of 10 m, U_{10}, from wind speed measurements at 2 m and 3.8 m. Derived values of U_{10} normalized to remove thermal stability effects (U_{10}-n) were significantly correlated with k_{600} ($R^2 = 0.71$, $p < 0.001$). A detailed analysis of surface roughness lengths estimated with this procedure showed the k_{600} versus U_{10}-n relationship to be sensitive to wind speed modification by the meteorological mast and sensors. With normalization to remove these effects, the correlation between k_{600} and U_{10}-n substantially improved ($R^2 = 0.86$, $p < 0.001$). In contrast to previous laboratory findings, relative humidity was not significantly correlated with k_{600} and rainfall rate (R_n) was only weakly correlated with k_{600}, possibly as a consequence of the effects of these variables being largely masked by the time scales of data averaging and SF_6 sampling. Similarly, k_{600} was not correlated with wind direction (i.e., fetch). An empirical gas exchange model accounted for 88% of the total variance in k_{600} ($p = 0.01$) at Coatenhill, with U_{10}-n and R_n accounting for 86% and 2%, respectively. Future field investigations of the meteorological controls of k_{600} will require careful experimental design to allow for more detailed sampling than hitherto has been possible.

Reactive trace gas exchange between water and air is an important process in global biogeochemistry. Quantifying gas fluxes and budgets accurately requires accurate estimates of the gas transfer velocity, k_w, a physical variable that has been determined experimentally using volatile tracers in a range of aquatic systems. For example, inert SF_6 has been used to evaluate k_w in lakes (Wanninkhof et al. 1985, 1987; Upstill-Goddard et al. 1990; Clark et al. 1995; Cole and Caraco 1998) and in rivers (Clark et al. 1994). SF_6 has also been used in combination with volatile ^3He to estimate k_w in coastal seas (Watson et al. 1991; Wanninkhof et al. 1993, 1997; Nightingale et al. 2000*b*) and in the open ocean (Nightingale et al. 2000*a*).

All of these tracer studies have tended to model k_w empirically as simple functions of wind speed because of the fundamental role of the wind in generating surface water turbulence. However, a detailed comparison of several of these studies (Wanninkhof 1992; Frost and Upstill-Goddard 1999) shows the relationship between k_w and wind speed to vary widely between them, an observation that cannot be ascribed to the analytical precision of the tracer analyses. On the other hand, wind speed can be difficult to measure reliably, especially at sea (Taylor et al. 1995). In addition, because the increase in k_w with wind speed is strongly nonlinear, the averaging of individual wind speed measurements can introduce biases in the results related to differences in the ambient wind speed distributions between studies (Wanninkhof 1992). Although these problems can be corrected for (Wanninkhof 1992; Yelland et al. 1998), the observed discrepancies between the various studies, although somewhat reduced, still remain, implicating other geophysical variables in the gas exchange process (Frost and Upstill-Goddard 1999).

Some potentially important controls of gas exchange in addition to wind speed include rainfall (Ho et al. 1997; Cole and Caraco 1998), the thermal stability of the air–water interface (Erickson 1993), humidity (Quinn and Otto 1971; Münnich et al. 1978; Liss et al. 1981), and wind fetch (Wanninkhof 1992). In addition, surfactant films associated with high organic productivity can influence gas transfer at low to intermediate wind speeds (Frew et al. 1990; Frew 1997), and bubble generation is important at high wind speeds during wave breaking (Asher and Wanninkhof 1995, 1998; Woolf and Thorpe 1991; Woolf 1993, 1997). Nevertheless, to date there have been few attempts to investigate the effects of several of these processes simultaneously. Cole and Caraco (1998) examined the role of rainfall during CO_2 transfer in a small lake at low wind speeds. However, other variables have previously been treated in isolation, either theoretically and/or in the laboratory (Liss et al. 1981; Wanninkhof and Bliven 1991; Erickson 1993; Asher and Farley 1995; Ho et al. 1997; Woolf 1997).

In this study, we investigated the relationships between k_w in a small oligotrophic lake, determined from the evasion rate of added SF_6, and wind speed normalized to remove thermal stability effects, wind direction (fetch), rainfall, and

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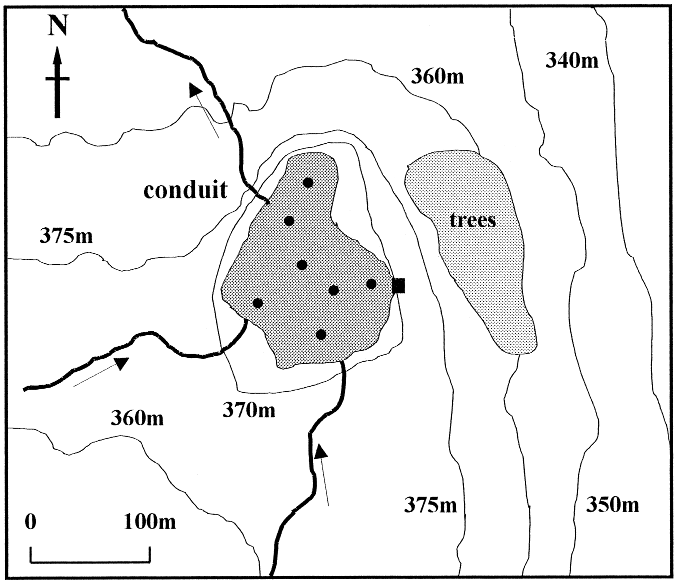

Fig. 1. Coatenhill Reservoir, 54°49.6′N, 2°14.4′W. The filled square gives the location of the meteorological mast and sensors. Filled circles indicate routine sampling locations.

relative humidity. The results were used to construct a simple empirical model of gas exchange. Because small lakes are typically characterized by much lower wind speeds than are large lakes or the open ocean, the opportunities they present for studying gas exchange processes unique to high wind speeds, such as wave breaking and bubble formation, are necessarily limited. Nevertheless, the sampling logistics for small lakes are relatively straightforward, and lateral and/or vertical chemical gradients are generally insignificant, simplifying interpretation of the tracer results. Consequently, gas exchange experiments can be relatively easily controlled, in principle facilitating the collection of highly temporally resolved data and subsequent detailed analysis for key meteorological variables.

