

## The use of photolytic rhodamines WT and sulpho G as conservative tracers of dispersion in surface waters

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### Abstract

We describe the use of sulpho rhodamine G (SG) and rhodamine WT (WT) as oceanographic tracers in tidally active waters of the southeastern North Sea. Ten kilograms of SG and 5 kg of WT dissolved in 1,000 liters of sea water were released to produce an initial tracer patch  $\sim 10 \times \sim 0.5$  km. Tracer dispersal was monitored for 11 d by high-performance liquid chromatography analysis of samples collected close to the patch center. The patch center was initially identified during surveys for sulfur hexafluoride released simultaneously, and its position was subsequently confirmed by use of a two-dimensional tracer dispersion model. Temporal changes in the SG/WT ratio were undetectable, so photolytic tracer losses were not directly quantified. A simple photolysis model was used to correct to conservative behavior for WT. Results are compared with the dispersal of spores of *Bacillus globigii* var. *niger* released simultaneously. Photolytic tracer pairs are ideally suited to tracer experiments in unconstrained water masses.

Large-scale experiments involving deliberate tracer releases are becoming increasingly important in limnology and oceanography. Sulfur hexafluoride ( $\text{SF}_6$ ) has been used in lakes (Wanninkhof et al. 1985; Upstill-Goddard et al. 1990),

in rivers (Clark et al. 1994), in coastal seas (Watson et al. 1991), and in the open ocean (Ledwell and Watson 1991; Ledwell et al. 1993, 1998) to calculate mixing rates and kinetic transport terms. More recently,  $\text{SF}_6$  has been deployed during deliberate in situ iron enrichment experiments in the Pacific Ocean (Coale et al. 1996) and during passive Lagrangian experiments on the Florida Shelf (Wanninkhof et al. 1997) and in the Atlantic Ocean (Law et al. 2001).

In surface waters  $\text{SF}_6$  is nonconservative, because it vents to the atmosphere. Consequently, it is of value in quantifying air-sea gas exchange in unconstrained water masses, if used in combination with a conservative tracer that facilitates correction for  $\text{SF}_6$  advection and dispersion. The unavailability of such a conservative tracer initially led Watson et al. (1991) to develop the so-called dual volatile tracer technique for gas exchange measurements. In this, two inert volatile tracers with a large diffusivity contrast ( $\text{SF}_6$  and  $^3\text{He}$ ) are released to seawater and their concentrations monitored with time as they decrease, by advection-dispersion and air-sea gas exchange. An inherent problem with this approach however, is that it corrects for advective and dispersive gas losses by use of an assumed gas diffusivity relationship that cannot be independently validated within the constraints imposed by the technique (Frost and Upstill-Goddard 1999). Bacterial spores have been used to monitor tidal dispersion nearshore (Pike et al. 1969), and their potential for dispersion correc-

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tions in open water gas exchange experiments has been recently demonstrated (Nightingale et al. 2000). Unfortunately, because the analytical precision of spore determinations is considerably poorer than that for SF<sub>6</sub> analysis, data quality tends to be compromised. Rhodamine B is a widely available and cheap tracer that has been used in studies of tidal mixing (Talbot and Talbot 1974), but its affinity for suspended particles renders it impractical as a truly conservative tracer in surface waters (Talbot and Henry 1968; Wilson 1968; Smart and Laidlaw 1977). Rhodamine WT (WT) and sulpho rhodamine G (SG) are superior candidates for such work because of their low octanol/water partition coefficients (Benoit-Guyod et al. 1979). Rhodamine WT has been successfully used in a lake (Suijlen and Buyse 1994), and WT and SG have been codeployed in the North Sea (Suijlen 1995).

As part of the 1996 Air-Sea Gas Exchange Marine Aerosol and Gas Exchange (ASGAMAGE) project, a European Union-funded investigation of the geophysical controls of air sea gas exchange, we used WT and SG considered as conservative tracers during an experiment to determine air-sea gas transfer velocities in tidally active North Sea waters adjacent to the Dutch coast. They were used with high precision to correct for the tidal dispersion of volatile tracers released simultaneously. Because WT and SG are both degraded by sunlight (Abood et al. 1969; Suijlen 1995), their photolytic losses were compensated for by use of a novel method first described by Suijlen and Buyse (1994). This is based on measuring the concentration ratio of the two rhodamines by improved high-performance liquid chromatography (HPLC) at the high dilution encountered. We describe here the preparation and release of 1,000 liters of seawater augmented with relatively modest amounts of the two rhodamines. We also give details of tracer dispersion and a photolytic loss correction for WT and compare the performance of photolysis corrected WT relative to inert spores of the bacterium *Bacillus globigii* var. *niger* (BG) released simultaneously.

The techniques described in this article are generic and are suitable for various applications under a wide range of environmental conditions. For ASGAMAGE, our particular interest was the precise quantification of advection and dispersion in order to determine rates of air-sea gas exchange accurately. Details of gas transfer velocities derived by use of combinations of these conservative and volatile (SF<sub>6</sub> and <sup>3</sup>He) tracer pairs will be discussed elsewhere.

