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Gas transfer velocities for SF_6 and ^3He in a small pond at low wind speeds

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Abstract. Gas transfer velocities for two gases, SF_6 (sulfur hexafluoride) and ^3He, were determined in a small pond by injecting a mixture of these gases into the water and monitoring the decline of their concentrations over the next eight days. For wind speeds between 1.5 - 2.5 m s^{-1}, no variations of gas transfer velocity with wind speed could be resolved with our data. Gas transfer velocities at wind speeds greater than 3 m s^{-1} were substantially larger and consistent with other lake tracer experiments. From the ratio of gas transfer velocities for SF_6 and ^3He, we calculated the Schmidt number exponent to be 0.57± 0.07.

Introduction

The gas transfer velocity is an important physical parameter needed to understand the exchange of gases between water bodies and the atmosphere. This parameter is used for evaluating water quality, cycles of trace gases, and evasion rates of gaseous contaminants.

Gas transfer across the air - water interface is regulated by the surface turbulence in the water (Jähne et al. 1987). The dominant source of surface turbulence for most water bodies is wind, although other parameters such as current speed, bubble formation, and surface films can influence the turbulence regime (Broecker et al. 1978; Broecker and Siems, 1984; Goldman et al., 1988). At low wind speeds, differential heating of the water body and cooling at the surface may dominate the surface turbulence field (Soloviev and Schlüssel, 1994). However, because of the relative ease of measuring wind speeds, gas transfer velocities are commonly related to this parameter.

Laboratory experiments in wind - wave tunnels have shown that the gas transfer velocity, k, increases with wind speed, U (Downing and Truesdale, 1955; Broecker et al., 1978; Broecker and Siems, 1984). These experiments have identified three distinct regions of wave formation which also characterize the slope of the correlation between k and U. In the first region which occurs before the formation of capillary waves (U<2-3 m s^{-1}) k increases only slightly with U. The second region is defined by the occurrence of capillary waves and the absence of breaking waves (2-3 m s^{-1}<U<10-13 m s^{-1}). The response of k to increased U is much greater in this region than in the first region. The final region occurs at wind speeds where breaking waves and bubble entrainment are common (U>10-13 m s^{-1}). In this region, the greatest response of k to increased U is found (Broecker and Siems, 1984).

The gas transfer velocities for different gases are related by their Schmidt numbers (Jähne et al, 1987). (The Schmidt number is defined as the kinematic viscosity of water divided by the molecular diffusion coefficient of the gas in water.) The dependence on the Schmidt number changes with the state of the surface boundary layer. At low wind speeds, the surface boundary layer is generally smooth while at moderate winds the surface boundary layer is generally covered with waves and considered to be rough (Liss and Merlivat, 1986).

With the development of the SF_6-method, the relationship between k and U has been empirically determined in natural environments (Wanninkhof et al., 1985, 1987, 1991; Upstill-Goddard et al., 1990). With this method, SF_6 (sulfur hexafluoride) is injected into the surface water of lakes and the decline in its concentration is monitored as the gas escapes to the atmosphere. SF_6, a synthetic gas, is an ideal tracer of gas exchange across the air-water interface because it can be measured at very low concentrations, it is chemically and biologically nonreactive in aqueous environments, and present background concentrations in natural waters are very low (<0.05x10^{-12} ml STP g^{-1}).

Previous experiments using the SF_6-method have shown that in lakes, the magnitude of k increases with U (Wanninkhof et al., 1985, 1987, 1991; Upstill-Goddard et al., 1990). Different lake experiments have produced slightly different correlations. A number of reasons have been postulated to explain these differences. Firstly, laboratory experiments have found that surface films decrease k (Broecker et al., 1978; Goldman et al., 1988), hence the local water chemistry can be important. Secondly, mean wind speeds over lakes are difficult to characterize. Anemometers having different starting thresholds can record different mean wind speeds, especially at low wind speeds, and wind speeds over lakes tend to be variable both spatially and temporally. Thirdly, the local geometry, in particularly the fetch, may influence the gas transfer velocity (Wanninkhof, 1992).

