Comparison of SF_6 and Fluorescein as Tracers for Measuring Transport Processes in a Large Tidal River

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Abstract: We present the first large-scale comparison of a fluorescent dye [fluorescein ($C_{20}H_{10}O_5Na_2$)] and a gas [sulfur hexafluoride (SF_6)] as tracers of advection and longitudinal dispersion from a dual tracer release experiment conducted in the tidal Hudson River. At the beginning of the experiment, 36 kg of fluorescein and ~4.3 mol of SF_6 were injected into the Hudson River at an averaged depth of 9.5 m, ~1 m above the bottom, near Hyde Park, N.Y. After injection, fluorescein distributions were surveyed for 4 days (until it became undetectable) and SF_6 distributions were surveyed for 10 days. The dye resolves initial vertical mixing on the day of injection, and then net advection and longitudinal dispersion, whereas SF_6 provides information on net advection and longitudinal mixing on larger spatial scales and longer time scales. Quantitative estimates of transport processes (net advection and longitudinal dispersion) calculated from the two methods are consistent for the first three days, and start to deviate on the fourth day when the signal-to-noise ratio of the dye deteriorated.

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CE Database subject headings: Advection; Dispersion; Mixing; Tracers; Dyes; Hudson River; Tides.

Introduction

Net advection and longitudinal dispersion play important roles in determining transport and mixing of substances and pollutants discharged into a river. Hence, the ability to predict the strength of these processes based on measured parameters such as river discharge and river geometry is desirable. Calculation of net advection in tidal rivers (or travel time in nontidal rivers) is fairly straightforward, but longitudinal dispersion is difficult to determine a priori. Many investigators have derived semiempirical equations to calculate longitudinal dispersion from measured parameters (e.g., Seo and Cheong 1998; Kashefipour and Falconer 2002), using data derived from field experiments conducted to quantify longitudinal dispersion.

These field experiments are typically conducted with fluorescent dyes, whose concentrations are easily measured at high frequency (1–5 Hz) with a field-portable fluorometer. While dyes are ideal for examining smaller spatial scale (m to km), and short time scale (hours to days) estuarine processes, the inert gas sulfur hexafluoride (SF_6) is more appropriate for use in large spatial scale (tens of km) and longer time scale (weeks) experiments (Clark et al. 1996; Ho et al. 2002). This is because fluorescent dyes have a smaller dynamic range of detection than SF_6, and may suffer from photodegradation. Also, fluorescent dyes are more expensive than SF_6.

In recent experiments, SF_6 has been shown to be a powerful tool for examining mixing, dispersion, and residence time on large scales in rivers and estuaries (Clark et al. 1996; Ho et al. 2002; Caplow et al. 2003, 2004a,b). Also, because SF_6 is a gas, its loss across the air–water interface can be used to quantify the gas transfer velocity, which affects the fate of volatile and semivolatile compounds. However, because the highest measurement frequency yet achieved for SF_6 with a gas chromatograph is lower than that for fluorescent dye with a fluorometer (one measurement per minute versus one per second), SF_6 is not well suited for examining small spatial scale (i.e., meters) and short timescale (i.e., minute to hours) processes.

Here, we present the first comparison of a fluorescent dye [fluorescein ($C_{20}H_{10}O_5Na_2$)] and SF_6 as tracers of advection and longitudinal dispersion from a dual tracer release experiment in the tidal Hudson River. After the tracer injection, fluorescein was surveyed for 4 days (until it became undetectable) and SF_6 was surveyed for 10 days. Fluorescein resolved vertical mixing on the day of injection, both the fluorescein and SF_6 provided information about net advection and longitudinal dispersion on subsequent days. The two tracer methods are compared where the data overlapped.

Study Location

Starting at the Federal Dam in Troy, N.Y., the tidal Hudson River flows south for about 244 km into New York Harbor. In its