Materials and methods

Environmental setting—Figure 1 shows the location of Coatenhill Reservoir, a small man-made lake located ~370 m above sea level on an exposed flank of the North Pennines, northeast England (54°49.6′N, 2°14.4′W). Relevant physical characteristics determined by Frost (1999) are summarized in Table 1. Detailed bathymetric mapping with a portable echo sounder (SupraPro-Eagle: precision ± 0.1 m) revealed a mean lake depth of 1.9 ± 0.1 m and a maximum of 3.9 ± 0.1 m (Table 1). The lake volume was determined from the bathymetric measurements, and the lake area was derived from U.K. ordnance survey data. Freshwater enters Coatenhill directly as storm runoff and exits via a concrete conduit (Fig. 1). During this study, the freshwater volume of the lake remained constant. Freshwater throughput rates were ~0.04% of total lake volume d^{-1}, corresponding to a freshwater residence time ~6.7 yr (Table 1).

Areas of dense reeds extending to ~3 m from the northern and southern shores cover <3% of the water surface. The presence of surface-active material was monitored by weekly measurements of surface tension with a capillary method. Data were indistinguishable from surface tension values for distilled water given in Lide (1991). Therefore, significant modifications to gas exchange by surface-active components (Frew et al. 1990; Frew 1997) can be excluded.

Table 1. Physical data for Coatenhill Reservoir, 54°49.6′N, 2°14.4′W.

Variable	Units	Value
Catchment area	(m^2)	1.3×10^5
Surface area	(m^2)	1.7×10^4
Maximum water depth	(m)	3.9 ± 0.1
Mean water depth	(m)	1.9 ± 0.1
Mean water volume	(m^3)	3.2×10^4
Mean water throughflow	($m^3\ d^{-1}$)	13.0
Mean water residence time	(yr)	6.7

Tracer deployment and sampling—SF_6 deployments were from a small boat, following the procedure of Upstill-Goddard et al. (1990). In brief, two 25-liter steel drums were each filled with fresh water less a 30-cm^3 headspace, which was continuously flushed with 200 $cm^3\ min^{-1}$ pure SF_6 (BOC Special Gases) and recirculated through the water at 2 L min^{-1}. This procedure achieved full SF_6 saturation in 50 min (Upstill-Goddard et al. 1990). The tank contents were distributed evenly around the lake at 1-m depth via 10-cm silicon tubing connected to a hand-held pump.

Water samples were collected by boat, at fixed locations marked by buoys (Fig. 1), and from around the lake perimeter, in 100-cm^3 gastight glass syringes (Samco), taking care to avoid air entrainment and disturbance to the bottom sediment. Near surface samples (i.e., down to ~0.3-m depth) were collected by hand, and deeper samples were collected with a peristaltic pump (RS Components) and 0.2-cm diameter Cu tubing. Filled sample syringes were returned to the laboratory immersed in ambient lake water in an insulated container in order to minimize sample outgassing and diffusive losses (Upstill-Goddard et al. 1990).

Meteorological variables—Because of the small size of Coatenhill Reservoir (Table 1), the difficulty of spatial wind speed variability commonly associated with large lakes (Wanninkhof 1992) does not arise. The meteorological station was of custom design and construction, with full sensor certification by the manufacturer (Delta-T Devices, model WS-UM-3). It was mounted on a mast secured to a submerged stock fence on the eastern lake shoreline and about 30 m from a small copse of trees to the east (Fig. 1). Hence the instruments were partially sheltered from easterly and northeasterly winds but fully exposed to winds from all other directions. Table 2 summarizes details of meteorological variables recorded. Data were logged by integrating each parameter over precisely determined preset time intervals (Table 2) selected as a compromise between sensor resolution and accuracy. Data storage was in binary format in semiconductor memory sufficient for 6 d continuous logging. Data were routinely downloaded to a laptop computer in situ.

Table 2. Details of meteorological variables measured at Coatenhill Reservoir. Operational limits and accuracy data are those supplied by the manufacturer; the latter includes both sensor and data logger derived errors. Data logger uncertainties were ±0.17°C temperature, ±0.2 mbar pressure, ±0.5° wind direction. The water temperature thermistor was secured to the stock fence about 10 m offshore from the mast. The precision of the humidity measurements is ±4% at relative humidities above 98% due to condensation on the sensor.

Variable	Sensor type and height	Measurement unit	Logging frequency (min)	Threshold measurement value	Maximum measurable value	Accuracy
Air pressure	Barometer (Delta-T BS3) 2 m	mbar	60	800	1,060	±0.6
Wind direction	Wind vane (Delta-T WD1) 3.8 m	degrees from north	5	0.6		±2
Wind speed	Anemometers (Delta-T AN1) 2 m and 3.8 m	$m\ s^{-1}$	5	0.2	75	±0.35
Humidity	Hygrometers (Delta-T TM1) 2 m and 3.8 m	% relative humidity	5	0	100	±<2
Air temperature	Thermistors (Delta-T UM-A) 2 m and 3.8 m	°C	5	−20	80	±0.27
Water temperature	Thermistor −0.2 m	°C	5	−20	80	±0.27

Rainfall data were obtained from a rain gauge located about 5 km from Coatenhill and operated by the U.K. Meteorological Office.

Water sample analysis—Each filled sample syringe was emptied to a predetermined volume and a headspace created by backfilling to 100 cm^3 with ultra-high purity (UHP) N_2. The extremely low solubility of SF_6, $\sim 2.4 \times 10^{-4}$ mol kg^{-1} at 25°C and 1 atmosphere (Gerrard 1980), meant that vigorous shaking for 4 min ensured quantitative transfer of SF_6 to the headspace. Although ambient water temperatures at Coatenhill ranged from 1 to 14°C during the experiments, partitioning errors due to variations in equilibration temperature were not significant.

Equilibrated headspace gases were analyzed by electron capture gas chromatography (Shimadzu GC-8) with chromatographic separation at 60°C on a 2 m × 0.2 cm internal diameter 5A molecular sieve column (80–100 mesh, Alltech). UHP N_2 was used as carrier gas (25 $cm^3\ min^{-1}$). Method calibration was by secondary standards pressure diluted from a primary mixture (Upstill-Goddard et al. 1990) and calibrated against high-accuracy standards prepared independently (Law et al. 1994). Analytical precision (1 σ) established from repeat analyses ($n = 20$) of a 50 parts per trillion by volume (pptv) SF_6 standard was ±0.5%.

