

# Gas transfer velocities in lakes measured with SF<sub>6</sub>

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## ABSTRACT

The experimentally-determined relationships between air–water gas transfer velocity and windspeed are presented for two small, rapidly wind mixed lakes in upland SW England. High-precision estimates of the gas transfer velocity,  $k$ , with daily resolution, were derived by monitoring the rate of evasion from the lakes of added sulphur hexafluoride, SF<sub>6</sub>, an inert, sparingly soluble, man-made gaseous tracer. Corresponding data on in situ wind speeds and directions, and surface water temperatures were automatically logged as a time series of 4 min averages, using a battery-powered device. The results significantly extend the existing field database and show a strong dependence of  $k$ , normalized to CO<sub>2</sub> at 20°C, on windspeed in the range ~2–13 m s<sup>-1</sup>, corrected to a height of 10 m. No correlation was found between  $k$  and wind direction. The data are fitted with two least-squares straight lines which intersect at a windspeed of  $9.5 \pm 3$  m s<sup>-1</sup> (at  $z = 10$  m), beyond which significant steepening of the  $k$  versus windspeed relationship implies a transition from the “rough surface” to “breaking wave” regime, in broad agreement with previous conclusions. Nevertheless, the data scatter about the fitted lines exceeds that which would be predicted from the associated analytical uncertainties. This implies the observed relationships between  $k$  and windspeed are not unique and therefore that additional factors must be important in determining  $k$ .

## 1. Introduction

The evaluation of gas exchange between the atmosphere and surface waters has important consequences for water quality assessment, for example in determining rates of river reaeration (Holley and Yotsukura, 1984; Devol et al., 1987) and lake eutrophication (Emerson, 1975). Recently, accurate estimates of gas fluxes have assumed a critical role in evaluating the biogeochemical cycles of important atmospheric trace gases. They are particularly relevant to such contentious issues as the partitioning of greenhouse gases between the atmosphere and the oceans (Peng and Broecker, 1984; Broecker et al., 1979, 1985), natural versus anthropogenic sources of acid-rain sulphur (Gorham et al., 1986; Bates et al., 1987; Holligan et al., 1987; Nriagu et al., 1987; Turner et al., 1988) and the origin of SO<sub>4</sub><sup>2-</sup> aerosols, over which there is controversy regarding their proposed role in climate regulation

(Charlson et al., 1987; Shaw, 1987; Schwartz, 1988; Wigley, 1989).

In lakes and in the oceans, water column turbulence produced by wind shear is the dominant control of interfacial transfer for gases of low solubility (i.e., high Henry's law constant), although in certain circumstances bubble formation may also be significant (Merlivat and Memery, 1983; Broecker and Siems, 1984). Accurate determination of the rate of air–water gas exchange requires reliable measurements of the interfacial gas concentration gradient and an appropriate transfer velocity,  $k$ .

Laboratory experiments, including those in wind tunnels, give reasonable agreement for  $k$  and its relationships to selected variables associated with turbulence (e.g., Broecker et al., 1978; Merlivat and Memery, 1983; Jähne et al., 1979, 1985, 1987). However, the complexity of the real environment largely precludes accurate quantification of the functionality of  $k$  by this means

alone; in wind tunnels waves are small and bubbles and spray are generally absent. In addition the results can be significantly modified by tunnel geometry (Liss, 1983). Direct field determinations of the  $k$  versus windspeed relationships are at present only poorly constrained. Measurements based on the surface ocean invasion rate of natural or bomb-derived <sup>14</sup>C<sub>2</sub>O<sub>2</sub> determined from in situ <sup>14</sup>C activity yield only long term global or regional averages (e.g., Broecker et al., 1985). The "radon deficit" method, in which the sea-air flux of volatile <sup>222</sup>Rn arising from in situ <sup>226</sup>Ra decay is linked to the imbalance in the mixed layer activities of the two nuclides, potentially gives better temporal and areal resolution (Peng et al., 1979; Kromer and Roether, 1983; Hartmann and Hammond, 1984; Broecker et al., 1985; Smethie et al., 1985; Glover and Reeburgh, 1987). However, in practice the accuracy with which  $k$  can be determined in this way is limited by a number of uncertainties. These principally arise from inhomogeneity in the mixed layer radionuclide activities, distortion of their profiles by variable high winds and entrainment across the thermocline (Liss, 1983).

In this paper we present the transfer velocity versus windspeed relationships for two small, rapidly wind mixed, upland lakes in rural SW England, determined from the rate of evasion of added sulphur hexafluoride, SF<sub>6</sub>, a sparingly soluble gaseous tracer. Protocols for tracer deployment and sampling, brief details of SF<sub>6</sub> analysis by electron capture gas chromatography (EC-GC) and method calibration are also described.

Wanninkhof et al. (1985, 1987) first used SF<sub>6</sub> to measure gas exchange in lakes. The method has a number of advantages over <sup>14</sup>C<sub>2</sub>O<sub>2</sub> and <sup>222</sup>Rn, which make it ideal for this type of work. Firstly, because SF<sub>6</sub> is chemically inert its aqueous dynamics are dictated solely by physical exchange and mixing processes. Secondly, it has a low atmospheric background, presently ~1.9 pptv but rising slowly (Watson and Liddicoat, 1985) and, thirdly, it can be detected in ultra-trace amounts in water. Ambient SF<sub>6</sub> levels in the upper thermocline of the ocean, for example, have been reliably quantified at ~2 × 10<sup>-16</sup> mol kg<sup>-1</sup> using EC-GC (Watson and Liddicoat, 1985). For these reasons SF<sub>6</sub> is already an es-

tablished tracer of atmospheric and oceanic diffusion (Brown et al., 1975; Watson and Liddicoat, 1985; Ledwell et al., 1986; Watson and Ledwell, 1988). A further advantage to this study is that the rate at which added SF<sub>6</sub> vents from shallow waters to the atmosphere is sufficiently rapid to allow daily resolution of  $k$  to high precision. Although exchange experiments can be designed to run on both local and regional oceanic scales, small lakes were favoured in this preliminary study for their ease of access and because the experiments can be strictly controlled. Unlike the case in oceanic work, complications arising from lateral and vertical dispersion of the tracer plume do not arise.