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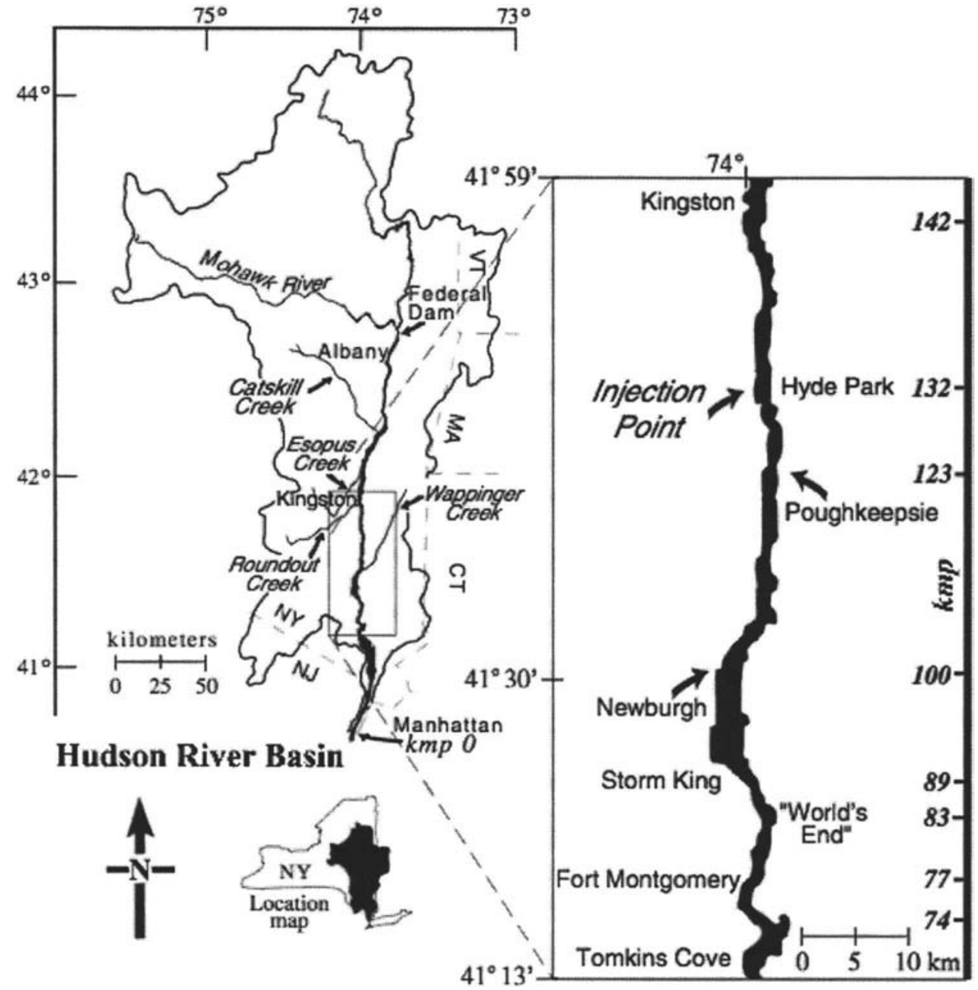

Fig. 1. Map of tidal Hudson River, showing location of tracer release experiment

course, the width of the river varies from ~300 to 5,700 m, while the mean depth varies between ~3 and 43 m. The tracer release experiment was performed between July 21 and August 1, 2003 in a stretch of the river from Tomkins Cove to near Kingston [67–142 kilometer points (kmp); locations along the tidal Hudson River are referred to as axial distance, or kilometer point, from the Battery (0 kmp) at the southern tip of Manhattan]. In this stretch of the river, the mean width ranges from 300 to 2,600 m, and the mean depth varies from 6 to 43 m. Fluorescein and SF_6 were injected into the river south of Esopus Island (132 kmp), near Hyde Park (Fig. 1).

During the experiment, the mean freshwater discharge rate over the Federal Dam was 257 ± 74 $m^3 s^{-1}$, which is higher than the 50-year climatological mean of 189 ± 93 $m^3 s^{-1}$, and surface water temperature along the river varied from about 25 to 29°C.

Experimental Section

Tracer Injection

On July 22, 2003, as the boat traversed the river twice near Hyde Park (132 kmp), 4.3 mol of SF_6 was injected by bubbling the gas through a 7 m length of diffusion tubing. The depth of injection was held at 1 m off the bottom, and monitored by using a pressure transducer. Overall, the injection depth ranged from 7.9 to 10.1 m, and based on subsequent measurements, we estimated that ~1 mol of SF_6 dissolved in the water. At the same time, 36 kg of fluorescein in a 23% water solution, mixed with 2-propanol to achieve in situ density, was injected into the water by pumping the dye through a hose.

