

UC Santa Barbara

UC Santa Barbara Previously Published Works

Title

SF6–3He Tracer Release Experiment: A New Method of Determining Longitudinal Dispersion Coefficients in Large Rivers

Permalink

<https://escholarship.org/uc/item/86k436v4>

Journal

Environmental Science and Technology, 30(5)

ISSN

0013-936X

Authors

Clark, Jordan F
Schlosser, Peter
Stute, Martin
[et al.](#)

Publication Date

1996-04-01

DOI

10.1021/es9504606

Peer reviewed

SF₆—³He Tracer Release Experiment: A New Method of Determining Longitudinal Dispersion Coefficients in Large Rivers

JORDAN F. CLARK,*†
PETER SCHLOSSER,
MARTIN STUTE, AND
H. JAMES SIMPSON

Lamont-Doherty Earth Observatory, Department of Geological Sciences, Columbia University, Palisades, New York 10964

Longitudinal dispersion coefficients have been determined in the tidal Hudson River using sulfur hexafluoride. For this purpose, SF₆, a nonreactive synthetic gas, was injected into the Hudson south of Albany, NY, and used in a fashion similar to a fluorescent dye. Three days after injection, SF₆ distributions along the main axis of the river were approximately Gaussian. The change in variance with time showed two periods of linear growth. During the first period (days 3–8), the longitudinal dispersion coefficient was estimated to be $47 \pm 6 \text{ m}^2 \text{ s}^{-1}$, and during the second period (days 8–13), it was $162 \pm 22 \text{ m}^2 \text{ s}^{-1}$. A second gas, ³He, which was injected simultaneously with SF₆, allowed for the determination of gas exchange rates across the air–water interface. Gas transfer velocities normalized to a Schmidt number of 600 ranged from 2.8 to 9.2 cm h⁻¹ and correlated well with mean wind speed.

Introduction

The fate of soluble material in rivers and streams is governed by a number of physical and chemical processes. The primary physical processes are currents, dispersion, and, for volatile substances, transfer across the air–water interface. While advective transport and gas transfer velocities can be estimated reasonably well from the channel geometry, discharge rate, and wind speed, longitudinal dispersion coefficients are difficult to predict from physical parameters in rivers (1, 2). Therefore, many studies of rivers have relied upon field experiments to determine these coefficients. Generally, these experiments have used fluorescent dyes as tracers (4–7).

Fluorescent dyes have a number of properties that have made them successful tracers of dispersion. First, they can be measured easily in the field using portable fluorimeters

(6). Second, they can be measured over concentration ranges of several orders of magnitude. Third, background concentrations are very low in most natural waters (6, 8). Nevertheless, these dyes are not “ideal” tracers because (i) both laboratory and field experiments have demonstrated that most fluorescent dyes are not conservative in natural waters (4, 5, 8), (ii) degradation products of some dyes, such as Rhodamine WT, can be toxic (9), and (iii) fluorescent dyes are relatively expensive. Hence the design and duration of experiments are often determined by the amount of dye that can be purchased (7).

A potential substitute for fluorescent dyes in river dispersion experiments is sulfur hexafluoride. SF₆ is a synthetic gas used primarily as an electrical insulator. It has many of the same properties as fluorescent dyes, which suggests that it can be used successfully as a tracer in rivers. Background concentrations in natural waters are extremely low (<1 fmol/L; 1 fmol = 10⁻¹⁵ mol) (10, 11); it can be measured precisely in water ($\pm 2-3\%$) over a concentration range of 6 orders of magnitude using a gas chromatograph equipped with an electron capture detector (10, 11); and field and laboratory experiments suggest that SF₆ does not adsorb onto suspended particles or into sediments and that it is nonreactive in oxygenated natural waters (12–14). SF₆ differs from fluorescent dyes in that it is a gas. Hence, it is lost from solution across the air–water interface to the atmosphere. However, by injecting a second nonreactive gas (for example ³He) along with SF₆ and monitoring the distributions of both gases, the gas transfer velocity can be quantified (15–17) and the mass balance closed.

The advantage of using SF₆ to estimate dispersion coefficients in rivers is that it is much less expensive than fluorescent dyes; thus, considerably more SF₆ can be injected. Therefore, it is possible to work in larger systems and for longer periods of time. SF₆ has been successfully used to estimate eddy diffusion coefficients in the open ocean (14, 18, 19) and lakes (20, 21) over periods of weeks to months and to estimate gas transfer velocities in lakes, rivers, and the open ocean (15–17, 23–25). The disadvantage of using SF₆ is that discrete samples must be collected. Thus, the spatial resolution of the tracer patch is generally not as well defined as in fluorescent dye studies.

Here, we present the results of a gas tracer experiment performed on the tidal freshwater reach of the Hudson River which examines the usefulness of SF₆ as a tracer for mixing. The experiment took place south of Albany, NY, in October 1994. ³He was injected simultaneously with SF₆ and an anemometer was placed within the river channel to quantify the relationship between wind speed and gas transfer velocities.