Our results extend the work of Wanninkhof et al. (1985, 1987), whose experiments using SF<sub>6</sub> covered windspeeds ~3–7 m s<sup>-1</sup> at 10 m, measured with a relatively simple meteorological apparatus. Our larger data base refers to windspeeds ~2–13 m s<sup>-1</sup> at 10 m, recorded as a high quality time-series. Because of this, our data are amenable to more detailed analysis than those obtained previously.

## 2. Environmental setting

Fig. 1 shows the locations of the two lakes, on an exposed NE flank of Bodmin Moor, SW England, and their major physical features. Other relevant physical data are summarized in Table 1. Both lakes are characterized by low organic fluxes and are free from significant algal blooms. Therefore, complications in the evaluation of gas exchange data which arise from the presence of organic surface films can be discounted. Dozmary Pool (Fig. 1) is a shallow depression of approximately uniform depth, with extensive marginal reed beds covering ~10% of its surface. Freshwater enters directly as storm runoff. Siblyback lake, a freshwater resource operated by the South West Water Authority, is somewhat larger (Fig. 1, Table 1) with a more complex bathymetry. Its southern limb is ~8–12 m deep, apart from a small area adjacent to the dam where it reaches ~12–16 m. The lake shallows considerably towards its northern end, where depths of 2–4 m are typical. Freshwater throughput, via a number of minor rivers, is routinely monitored by South West Water. Dur-

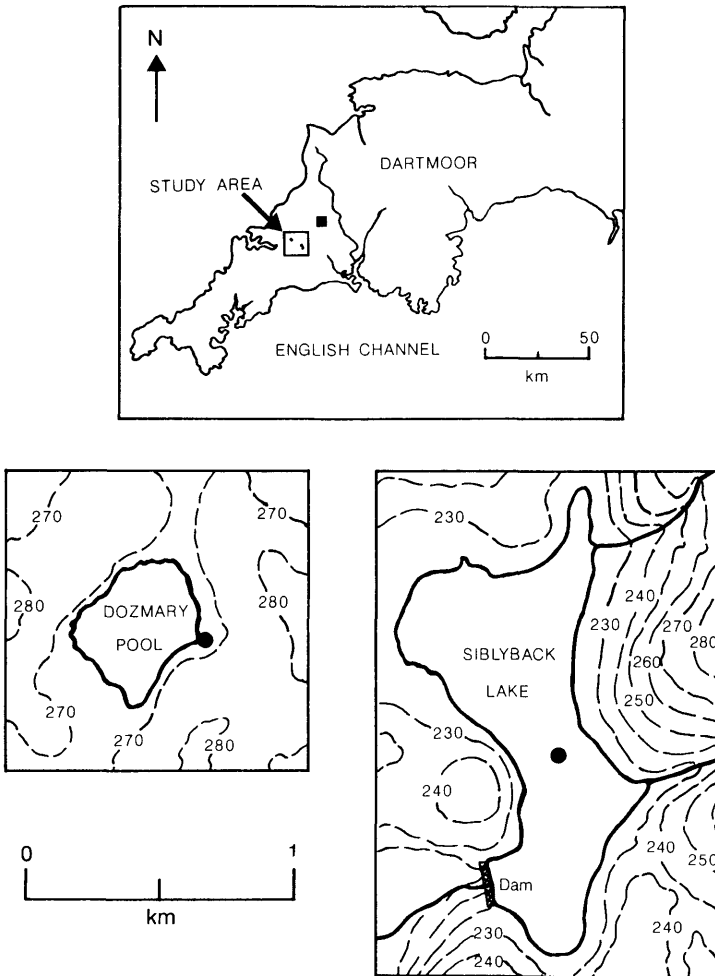


Fig. 1. (a) Physical setting of the lake study area and, ■, Coombe Mill experimental station; (b) relative physical dimensions of the two lakes, local topography and, ●, locations of the wind logging apparatus. Numbers refer to contour intervals in metres above mean sea level.

Table 1. Physical data for Siblyback Lake and Dozmary Pool

Location	Siblyback Lake lat. 4°29' W long. 50°31' N	Dozmary Pool lat. 4°33' W long. 50°33' N
Surface area (m <sup>2</sup> )	5.6 × 10 <sup>5</sup>	1.4 × 10 <sup>5</sup>
Mean water depth (m)	5.7	0.7
Depth range (m)	2–16	0.6–0.8
Mean water volume (× 10 <sup>5</sup> m <sup>3</sup> )	31.8	1.0

ing the experiments the reservoir operated in a constant head mode with freshwater throughput rates in the range 0.5–0.7% of total lake volume d<sup>-1</sup>, corresponding to an overall freshwater residence time ~ 5–7 months.

### 3. Experimental procedures

#### 3.1. Tracer deployment and sampling

SF<sub>6</sub> deployments were from a small boat.

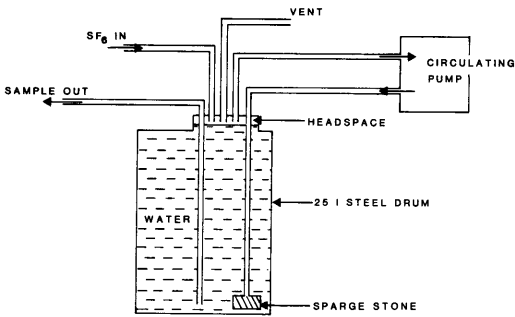


Fig. 2. Saturation apparatus used for routine SF<sub>6</sub> deployments. For description of operation see text. Subsamples taken via the "sample out" line were used to evaluate the degree of saturation. Analysis was by Thermal Conductivity G.C., following equilibration of 25 cm<sup>3</sup> of sample with 25 cm<sup>3</sup> of O<sub>2</sub>-free N<sub>2</sub>.