## Materials and methods

*Tracer preparation*—During our initial tests, SG was found to be only sparingly soluble in seawater, and it had a tendency to settle out of solution. Therefore, solutions of SG were initially prepared in CH<sub>3</sub>OH and needed to be continuously and vigorously stirred, conflicting with the need to preserve the SF<sub>6</sub>:<sup>3</sup>He ratio during deployment by minimizing their potential for outgassing (Watson et al. 1991). Additional concerns were the possible affinity of WT and SG for BG at high concentrations and the potential effects on BG viability of the high CH<sub>3</sub>OH concentrations required during SG preparation.

WT and SG were therefore prepared separately from the other tracers. Preparation was onboard RRS *Challenger* prior to leaving port, to preclude accidental gross contamination of the selected tracer release site. In a 1,000-liter steel tank, 25 kg of WT (20% w/v solution), 10 kg of SG powder, 60 kg of CH<sub>3</sub>OH, and 100 kg of ambient seawater (Portsmouth Harbour, UK) were stirred for 1 h by use of a high-capacity borehole drainage pump (Junge Pumps). The tank was then filled to capacity with more seawater with further continuous stirring, and the tank was sealed. Preparation of the other tracers followed previously published protocols (Upstill-Goddard et al. 1991; Nightingale et al. 2000). Subsequently, the ship's afterdeck, the tank exteriors, and all tracer preparation materials were thoroughly flushed with more seawater to remove residual amounts of the tracers. The rhodamine mixture continued to be stirred en route to the release site and throughout its subsequent deployment.

*Tracer release*—The selected release site was in tidally well-mixed North Sea waters of relatively shallow and uniform bathymetry (20 ± 1 m), ~20 km off the Dutch Coast near Ijmuiden (i.e., at 52°16'N, 004°02'E–52°20'N, 004°05'E). This site is in a region used previously by us for the release of SF<sub>6</sub> and <sup>3</sup>He (Upstill-Goddard et al. 1991; Watson et al. 1991) and SF<sub>6</sub>, <sup>3</sup>He, and BG (Nightingale et al. 2000). Prior to tracer release, a series of vertical casts along the release axis by use of a combined conductivity temperature depth (CTD) probe and rosette water sampler ensured that the water column was well mixed, which simplifies the subsequent interpretation of tracer distributions (Watson et al. 1991). This procedure also established ambient tracer backgrounds and provided a further check on possible tracer contamination from *Challenger*.

Tracer release was initiated at the end of high water slacks and continued for 5.5 h during the cycle to low water slacks, on 18 October 1996. The mean tidal velocity was ~0.5 m s<sup>-1</sup> to the north-northeast. *Challenger* held station along the tidal axis with her stern down tide, and the tracers were deployed over the stern by displacement with seawater pumped into header tanks. This procedure prevented excessive internal tank pressures, which might have occurred with direct connection to the incoming seawater supply. For the volatile tracers, this also minimized the possibility of air contact, which would otherwise have modified their release ratio and complicated subsequent data interpretation (Watson et al. 1991). Deployment was through 10-cm subsurface hoses buoyed at 10 m depth. In-line flow meters were used to maintain a constant ratio between the tracer displacement rates from the two tanks, and the flow rates were increased stepwise with time to compensate for continual dilution of the tank contents. Using

$$C_t = C_i e^{-\lambda t}, \quad (1)$$

where  $C_t$  and  $C_i$  are, respectively, the tracer concentrations in the tank at time  $t$  and time zero and  $\lambda$  (s<sup>-1</sup>) is the ratio of tank flow rate to tank volume, >90% of the individual total tracer masses were released during the 5.5-h deployment. We anticipated that, after the release of SG, tidal stirring would be sufficiently vigorous to maintain it in suspension. The tracer-tagged water streamed away with the tide in

a northeasterly direction, producing a line release roughly the dimensions of the tidal ellipse,  $\sim 10 \times \sim 0.5$  km—that is, covering an area  $\sim 4$  km<sup>2</sup>. Three drogued surface-drifting buoys were deployed at equal intervals along the tracer axis and subsequently tracked by use of the Argos satellite network and with direction finding (DF) receivers. *Challenger* then left the release site for an area  $\sim 35$  km to the northwest, where the tanks, afterdeck, and all ancillary equipment used in the release were thoroughly cleaned by use of the seawater fire hoses. With these precautions, tracer measurements in the patch were possible within several hours of the release, and residual contamination from the ship was insignificant.

**Rhodamine sampling and analysis**—The approximate position of the tracer patch was initially determined by use of DF or Argos satellite updates and its center located by use of a system for continuous underway SF<sub>6</sub> analysis (Upstill-Goddard et al. 1991; Law et al. 1998). Water samples were collected at the patch center, from near surface, middepth and near bottom, by use of the CTD rosette. Because WT and SG are both susceptible to photolytic decomposition, seawater aliquots were decanted into 0.5-liter opaque glass bottles and stored in light-proof boxes for subsequent rhodamine analysis postcruise. When stored in this way, samples have been shown to remain stable for several months (Suijlen and Buyse 1994). All analyses were completed within 3 months of collection.