SF_6 Measurement

For 10 days after the injection (Days 1 to 10), as the boat traversed the tracer patch, surface water SF_6 was measured by using a continuous SF_6 analysis system, described in detail by Ho et al. (2002). The system consists of a submersible pump, a gas extraction system, and a gas separation and measurement system. SF_6 depth profiles were obtained by attaching a lowered submersible pump to the continuous SF_6 analysis system. The depth of the pump was determined with an attached pressure transducer. The pump was lowered to a predetermined depth (usually about 1 m off the bottom), and SF_6 was analyzed after the extraction system was flushed for a sufficient time. The pump was then raised at predetermined increments and the procedure repeated until the desired tracer profile was obtained.

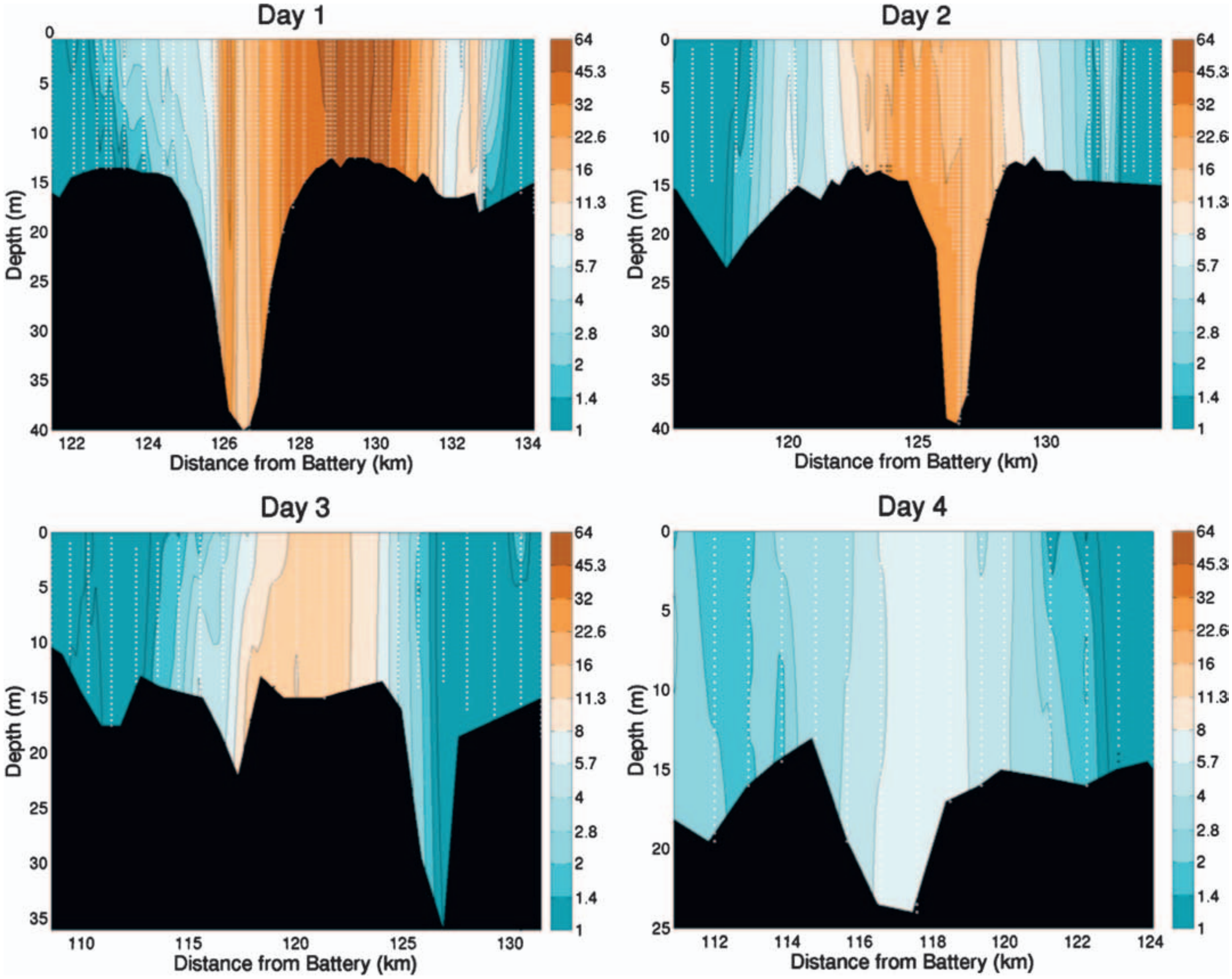

Fig. 2. (Color) Selected vertical profiles of fluorescein distribution for Days 1 to 4. Fluorescein concentration from each station was vertically averaged to yield a mean concentration for each station. These vertically averaged fluorescein distributions are shown in Fig. 3(b). The standard deviations in the mean-depth-averaged concentration are 103, 81, 55, and 41% for Days 1 to 4, respectively, indicating that the dye became vertically well mixed with time.