Initially we used direct bubbling through a gas sparger towed slowly around the lake at mid depth and connected to an onboard gas source. However, because most of the gas injected in this way vented directly to the atmosphere, subsequent deployments involved slow pumping of 25 litres of lakewater previously saturated with SF<sub>6</sub> on site. The saturation procedure devised for routine fieldwork uses a 25 litre steel tank filled with lakewater and sealed to leave a small headspace ~20 cm<sup>3</sup> (Fig. 2). Saturation is initiated by continuous flushing of the headspace with pure SF<sub>6</sub> with simultaneous circulation through the water at ~6 litres min<sup>-1</sup> via a diaphragm pump and sparge stone. The time taken to reach saturation is inversely related to the rate at which the headspace is flushed (Fig. 3). For routine deployments a flow rate of 200 cm<sup>3</sup> SF<sub>6</sub> min<sup>-1</sup> was used, giving complete saturation in ~40 min (Fig. 3). Each tracer deployment gave initial average lakewater concentrations ~2 pmol SF<sub>6</sub> kg<sup>-1</sup> in Siblyback Lake and ~55 pmol SF<sub>6</sub> kg<sup>-1</sup> in Dozmary Pool. Following deployment, several days were allowed for thorough mixing. Time-series data on wind speeds at two fixed heights above the lake surface (1.5 m and 2.5 m for Dozmary Pool, 1.5 m and 3 m for Siblyback Lake), wind directions and surface water temperatures were recorded on a specially built battery powered logger which could be interrogated in the field by portable computer via an RS232 link. The logger operates by integrating each measured parameter over precisely deter-

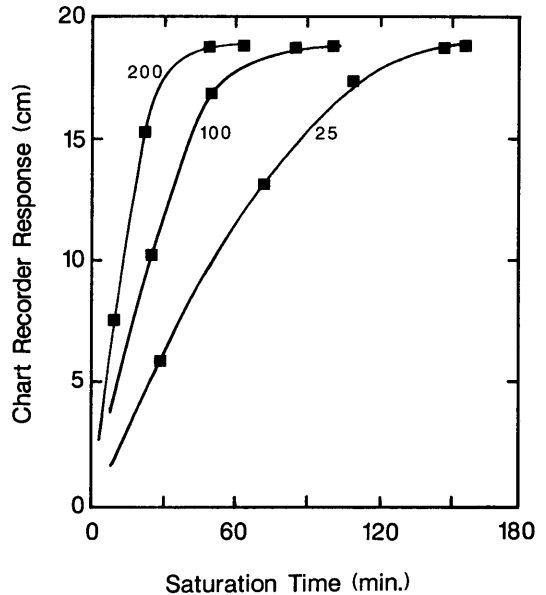


Fig. 3. Relative chart response versus SF<sub>6</sub> saturation time for the 25-litre tank. Numbers refer to rates of SF<sub>6</sub> flushing of the headspace in cm<sup>3</sup> min<sup>-1</sup>. Analysis was as outlined in Fig. 2.

mined preset time intervals. Data are stored in 8 bit binary format in semiconductor memory. For this work, a 4-min recording interval was selected. Under these conditions memory capacity is sufficient for 15 days continuous operation. Windspeed and direction signals were measured using commercial masthead transducer sets (Simpson-Lawrence Instruments Ltd., Glasgow; T. Walker and Sons Ltd., Birmingham, UK) secured to a rigid pole at the requisite heights. Windspeeds were recorded as frequency pulses per anemometer revolution and subsequently converted to m s<sup>-1</sup> using predetermined calibration equations. With the two anemometers fixed at the same height during trials, their measured windspeeds were not significantly different. The direction transducer used a three-phase potentiometer with analogue outputs spaced 120° apart. Measurement precisions were ±0.15 m s<sup>-1</sup> windspeed, ±1° wind direction. The temperature transducer used a current generator yielding 1 μA °C<sup>-1</sup>. The working temperature range was -11 to 40°C. Calibration was by immersion in melting ice and in water at 40°C, with output frequency adjustment as necessary.

Measurement precision was  $\pm 0.2^\circ\text{C}$ . At Siblyback the apparatus was lashed to a raft moored in the centre of the lake. At Dozmary Pool recording was on the NW shoreline (Fig. 1). At Siblyback, temperature–depth profiles were also monitored routinely using a standard T-S probe having a precision of  $\pm 0.1^\circ\text{C}$ . Water samples were collected at intervals from a number of stations around the lakes in 100 ml glass syringes, taking precautions to avoid air entrainment. Near-surface samples were withdrawn by hand and the remainder by peristaltic pump through 0.2 cm i.d. Cu tubing. Filled syringes were returned to the laboratory immersed in ambient lake water in order to minimize sample outgassing and diffusive losses.

### 3.2. Analytical methods

SF<sub>6</sub> was transferred to the gas phase by vigorous shaking of 50 cm<sup>3</sup> of sample in a 1:1 volume ratio with N<sub>2</sub>, introduced via a luer fitting. A constant headspace pressure was maintained by a ventline which opened at 0.02 atm overpressure when movement of the syringe barrel was stopped. Due to the low solubility of SF<sub>6</sub>,  $\sim 2.4 \times 10^{-4}$  mol kg<sup>-1</sup> at 25°C and 1 atm (Gerrard, 1980), essentially all of the gas partitions into the headspace during the procedure and small variations in equilibrium temperature are not a significant source of analytical error.

Analysis of the equilibrated headspace gases was by gas chromatography (Hewlett-Packard, 5880A) with electron-capture detection (ECD). The analytical system is similar to that described by Wanninkhof et al. (1989) but with substantial modification, and will be described in detail elsewhere. In brief, chromatographic separation was at room temperature on a molecular sieve 5A, 80–100 mesh (Alltech Ltd.), 100 × 0.2 cm i.d. column using N<sub>2</sub> as carrier gas and with column backflushing to enhance the sample throughput rate. The detector temperature was 250°C. For aqueous concentrations >0.2 pmol SF<sub>6</sub> kg<sup>-1</sup>, injection of samples and standards was via a 2 cm<sup>3</sup> loop, following pre-drying with K<sub>2</sub>CO<sub>3</sub>. For concentrations <2 pmol SF<sub>6</sub> kg<sup>-1</sup>, sensitivity was enhanced by N<sub>2</sub>-sparging of samples followed by cryogenic trapping of headspace gases on Porapak-Q (Waters Associates). Fig. 4 shows the “retention volume” for SF<sub>6</sub>, using 1 cm<sup>3</sup>

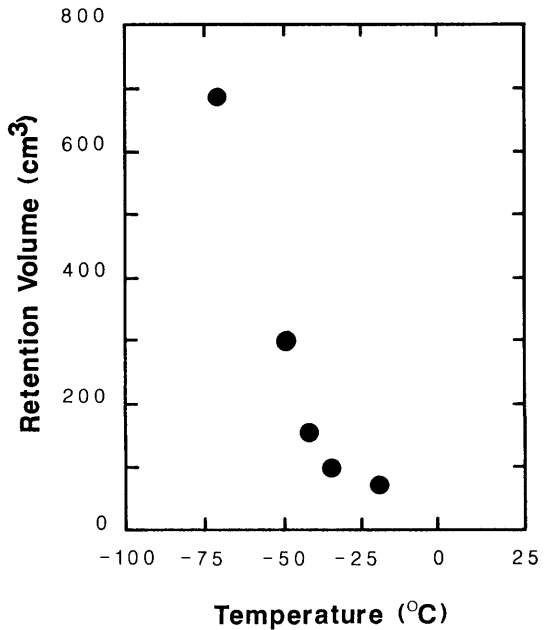


Fig. 4. The “retention volume” of SF<sub>6</sub> on 1 cm<sup>3</sup> Porapak-Q “traps” as a function of temperature. In routine analyses trapping was at  $-75^\circ\text{C}$ .