For rhodamine analysis, we used a slightly modified version of the procedure described by Suijlen et al. (1994). Full details of the modified method are given elsewhere (Den Das et al. 1997). In brief, 100 ml of sample, standard, or blank was buffered to pH 4.8 with 0.04 M CH<sub>3</sub>COONa and pre-concentrated by on-line solid-phase extraction by use of  $5 \times 100$  mm C<sub>18</sub> “Novapak” (4  $\mu$ m packing) or  $5 \times 50$  mm C<sub>18</sub> “Symmetry” (3.5  $\mu$ m packing) cartridges (Waters Chromatography). During initial tests, cartridge performance was identical within the resolution of the measurements. Subsequent separation was by gradient HPLC using pentane sulfonic acid and tetrabutyl ammonium phosphate (both  $5 \times 10^{-3}$  M), followed by fluorescence detection with 545 nm excitation and 575 nm emission. The monochromator settings are a compromise that facilitates the simultaneous detection of SG and WT. The technique was optimized for a relatively fast throughput rate of 4 samples h<sup>-1</sup> while maintaining acceptable detection limits of 45 pg L<sup>-1</sup> WT and 80 pg L<sup>-1</sup> SG (for a signal:noise ratio of 2). Distilled water blank values never exceeded these thresholds. Although such detection limits were fully acceptable for our current purpose, much lower thresholds are routinely possible in other applications of this technique (Suijlen et al. 1994).

## Tracer theory

**Tracer dispersion model**—Dispersion of an aqueous tracer is initially in three dimensions. Because of the shallow and tidally active nature of the ASGAMAGE release site, we anticipated that WT and SG would be vertically homogenized within a few hours and that two-dimensional dispersion would subsequently apply. We have previously observed that tracers are uniformly mixed through the water

column at this study site within a few hours after tracer release (Nightingale et al. 2000). Following the reasoning of Okubo (1974) and van Dam (1982), for an instantaneous release the rate of decline in maximal tracer concentration at the patch center,  $C_{max}$  can be closely approximated by a power function of the form

$$C_{max}(t) = [M/h]C_o t^{-b}, \quad (2)$$

where  $M$  is the mass of tracer released (kg),  $h$  is the depth of the well-mixed water column (m), and  $t$  is the time from release (s). For numerous earlier rhodamine release experiments in the southern North Sea, the data are adequately described by  $b = 2$  and  $C_o = 600$  s<sup>2</sup> m<sup>-2</sup>, for  $t$  in the range  $10^2$ – $5 \times 10^5$  s (Van Dam et al. 1999). In a situation where the release is not instantaneous from a point source, as in the case of ASGAMAGE, a correction is required for  $t$ . Where  $A$  is the horizontal area enclosed by the isoline of concentration  $C$ , the concentration distribution  $C(A,t)$  is expressed as

$$C(A,t) = [M/h][C_o t^{-b}] \exp\{-A[C_o t^{-b}]\}. \quad (3)$$

Hence, the fraction of the tracer mass enclosed by an area  $n/[C_o t^{-b}]$  is equal to  $1 - e^{-n}$ . For  $n = 2$  and  $n = 3$ , the enclosed tracer masses are, respectively,  $\sim 87\%$  and  $\sim 95\%$  of the total tracer mass. The appropriate time shift,  $\Delta t$ , is given by

$$\Delta t = [C_o A_o/n]^{1/b}, \quad (4)$$

where  $A_o$  is the observed horizontal area at  $t = 0$ .

**Photolysis model**—By use of a first-order photolysis model (Suijlen and Buyse 1994), the tracer concentration in a vertically homogeneous water column with no dilution,  $C(H_\mu)$ , is given by

$$C[H_\mu(t)] = C(0)\exp[-k H_\mu(t)], \quad (5)$$

with

$$H_\mu(t) = \int_0^t \mu(\vartheta) E_{tot}(\vartheta) d\vartheta, \quad (6)$$

where  $\mu$  is the time dependent dimensionless underwater light parameter,  $k$  is the photolysis coefficient (m<sup>-2</sup> J<sup>-1</sup>),  $E_{tot}$  is the time dependent daily irradiance (J m<sup>-2</sup> d<sup>-1</sup>) at the sea surface over the 300–2,000 nm wavelength interval, and  $H_\mu(t)$  is the ambient under water irradiation (J m<sup>-2</sup>). Following from Eq. 5, the photolysis correction factor  $f_{ph}(t)$  of any photolytic tracer  $x$  is given by

$$f_{ph}(t) = \exp[k_x H_\mu(t)], \quad (7)$$

where  $f_{ph}(t)$  is always greater than unity. In the case of two photolytic tracers  $x$  and  $y$  with similar excitation spectra, the value of  $\mu$  will be about the same for both. Hence, the unknown parameter  $H_\mu(t)$  can be determined from

$$H_\mu(t) = [\ln R(t)/R(0)]/(k_x - k_y) \quad (8)$$

(Suijlen and Buyse 1994), where  $R(t) = C_y(t)/C_x(t)$  is the ratio of the two tracer concentrations. Because  $H_\mu(t)$  can be determined from this ratio, the correction factor  $f_{ph}(t)$  can be computed from Eq. 7. However, in situations where the total daily irradiance is low and/or where the experimental dura-

Table 1. Concentrations of rhodamines SG and WT ( $\text{ng L}^{-1}$ ) and BG (individuals  $\text{L}^{-1}$ ) determined during ASGAMAGE, 18–30 October 1996. All values are averages over the depth of the water column; Sta. 1 and 3 are ambient backgrounds prior to tracer release;  $\sigma_t$  is density;  $R(t)$  is the concentration ratio of SG to WT; numbers in parentheses are standard errors;  $n$  ( $\sigma_t$ ) is the number of individual density calculations;  $n$  (SG, WT) is the number of individual rhodamine analyses; and  $n$  (BG) is the number of individual *Bacillus globigii* analyses.

