Relationship between Gas Transfer Velocities and Wind Speeds in The Tidal Hudson River Determined by the Dual Tracer Technique

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Abstract

Gas transfer velocities were determined using the dual tracer technique (^{3}He and SF_6) for two 40–60 km reaches of the tidal Hudson River. The experiments were performed near Poughkeepsie, NY, in 1993 and near Catskill, NY, in 1994. During both experiments, wind speeds were measured above the river. The shape of daily axial SF_6 distributions and the evolution of peak concentrations followed patterns predicted by the one-dimensional advection-diffusion equation. Mean gas transfer velocities calculated from the 1994 data using the temporal change in SF_6 inventory (4.6 ± 0.4 cm hr^{-1}) and the tracer ratio (5.3 ± 0.2 cm hr^{-1}) are in good agreement, suggesting that the dual tracer technique yields reasonable results. The relationships between gas transfer velocity and wind speed found during these experiments are very similar to those observed previously for lakes, suggesting that wind is the primary source of surface turbulence in these reaches of the tidal Hudson River. The results of the 1993 and 1994 experiments agree very well, indicating that the local geometry of the river is of secondary importance.

1 Introduction

Exchange of dissolved gases across the air-water interface is an important physical process which influences many properties of natural waters. Water quality assessment often requires quantitative estimates of this parameter both for calculations of reaeration rates and for loss rates of volatile pollutants (e. g., *O'Connor* [1962], *Dyrssen et al.* [1990], *Thomann et al.* [1991]). Quantitative relationships which can be used to predict gas transfer velocities from easily measurable parameters such as wind and current speeds are particularly important. Such relationships can be used directly in model simulations and mass balance calculations. For instance, precise *gas transfer* velocities are needed to accurately measure whole-ecosystem respiration

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rates using diurnal dissolved oxygen methods (*Odum* [1956], *Edwards and Owens* [1962], *Howarth et al.* [1992]) or to constrain mass balance calculations of volatile contaminants such as PCBs [*Thomann et al.*, 1991].

Most experiments which quantified gas transfer velocities in estuaries have used either the helmet or mass balance methods (*Juliano* [1969], *Hartman* and *Hammond* [1984], *Clark et al.* [1992], *Marino and Howarth* [1993]). While such experiments can potentially lead to parameterizations of gas transfer velocities, the results are questionable because of a number of methodological uncertainties. The problem with the helmet method is that the surface turbulence regime, the physical driving force behind gas exchange, is disturbed during the measurement. Thus, the measured gas transfer velocity may be influenced by the helmet. Laboratory experiments have found little agreement between gas transfer velocities determined by the helmet method and other approaches (*Stephens* [1978], *Belanger and Korzum* [1991]), suggesting that the surface turbulence regime is indeed disturbed. A central weakness of the mass balance method is that the magnitude and variability of sources and sinks of the dissolved gas must be well known. Uncertainties associated with these terms influence calculated gas exchange rates. Despite these problems, both methods have shown that gas transfer velocities correlate well with wind speed in most estuaries (*Hartman* and *Hammond* [1984], *Kim and Holley* [1988], *Marino and Howarth* [1993]).

Recently, a new method, the *dual tracer technique* (*Watson et al.* [1991], *Wanninkhof et al.* [1993]), has been developed which can be used to quantify gas transfer velocities in large tidal rivers [*Clark et al.*, 1994]. Because the surface turbulence regime is not disturbed during the measurements and because the gas tracers are added in a controlled fashion, the dual tracer technique does not have the methodological problems associated with the helmet and mass balance approaches. With the dual tracer technique, mean gas transfer velocities over periods of days to weeks can be estimated. By simultaneously measuring other environmental variables, parameterizations of the gas transfer velocity can be established for use in future experiments.

Here we present the results of two gas tracer experiments performed on the tidal *Hudson River* during summer and autumn months in 1993 and 1994. The focus will mainly be on the results of the 1994 experiment because the results of the 1993 experiment have been described earlier [*Clark et al.*, 1994].