Porapak-Q “traps”, as a function of temperature. The retention volume is the maximum throughput of N<sub>2</sub> for which complete trapping of injected SF<sub>6</sub> occurs. In practice the retention volume is likely to be exceeded during analysis at all trap temperatures above  $\sim -50^\circ\text{C}$ . Therefore, routine trapping of samples was at  $-75^\circ\text{C}$ . Analytical results obtained by the two methods were not significantly different at the 0.2 pmol kg<sup>-1</sup> threshold. The analytical detection limit was  $\sim 10^{-17}$  mol, equivalent to a mixing ratio of <1 pptv SF<sub>6</sub> in a 2 cm<sup>3</sup> injection. Analytical precision (1  $\sigma$ ), determined from repeat analyses of a mixture of  $\sim 10$  pptv SF<sub>6</sub> in N<sub>2</sub>, was  $\pm 1\%$ .

### 3.3. Calibration

A series of four high quality primary standards with nominal mixing ratios of 10, 20, 150 and 1500 ppt SF<sub>6</sub>, to be used for the absolute calibration of the method, were prepared in a dilution chamber at the Coombe Mill Experimental Station, located in a remote rural region of SW England close to the open Atlantic (Fig. 1). Details of the construction and routine use of

the facility for gas standard preparation are given in Rasmussen and Lovelock (1983). In brief, the facility comprises a sealed chamber of accurately known volume,  $5 \times 10^7 \text{ cm}^3 \pm 1\%$ , above a small laboratory sited in an old barn. Standards may be prepared by injecting precisely measured volumes of pure or pre-diluted gas into the chamber from outside and downwind of the barn via 0.2 cm i.d. Cu tubing. Rapid circulation and mixing of chamber air, which is more than 95% complete after  $\sim 20$  s, is achieved with a centrally mounted, high capacity axial flow fan. For this work standards were prepared when the ambient air mass was oceanic and blowing steadily from the west. Under these conditions low, approximately constant SF<sub>6</sub> mixing ratios  $\sim 1.9$  pptv, corresponding to ambient levels predicted for the "clean" atmosphere (Watson and Liddicoat, 1985), were observed in background air.

Because of the small volume of the dilution chamber relative to the dilution factors required from pure SF<sub>6</sub>, i.e.,  $\sim 10^8$ – $10^{11}$ , it was impractical to prepare standards by a single stage dilution. Therefore an intermediate dilution vessel was used, consisting of a 1 litre glass bulb with shut-off valves fitted at its two open ends (Fig. 5). Interchangeable sample loops of accurately known capacities may be connected in-line and filled with pure SF<sub>6</sub>, which can be transferred to the bulb via a 6-port switching valve. A metered volume of the resultant diluted tracer can then be transferred to the dilution chamber via the same assembly. For this work loops of 1, 5 and 10 cm<sup>3</sup> nominal capacity were used to give initial dilution factors of up to  $\sim 10^3$  from pure SF<sub>6</sub>. Bulb and fitted loop volumes were determined gravimetrically with distilled water at 20°C. Precisions were better than  $\pm 0.1\%$  in all cases.

Throughout the dilution procedures, possible contamination of barn air was continuously appraised by monitoring of ambient SF<sub>6</sub> levels every 3 min on the G.C. Ambient pressures and temperatures were recorded routinely. Prior to each dilution the apparatus was flushed with  $\sim 10$  litres of O<sub>2</sub>-free N<sub>2</sub> and the bulb evacuated to  $\sim 0.2$  atm with a filter pump. With the 6-port valve "closed" (Fig. 5) the fitted sample loop was flushed with at least 20 loop volumes of pure SF<sub>6</sub>. The upper shut-off and 6-port valves were then simultaneously opened in order to draw in air

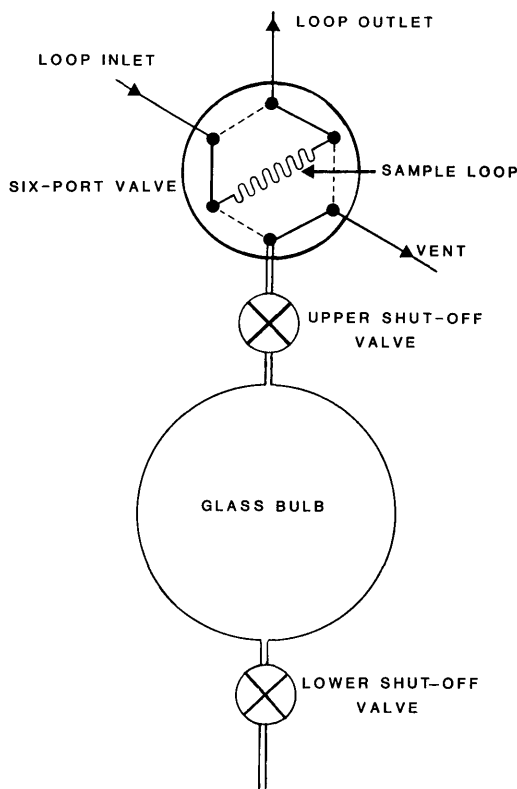


Fig. 5. Schematic representation of the 1-litre dilution vessel used for standard preparation. For description of operation see text.