Sta.	Time from release (h)	$\sigma_t$	$n$ ( $\sigma_t$ )	SG	WT	$R(t)$	$n$ (SG, WT)	BG	$n$ (BG)
1	Background	25.155 (0.000)	14	0.61 (0.140)	0.00		7		
3	Background	25.119 (0.002)	16	0.00	0.00		5		
4	21.2	25.296 (0.001)	17	2.55 (0.286)	1.07 (0.102)	2.38 (0.092)	7	573 (30)	30
5	23.5	25.316 (0.001)	15	3.45 (0.200)	1.16 (0.053)	2.97 (0.082)	10	436 (15)	30
6	37.3	25.128 (0.002)	16	16.53 (0.392)	7.37 (0.273)	2.24 (0.028)	4		
7	41.9	25.134 (0.000)	16	6.98 (0.234)	3.01 (0.119)	2.32 (0.036)	8	298 (12)	29
11	68.6	25.170 (0.001)	15	6.06 (0.208)	2.67 (0.091)	2.27 (0.051)	6	303 (12)	30
12	83.4	25.410 (0.001)	11	2.53 (0.067)	1.14 (0.018)	2.21 (0.038)	6	171 (6)	30
13	85.7	25.357 (0.002)	13	1.66 (0.085)	0.77 (0.049)	2.16 (0.027)	4	73 (9)	9
14	95.1	24.895 (0.036)	13	2.10 (0.123)	0.97 (0.057)	2.16 (0.044)	11	151 (25)	10
15	105.2	25.072 (0.009)	13	1.42 (0.063)	0.61 (0.016)	2.33 (0.082)	12	52 (3)	10
16	115.4	25.208 (0.002)	12	1.92 (0.056)	0.87 (0.026)	2.21 (0.091)	11	78 (6)	10
17	131.2	25.094 (0.018)	12	0.86 (0.056)	0.36 (0.025)	2.40 (0.130)	8	59 (6)	10
18	141.6	24.926 (0.018)	12	1.09 (0.025)	0.46 (0.007)	2.38 (0.072)	6	45 (4)	10
19	151.1	25.083 (0.005)	15	1.02 (0.011)	0.43 (0.013)	2.37 (0.072)	6	47 (2)	10
27	159.1	24.798 (0.039)	13	0.79 (0.049)	0.36 (0.024)	2.20 (0.099)	5	31 (3)	10
31	163.1	24.916 (0.001)	13	0.82 (0.015)	0.39 (0.010)	2.09 (0.029)	5	37 (2)	9
32	177.7	24.569 (0.000)	11	0.75 (0.031)	0.31 (0.012)	2.42 (0.033)	3		
34	186.0	24.471 (0.001)	12	1.18 (0.129)	0.42 (0.021)	2.81 (0.217)	3	25 (2)	10
36	277.1	25.784 (0.001)	16	0.48 (0.068)	0.123 (0.015)	3.94 (0.329)	3	20 (2)	10
37	278.8	25.790 (0.000)	15	0.47 (0.002)	0.147 (0.003)	3.20 (0.075)	3	19 (2)	10

tion is comparatively short, conditions that are both fulfilled during ASGAMAGE, significant changes in  $R(t)$  can become difficult to detect, with the result that  $R(t)/R(0)$  or  $f_{\text{ph}}(t)$  tend toward unity. In this case, tracer photolysis can be estimated from vertical profiles of the downward irradiance attenuation coefficient  $K_d$ . The relationship between  $\mu$  and  $K_d$  is

$$\mu = 0.8[1 - \exp(-K_d h)] / (K_d h) \quad (9)$$

(Suijlen and Buyse 1994). Because vertical light attenuation is wavelength dependent, the available  $K_d$  values are averages over the wavelength range 400–700 nm, whereas the wavelength range relevant to WT and SG photolysis is 525–575 nm (Suijlen et al. 1994). However, by use of data from Jerlov (1976) for coastal waters, it can be shown that

$$K_{d,525-575\text{nm}} = 0.6 \pm 0.05 K_{d,400-700\text{nm}} \quad (10)$$

Although the above approach can be applied to time-varying parameters, we have used an approximation based on mean values for  $K_d$  and  $\mu$ , with the assumption of a constant daily irradiance, because the relevant observations are unavailable for ASGAMAGE. The associated errors are, however, negligible, because for tracer experiments of short duration in this region and season, changes in daily irradiance are small enough that the assumption of a constant daily mean irradiance  $E_{\text{tot}}$  suffices. In this simplified case, the photolysis correction factor  $f_x(t)$  for the tracer  $x$  is given by

$$f_x(t) \approx \exp(k_{x,525-575} E_{\text{tot}} t), \quad (11)$$

where  $\mu_{525-575}$  is the underwater light-climate parameter for the wavelength range 525–575 nm. Extending this treatment,

the change in the ratio of the two tracer concentrations,  $R(t)$ , is described by

$$R(t) \approx R(0) \exp[(k_y - k_x) \mu_{525-575} E_{\text{tot}} t]. \quad (12)$$

With the condition that the power of the exponential function is smaller than 0.2,  $R(t)$  can be approximated by

$$R(t) \approx R(0) \{ [1 - (k_y - k_x) \mu_{525-575} E_{\text{tot}} t] \}. \quad (13)$$

If  $k_y > k_x$ , as in the case of SG relative to WT,  $R(t)$  will be a decreasing function of time.