1.1 Principles of the Dual Tracer Technique

Most *tidal rivers* such as the Hudson can be approximated as one-dimensional systems. Dilution and first-order decay of a pulse of a non-reactive gas tracer added to such a system can be described by the following advection-diffusion equation:

$$\frac{\partial C}{\partial t} + u\frac{\partial C}{\partial x} = D\frac{\partial^2 C}{\partial x^2} - \alpha C \tag{1}$$

where C is the average cross sectional concentration of the gas tracer; u is the average cross sectional current velocity; D is the longitudinal dispersion coefficient; and α is the first order loss term due to transfer across the air-water interface (i. e., reaeration coefficient). *O'Connor* [1963] and *O'Loughlin and Bowmer* [1975] showed that the solution of equation (1) for an instantaneous injection of a gas tracer is:

$$C(x,t) = \frac{M}{A\sqrt{4\pi Dt}} \exp\left[-\frac{(x-ut)^2}{4Dt}\right] \exp(-\alpha t) \tag{2}$$

where M is the mass of trace gas added and A is the cross sectional area. This model predicts that longitudinal distributions of the tracer should be gaussian in shape and that the peak concentrations should decay linearly as a function of $e^{-\alpha t}t^{-1/2}$.

The gas transfer velocity, k, is defined in the following manner:

$$k = F/(C_{sur} - C_{eq}) = \alpha/h \tag{3}$$

where F is the mass flux of gas across the air-water interface, C_{sur} and C_{eq} are the concentrations of the gas in the water at the air-water interface and in equilibrium with the atmosphere, respectively, and h is the mean depth.

Solving the advection-diffusion equation with first order decay (eq. 1 and 2) for two instantaneously injected gases, such as ^{3}He and SF_6, and assuming that the gas transfer velocities, $k_{^3He}$ and k_{SF_6}, are related by their Schmidt numbers [*Jähne et al.*, 1987]:

$$k_{SF_6}/k_{^3He} = \left(Sc_{(SF_6)}/Sc_{(^3He)}\right)^{-n} \tag{4}$$

leads to the following expression for the gas transfer velocity of ^{3}He (*Watson et al.* [1991], *Wanninkhof et al.* [1993]):

$$k_{^3He} = \frac{1}{h}\frac{d}{dt}\left(\frac{\ln(\Delta[^3He]/\Delta[SF_6])}{1-\left(Sc_{(SF_6)}/Sc_{(^3He)}\right)^{-n}}\right) \tag{5}$$

where $Sc_{(^3He)}$, and $Sc_{(SF_6)}$ are the Schmidt numbers for ^{3}He and SF_6 calculated using the relationships given by *Wanninkhof* [1992] and the observed water temperature, $\Delta[^3He]$ and $\Delta[SF_6]$ are the differences between observed and atmospheric equilibrium concentrations for ^{3}He and SF_6, respectively, and

n is the Schmidt number exponent. The Schmidt number is defined as the kinematic viscosity of water divided by the molecular diffusion coefficient of the gas in water. For wavy surfaces not broken by white caps, n has been determined to be 1/2 in both laboratory and field experiments (*Ledwell* [1984], *Jähne et al.* [1987], *Watson et al.* [1991]).

1.2 Study Location

The Hudson is a tidal river for more than 130 km south of the Federal Dam at Troy, NY (kmp 248[1]) (Fig. 1). The position of the salt/fresh water interface varies seasonally. Typically, during spring runoff, it is located about 15 to 30 km north of New York City (kmp 25–40) and during late summer low runoff, it lies near Newburgh, NY (kmp 100).

Of the total freshwater discharge into the tidal Hudson River, 50–80 % enters at the Federal Dam. Flow from four large tributaries, Wappinger Creek (kmp 108), Rondout Creek (kmp 148), Esopus Creek (kmp 166), and Catskill Creek (kmp 183), account for most of the remaining freshwater discharge. Mean flow at the Federal Dam varies seasonally. Maximum (> 800 m^3 s^{-1}) and minimum flows (50 to 200 m^3 s^{-1}) occur during spring and late summer respectively. Mean depths of cross sections vary between 4 and 9 m for most of the tidal river except for a 30 km reach downstream of Rondout Creek where the river deepens and mean depths of cross sections vary between 10 and 20 m (Fig. 2a). The cross sectional area of the channel increases downstream from 2,000 m^2 near the Federal Dam to 12,000 m^2 near the salt/fresh water interface (Fig. 2b).

The tracer release experiments were performed at different locations in the tidal Hudson River. During the 1993 experiment, a mixture of SF_6 and ^3He was injected about 10 km south of Rondout Creek (kmp 138). The center of the tracer patch was confined to a 40 km reach of river between the injection point and Wappinger Creek. Here, the axis of the river trends north-south with only one significant bend in the river (Fig. 1). No major tributaries enter and no extended area of shallow water occurs along this stretch of river. The geometry is complicated only by Esopus Island, which lies about 3 km south of the injection point. The cross sectional area of the channel does not vary much along this reach (Fig. 2b). The mean depth and width of the channel is 14 m and 800 m, respectively (Fig. 2). During this experiment, the mean freshwater discharge rate over the Federal Dam was 160 ± 24 m^3 s^{-1} and the temperature of the river averaged 26°C.