Methodology

Most tidal rivers such as the Hudson can be approximated as one-dimensional systems. Dilution and first-order decay of a pulse of a nonreactive gas tracer in such a system can be described by the following advection–diffusion equation (1, 2, 4):

$$\frac{\partial C}{\partial t} + u \frac{\partial C}{\partial x} = D \frac{\partial^2 C}{\partial x^2} - RC \quad (1)$$

† Present address: Department of Geological Sciences, University of California, Santa Barbara, CA 93106; phone: (805) 893-3471; fax: (805) 893-2314; e-mail address: clark@magic.ucsb.edu.

where C is the concentration of the gas tracer averaged over the cross section, u is the net downstream current velocity averaged over the cross section, D is the longitudinal dispersion coefficient, and R is the first-order loss term due to transfer across the air–water interface (reaeration coefficient). It can be shown that, by assuming a constant geometry, D , and R , the solution of eq 1 for an instantaneous injection of a gas tracer is

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

where M is the mass of trace gas added and A is the cross-sectional area. This model predicts that longitudinal distributions of an instantaneously injected tracer should be Gaussian in shape and that the peak concentration should decrease linearly as a function of $e^{-Rt}t^{-1/2}$. Equation 2 holds only after an initial period of transverse mixing (1–3).

Longitudinal Dispersion Coefficients. A number of methods have been developed to calculate longitudinal dispersion coefficients, D , from experimental data (1–6), with the “change-of-moment method” being commonly used (1–3). D can be calculated in the following manner:

$$D = \frac{1}{2} \frac{d\sigma^2}{dt} \quad (3)$$

where σ^2 is the spatial variance of concentration at a particular time.

Gas Transfer Velocities. In addition to the longitudinal dispersion coefficient, gas transfer velocities can be determined from gas tracer experiments if two gas tracers are injected simultaneously (15–17). Typically, the two gases used have been SF_6 and ^3He . Assuming that the gas transfer velocities are related by their Schmidt numbers (26)

$$k_{\text{SF}_6}/k_{^3\text{He}} = (Sc_{(\text{SF}_6)}/Sc_{(^3\text{He})})^{-n} \quad (4)$$

$k_{^3\text{He}}$ can be calculated in the following manner (15–17):

$$k_{^3\text{He}} = \frac{1}{h} \frac{d}{dt} \left(\frac{\ln(\Delta[^3\text{He}]/\Delta[\text{SF}_6])}{1 - (Sc_{(\text{SF}_6)}/Sc_{(^3\text{He})})^{-n}} \right) \quad (5)$$

where $k_{^3\text{He}}$ and k_{SF_6} are the gas transfer velocity for ^3He and SF_6 , respectively; $Sc_{(^3\text{He})}$, and $Sc_{(\text{SF}_6)}$ are their Schmidt numbers (27, 28); $\Delta[^3\text{He}]$ and $\Delta[\text{SF}_6]$ are the differences between the observed and atmospheric equilibrium concentrations for ^3He and SF_6 in the peak region, respectively; h is the mean depth; 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 (15, 26, 29). Gas transfer velocities, k , are equal to first-order loss terms due to transfer across the air–water interface, R , divided by the mean depth in vertically well-mixed systems.

Experimental Section

Study Location. The Hudson is a tidal river for more than 140 km between the Federal Dam at Troy, NY (kmp 248) and the saltwater–freshwater interface (Figure 1). [Locations along the Hudson River are referred to by the axial distance, kilometer point (kmp), upstream (+) and down-

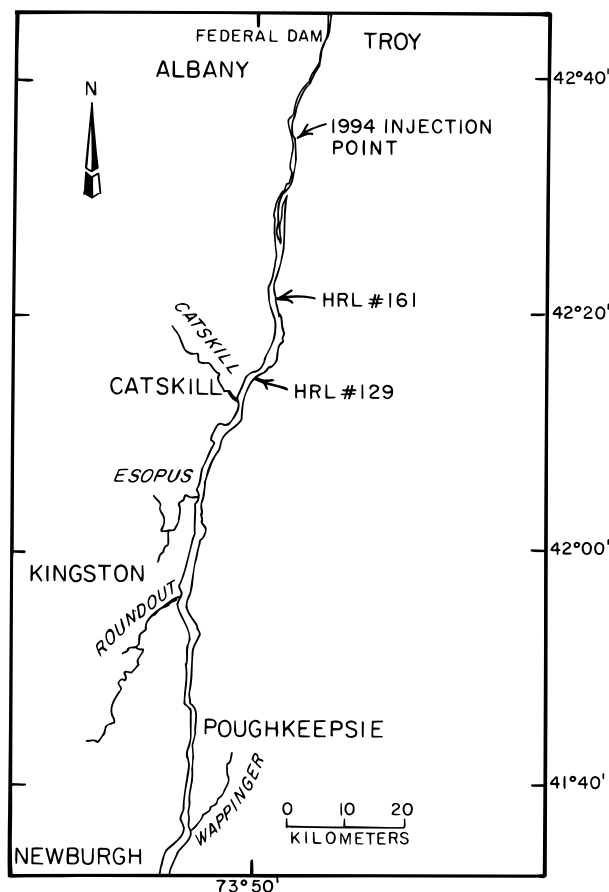


FIGURE 1. Map of tidal Hudson River.