Fluorescent Dye, Temperature, and Salinity Profile Measurements

For the first five days (Days 0 to 4; day of injection=Day 0) of the experiment (including day of injection), dye profiles were obtained at 217 stations spaced between 0.1 and 3.7 km apart. Three longitudinal dye distributions were obtained on Day 0, two on Day 1, and one on each subsequent day.

For each dye profile, an in situ fluorometer (AQUA^{tracka} III; Chelsea Technologies Group, Surrey, U.K.) attached to a CTD with sampling rate of 4 Hz (Sea-Bird SBE 19*plus* SEACAT Profiler, Sea-Bird Electronics, Inc., Bellevue, Wash.) was lowered through the water column using a winch to obtain profiles of fluorescein concentration, temperature, and salinity. The accuracies for temperature, salinity, and pressure measurements were 0.005°C, 0.005, and 0.35 dbar, respectively. Data were transmitted in real time to a personal computer, where they were stored for postexperiment processing.

ADCP Measurement and Tidal Correction

Tidal velocities during the study period were measured with a 1,200 kHz acoustic Doppler current profiler (ADCP) moored at 129 kmp, near Hyde Park. In addition, data from a 600 kHz ADCP, deployed and maintained by the United States Geological Survey (USGS) at 114 kmp, near Poughkeepsie, N.Y., was used.

Results

In order to obtain a synoptic view of the tracer distribution for each day, the longitudinal tracer distributions were corrected for tidal motion according to the method described in Ho et al. (2002), using the tidal velocities and timing from the two moored ADCPs. Water column fluoroscein concentration from each station (Fig. 2) was averaged to yield one value for each station. The resulting fluorescein and SF_6 distributions are shown in Figs. 3(a