During the 1994 experiment, the injection point (kmp 227) was about 7 km south of Albany, NY. The center of the tracer patch was confined to a 60 km reach of the river between the injection point and Esopus Creek. The cross sectional area increases south of the injection point from about

[1]Locations along the Hudson River are referred to by the axial distance, kilometer point (kmp), upstream (+) and downstream (-) from the Battery at the southern tip of Manhattan Island.

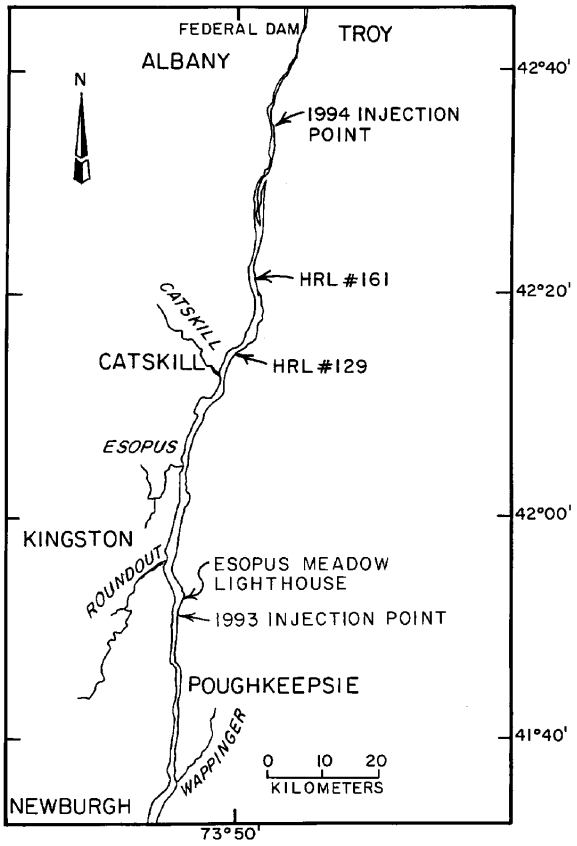

Figure 1: Map of the tidal Hudson River.

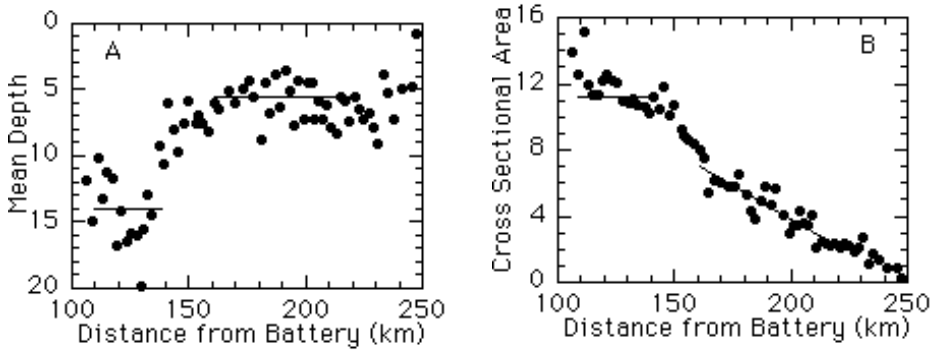

Figure 2: Geometry of Hudson River cross sections calculated from Stedfast (1980). ***a*** *mean depth (m) and* ***b*** *cross sectional area (10^3 m^2). The lines represent the regions of the two tracer experiments.*

Table 1: Results of Hudson River gas tracer experiments.

