Massachusetts Water Resources Authority
Effluent Outfall Dilution:
April 2001

Massachusetts Water Resources Authority

Environmental Quality Department
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MASSACHUSETTS WATER RESOURCES AUTHORITY EFFLUENT OUTFALL DILUTION: APRIL 2001

Submitted to

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EXECUTIVE SUMMARY

The Massachusetts Water Resources Authority (MWRA) is responsible for the operation and monitoring of the new sewage effluent outfall from the Deer Island Wastewater Treatment Plant, which began discharging into Massachusetts Bay on September 6, 2000. The outfall is regulated under a National Pollutant Discharge Elimination System (NPDES) permit issued by the U.S. Environmental Protection Agency (EPA) and the Massachusetts Department of Environmental Protection (EPA/MADEP 1999) with an effective date of August 19, 2000. Part I, Section 18.e of the permit requires that MWRA "field test and certify whether the outfall's minimum dilution is equal to, or greater than, the predicted minimum dilution" specified in a hydraulic study published in 1993 (Roberts and Snyder (1993a,b). MWRA addressed this permit condition in the summer of 2001. The primary objectives of the Plume Tracking Program are to 1) determine the initial dilution characteristics of the outfall and 2) to track the longer-term location and mixing dynamics of the outfall plume. The evaluation of effluent plume dilution characteristics and transport was conducted using Rhodamine WT dye as a tracer during April and July of 2001. The April study is the subject of this report.

The April 2001 plume tracking study was conducted under typical treatment plant flows. The flows during the period rhodamine dye was added to the effluent decreased from 470 to 320 mgd early morning then increased to ~410 mgd as dye addition was being completed. Flow remained steady over the period the dye exited the diffuser system in Massachusetts Bay (~11 AM through 5PM). The plant achieved a high quality effluent as secondary treatment resulted in total suspended solids averaging 13 mg/L. Representative metals concentrations were measured at low levels (Cu < 10 µg/l and Ag < 0.56 µg/L). Nutrient levels during the addition were also constant and typical for this time of year (ammonia ~1020 µM, phosphate ~24 µM). Bacterial indictors in the effluent varied in abundance over the dye addition but were within the range expected at the sampling point in the west disinfection basin.

Offshore, the dyed effluent exited from the diffusers into a water column that was slightly stratified with a weak pycnocline at about five meters depth. The water column in Massachusetts Bay was being transported to the north at about 6 cm/s during the period dye was exiting the diffuser. The northerly set continued through the next day as the dyed effluent was found north and west of the diffuser line. The current velocities were stronger in the upper water column decreasing from ~20 cm/s in the upper 10 meters to 1-5 cm/s at below 20 meters depth.

Near-surface shears that were strong on April 19 did not have a strong influence on the conditions at the depth of the dye during the plume tracking. The survey was conducted near neap tide conditions, which resulted a minimal amount of energy for vertical mixing, thus there was lower than average mixing energy during the study. The vertical stratification observed during the study is also related to large vertical shears, both mean and fluctuating, which may have contributed to more horizontal spreading of the patch than might have been encountered under during vertically well-mixed conditions.

The current direction and velocities provided a good condition for comparing the initial dilution measurements against a dilution scenario modeled during the design of the diffuser (i.e., currents perpendicular to the diffuser). Although a typical non-stratified winter condition was not present during the study, the weak stratification provided sufficient conditions against which the model predictions could be performed and compared the engineering study results.

The effluent dilutions measured based on the initial dye concentration in the effluent (59.7 ppb Rhodamine) and in the receiving waters (0 to ~0.8 ppb) found initial mixing of the effluent was completed very close to the diffuser line. The lowest dilution measured during the survey was ~56 measured within 20 meters of a riser. Intensive high-resolution *in situ* measurement of dye concentrations

near the diffuser line generally found the effluent dilution was at least 85 fold by the time the effluent was ~50 m from the risers. Measured dilution increased from 85 to ~110 as the effluent was transported ~300 m from the diffusers.

The plume dilution measured in Massachusetts Bay was compared to dilution results derived from the RSB model using current velocities and direction observed during the plume tracking and under scenarios with all 440 diffuser ports open and the present configuration of 275 ports open. The model closely simulated the plume rise height and wastefield thickness. Modeled dilution overestimated measured dilution by less than 20% (109 modeled using 275 open diffuser ports versus 88 to 95 measured within 100 m of the diffusers). Although the field conditions were not identical to those of the original model studies, the results from the modeling were generally consistent with expected results. Some of the difference is likely related to differences in shapes in the density profiles used in the original modeling and relative to those from this field study. Overall, the results of this RSB model run and field results compared well with the physical model studies on which the diffuser design was based.

A more sophisticated three-dimensional laser-induced florescence (3DLIF) measurement approach for determining dilution was also run at Georgia Institute of Technology. This physical simulation was completed under conditions that closely match those actually observed during the field experiment. The dilution results compared very closely to the field observations (101 versus 88-95). The 3DLIF results also provided more insight into the mixing processes and show that plumes from the individual ports on each riser merge quickly forming a riser plume that then merges with those from the neighboring risers. This merging begins about 17 m downstream from the risers. After merging, transverse internal mixing erases lateral concentration gradients. The wastefield under the conditions evaluated during the survey becomes laterally homogeneous about 26 m from the risers. The 3DLIF model results indicate that field sampling within less than ~26 m from the risers, would probably result in widely fluctuating results that would be difficult to interpret. Beyond this distance, however, wastefield characteristics do not vary rapidly so field sampling positioning for confirming the initial mixing is not as critical.

The initial dilution resulted in acceptable water quality characteristics within the plume as measured from discrete samples collected from within the dye field after initial dilution is complete. Copper concentrations after initial mixing were slightly higher (~25%) than background levels obtained approximately 1,000 meters south of the diffuser system. Bacterial indictors were near or below the detection limits of the methods. The metals and bacterial indicators were well below applicable water quality standards. In contrast, nutrient measurements of the diluted effluent found relatively high levels of ammonia and phosphate. The levels were consistent with dilution of the concentrations measured in the effluent upon entry to the discharge tunnel on Deer Island.

The discrete sample data were also used to estimate the dilution achieved in the samples. Only ammonia showed reasonably good agreement with the dye results and suggests ammonia can provide an excellent short-term measure (minutes to a few hours) of the dilution near the diffuser. However, because it is biologically active and not conserved over longer time scales, it is less effective as a long-term measure of dilution in the bays. The other discrete parameters either over or underestimated the dilution relative to the dye, possibly due to any of three factors: 1) inappropriate assumed background concentrations due to neglecting mixing of dyed effluent into previous plume, 2) loss or of a gain of a chemical through non-conservative processes, and 3) poor precision on the data that was obtained. The data from the survey are inadequate to differentiate any of the three possible causes, although the data make it clear that additional samples are required on future surveys if the first two causes are to be addressed.

One additional observation from the discrete samples is an apparent increase in total suspended solids in the plume relative to increases expected based on the dilution and concentration in the effluent. The data from the discrete samples suggest an increase of about ~0.3 mg/L versus an estimated increase of 0.11

mg/L, if the TSS was conservative. Results from the *in situ* tracking also demonstrate an increase in the concentrations of the particle field near the diffuser as measured with a transmissometer. The correspondence converged with background beam attenuation values at dilutions of about 300 to 400 and did not show evidence of particle settling relative to the dispersion of the dye, either during the HMZ surveys nor 24 hours after the dyed effluent entered the offshore environment. Thus, particles within the precision of these measurements appear to be behaving conservatively after discharge. Further studies are required to better understand this potential loss of effluent-derived particles from the water column on the time scales of the plume dilutions studied

Conclusions

Both the field and modeling results show the outfall is performing as expected. Measured dilutions and other wastefield characteristics are consistent with results from the original physical model studies and the RSB mathematical model, reanalysis with the RSB model using data specific to this plume tracking study, and a new physical model study. Dilution of ~85 was observed in the field data within ~50 meters of the diffuser line which slowly increased to ~105 three hundred meters from the diffusers. Oceanographic mixing and dispersion further increased the dilution after the dye had exited the outfall system. Dilutions of 200 to 400 were measured 24 hours following discharge.

It is concluded that the outfall is behaving as expected and that acceptable water quality is being achieved at the outfall. Ammonia appears to be an excellent short-term tracer of the effluent and may serve as a check on initial dilution in the future.

Particle settling on time scales of 24 hours is not apparent in the data, thus rapid loss of particles to the seafloor is not occurring.

The survey met its goals of validating the data collection methods while obtaining quality information on the dilution characteristics of the plume. The modifications recommended in Mansfield *et al*. (2001a) will substantially improve the certification survey in July 2001. These include improved logistics for sampling at Deer Island and the sensor package on the tow-yo unit. The offshore component of the survey resulted in several recommended changes to the sampling protocols. These recommended changes were confirmed through the additional data synthesis included in this report. These logistical issues, recommendations, and confirmations include.

1) Defining the HMZ proved difficult in the field. It was recommended that a series of rapid tow-yos extending perpendicular to the diffuser array be conducted to better define the direction of plume transport. This would include some measurements very close to the risers to find high dye concentrations and high variability. This would help define the point at which hydraulic mixing gives way to oceanic dispersion effects, although the new modeling information presented in this report suggests the spatial scales and variability near the diffusers will be so short that collection of useful data near the diffuser will prove problematic. Also recommended in the survey report was an effort to hold the sensor unit at selected depths for least 1-2 minutes to define stable dye levels. Instability in the dye concentrations at a given point over time was considered as indicative of hydrodynamic mixing. The modeling reaffirms this expectation. Moreover, the field team recommended that more discrete samples be collected to provide a greater range of concentrations, allowing for better verification of the *in situ* data from the discrete values. The data from the laboratories confirms that added discrete samples would increase the ability to extrapolate the discrete results against the dye data.
2) Background operations completed before dye began to emerge from risers provided substantial insight about dye transit times and dispersion from the diffuser array. It is recommended that more time be spent conducting pre-dye *in situ* measurements prior to the emergence of the dye.

3) The six-hour 59 µg/L dye addition produced an easily-defined plume field on both the nearfield and farfield days. The summer survey plan calls for a dye addition of 28 hours at 50 µg/L. The April dye study clearly identified that this long-term addition could result in an "old" dye plume confounding the ability to track the initial dilution associated with the "new" plume field where an HMZ is being conducted. The results from the winter survey presented in this report reaffirm that recommendation by showing the diluted plume is easily monitored within a few hundred meters of the diffuser line, thus six-hour addition will be sufficient to reliably track the effluent plume. The farfield data from this survey suggests also that the plume could be tracked for at least 3 days in Massachusetts with a 50 ppb dye concentration in the effluent. Higher concentrations would enable longer tracking.

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1.0 INTRODUCTION

The Massachusetts Water Resources Authority (MWRA) is responsible for the operation and monitoring of the sewage effluent outfall (Figure 1-1) from the Deer Island Wastewater Treatment Plant (DITP), which began discharging into Massachusetts Bay on September 6, 2000. The outfall is regulated under a National Pollutant Discharge Elimination System (NPDES) permit MA0103284 issued by the U.S. Environmental Protection Agency (EPA) and the Massachusetts Department of Environmental Protection (EPA/MADEP 1999) with an effective date of August 19, 2000. Part I, Section 18.e of the permit requires that MWRA "field test and certify whether the outfall's minimum dilution is equal to, or greater than, the predicted minimum dilution" specified in a hydraulic study published in 1993 (Roberts and Snyder (1993a,b). Thus, the primary objective of the Plume Tracking Program is to determine the initial dilution characteristics of the outfall. The effluent plume dilution characteristics and transport assessment study was scheduled to be evaluated using Rhodamine WT dye as a tracer during winter (unstratified) and summer (stratified) conditions. The summer survey was specifically designed to address the permit condition. The winter survey was designed to ensure the approach to the plume tracking would result in effective data collection methods and obtain initial information on the dilution characteristics as described in the *Combined Work/Quality Assurance Project Plan for Plume Tracking: 2001* (Bruce *et al*. 2000). The winter study is the subject of this report.

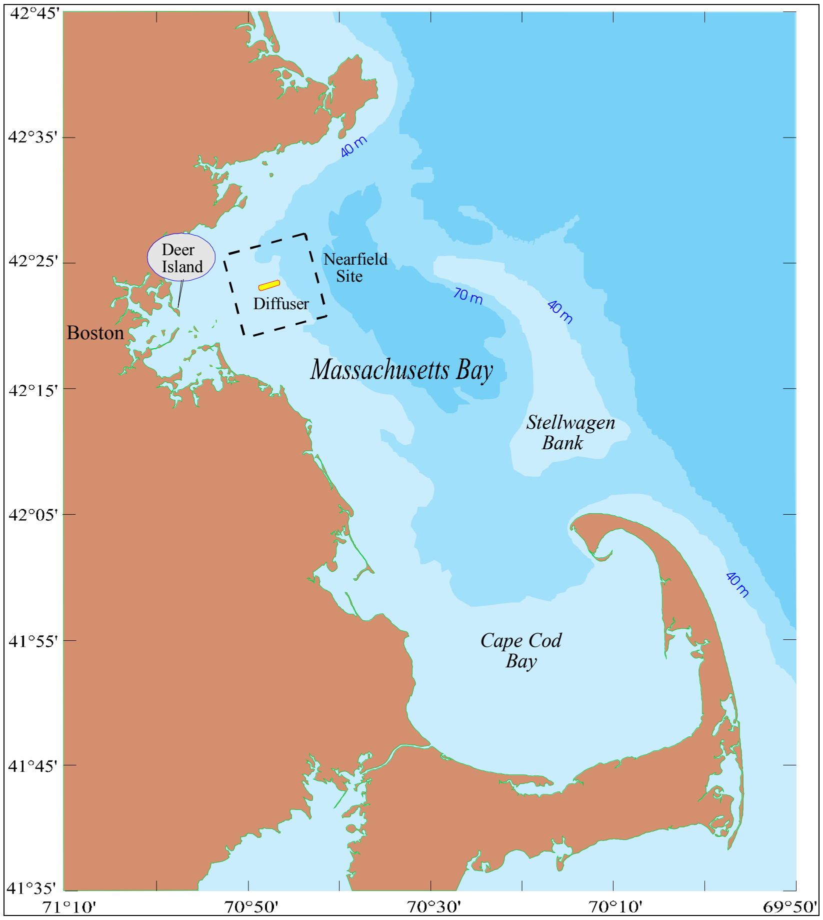

Figure 1-1. Location of the MWRA effluent outfall in Massachusetts Bay.

The winter plume tracking survey was designed to provide information on the effluent plume characteristics under unstratified conditions but its primary purpose was to test and evaluate field methods and explore plume-tracking options for the summer 2001 NPDES certification survey. All aspects of the technical approach, including methods and equipment employed, data quality objectives, and quality assurance activities were developed in the planning process and are described in the (Bruce *et al.* 2000) and are further elaborated in a survey plan prepared for the survey (Battelle 2001a).

The Winter Plume Tracking survey WP011 was conducted at Deer Island Treatment Plant (DITP) and Massachusetts Bay on April 19 and 20, 2001, (Mansfield *et al*., 2001a). Rhodamine WT dye was added at the MWRA Deer Island Treatment Plant (DITP) and the effluent plume dilution characteristics and transport traced offshore over these two days. Data collected during the plume tracking exercise were used to determine the location of the effluent discharge plume as it exited the diffuser and mixed with ambient waters. The dilution performance of the outfall was evaluated and compared with results of the RSB model (Roberts and Snyder 1993a,b).

Several laboratory studies associated with the plume–tracking surveys were conducted 2001. These studies primarily addressed the stability of Rhodamine WT in chlorinated effluent and in seawater, simulating conditions occurring during the full cycle of survey activities beginning with dye addition at the DITP and ending with the last dye tracking exercise 2-days later in Massachusetts Bay. The planning and design for the laboratory studies are described in a separate work plan (Battelle 2001b) and further described in separate reports that are included in Appendix A to this report.

This report is organized into five major sections. Section 1 introduces the report and establishes the purpose and goals of the study. Section 2 summarizes the methods used during the plume tracking including the special studies conducted to validate temperature calibration of the rhodamine and the evaluation of potential degraded by environmental factors, the dye addition at Deer Island, and field activities offshore. The results of the special studies and the field measurement program, including the physical oceanographic conditions during the survey and factors affecting the transport of the plume, are presented in Section 3. Section 4 presents the results of the modeling study including comparison of model results to the field results. Section 5 provides a summary-level discussion of the findings, conclusions, and recommendations derived from the study.

2.0 METHODS

2.1 Dye Tracer Study

The data acquired in support of the 2001 winter plume tracking survey were collected in three study components: 1) Ancillary dye studies and sensor calibration, 2) Deer Island Treatment Plant (DITP) and 3) the offshore field program. The ancillary dye studies addressed the stability of dye and dye fluorescence under the conditions found at the DITP or at sea. Additionally, robust calibrations of the sensors used on the survey were obtained under laboratory conditions. Activities conducted at DITP included dye addition, *in situ* effluent monitoring, and discrete effluent sampling. Figure 2-1 provides a summary of the DITP and offshore survey components, showing the juxtaposition of the activities in the tidal cycle. The general chronology of events is also is also presented in Table 2-1. Further details of the survey chronology are presented in the Winter Plume Tracking Survey Report (Mansfield *et al.* 2001a). Four distinct survey activities comprised the offshore component of the study:

1. background survey,
2. segment survey,
3. hydraulic mixing zone (HMZ)[1] surveys, and
4. farfield plume tracking survey.

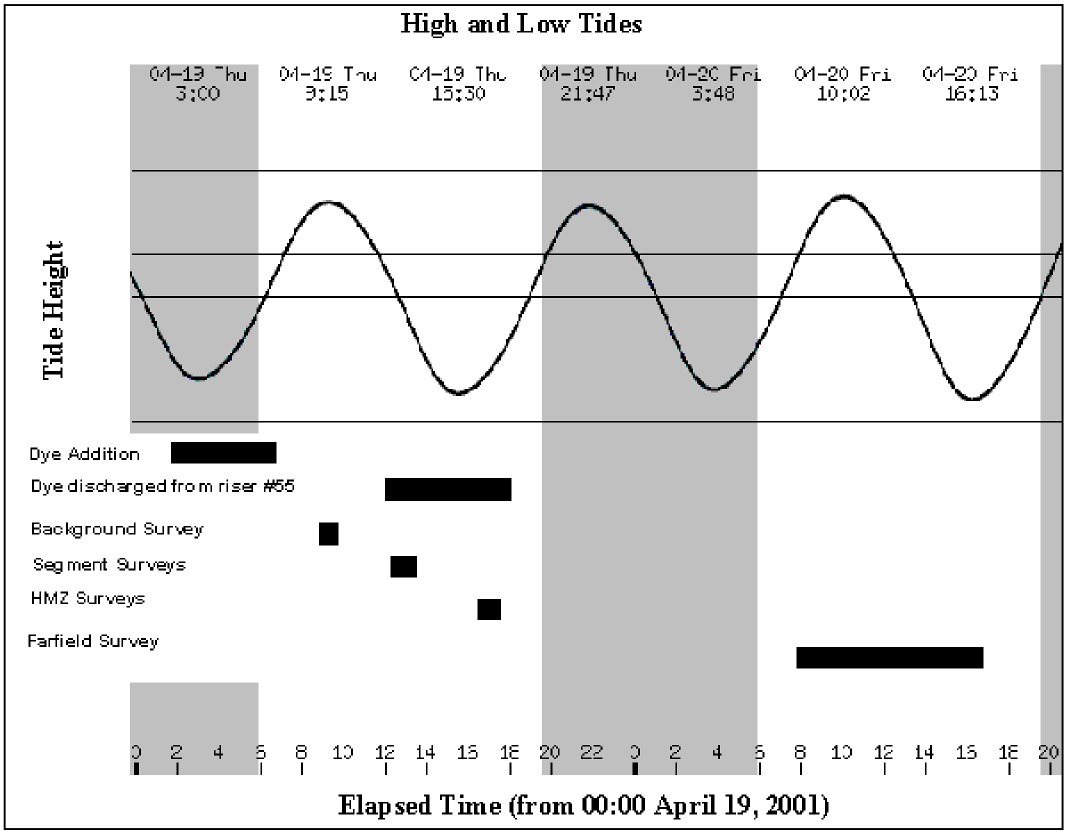

Figure 2-1. Timeline of the winter survey plume tracking activities showing juxtaposition with the tides with survey activities. (Times are EDT.)