Most of the lake experimental data have been collected during periods of moderate wind speeds (3 m s^{-1} <U< 10 m s^{-1}). The little data that has been collected at low wind speeds (<3 m s^{-1}) suggests that the break in slope of the correlation between k and U, which develops in laboratory experiments with the formation of capillary waves also occurs in lakes (Wanninkhof et al., 1985; 1991; Crusius, 1992).

Here we present the results of a tracer experiment in a small lake, Sutherland Pond, which examines gas transfer velocities at low wind speeds. In addition to SF_6, we also injected ^3He to assess the Schmidt number relationship between gas transfer velocity and gas type. Very few field studies examine this relationship. ^3He, like SF_6, is chemically and biologically nonreactive in natural waters and can be measured with high precision at low concentrations.

Study Location

Sutherland Pond is located at an elevation of 380 m above sea level in Black Rock Forest about 100 km north of New York City (figure 1). The pond has a surface area of 0.041 km^2 and a drainage area of 0.21 km^2. We have estimated the mean depth to be 1.6±0.2 m from a bathymetric map produced by the Adirondack Lakes Survey Corporation. Northwest and east of the pond, cliffs rise more than 30 m above the water's surface sheltering it from winds out of these directions. To the south lie open wetlands. There are no surface streams which drain into Sutherland Pond and the only outflow of surface water is through Mineral Spring Brook.

Sutherland Pond supports a diverse ecosystem. However, the surface tension of the pond water (71.9±0.2 dynes cm^{-1}) was indistinguishable from distilled water (72.1±0.2 dynes cm^{-1}). This indicates that the pond surface is free of any compounds which may form surface films.

Our tracer experiment was performed during mid summer in the midst of a drought. The flow out of Sutherland Pond through Mineral Spring Brook was negligible. Sunny days persisted throughout the experiment

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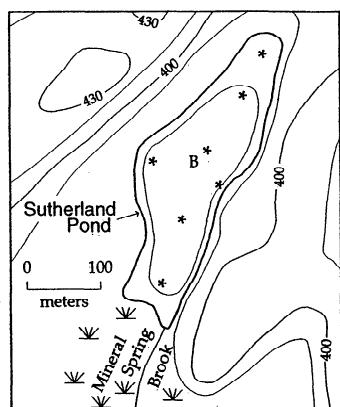
Figure 1. Map of Sutherland Pond and surrounding area. Contour lines are drawn every 15 m. Within the pond, the light inner line is the 1.5 m isobath. * represent the approximate locations of the sampling stations and B represents the approximate location of the buoy.

Figure 2. (A) Decline of mean SF_6 and excess ^3He with time. Only SF_6 was collected 0.1 days after the injection. Filled circles = SF_6 and crosses = excess ^3He. (B) Decline in the excess $^3He/SF_6$ ratio with time.

until the last day when about 9 mm of rain fell. Daily temperature variations of 5° C were observed in the pond water. Surface waters reached a minimum temperature of 21° C during the early morning and a maximum of 26° C during the late afternoon.

Principle of the SF6 - Method

The theory of the SF_6-method of determining gas transfer velocities has been presented in detail elsewhere (Wanninkhof et al. 1985, 1987). Briefly, the gas transfer velocity, k, is defined in the following manner:

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

where F is the flux of a gas crossing the air-water interface, C_{sur} is the concentration of the gas adjacent to the air-water interface, and C_{eq} is the gas concentration in water at solubility equilibrium with the atmosphere. The flux of a gas in a well-mixed closed water body, such as frequently found in lakes, can be estimated in the following manner:

$$F = \frac{-1}{A}\frac{dM}{dt} = h\frac{-dC_m}{dt} \qquad (2)$$

where M is the total amount of a gas in the system, A is the surface area of the water body, h is the mean water depth, and C_m is the mean concentration of the gas in the water. Combining equations (1) and (2) leads to the following expression for the gas transfer velocity:

$$k = \frac{h}{\Delta t}\frac{\ln(C_i - C_{eq})}{\ln(C_f - C_{eq})} \qquad (3)$$

where C_i and C_f are the mean concentration of gas in the water at time t_i and t_f, respectively, and Δt is the time elapsed between t_i and t_f. We have assumed that the mean concentration of the gas in the pond is equal to the concentration of the gas adjacent to the air-water interface. As we will show below, the water column was vertically well mixed. The atmospheric equilibrium concentration of SF_6 in natural waters is very low and we have assumed it to be equal to zero in our study. This is not the case for ^3He and we have defined the difference between the observed ^3He concentration and the atmospheric solubility equilibrium concentration to be the excess ^3He concentration.