Time after Injection (day)	Peak SF_6 (pmol l^{-1})	Peak Excess ^3He (10^{-16} ml STP g^{-1})	Excess $^3He/SF_6$	k_{600} (cm hr^{-1})	U_{10} (m s^{-1})
		1993 Experiment			
1.1	3.28	1524	501 ± 15	–	–
2.0	1.98	1040	530 ± 16	–	0.7
3.1	1.64	791	483 ± 15	–	1.6
5.2	1.04	431	413 ± 12	3.9 ± 1.5	3.9
7.0	0.81	323	387 ± 12	1.5 ± 1.8	2.5
8.2	0.69	216	315 ± 10	9.0 ± 2.4	4.9
10.1	0.53	131	248 ± 7	6.3 ± 1.6	3.1
12.1	0.45	96	214 ± 6	3.5 ± 1.4	3.2
14.2	0.34	63	189 ± 6	3.6 ± 0.7	2.8
16.2	0.26	38	144 ± 4	5.9 ± 1.5	3.2
		1994 Experiment			
1.1	41.3	–	–	–	–
2.1	20.0	–	–	–	–
3.1	11.6	–	–	–	–
4.1	7.84	2031	260 ± 5	–	–
5.2	4.73	940	199 ± 6	5.3 ± 1.0	–
6.3	3.06	437	143 ± 5	6.7 ± 1.3	2.9
7.3	2.24	251	109 ± 3	6.1 ± 1.4	3.1
8.2	1.79	166	92.4 ± 3	4.2 ± 1.5	2.7
9.2	1.42	115	81.1 ± 1	2.8 ± 1.0	1.3
10.1	1.17	77	65.5 ± 2	5.6 ± 1.2	2.4
11.0	0.86	38	43.9 ± 1	9.1 ± 1.2	5.1
12.0	0.66	21	32.5 ± 2	6.7 ± 1.9	4.2
13.1	0.51	12	24.1 ± 3	6.5 ± 4.2	3.4

2,000 m^2 to about 7,000 m^2 near Esopus Creek (Fig. 2b). Throughout this region, the main channel is dredged to a depth of about 10 m. However, because of extensive areas of shallow water (<2 m), the mean depth varied between 4 and 8 m and averaged about 5.5 m (Fig. 2a). Many islands and coves further complicate the geometry. During this experiment, the mean freshwater discharge rate over the Federal Dam was 210 ± 40 m^3 s^{-1}. During the first week, the surface water temperature decreased from 19°C to about 15°C where it remained constant thereafter.

2 Methods

Prior to each Hudson River experiment, about 0.045 moles of 99.8 % pure ^{3}He gas and 31 moles of pure *sulfur hexafluoride* (SF_6) gas were mixed into a large gas cylinder (43.8 l). The gas mixtures were injected into the river on August 24, 1993 and September 28, 1994 through two diffusing stones which were suspended at a depth of 10 m behind a small boat. The injection occurred over a period of about 20 minutes as the boat crossed the channel perpendicular to the main axis of the river. During the 1993 experiment about 0.6 moles of the gas mixture were injected as the boat crossed the channel twice and during the 1994 experiment about 1.4 moles were injected as the boat crossed the channel 7 times. Approximately 20–40 % of the gases dissolved during the injection (see below; *Clark et al.* [1994]). Because of drag caused by the rope and diffusion stones, the injection depth of the gas mixture was shallower than 10 m.

For approximately two weeks after both injections, samples were collected in sequence along the main axis of the river from a small boat every 1 to 2 days using either a 1.5 l or 5 l Niskin bottle. Station locations were determined using a field Global Positioning System unit. During the 1993 experiment, stations were occupied at either slack high or slack low tide and spaced at intervals of 1 to 2 km. At each station, samples for SF_6 and ^{3}He were collected about 1 meter below the surface of the water and about 1 meter above the sediment. SF_6 samples were stored submerged in a bucket of river water and analyzed on shore 2 to 12 hours after collection.

During the 1994 experiment, the analytical equipment was set up in the cabin of our boat, enabling us to obtain nearly real time SF_6 data. Spacing between stations was determined by location within the tracer patch. At the edges, stations were separated by 2 to 4 km. This distance was shortened nearer to the center of the patch where the distance between stations was 0.3 to 0.5 km during the first week of the experiment and 0.5 to 1.5 km during the second week. Surface samples were collected at all stations, bottom samples were collected at every 3^{rd} or 4^{th} station and at all stations near the center of the patch, and mid-depth samples were collected at about one third of the center stations. While SF_6 was collected at all stations and measured on the boat, ^{3}He samples were collected only near the center of the patch and measured later on shore.

SF_6 samples were collected in either 50 ml glass syringes or 60 ml BOD bottles. All samples were analyzed with a gas chromatograph equipped with an electron capture detector using the head space method described by *Wanninkhof et al.* [1987, 1991]. SF_6 was separated from other gases with a molecular sieve 5A column held at room (cabin) temperature. All samples were measured within 12 h of collection. The reproducibility of the SF_6 measurements was ± 2 to 3 %.