through the loop and drive its contents into the bulb. After allowing  $\sim 3$  min for pressure equilibration, the upper shut-off valve was closed and the bulb contents left to mix thoroughly. The loop was then flushed with  $\sim 50$ – $100$  loop volumes of N<sub>2</sub> and another loop substituted as necessary for the desired dilution. With the 6-port valve open, a syringe containing 100 cm<sup>3</sup> of water was connected via the lower shut-off valve with the loop outlet connected to the chamber injection line. The two shut-off valves were simultaneously opened and the syringe contents pushed into the bulb, in order to drive the SF<sub>6</sub> air mixture out through the sample loop. Following displacement of  $\sim 10$ – $20$  loop volumes of the mixture in this way, the 6-port valve was switched and the loop contents flushed into the chamber with  $>10$  litres of N<sub>2</sub> from a cylinder connected to the loop inlet. With the chamber

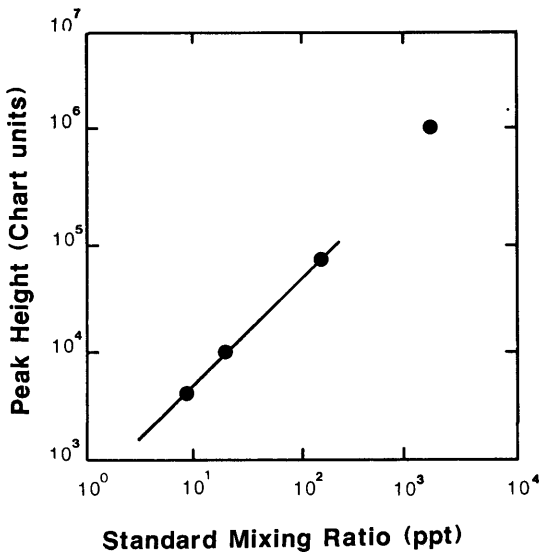


Fig. 6.  $\text{SF}_6$  mixing ratios in the primary standards versus detector response for a  $2 \text{ cm}^3$  injection.

circulation fan on, and after allowing 2 min for thorough mixing, chamber air was pumped through an open-ended steel 4 litre sample bottle in the laboratory at  $2 \text{ litres min}^{-1}$ . The bottle was thoroughly flushed, filled to a pressure of 2 atm and sealed. The chamber was subsequently ventilated by blowing in air from upwind of the barn at  $\sim 10^6\text{--}10^7 \text{ cm}^3 \text{ min}^{-1}$  until ambient  $\text{SF}_6$  levels declined to the pre-experimental value. In order to minimize possible cross-contamination of standards, preparation was on consecutive days in order of ascending mixing ratio. We estimate the overall accuracy of the whole procedure to be better than  $\pm 2\%$ .

Fig. 6 shows  $\text{SF}_6$  mixing ratios in the primary standards versus detector response for a  $2 \text{ cm}^3$  injection. Response is linear from the detection limit up to at least 160 pptv, a range  $\sim 10^3$  which is typical for ECD analysis (Lovell and Watson, 1978).

In view of the limited amounts of the primary standards, a series of secondary high pressure standards, with nominal mixing ratios of 10, 20, 60, 120 and 180 ppt, were prepared for day to day use by pressure dilution. About  $0.2 \mu\text{l}$  of pure  $\text{SF}_6$  were first introduced through a septum into a 10 litre gas bottle previously evacuated to  $\sim 0.2 \text{ atm}$ . The bottle contents were then pressurized

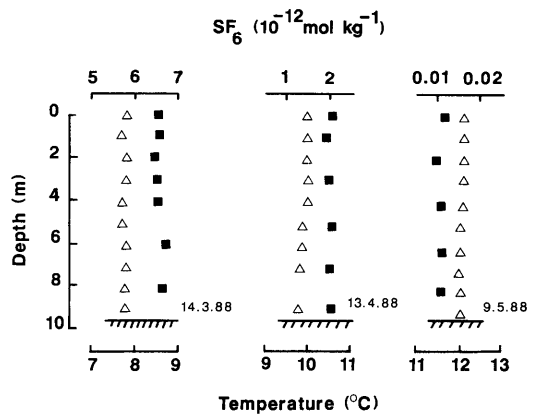


Fig. 7. Typical profiles of temperature,  $\Delta$ , and  $\text{SF}_6$ ,  $\bullet$ , in Siblyback Lake during the tracer experiment.

isothermally to 100 bar with  $\text{N}_2$ , to give an initial nominal mixing ratio  $\sim 180 \text{ pptv}$   $\text{SF}_6$ . Bottle wall temperatures were measured using a thermocouple with a precision of  $\pm 0.1^\circ\text{C}$ . Pressure was monitored on a specially commissioned master test gauge with a certified overall accuracy of  $\pm 0.3\%$  (model 315GP, Budenberg Gauge Co., Altrincham, UK). The remaining standards were made by further pressure dilution from the 180 pptv standard, yielding a range of standards in  $\text{N}_2$  at 50 bar. Absolute calibration was against the primary standards.

## 4. Results

### 4.1. Tracer mixing

Initial sampling indicated that both lakes became well mixed with respect to  $\text{SF}_6$  concentrations within  $\sim 48 \text{ h}$  of tracer deployment. Fig. 7 shows three representative vertical profiles of  $\text{SF}_6$  and temperature during the Siblyback Lake experiment. The data demonstrate strong thermal and chemical homogeneity. At no stage during the experiments were significant vertical  $\text{SF}_6$  gradients or a measurable thermocline detected. However, some diurnal surface warming, by up to  $0.3^\circ\text{C}$  relative to 1 m, occurred as a result of solar heating, although any resultant effects on  $\text{SF}_6$  profiles remained undetectable. Similarly for Dozmary Pool, no significant differences in  $\text{SF}_6$  concentration were evident between surface and bottom water samples.

Following periods of average 1.5 m winds > 3 m s<sup>-1</sup>, SF<sub>6</sub> concentrations in the shallower areas of Siblyback Lake were always within a standard deviation of the average for its deeper regions, demonstrating rapid wind-induced mixing relative to the rate of gas exchange. However, although both lakes remained vertically well mixed throughout the experiments, significant lateral concentration differences did occasionally develop following periods in which 1.5 m winds averaged < 2.5 m s<sup>-1</sup>. At Siblyback Lake such differences were generally ~10% or less, and most probably reflect the influence of local topography on surface winds. In contrast, lateral variations in SF<sub>6</sub> content were generally greater in Dozmary Pool, occasionally exceeding 40%, despite its comparatively small size and uniform shape, and the low lying local topography (Fig. 1). During the experiments substantial damping of surface waves was observed amongst the marginal reed beds which cover ~10% of the lake surface and it seems likely that such features could give rise to periodic isolation of a significant volume of water from the bulk of the lake. Therefore, we interpret the results to reflect incomplete mixing following periodic release of high-SF<sub>6</sub> water previously trapped amongst the reeds. Nevertheless, despite this occasional complication, in both lakes decreases in SF<sub>6</sub> concentration between sampling intervals were generally far greater than the individual uncertainties due to inhomogeneity. Therefore, representative values for whole lake concentrations were determined by averaging the data collected from individual stations. Tracer concentrations in Siblyback Lake were corrected for freshwater throughput using daily spillway discharge data supplied by South West Water.