Jähne et al., (1987) showed that gas transfer velocities are related in the following manner:

$$k_1/k_2 = (Sc_1/Sc_2)^{-n} \qquad (4)$$

where Sc is the Schmidt number for each gas and n is the Schmidt number dependence. They experimentally determined n using a wind-wave fac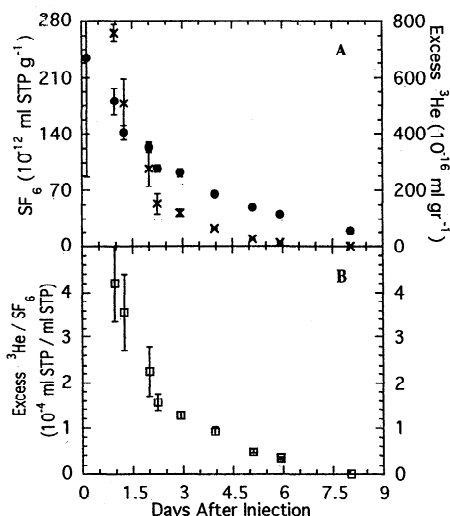ility and found that at very low wind speeds n=2/3. At these wind speeds, the boundary layer could be approximated by a smooth surface. With the formation of capillary waves and a rough surface they found that n abruptly changed to 1/2 and remained constant at moderate wind speeds. Ledwell (1984) also found n to equal 1/2 at moderate wind speeds in wind-wave tunnel experiments.

Experimental Methods

Approximately 10 mmoles of pure SF_6 gas and 0.02 mmoles of 99.8% pure ^3He gas were transferred to a small evacuated cylinder (6.9 l) in the laboratory. High purity N_2 gas was then added until a final pressure of 9 bars was achieved. During the morning of July 20, 1993, the gas mixture was injected into the pond water through a diffusion stone which was suspended from the back of a canoe. The injection took about 20 minutes as the canoe was paddled around the center of the pond. The depth of the diffusion stone varied throughout the injection.

Samples of pond water were collected every 6-48 hrs for the next eight days using a 1.5 l Niskin bottle. Each time, surface samples (approximately 0.5 m below the surface) were collected from four shallow stations along the perimeter and surface and bottom (approximately 0.5 m above the sediments) samples were collected at three station along the center axis of the pond (figure 1). While SF_6 samples were collected from all the stations and depths, ^3He samples were collected from only one depth at each of the three center stations.

SF_6 samples were collected in either 50 ml glass syringes or 60 ml BOD bottles and stored submerged in pond water until analysis. All samples were analyzed within 24 h of collection using the head space method described by Wanninkhof et al. (1987). The reproducibility of duplicate samples was ±3%.

About 40 ml of water was collected in copper tubes which were sealed by pinch-off clamps at each end for ^3He analysis. All samples were analyzed on a VG-5400 helium isotope mass spectrometer using methods similar to those described by Bayer et al., (1989). Precision of ^4He concentrations and $^3He/^4He$ ratio measurements were about ±0.5% and ±0.2%, respectively.

Excess ^3He concentration was calculated from the measured $^3He/^4He$ ratio and ^4He concentration in the following manner:

$$\text{Excess }^3He = [^4He]_s (R_s - R_a) + [^4He]_{eq} R_a (P_z/P_0) (1 - \alpha) \qquad (5)$$

where $[^4He]_s$ is the measured ^4He concentration; $[^4He]_{eq}$ is the atmospheric equilibrium concentration of ^4He (Weiss, 1971); P_z is the atmospheric pressure at the elevation of the pond (380 m); P_0 is the atmospheric pressure at sea-level; R_s is the measured $^3He/^4He$ ratio; R_a is

Table 1. Results of the Sutherland Pond tracer experiment.