The first three offshore activities occurred on April 19, 2001. The farfield survey took place on April 20, 2001, the day after the dye addition. The *R/V Aquamonitor,* a 45-foot research vessel, served as the sampling platform during all offshore survey activities. Over the course of the offshore surveys, both *in situ* and discrete samples were collected. A summary of the methods of each of these components is presented below.

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[1] Note: The term nearfield in this document refers to the general vicinity of the diffuser line. The term is not to be confused with the term near field used by plume modelers to mean the region in which mixing and dilution occur as a result of the turbulence generated by the discharge itself. This latter region is often referred to as the initial mixing zone. We will refer to the modeler's near field as hydraulic mixing zone or HMZ. The term farfield is not to be confused with the modelers use of the term far field. The later is used to mean the region where plume mixing and dilution is due to oceanic turbulence. The farfield surveys described herein will encompass the modeler's farfield, as will most of the nearfield survey. It is the transition point between the hydraulic mixing zone and the farfield that initial dilution is set. Sampling this location was the goal of the hydraulic mixing zone surveys.

Table 2-1. General survey chronology, winter plume tracking survey.

Date	Time (EDT)	Activity
April 18, 2001	All day	Mobilization at DITP and marina, Hingham MA
April 19, 2001	0132 to 0845	Dye monitoring at DITP
	0142 to 0750	Dye addition at DITP
	0900 to 0930	Background survey
	1205 to 1340	Segment surveys
	1500 to 1720	HMZ surveys
April 20, 2001	0800 to 1725	Farfield survey

The plume tracking Combined Work/Quality Assurance Project Plan (Bruce *et al.,* 2000) and The Survey Plan for the March 2001 plume tracking survey (Battelle 2001a) contain additional details on survey/sampling methods. Details of the methods and equipment employed for the ancillary studies are presented in a work plan (Battelle 2001b) and in letter data reports appended (Appendix A1-A6) to this report (Battelle 2001c – h). The survey report for the winter survey provides additional information the activities and accomplishments of the winter plume tracking survey (Mansfield *et al.* 2001a).

2.1.1 Ancillary Dye Studies

Several ancillary experiments were conducted before and after the winter plume tracking survey to address potential interferences on Rhodamine WT dye detection that may be encountered either at the DITP or in the offshore survey area. A critical element of these studies was development of accurate estimates of the response of dye as a function of changing temperature. These data were required to establish calibration coefficients for the sensors used to measure *in situ* the dye concentrations during the survey and in the laboratory. Potential interferences that were examined included background fluorescence, turbidity (measured as light beam attenuation), photochemical decay, adsorption to particulate matter, pH, agitation, biodegradation, degradation by chlorine, and degradation by chlorine in the presence of bromine in seawater. The methods used to examine the potential interferences are described in the following sections.

2.1.1.1 Effect of Temperature and Instrumentation on Fluorescence Measurements

Previous studies have shown that Rhodamine WT fluorescence intensity increases with decreasing temperature (Feuerstein and Selleck 1963, Wilson *et al*. 1986) and also varies with total suspended solids concentrations in natural samples (Feuerstein and Selleck 1963). Further, Wilson *et al.* (1986) state that fluorescence measurements are instrument-specific. To address how these issues could affect the plume tracking study, a series of experiments were performed to assess the effect of temperature on Rhodamine WT fluorescence across the concentrations and media used during the 2001 MWRA plume tracking surveys. The resulting data were used to develop a temperature compensation equation for each instrument package used during the 2001 plume tracking surveys and compare the equation with that previously reported (Feuerstein and Selleck 1963).

The data used to develop the temperature -fluorescence relationship equation were derived from three separate sets of experiments:

1. Fluorescence in de-ionized (Milli-Q) water – Solutions of 2.5, 25, and 50 μppb Rhodamine WT dye were prepared. Fluorescence was measured with the two fluorometers that were used in the field during the winter plume tracking survey, each at the range setting that was used in the field -- either 0 – 5 ppb range or 0 – 150 ppb range. The fluorescence and temperature in each test

solution were measured independently over a range of temperatures while the solutions were well mixed.

2. Fluorescence in filtered seawater and effluent – The seawater experiments were conducted on filtered seawater from Nantasket Roads, Massachusetts Bay that was collected during the Summer 2001 MWRA plume tracking survey (Mansfield *et al*. 2001b). The seawater was filtered through Whatman GF/F glass fiber filters with mean pore size of 0.45 µm. The seawater dye solutions were intended to represent the matrix and dye conditions of samples collected during the offshore plume tracking surveys, thus, they were prepared at a concentration of 1 ppb Rhodamine WT. The whole effluent solutions were intended to represent the DITP samples that were collected during the Winter and Summer 2001 MWRA plume tracking surveys, thus they were prepared at a concentration of 60 ppb Rhodamine WT. All test solutions were prepared in triplicate. A background matrix sample for each matrix was also prepared and processed. The fluorescence response in each of the eight test solutions (3 x 1 ppb seawater plus seawater blank; 3 x 60 ppb effluent plus effluent blank) was analyzed independently over a range of temperatures.

3. Sensor calibrations performed for the analysis of discrete water samples – The analysis of discrete water samples collected during the Summer 2001 plume tracking survey provided an additional opportunity to record the fluorescence-temperature relationship with the instrumentation used for dye monitoring at DITP and offshore during the winter and summer plume tracking surveys. A set of calibration standards was prepared for each media (Rhodamine WT in either filtered seawater or effluent) for which discrete samples were collected during the Summer 2001 MWRA plume tracking survey. These included:

   Filtered Seawater: Blank, 0.25 ppb, 0.50 ppb, 1.00 ppb, 1.25 ppb, 2.5 ppb
   Effluent: Blank, 50 ppb, 60 ppb, 80 ppb, 90 ppb, 100 ppb

   These concentrations were intended to bracket the dye values observed during the survey. Seawater and effluent blank solutions were also prepared and processed along with the dilute dye solutions to ensure any non-dye background fluorescence was understood. The fluorescence of the calibration solutions (as well as the discrete samples) was measured at approximately the same temperature that the respective matrices were measured in the field. The fluorescence of the seawater calibration solutions was measured within a range of 6 to 8°C; effluent between 18 and 20°C.

The study performed on filtered seawater and effluent (number 2 above) provided the primary basis to determine the fluorescence-temperature relationship. Details of the methods and instrumentation used for the temperature study are presented in the Final Temperature Effect Letter Report (Battelle 2001d, Attachment 1). Battelle (2002d) also describes the methods followed to understand the effect of the specific sensors on recorded dye concentrations. Additional method details related to instrument intercalibration are presented in Battelle (2000e; Attachment 6).

2.1.1.2 Background Fluorescence and Turbidity

A previous plume tracking study (Albro 1994) found "false" dye fluorescence readings proportional to transmissometer (turbidity) readings. In 1994, the "false" readings were removed by acquiring fluorescence data in and out of the effluent plume before the dye appeared in the discharge plume. Using the relationship between the fluorometer readings to transmissometer readings, an equation relating the "false" reading to turbidity was determined using linear regression. Since that time, the deployment of new rhodamine fluorometers with relatively narrow bandwidths for excitation and emission spectra appeared to have eliminated problems of "false" fluorescence caused by turbidity. This was confirmed by obtaining concurrent turbidity and fluorescence measures from the *in situ* sensors in the nearfield area prior to dye exiting the diffuser (Figure 2-2). Background dye fluorescence remained constant and very close to zero in spite of changes in beam attenuation from ~0.5 to 1.0 m^{-1}. Similar results were obtained during the summer survey.

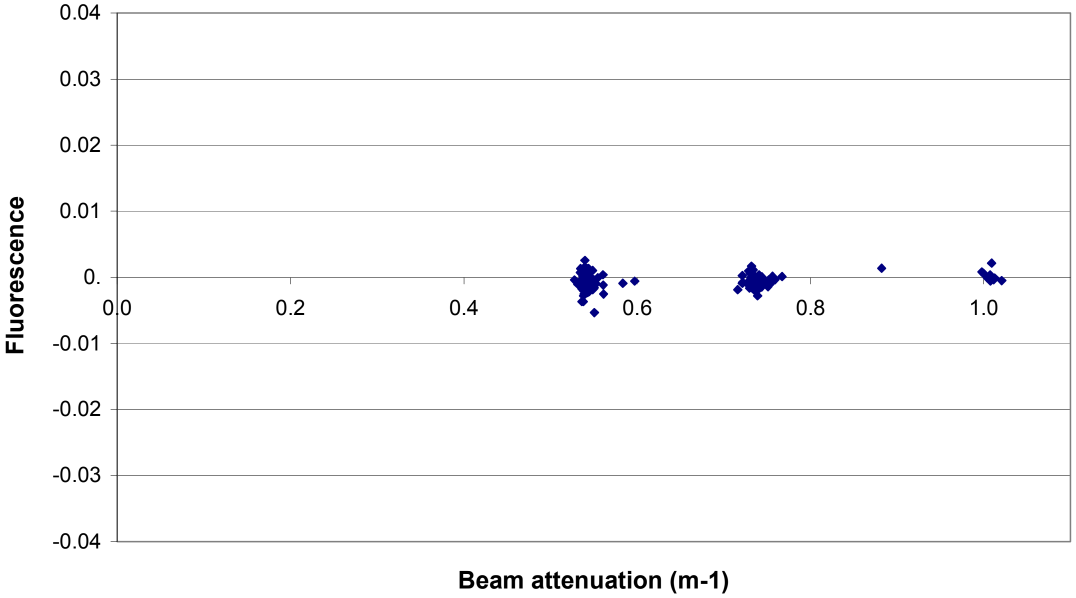

Figure 2-2. Pre-dye emergence comparison of *in situ* beam attenuation versus dye fluorescence response in the vicinity of the MWRA effluent diffuser in April 2001.

In addition, the background fluorescence of effluent, seawater, and effluent in seawater were addressed in laboratory studies. The laboratory study is presented below. The field study is presented in Section 2.1.3.

The laboratory turbidity experiments were conducted on serially diluted solutions of three separate test solutions: 1) undiluted DITP effluent with no dye added was used to establish turbidity levels of the effluent, 2) de-ionized water at a dye concentration of 100 µppb was used to represent true fluorescence of the dye without the effects of turbidity or other factors attributable to the effluent, and 3) DITP effluent with a dye concentration of 100 µppb. Each solution was serially diluted with de-ionized water and fluorescence measured. The fluorescence response from the test solution was compared to the other solutions to determine the influence of turbidity on Rhodamine WT dye fluorometric readings. Further description of the equipment and methods used in the laboratory study can be found in the Final Background Fluorescence Letter Report (Battelle 2001c, Attachment 2).

2.1.1.3 Effect of Chlorine, pH, Agitation, and Particle Adsorption on Fluorescence

The rhodamine dye injected into the effluent stream may be degraded or the dye signature masked by a number of factors, including agitation, biological degradation, adsorption onto particles, variable and extreme pH, and contact with chlorine (added to the effluent in the form of NaOCl). Of these, degradation by reaction with chlorine is perhaps the most important. Deaner (1973) reported that chlorine concentrations of 2 to 9 mg/L in an effluent should not significantly alter the fluorescent properties of the dye. However, Turner Designs (2001) reports that chlorine in any amount appears to destroy Rhodamine WT within a few minutes. Wilson *et al.* (1968) also report that chlorine is known to quench the fluorescence of rhodamine dyes. Because of the difficulty in separating the effects of individual factors, the total effect of the above were addressed in one single experiment. This study determined if combined conditions in the effluent stream after dye addition until discharge to Massachusetts Bay could impact dye measurements.

The primary parameters that were measured included fluorescence, temperature, and pH. These parameters were measured with the sensor packages that were used in the field for plume tracking. Additionally, residual chlorine was measured with a HACH colorimetric test kit. A detailed description of the equipment and methods used in the laboratory study can be found in the Dye Loss Letter Report, Final Chlorine Study Letter Report (Battelle 2001f, Attachment 3). The study employed two 10-liter tanks of effluent. One was primary tank for measuring all parameters except residual chlorine and one tank was used to measure residual chlorine (Rhodamine WT interferes with the colorimetric analysis of chlorine). The two test solutions were of the same volume and were maintained under the same conditions throughout. Equivalent amounts of chlorine were added to both tanks; however, no dye was added to the second tank. The second tank was monitored for residual chlorine only.

Once the temperature stabilized to room temperature, Rhodamine WT was added to tank 1 to achieve a concentration of 62 μppb, the approximate concentration achieved at DITP during the plume tracking study. To mimic the turbulence at DITP, the effluent was rapidly mixed for 1 h while data were continuously collected. The data collected during this period were used to address any biodegradation, adsorption, and agitation effects that the dye may be subjected to in the channel from the point of injection downstream to the hypochlorite addition and mixers. After 1 hour, chlorine (as $NaOCl_2$) was added to both tanks to simulate the DITP hypochlorite dosing point. The chlorine was added as a single injection to achieve a chlorine residual of ~4.0 mg/L, also approximating conditions at DITP. After this time, residual chlorine (in the second tank) was measured approximately every half-hour for 7.5 hours (t – 12.5 h). At t = 24.4 h, a second chlorine dose (NaOCl) was added to the tanks to bring the chlorine residual up to ~10 mg/L. The solution was monitored for an additional 5 hours before termination. During the post-chlorination portion of the experiment, the recorded temperature in the tanks fluctuated slightly with room temperature. Dye concentrations were monitored in tank 1 before and after chlorine additions to assess the affect of chlorine on dye concentration.

2.1.1.4 Effect of Chlorine/Bromine

It has been suggested that free chlorine may react with the bromine salts found in seawater (Turner Designs, 1995), which then may react with the rhodamine. Thus, while rhodamine may be stable in chlorinated effluent, it may not be stable in chlorinated effluent diluted with seawater. (The mean abundance of bromine in seawater is 65 mg/L, most of which is bromide ion [Riley and Skirrow, 1965]). To determine whether or not this is the case, a separate set of experiments specifically addressing the potential for interactions of residual chlorine and bromine in seawater on the dye were designed and performed. These experiments were designed to determine if conditions at the diffuser; i.e., chlorinated effluent diluted in seawater as it is discharged to Massachusetts Bay, could impact dye measurements. The study involved four experiments, including the collection of data on background levels for the acquired parameters. A detailed description of the equipment and methods used in the laboratory study can be found in the Dye Loss Letter Report, Final Chlorine/Bromine Interaction Study Letter Report (Battelle 2001g, Attachment 4). The experiments included:

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[2] Commercial sodium hypochlorite solution used at DITP for the purpose of effluent disinfection was provided by MWRA.

1. Dye in Seawater – The initial experiment was designed to address the chlorine/bromine/rhodamine interaction by adding known amounts of NaOCl in a 100% seawater medium containing several concentrations of dye. While solutions were prepared at four rhodamine concentrations, approximately 20, 10, 1, and 0 ppb, only the data from the 20 ppb solution was used and is discussed below. The experiment was conducted by adding chlorine to the seawater/rhodamine solution. The solution was continuously stirred in a 1-liter test tank and continuously monitored for temperature and salinity with an OS200 CTD unit and for rhodamine dye fluorescence with a Seapoint *in situ* rhodamine fluorometer. After baseline readings of temperature, salinity, and rhodamine were established, the solution was injected with a quantitative amount of sodium hypochlorite solution to achieve the desired chlorine concentration (~ 0.5 mg/L). However, chlorine concentrations were not measured in this experiment.

2. Dye in De-Ionized Water –The second experiment was designed to address the effects of low bromine levels on the rhodamine fluorescence in de-ionized water. The procedures described above were repeated in de-ionized water, except that the design was modified to include the addition of 25 ml of seawater after chlorine effects were measured (to provide a low concentration of bromine).

3. Dye in Effluent – A third experiment was designed to assess bromine/chlorine/rhodamine interaction in the presence of DITP effluent. Secondary effluent, collected prior to chlorination, comprised the starting material for the test solutions. The primary parameters measured as seawater was added to the effluent included fluorescence, temperature, and conductivity, which were measured with the sensors that were used in the field for plume tracking. Additionally, residual chlorine was measured with a HACH colorimetric test kit.

   The experiment consisted of adding a 500-mL of seawater or de-ionized water to 1-L effluent test solutions containing ~45 ppb rhodamine and ~0.39 mg/L Total Residual Clorine (TCR, from NaOCl). The seawater addition served as the experimental test, whereas the de-ionized water served as the control for dilution effects. Both dye stability and TCR stability were monitored before the start of the experiment, which were run side-by-side. During the set-up period, fluorescence was stable but the TCR decreased in each solution, apparently consumed by the effluent. Each solution was dosed again with NaOCl, raising the TCR to 0.39 mg/L in each solution just before the start of the experiment. Fluorescence, temperature, and conductivity were measured in the solution to which seawater was added. Fluorescence only was measured in the dilution control solution. Before the addition of seawater or de-ionized water, each fluorometer sensor was removed from its tank and placed in the opposite solution to compare sensor values. The solutions were again monitored for several minutes to measure any effect of the increased chlorine concentration on the dye concentrations. The sensors were then switched back to their initial orientation. Upon verification of solution stability, 500 mls of either seawater or de-ionized water were added into their respective test tanks. Data were recorded for approximately 20 minutes.

4. Background Measurements – Separate measurements were taken to establish the background fluorescence and salinity of each of the three media used in this study (effluent, seawater, and de-ionized water).

2.1.1.5 Effect of Photodegradation

Photochemical decay of fluorescent dyes has been previously documented (Feuerstein and Selleck, 1963 and Tai and Rathburn, 1988) and some photodecay of dye in the field may be expected during prolonged exposure to sunlight. Photochemical decomposition of rhodamine dye is dependent on light intensity, which can vary substantially from season to season and day to day as well as over the course of each day. To partially address this variability and to estimate the photodegradation that might occur during each day of the winter and summer plume-tracking surveys, photodegradation experiments were conducted outside in sunlight on the days the April and July plume tracking surveys were conducted. Light intensity in the water column is depth dependent and hence photodegradation is also depth dependent. The study was designed to address only the "worst-case" situation (i.e. photodegradation of dye at the ocean's surface). Potential for photodegradation at depth was estimated based on depth-dependent decay rates derived in previous experiments (Tai and Rathburn, 1988).

Two separate experiments were conducted at Battelle over the periods of the plume tracking exercises -- on April 18-20 and July 16-19, 2001. For each study, two 10-liter Rhodamine WT dye solutions in seawater, nominal concentrations of 1.4 ppb and 0.7 ppb, were prepared and placed in open top, white 13-liter polyethylene bucket (diameter = 285 cm, depth = 270 cm, water depth = 175 cm). The test solutions were placed, uncovered, outside at the Battelle laboratory in an area that receives direct sunlight during all daylight hours. One-liter samples were removed at T = zero and again near the end of the photoperiod (21:00) on each survey day. All collected samples were stored in sealed HDPE bottles held in the dark at 4° C until analysis following the surveys (maximum holding time: winter 8 days, summer 22 days). The fluorescence was measured *in situ* with a Seapoint rhodamine fluorometer set in the 0 – 5 ppb range. Additionally, conductivity and temperature were measured with an Ocean Surveys OS200 conductivity/temperature/depth (CTD) sonde. The analog signals from the fluorometer, conductivity, and temperature sensors were processed through analog channels of the CTD into the Battelle NavSam© database. The fluorescence data were temperature corrected based on media specific coefficients previously described (Battelle 2001d). The fluorescence correction for temperature was applied after the end of the experiment because final temperature coefficients had not been established at the time of the analysis. Details of the methods and instrumentation used for the photodegradation study are presented in the Final Photodegradation Letter Report (Battelle 2001h, Attachment 5).