#### 4.2. Gas transfer velocities

The water-air gas transfer velocity,  $k$ , may be determined from the expression

$$k = F/(C_w - C_o), \quad (1)$$

where  $F$  is the interfacial gas flux,  $C_w$  is the gas concentration in the water immediately below the interface and  $C_o$  is the gas concentration in water in equilibrium with ambient air. In a given time period,  $\Delta t$

$$F = (dM/dt)/A \quad (2)$$

where  $M$  is the total mass of gas in the lake and  $A$  is the lake surface area. For the case of a well mixed water body

$$F = (dC/dt)h, \quad (3)$$

where  $C$  is the gas concentration in the water and  $h$ , the mean water depth,  $= V/A$ , where  $V$  is the water volume. In the experiments,  $C = C_w$ ; the lakes were well-mixed. Therefore, combining eqs. (1) and (3) gives

$$dC_w/dt = k/h(C_w - C_o). \quad (4)$$

During sampling,  $C_w$  for SF<sub>6</sub> was  $\sim 10^{-11}$ – $10^{-14}$  mol kg<sup>-1</sup>, whereas  $C_o$  is  $\sim 3 \times 10^{-16}$  mol kg<sup>-1</sup> (Gerrard, 1980). Therefore, for practical purposes  $C_o$  can be ignored in eq. (4) which, on integration gives

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

where  $C_i$  and  $C_f$  are the initial and final gas concentrations in the water respectively during time period  $\Delta t$ .

The results of the lake gas exchange experiments are summarized in Table 2 where the calculated transfer velocities are listed as corresponding values for CO<sub>2</sub> at 20°C. The relationship  $k_{SF_6}/k_{CO_2} = (Sc_{SF_6})^n/(Sc_{CO_2})^n$  was used for the conversion. The Schmidt number,  $Sc$ , is the ratio of the kinematic viscosity of water to the molecular diffusivity,  $D$ , of the gas at the stated temperature. Values of  $D$  were estimated from the empirical relationship of Hayduk and Laudie (1974). We have assumed  $n = -\frac{1}{2}$ , corresponding to the case of turbulent flow below a free surface (Ledwell, 1984; Jähne et al., 1984, 1987). The average windspeeds recorded during each sampling interval are listed as  $U_{10}$ , the corresponding value at  $z = 10$  m, in order to facilitate comparisons with previous work. Values of  $U_{10}$  were estimated assuming a logarithmic wind profile, from the equation  $\ln(z) = [(K/U^*)U(z)] + \ln(z_o)$ , where  $K$  is Von Karman's constant,  $= 0.4$ ,  $U^*$  is the friction velocity and  $z_o$  the surface roughness parameter (Mackintosh and Thom, 1973). The ratio  $K/U^*$  was determined graphically for each sampling interval from the slope of  $\ln z$  versus  $U(z)$ , using average windspeed data for the two known heights, with  $\ln(z_o)$  evaluated by substitution.



Table 2. Results of the SF<sub>6</sub> exchange experiments

Date	Surf. water temp. (°C)	$\Delta t$ (h)	$C_i/C_f$	$k_{20}$ SF <sub>6</sub> (cm h <sup>-1</sup> )	$k_{20}$ CO <sub>2</sub> (cm h <sup>-1</sup> )	$\Delta k$ (cm h <sup>-1</sup> )	$U_{10}$ (m s <sup>-1</sup> )
<b>Siblyback Lake</b>							
24.3.88	6.6	49.5	2.10	13.0	16.1	0.3	10.3
8.4.88	6.4	24.3	1.15	4.7	5.8	0.3	5.1
11.4.88	6.5	71.4	1.36	3.7	4.5	0.1	3.9
12.4.88	6.4	24.2	1.21	6.9	8.6	0.4	4.8
13.4.88	6.8	23.2	1.15	5.0	6.1	0.5	5.7
15.4.88	5.0	47.5	1.62	9.4	11.7	0.2	10.3
18.4.88	7.4	71.9	1.56	6.3	7.8	0.3	6.1
19.4.88	7.6	24.4	1.15	4.8	6.0	0.7	6.0
20.4.88	7.6	23.6	1.11	4.5	3.6	0.6	4.2
21.4.88	8.0	24.5	1.20	5.9	7.1	0.8	4.6
22.4.88	8.1	22.5	1.29	6.5	8.1	0.9	5.9
23.4.88	8.5	31.2	1.31	9.0	11.1	0.4	9.5
25.4.88	6.5	38.5	1.39	6.2	7.6	0.3	4.1
1.5.88	7.5	53.5	2.74	13.2	16.1	0.5	12.2
3.5.88	7.8	43.5	2.40	16.7	20.7	0.6	12.9
4.5.88	7.3	22.4	1.29	5.5	6.8	0.9	5.2
9.5.88	10.0	70.7	1.79	6.4	7.9	0.4	8.3
10.10.88	9.8	72.2	2.44	9.5	11.8	0.4	6.7
14.10.88	10.3	46.1	1.47	6.5	8.1	0.7	6.1
17.10.88	10.0	71.5	1.57	4.9	6.1	0.2	6.2
19.10.88	10.6	46.9	1.42	5.7	7.1	1.2	8.4
21.10.88	10.9	48.5	1.31	4.4	5.5	2.7	6.0
24.10.88	11.0	72.5	1.87	6.6	8.1	1.4	8.6
26.10.88	10.9	47.3	1.53	6.9	8.5	1.0	9.1
23.11.88	7.6	46.5	1.20	3.4	4.2	0.9	3.8
25.11.88	7.2	47.1	1.26	4.2	5.2	0.7	5.2
28.11.88	6.2	71.7	1.50	5.1	6.4	0.4	5.8
30.11.88	6.2	47.3	1.32	5.3	6.6	1.1	5.3
2.12.88	6.5	48.3	1.22	3.6	4.5	1.1	4.2
5.12.88	5.9	72.0	2.08	9.2	11.4	0.4	7.9
7.12.88	5.6	49.3	1.74	10.3	12.8	0.5	8.8
9.12.88	5.3	46.3	1.43	7.1	8.8	0.3	6.4
12.12.88	5.8	71.9	1.56	5.6	6.9	0.2	6.7
14.12.88	5.8	47.9	1.33	5.4	6.6	0.3	7.1
<b>Dozmary Pool</b>							
22.7.88	17.2	22.5	5.70	6.0	7.4	0.9	5.7
25.7.88	15.0	75.7	76.1	4.8	5.8	0.2	5.5
26.7.88	14.7	6.5	1.49	5.1	6.3	2.3	8.0
10.8.88	18.8	22.2	1.69	2.3	2.9	1.0	2.5
11.8.88	16.0	24.7	3.17	3.7	4.6	0.6	6.9
12.8.88	14.7	22.9	8.17	7.6	9.4	0.3	7.5
12.8.88	15.9	7.8	2.34	8.6	10.7	0.8	8.6