Results

Tracer mixing—Initial surveys conducted 2 to 4 d after each SF_6 deployment demonstrated strong thermal and chemical homogeneity. Vertical and lateral variations in SF_6 were generally <5%. However, samples collected in areas of peripheral reed coverage occasionally had SF_6 concentrations significantly above the mean for open lake samples, especially during the warmer months when reed coverage was most extensive and wind speeds were comparatively low. Wave damping in reed covered sites was evident at all wind speeds, presumably leading to decreased gas exchange and excess SF_6. We observed a similar phenomenon during an earlier study (Upstill-Goddard et al. 1990). The maximum concentration difference observed between open lake and reed covered sites at Coatenhill was ~15%. Subsequent release of this water during higher wind speed periods or following reed die back has potential implications for the subsequent calculation of k_w. However, we estimated the reed beds to occupy <2% of the total lake volume. Although periodic release of this water could cause significant SF_6 inhomogeneity during its initial mixing with adjacent lake water, following complete mixing the resulting increase in mean SF_6 concentration would not exceed 0.5%. Because decreases in SF_6 concentration between sampling intervals were always far greater than 0.5%, representative SF_6 concentrations were determined by averaging the data obtained at individual stations.

Gas transfer velocities—The flux of a gas, F, across an air–water interface is related to k_w by

$$F = k_w(C_w - \beta C_a) \tag{1}$$

where C_w is the gas concentration in water directly below the interface, C_a is the equilibrium gas concentration in air just above the interface, and β is the Ostwald solubility coefficient. In a given time period Δt

$$F = (\Delta M/\Delta t)/A \tag{2}$$

where M is the total mass of gas contained under an air–water interface of surface area A. Because Coatenhill was always well mixed with respect to SF_6 concentrations

$$F = (\Delta C_w/\Delta t)h \quad (3)$$

where h is the mean water depth. Combination of Eqs. 1 and 3 gives

$$\Delta C_w/\Delta t = k_w/h[C_w - (\beta C_a)] \quad (4)$$

Because the condition $C_w \gg \beta C_a$ was always fulfilled during sampling, βC_a can be ignored and integration gives

$$k_w = h/\Delta t \ln(C_i/C_f) \quad (5)$$

where C_i and C_f are, respectively, the initial and final gas concentrations in the water during time period Δt.

Non–gas exchange losses of SF_6—In addition to its direct evasion to air, SF_6 is lost from Coatenhill by water through flow, requiring the inclusion of a dilution term, F_d, in Eq. 3

$$F + F_d = (\Delta C_w/\Delta t)h \quad (6)$$

(Ho et al. 1997). Because Coatenhill operated at constant water volume, F_d can be determined from

$$F_d = C_w h(j/V_l) \quad (7)$$

where V_l is the lake volume and j is the water outflow rate measured at the conduit (Ho et al. 1997). Combining Eqs. 6 and 7 and integrating over Δt gives

$$k_w = h/\Delta t \ln[(C_i/C_f) - (j/V_l)] \quad (8)$$

For the time intervals used here, such corrections to k_w were always <2%.

Other potential SF_6 losses include scavenging by sediments (Wanninkhof 1986) and coebullition with biogenic gases such as CH_4 (Cole and Caraco 1998). Replicate sediment samples routinely collected in 100-cm^3 gastight syringes at the end of each gas exchange experiment and equilibrated with UHP N_2 failed to elicit a measurable analytical response, implying any reversible adsorption of SF_6 to be weak, in agreement with previous conclusions (Wanninkhof 1986). Cole and Caraco (1998) found SF_6 coebullition losses from Mirror Lake to be at most 200-fold slower than losses due to gas exchange. Based on their data, a change in k_w of 0.1 cm h^{-1} at Coatenhill would require an ebullition rate in excess of 10 L m^{-2} d^{-1}. Ebullition rate data are not available for our experiments, but because we only ever observed the phenomenon as a short-lived consequence of direct sediment disturbance during sampling, a significant effect from this process can be excluded.

Wind speed derivation—The derivation of meaningful wind speeds from cup anemometers can be problematic (DeFelice 1998). In this study, wind speed measurements from anemometers at two fixed heights (Table 2) were required for estimating vertical wind profiles and for deriving additional variables. In order to ensure data integrity, stringent anemometer calibration is essential. The meteorological sensors and data logger used at Coatenhill were an integrated package designed specifically for high-accuracy scientific applications. The two anemometers were rigorously precalibrated by the manufacturer in a wind tunnel over the wind speed range 0–30 m s^{-1} and certified to ±1% accuracy by metering their performance against a standard rotor calibrated by the U.K. National Maritime Institute. Relative calibration factors (revolutions s^{-1} m^{-1} s^{-1} wind speed) supplied for the two anemometers were 48.3 (2 m) and 48.4 (3.8 m), a discrepancy of <0.2% in measured wind speeds.

Measured wind speeds were graphically extrapolated to U_{10}, the corresponding wind speed at 10 m, by assuming a logarithmic vertical wind distribution

$$\ln z = [(K/u^*)U(z)] + \ln z_0 \quad (9)$$

where $U(z)$ is the measured wind speed at height z; K is von Karman's constant, 0.4; u^* is the friction velocity in air; and z_0 is the surface roughness length (Mackintosh and Thom 1973). The ratio K/u^* was evaluated graphically for each sampling interval from the slope of ln z versus $U(z)$, with ln z_0 derived by substitution.