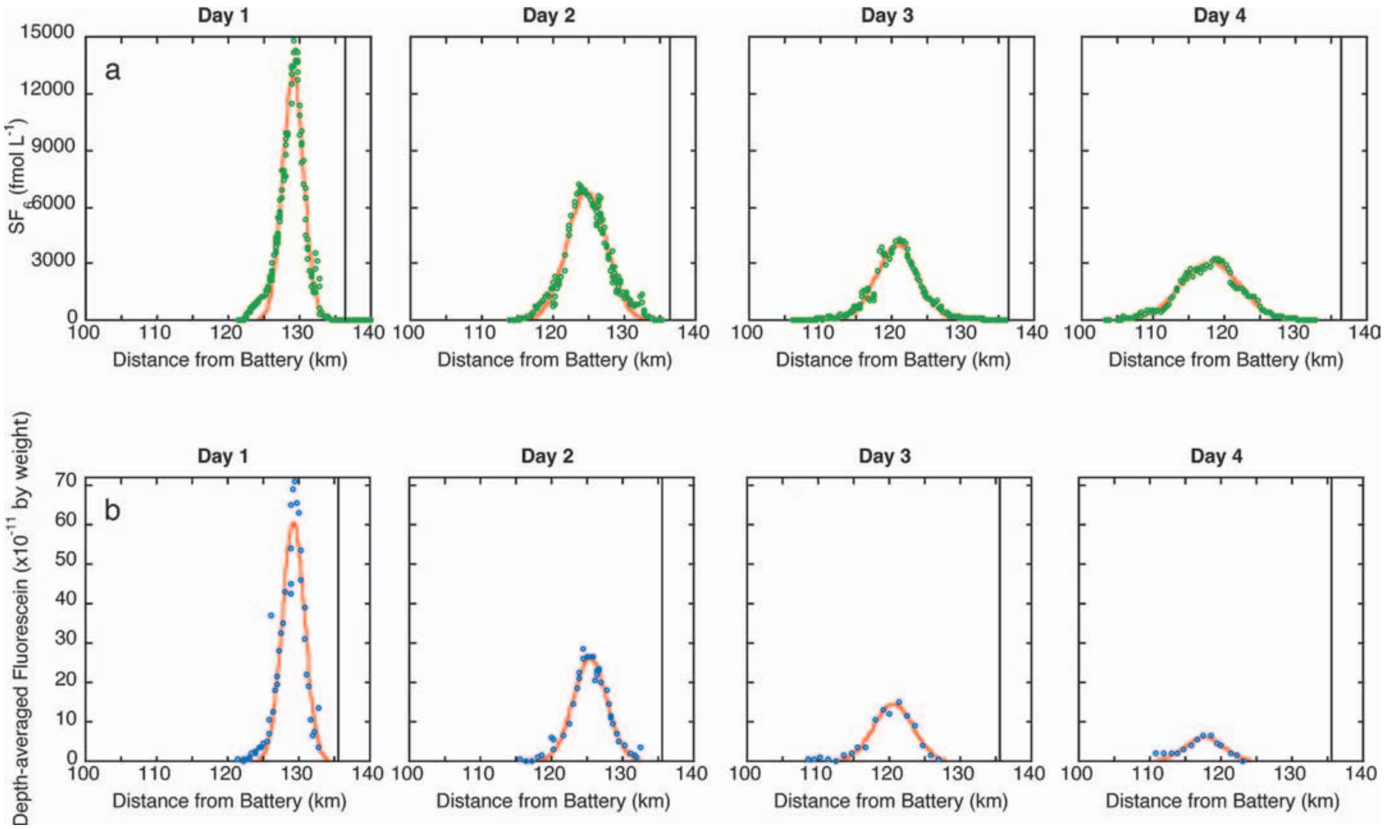

Fig. 3. (Color) Daily distributions of (a) SF_6; (b) fluorescein for Days 1 to 4. Vertical line denotes injection point near Hyde Park. Red lines are Gaussian fits to the measured tracer data.

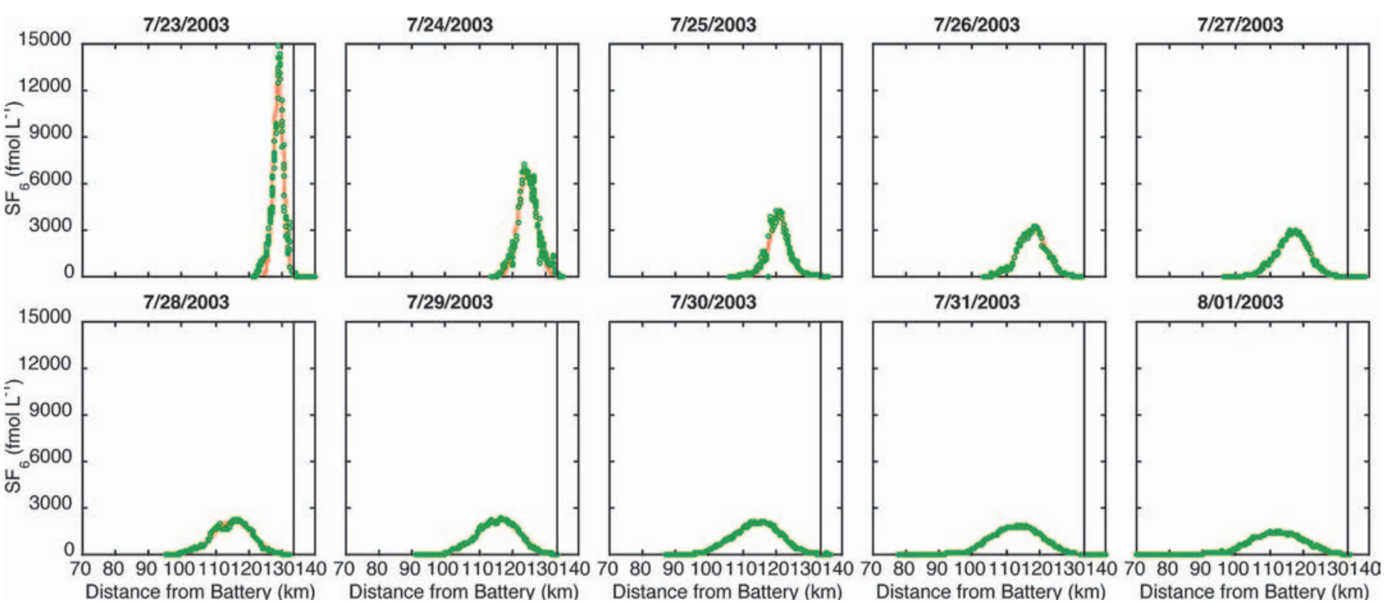

Fig. 4. (Color) Daily distributions of SF_6 in the tidal Hudson River for Days 1 to 10. Vertical line denotes injection point near Hyde Park. Red lines are Gaussian fits to the measured tracer data.