Equations 7 and 8 contain all the information theoretically required for a photolysis correction under any ambient light intensity or degree of water stratification, and Eqs. 9–13 only apply in situations where accurate estimates of extremely low photolysis rates are required. Hence, the methods described here are universal, yielding solutions under all environmental conditions.

## Results

Table 1 shows depth averaged concentrations of SG and WT and mean SG/WT weight ratios,  $R(t)$ , during ASGAMAGE as a function of time, with time measured from the midpoint of the 5.5-h release. The original data can be found in Den Das et al. (1997). In two depth casts collected along the release axis several hours prior to tracer deployment (Sta. 1 and 3), WT was undetectable in all samples. In contrast, although SG was undetectable at Sta. 3, Sta. 1 returned a mean SG concentration of  $0.61 \text{ ng L}^{-1}$  (Table 1). One possibility is the existence of an unidentified fluorescent source

in the water column with the same method response characteristics as SG. If present, such a source must have a somewhat restricted small-scale distribution. Our tracer release was in a region influenced by strong Rhine outflow (Upstill-Goddard et al. 2000). However, in a previous rhodamine release in this area, the measured SG backgrounds in samples for which the estimated Rhine outflow contributions were  $\sim 10\%$  were all  $< 0.02 \text{ ng L}^{-1}$  (Suijlen 1995). Our estimate for the maximum Rhine outflow contribution during ASGAMAGE is also  $\sim 10\%$  (Upstill-Goddard et al. 2000), so the observed background signal is not likely to have arisen from this source. We also exclude the possibility of contamination during SG analysis, because we randomized all samples prior to analysis and detected no systematic change in analytical concentrations with time (Den Das et al. 1997). Our favored explanation is residual SG contamination during initial sample handling. Because SG is supplied as a fine powder and is difficult to force into solution, it presents much greater handling difficulties than WT. A particular problem is the far greater risk of personal contamination, and one of us (J.S.) has previously experienced such difficulties while handling rhodamine B powder.

After tracer deployment, on most sampling occasions SG and WT both were homogeneously distributed with depth. The mean relative standard errors in concentration for all stations were SG, 5.0% and WT, 4.7% (Table 1). However, rhodamine concentrations at Sta. 4 and 36 were vertically inhomogeneous, as evidenced by their comparatively large standard errors. Neither of these stations had a significant vertical density structure; however, the mean density at Sta. 36 was comparatively high (Table 1). These data may reflect movement of the ship relative to the water during sampling, as a consequence of the strong tides prevailing in this area, particularly during the early phase of the experiment, when the tracer patch was rather narrow. At Sta. 4,  $^3\text{He}$ ,  $\text{SF}_6$ , and BG were all distributed similarly to WT and SG. If these stations are excluded, the mean relative standard errors reduce to SG, 4.1% and WT 3.9%, about a factor of 1.5 better than those in our previous work (Suijlen and Buyse 1994; Suijlen et al. 1994). The mean relative standard error in  $R(t)$  was 2.8% on the basis of all stations but is not reduced by the exclusion of Sta. 4 and 36 (Table 1). Thus, the precision of the ratio measurements was better than that of the individual concentration measurements. Because each ratio is effectively that of two peaks in a single chromatogram, the effects both of small-scale inhomogeneities in the water column and of possible movement within the patch during vertical sampling are therefore eliminated.

All measured values of  $R(t)$  exceeded the theoretical SG/WT mass ratio of 2 (Table 1), which is based on the notional tracer masses initially added to the tank. Because significant settling out of SG from suspension should give rise to initial values of  $R(t) < 2$ , our assertion regarding effective tidally driven suspension of SG seems justified. Significant WT losses during tracer preparation need not be invoked, because, in most cases, the observed value of  $R(t)$  can be explained by analytical uncertainty. Nevertheless, at Sta. 5 and 34–37,  $R(t)$  is significantly higher than the theoretical initial value and cannot be easily explained in this way. Neither can the discrepancy be ascribed to photolysis, because the rate

constants for this process are several orders of magnitude too slow to account for the implied WT losses (Suijlen and Buyse 1994). Although Sta. 32 and 34 were of relatively low density, consistent with significant mixing of this part of the patch with Rhine outflow waters, a significant SG background from this source has already been discounted. Moreover, Sta. 5, 36, and 37 have the highest values of  $R(t)$  but also some of the highest densities, which implies that they are less strongly influenced by continental outflow than some other stations. Toward the end of ASGAMAGE, weather conditions significantly worsened, with mean 10-m wind speeds ( $U_{10}$ ) steadily increasing from  $\sim 5\text{--}6 \text{ m s}^{-1}$  prior to Sta. 34 to values  $> 17 \text{ m s}^{-1}$  prior to Sta. 36 and 37. It is conceivable that the high levels of suspended sediment that we observed during this period could have contributed to the high  $R(t)$  values for these samples. Partition coefficients for WT and SG reported by Benoit-Guyod et al. (1979) imply that WT has an  $\sim 25\%$  greater affinity than SG for suspended particles. If so, such a correction for WT scavenging by particles would reduce the  $R(t)$  values for these stations to levels more consistent with the other measurements.