^{3}He was analyzed from about 40 ml of water which was collected in copper tubes and sealed by pinch-off clamps. All samples were analyzed

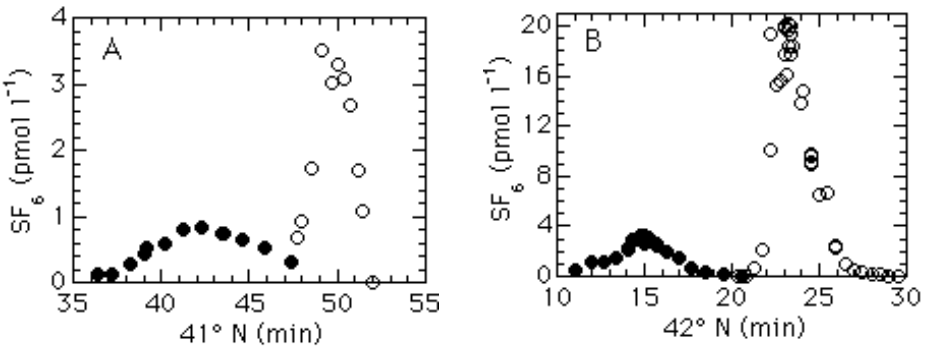

Figure 3: ***a*** *Axial distributions of SF_6 from the 1993 experiment. Open circles = day 1 and solid circles = day 6.* ***b*** *Axial distributions of SF_6 from the 1994 experiment. Open circles = day 2 and solid circles = day 6.*

on a VG-5400 helium isotope mass spectrometer using methods similar to those described by *Bayer et al.* [1989]. Precision of ^{4}He concentrations and ^{3}He/^{4}He ratios were about ±0.5 % and ±0.2 %, respectively.

Excess ^{3}He concentrations, $[^3He]_{exc}$, were calculated from the measured ^{3}He/^{4}He ratio and ^{4}He concentration in the following manner:

$$[^3He]_{exc} = [^4He]_s(R_s - R_a) + [^4He]_{eq}R_a(1 - a) \quad (6)$$

where ^4He_s is the measured ^{4}He concentration; $^4He_{eq}$ is the atmospheric equilibrium concentration of ^{4}He [*Weiss*, 1971]; R_s is the measured ^{3}He/^{4}He ratio; R_a is the atmospheric ^{3}He/^{4}He ratio (1.386×10^{-6}; *Clarke et al.* [1976]); and a is the solubility isotope effect (0.983; *Benson and Krause* [1980]).

During each experiment an anemometer was placed within the river's channel (Fig. 1). In 1993, it was placed on top of the Esopus Meadow Lighthouse (kmp 141), 16 m above the high water mark. The lighthouse is located about 600 m from the western shore. In 1994, the anemometer was placed on Hudson River Light (HRL) #161 (kmp 203) for the first week and on HRL #129 (kmp 188) for the second week. The height of the anemometer above the high water mark was 9.6 m and 9.7 m, respectively. Both of these lights were more than one third of the way across the channel. Hourly mean wind speeds and prevailing wind direction (using 16 compass directions) were recorded. The same instrument was used during the two experiments.

3 Results

Because continental waters are potentially contaminated with SF_6 [*Clark et al.*, 1995a], background concentrations were measured prior to injecting the

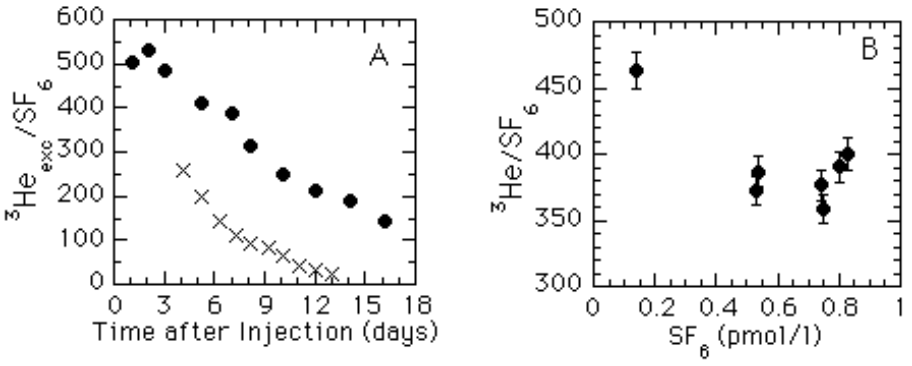

Figure 4: ***a*** *Temporal change of the excess $^3He/SF_6$ ratios: solid circles = 1993 and crosses = 1994.* ***b*** *Excess $^3He/SF_6$ plotted as a function of SF_6 concentration. Transect collected on Aug. 31, 1993.*

gas tracers. We found that background SF_6 concentrations were below our detection limit (0.01 pmol l^{-1}) in areas of our gas exchange experiments suggesting that the tidal Hudson River is free of any significant local contamination. At the same locations, ^3He was determined to be in solubility equilibrium with the atmosphere.