2.1.2 DITP Field Activities

The primary activities occurring at DITP supporting the plume tracking survey included addition of Rhodamine WT dye into the effluent stream and *in situ* monitoring of the dye concentrations throughout the period it was being added. Additionally, discrete effluent samples were collected for the purpose of comparing laboratory-derived dye concentrations with *in situ* data, comparing dye concentrations in the west and east disinfection basins, determining the concentrations of selected parameters in the effluent, and to intercompare laboratory results for selected parameters. Dye was added to the effluent stream from 1:42 to 7:50 AM (EDT) March 19, 2001 (Table 2-1.) Dye monitoring at DITP was conducted from 01:32 AM until 8:45 AM (EDT), when dye concentrations returned to pre-addition levels.

Dye Addition -Rhodamine WT dye solution was added to the primary/secondary blended effluent channel at the Deer Island Treatment Plant downstream of the secondary clarifiers at a location near the riser shaft for clarifier B (Figure 2-3). At this location, the effluent undergoes vigorous mixing before the flow splits into the two streams that lead to the sodium hypochlorite dosing points, the hypochlorite mixers, and the two disinfection basins. The hypochlorite mixers blend the effluent with chlorine (as sodium hypochlorite (NaOCl); pre-diluted to ~500 mg/L). The target dye concentration was 100 ppb.

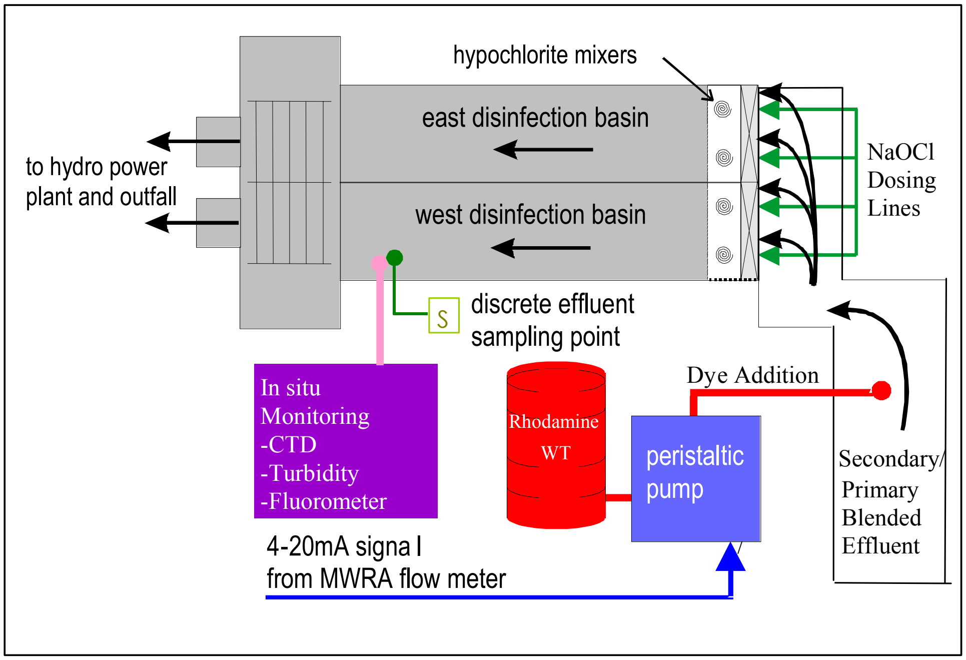

Figure 2-3. Schematic of Deer Island Treatment Plant dye addition and sampling locations.

Rhodamine WT dye (assumed 20% wt/wt active ingredient), purchased from Keystone Aniline Corporation, Chicago IL, was metered directly into the primary/secondary blended effluent channel using a peristaltic pump. The pumping speed was proportional to the "official plant flow" measured by MWRA and derived as the sum of readings from flowmeters located in four parallel streams in the treatment plant. The pumping speed and plant volume were periodically monitored throughout the period of dye addition.

Dye Monitoring (*in situ* sampling) – The dye-dosed effluent was monitored with *in situ* instrumentation and also sampled periodically at the most downstream end of the west disinfection basin. Fluorescence, temperature, conductivity, density, pH and turbidity were measured *in situ*. A Seapoint Rhodamine WT fluorometer, Seapoint turbidity sensor, and an Ocean Sensors OS200 CTD unit containing conductivity, temperature, pressure (depth), and pH sensors comprised the *in situ* sensor package. The fluorometer and turbidity sensors were powered by and their analog signals were processed through the CTD unit. The *in situ* data were collected and stored by the Battelle Ocean Sampling System (BOSS). The effluent was monitored continuously at a single depth approximately 1 meter below the surface. Additionally, 1 hour after the start of dye addition, vertical profiles were conducted at three locations within the west disinfection basin to determine dye homogeneity. These profiles showed that dye concentrations were uniform across all locations and depths sampled. Details of the DITP monitoring are provided in Mansfield *et al.* (2001a).

Discrete Effluent Sampling – In addition to the continuous *in situ* monitoring of the effluent, discrete effluent samples were collected to verify the *in situ* data and provide additional information on the waste stream. Samples were obtained for analysis of Rhodamine WT, chloride, total suspended solids (TSS), ammonium (NH_4), phosphate (PO_4), silver (Ag), copper (Cu), fecal coliform and *Enterococcus* and chlorophyll (Table 2-2). These samples were collected just prior to dye addition and then periodically during the 6-hour period that the dye was released. The discrete samples were collected as grab samples from the flow of a submersible pump that was placed near the *in situ* monitoring point in the west disinfection basin. Additionally, four samples were collected from the east disinfection basin to compare the dye concentrations in the two basins. These latter samples were analyzed for rhodamine only. The discrete samples were analyzed by the MWRA Deer Island Laboratory (DIL), Battelle, or University of Rhode Island (URI). Total suspended solids (TSS) and nutrients were measured by DIL and URI to allow comparison of standard-oceanographic to EPA-approved methods.

Table 2-2. Discrete samples obtained for analysis and analytical methods used for the April plume tracking survey.

Parameter	Units	Instrument	Reference	Sample source	Lab
Rhodamine WT	ppb (µg/L)	Seapoint rhodamine fluorometer	Seapoint Rhodamine WT Fluorometer Manual	DITP and offshore	Battelle
Chloride (effluent only)	mg/L	Mettler autotitrator	MWRA (1997c) SOP 10-ORNG-TAR-01.1	DITP	DIL
Total suspended solids	mg/L	Mettler 5-place balance (0.01 mg)	Battelle SOP 5-053	DITP and offshore	URI
Total suspended solids	mg/L	Mettler 4-place balance (0.1 mg)	MWRA (1999) SOP 1012.0	DITP	DIL
Dissolved ammonium	µM	Technicon Autoanalyzer II	Lambert and Oviatt (1986); Solorzano (1969)	DITP and offshore	URI
Dissolved ammonium	µM	Skalar autoanalyzer	MWRA (1998a) SOP 1005.0	DITP	DIL
Dissolved phosphate	µM	Technicon Autoanalyzer II	Murphy and Riley (1962)	DITP and offshore	URI
Dissolved inorganic phosphorus	µM	Skalar autoanalyzer	MWRA (1998b) SOP 1006.0	DITP	DIL
Silver – total	µg/L	inductively coupled plasma mass spectrometry (ICP-MS) or graphite furnace atomic absorption	EPA Method 200.8, 200.9 (EPA 1991); EPA Method 1638 and EPA 1640 Battelle MSL SOP I-022; Battelle MSL SOP I-029	DITP and offshore	Battelle
Copper – total	µg/L	inductively coupled plasma mass spectrometry (ICP-MS)) or graphite furnace atomic absorption	EPA Method 200.8 , 200.9 (EPA 1991); EPA Method 1638 and EPA 1640 Battelle MSL SOP I-022; Battelle MSL SOP I-029	DITP and offshore	Battelle
Fecal Coliform/ *Enterococcus*	#/100 mL	Microscope	MWRA (1996a) and MWRA (1996b)	DITP and offshore	DIL
Chlorophyll a/phaeopigments	µg/L	Turner Designs fluorometer Model 10AU	Arar and Collins (1992); Battelle SOP 5-265	Offshore	UMD

2.1.3 Offshore Field Activities

The Winter Plume Tracking survey WP011 was conducted in Massachusetts Bay in the vicinity of the ocean outfall on April 19 and 20, 2001. During the first day of survey operations, the survey focused on the environment in the immediate vicinity of the outfall location in Massachusetts Bay. Additional monitoring of the plume at distance was conducted on second day. The BOSS towfish with rhodamine fluorometer, towed in a tow-yo fashion, provided measurements of Rhodamine WT dye that indicated the vertical and horizontal distribution of the effluent and its dilution. The combined data from the nearfield surveys were used to develop contours of dilution over relatively small scales in the immediate vicinity of the outfall. Data collected during the farfield survey day were used to demonstrate the dispersion of the plume over longer time scales. In support of the interpretation of dilution assessments, current velocities in the study area were measured using a downward looking Acoustic Doppler Current Profiler (ADCP) on board the survey vessel. Density profiles were measured with a CTD system housed in the towed sensor unit. The ADCP measurements documented the ambient currents (particularly tidal and wind-driven) that affect the dilution and trajectory of the plume. Contour plots of temperature, salinity, and Rhodamine WT dye were used to visualize the data both during the survey to guide decision-making and during subsequent data analysis. Details of the equipment, methods, and survey strategy can be found in Bruce *et al.* 2000, Battelle 2001a, Battelle 2001b, and Mansfield *et al.* 2001a).

The offshore field component included the following four components:

- Background survey –*The objective was to obtain measurements of background fluorescence in the environment prior to dye release at the diffuser and to obtain discrete background water samples from locations outside the region influenced by the effluent.*

- Segment survey –*The objective was to determine plume structure and behavior in the nearfield by examining the influence of tides and ambient stratification on its vertical and horizontal distribution.*

- Hydraulic mixing zone (HMZ) surveys – *The objective of these surveys was to measure dilution at the edge of the hydraulic mixing zone to determine compliance with the requirements of the NPDES permit. Discrete samples were collected during the HMZ surveys.*

- Farfield plume tracking survey – *The objective was to determine plume structure and behavior in the farfield by tracking the spread of the dye to dilutions of at least 1:1000 (down to 0.10 µppb active dye ingredient).*

The first three offshore activities occurred on April 19, whereas the survey activities on April 20 were devoted exclusively to the farfield plume tracking (Table 2-1). Over the course of the offshore surveys, both *in situ* data and discrete samples were collected supporting dye tracking and hydrographic characterization.

The dye plume tracking was conducted using a second *in situ* sensor package deployed from the *R/V Aquamonitor* in the BOSS towfish. The sensor suite used for offshore monitoring included the same model sensors used for DITP monitoring. Additionally, the offshore sensor package included a chlorophyll fluorometer and a transmissometer. The depth of the towed sensor package was controlled by winch and vessel speed. The offshore plume tracking used the BOSS towfish in three sampling modes 1) vertical profile, 2) constant-depth towing, and 3) towyo. In vertical profiling mode, data were acquired as a function of depth while the vessel remained stationary. During towyo mode the BOSS was operated in a vertically undulating (ascent and descent) pattern to obtain data continuously at different depths while underway.

Battelle's software, NavSam© acquired data from all electronic sampling systems and navigation systems at the rate of four times per second. The software displayed all of the information on a color monitor updated once per second. The screen is split to show sensor data on the left and navigation data on the right. Once the data were acquired, they were automatically written to a data file and logged concurrently with position data from the navigation system. The navigation portion of the display showed the position of the vessel compared to the coastlines digitized from standard NOAA charts, navigation aids, preset sampling locations, and vessel track. During towing operations, position fixes were electronically recorded at 2-second intervals. The software system allowed the viewing of all hydrographic measurements and dye measurements in real time and was invaluable in this application.

Two different types of towfish cables were used during this experiment. During the first day of operations, an electrical-mechanical cable with a Teflon tube down the middle of the cable enabled the collection of discrete water samples. However, since discrete samples were not required during the farfield surveys, a standard electrical mechanical cable (500 ft long) was used, allowing the vessel to tow at a greater speed.

The use of the cable with tube during the first survey day allowed the collection of discrete water samples, which were all collected during vertical BOSS profiling as part of the HMZ surveys. The discrete samples were collected as a secondary measurement of dilution and to demonstrate the effectiveness of effluent treatment and dilution. The discrete samples collected in the plume were collected only where dye concentrations appeared to be relatively high. Discrete samples of the background condition near the diffuser were also collected. A summary of the parameters measured in the discrete samples is presented in Table 2-2. During the vertical profiles when discrete water samples were collected, hydrographic data and other parameters were also collected with *in situ* sensors (Table 2-3).

Table 2-3. Summary of shipboard instrumentation.

Parameter	Lab	Units	Instrument	Reference
Rhodamine fluorescence	Battelle	ppb (µg/L)	Seapoint rhodamine fluorometer	Seapoint Rhodamine WT Fluorometer Manual
Conductivity	Battelle	mmhos/cm	OS200 CTD	Ocean Sensors CTD manual (1999)
Temperature	Battelle	C	OS200 CTD	Ocean Sensors CTD manual (1999)
Pressure	Battelle	m	OS200 CTD	Ocean Sensors CTD manual (1999)
Chlorophyll fluorescence	Battelle	µg/L	Wetstar WS-3-MF	Wet Labs manual (1998)
Transmissometry	Battelle	m-1	Seatech 20-cm (660nm)	Seatech manual (1998)
Altitude	Battelle	m	Datasonic PSA-916	Datasonic manual (1997)
Bottom depth	Battelle	m	Furuno FCV-52	Furuno manual (1998)
Navigational position	Battelle	Degrees	Northstar 942X	Northstar manual (1998)
Ocean current velocity	Battelle	cm/sec	RD Instruments ADCP WHM600-I-UG6	RD Instrument manual (2000)
Sigma-T*	Battelle	no units	OS200 CTD	Fofonoff and Millard (1983)
Salinity*	Battelle	PSU	OS200 CTD	Fofonoff and Millard (1983)

* Sigma-T and salinity are calculated from conductivity, temperature, and pressure.

The location for discrete sample collections was identified in the field using the tow-yo data. The vessel then returned to the identified location and conducted vertical hydrographic profile operations. After an initial profile, the pumped system was raised through the plume to collected the discrete samples at selected depths as follows:

- TSS, NH_4, PO_4, and chlorophyll samples at the depth of maximum dye concentration, minimum dye concentration, and at 3 other depths to obtain a range of values at different dye concentrations

- Bacterial indicator samples at 5 depths plus 3 additional samples taken from the area of maximum dye concentration. The bacteria indicator samples were collected only on one HMZ survey to facilitate delivery of samples to the shore laboratory within prescribed holding times.
- Silver and copper at the depth of maximum dye concentration and one other depth of high dye concentration.

While real-time survey data (both at DITP and offshore) were used to make decisions in the field, all survey and laboratory data were subsequently entered into the MWRA Environmental Monitoring and Management System and subjected to a quality assurance review before use in the plume tracking assessment. During data post-processing, the background fluorescence of seawater at the rhodamine wavelength outside the direct influence of the outfall was subtracted from the rhodamine fluorescence values obtained from the plume tracking surveys. Additionally, all fluorescence data were temperature corrected as described in Section 3.1.1.

The contouring and surface mapping software Surfer® was used to plot nearfield and farfield data in this report. Grid files of dilution, depth and latitude or longitude, or dilution, latitude and longitude were created from data in the MWRA database. Gridding allowed the interpolation or extrapolation of data following the *inverse distance to a power* method (Golden Software 1999). The inverse power method was selected over the kriging method because the wide range of dye dilution values caused the kriging method to overshoot data during extrapolation. The inverse distance to power did not allow data extrapolation beyond the range of the data. For horizontal plume dispersion plots the highest dye concentration from each towyo pass (up or down) was selected, then the inverse distance to a power method was used to generate the grid data. For each gridded plot contained in this report the grid search ellipse is identified.

The data collected during the plume tracking exercise were used as input to the environmental discharge model RSB (described in Baumgartner *et al*. 1992). RSB was developed based on experiments on multiport diffusers in density-stratified currents. This model predicts the spread of the plume and calculates the minimum dilution and the flux-average dilution based on the physical characteristics of the outfall, diffuser flow rate, effluent density, ambient water density, and the current speed at one depth.

2.2 Physical Oceanographic Study

During the offshore surveys, data were also collected supporting a physical oceanographic study to assess the forcing conditions and current regime at the vicinity of the outfall in support of the interpretation of dye dilution and transport assessments. Water properties were obtained from conductivity, temperature and depth profiles acquired from Battelle's BOSS profile data (Table 2-3). Data on the current field were obtained in several ways. Currents were obtained from the ship-mounted acoustic Doppler current profiler (ADCP), which was deployed continuously throughout both days of the offshore survey. The ADCP provided real-time current measurements at 0.5 m or 1.0-m vertical increments between 2.5-m depth and 26-m depth (in 30 m of water). Tidal information was obtained by the NOAA tidal predictions and wind data were obtained from the NOAA web site http://seaboard.ndbc.noaa.gov. Additional information on the movement of the plume was obtained with the deployment of a sub-surface satellite-tracked drifter. The drifter, with drogue positioned at 15-meters depth, was deployed at the end of the nearfield day in the center of the plume. The following day, the vessel used the drifter to locate the plume to begin farfield plume tracking operations. The drifter remained in the water providing information on the general drift of the plume until the end of the farfield data, when it was retrieved.

3.0 RESULTS

3.1 Dye Tracer Study

3.1.1 Results of Ancillary Studies

Each of the ancillary studies was intended to address a specific technical issue associated with the use of rhodamine dye for dispersion studies. Presented as attachments to this report, the ancillary study reports demonstrate few technical problems with Rhodamine WT dye in either the effluent stream or in seawater. The results of the ancillary studies are summarized below.

Study objective: *To determine if there is a substantial background fluorescence in the effluent at the Rhodamine WT dye measurement wavelength.*
The measured dye fluorescence in the effluent was similar to that in the Milli-Q water, indicating that the presence of effluent did not have a significant effect on the fluorescence signal. The majority of effluent turbidity values ranged from 9 to 12 nephelometric turbidity units (NTU). No correlation between fluorescence and turbidity was observed (Battelle 2001c, Attachment 2).

Study objective: *To determine if turbidity in the effluent could interfere with the Rhodamine WT dye fluorescence readings*
A series of measurements of Rhodamine WT dye in effluent and in de-ionized water at concentrations ranging from 1 to 100 ppb indicated no difference in the dye signal measured by the fluorometer indicating that the presence of effluent did not have a significant effect on the fluorescence signal (Battelle 2001c, Attachment 2).

Study Objective: *To assess the effect of temperature on Rhodamine WT fluorescence across the concentrations and media used during the 2001 MWRA plume tracking surveys.*
The study results confirmed the effect of temperature on fluorescence intensity first described by Feuerstein and Selleck (1963), which can be described with the following relationship:

$$F_c = F_r e^{d(T - To)}$$

Where, F_c is the temperature corrected fluorescence concentration
F_r is the uncorrected fluorescence concentration
d is a constant for a given fluorescent dye
T is the temperature at which the fluorescence is measured
T_o is the temperature at which F_c/F_r is unity

Seawater and effluent were both tested in the ranges of concentrations expected offshore or at the treatment plant during the dye tracing study and both were found to behave slightly different. The slight differences in fluorescence responses were attributed to the specific instrument suite used to measure the fluorescence (see below) (Battelle 2001d, Attachment 1).

Study Objective: *To develop a temperature compensation equation for each instrument package used during the 2001 plume tracking surveys and compare the equation with that previously reported (Feuerstein and Selleck 1963).*
The above equation was rearranged as follows to regress the data from the temperature series experiments.

$$T = (1/d)*\ln(F_c/F_r) + T_o$$

Plotted in this fashion, the slope of the regression equals 1/d and the regression intercept equals T_o. Similar data transformations were performed on the other temperature series. The calculated slope (d) and T_o for each of the experiments are presented in Table 3-1. The slopes of the temperature calibrations are close to, but do not precisely align with, the theoretical slopes described in the literature *(Feuerstein and Selleck 1963).*

Table 3-1. Final calibration coefficients developed for temperature compensation under the MWRA plume tracking study.