## Discussion

*Tracer dispersion*—At the periphery of a typical tracer patch, tracer concentration ratios can be modified by edge diffusion effects and suffer reduced precision due to dilution, thereby compromising their value. In view of this, it is important to establish that sample collection was in or close to the region of maximal tracer concentrations at the patch center. By making the reasonable assumption that the dispersion was comparable to the mean results of earlier tracer-release experiments in this region (van Dam et al. 1999), the validity of the observations (Table 1) can be established. Figure 1 shows mean WT concentrations as a function of time by use of data from Table 1. The fitted line in Fig. 1A is a prediction based on the dispersion model, for  $b = 2$  and  $C_0 = 600 \text{ s}^2 \text{ m}^{-2}$ , as in other tracer releases over timescales  $\sim 10\text{--}500 \text{ h}$  (van Dam et al. 1999). With  $A_0 = 4 \pm 1 \text{ km}^2$  and with  $n = 2$ , corresponding to  $\sim 87\%$  recovery of the tracer mass,  $\Delta t$  is  $\sim 8 \pm 1.5 \text{ h}$  and is relatively insensitive to the choice of  $A_0$  within the range  $1.5\text{--}6 \text{ km}^2$ . In Fig. 1B, these data have been replotted by use of the calculated time shift. Figure 2 is a similar plot for BG, based on our initial BG release and time shifted in the same way. The BG data less strongly conform to their predicted line than do the WT data, reflecting their comparatively poor analytical precision. Nevertheless, the behavior of both tracers allows us to conclude that the majority of the sampled stations, with the notable exception of Sta. 4 and 5, are representative of the tracer patch center. In order for Sta. 4 and 5 to satisfy the linear fits, their WT and BG concentrations would need to be several times higher than those observed. On the basis of this evidence, it therefore seems likely that Sta. 4 and 5 were from the patch periphery.

*Photolysis*—Figure 3 shows that there was no significant temporal trend in  $R(t)$  during ASGAMAGE. The solid line is a linear regression on the data, from which Sta. 5 and 34–37, discussed earlier, are excluded. The value of  $K_{d,400\text{--}700\text{nm}}$

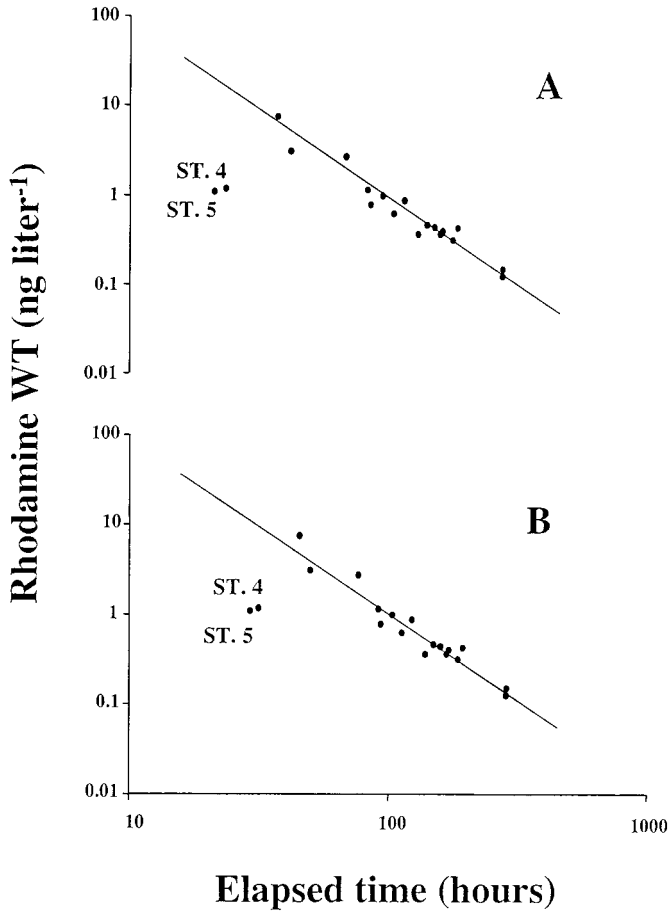


Fig. 1. (A) Temporal trend in mean rhodamine WT concentrations ( $\text{ng liter}^{-1}$ ) plotted by use of data from Table 1. (B) A replot of the data from (A), time shifted by 8 h according to the results of the tracer dispersion model. The fitted line in both plots is the predicted rate of decline in maximal tracer concentration at the patch center,  $C_{\text{max}}$ , for  $b = 2$  and  $C_o = 600 \text{ s}^2 \text{ m}^{-2}$ .

measured over the course of ASGAMAGE was  $0.48 \pm 0.15$ , corresponding to  $\mu_{525-575} = 0.15 \pm 0.05$  for a mean water depth of 20 m. By use of  $k_{\text{WT}} = 3.5 \text{ m}^2 \text{ GJ}^{-1}$  (Suijlen and Buyse 1994),  $k_{\text{SG}}/k_{\text{WT}} = 3.2$  (Suijlen 1995) and  $E = 5.9 \text{ MJ m}^{-2} \text{ d}^{-1}$ , as determined from contemporary measurements at a Dutch coastal station  $\sim 60 \text{ km}$  northeast of the tracer release site (Den Das et al. 1997):

$$R(t)/R(0) = \exp(0.00681t) \approx [(1 - 0.00681)t], \quad (14)$$

where  $t$  in this instance is in days. This relationship, shown by the dotted line in Fig. 3, predicts a decrease in  $R(t) \sim 5\%$  after 8 d, which is not detectable within the precision of the measurements. On the basis of the same assumptions, the photolysis correction factor for WT is

$$f_{\text{ph}}(t) = \exp(0.0031t). \quad (15)$$

Table 2 shows values of  $f_{\text{ph}}(t)$  for WT for  $\mu_{525-575} = 0.15$  and  $\mu_{525-575} = 0.2$  and resultant photolysis corrected WT concentrations derived from Eq. 7. For  $\mu_{525-575} = 0.15$ , computed daily photolytic WT mass losses were  $\sim 0.2\% - 0.4\%$ , and the cumulative loss over the 11.5-d duration of the measure-