Daily distributions of SF_6 concentrations along the axis of the tidal Hudson River and the evolution of peak concentrations followed patterns predicted by the one-dimensional advection-diffusion equation (eq. 1 and 2) suggesting that this system can be approximated as a one-dimensional system. During both experiments, longitudinal distributions were approximately gaussian in shape (Figs. 3a and 3b) and peak SF_6 concentrations and excess $^3He/SF_6$ ratios decreased by 1 to 2 orders of magnitude (Tab. 1, Fig. 4a). The ratio observed near the center of the tracer patch ([SF_6] > 0.5 $*$ [SF_6]max) was approximately constant (Fig. 4b). Plots of peak SF_6 concentrations versus $e^{-\alpha t} t^{-1/2}$ were linear (Fig. 5). The change in slope in the 1994 data set appears to be related to a change in the longitudinal dispersion coefficient [*Clark et al.*, 1995b].

While small vertical gradients in the tracer concentrations were observed during the 1993 experiment [*Clark et al*, 1994], they were not observed during the 1994 experiment.

Hourly mean wind speeds corrected to a height of ten meters, U_{10}, were highly variable during the two tracer experiments (Fig. 6). The wind speeds were corrected assuming a neutrally stable boundary layer, a logarithmic wind profile, and a drag coefficient of 1.3×10^{-3} (*Large and Pond* [1981]). Hourly mean wind speeds recorded during periods between sampling events varied by a factor of 3 to 6 and the prevailing wind directions were generally along the axis of the river. During the two experiments, mean U_{10} between

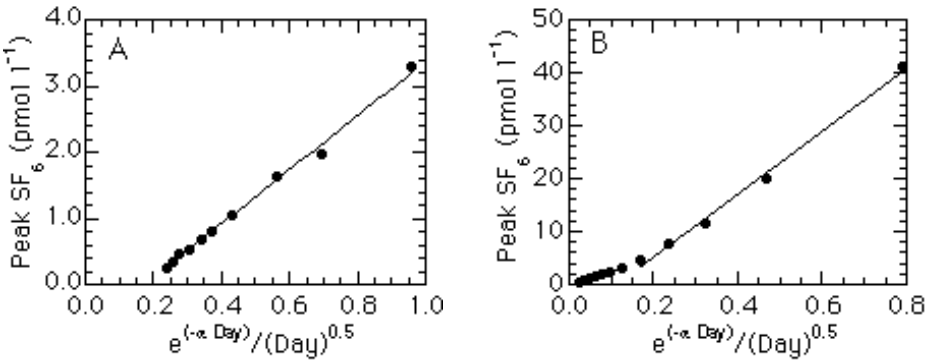

*Figure 5: Peak SF_6 concentrations plotted as a function of $e^{-\alpha t}\ t^{-1/2}$: **a** results of the 1993 experiment and **b** results of the 1994 experiment.*

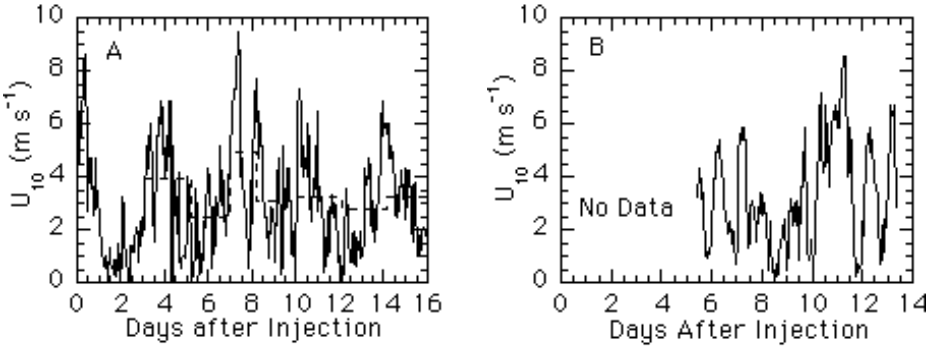

*Figure 6: Mean wind speeds observed during the experiments, corrected to a height of 10 m. The solid and dashed lines are the hourly mean wind speed and the mean wind speeds between sampling events, respectively. **a** 1993 and **b** 1994.*

sampling periods ranged between 0.7 and 5.1 m s^{-1}. Wind speeds over the river are not available for the first 5 days of the 1994 experiment because the anemometer failed to record the data.