Media	Slope	T_0 (Intercept) °C
Seawater	0.0250	4.876
Effluent	0.0231	5.365

The study concluded that media specific temperature calibration coefficients were difficult to separate from sensor specific effects. Because the same sensors that were used in the field were used in the temperature experiment, the coefficients that were developed eliminated this problem. The above coefficients were used to calibrate the sensors that were used in both the winter and summer plume tracking surveys and were also used to calibrate the same sensor data from all of the ancillary studies.

Study Objective: *To determine whether chlorine added to the MWRA effluent causes degradation of Rhodamine WT dye.*
Chlorine residual in DITP effluent at the time and point of collection measured 2.4 mg/L. At the start of the experiment a day later, this concentration had decreased to 0.04 mg/L. At t = 5 h, chlorine was added to achieve a concentration of residual chlorine of 4.0 mg/L and over the next 19.3 h (until t = 24.3 h) this concentration slowly decreased to 2.1 mg/L. At 24.3 h, NaOCl was again added to increase residual chlorine to 10 mg/L at which time no additional chlorine measurements were taken. Following dye addition, the temperature corrected rhodamine fluorescence was stable at 62.46 uppb (Std. Dev. = 0.059) throughout the course of the 29-h experiment. No immediate drop in rhodamine concentration was observed upon initial chlorine addition (at residual chlorine levels of 4.0 mg/L), nor was any rhodamine concentration decrease observed when the residual chlorine levels were increased to 10 mg/L toward the end of the experiment (Battelle 2001f, Attachment 3).

Study Objective: *To determine if biodegradation, adsorption, and agitation could have a net effect on rhodamine dye fluorescence*
Rhodamine fluorescence was continuously measured for 1 hour after dye addition and chlorine addition. During this time, no decrease in temperature-corrected fluorescence was observed. The fluorescence was then measured for an additional 24 hours after chlorine addition. No decrease in temperature-corrected fluorescence was observed during this period. Because the entire experiment was conducted in whole effluent undergoing constant mechanical agitation, the results indicate that there is no combined effect of biodegradation, adsorption, or agitation during the observational timeframe (Battelle 2001f, Attachment 3).

Study Objective: *To determine whether bromine in seawater interacts with chlorinated effluent to degrade (bleach) Rhodamine WT dye.*
Data from the chlorine/bromine experiments showed that, while rhodamine dye reacted rapidly in seawater upon the addition of chlorine (immediate and complete loss of dye signal), the presence of effluent protected the dye from similar rapid degradation. The results of the effluent experiment verified that rhodamine was stable in chlorinated effluent solutions even at total chlorine residual levels up to 0.39 mg/L (as previously observed in Battelle 2001c) and that the addition of seawater or de-ionized water each reduced the rhodamine concentration similarly; i.e., all dye signal reduction resulted from dilution.

This study verified a previous study that rhodamine dye was stable in effluent (Battelle 2001d) and provided new information leading to the conclusion that rhodamine dye is also stable during the rapid mixing process that occurs during effluent discharge into seawater. The results of the chlorine/bromine study are described in Battelle (2001g), (Attachment 4).

Study Objective: *To determine whether exposure to sunlight would result in a decreased fluorescent signal from Rhodamine WT dye in seawater.*
A decrease in rhodamine fluorescence in seawater was seen in both photodegradation experiments. In the experiment run parallel with the winter plume tracking survey, a decrease in rhodamine fluorescence was seen observed in both the 0.7 and 1.4 ppb dye solutions. The largest percent decrease was seen at the lower concentration, where at the end of the first day (13 hours 37 minutes of daylight exposure), the fluorescence had dropped by as much as 3%. At the end second day (27 hours and 17 minutes of total daylight exposure) a 4.3% total decrease was observed. This corresponds to an average rate of decrease of 2.2 %/day. A decrease in rhodamine fluorescence was also seen at both dye concentrations in the experiment run parallel with the summer survey. The highest percent decrease was observed in the 1.4 ppb solution where at the end of the first day (14 hours 55 minutes of sunlight exposure), the fluorescence had dropped by 0.7% and at the end of three days (42 hours 41 minutes of sunlight exposure), a 5.7 percent decrease was observed. This corresponds to an average rate of decrease of 1.9 %/day (Battelle 2001h, Attachment 5).

Study Objective: *To determine a photochemical decay rate for the specific survey days, which will be applied to the survey data if necessary.*
During the winter plume tracking survey, the dye plume was primarily located between 7 and 20 meters deep. During the summer plume tracking survey the dye plume was primarily located below 10m deep although the upper boundaries were occasionally seen up to 5m deep. Tai and Rathburn (1988) developed depth-dependent decay rates for Rhodamine WT in seawater. Applying the Tai and Rathburn attenuation rates to the observed losses from the Battelle photodegradation study, the dye loss due to photodegradation at the depths the dye was observed is estimated to be < 1% per day for both surveys. For several reasons, including the timing of dye release at the risers, the cloud cover at the site during portions of the surveys, and the subsurface nature of the plume, it was concluded that the field data would not be corrected for photodegradation during either of the two 2001 MWRA Plume Tracking Surveys. Details of rationale used to arrive at this conclusion can be found in Battelle 2001h.

In summary, the results of the ancillary experiments reinforce that rhodamine dye serves as a conservative sewage effluent tracer from its point of entry at DITP to and during the period of initial dilution in Massachusetts Bay. Further, the dye appears stable over longer periods, allowing use of the dye for tracing plumes in the farfield.

3.2 Dye Addition – DITP Results

Rhodamine WT dye was introduced into the effluent stream at DITP from 1:42 to 7:50 AM (EDT), April 19, 2001. During this time the DITP effluent flow rate varied from 412 MGD at the start of dye injection to 346 MGD at the end of dye injection (Figure 3-1). The flow was about 460 MGD over the period the dye exited the diffuser system.

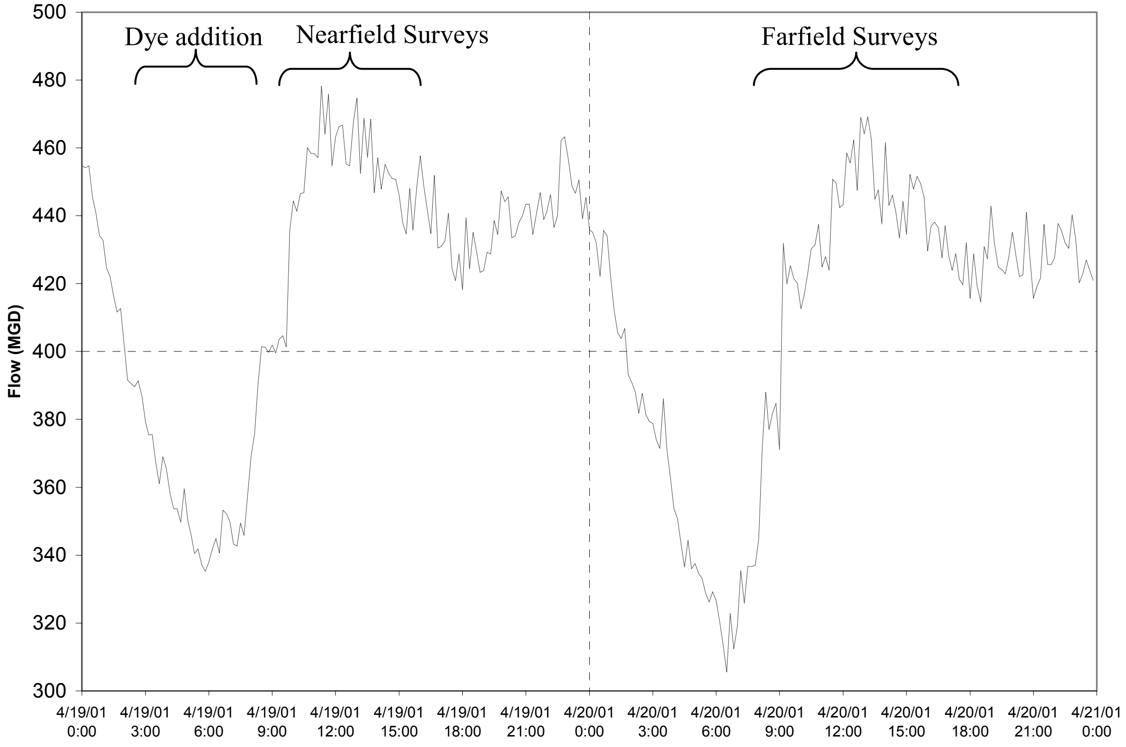

Figure 3-1. Flow rates at Deer Island Treatment Plant during and after the dye addition (Times are EDT).

Figure 3-2 shows dye concentration as measured by the *in situ* fluorometer in the west disinfection basin throughout the period of dye injection. Once the dye concentration stabilized in the disinfection basin (at approximately 45 minutes after start of dye addition), concentrations remained extremely uniform until dye injection was discontinued. Dye concentration in the west disinfection basin was also uniform with depth as determined by *in situ* depth profiling. (Note that the discontinuities in the sensor data shown in Figure 3-2 between 0200 and 0230 [~50 minutes after dye addition was started] are related to difficulties encountered in conducting vertical profiles and not an indication of problems with the sensors. These data also show when the sensors were removed from the effluent during the profiling. The mean *in situ* dye concentration, calculated from data acquired between 3:15 to 8:00 AM (t=92 to 378 minutes after start of dye addition) after the removal of "noisy data" associated with depth profiling and the associated removal and movement of the equipment, was 57.36 (Table 3-2).

The DITP dye monitoring strategy; i.e., continuous *in situ* monitoring in the west disinfection basin only, was designed given the assumption that the dye concentrations would be the same in both the east and west disinfection basins. However, data from the discrete samples collected in both basins indicated that dye concentrations in the east disinfection basin were ~12% higher than in the concurrent *in situ* readings from the west basin (Table 3-2). The discrete samples collected from the two disinfection basins during dye addition were analyzed on April 26th. Each sample was measured with both fluorometers used during the plume tracking study to ensure their intercalibration. Details of the sampling and analysis procedures are presented in Mansfield *et al.* (2001a).

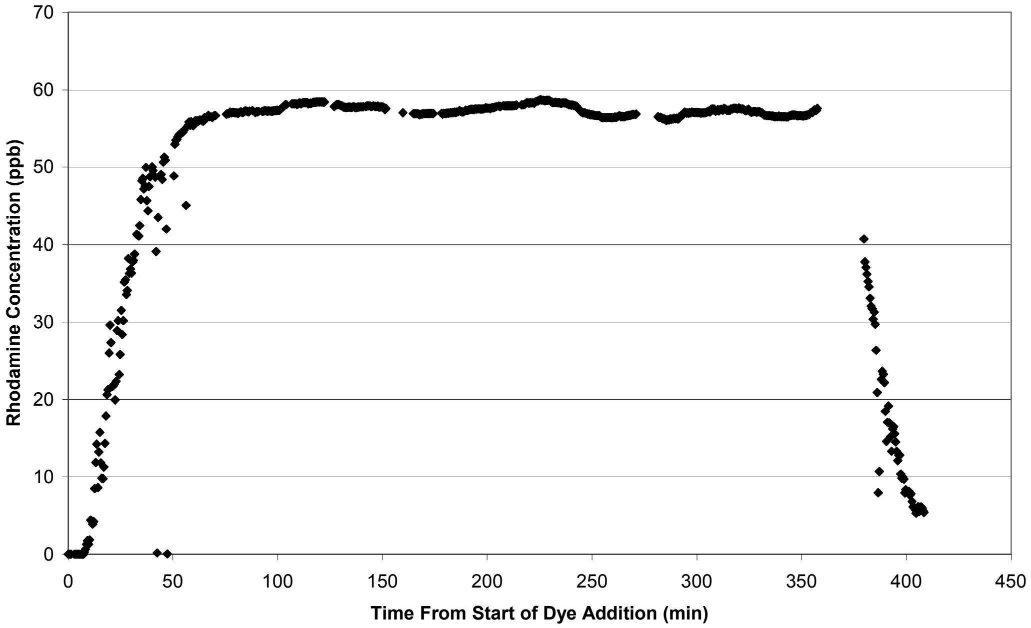

Figure 3-2. Dye concentration in the West Disinfection Basin.

Table 3-2. Rhodamine dye concentrations in discrete effluent samples collected April 19, 2001 and *in situ* dye concentrations measured in the west basin.

		Dye Concentration (ppb)			
Sample ID	**Time of Collection (EST)**	**West Basin In Situ**	**West Basin Discrete**	**East Basin Discrete**	**DITP Grand Mean**
P011A03A	2:10		55.32		
P011A049	2:40		55.27		
P011A060	4:07		56.43		
P011A06C	5:03		54.12		
P011A078	6:03		54.88		
P011A03F	2:10			60.50	
P011A046	2:17			64.03	
P011A063	4:07			63.30	
P011A06F	5:03			60.59	
PO11A07B	6:05			61.50	
Mean		57.36[A.]	55.20	61.98	59.67[B.]
Std.Dev.		0.71	0.84	1.61	

A. Only the in situ data are used in this column: Range 51.57 to 58.82 ppb, n = 46,270
B. Average of West Basin In Situ and East Basin Discrete values

The difference in dye concentrations between the basins was attributed to incomplete mixing of the dye in the effluent channel before the effluent stream splits into the east and west disinfection basins. Of the several approaches evaluated to account for the concentration difference, averaging the mean *in situ* dye concentration from the west basin and the mean dye concentration from the discrete sample analyses from the east basin was deemed the most defensible. The resulting overall mean dye concentration in the effluent is 59.67 ppb (Table 3-2). This value represents C_0, which is used for the calculation of dye dilution in the nearfield and farfield surveys.

3.3 Dye Tracking –Plume Tracking Results

All *in situ* fluorescence, as well as the fluorescence of the discrete samples analyzed after the survey, were measured with the same rhodamine fluorometer. The concentration of dye in the plume or discrete sample (C_{plume}) measured directly in ppb using the *in situ* rhodamine fluorometer was used to determine dilution (S):

$$S = \frac{C_o}{C_{plume}}$$

where C_o is the concentration of dye in the effluent at the Deer Island Treatment Plant and C_{plume} is the concentration of dye in the plume in the ocean. The C_O value calculated from the DITP data was 59.67 ppb as active dye ingredient (Table 3-2). All dye values in the MWRA database were corrected for the decrease in rhodamine fluorescence with increasing temperature (see Section 3.1.1).

3.3.1 Background Survey

The pre-dye emergence background survey was conducted near the western end of the MWRA diffuser system on April 19, 2001 Figure 3-3 shows the position of the vessel during this survey. Starting approximately 1800 meters west of the diffuser array [1], the sensor package was towed towards the diffusers [2] in towyo mode. The track continued straight down the diffuser line from riser 55 to riser 30 [3]. At riser 30, the sensors were towed north (perpendicular to the diffuser line) for ~300 m [4]. The vessel turned and headed south [5] then west [6] to approximately 1000 meters due south of riser 55 [7]. At location [7], discrete water samples representative of background conditions were collected at four depths (2.4, 10.4, 21.9, and 31.4 meters). See Table 2-2 for the parameters measured in the discrete samples. After the background samples were collected, the sensors were towed back to the diffuser line [8] where short perpendicular [9] and parallel [10] tracks were conducted in the segment between risers 55 and 30 until dye began to emerge from riser 55 at 12:06 PM (EDT).

The mean background fluorescence of seawater outside the direct influence of the outfall, measured *in situ* during the vertical profile when discrete samples were collected (position [7], Figure 3-3) was 0.0291 ppb. During post-survey processing, the mean background *in situ* fluorescence was subtracted from all *in situ* fluorescence measured during the nearfield and farfield plume tracking exercises to correct for this background contribution.

The conductivity sensor failed at the beginning of the background survey and was not operational for the duration of the nearfield day. Thus, conductivity measurements were not made during the background survey or the nearfield plume tracking surveys (segment surveys and HMZ surveys).

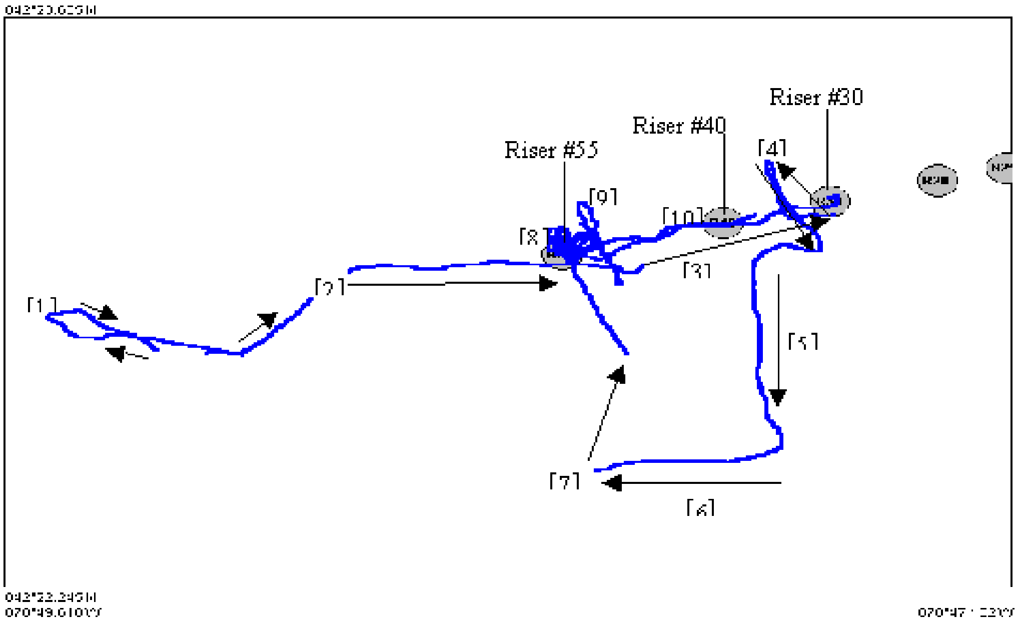

Figure 3-3. Track lines for the background survey conducted on April 19, 2001.

Beam attenuation measures the percent transmission of light over a given path length in water and is indicative of particulate concentration in the water. The two primary sources of particles in coastal water are biogenic material (plankton or detritus) and suspended sediments. Beam attenuation measured in the water column synoptically with dye fluorescence in the background station vertical profile (Figure 3-4) ranged from 0.51 to 1.0 m^{-1} (mean 0.60 m^{-1}). The particle field was relatively uniform between 1 and 28 m before increasing in the near bottom waters to slightly more than 1m^{-1} at 32 meters depth. The relatively low values reflect the low levels of particulate matter (background TSS ~0.3 mg/L, see Section 3.3.2 and chlorophyll *a* present in the bay at the time of the survey.

3.3.2 Segment Survey

Segment surveys were planned to determine the structure and position of the dye plume in the nearfield under a fixed depth-towing scenario. Each planned segment survey was designed to evaluate the dye field over a portion of the diffuser line as way of optimizing survey activities. The first planned segment survey was started ~ 45minutes after the dye began to emerge from Riser 45 and after a number of exploratory towyo transects were conducted at the west end of the diffuser line (Mansfield *et al*. 2001a). These exploratory transects were conducted from north or south of the diffuser line (perpendicular the diffuser) at fixed depths and under towyo operations while the sensors were towed. Because these surveys were conducted shortly after the dye emerged from the diffusers, the operations were concentrated along the western part of the diffuser line (the dye emerged from west to east). From the exploratory transect data it appeared that the plume field was centered along the diffuser line with little net movement to the north or south. As a result, the segment survey was conducted along the diffuser line as planned. The segment survey was composed of several oval transects conducted near a subset of the diffusers (between diffusers 55 and 47). During this segment profiling, the *in situ* sampling system acquired data from a set of fixed depths sampled in rapid succession. Information obtained by the exploratory transects and the initial segment survey suggested that modifications to the planned field design were necessary (Mansfield *et al*. 2001a). The field team confirmed this part way through the first planned HMZ survey conducted parallel to the diffuser. Thus, it was decided to refine the final HMZ transects (See Section 3.3.3).