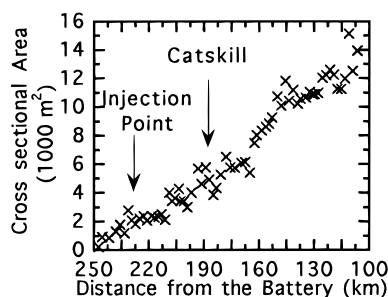


FIGURE 2. Cross-sectional area plotted as a function of distance from the Battery. Data from Stedfast (30).

stream (–) from the Battery at the southern tip of Manhattan Island.] The position of the saltwater–freshwater interface varies seasonally with freshwater discharge. Typically, during maximum spring runoff, it is located ~15 km north of New York City (kmp 25), 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), makes up most of the remaining freshwater discharge. Mean flow at the Federal Dam varies seasonally. Maximum ($>800 \text{ m}^3 \text{ s}^{-1}$) and minimum ($50\text{--}200 \text{ m}^3 \text{ s}^{-1}$) flows occur during spring and late summer, respectively. The cross-sectional area of the channel increases downstream from the Federal Dam to the saltwater–freshwater interface (Figure 2). 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.

During the 1994 experiment, the trace gases were injected ~7 km south of Albany, NY (42°34.7' N; kmp 227). The center of the tracer patch was always found along a 60 km reach of the river between the injection point and Esopus Creek (kmp 166). The axial trend is, respectively, north-south and southwest-northeast along the northern and southern half of this reach. The cross-sectional area increases south of the injection point from ~2000 to ~6000 m² near the confluence with Esopus Creek (Figure 2). Throughout this reach of the Hudson, the navigation channel is dredged to ~10 m. However, because of extensive areas of shallow water (<2 m), the mean depth varied between 4 and 8 m and averaged ~5.5 m. Many islands and coves further complicate the geometry. During this experiment, the mean freshwater discharge rate over the Federal Dam was 210 ± 40 m³ s⁻¹.

Tracer Injection. Prior to the Hudson River tracer experiment, ~0.045 mol of 99.8% pure ³He gas (1994 cost, \$120) and 31 mol of pure SF₆ gas (1994 cost, \$230) were mixed into a large cylinder (43.8 L). About 1.4 mol of this mixture (1994 cost, \$16) was injected into the river on September 28, 1994, through two diffusing stones which were suspended at a depth of 10 m behind a small boat. We estimated from inventories that were calculated during the first 2 days of the experiment that ~0.4 mol (28% of the total) dissolved during the injection. At the injection point, the channel depth was ~11 m and the cross-sectional area was ~2250 m². The injection occurred 3 h before high tide as the river was flowing to the north (upstream). The gas mixture was injected for a period of ~20 min as the boat crossed the channel perpendicular to the main axis of the river 7 times. Because of drag caused by the rope and diffusion stones, the injection depth of the gas mixture was shallower than 10 m.

Sampling Procedure and Analysis. For ~2 weeks after the injection, samples were collected in sequence along the main axis of the river from a small boat every day using a 5 L Niskin bottle. The analytical equipment was set up in the cabin of the boat enabling us to have nearly real-time SF₆ data. Spacing between stations was determined on the basis of location within the tracer patch. At the edges of the patch, stations were separated by 2–4 km. This distance was reduced nearer to the center of the patch where the spacing between stations was 0.3–0.5 km during the first week of the experiment and 0.5–1.5 km during the second week. Surface samples (<1 m below the air-water interface) were collected at all stations, and bottom samples (1–2 m above the sediments) were collected at every third or fourth station and at all stations near the center of the patch. Additionally, middepth samples were collected at about one-third of the stations near the center of the patch. ³He samples were collected only near the center of the patch because it is only necessary to resolve the gas tracer ratio in this region of the patch. This strategy helped to keep the ³He analysis cost (\$250 each) down. The total sampling time for each transect was 2–3 h. Station locations were determined using a field global positioning system (GPS) unit.

SF₆ samples were collected in 50 mL glass syringes. Most samples were analyzed immediately after collection (total collection and analysis time was ~5 min) using the headspace method described by Wanninkhof et al. (23). Replicates and occasional samples from stations with

multiple depth intervals could not be analyzed immediately after collection. These samples were stored submerged in river water and analyzed later, generally within 2 h of collection.