In our earlier use of the graphical method for U_{10} at Siblyback Lake and Dozmary Pool, our wind speed data were obtained using commercial yacht masthead transducers of contrasting designs (Upstill-Goddard et al. 1990). Therefore the possibility of a significant measurement offset could not be discounted. Our results were subsequently criticized on the basis that our z_0 estimates were too high for a free water surface (Kwan and Taylor 1993). These authors concluded that the lower of our two anemometers (Upstill-Goddard et al. 1990) may have underestimated true wind speeds, and they subsequently reworked our data using wind speeds from the higher anemometer only and using a fixed z_0 more typical of a free water surface. The resulting modifications to the Siblyback/Dozmary Pool k_w versus U_{10} curve (Kwan and Taylor 1993) more closely allied it with other published relationships (Liss and Merlivat 1986; Crucius and Wanninkhof 1990). Nevertheless, many of our z_0 estimates for Coatenhill (mean ~0.1 m; range 10^{-7}–1.3 m) are closer to those derived for Siblyback Lake and Dozmary Pool (mean ~0.26 m; range 0.06–0.5 m) than to the value of 10^{-4} m adopted by Kwan and Taylor (1993). Unlike the situation for Siblyback Lake and Dozmary Pool, the possibility of anomalous z_0 estimates at Coatenhill arising from measurement offsets is precluded by the choice of higher quality anemometers in the present study and the care taken over their calibrations.

According to Mason (1988), for z_0 variations over short length scales, the effective value of z_0 approaches the largest z_0 values encountered over the averaging length. Adoption of this reasoning at Coatenhill and consideration of its relatively small surface area lead to the conclusion that the surrounding terrain should exert a greater influence on z_0 than does the water surface itself. Consequently, higher z_0 values for Coatenhill than for larger water bodies should be expected. The effect of the surrounding terrain on z_0 was investigated by examining the relationship between z_0 and wind direction. Individual z_0 estimates for each of 45,001 5-min logging intervals were allocated to one of 11 equally sized bins. Data allocation produced 11 consecutive ranges in z_0, each compiled from 4,091 individual estimates (Table 3). Figure 2 is a wind direction frequency plot for selected bins and reveals some important features of the data. Most importantly, the highest z_0 values (90–100% category, Table 3) were primarily associated with wind directions of 280°–330° (Fig. 2). These correspond to an approach across open ground and the free lake surface (Fig. 1) and on initial in-

Table 3. Ranges of z_0 for Coatenhill Reservoir, based on allocating individual 5 min z_0 estimates to one of 11 equally sized bins in order to produce 11 ranges in z_0.

Category (%)	z_0 range (m)
0–10	$\sim 1 \times 10^{-7}$–8×10^{-4}
10–20	8×10^{-4}–0.008
20–30	0.008–0.02
30–40	0.02–0.03
40–50	0.03–0.05
45–55	0.04–0.07
50–60	0.05–0.09
60–70	0.09–0.15
70–80	0.15–0.3
80–90	0.3–0.6
90–100	0.6–1.3

spection seem somewhat high for such terrain (Mackintosh and Thom 1973; Mason 1988). However, the apparent anomaly can be ascribed to likely interference by the mast assembly and additional sensors, which partly obstructed airflow to the 2-m anemometer from these directions. By contrast, the 3.8-m anemometer had a different boom orientation, such that 280°–330° winds were unhindered but 60°–90° winds were partially obstructed. For this situation Eq. 9 underestimates the decay in wind speed to ground level for 280°–330° winds, leading to an overestimate of z_0. By way of comparison, winds from directions directly adjacent to these coordinates (i.e., 260°–280° and 330°–360°) were unaffected by the mast structure, and the associated z_0 estimates are correspondingly lower. The cluster of relatively high values in the 0–10% z_0 category (Table 3) for wind directions between 60° and 90° (Fig. 2) reflects shielding of the 3.8-m anemometer by its boom. Winds from these directions pass over a copse of trees (Fig. 1) and should give z_0 values somewhat higher than estimated. In this situation, the suppression of measured 3.8-m wind speeds by the boom structure gives an overestimate of the decay in wind speed to ground level and an underestimate of z_0. Based on this reasoning, all U_{10} values associated with wind directions of 60°–90° and 280°–330° (~5% and 15% of the total data set, respectively) have been corrected for these effects. For 60°–90° winds, U_{10} was estimated using the 2-m anemometer data only and adopting the median z_0 value of 0.2 m for the 70–80% z_0 bin, a value compatible with winds flowing directly across the copse (Mackintosh and Thom 1973; Mason 1988). For 280°–330° winds, U_{10} was estimated using the 3.8-m anemometer data only and the median z_0 value of 9×10^{-5} m for the 0–10% z_0 bin. This value is consistent with winds flowing directly across open ground and the lake surface (Mackintosh and Thom 1973; Mason 1988).

Gas transfer velocities and wind speed—The results of the gas exchange experiments are summarized in a Web Appendix on the Limnology and Oceanography web site (Web Appendix 1: http://www.aslo.org/lo/toc/vol_47/issue_4/1165a1.pdf). All k_w estimates derived from Eq. 8 have been converted to k_{600}, the corresponding value for a Schmidt number of 600 being the value for CO_2 in freshwater at 20°C