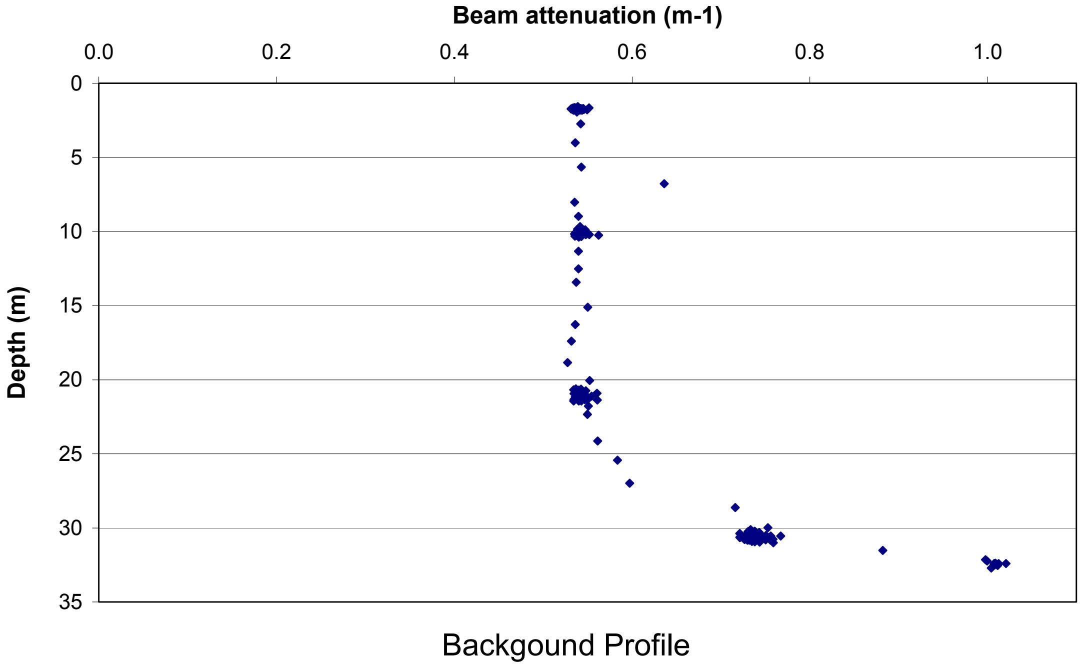

Figure 3-4. Beam attenuation versus depth at the station where background samples were collected.

3.3.3 HMZ Surveys

The goal of the HMZ surveys was to collect *in situ* data and discrete samples at the edge of the HMZ for the purpose of measuring dilution after the hydraulically-driven mixing at the diffuser was complete. Defining the edge of the HMZ in the field proved difficult because no distinct HMZ was observed in the real-time data. During the segment survey transects, including those running perpendicular to the diffuser line, no distinct dye gradient indicative of hydraulic mixing was apparent. Dye concentrations were relatively constant from 0 to 100 meters north of the diffuser line. Based on this information, the planned HMZ transect was conducted along the diffuser line from east to west (Figure 3-5). *In situ* data were acquired from the sensor towfish in the tow-yo mode from riser #10 to riser #40 along a line approximately 90 meters to the north and parallel to the diffuser line. The position (as longitude) and depth (m) of the tow fish shown in Figure 3-6 shows where the data points were collected during the tow-yo operation. The Y-axis presents depth in meters. The X-axis presents decimal east longitude. The tow-yo depths along this transect ranged between 4 and 33 meters deep. During the data acquisition, it was determined that surface light interfered with the dye recordings above 5 meters depth, consequently, these data were not included in the analysis of dye dilution. Subsequently, a small light shield was attached to the fluorometer to eliminate this problem.

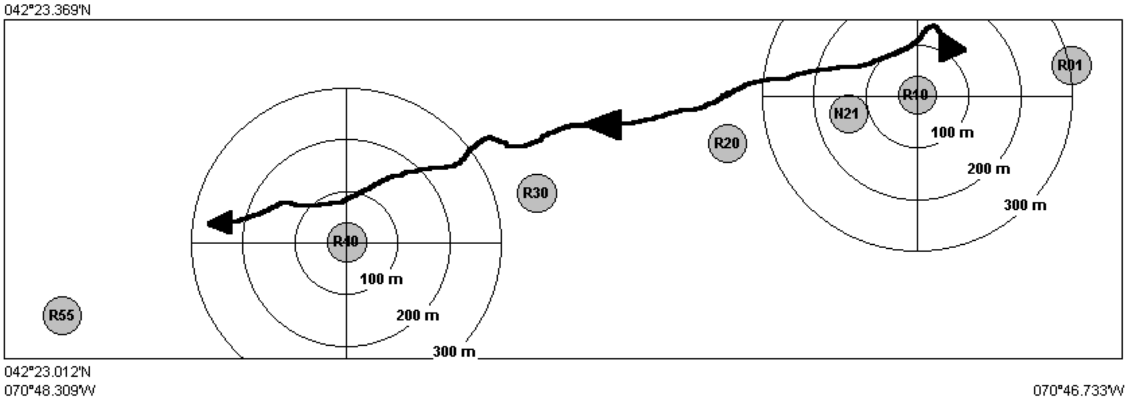

Figure 3-5. Nearfield/HMZ Survey Tow-Yo Trackline Along Diffuser Line, April 19, 2001. The vertical excursion of the towfish along the trackline is presented in Figure 3-6.

The vertical structure of the plume along the diffuser is presented in Figure 3-6. The calculated dilution data were plotted against depth and longitude using Surfer® contouring software to provide a vertical 2-D view of the plume. For this presentation, the Surfer® program interpolated the dilution data by the inverse distance to a power method across an area of 0.01° longitude (~ 820 m) by 3m depth. The core of the plume was found between 12 and 22 meters depth. At these depths, dilution generally ranged between 50 and 100, as calculated from measured dye concentrations. The highest dye concentration (~0.95 ppb) (lowest dilution) was found at –70.79382 W at 21 meters depth, where a 62.2 fold dilution was observed. Above 12 meters and below 22 meters dye concentrations rapidly diminished. The bottom edge of the dye plume was sharply defined and dye was generally not found below 25 meters of water depth. The top edge of the plume was less distinct and appeared to rise from west to east. West of –70.786 W, dye dilutions in waters shallower than 10 meters were generally greater than 100, whereas, the single towyo cycle with an excursion above 10 meters in the east half of the transect (near -70.78 W) revealed dilution between 80 and 100 at 7 – 8 meters water depth. The dye plume also became more dilute in an easterly direction; this may have been a function of the amount of dye that had been discharged (the dye first emerged from the most westerly diffuser) or differences in the vertical density structure near the eastern end of the diffuser. The failed salinity sensor on this day precludes further evaluation of the latter.

3.3.3.1 Revised HMZ dye results

In the field, the data being observed from the along diffuser transect did not appear to be addressing the need to define the hydraulic mixing zone. Therefore, the field team modified the survey design and conducted HMZ towyo transects perpendicular to the diffuser line (Figure 3-7). The perpendicular HMZ transects represented a concerted effort to follow the dye plume away from the diffuser line to determine the location of the edge of the hydraulic mixing zone (where confirmatory discrete samples were to be collected). The onboard data from the transects from HMZ1 (Figure 3-7) showed that dye concentrations in the core of the plume were fairly uniform extending from the diffuser line to as far as 400 m to the north and 50 m to the south of the diffuser line (Mansfield *et al.* 2001a).

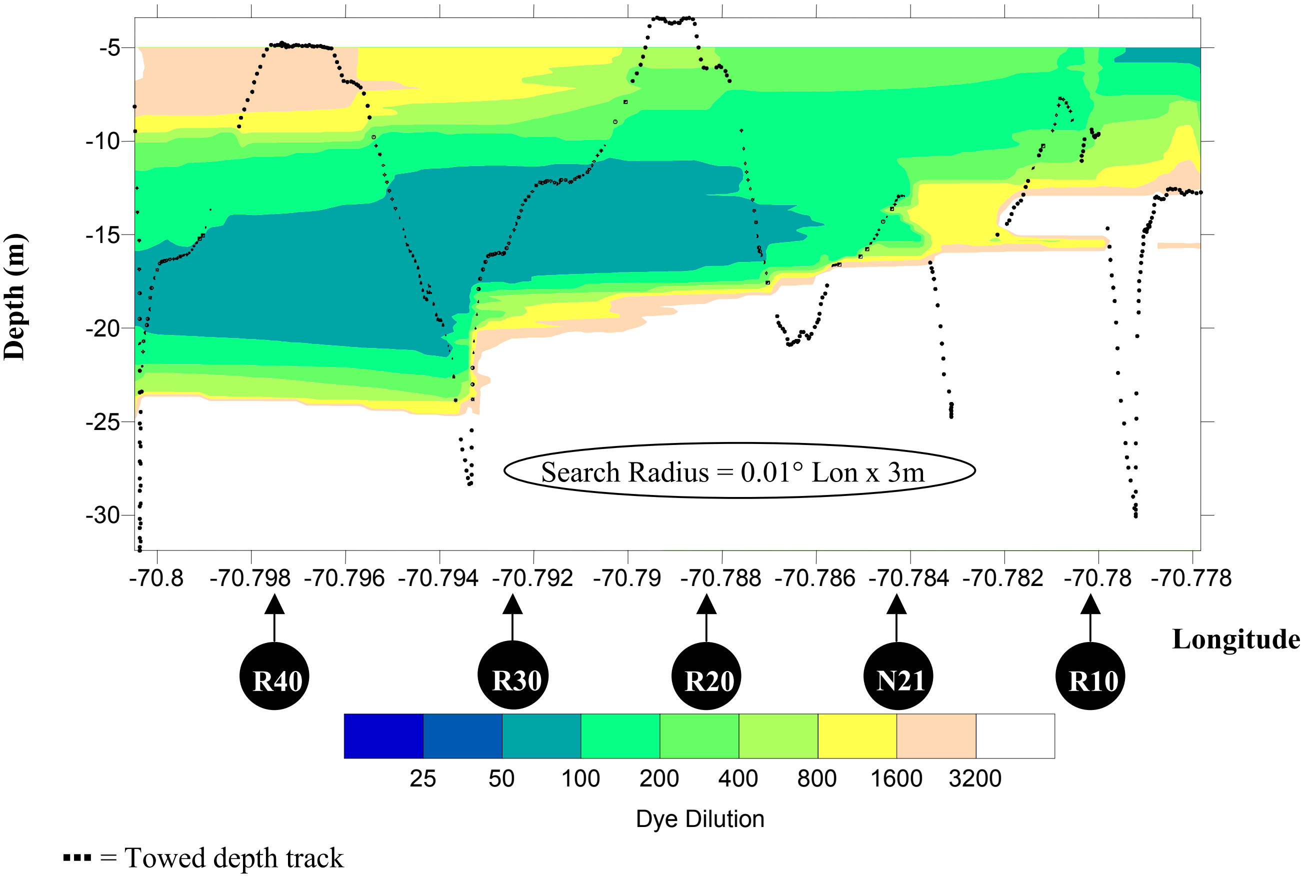

Figure 3-6. Dilution based on *in situ* dye measurements along the diffuser line, April 19, 2001 (See trackline in Figure 3-5.).

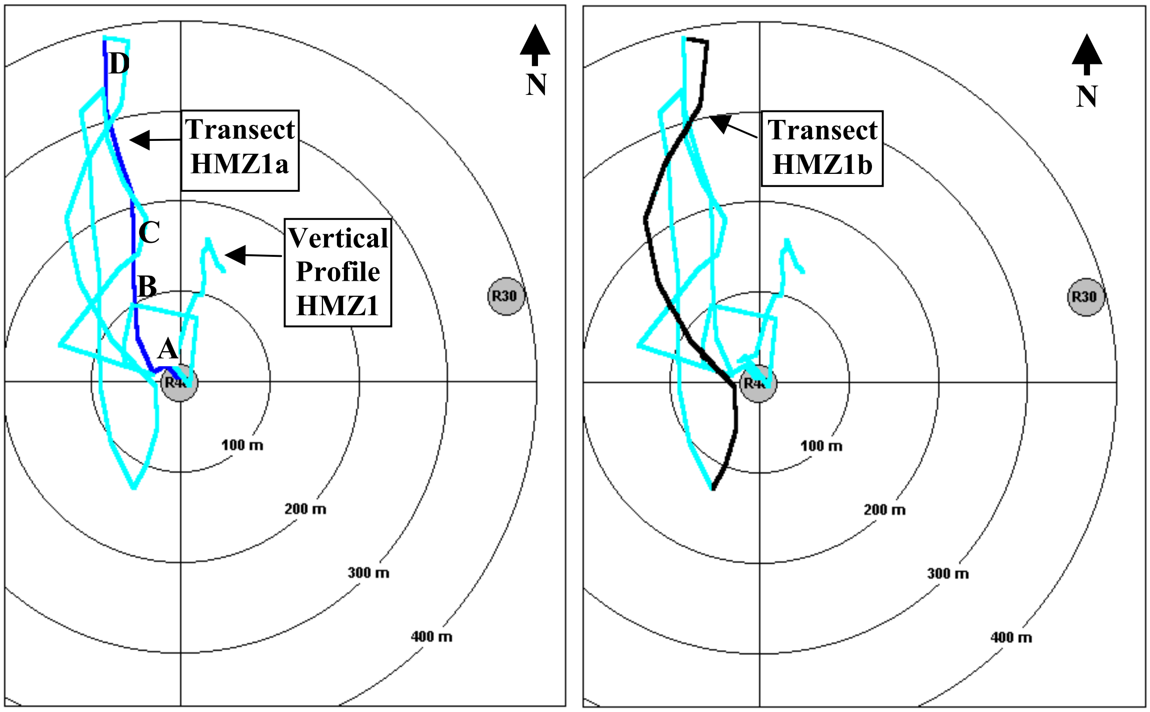

Figure 3-7. Tow-yo tracklines conducted perpendicular to diffuser line from the modified HMZ surveys on April 19, 2001.

The dilution data from HMZ1 were plotted with Surfer® contouring software to provide a 2-D view of the plume. Data from two tracklines (HMZ1A and HMZ1B in Figure 3-7) were contoured. The vertical contour of estimated dilution north of the diffuser line from trackline HMZ1A is presented in Figure 3-8. In Figure 3-8 dilution data was interpolated across an area 100m by 3m depth by the inverse distance to a power method. The core of the plume was observed between 12 and 23 meters depth as observed along the diffuser transect. Viewed in another manner, the individual data points for dilution, depth, and position (as distanced from the diffuser) are presented for tracklines HMZ1A and HMZ1B in Figure 3-9 and Figure 3-10, respectively. The southerly extent of the dye plume was found ~ 70 meters south of the diffuser. The highest dye concentration (lowest dilution) was found on transect HMZ1A approximately 10 meters north of the diffuser line where a 56.5 fold dilution was observed at 30 meters water depth. These figures show that dye dilution in the plume core slowly increased in a northerly direction, away from the diffuser line. The data from trackline HMZ1B is particularly demonstrative of this slow increase in dilution as the transect was conducted at a constant tow depth between ~50 m and 300 m north of the diffuser line. Within ~25 m of the diffuser, dilutions generally range from 60 to 70, whereas about 250 meters to the north minimum dilutions of 100 were consistently found.

The HMZ1B data were particularly interesting in that along the transect, the minimum observed dilution in the core of the dye field at constant depth appear to change systematically with distance from the diffuser line. Assuming a constant effluent flow rate and dye concentration and ~6cm/s northward movement of the water column (see Section 3.5), the data were used to estimate the rate of dye dilution as a function of distance from the diffuser. To derive this relationship dilutions that were greater than the minimum were removed from the regression (Figure 3-11). The higher observed dilution values likely reflect local heterogeneity in the dye field related to merging of dye from the risers. The linear fit of the retained data show a high correlation ($r^2 = 0.98$) of dilution with distance from the diffuser line. The slope of the regression is 0.128 dilution/m with an intercept of 76. On a dye concentration basis, the rate of change with distance was 0.00082 ppb dye per m ($r^2 = 0.97$) and the intercept was equal to 0.77 ppb dye. These data suggest that the dispersion of the plume after initial mixing was relatively rapid with a loss of 0.44 ppb dye 400 m from the diffuser. This is a reduction of 57% of the dye concentrations relative to the values measured after initial mixing.

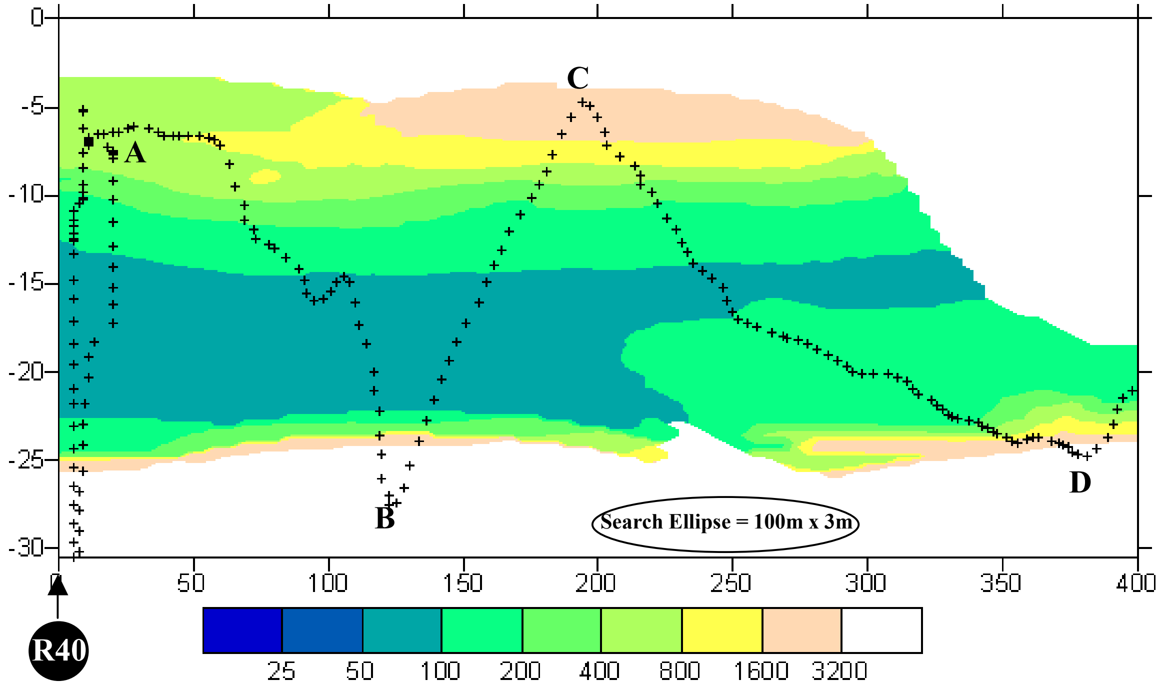

Figure 3-8. Vertical structure of calculated dilution perpendicular to the diffuser line, transect HMZ1A April 19, 2001 (See trackline in Figure 3-7). Dilution calculated from *in situ* dye measurements. The Y-axis presents depth in meters. The X axis distance to the north from the Riser #40 (m).