The glass syringes were filled to a predetermined volume of water (15–36 mL) and then a headspace was created with a known volume of high-purity nitrogen gas (14–35 mL). After 3 min of shaking to equilibrate the N₂ with the water sample, the headspace gas was injected through a column of Mg(ClO₄)₂ (to remove water vapor) into a small sample loop of known volume (~1 mL). Subsequently, the gas in the sample loop was flushed into a gas chromatograph equipped with an electron capture detector with high-purity N₂ carrier gas. SF₆ was separated from other gases with a molecular sieve 5A column held at cabin temperature. Multiple equilibrations between sample and N₂ gas showed that more than 98% of the SF₆ was extracted during the first equilibration. Using this method, we were able to analyze ~12 samples/h. Our detection limit was ~0.01 pmol L⁻¹ (1 pmol = 10⁻¹² mol), and the precision determined through duplicate measurements was ±3%.

³He was extracted from ~40 mL of water which was collected in copper tubes and sealed by pinch-off clamps. All samples were analyzed on a VG-5400 helium isotope mass spectrometer using methods similar to those described by Bayer et al. (31). Precision of ⁴He concentrations and ³He/⁴He ratio measurements were about ±0.5% and ±0.2%, respectively.

Excess ³He concentrations, [³He]_{exc}, were calculated from the measured ³He/⁴He ratios and ⁴He concentrations using the following formula:

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

where [⁴He]_s is the measured ⁴He concentration, [⁴He]_{eq} is the atmospheric equilibrium concentration of ⁴He (32), R_s is the measured ³He/⁴He ratio, R_a is the atmospheric ³He/⁴He ratio (1.384 × 10⁻⁶) (33), and α (0.983) is the solubility isotope effect (34).

Wind Measurements. An anemometer was placed within the river's channel on top of Hudson River Lights (HRL). From days 5 to 8, it was set up on HRL 161. On day 8, it was moved downstream to HRL 129. Both of these lights were near the midchannel. The anemometer recorded hourly mean wind speeds and prevailing wind direction using 16 compass directions.

Results and Discussion

Background SF₆ Concentrations. Concentrations of SF₆ can be significantly higher than solubility equilibrium with the atmosphere (~0.5 fmol/l) in coastal waters that receive large quantities of wastewater (35). Background SF₆ concentrations in the different reaches of the Hudson estuary vary considerably. While Clark et al. (35) observed SF₆ concentrations as high as 9 pmol L⁻¹ in New York harbor, the tidal Hudson River between Kingston and Poughkeepsie, NY, was not contaminated locally with SF₆ (17). Prior to the 1994 tracer experiment, surveys were completed to determine background SF₆ concentrations between Albany and Catskill, NY. We found that background SF₆ concentrations in this reach of the Hudson were less than our detection limit of 0.01 pmol L⁻¹. Although the Hudson estuary near New York City is locally contaminated with SF₆, the tidal Hudson River between the Federal Dam and the saltwater-freshwater interface appears not to be.

TABLE 1

Gas Tracer Experiment Results

time after injectn (d)	peak [SF ₆] (pmol L ⁻¹)	peak [³ He] _{exc} (10 ⁻¹⁶ mL STP g ⁻¹)	[³ He] _{exc} /[SF ₆]	k ₆₀₀ (cm h ⁻¹)	U ₁₀ (m s ⁻¹)	σ (m)		r ² corr
						raw	corrected	
1.08	20.7							
2.10	10.1							
3.08	5.80					2572	3134 ± 101	0.98
4.10	3.93	2031	519 ± 11			2837	3933 ± 226	0.96
5.21	2.37	940	396 ± 12	5.4 ± 1.0		3956	4212 ± 162	0.98
6.29	1.53	437	285 ± 11	6.7 ± 1.4	2.9	5771	5806 ± 237	0.97
7.28	1.12	251	219 ± 6	5.9 ± 1.5	3.1			
8.20	0.90	166	184 ± 6	4.2 ± 1.5	2.7	6158	6949 ± 606	0.90
9.23	0.71	115	162 ± 2	2.8 ± 1.0	1.3			
10.06	0.59	77	133 ± 4	5.3 ± 1.2	2.4	9905	10527 ± 1060	0.94
11.04	0.43	38	88.4 ± 2.7	9.2 ± 1.4	5.1	14463	12284 ± 325	0.98
12.04	0.33	21	64.7 ± 3.6	6.9 ± 1.9	4.2	12548	13489 ± 450	0.97
13.06	0.26	12	46.9 ± 5.8	7.0 ± 4.0	3.4	11847	12792 ± 770	0.98