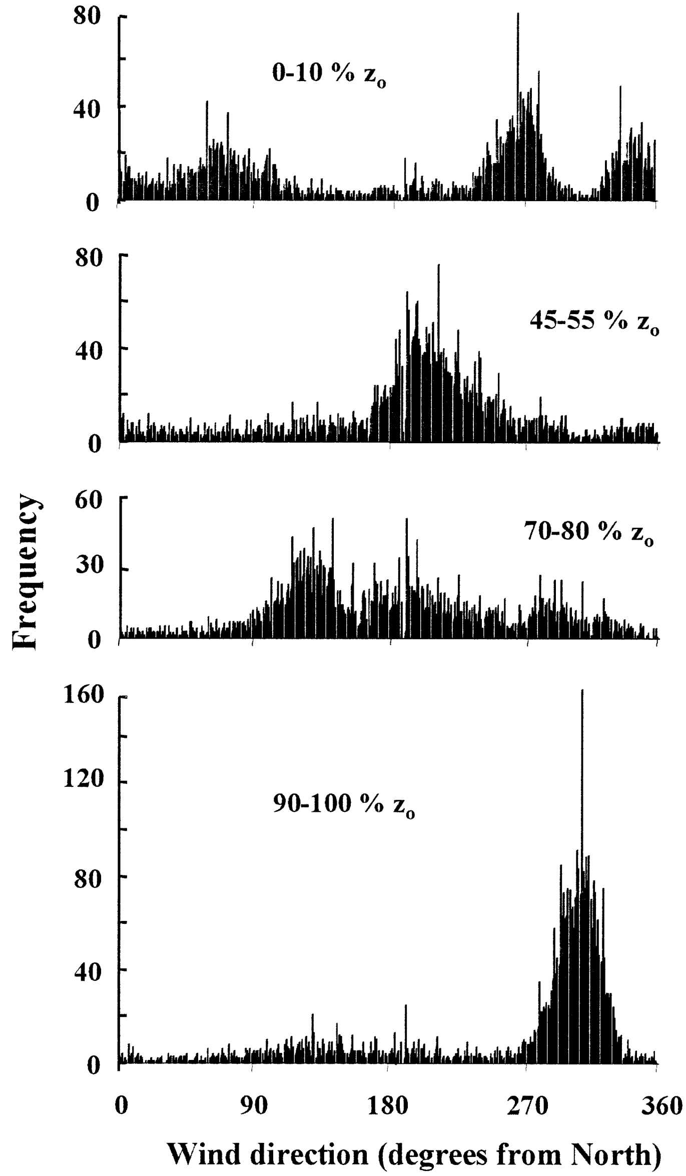

Fig. 2. Wind direction frequency plot for selected z_0 bins summarized in Table 3. *See text for details.*

$$k_{600} = k_w(S_c/600)^n \qquad (10)$$

where S_c is the Schmidt number of SF_6 at the measurement temperature, derived from the empirical relationship of Wanninkhof (1992). We used $n = -0.67$ for $U_{10} < 3.6$ m s^{-1} and $n = -0.5$ for $U_{10} > 3.6$ m s^{-1} (Liss and Merlivat 1986; Frost and Upstill-Goddard 1999).

In the hypothetical case of two identical lakes with identical wind speeds but with contrasting temperature structures across their water–air interfaces, their respective k_{600} versus U_{10} relationships will differ, reflecting differences in buoyancy-induced turbulence associated with thermal stability. Therefore, in comparing the results from different gas exchange studies, this effect should be removed by normalizing U_{10} to U_{10}-n, the equivalent wind speed for neutral stability conditions (e.g., Nightingale et al. 2000*b*). Both the original (U_{10}) and the stability normalized (U_{10}-n) 10-m wind speeds

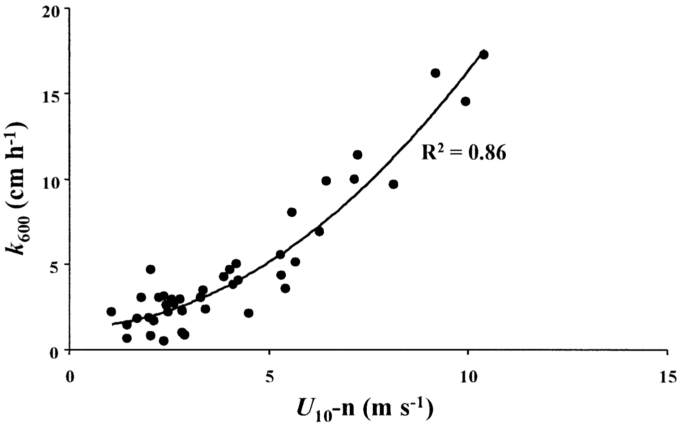

Fig. 3. k_{600} versus U_{10}-n relationship at Coatenhill, derived from Eq. 9, with the exclusion of mast and sensor artifacts from the 2-m and 3.8-m wind speed data (*see text*).

for Coatenhill are listed in the Web Appendix. We used the approach detailed in Erickson (1993) and derived from Large and Pond (1982) to generate estimates of the neutral drag coefficient (Cd_n), which could be converted to U_{10}-n. This required estimating the bulk stability parameter z/L, where L is the Monin-Obukhov length (Monin and Obukhov 1954). These estimates were derived from functions of $\Delta\theta$, where $\Delta\theta$ (K) is the water temperature immediately below the air–water interface (θ_w) minus the boundary layer air temperature (θ_a). For stable conditions ($\Delta\theta < 0$)

$$z/L = -[70z/U(z)^2T_0] \times [\Delta\theta + (2.5 \times 10^{-6}T_0^2(Q_s - Q_a))] \quad (11)$$

and for unstable conditions ($\Delta\theta > 0$)

$$z/L = -[100z/U(z)^2T_0] \times [\Delta\theta + (1.7 \times 10^{-6}T_0^2(Q_s - Q_a))] \quad (12)$$

Q_s, Q_a, and T_0 are defined as follows

$$Q_s = [62{,}757 \times 10^4e^{-5107.4/\theta_w}] \quad (13)$$

$$Q_a = [48{,}029 \times 10^4e^{-5107.4/\theta_a}] \quad (14)$$

$$T_0 = \theta_a[1 + (1.7 \times 10^{-6}\theta_aQ_s)] \quad (15)$$

(Large and Pond 1982; Erickson 1993). In this treatment we assumed θ_w to be equal to the water temperature measured 0.2 m below the water–air interface (*see Web Appendix*). Estimates of Cd_n were obtained from z/L and neutral drag coefficients over the oceans given in Trenberth et al. (1989), using a bulk aerodynamic approach (Large and Pond 1982; Erickson 1993). U_{10}-n was calculated from Cd_n adopting the U_{10}-n versus Cd_n functional dependence determined by Oost (1998). For these conditions, the wind speed normalizations to neutral stability at Coatenhill are rather small (mean = 5 ± 10%, *see Web Appendix*), consistent with the predictions of Erickson (1993) based on similar ranges in U_{10} and $\Delta\theta$.

In order to interrogate the validity of our protocol for estimating U_{10} (i.e., by excluding wind mast/sensor interference on the basis of derived z_0 values), we evaluated alternative approaches to deriving the k_{600} versus U_{10}-n relationship at Coatenhill. With U_{10}-n derived from U_{10} calculated from Eq. 9 applied to the full data set, this relationship was best described by a quadratic relationship ($R^2 = 0.54$, $p < 0.001$, $n = 44$). With U_{10}-n derived from U_{10} estimated logarithmically using the 3.8-m wind speeds only and with z_0 set to 10^{-4} m (Kwan and Taylor 1993), the data fit improved ($R^2 = 0.71$, $p < 0.001$, $n = 44$). However, the strongest relationship (Fig. 3) was derived by applying Eq. 9 to both sets of anemometer data, filtered to remove mast/sensor artifacts as described earlier ($R^2 = 0.86$, $p < 0.001$, $n = 44$). Based on this comparison, our preferred procedure for estimating U_{10} seems justified.