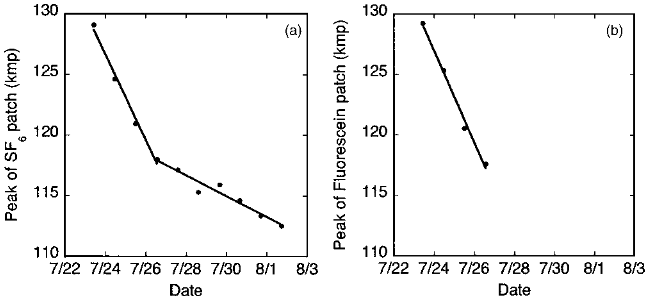

Fig. 5. Tidally corrected net movement of tracer peak concentration as a function of time for (a) SF_6; (b) fluorescein. At Day 4, the net advection decreased due to a combination of increase in river cross-sectional area and decrease in freshwater discharge.

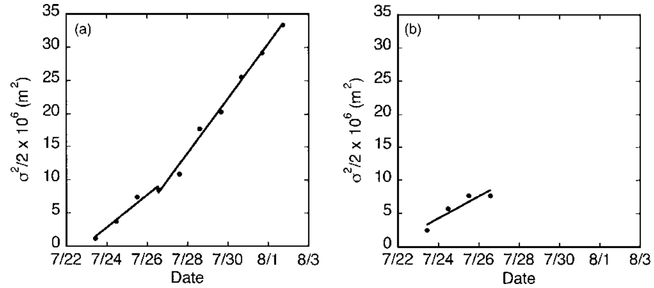

Fig. 6. Second moments of the tracer distributions as a function of time calculated from (a) SF_6; (b) fluorescein distributions. These data are used to estimate the longitudinal distribution.

and b), respectively. On the last day of surveying (Day 10), the SF_6 patch spanned from 142 kmp (near Kingston) to 67 kmp (Tomkins Cove), a stretch of 75 km (Fig. 4).

During the day of injection (Day 0) there was considerable vertical and cross-channel structure in the fluorescein concentration within the patch. By Day 1, the fluorescein was well mixed both vertically and across the channel. The only structure that persisted was a decrease in fluorescein concentration in the top 1 m of the water column due to photodecay. The high turbidity of the river water (with Secchi depths of ~1 m) limited this loss. Survey of the fluorescein was halted on Day 4 when the signal-to noise ratio fell to 4.

Vertical Mixing

The fluorescein distributions measured on Day 0 were used to estimate a lower bound for vertical diffusivity, K_z using the scaling $K_z \propto L^2 t^{-1}$ (Rutherford 1994), where L and t are length and time scales, respectively. Taking $L \sim 15$ m and $t=1$ day yields $K_z = 2.6 \times 10^{-3}$ m^2 s^{-1}. This value is within the range of values derived for the Hudson River by Lung and O'Connor (1984), despite the slight stratification in the water column of $\Delta\rho \sim 0.1-0.2$ kg m^{-3} over 15 m from a weak temperature gradient. The stratification in the upper 2 m of $\Delta\rho \sim 0.2$ kg m^{-3} is due to daily solar heating, and this gradient disappeared during nighttime due to heat loss by radiation.

Because of its lower temporal measurement resolution and high initial concentrations, SF_6 was not measured during Day 0. On subsequent days, SF_6 profiles were taken at selected places. These measurements show that the tracer was well mixed throughout the water column during the experiment.

Net Advection

During the experiment, the tracer patch moved downriver due to freshwater input. After correcting the daily tracer distribution for tidal motion, the net advection can be calculated by examining the movement of the dye and SF_6 distributions with time (Fig. 5). Least-square fit to the SF_6 peak locations indicates that net advection was initially 3.5 ± 0.2 km d^{-1} (Days 1 to 4) but then slowed down to 0.9 ± 0.1 km d^{-1} (Days 5 to 10). Net advection calculated from the dye concentration averaged over the water column indicates that for Days 1 to 4, net advection was 3.8 ± 0.2 km d^{-1}.