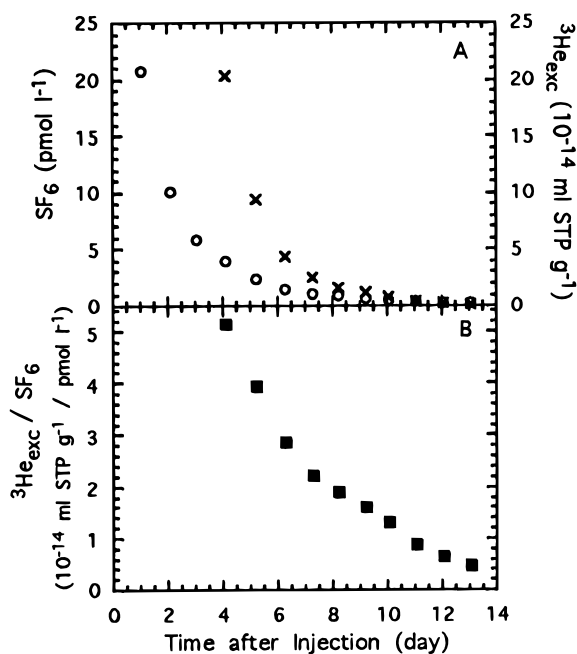


FIGURE 3. Decline in SF₆ (open circles), excess ³He (crosses), and excess ³He/SF₆ ratio (filled squares) at peak stations with time.

Tracer Distributions. One day after injecting the gas tracers, maximum SF₆ concentrations were ~21 pmol L⁻¹ (Table 1). ³He was not measured until the fourth day of the experiment. On that day, maximum excess ³He concentrations were ~2000 × 10⁻¹⁶ mL STP g⁻¹. Daily maximum concentrations of both trace gases decreased exponentially thereafter, reaching, respectively, about 0.3 pmol L⁻¹ and 12 × 10⁻¹⁶ mL STP g⁻¹ after 13 days (Figure 3A). Surface and bottom samples from the same station were indistinguishable, suggesting that the water column was vertically well mixed. Excess ³He/SF₆ ratios also decreased during the experiment (Figure 3B).

The tracer patch grew from the initial injection "line" (0.3–0.5 km wide) to a length of more than 40 km by the end of the experiment. During the first 3 days of the experiment, the patch moved downstream with a net velocity of ~8 km d⁻¹. Thereafter, the net downstream movement was much slower, 2–3 km d⁻¹. The decrease in the movement of the tracer patch probably reflected both the increase in cross-sectional area and a decrease in the daily freshwater discharge rate over the Federal Dam.

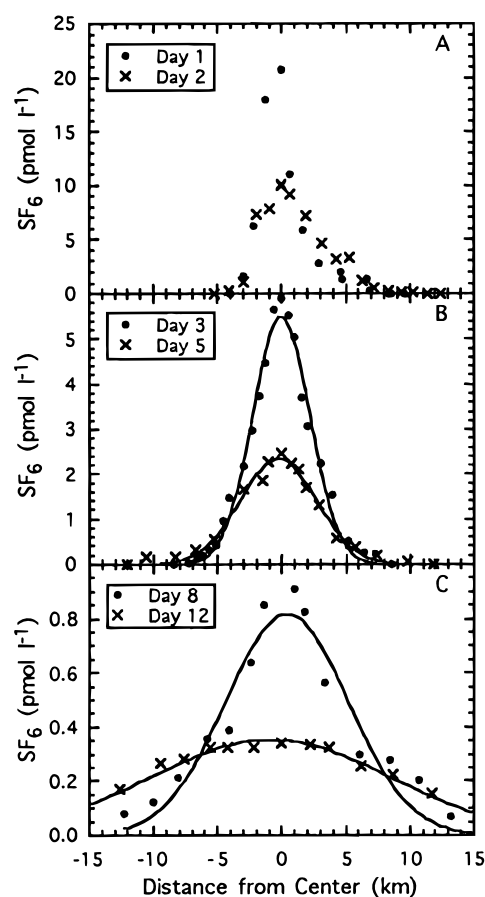


FIGURE 4. Distributions of SF₆ along the main axis of the tidal Hudson River. Solid lines in (B) and (C) are Gaussian fits to the data. SF₆ distributions have been corrected for tidal movement. Distances upstream of the peak are plotted as positive numbers.

During the first two days of the tracer experiment, distributions of SF₆ concentrations along the main axis of the Hudson River were skewed, with steeper rates of decline downstream of the peak (Figure 4A). Distances from background to peak were 1.5–2 times greater upstream of the peak as downstream. Skewed distributions are often found during the initial phase of river experiments (1, 2). The transition between skewed and Gaussian distributions occurred between the second and third day. From day 3 to the end of the experiment, distributions along the main axis were approximately Gaussian (Figure 4B,C). Assuming a transverse mixing coefficient of 0.2 m² s⁻¹ and a length

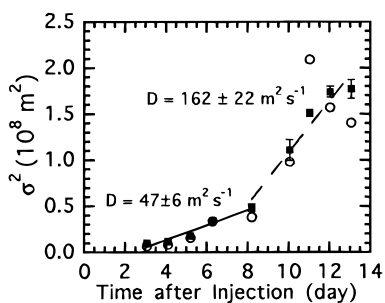


FIGURE 5. Plot of variance determined from the Gaussian fits vs time. The solid and dashed lines are linear fits to the data for the periods between days 3–8 and days 8–13, respectively. Longitudinal dispersion coefficients, D , were calculated from the slopes of these lines. Solid squares are data corrected for tidal movement, and open circles are raw data.

scale of 350 m (the mean width of the river near the injection point), the transition to the Taylor dispersive period (I) should have occurred 1.5–3 days after injection. This is consistent with the field data.