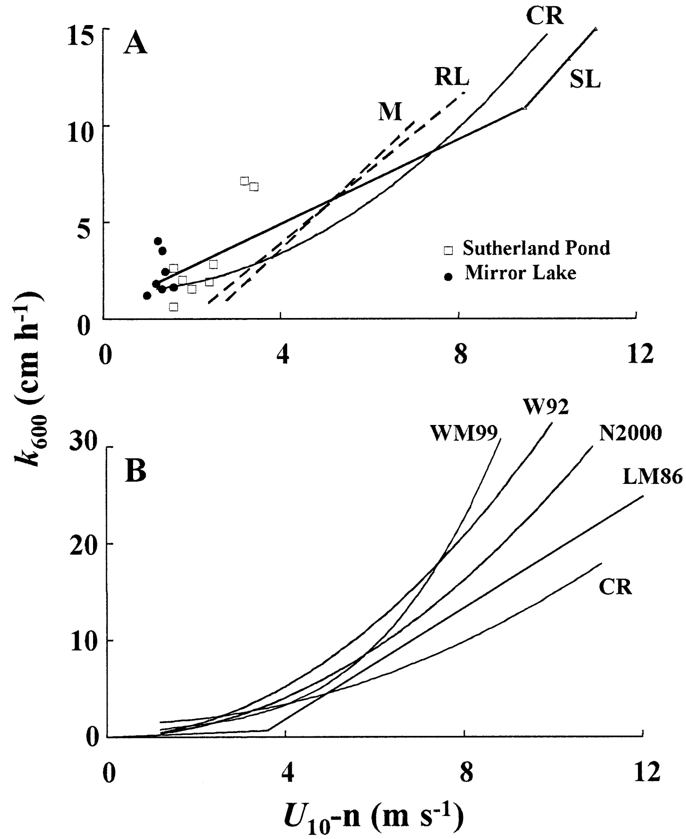

Fig. 4. (A) k_{600} versus U_{10} relationships in lakes. CR is Coatenhill Reservoir, SL refers to Siblyback Lake and Dozmary Pool (Upstill-Goddard et al. 1990), M is Mono Lake (Wanninkhof et al. 1997), and RL is Rockland Lake (Wanninkhof et al. 1985). Sutherland Pond data are from Clark et al. (1995) and Mirror Lake data are from Cole and Caraco (1998). (B) Comparison of the Coatenhill relationship with contemporary gas exchange parameterizations. CR is Coatenhill Reservoir, LM86 is the Liss and Merlivat (1986) curve, W92 is the relationship for instantaneous winds derived by Wanninkhof (1992), N2000 is a best fit to North Sea dual tracer data (Nightingale et al. 2000*b*) and WM99 is the cubic relationship of Wanninkhof and McGillis (1999).

Discussion

Wind parameters and k_{600}—Figure 4 compares the k_{600} versus U_{10}-n relationship shown in Fig. 3 with k_{600} versus U_{10} data for prior lake studies and some other contemporary

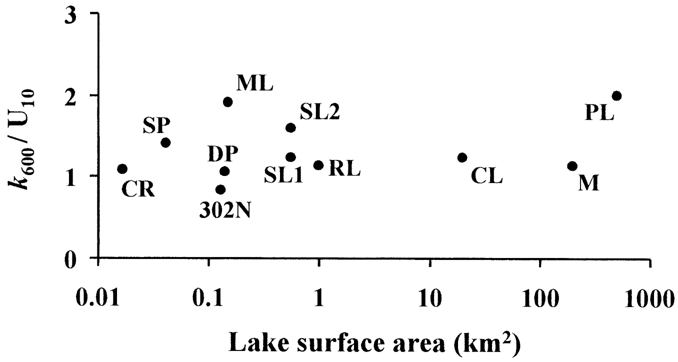

Fig. 5. Relationships between wind speed normalized mean k_{600} and lake surface area. CR is Coatenhill Reservoir, CL and M are Crowley Lake and Mono Lake (Wanninkhof et al. 1997), DP is Dozmary Pool (Upstill-Goddard et al. 1990), and ML is Mirror Lake (Cole and Caraco 1998). PL is Pyramid Lake (Wanninkhof et al. 1991), RL is Rockland Lake (Wanninkhof et al. 1985), SP is Sutherland Pond (Clark et al. 1995), and 302N is from Crucius and Wanninkhof (1990). SL1 is Siblyback Lake (Upstill-Goddard et al. 1990) and SL2 is Siblyback Lake with the revised U_{10} estimates of Kwan and Taylor (1993).

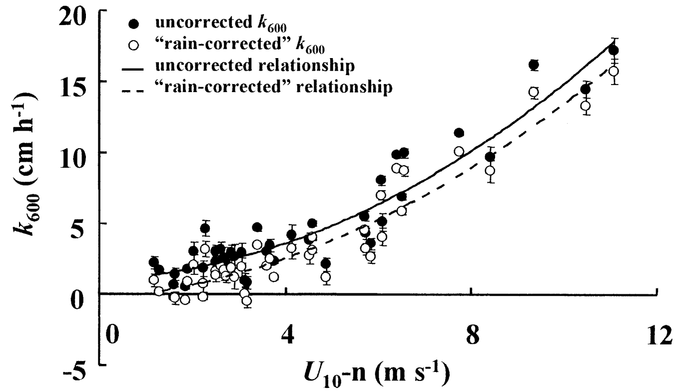

Fig. 6. A comparison of k_{600} and rain-corrected k_{600} versus U_{10}-n at Coatenhill. There is no significant difference between the two correlations; $R^2 = 0.86$ for both.