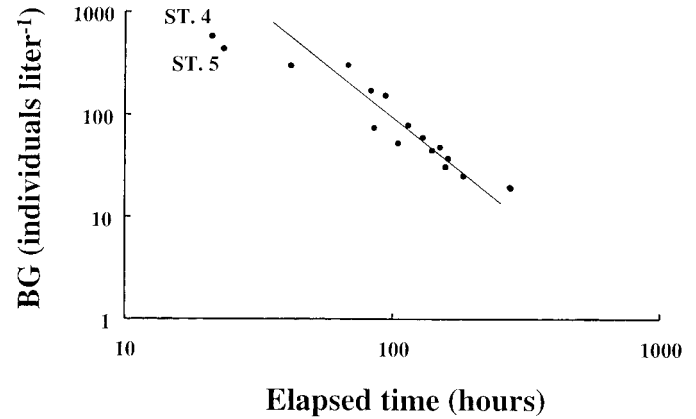


Fig. 2. Temporal trend in mean BG concentrations ( $\text{individuals L}^{-1}$ ) plotted by use of data from Table 1 and time shifted by 8 h according to the results of the tracer dispersion model. The fitted line is the predicted rate of decline in maximal tracer concentration at the patch center,  $C_{\text{max}}$ , for  $b = 2$  and  $C_o = 600 \text{ s}^2 \text{ m}^{-2}$ .

ments was  $\sim 3.7\%$ . Even for  $\mu_{525-575} = 0.2$ , which seems unrealistically high, this figure only increases to  $\sim 5\%$  (Table 2). Hence, within the experimental uncertainties, WT can therefore be treated as a conservative tracer for the conditions experienced during ASGAMAGE.

It is instructive to examine the conditions under which the WT-SG tracer combination would be of value in determining a reliable value for  $\mu_{525-575}$ , and hence for  $K_{d,525-575}$ , in coastal waters. Under the assumption that a decrease in  $R(t) \sim 10\%$  would be detectable in the data, the corresponding minimum value for the sea surface irradiation,  $H_{\text{min}}$ , is given by

$$H_{\text{min}} \geq 0.1/[\mu_{525-575}(k_{\text{SG}} - k_{\text{WT}})]. \quad (16)$$

For  $\mu = 0.15$ , this gives  $H_{\text{min}} \geq 85 \text{ MJ m}^{-2}$ . Because the total irradiation received during the 11.5-d duration of the

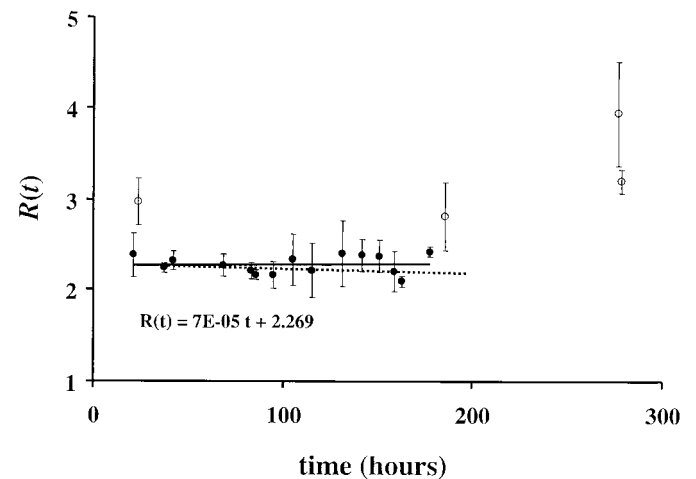


Fig. 3. Time-dependent behavior of  $R(t)$  during ASGAMAGE. Open symbols refer to Sta. 5 and 34–37; closed symbols refer to all other stations. Error bars are the standard errors listed in Table 1. The solid line is a linear regression on the closed symbols. The dotted line is the predicted decrease in  $R(t)$ , as determined from Eq. 14.

Table 2. Measured and predicted concentrations of rhodamine WT (ng L<sup>-1</sup>) during ASGAMAGE, 18–30 October 1996; predictions based on photolysis correction factors,  $f_{ph}(t)$ , derived from Eq. 7 for  $\mu_{525-575} = 0.15$  and  $\mu_{525-575} = 0.2$ ;  $k_{WT} = 3.5 \text{ m}^2 \text{ GJ}^{-1}$ ;  $E = 5.9 \text{ MJ m}^{-2} \text{ d}^{-1}$ .