Longitudinal Dispersion Coefficients. The axial distributions of SF_6 were sampled over a period of 2–3 h. Prior to calculating longitudinal dispersion coefficients, distributions were corrected for tidal movement which occurred during sampling in an attempt to provide a synoptic distribution. Tidal velocities, which were $\sim 0.4 \text{ m s}^{-1}$ during peak flow, were estimated from a hydrodynamic model developed by HydroQual, Inc. (36). Standard deviations (σ) of each transect were estimated by fitting a Gaussian curve to the observed data (Table 1, Figure 4). The Gaussian curves approximated the distributions collected after day 2 very well ($R^2 > 0.90$).

Longitudinal dispersion coefficients were calculated from the change in the variance (σ^2) with time (eq 3). Two distinct periods of linear growth of the variance were observed during this experiment (Figure 5). During the initial period, days 3–8, the apparent longitudinal dispersion coefficient was $47 \pm 6 \text{ m}^2 \text{ s}^{-1}$ and during the second period, days 8–13, it increased to $162 \pm 22 \text{ m}^2 \text{ s}^{-1}$. These results are in good agreement with earlier measurements made by Hohman and Parke (7). During a week-long experiment, they estimated the longitudinal dispersion coefficient to be between 20 and $200 \text{ m}^2 \text{ s}^{-1}$ in this reach of the Hudson using 300 lb of Rhodamine B, a fluorescent dye. The change in the dispersion coefficient which occurred at day 8 may reflect a change in the river geometry and increased size of the tracer patch. However, a more systematic investigation of the river hydraulics is needed to confirm our hypothesis.

Gas Transfer Velocities. Gas transfer velocities, k , were calculated using the change in the excess $^3\text{He}/\text{SF}_6$ ratio with time from the peak stations using eq 5. Mean wind speeds were calculated from the hourly data and corrected to a height of 10 m (17). After being normalized to a Schmidt number of 600 (26), k_{600} ranged between 2.8 and 9.2 cm h^{-1} (Table 1) and correlated well with mean wind speed, U_{10} (Figure 6). (k_{600} is equivalent to the gas transfer velocity of CO_2 in freshwater at $\sim 20^\circ \text{C}$.)

Plotted along with the results of this experiment in Figure 6 are the results of a gas tracer experiment which was performed on the tidal Hudson River between Kingston and Newburgh, NY, during the late summer of 1993 (17). The relationships between k_{600} and U_{10} were similar for the two experiments and agree well with relationships found

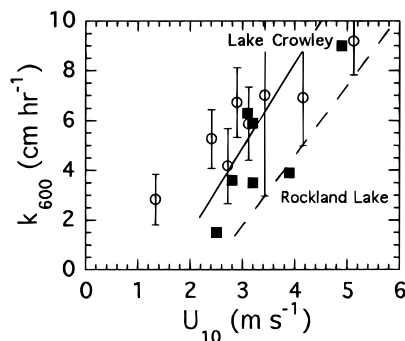


FIGURE 6. Normalized gas transfer velocities, k_{600} , plotted against mean wind speed corrected to a height of 10 m, U_{10} . The open circles and solid squares are the results of this experiment and of Clark et al. (17), respectively. The solid and dashed lines are trends observed in lake studies (22, 23).

in earlier lake experiments (22, 23). These results suggest that gas transfer velocities for the entire tidal Hudson river can be estimated from the mean wind speed using a single parameterization (37). The dominance of wind in generating surface turbulence probably results from the relatively low current velocity and high mean depth of the river channel.

Conclusions

SF_6 was used successfully as a tracer for dispersion in the tidal Hudson River. A practical method of injection has been developed and approximately real-time measurements (within 5 min of collection) can be made from small boats. Hence, the distribution of the tracer patch can be located and sampling strategies can be determined in the field. The main advantages of using SF_6 are that it is less expensive than fluorescent dyes, has a loss term which can be used to quantify gas transfer velocities, and has sufficient sensitivity to permit extended experiments in time and space. The disadvantage of using SF_6 is that discrete samples must be collected. Thus, fine-scale features of the tracer patch are difficult to resolve.

Distributions of SF_6 along the main axis of the river followed a predictable pattern. During the first 2 days of the experiment, distributions were skewed; thereafter, they were approximately Gaussian in shape. The change in variance with time showed two periods of linear growth. During the first period, days 3–8, we estimated a longitudinal dispersion coefficient of $47 \pm 6 \text{ m}^2 \text{ s}^{-1}$; during the second period, days 8–13, it increased to $162 \pm 22 \text{ m}^2 \text{ s}^{-1}$. The 3.5-fold increase may be related to a change in the river's geometry and increased size of the tracer patch.