relationships for short-term (~1 d) steady winds: a trilinear function derived from wind tunnel results and lake tracer data (Liss and Merlivat 1986), a quadratic relationship derived using an assumed global wind frequency distribution modeled with ocean ^{14}C (Wanninkhof 1992), a best fit to all existing tracer results from the southern North Sea (Nightingale et al. 2000*b*), and a cubic relationship derived from CO_2 covariance measurements compatible with global ^{14}C constraints (Wanninkhof and McGillis 1999). For all wind speeds >2 m s^{-1}, the Coatenhill results generally predict a lower k_{600} for any given value of U_{10}-n than for any of the other lakes studied to date. Momentum transfer from the wind to a water surface has been shown to be partly wind fetch dependent (MacIntyre 1984), and the data in Fig. 4 are for systems of widely differing physical scales. Wanninkhof (1992) showed that for several lakes spanning a wide range of surface areas, for any given value of mean wind speed the value of k_{600} averaged over the experiment increased with lake surface area and, by implication, wind fetch. Although this does not seem to apply to the results of subsequent lake experiments (Fig. 5), for the majority of these the mean wind speed was rather low and presumably wind fetch would also have been small. Therefore, because Coatenhill Reservoir has approximately the same surface area as the smallest of the lakes compared by Wanninkhof (1992), a significant influence of wind fetch in the data of Fig. 4 cannot be excluded. Even so, as in an earlier study (Upstill-Goddard et al. 1990), we could find no relationship between our individual estimates of k_{600} and wind direction. Similarly, Nightingale et al. (2000*b*) could find no such relationship for the southern North Sea. Such lack of a significant k_{600} versus wind fetch relationship for individual measurements is perhaps not surprising given that the data inevitably incorporate the complicating effects of short-term fluctuations in wind direction and other controlling variables between sampling.

Rainfall effects on k_{600}—Raindrops striking a water surface cause small increases in turbulence, leading to enhancements of k_{600} (Ho et al. 1997). Quantification of this effect for Coatenhill requires the influence of U_{10}-n on k_{600} (Fig. 3) to be removed from the data. Therefore, we initially calculated the differences between our k_{600} values and those determined from both the Liss and Merlivat (1986) and Wanninkhof (1992) relationships (Cole and Caraco 1998), for wind speeds below 3 m s^{-1} where the wind speed effects on k_{600} are smallest (Liss and Merlivat 1986; Wanninkhof 1992). However, no significant relationships between these residual k_{600}s, and rainfall rate were derived. An alternative approach to removing the effects of wind speed by plotting the relationship between rain rate and the ratio k_{600}/U_{10}-n did give a correlation that, although significant, was rather weak ($R^2 = 0.25$, $p = 0.001$). In contrast, using laboratory data for fixed raindrop sizes at zero wind speed Ho et al. (1997) derived a strong relationship between rain rate and k_{600}. This involved calculating the rainfall transfer of kinetic energy flux (KEF) to a water surface using a robust relationship between KEF and raindrop size (Marshall and Palmer 1948) in order to negate the effects of a limited drop size spectrum on their results. Their treatment gave

$$k_{600} = 0.679R_n - 0.0015R_n^2 + 0.929 \qquad (16)$$

(Ho et al. 1997), where R_n is the rainfall rate (mm h^{-1}). The lack of a strong relationship at Coatenhill Reservoir of the type found by Ho et al. (1997) highlights the difficulty of deriving meaningful data under field conditions where rainfall occurs as discrete events of a duration unrelated to the frequency of tracer sampling. In addition, it is conceivable that any relationship with rainfall is at least partly obscured by systematic errors in the measurement of U_{10}-n and in the applied stability correction. Notwithstanding such possibilities, a useful insight into the relationship between k_{600}, U_{10}-n, and R_n at Coatenhill can be derived by initially assuming the turbulence effects of rain and wind upon k_{600} to be additive (Cole and Caraco 1998) and applying Eq. 16 to derive rain-corrected values of k_{600}. The corollary of additive turbulence is that U_{10}-n should be more closely correlated with rain-corrected k_{600} than with the initial k_{600} value. However, this procedure does not improve the fit of the Coatenhill data

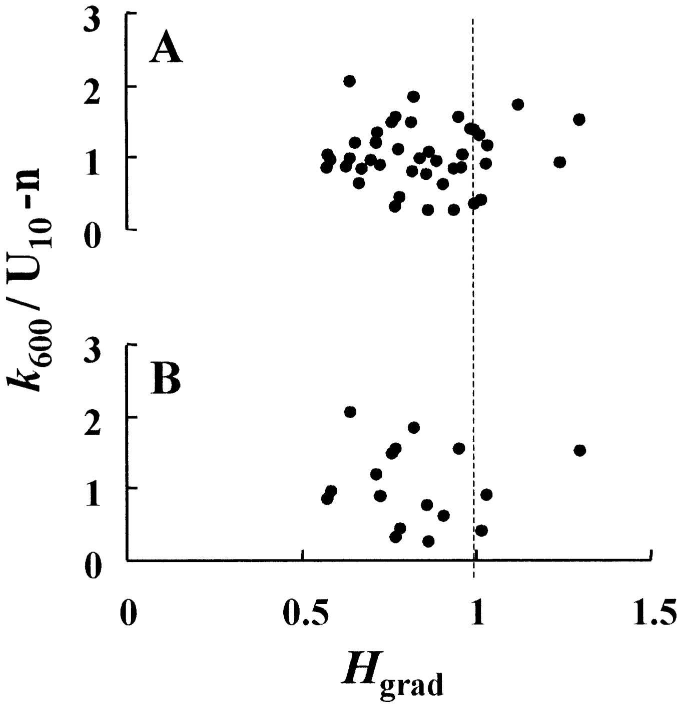

Fig. 7. The relationship between gas exchange and humidity at Coatenhill: (A) all data; (B) data for U_{10}-n < 3 m s^{-1}.

(Fig. 6), and given the robust basis of the Ho et al. (1997) formulation (Marshall and Palmer 1948), the assumption of additive turbulence effects for rain and wind upon k_{600} may be inappropriate. This conclusion is consistent with a previous contention that the effects of rainfall and wind speed on k_{600} are intrinsically interlinked (Poon et al. 1992). These authors demonstrated significant rain suppression of wind waves for wind speeds below ~6 m s^{-1} in a laboratory tank but could show no observable rain effect above 6.34 m s^{-1}. Unfortunately present data are inadequate for a further examination of these conclusions.