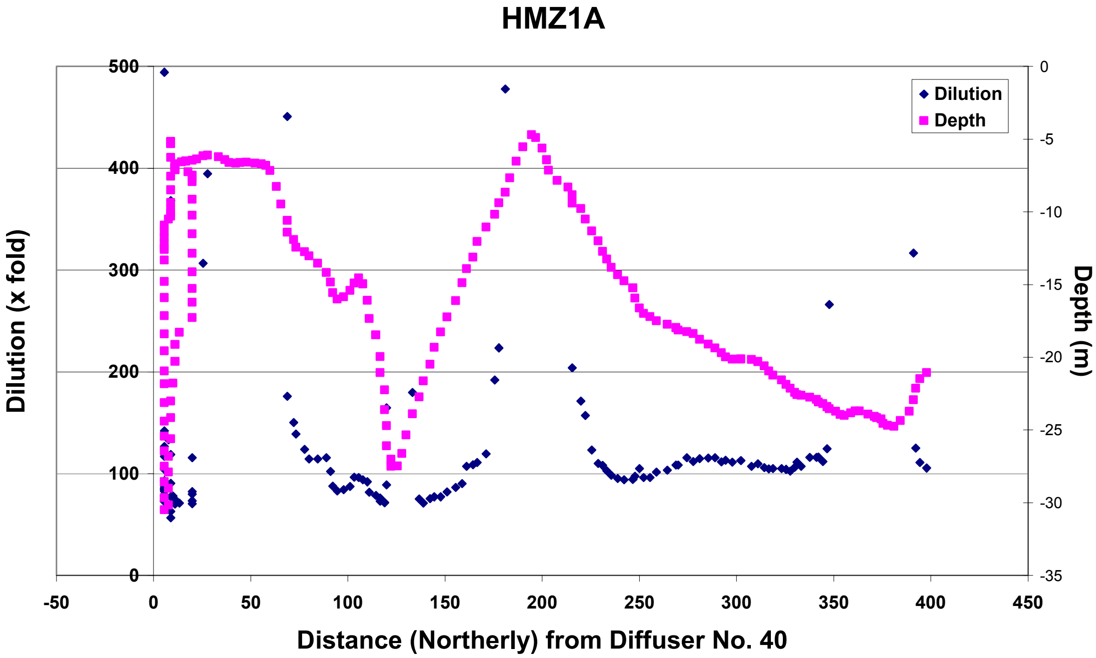

Figure 3-9. Dye dilution and depth, Transect HMZ1A, April 19, 2001.

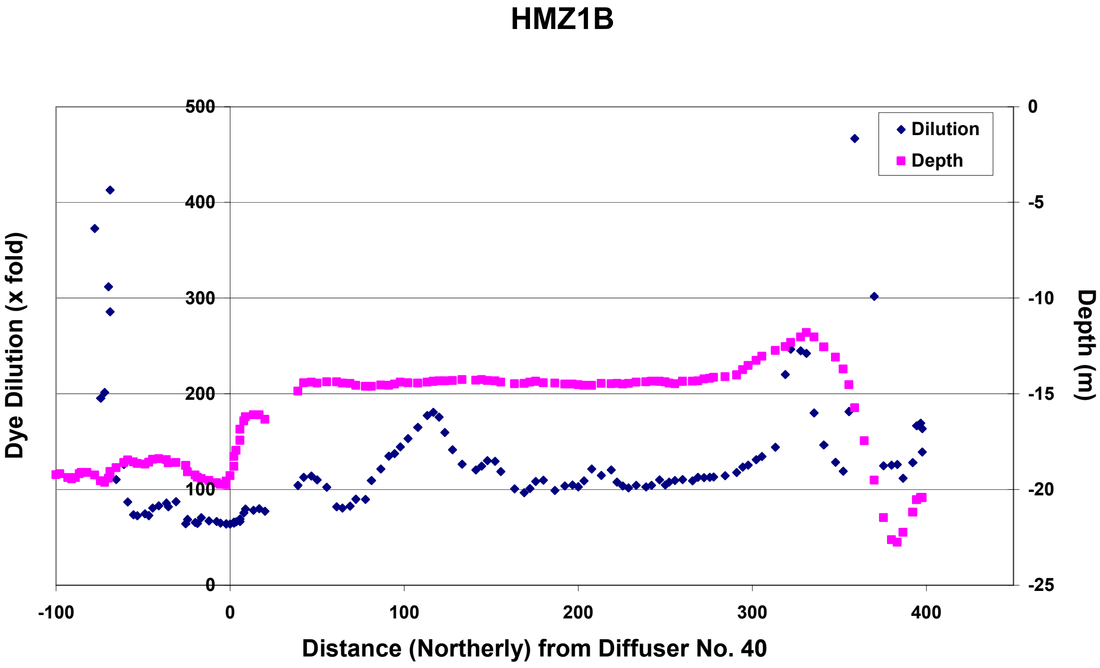

Figure 3-10. Dye dilution and depth, Transect HMZ1B, April 19, 2001.

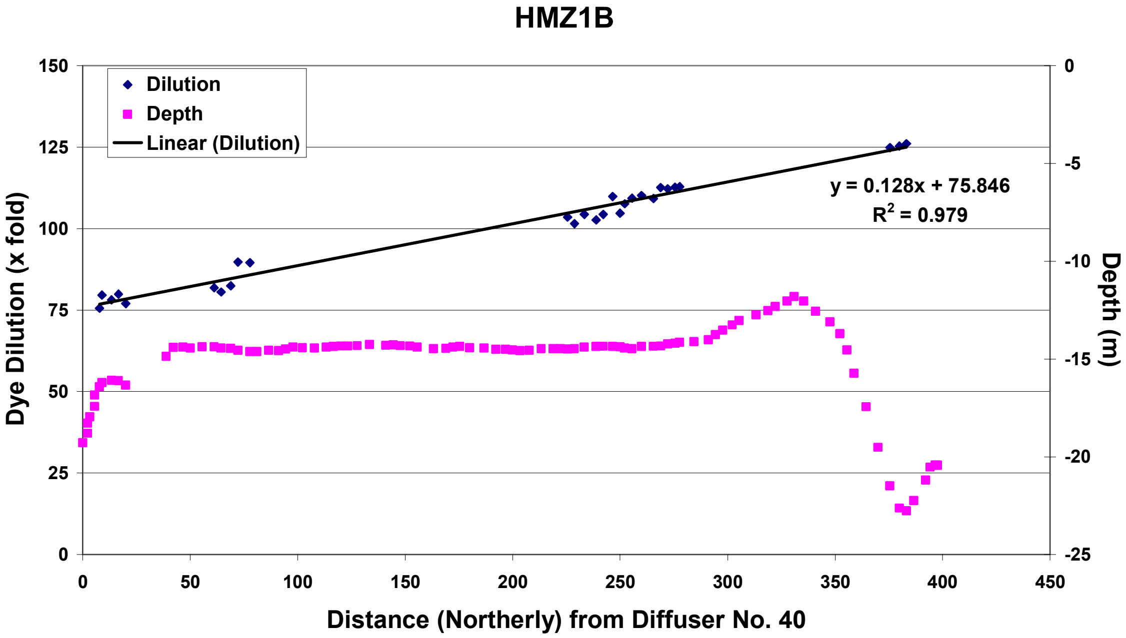

Figure 3-11. Change in minimum dilutions at constant depth as a function of distance from the diffuser line observed along the HMZ1B transect.

Based on the field data from these and other transects conducted on April 19th, a position approximately 125 meters north of riser #40 was chosen for vertical profiling and discrete sampling (see Vertical Profile position for HMZ1, Figure 3-12). While the vertical profile associated with HMZ1 was not conducted during either the HMZ1A or HMZ1B transect operations, the characteristics of the plume at this distance from diffuser #40 can be derived using the data from these transects. Dilution based on the fluorescence of the water samples collected at 11, 15 and 20 meters depth clearly fit onto the dilution curves for the HMZ1A and HMZ1B transects at dilutions of ~85. While this post-survey analysis shows that the vertical profile and discrete sampling could have been conducted closer to the diffuser line, this was not apparent from the real time data. Because a distinct dye gradient was not found at any distance from the diffuser line, the location 125 meters north was selected to ensure that the samples were taken outside the HMZ (e.g., dye concentrations were not rapidly changing). This was clearly achieved as the samples in the core of the dye plume were collected at a dilution of ~90 and show the samples are representative of the dye plume outside of the HMZ.

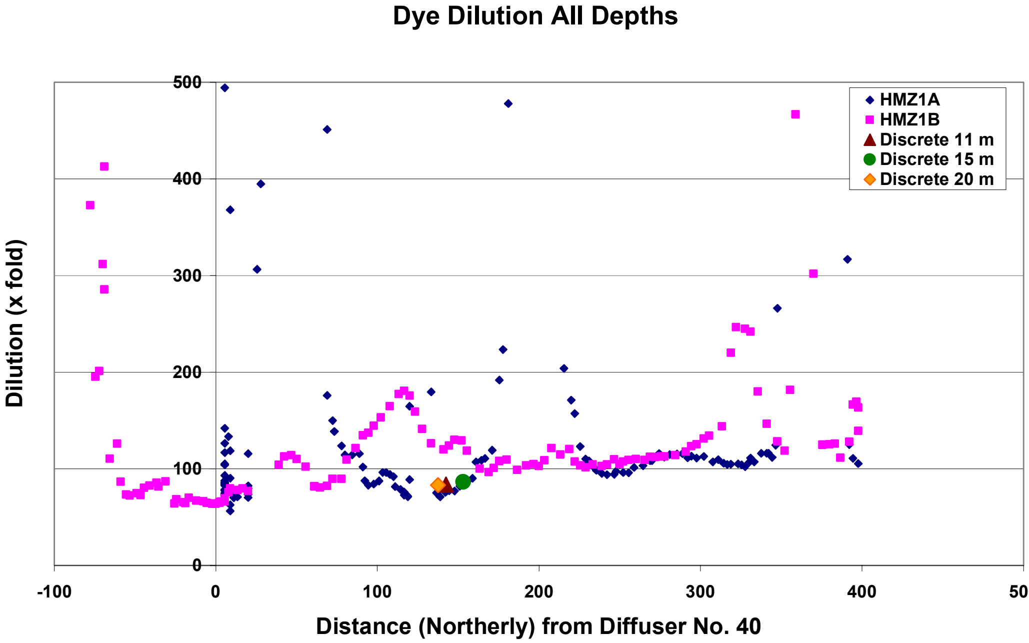

Figure 3-12. Dye dilution in the core of the effluent plume (14 – 22 m depth) along transects HMZ1A and HMZ1B and at points of discrete sample collection from the vertical profile obtained during HMZ1. The locations of discrete sample collection (depth and distance from diffuser # 40).

A second HMZ sampling (HMZ2) was conducted near riser #10. This location was selected to capture the properties of the plume and HMZ at the eastern end of the diffuser line. Tow-yo operations were not conducted at this HMZ. Rather the tow fish was used to locate the core of the dye plume and the sensor suite towed at a fixed depth to a location ~80 meters north of the riser where vertical profiling was conducted and water samples collected for measurement of the ancillary parameters including bacterial indicators (see Section 2.1.2). The dye dilution observed at this station was lower than observed during HMZ1, which is consistent with the higher dilution observed along the eastern end of the diffuser in Figure 3-6.

3.3.3.2 Water Clarity during revised HMZ surveys

The impact of the discharge on water clarity in the immediate vicinity of the diffuser is shown in Figure 3-13. The beam attenuation is shown as a function of depth at the background station located south of the diffuser and from the background towyo's conducted in the vicinity of the outfall prior to dye emergence (see Figure 3-3 for the tracklines) is shown. The background data is relatively homogeneous (0.54 ± 0.01 m^{-1}) from the surface to 28 m before increasing to approximately 1.0 m^{-1} at 32 meters depth. In contrast, the beam attenuation near the diffuser shows large number of points between the surface and 28 meters that are higher than at the background station and range up to ~0.9 m^{-1}. Note also the large number of data points that overlap the background data. Recalling that these tracklines were conducted both within and without the effluent plume, the high beam attenuation data are indicative of the particle field resulting from the effluent discharge. Note further that the beam attenuation below 32 m depth near the diffuser is similar to that at the background station.

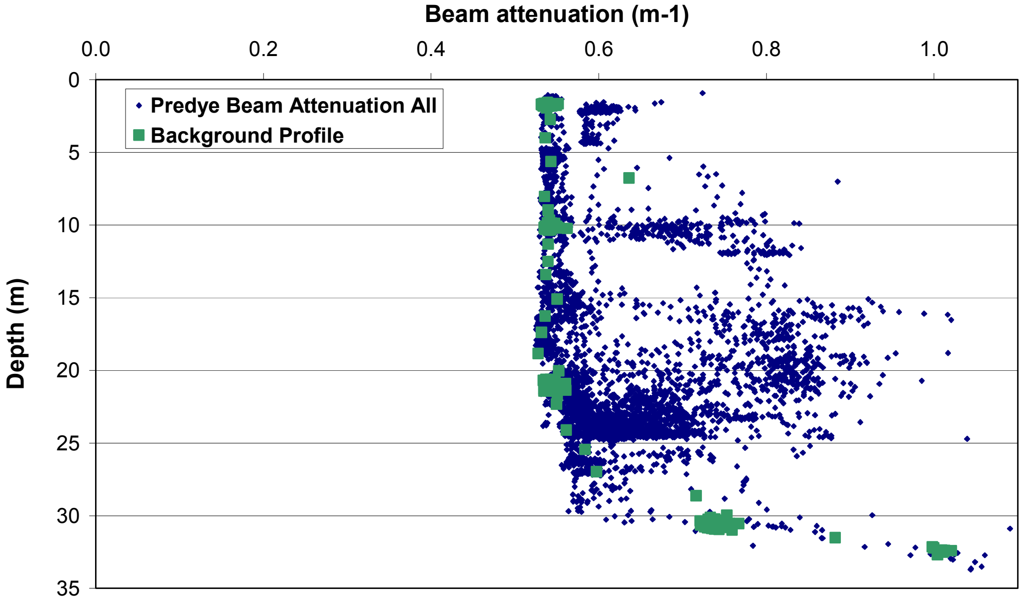

Figure 3-13. Water clarity in at the background stations and in the effluent plume prior to dye emergence.

A similar range in beam attenuation (0.55 to 0.95 m^{-1}) was observed on the HMZ surveys. However, the dye provided an additional way to evaluate these data and to place the observations in context of the diluting effluent. In Figure 3-14, the beam attenuation from HMZ1A and HMZ1B are plotted as a function of dye concentration. An increase in water clarity (decrease in beam attenuation) with increasing dye dilution is clearly observed. Beam attenuation values for MHZ1A returned to values close to the mean background level above 28 m depth (0.57 m^{-1}) at dye concentrations of about 0.1 ppb (dilution of ~ 500 fold). These dye values were measured 400 to 500 m from the diffuser line. Note that most of the increase in water clarity is completed at dye concentrations of ~ 0.2 ppb (see Figure 3-14). The data from the HMZ1B showed a similar decrease in the relationship between dye concentration and beam attenuation, although the particle field appears to split into two distinct the relationship. One set of data falls directly on the results from HMZ1A, while another set of points that are associated with dye concentrations between 0.05 and 0.5 ppb shows a slightly higher beam attenuation. Examination of the dye and beam attenuation data (Figure 3-15) shows that this set of points is from south of the diffuser where dye readings are low, yet beam attenuation values are high. These data suggest these data were obtained in an area that had pre dye effluent, thus reflect the high particles but low dye concentrations. The linearity in the beam attenuation versus dye data suggest that rapid removal and settling of the particles is not occurring, otherwise substantial curvature in the plot, indicative of nonconservative processes, would be evident in the plot.

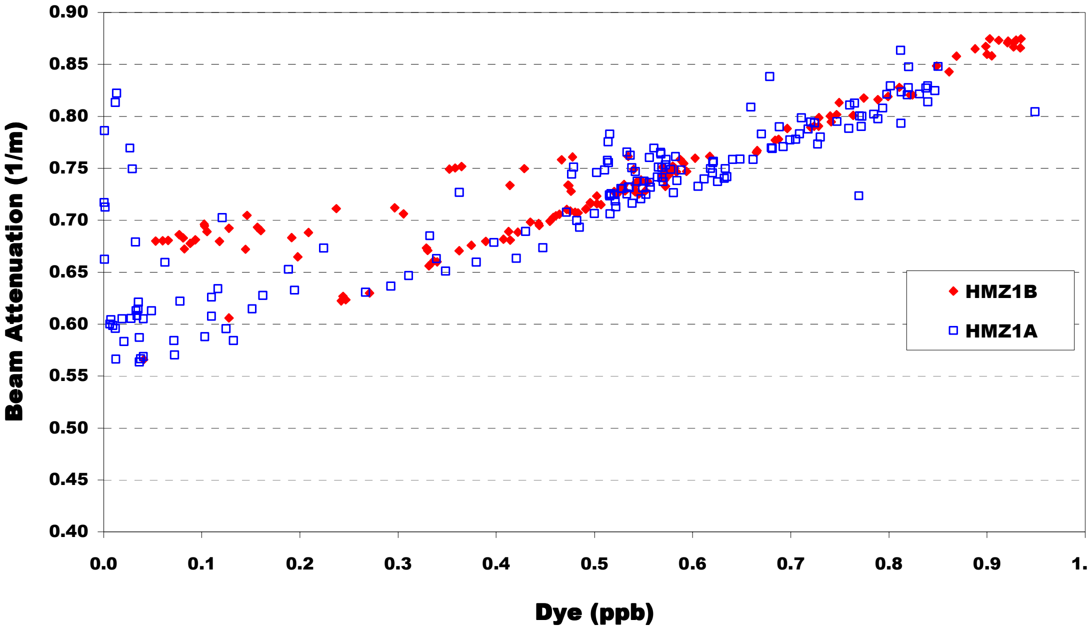

Figure 3-14. Beam attenuation (m^{-1}) versus dye concentration for transects HMA1A and HMZ1B. The mean background beam attenuation from background survey above 28 m water depth was 0.57 m^{-1}.

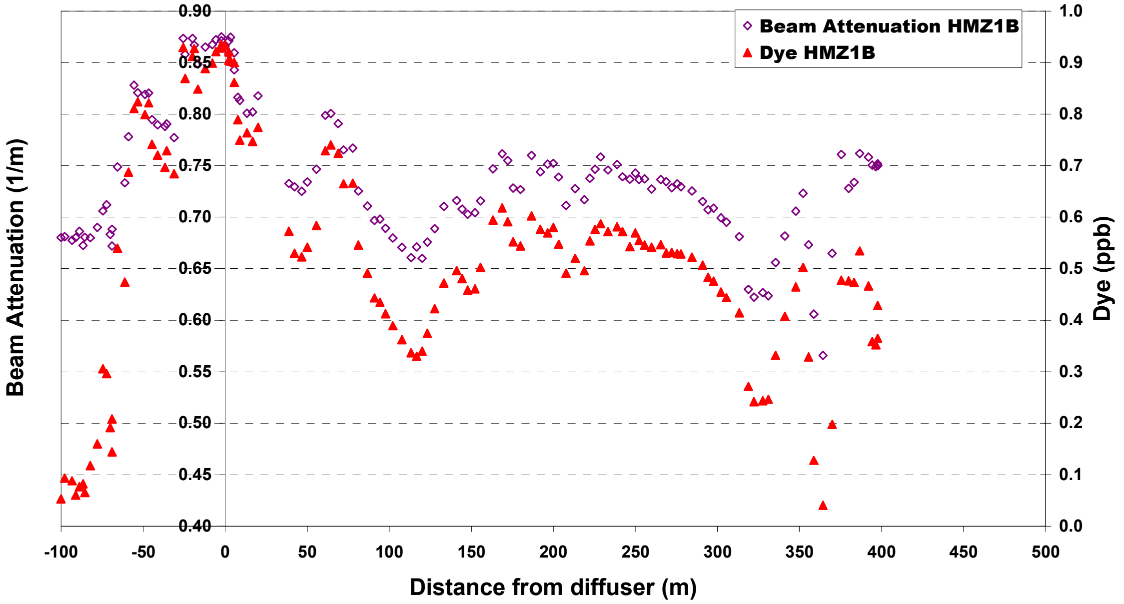

Figure 3-15. Comparison of *in situ* dye and beam attenuation data for as a function of distance from the diffuser during HMZ1B.