Mean gas transfer velocities, k_{600}, were calculated from the change in the excess $^3He/SF_6$ ratio with time and normalized to a Schmidt number of 600 using equations (4) and (5) (Tab. 1). Daily ratios were determined from one station in 1993 and from 1 to 4 stations in 1994. In 1994, the mean standard deviation of the excess $^3He/SF_6$ ratios from stations near the peak was about ± 3 %, approximately the same as the analytical error.

We have assumed that during the 1993 experiment, the error in the ratio was also approximately equal to the analytical uncertainty. Small corrections were applied to k_{600} calculated during the 1993 experiment to account

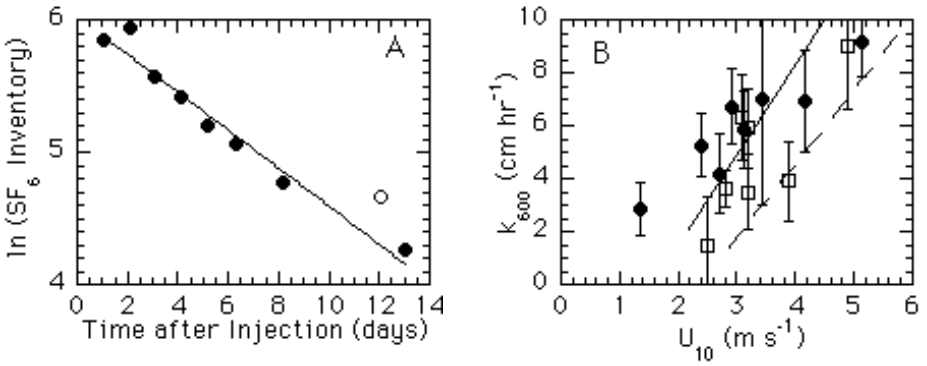

Figure 7: ***a*** *SF_6 inventory (mmol) plotted as a function of time. The open circle was not used in the fit.* ***b*** *Results of Hudson tracer experiments. Open squares: 1993 data and filled circles: 1994 data. Dashed and plain lines represent trends from Rockland and Crowley lakes, respectively [Wanninkhof et al., 1985, 1987].*

for observed vertical gradients [*Clark et al.*, 1994]. Mean values of k_{600} calculated for the 1993 and 1994 experiments were 4.4 ± 0.2 cm hr^{-1} (day 3 to 16; U_{10} = 3.1 m s^{-1}) and 5.3 ± 0.2 cm hr^{-1} (day 4 to 12; U_{10} = 3.2 m s^{-1}), respectively.

Gas transfer velocities were not calculated for the initial period during either experiment for a variety of reasons. In 1993, an injection bias persisted for the first two days of the experiment [*Clark et al.*, 1994]. In 1994, ^{3}He samples were not measured during the first three days because of their high concentrations (δ^3He > 350 %) and because of the failure of the anemometer during initial phase of the experiment.

4 Discussion

In 1994, the density of stations along the axis of the Hudson was sufficiently high to allow for examination of inventories of SF_6. These inventories were calculated assuming that cross sectional mean concentrations were equal to the observed concentrations in the center of the channel. The distributions were corrected for tidal movement which occurred during sampling in an attempt to provide synoptic distributions. Tidal current velocities, which were about 0.4 m s^{-1} during peak flow, were estimated from a hydrodynamic model developed by HydroQual, Inc. [*Blumberg and St. John*, 1995]. The corrections applied for tidal movement during sampling were as large as 20 % and averaged about 10 %. The assumption that the observed and cross sectional mean concentrations are equal is not entirely correct. Cross sectional surveys that were carried out on day 7 and 9 showed that concentrations outside of the channel and near the shore were often less than half

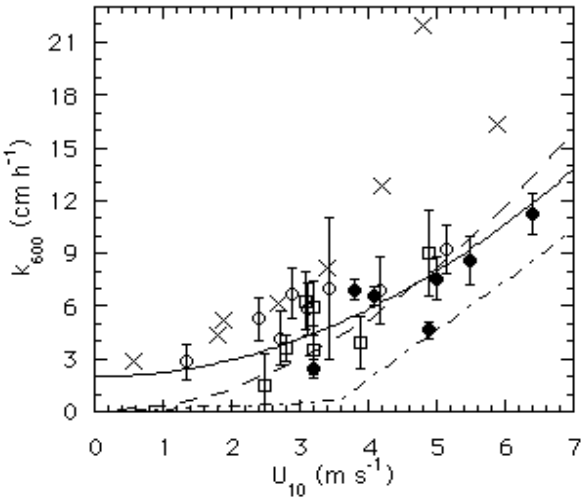

Figure 8: Relationship between gas transfer velocity, k_{600}, and wind speed, U_{10}, for estuaries. Open squares = 1993 Hudson River data [Clark et al., 1994]; filled circles = 1994 Hudson River data [this work]; open triangles = San Francisco Bay data [Hartman and Hammond, 1984]; crosses = Hudson River data [Marino and Howarth, 1993]. The dashed-dotted, dashed, and solid lines are the empirical relationships of Liss and Merlivat [1986], Wanninkhof [1992], and this study, respectively.

of those observed in the main channel. However, because the navigational channel typically made up 75-90 % of the cross sectional area [*Steadfast*, 1980], the error introduced by this assumption is probably small.