Longitudinal Dispersion

From the daily tidally corrected tracer distributions, the longitudinal dispersion coefficients K_x were determined using the change of moment method as follows (Fischer et al. 1979; Rutherford 1994):

$$K_x = \frac{1}{2}\left(\frac{d\sigma_x^2}{dt}\right) \approx \frac{1}{2}\frac{\sigma_x^2(t_2) - \sigma_x^2(t_1)}{t_2 - t_1} \quad (1)$$

where $\sigma_x^2(t_1)$ and $\sigma_x^2(t_2)$=second moments of the tracer distribution at times t_1 and t_2, respectively. σ_x^2 for each day was found by fitting a Gaussian curve to the daily tracer distribution, while minimizing the chi square. K_x was then derived by fitting a linear least-square curve to a plot of $\sigma_x^2/2$ versus time t (Fig. 6).

Longitudinal dispersion K_x calculated from water column averaged Fluoroscein concentration was 19.5 ± 5.6 m^2 s^{-1} (Days 1 to 4), while K_x calculated from SF_6 increased from 28.6 ± 4.1 m^2 s^{-1} (Days 1 to 4) to 48.0 ± 1.9 m^2 s^{-1} (Days 5 to 10).

Discussion

Comparison between Dye and SF_6

SF_6 and fluorescein measurements overlapped on Days 1 to 4. Hence, the two tracers could be directly compared with respect to calculation of longitudinal dispersion coefficients. Over this period, K_x determined from SF_6 was about 47% higher than from fluorescein (28.6 ± 4.1 versus 19.5 ± 5.6 m^2 s^{-1}). However, K_x calculated from fluorescein for Days 1 to 3 was 28.8 ± 4.0 m^2 s^{-1}, which is similar to that derived from SF_6. K_x for SF_6 and fluorescein diverge on Day 4 (Fig. 6). These results are similar to those reported by Clark et al. (1996), 23 ± 3 m^2 s^{-1}, from the same stretch of the river. Given the similarity from Days 1 to 3, the difference observed on Day 4 is most likely due to K_x being underestimated from the dye, because the signal-to-noise ratio of the dye had dropped to 4 (10% of the dye is at concentrations below detection). Furthermore, the difference is exacerbated by the fact that the K_x increases on Day 4, due to a change in the river geometry. The relationship between longitudinal dispersion coefficient and river geometry in the tidal Hudson River is beyond the scope of this contribution, and will be discussed elsewhere.

This comparison shows that fluorescent dyes have the advantage over SF_6 in being able to examine short timescale (hours), and small spatial scale processes (meters). This advantage is a feature of the measurement equipment (i.e., higher sampling frequency of the fluorometer versus the gas chromatograph) and not of the tracers themselves. On the time scale of a couple of days, dye is comparable to SF_6, but it cannot resolve processes on long timescales and large spatial scales. By Day 4, the fluorescein had degraded to the point that it no longer appeared to yield accurate information, and after Day 4, it was no longer useful at all. By comparison, at the end of the experiment (Day 10), the SF_6 signal was still robust (signal-to-noise ratio of 1,500). Furthermore, because SF_6 is a gas, it could be used to measure gas transfer velocities, either by closing the tracer mass balance or by using it in conjunction with ^{3}He (e.g., Clark et al. 1994).

Based on the longitudinal dispersion coefficient and the signal-to-noise ratio necessary for accurate measurements, if an experiment were to be conducted with fluorescein for the same length of time, $\sim$5,700 kg of fluorescein would be necessary, costing \$150,000 (U.S. dollars) in 2004 for the dye. The material cost of the $\sim$0.6 kg of SF_6 used for this experiment was $\sim$\$20.

Conclusions

The dual tracer release experiment conducted in the tidal Hudson River with SF_6 and fluorescein has shown that the two techniques yield consistent results over small spatial and short temporal scales, with respect to measurements of net advection and longitudinal dispersion. At the same time, the experiment has shown that with SF_6, longer timescale and larger spatial scale experiments are possible, at a much lower cost (the equipment cost for the two methods is similar; $\sim$\$20,000). In addition to the utility of SF_6 as a tracer for net advection and longitudinal dispersion in large rivers, SF_6 has also been shown to be an effective tracer for examining flushing from bays and estuaries (Caplow et al. 2004a,b).

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