The *in situ* transmissometry and dye data collected during the transit from HMZ1 to HMZ2 were examined in a similar manner (Figure 3-16). The data show a correspondence between transmissometry and dye concentration that appears to fit two relationships. The transmissometry data between 2 and 130 m north of the diffuser line decrease as dye concentration decreases. The pair values at the high and low ends of the correspondence are similar in values observed in the HMZ1 data. For example, 0.9 ppb dye concentrations have corresponding beam attenuation data of ~ 0.85 m^{-1} and the limited set of dye at ~0.2 ppb has an associated transmissometry of ~0.6 m^{-1}. In contrast, the data from the HMZ transect run to the north of the diffuser line had higher transmissometry (0.70 to 0.75 m^{-1}) for dye concentrations ranging between 0.1 and 0.6 ppb. The data clearly show differential responses which can only be ascribed to dyed effluent discharging into previously discharged effluent (e.g., into waters with relatively high turbidity). Plotting the HMZ2 transect data (Figure 3-17) amplifies this point. On this transect low dye concentrations found between 40 to 120 m north of the diffuser did not show decreasing transmissometry as observed in HMZ1. Possible explanations are that the lower dye represents the interface between the dyed and previously discharged undyed effluent or that the dyed effluent is in fact mixing into remnant effluent discharged before the dye was added. The data suggest the former, however, a definite explanation cannot be drawn from the available data. One last confounding factor may be the current field at the time of sampling. Figure 4-1 in Section 4.0 suggests the current field was changing in the hour immediately preceding the sampling, which also could have caused local variation in the dye and turbidity fields, confounding the ability to identify clear causes. These potential reasons are further explored in Section 3.4.2.

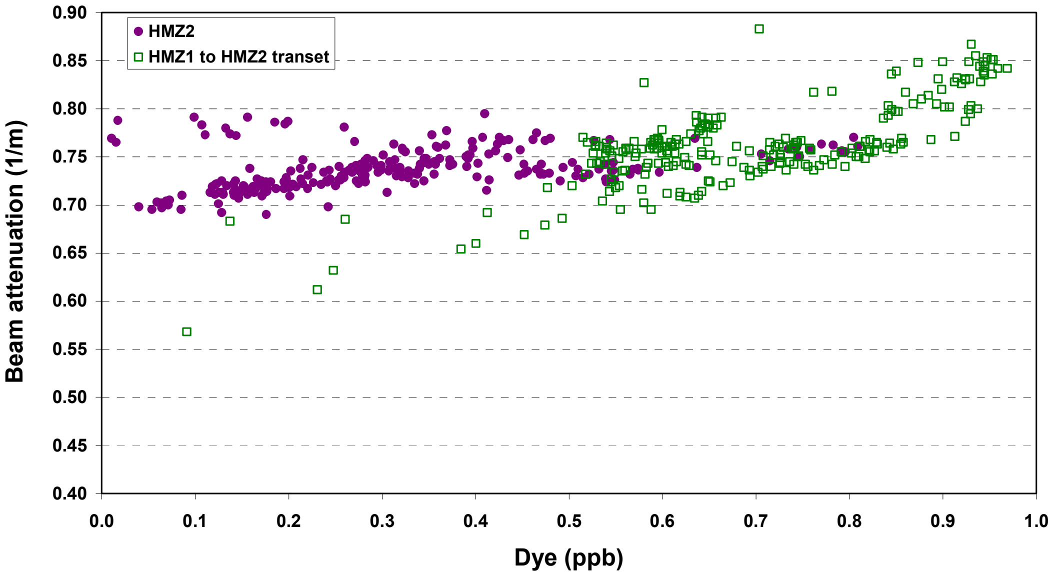

Figure 3-16. Beam attenuation (m^{-1}) versus dye dilution from the transect between HMZ1 and HMZ2 and from the HMZ2 transect.

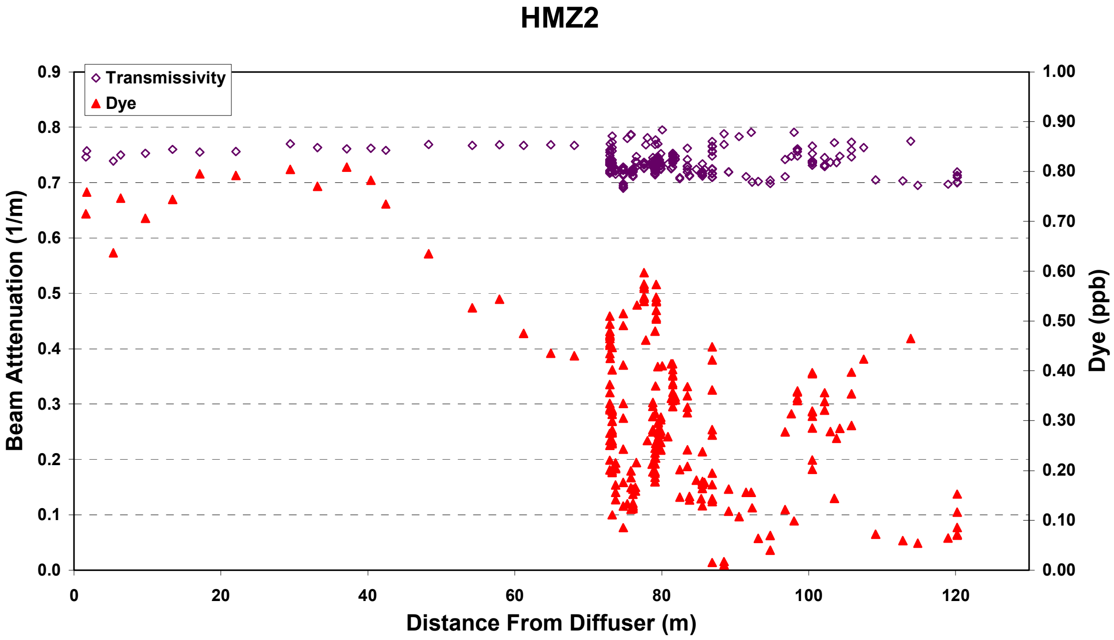

Figure 3-17. Comparison of *in situ* dye and beam attenuation data for as a function of distance from the diffuser from the HMZ2 transect.

From previous studies (Libby *et al*. 2000), it is known that the beam attenuation provided a good indication of the effluent field in the Bay. The data from the plume tracking survey reaffirm this finding and suggest *in situ* turbidity measurements, at least under the conditions evaluated during this survey, can document the plume excursions within a few hundred meters of the diffuser.

3.3.4 Farfield Survey

The objective of the farfield survey was to determine plume structure and behavior in the Farfield by tracking the spread of the dye to dilutions of at least 1:1000.
At the end of the nearfield day a satellite-tracked drifter, with drogue depth set at a depth of 15 meters, was deployed at approximately 60 m due north of riser #14 (42° 23.301'N 70° 47.121W). At the start of the farfield day, the vessel followed the drifter signal and located the unit 1.25 nmi north of the diffuser array. Using the drifter location to initiate survey activities, towyo transects were conducted to define the physical extent of the dye plume one day after the dye entered the offshore environment (Figure 3-18). The first trackline, run perpendicular to the diffuser line, was continued until the dye was no longer detected (~3 nautical miles to the northwest of the diffuser array). After this, perpendicular and parallel tracklines were run in and out of the plume field. The farfield tracking operations shown in Figure 3-18 comprised over 8 hours of towing. The drifter continued to provide positional information on drift of the plume throughout the survey.

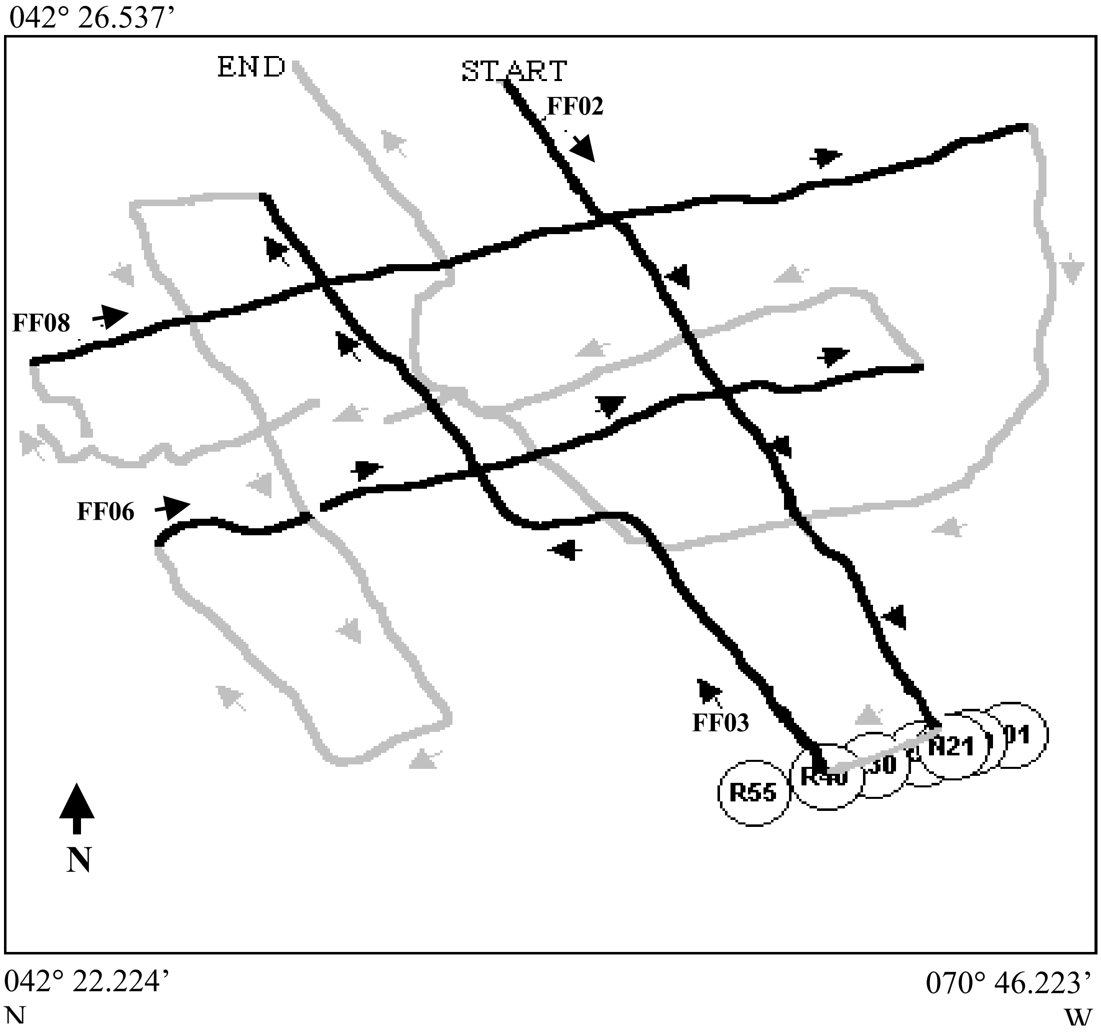

Figure 3-18. Farfield survey transects, April 20, 2001.

A depiction of the aerial extent of the dye plume surveyed on the farfield day is presented in Figure 3-19. In visualizing the extent of the plume, the location and dilution of the two maximum dye values observed in each towyo cycle (maximum values from each the peak to valley and valley to peak half-cycles) were plotted in 2-D using the Surfer® contouring software. The dilution contours result from the interpolation of the maximum values using a 0.01° Lat by 0.01°Lon search pattern and the inverse distance to a power gridding method.

The overall plume field was approximately 3.8 nmi miles across in an east-west direction and 3.1 nmi in a north-south direction. During the day of tracking operations, there appeared to be some dispersion of the plume as well as a net movement of the plume field towards the north.

These two factors made it difficult to completely capture the northern extent of the plume boundary at any given time, as shown in Figure 3-19. Two areas of relatively high dye concentration were observed; one near the center of the plume approximately 2 nmi northwest of the diffuser and one northeast of the first center, approximately 3 nmi north of the diffuser. Minimum dye dilutions within these areas ranged from 100 to 200 fold. The tidal oscillation during dye discharge (Figure 2-1) and later observed in the drifter movement throughout the survey may have contributed to the splitting of the core of the plume.

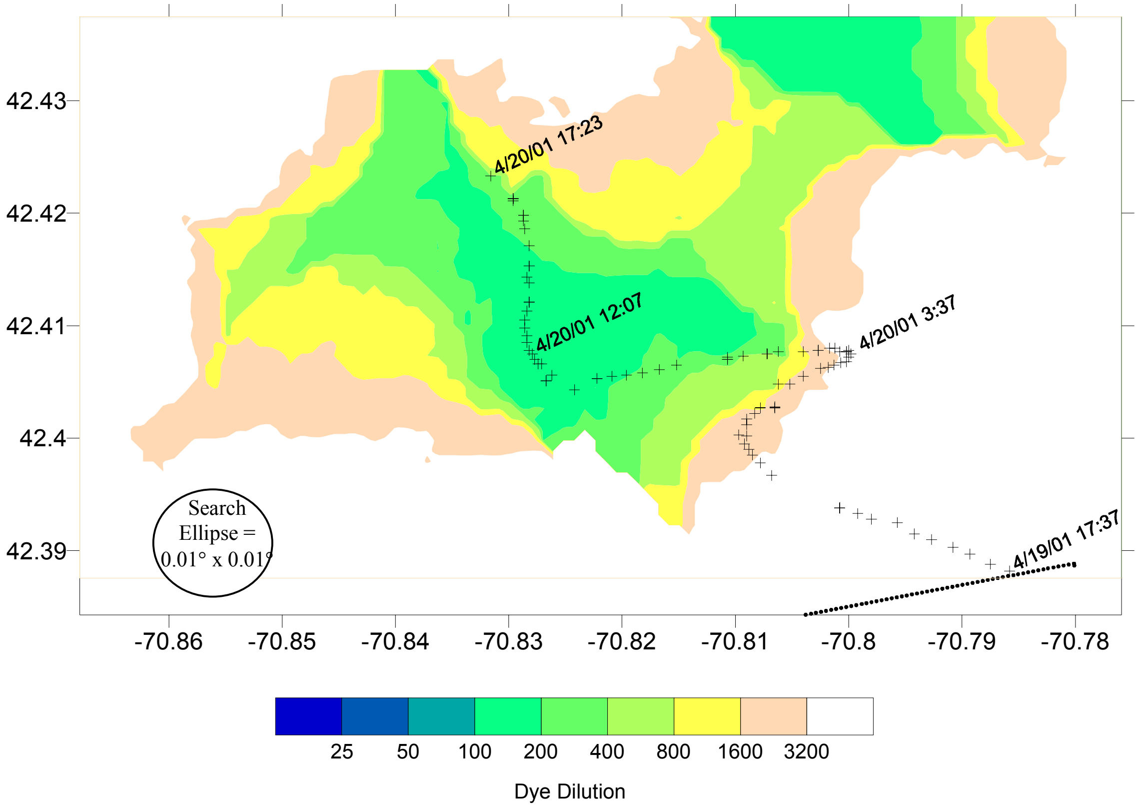

Figure 3-19. Dye plume boundaries measured during Farfield Survey, April 20, 2001. The dilutions shown are calculated from the highest dye concentrations observed during towing operations. The drifter position from the time of deployment at the end of the nearfield day to time of retrieval at the end of the farfield day, presented as a series of +'s, shows general movement of the water to the northwest. The MWRA diffuser line is shown in the lower right corner of the figure.

The vertical dimensions of the dye plume along four of the farfield transects, transects FF02, FF03, FF06, and FF08, are presented in Figure 3-20 and Figure 3-21. The location of each of these transects is presented in Figure 3-18. As with the nearfield data, the calculated dilution data were plotted against depth and longitude or latitude using Surfer® contouring software. The search radius for each data set is shown on the figure.

Figure 3-20 and Figure 3-21 show that, generally, the dye plume had not dispersed into waters above 9 m or below 26 m depth. Although there were exceptions, above 10 and below 26 meters dilutions generally exceeded 3200 fold, beyond which the dye signal could not be seen above the background. The core of the plume, defined here as dye dilution less than 200 fold, was more constrained vertically. Dilutions less than 200 fold were not observed in waters less than 10.8 meters or greater 23.8 meters depth (Table 3-3). The minimum dilution found in the farfield was 96.9 at a water depth of 19.6 meters. This dilution is similar to that seen within ~300 m of the diffuser line during the HMZ1 and indicates a slow dispersion of this portion of the plume relative to the other observed farfield data.

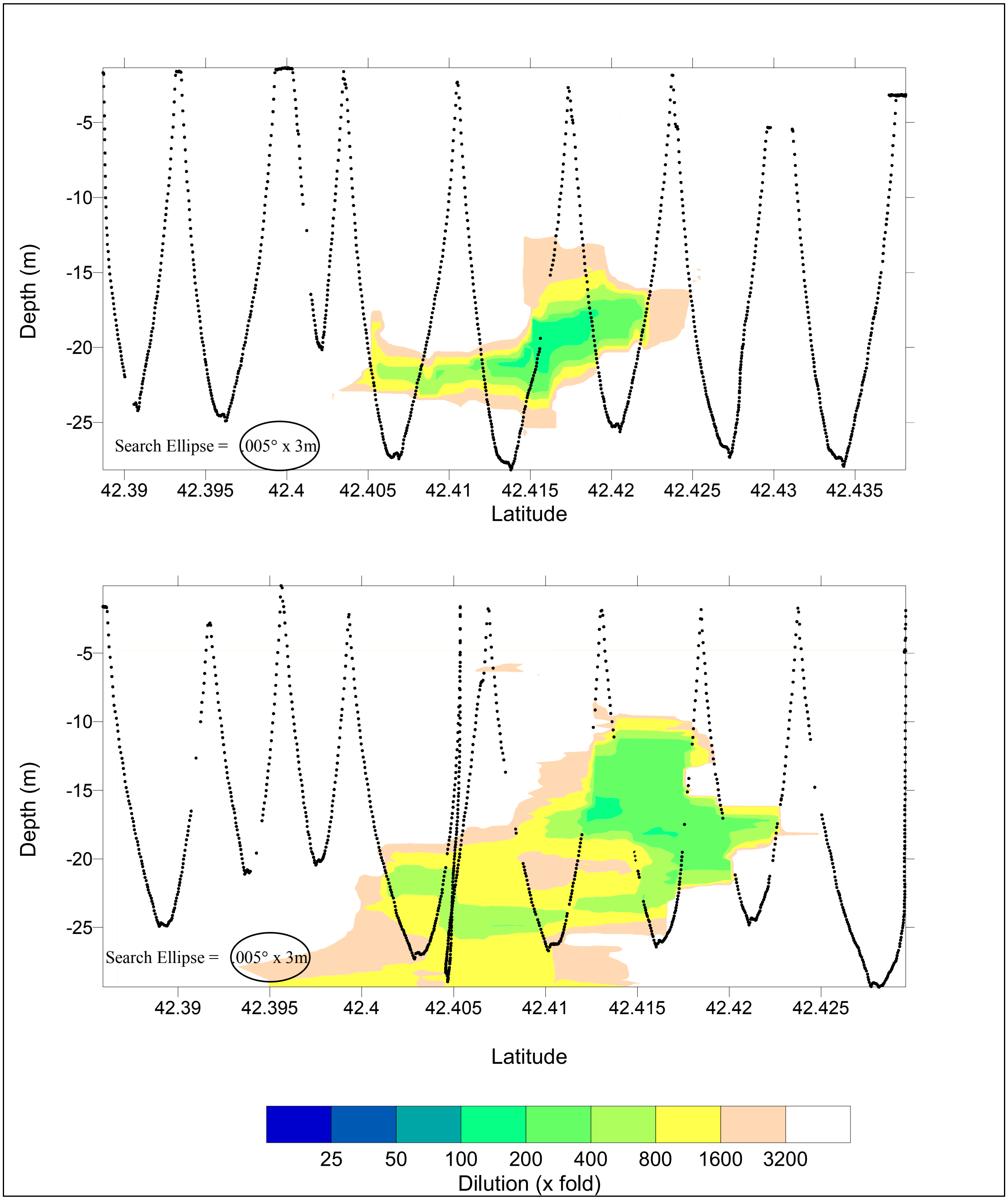

Figure 3-20. Vertical Structure of Calculated Dilution, Farfield Survey North-South Transects FF02 (top panel) and FF03 (bottom panel). See trackline in Figure 3-18. Dilution calculated from *in situ* dye measurements.