Day	SF$_6$[a] 10^{-12} ml STP g^{-1}		Excess ^{3}He[b] 10^{-16} ml STP g^{-1}		U$_{10}$ m s^{-1}	k$_{600}$[c] cm hr^{-1}	
0.1	234	± 147					
1.0	180	16	758	± 32	1.7		
1.3	142	9	506	93	3.4	6.8	± 4.3
2.0	123	6	276	63	2.0	1.5	1.2
2.3	97	5	152	37	3.2	7.1	3.0
2.9	92	5	119	13	1.6	0.6	1.1
4.0	66	2	62	2	1.6	2.6	0.6
5.1	49	2	24	2	1.8	2.0	0.5
5.9	40	2	14	1	2.4	1.9	0.9
8.0	19	1	0	1	2.5	2.8	0.4

[a]Mean and standard deviation of 10 - 19 samples.
[b]Mean and standard deviation of 3 samples.
[c]k$_{600}$ calculated from the change in SF$_6$ concentration with time and normalized to a Schmidt number of 600 assuming n=0.57.

the atmospheric ^{3}He/^{4}He ratio (1.386x10^{-6}, Clarke et al., 1976); and α is the isotope solubility effect (0.983; Benson and Krause, 1980).

A buoy holding an anemometer which recorded hourly mean wind speed was deployed near the center of the pond (figure 1).

Results and Discussion

The concentrations of SF$_6$ and excess ^{3}He in pond water collected one day prior to the injection of the gases were below the limit of detection (<0.1x10^{-12} ml STP g^{-1}) and 1±1x10^{-16} ml STP g^{-1}, respectively. After 24 hours, the injected gases were nearly homogeneously mixed throughout the pond; mean SF$_6$ and excess ^{3}He concentrations were 180 ±16x10^{-12} ml STP g^{-1} and 758±32x10^{-16} ml STP g^{-1}, respectively (figure 2; table 1). After eight days, the concentration of excess ^{3}He had reached background levels (0.2±1x10^{-16} ml STP g^{-1}) and SF$_6$ concentrations had decreased by an order of magnitude (19±1x10^{-12} ml STP g^{-1}). Over the same time period the excess ^{3}He/SF$_6$ ratio decreased from 4.2±0.2 to 0.0±0.05 (figure 2). Throughout the experiment ^{4}He concentrations were equal to 4.33±0.04x10^{-8} ml STP g^{-1}.

Hourly mean wind speeds corrected to a height of ten meters, U$_{10}$, varied between 0.2 and 5.0 m s^{-1} (bouy height=1.8 m; figure 3). The wind speeds were corrected assuming a neutrally stable boundary-layer, a logarithmic wind profile, and a drag coefficient of 1.3 x 10^{-3} (Large and Pond, 1981). Mean U$_{10}$ calculated for periods between sampling events varied between 1.6 and 3.4 m s^{-1} (table 1).

During each sampling period, the standard deviation of the sample concentrations were greater than the measurement errors. The standard deviations of the SF$_6$ samples were 2-3 times smaller than those for ^{3}He samples despite a more diverse sampling strategy. The direction of
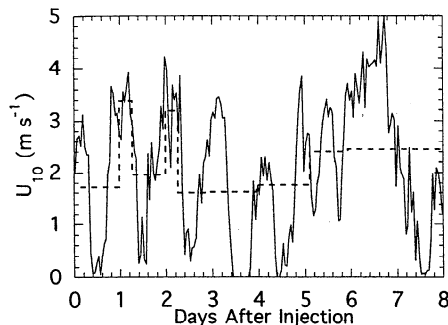
Table 2. Schmidt number exponent.

Period Days	U$_{10}$ m s^{-1}	k$_{SF_6}$ cm hr^{-1}		k$_{He}$ cm hr^{-1}		k$_{600}$[a] cm hr^{-1}		n	
1.0 to 2.9	2.2	2.3	± 0.5	6.3	± 0.5	2.7	± 0.6	0.59	± 0.17
2.9 5.9	1.9	1.8	0.2	4.8	0.3	2.2	0.2	0.56	0.11
1.0 5.9	2.0	2.0	0.2	5.4	0.1	2.4	0.2	0.57	0.07

[a]k$_{600}$ was calculated from k$_{SF_6}$ assuming n = 0.57.

vertical gradients in SF$_6$ concentrations were never the same at all three center stations suggesting that the pond was vertically well mixed. The greater range in sample concentrations than expected from the measurement error resulted from lateral variability in concentration. This suggests that either horizontal mixing between areas with different mean depths was slower than gas transfer across the air-water interface or that the gas transfer velocity was not uniform over the surface of the pond. ^{3}He which is transferred across the air-water interface at a rate about 2.5 times greater than SF$_6$ displayed a greater range in concentrations than SF$_6$ supporting either of these suggestions.