## 5. Discussion

The relationships between  $k$  and windspeed determined during the Lake experiments are shown in Fig. 8 where they are compared with some averages determined at sea using <sup>222</sup>Rn (Broecker and Peng, 1974; Peng et al., 1979;

Kromer and Roether, 1983) and the global <sup>14</sup>C inventory (Broecker et al., 1985), and some recent SF<sub>6</sub> results from two US lakes (Wanninkhof et al., 1987). Also shown is the model "curve" of Liss and Merlivat (1986) applicable to a range of gases and sea surface temperatures, derived from an extrapolation of the early SF<sub>6</sub> results of

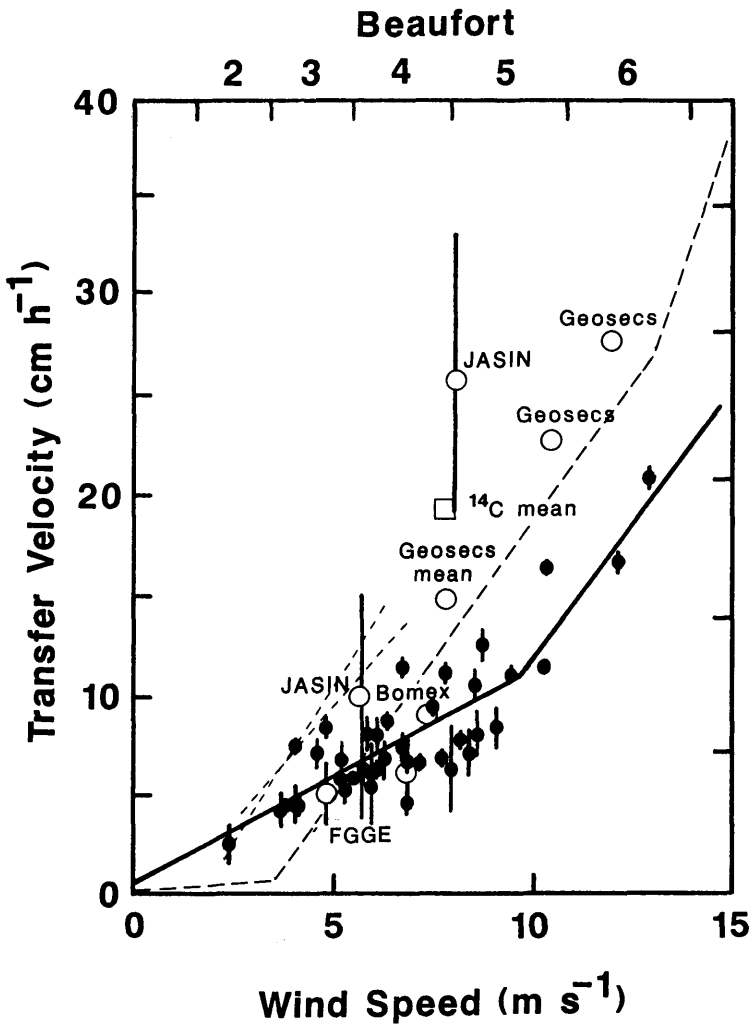


Fig. 8. Gas transfer velocities as a function of windspeed and the corresponding Beaufort Scale number: ●, results from this work; ○, ocean radon averages (Broecker and Peng, 1974; Peng et al., 1979; Kromer and Roether, 1983); □, global ocean bomb-<sup>14</sup>C mean (Broecker et al., 1985); solid lines, least squares fit to field data (this study); small dashed lines, recent SF<sub>6</sub> results for US lakes (Wanninkhof et al., 1987); large dashed line, extrapolation of the SF<sub>6</sub> results of Wanninkhof et al. (1985) using model equations (Liss and Merlivat, 1986). All data refer to CO<sub>2</sub> at 20°C with windspeeds normalized to 10 m.

Wanninkhof et al. (1985) using model and wind tunnel data (e.g., Deacon, 1977; Broecker and Siems, 1984).

Our results show a reasonably good correlation between transfer velocity and windspeed, even over time scales as short as 12 h (Fig. 8, Table 2). The difference between the individual relationships for Dozmary Pool and Siblyback Lake is of

the order of experimental uncertainty. No correlation between  $k$  and wind direction was evident during the experiments. Our findings contrast with those recently reported for two US lakes by Wanninkhof et al. (1987), in which little or no correlation of  $k$  with windspeed was evident on time scales shorter than about 48 h due to inherently large uncertainties in whole lake

average tracer concentrations. Consequently, their data were averaged over significantly longer periods than ours, a procedure which tends to "dilute" high windspeeds and underestimate their true average. This is particularly relevant when the calculated average is close to one of the breaks of slope predicted from the Liss and Merlivat (1986) curve.

Our results generally fall below both the Liss and Merlivat (1986) curve and the trend of the  $^{222}\text{Rn}$  results, particularly at intermediate to high windspeeds. However, it should be recognized that the  $^{222}\text{Rn}$  results are averages of extensive data sets in which the individual measurements themselves are often only weakly correlated with windspeed (e.g., Peng et al., 1979). This is because the wind data were averaged over the ships track of up to 200 km during the preceding 0–24 or 24–48 h periods and as such contain substantial uncertainties (e.g., Peng et al., 1979).