Daily mean gas transfer velocities were determined by injecting ^3He simultaneously with SF_6 . In the tidal Hudson River, gas transfer velocities were found to correlate with mean wind speed. This relationship is similar to those observed for lakes suggesting that, in the tidal Hudson River, wind is the dominant source of surface turbulence.

A number of technique changes could be made to improve the gas tracer methodology. Continuous underway measurements of surface SF_6 concentrations (every 2–3 min) could be made using an equilibrator (16). Such a system would decrease the sampling time and allow for cross-sectional surveys in addition to axial transects. Similarly, a depth-averaging sampler such as the one that Maiss et al. (20) employed during their tracer experiment would improve the results.

Acknowledgments

We thank S. Chillrud, B. Ekwurzel, and D. Ho for helping with the field work. Special thanks go to T. P. Dernago, Jr., of the United States Coast Guard for granting permission to place anemometers on the Hudson River Lights. A. Ludin and R. Weppernig measured the ^3He samples. The ^3He analyses were made possible by a generous donation by the W. M. Keck foundation. Financial support was provided by the Hudson River Foundation (Grants 011/92A and 009/94P) and by Columbia University Strategic Research Initiative Program. This is contribution no. 5432 from the Lamont-Doherty Earth Observatory of Columbia University.

Literature Cited

- (1) Fischer, H. B.; List, E. J.; Koh, R. C. Y.; Imberger, J.; Brooks, N. H. *Mixing in Inland and Coastal Waters*; Academic Press: New York, 1979.
- (2) Rutherford, J. C. *River Mixing*; Wiley and Sons: New York, 1994.
- (3) Fischer, H. B. *U.S. Geol. Surv. Prof. Pap.* **1968**, No. 582-A.
- (4) O'Connor, D. J. *Int. J. Air Water Pollut.* **1963**, 7, 1073-1084.
- (5) Hetling, L. J.; O'Connell, R. L. *Water Resour. Res.* **1966**, 2, 825-841.
- (6) Pitchard, D. W.; Carpenter, J. H. *Bull. Int. Assoc. Sci. Hydrol.* **1960**, 20, 37-50.
- (7) Hohman, M. S.; Parke, D. B. *Hudson River Ecology*, Hudson River Valley Commission of New York: Albany, NY, 1969; pp 60-81.
- (8) Smart, P. L.; Laidlaw, I. M. S. *Water Resour. Res.* **1977**, 13, 15-33.
- (9) Abidi, S. L. *Water Res.* **1982**, 16, 199-204.
- (10) Wanninkhof, R.; Ledwell, J. R.; Watson, A. J. *J. Geophys. Res.* **1991**, 96, 8733-8740.
- (11) Law, C. S.; Watson, A. J.; Liddicoat, M. I. *Mar. Chem.* **1994**, 48, 57-69.
- (12) Wanninkhof, R. Ph.D. Dissertation, Columbia University, **1986**.
- (13) Wilson, R. D.; Mackay, D. M. *Groundwater* **1993**, 31, 719-724.
- (14) Ledwell, J. R.; Watson, A. J.; Broecker, W. S. *Nature* **1986**, 323, 322-324.
- (15) Watson, A. J.; Upstill-Goddard, R. C.; Liss, P. S. *Nature* **1991**, 349, 145-147.
- (16) Wanninkhof, R.; Asher, W.; Weppernig, R.; Chen, H.; Schlosser, P.; Langdon, C.; Sambrotto, R. *J. Geophys. Res.* **1993**, 98, 20,237-20,248.
- (17) Clark, J. F.; Wanninkhof, R.; Schlosser, P.; Simpson, H. J. *Tellus* **1994**, 46B, 274-285.
- (18) Ledwell, J. R.; Watson, A. J. *J. Geophys. Res.* **1991**, 96, 8695-8718.
- (19) Ledwell, J. R.; Watson, A. J.; Law, C. S. *Nature* **1993**, 364, 701-703.
- (20) Maiss, M.; Ilmberger, J.; Zenger, A.; Münnich, K. O. *Aquat. Sci.* **1994**, 56, 307-328.
- (21) Maiss, M.; Ilmberger, J.; Zenger, A.; Münnich, K. O. *Aquat. Sci.* **1994**, 56, 329-347.
- (22) Wanninkhof, R.; Ledwell, J. R.; Broecker, W. S. *Science* **1985**, 227, 1224-1226.
- (23) Wanninkhof, R.; Ledwell, J. R.; Broecker, W. S.; Hamilton, M. J. *Geophys. Res.* **1987**, 92, 14567-14580.
- (24) Wanninkhof, R.; Mulholland, P. J.; Elwood, J. W. *Water Resour. Res.* **1990**, 26, 1621-1630.
- (25) Cirpka, O.; Reichert, P.; Wanner, O.; Müller, S. R.; Schwarzenbach, R. P. *Environ. Sci. Technol.* **1993**, 23, 2086-2097.
- (26) Jähne, B.; Münnich, K. O.; Börsinger, R.; Dutzi, A.; Huber, W.; Libner, P. *J. Geophys. Res.* **1987**, 92, 1937-1949.
- (27) Wanninkhof, R. *J. Geophys. Res.* **1992**, 97, 7373-7382.
- (28) King, D. E.; Saltzman, E. S. *J. Geophys. Res.* **1995**, 100, 7083-7088.
- (29) Ledwell, J. R. In *Gas Transfer at Water Surfaces*; Brutsaert, W., Jirka, G. H., Eds.; Reidel: Dordrecht, The Netherlands, 1984; pp 293-302.
- (30) Stedfast, D. A. *U.S. Geol. Surv. Water Resour. Invest.* **1980**, No. 80-24.
- (31) Bayer, R.; Schlosser, P.; Bönisch, G.; Rupp, H.; Zaucker, F.; Zimmek, G. *Performance and blank components of a mass spectrometric system for routine measurement of helium isotopes and tritium by ^3He in growth method*; Springer-Verlag: New York, 1989; pp 241-279.
- (32) Weiss, R. *J. Chem. Eng. Data* **1971**, 16, 235-241.
- (33) Clarke, W. B.; Jenkins, W. J.; Top, Z. *Int. J. Appl. Radiat. Isot.* **1976**, 27, 217-225.
- (34) Benson, B. B.; Krause, D., Jr. *J. Solution Chem.* **1980**, 9, 895-909.
- (35) Clark, J. F.; Simpson, H. J.; Bopp, R. F.; Deck, B. L. *J. Environ. Eng. (N.Y.)* **1995**, 121, 760-763.
- (36) Blumberg, A.; St. John, J., personal communication, 1995.
- (37) Clark, J. F.; Schlosser, P.; Simpson, H. J.; Stute, M.; Wanninkhof, R.; Ho, D. T. In *Air-Water Gas Transfer*; Jähne, B., Monahan, E., Eds.; AEON Verlag: Hanau, Germany, 1995; pp 785-800.