Hours from release	WT observed	$f_{ph}(t)$ ( $\mu_{525-575} = 0.15$ )	WT predicted ( $\mu_{525-575} = 0.15$ )	$f_{ph}(t)$ ( $\mu_{525-575} = 0.2$ )	WT predicted ( $\mu_{525-575} = 0.2$ )
21.2	1.07	1.003	1.07	1.004	1.07
23.5	1.16	1.003	1.16	1.005	1.17
37.3	7.37	1.005	7.41	1.008	7.43
41.9	3.01	1.005	3.03	1.009	3.04
68.6	2.67	1.009	2.69	1.015	2.71
83.4	1.14	1.011	1.15	0.018	1.16
85.7	0.77	1.011	0.78	1.018	0.78
95.1	0.97	1.013	0.98	1.020	0.99
105.2	0.61	1.014	0.62	1.022	0.62
115.4	0.87	1.015	0.88	1.025	0.89
131.2	0.36	1.017	0.37	1.028	0.37
141.6	0.46	1.019	0.47	1.030	0.47
151.1	0.43	1.020	0.44	1.032	0.44
159.1	0.36	1.021	0.37	1.034	0.37
163.1	0.39	1.022	0.40	1.035	0.40
177.7	0.31	1.024	0.32	1.038	0.32
186.0	0.42	1.025	0.43	1.040	0.44
277.1	0.123	1.037	0.128	1.060	0.130
278.8	0.147	1.037	0.152	1.060	0.156

experiment was only  $\sim 68 \text{ MJ m}^{-2}$ , determination of a reliable value for  $\mu$  was not possible during ASGAMAGE and would have required both a longer experimental timescale and improved measurement precision for the two tracers.

Figure 4 shows the relationship between photolysis-corrected WT ( $\mu_{525-575} = 0.15$ ) and the number concentration of

BG. The solid line is a best fit to the data, excluding Sta. 4 and 5. Notwithstanding these stations, the remarkable constancy of the spores/WT relationship in Fig. 4 is extremely gratifying because it shows the two tracers to be mutually supportive and vindicates our decision to use separate tracer tanks for their preparation and release.

### Conclusions

With the application of small photolytic loss corrections, rhodamines WT and SG can be used to derive a conservative tracer (WT) for aqueous transport studies. By deploying relatively modest amounts of these tracers in air-sea gas exchange work, complications due to advective and dispersive effects in tidally active coastal waters can be routinely accounted for on a timescale of  $\sim 2$  weeks. Such information is difficult to obtain directly by use of alternative conventional methods such as drifting buoys.

With recent advances in HPLC analysis, detection limits  $\sim 0.2\text{--}1 \text{ pg L}^{-1}$  can now be routinely achieved for fluorescent tracers (Van Soest et al. 1996). Hence, the major constraint on future experimental sensitivity lies in the availability of tracers for which the potential for contamination during handling is minimized. We foresee the need for a new generation of such fluorescent tracers that span a range of photolysis coefficients—that is, with characteristic  $k$ 's  $\sim 30\text{--}100 \text{ m}^2 \text{ GJ}^{-1}$ . Such tracers would facilitate long-term experiments and would be ideally suited to the determination of underwater light parameters under ambient light conditions similar to those experienced during ASGAMAGE. With future improvements such as these, we predict that techniques of the type outlined here will find increasing application in aquatic science.

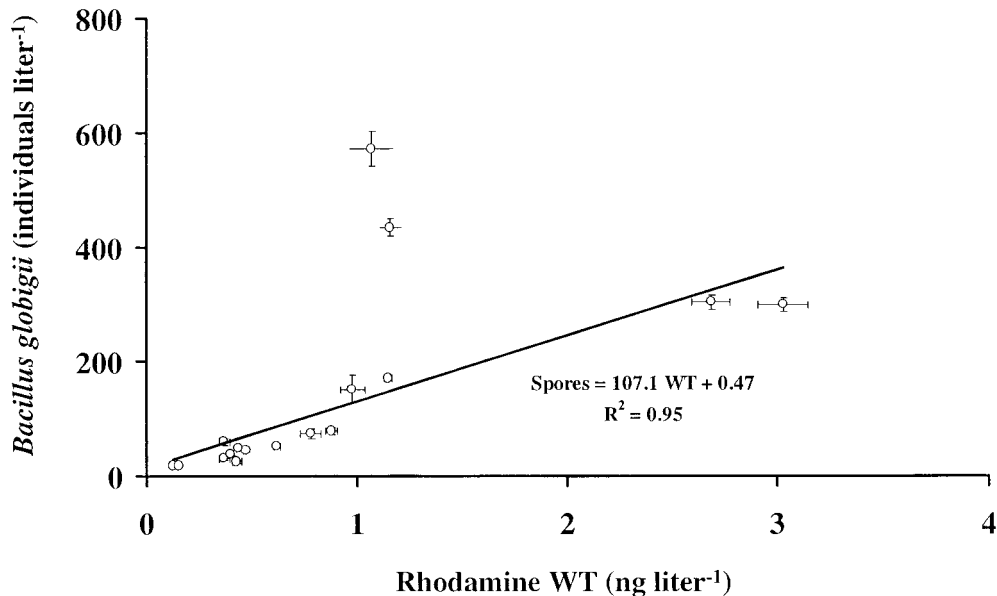


Fig. 4. The relationship between mean WT concentrations corrected for photolysis losses ( $\mu_{525-575} = 0.15$ ) and the mean number concentration of BG for each station. The solid line is a best fit to the data, excluding Sta. 4 and 5. Error bars are the standard errors listed in Table 1.

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