In their synthesis, Liss and Merlivat (1986) reason that for  $\text{CO}_2$  with  $U_{10} < \sim 3.6 \text{ m s}^{-1}$  (Fig. 8), the so-called "smooth-surface" regime in which surface waves are absent (Deacon, 1977),  $k$  increases only very gradually with windspeed, with  $k \propto \text{Sc}^{-2/3}$  (e.g., Jähne et al., 1984, 1987). In the "rough-surface" regime, with  $U_{10}$  between 3.6 and  $\sim 13 \text{ m s}^{-1}$  (Fig. 8), the onset of capillary waves leads to steepening of the  $k$  versus windspeed curve by a factor  $\sim 10$  relative to the smooth surface, with  $k \propto \text{Sc}^{-1/2}$  (e.g., Ledwell, 1984; Jähne et al., 1984, 1987). With  $U_{10} > \sim 13 \text{ m s}^{-1}$ , when whitecap coverage of the sea surface is significant (Monahan and O'Muirchaertaich, 1980), bubble and spray formation by breaking waves leads to further enhancement of  $k$  (Fig. 8), with less soluble gases showing correspondingly earlier breaks of slope (Merlivat and Memery, 1983; Broecker and Siems, 1984).

In our data set only one result, with  $k = 2.9$ , corresponds to the smooth surface regime of Liss and Merlivat (1986). According to their model this value of  $k$  must be an underestimate because it was derived using a  $\text{Sc}^{-1/2}$  dependence. However, in this case recalculation with  $\text{Sc}^{-2/3}$  would increase  $k$  by only  $\sim 9\%$ , which does not significantly affect the overall result. During the experiments, 10 m windspeeds  $< 3.6 \text{ m s}^{-1}$  rarely persisted for periods in excess of a few hours and therefore tended to be averaged out over typical sampling intervals  $\sim 24\text{--}72 \text{ h}$ . Inspection of the

remainder of the data (Fig. 8) indicates a steepening of the  $k$  versus windspeed relationship beyond about  $10 \text{ m s}^{-1}$ . Although ocean whitecaps do not appear to be important at this windspeed (Monahan and O'Muirchaertaich, 1980), breaking waves were commonly observed on both lakes under such conditions. In view of this, we have fitted our data with two straight lines using the method of least squares, taking their intercept to define the transition from the rough surface to breaking wave regime for our field data. Minimum sums-of-squares were determined after individually weighting each data point with the inverse square of its associated statistical uncertainty in  $k$ . The results of the line fitting exercise are also shown in Fig. 8. The synthesis yielded, for  $U_{10} < 9.5 \pm 3 \text{ m s}^{-1}$ ,  $k = 1.11U_{10} + 0.35$  and, for  $U_{10} > 9.5 \pm 3 \text{ m s}^{-1}$ ,  $k = 2.53U_{10} - 13.09$ . Although the uncertainty in the value of  $U_{10}$  at the transition point is considerable ( $1\sigma \sim 30\%$ ), the lower figure of  $6.5 \text{ m s}^{-1}$  can be confidently rejected because whitecaps and spray were not observed under such conditions. With the transition point constrained at  $9.5 \text{ m s}^{-1}$ , the corresponding  $1\sigma$  error ranges for  $U_{10}$  are  $0.98\text{--}1.24 \text{ m s}^{-1}$  below it and  $2.9\text{--}2.2 \text{ m s}^{-1}$  above.

In formal least squares solutions incorporating statistical weighting, the predicted value for the minimum sum-of-squares should correspond to the number of degrees of freedom in the problem (Bevington, 1969). In other words, provided that the selected model is appropriate, the fitted lines should lie within the uncertainty limits of the data. However, this is clearly not the case with the present results (Fig. 8); the data show far greater scatter than would be predicted from the experimentally determined uncertainties (Table 2). Therefore, it seems likely that the relationship between transfer velocity and windspeed observed during our experiments is not unique and that additional parameters should be considered.

Some recent results for  $k$ , determined using the Liss and Merlivat (1986) equations and based on data from satellite scatterometry (Etcheto and Merlivat (1988), climatic models (Erickson, 1989) and meteorological analysis of archived winds (Heimann and Monfray, 1989), show good agreement amongst themselves. Nevertheless, they are all a factor of 1.6–1.8 lower than those derived from the  $^{14}\text{C}$  inventory and the discrepancy

cannot be ascribed to uncertainties in the available <sup>14</sup>C or wind data (Heimann and Monfray, 1989). It has been suggested that differences in wave spectra between seas and lakes could account for the apparent discrepancies in the Liss and Merlivat (1986) equations (Heimann and Monfray, 1989). However, in contrast some other recent estimates of *k* for the upper ocean derived from seasonal gas budgets are actually ~17% lower than predicted from the Liss and Merlivat (1986) curve (Spitzer and Jenkins, 1989) and are therefore more consistent with our own lake data. Unfortunately, no adequate explanation of these differences so far exists and further work is therefore necessary.

Recent studies from a number of wind tunnels indicate that *k* may be more closely allied with mean square wave slope than with windspeed (Jähne et al., 1987). Although such findings remain to be tested in field experiments, they could conceivably account for at least some of the scatter observed in our results. Nevertheless, in the case of a small lake and neglecting the influence of surface films, it must be the time variant wind speed and direction which fundamentally determine initial conditions at the interface. Therefore, development of an accurate predictive model for *k* should be possible given sufficiently comprehensive data on relevant wind parameters.

## 6. Conclusions

This study has shown that SF<sub>6</sub> can be deployed routinely in the field and used to provide high

precision measurements of gas transfer with daily resolution. Our results contribute significantly to the available data base, confirming previous conclusions that gas exchange rates are strongly windspeed dependent and that the rate of increase of *k* is enhanced at higher windspeeds. However, additional experiments are required in order to more fully constrain the functionality of *k* at windspeeds below 5 and beyond 10 m s<sup>-1</sup>, and to help identify reasons for the differences between the various published data sets. Such experiments should, as a first step, incorporate more frequent water sampling in an attempt to reduce the uncertainties associated with variable winds. Our work is presently progressing in this direction.

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