The SF_6 inventory decreased exponentially during the 1994 experiment (Fig. 7a) with a mean loss rate of SF_6, α, of 0.144 ± 0.011 d^{-1}. The mean gas transfer velocity, k_{600}, calculated from α is 4.6 ± 0.4 cm hr^{-1}, using equation (3) and a mean depth of 5.5 m.

This value is slightly lower than the mean k_{600}, 5.3 ± 0.2 cm hr^{-1}, calculated from the change in the excess $^3He/SF_6$ ratio between day 4 and day 12.

Daily mean gas transfer velocities calculated from the change in the excess $^3He/SF_6$ ratio with time correlate well with mean wind speed (Fig. 7b). Results from the 1993 and 1994 experiments were similar, suggesting that the local geometry of the channel has relatively little effect and that a single parameterization of k_{600} with U_{10} can be used for the entire tidal Hudson River. The observed trend is very similar to trends reported in lake experiments [*Wanninkhof et al.*, 1985, 1987]. This agreement suggests that the tidal Hudson River behaves like a lake in terms of gas transfer across the air-water interface. Surface turbulence appears to be forced primarily by wind; surface turbulence resulting from boundary shear appears to be of minor importance.

Earlier gas exchange experiments in *estuarine* environments have found strong correlations between wind speed and gas transfer velocity (*Hartman and Hammond* [1984], *Kim and Holley* [1988], *Marino and Howarth* [1993]). *Hartman and Hammond* [1984] determined the relationship between gas transfer velocity and wind speed using both the mass balance and helmet methods in San Francisco Bay. The slope of the correlation ($\Delta k/\Delta U$) was higher for the results of the helmet experiment than for the mass balance experiment. Their results using the mass balance approach agree very well with our results using the dual tracer technique (Fig. 8). *Marino and Howarth* [1993] determined the relationship using the helmet method on the tidal Hudson River near the location of our 1993 experiment. Their results plot systematically higher than ours especially at high wind speed (Fig. 8). In both the tidal Hudson River and San Francisco Bay, results from helmet experiments tend to show higher gas transfer velocities than other approaches. This suggests that the helmet tends to increase the gas transfer rate.

Plotted in figure 8 along with the experimental data are the empirical equations of *Liss and Merlivat* [1986] and *Wanninkhof* [1992]. Liss and Merlivat's equation falls well below the tidal river and estuarine data. Wanninkhof's equation fits the estuarine results quite well at wind speeds above 4 m s^{-1}. However, at low wind speeds, it tends to underestimate the gas transfer velocity substantially.

A better relationship between wind speed and gas transfer velocity can be achieved by assuming a non-zero y-intercept. A number of studies in lakes suggest that at very low wind speeds k_{600} does not approach zero (*Wanninkhof et al.* [1985], *Clark et al.* [1995c]). In these settings a non-wind source of surface turbulence regulates gas transfer. Assuming that a similar process occurs in estuaries, we propose the following relationship for estuaries based on a 2^{nd} order polynomial fit of the empirical data determined with the dual tracer technique in the tidal Hudson River and mass balance method in San Francisco Bay (Fig. 8):

$$k_{600} = 2.0 + 0.24U_{10}^2 \qquad R^2 = 0.58 \tag{7}$$

where k_{600} is in cm hr^{-1} and U_{10} is in m s^{-1}.

5 Conclusions

The dual tracer technique of determining gas transfer velocities has been successfully used in the tidal Hudson River. The daily distributions of SF_6 followed patterns predicted by the one-dimensional advection-diffusion equation. Mean gas transfer velocities calculated with the dual tracer technique and from the temporal change in SF_6 inventory agree quite well, verifying the accuracy of the dual tracer technique.

Gas transfer velocities in the tidal Hudson River were found to correlate strongly with wind speed. The relationship between wind speed and gas

transfer velocity falls close to those observed for lakes, suggesting that the tidal Hudson River behaves like a lake in terms of gas transfer.

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