Received for review June 29, 1995. Revised manuscript received November 20, 1995. Accepted November 25, 1995.®

ES9504606

® Abstract published in *Advance ACS Abstracts*, February 15, 1996.

1996, Volume 30, Pages 1527–1532

Jordan F. Clark,* Peter Schlosser, Martin Stute, and H. James Simpson: SF₆-³He Tracer Release Experiment: A New Method of Determining Longitudinal Dispersion Coefficients In Large Rivers

The standard deviation and calculated dispersion coefficients were uniformly too large because the axial distributions were fit with a function of the form:

$$f(x) = a \exp\left(-\frac{x^2}{\sigma^2}\right) \quad (1)$$

rather than with the appropriate function:

$$f(x) = a \exp\left(-\frac{x^2}{2\sigma^2}\right) \quad (2)$$

The values of the standard deviation, σ , listed in Table 1 and variances, σ^2 , plotted in Figure 5 should be replaced with the following:

TABLE 1

time after injection (day)	σ raw (m)	σ corrected (m)	r^2 corrected
1.08			
2.10			
3.08	1819	2216 ± 72	0.98
4.10	2005	2781 ± 160	0.96
5.21	2798	2979 ± 114	0.98
6.29	4081	4106 ± 168	0.97
7.28			
8.20	4360	4917 ± 338	0.90
9.23			
10.06	7004	7444 ± 749	0.94
11.04	10227	8686 ± 249	0.98
12.04	8873	9533 ± 319	0.97
13.06	8377	9046 ± 545	0.98

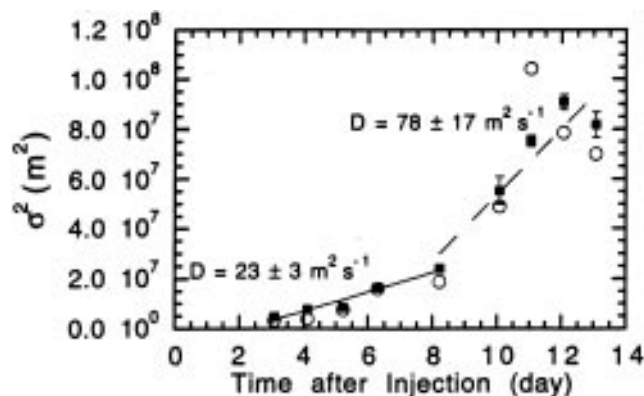


FIGURE 5.

Throughout the abstract and text, the values of the longitudinal dispersion coefficients should be replaced with $23 \pm 3 \text{ m}^2 \text{ s}^{-1}$ and $78 \pm 17 \text{ m}^2 \text{ s}^{-1}$, respectively, for the first (days 3–8) and second (days 8–13) periods.

ES962016O