To minimize the uncertainty in the calculation of k$_{He}$, we used only the data collected on day 1.0, 2.9, and 5.9 (table 2). The k$_{He}$ combined with the k$_{SF6}$ calculated for the same periods can be used to calculate the Schmidt number exponent with equation (3). In these calculations we assumed that Schmidt numbers for SF$_6$ and ^{3}He at 23.5° C are 811 and 144, respectively (Wanninkhof, 1992). The errors of the Schmidt numbers are of the order of ±5-10%. Using the maximum change of tracer concentrations (day 1.0 to day 5.9), we calculated n = 0.57±0.07.

Our upper and lower values for n are consistent with the laboratory results of Jähne et al. (1987). The mean value falls between the laboratory values of 1/2 and 2/3. This may have resulted from averaging periods of low and moderate wind speeds. However, the large uncertainty in our value for n makes it difficult to distinguish between the laboratory end members and our intermediate value. In a similar lake experiment using SF$_6$ and ^{3}He as tracers for gas transfer, Watson et al., (1991) found the Schmidt number exponent to be 0.510±0.005 at wind speeds greater than 3.5 m s^{-1}. Their results agree well with results from wind-wave tunnel experiments (Ledwell, 1984; Jähne et al., 1987).

The SF$_6$ data showed smaller variations during each sampling event than the ^{3}He data. Thus, it can be used to calculate k$_{SF_6}$ for shorter periods of time (table 1). Figure 4 shows the results of these calculation plotted against mean wind speeds referenced to a height of 10 m, U$_{10}$. The gas transfer velocity has been normalized to a Schmidt number of 600 (k$_{600}$) using equation (3) and a Schmidt number exponent of 0.57. (In freshwater, the Schmidt number for oxygen at 17.5° C is approximately 600.) For U$_{10}$ between 1.5 and 2.5 m s^{-1}, no significant variation in the gas transfer velocity was observed with wind speed.
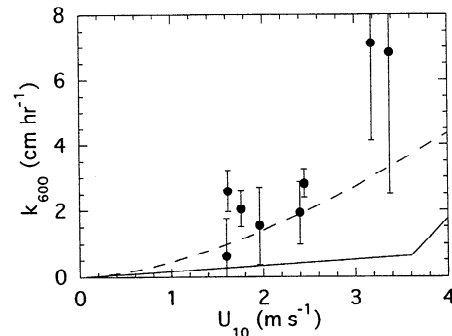

Figure 3. Mean wind speeds corrected to a height of 10 m, U$_{10}$, recorded during the tracer experiment. Solid line = hourly mean wind speeds and dashed line = mean wind speeds between sampling events.

Figure 4. Mean gas transfer velocities corrected to a Schmidt number of 600, k$_{600}$, plotted against mean wind speed corrected to 10 m, U$_{10}$. The plain line shows the empirical relationship of Liss and Merlivat (1986) and the dashed line show the empirical relationship of Wanninkhof et al. (1991).

However, the large uncertainty in k_{600} makes the analysis difficult. At U_{10} greater than 3 m s^{-1}, k_{600} increased dramatically. Our results at these higher wind speeds are consistent with other lake data (Wanninkhof, 1985; 1987; 1991; Upstill-Goddard, 1990).

Plotted along with the Sutherland pond results in figure 4 are the empirical equations proposed by Liss and Merlivat (1986) and Wanninkhof et al. (1991). Liss and Merlivat developed their equation by considering the three distinct regions of wave formation identified in laboratory experiments and the Rockland Lake data of Wanninkhof et al. (1985). Their relationship falls well below our Sutherland pond data. Wanninkhof et al. (1991) developed their relationship by fitting all available lake data to an exponential function. Their relationship fits our data better.

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