Humidity and k_{600}—So-called condensing conditions, for which the specific humidity of air immediately above a water surface exceeds that of the bulk boundary layer air, have been associated with k_{600} suppression in wind tunnels (Liss et al. 1981). In order to examine this phenomenon at Coatenhill, air immediately above the water surface was assumed to be at the same temperature as the water and to have a relative humidity of 100%. This and measured relative humidities in bulk air (web appendix 1) were converted to specific humidities using data from Lide (1991) and used to generate values of H_{grad}, the ratio of the specific humidity in interfacial air to that in bulk air. Hence, H_{grad} values less than one describe condensing conditions and H_{grad} values more than one refer to evaporating conditions. A plot of H_{grad} versus k_{600}/U_{10}-n for values of U_{10}-n < 3 m s^{-1} (Fig. 7) shows no significant correlation. Cole and Caraco (1998) similarly found no correlation between k_{600} and specific humidity at Mirror Lake. The range in H_{grad} at Coatenhill (0.6–1.3) was similar to that in the laboratory study of Liss et al. (1981), 0.5–1.6. Given that conditions in the latter were kept constant but that the Coatenhill data were necessarily averaged over several days, and assuming the experimental protocols of Liss et al. (1981) to be robust, the lack of any observed humidity control of k_{600} at Coatenhill is somewhat equivocal. The possibility that temporal variations in other controlling parameters during the averaging procedure act to mask any humidity effects on k_{600} in field experiments should not be discounted, highlighting a need for more detailed field sampling.

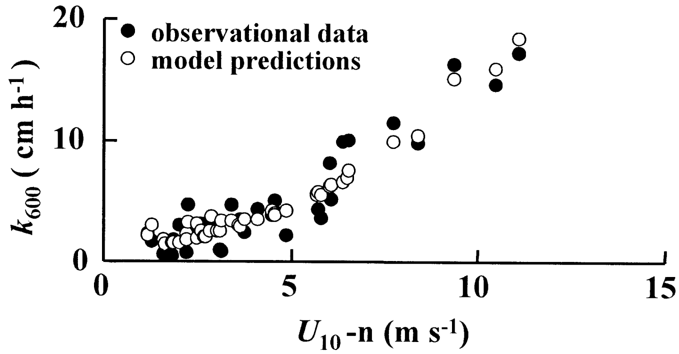

Fig. 8. A comparison of the model predicted k_{600} versus U_{10}-n relationship with the observational results.

Empirical gas exchange model—A multiple regression procedure (Altman 1996) was used to examine the extent to which variability in k_{600} could be explained by the meteorological variables measured. The model was initially of the form

$$k_{600} = a + b_1(U_{10}\text{-n})^2 + b_2(U_{10}\text{-n})^3 + b_3(H_{grad}) + b_4(R_n) \quad (17)$$

All potential controlling variables were included in a preliminary model and a sequential backward stepwise technique was employed to individually exclude them. Only those variables accounting for significant variability ($p < 0.05$) in the data were subsequently reinstated in the model. The resulting model accounted for 88% of the total variance in the data ($p = 0.01$) and was of the form

$$k_{600\text{-mod}} = 1.03 + 0.129(U_{10}\text{-n})^2 + 19.99(R_n) \quad (18)$$

with U_{10}-n (m s^{-1}) and R_n (cm h^{-1}) accounting for 86% and 2%, respectively, of the total variance. Figure 8 compares observational data with the model predictions. In order to adequately assess the robustness of the model, it is necessary to consider its predictive capacity for individual values of k_{600} (Altman 1996). This was done by examining the residuals generated by subtracting $k_{600\text{-mod}}$ from the measured k_{600} values and plotting the results against the standard normal deviates of k_{600}, determined by subtracting the mean k_{600} from each measured value and dividing by the standard deviation (Altman 1996). The results of this treatment (Fig. 9) show that although the majority of the data conform to a linear relationship, there are clearly five outliers. These were generated from k_{600} estimates for the five highest mean values of U_{10}-n (7.7–11 m s^{-1}). One possibility for this apparent weakening of the k_{600} versus U_{10}-n relationship at high U_{10}-n may be that the onset of breaking waves observed at Coa-

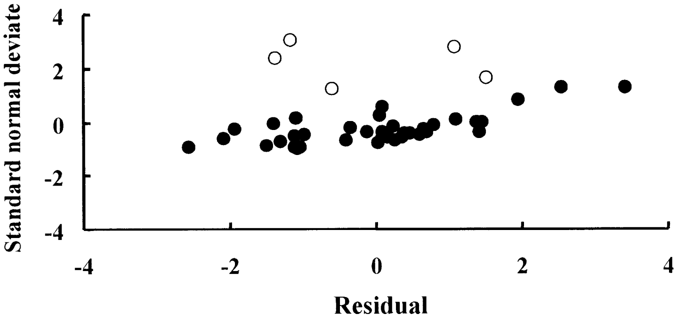

Fig. 9. The relationship between standard normal deviates of k_{600}, determined by subtracting the mean k_{600} from each measured value and dividing by the standard deviation, and the model residuals, generated by subtracting $k_{600\text{-mod}}$ from the measured k_{600} values. Open circles are outliers discussed in the text.

tenhill during these high wind speed events coupled with the low solubility of SF_6 (Gerrard 1980) results in a significant bubble contribution to SF_6 exchange. This possibility highlights the persistent difficulty of determining the functionality of k_{600} at high wind speeds.

The inherent design of the SF_6 evasion technique, which necessarily involves the averaging of data over time scales that are long in the context of meteorological variability, means that meteorological controls of k_{600} demonstrated under well-constrained laboratory conditions can fail as k_{600} predictors in the field. One important example is the effect of rainfall, the detailed investigation of which will require a much more frequent and flexible sampling strategy than has hitherto been employed. Future gas exchange studies should therefore aim to include some form of automated sampling and analysis, such as by deploying semipermanent measurement buoys. With such refinements, and assuming that lakes with wind speed distributions similar to those at sea are selected, future such studies should have great potential for defining more clearly the constraints on k_{600}. Although directly applying such results in an oceanic situation may currently be contentious, ongoing developments in the measurement of meteorological variables at sea (Walsh and Portis 1999; Wong et al. 1999; Lebedev and Tomczak 1999) make the direct extrapolation of lake-based results to the oceans a realistic prospect.

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