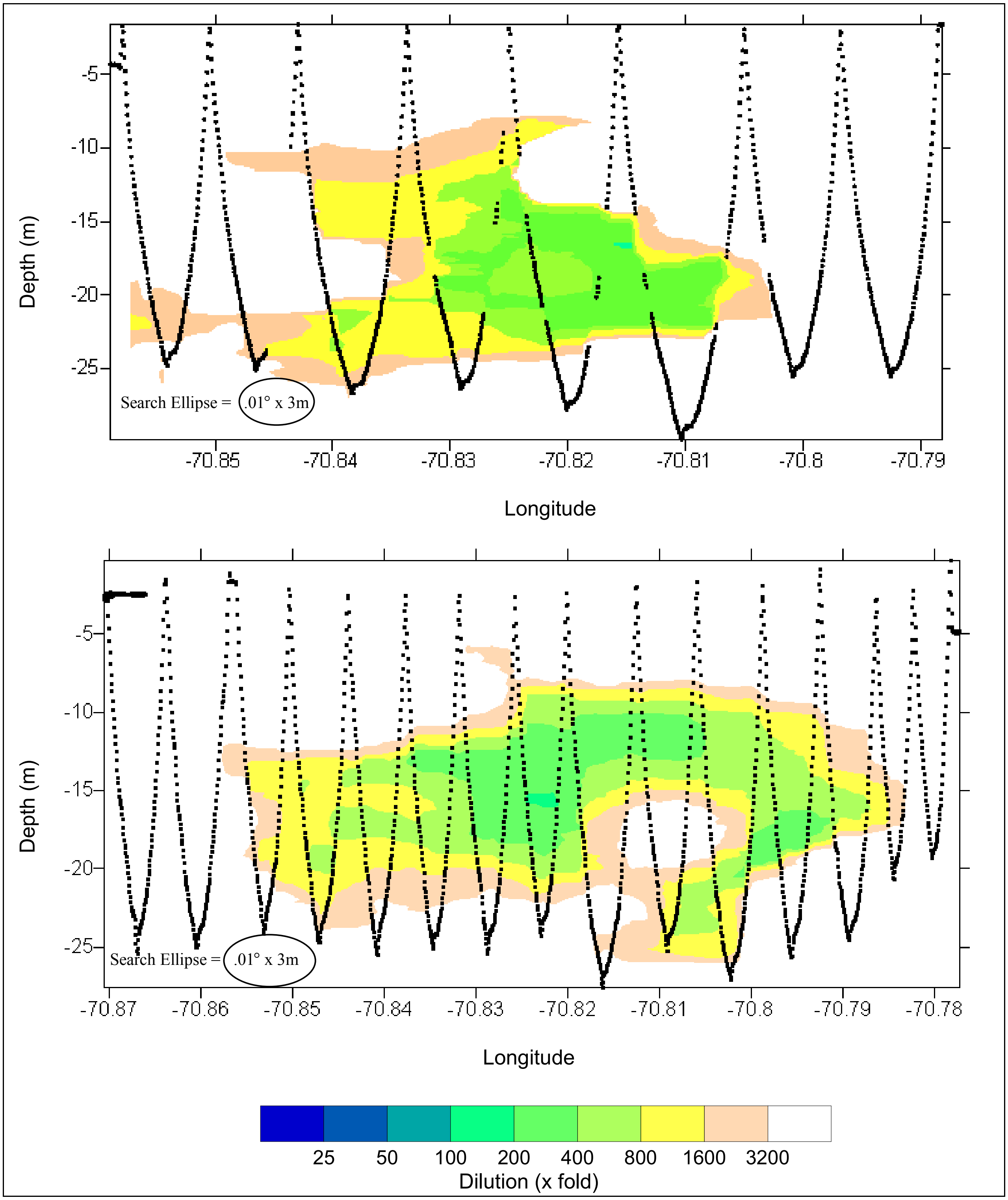

Figure 3-21. Vertical structure of calculated dilution, Farfield Survey East-West Transects FF06 (top panel) and FF08 (bottom panel). See Trackline in Figure 3-18. Dilution calculated from *in situ* dye measurements.

Table 3-3. Summary of key dye observations from farfield transects FF02, FF03, FF06, and FF08.

Farfield Transect	Minimum Dilution Observed		Observations Where Dilution <200x		
	Value	Depth (m)	n/total observations	Depth Range (m)	Median Depth (m)
FF02	83.8	5.33	28/1176	5.3 – 21.6	20.8
FF03	96.9	19.8	53/1254	12.7 – 23.8	17.6
FF06	120.6	19.2	62/1125	11.6 – 23.3	17.6
FF08	139.7	19.0	56/1805	10.8 – 20.8	16.7

Beam attenuation data from the farfield surveys were plotted against dye concentration to determine if the relationship differed from that observed in the during the HMZ surveys. Of particular interest is whether there was differential behavior of the dissolved and particulates in the effluent. For example, assuming the dye is conserved over a 24-hour period, beam attenuation would be lower for a given dye concentration if a significant amount of suspended matter settled to deeper waters over the same 24 hours (Figure 3-22).

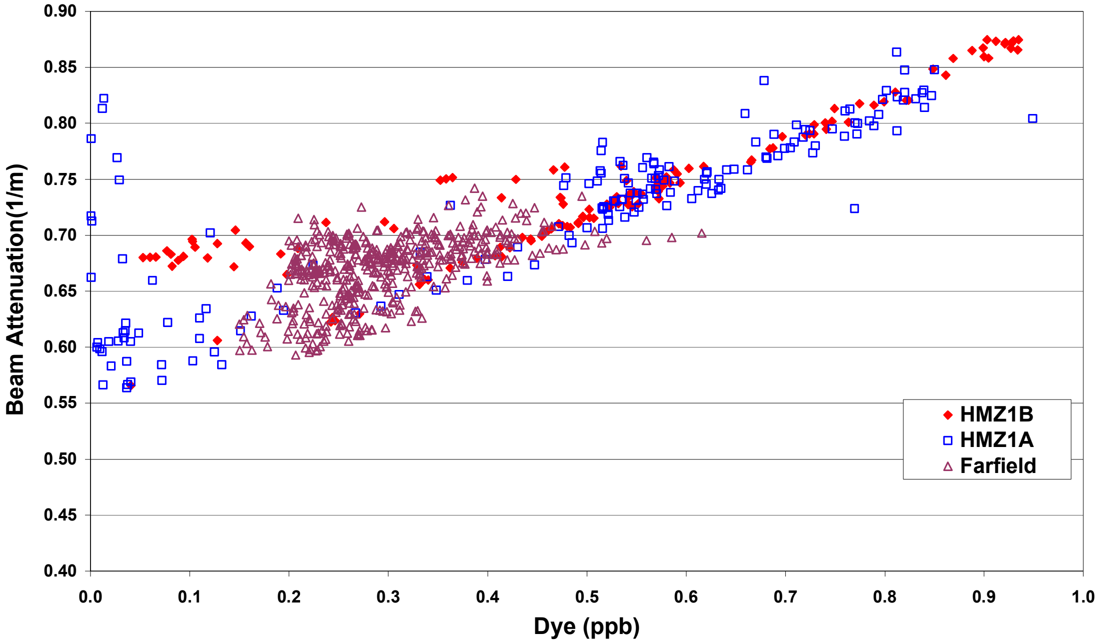

Figure 3-22. Beam attenuation (m^{-1}) versus dye dilution, nearfield (HMA1A and HMZ1B) and farfield (FF02, FF03, FF06, FF08) transects. Mean background beam attenuation at depths above 28 meters was 0.57 m^{-1} (range 0.51 to ~1.0 m^{-1}).

In general the beam attenuation during the farfield survey was lower than the previous day and the decrease is consistent with the higher dilutions observed during the farfield day. The beam attenuation ranges between 0.60 and 0.70 m^{-1} at dye concentrations of 0.2 to 0.5 ppb (equivalent to dilutions between 100 and 300). This set of values is consistent with the values observed at dilution greater than 300 from the HMZ1 studies. The transmissometry data tend to spread over a broad range at dye concentrations between 0.2 to 0.3 ppb, and possibly show a split along the two responses observed between HMZ1A and HMZ1B. If so the data suggests that the dye field in the farfield may have been mixing with pre-dye effluent. Further farfield studies conducted over greater spatial and temporal scales are required to validate this speculation.

In Section 3.3.3.2 the nearfield data were interpreted to be responding in a conservative manner. Using a similar logic with the caveat of the dyed effluent mixing with waters having an effluent background signal, differential behavior of the particles relative to the dye were not apparent in the farfield data. Thus, settling of the particles from the outfall over 24 our time frames is not apparent in the data obtained from this survey. However, there is one possible exception to this observation. Close examination of Figure 3-22 shows a set of beam attenuation data at the highest dye values measured in the farfield that were less than values in any corresponding nearfield dye levels. This suggests in the core of the plume that some settling may have been occurring. Unfortunately, very few of the farfield data showed dye levels this high and the data are too limited to draw definitive conclusions.

3.4 Discrete Sample Data

The discrete sample data obtained from the effluent and offshore environment provide information on effluent characteristics and the dilution at the outfall. The samples collected from the effluent provide information on the characteristics of the effluent and variability of these parameters in the effluent over the dye addition period, and establish the concentrations in the effluent by which additional dilution calculations can be made. The offshore discrete sample data provide information on concentrations of the selected parameters away from the direct influence of the plume (background) and within the plume after initial dilution is complete. Background measurements were required to enable adjustment of the concentrations measured in the plume for background conditions when estimating dilution (e.g., metals, nutrients). These background samples also provide limited data for comparison to historic data for parameters not routinely measured under the MWRA ambient monitoring program (e.g., selected metals) or that are not measured during initial mixing (nutrients, TSS, bacterial indicators). These data, coupled with the dye study enables extrapolation of the dye results to other water quality measures and evaluating whether federal marine water quality standards are exceeded.

The study design also included an inter-laboratory comparison of standard-oceanographic methods to EPA-approved methods for ammonia, phosphate, and TSS in the MWRA effluent. These measurements were performed by University of Rhode Island’s Marine Ecosystems Research Laboratory and the MWRA central laboratory.

This section first examines the results of discrete samples in the effluent and the laboratory inter-comparison. The ambient offshore results are then considered. The background data are compared with historical data, while the data from within the effluent plume are compared with federal and state water quality standards. The last section presents estimates of dilution based on nutrients and metals and compares these to estimates derived from the dye addition.

3.4.1 Effluent Discrete Sample Results

In general, the effluent data obtained from the discrete samples during the dye addition (Table 3-4) are consistent with results generated during MWRA’s routine effluent monitoring. The small amount of chloride measured in the effluent (~360 ppb) is typical of the effluent and reflects the intrusion of seawater into the MWRA sewer collection system (M. Hall, personal communication, 2001). Systematic changes in the chloride concentrations were not apparent even though the flow decreased from 390 to 330 mgd during the first 3 hours of the dye addition before returning to about 380 mgd when the last samples were taken.

Table 3-4. Results from the discrete samples collected from the MWRA effluent during the April 2001 MWRA plume tracking survey.

Sample Time (EST)	Dye east basin (ppb)	Dye west basin (ppb)	Ammonia μM	Phosphate μM	TSS mg/L	Chloride mg/L	Copper μg/L	Silver μg/L	Enteroccus #/100 mL	Fecal Coliform #/100 mL
00:22		-0.38	1035	22.6	12.6	409	9.41	0.430	31,000	4800
01:10						295				
02:10	60.50	55.32	1012	23.0	13.8	390	9.48	0.443	26,000	2500
02:17	64.03									
02:40		55.27	1007	22.4	12.8	368	9.54	0.534	18,000	640
02:40						383				
03:40						363				
04:07	63.30	56.43	1027	27.2	13.3	367	9.78	0.635	14,000	415
04:40						296				
05:03	60.59	54.12	1014	23.4	12.0	381	9.81	0.482	8,000	365
05:40						345				
06:05	61.50	54.88	1009	25.0	14.0	351	9.86	0.816	8,100	615
06:40						367				
Mean	**61.98**	**55.20**	**1017**	**23.94**	**13.08**	**359.58**	**9.65**	**0.56**	**17,520**	**1,556**
STDEV	**1.61**	**0.84**	**11.15**	**1.84**	**0.76**	**34.47**	**0.19**	**0.15**	**9,440**	**1,781**
CV%	**2.59**	**1.52**	**1.1**	**7.7**	**5.8**	**9.6**	**2.0**	**26.5**	**54**	**114**

In contrast, the abundance of both bacterial indictors generally decreased over the dye addition period (Table 3-4). Fecal coliform counts at the sampling point for the dye study ranged from 365 to 4800 /100mL. The geometric mean in the fecal coliform levels in the effluent between late June through the end of August 2001 was 10.8 colonies per 100 mL (Dave Duest, MWRA, personal communications, February 2002. This point is ~15 minutes into the disinfection time, thus the values are higher than those reported under routine monitoring. The *Enteroccous* levels were 10 times higher on average than the fecal coliform levels. The counts in the effluent during the dye addition were generally lower when the flow was lower.

The concentrations of the two metals measured in the effluent during the dye study were low and relatively constant. Total copper was less than 10 ppb (average 9.7 ppb). Total silver was measured at <0.82 ppb (average 0.56 ppb). The silver data tended to be more variable than Cu (27 versus 2.0 percent coefficient of variation).

The three parameters that were measured in two laboratories showed very tight agreement (Table 3-5). Ammonia levels throughout the dye addition were constant at about 1,000 μM. The paired ammonia data returned average values of 1017 and 1024 μM ammonia with overlapping standard deviations. Phosphate concentrations were also constant at ~24 μM. The paired data returned average values of 23.9 and 23.4 μM phosphate with overlapping standard deviations for the two laboratories. The TSS results were slightly different (11.7 versus 13.1 mg/L) based on all of the data, although the standard deviations of the measurements from the two laboratories overlapped. The paired data returned average values of 11.7 and 13.1 mg/L TSS. The average concentration using the data both from laboratories was 12.4 mg/L. The data are consistent with the weekly and monthly averages generally achieved by the treatment plant (Werme and Hunt 2001). The daily average TSS in the effluent from late June to late August was 10 mg/L (Dave Duest, Personal communication, February 2002). The overall variability for the intercomparison data was small. Reported as the coefficient of variation the variability was about 1 % for ammonia, 2 to 5% for phosphate; and 5 to 10 % for TSS.

Table 3-5. Laboratory intercalibration data for ammonia, phosphate and total suspended solids.

Sample time	Ammonia (μM)		TSS (mg/L)		Phosphate (μM)	
	DI	URI	DI	URI	DI	URI
00:22	1029	1035	14.0	12.6	22.2	22.6
01:40	1014		11.0		22.7	
02:10	1036	1012	11.0	13.8	24.0	23.0
02:40	1029	1007	12.0	12.8	23.7	22.4
02:40	1029		12.0		23.7	
03:40	1050		11.0		23.6	
04:07	1029	1027	11.0	13.3	23.7	27.2
04:40	1021		12.0		23.5	
05:03	1021	1014	11.0	12.0	23.6	23.4
05:40	1000		13.0		22.9	
06:05	1014	1009	10.0	14.0	23.5	25.0
06:40	1021		12.0		23.7	
Mean	**1024**	**1017**	**11.7**	**13.1**	**23.4**	**23.9**
STDEV	**12.4**	**11.15**	**1.1**	**0.76**	**0.5**	**1.84**
CV%	**1.2**	**1.1**	**9.2**	**5.8**	**2.2**	**7.7**

3.4.2 Ambient Discrete Sample Results

As discussed in previous sections, the Rhodamine dye concentrations in the dyed effluent plume in Massachusetts Bay were generally <0.8 ppb. A low background fluorescence signature (Table 3-6) was measured in the discrete samples collected before the dye exited the diffuser system in the bay (the depths of the sample collection are shown as the cluster of points within the beam attenuation profile shown Figure 3-4). This reflects natural compounds that fluoresce at the wavelengths used to measure the Rhodamine. The analytical results from the discrete samples collected at the background location confirmed that the location sampled was appropriate as a background station. This determination is based on the concentrations of the ammonia and metals at the background site relative to known levels prior to discharge or measured in surrounding waters during MWRA's summer 2001 nearfield monitoring surveys. Ammonia concentrations in the bay have been particularly effective as an indicator of the effluent plume in the bay (Libby *et. al*. 2002a; Werme and Hunt 2001). Ammonia levels at the background station ranged between 1 and 2 μM, values that are typical of those measured in areas outside of the influence of the effluent plume during MWRA's the early and late April water quality monitoring surveys (Libby *et al*. 2002b). Dissolved phosphate and TSS values were also indicative of Massachusetts Bay waters not influenced by the effluent plume. Thus, the background samples were obtained in waters unaffected by the ongoing discharge.

Table 3-6. Background water quality in vicinity of the MWRA outfall, April 19, 2001 as measured in discrete samples collected at position [7] in Figure 3-3.

Depth (m)	Dye (ppb)	Ammonia (µM)	Phosphate (µM)	TSS (mg/L)	Copper (µg/L)	Silver (µg/L)	Chlorophyll a (µg/L)	Phaeophytin (µg/L)
2.4	0.052	1.34	0.45	0.18			0.34	0.07
10.4	0.048	1.16	0.44	0.29	0.37	0.014	0.25	0.22
21.9	0.048	1.26	0.46	0.30			0.55	0.16
31.4	0.047	2.05	0.56	0.52	0.32	0.016	0.63	0.38
Mean	**0.049**	**1.45**	**0.48**	**0.32**	**0.34**	**0.02**	**0.44**	**0.21**
STDEV	**0.002**	**0.41**	**0.06**	**0.14**	**0.04**	**0.00**	**0.18**	**0.13**
CV%	**4.1**	**27.9**	**11.6**	**44.4**	**11.7**	**9.4**	**39.9**	**62.7**

Total metals concentrations at the background station were low (Cu ~0.32 to 0.37 µg/L; Ag ~ 0.015 µg/L) (Table 3-6). The copper data are comparable to data from Massachusetts Bay collected in August 1994 and September 1996 (Christian Krahforst, personal communication, December 2001). His total copper results, summed from separate measures of the dissolved and particulate phases, range from 0.34 to 0.35 µg/L. Thus, total copper at the background station is in the range expected for Massachusetts Bay. Total silver concentrations in Massachusetts Bay reported by Krahforst range from 0.002 to 0.004 µg/L. In contrast to the copper data, the two background data points from the plume tracking survey are 4 to 7 times higher than these values. Thus, the background silver data from the plume tracking study do not appear to represent background levels typically found in Massachusetts Bay.

Background concentrations of the parameters measured from the discrete samples in the bay are substantially lower than in the effluent: background ammonia levels are about 1000 times; PO_4 ~50 times; TSS ~35 times; and Cu and Ag each ~28 times lower than measured in the effluent. Monthly MWRA surveys for bacterial indicators, including data from adverse condition surveys conducted in 2001 have not detected fecal coliform (MDL = 1 colony /100mL) in the receiving water near the outfall (K. Coughlin, MWRA, personal communications, February 2002).

The other discrete parameters measured at the background station included chlorophyll and phaeophytin. The data from the survey show low concentrations (0.25 – 0.63 µg chl a /L) throughout the water column. Values at depths shallower than 10 m were about one-half those at depth.

The sample collection depths during the HMZ surveys are shown in Figure 3-23, which includes the *in situ* data for dye, temperature and beam attenuation.

The discrete data collected from within the dye field during the HMZ surveys (Table 3-7) were generally higher than measured at the background station, although by varying amounts. The increase varied both within an HMZ profile and between the two HMZ sampling events. In general, ammonia within the plume was about 10 times higher and phosphate and TSS about ~1 to 2 times higher than background levels. The TSS results from the MHZ2 appeared to be slightly higher than measured in HMZ1. Regression pots of the TSS data against *in situ* beam attenuation data showed a strong correlation to TSS (R^2 = 0.70, slope = 0.424 m^{-1} per mg TSS/L; intercept 0.456 m^{-1}) indicating the beam attenuation data discussed in Section 3.3.3.2 is also indicative of the general particle fields in the area. The measured increases were ~10 µM for ammonia, 0.5 to .7 µM for phosphate, ~0.3 mg/L for TSS. Copper levels increased by less than 20 percent (~0.06 µg/L increase) in the plume samples. Variably among the metal sample results is relatively high, making a definitive conclusion difficult to draw. Silver levels did not appear to change within the measurement precision. The chlorophyll and phaeophytin levels were similar in background versus plume.

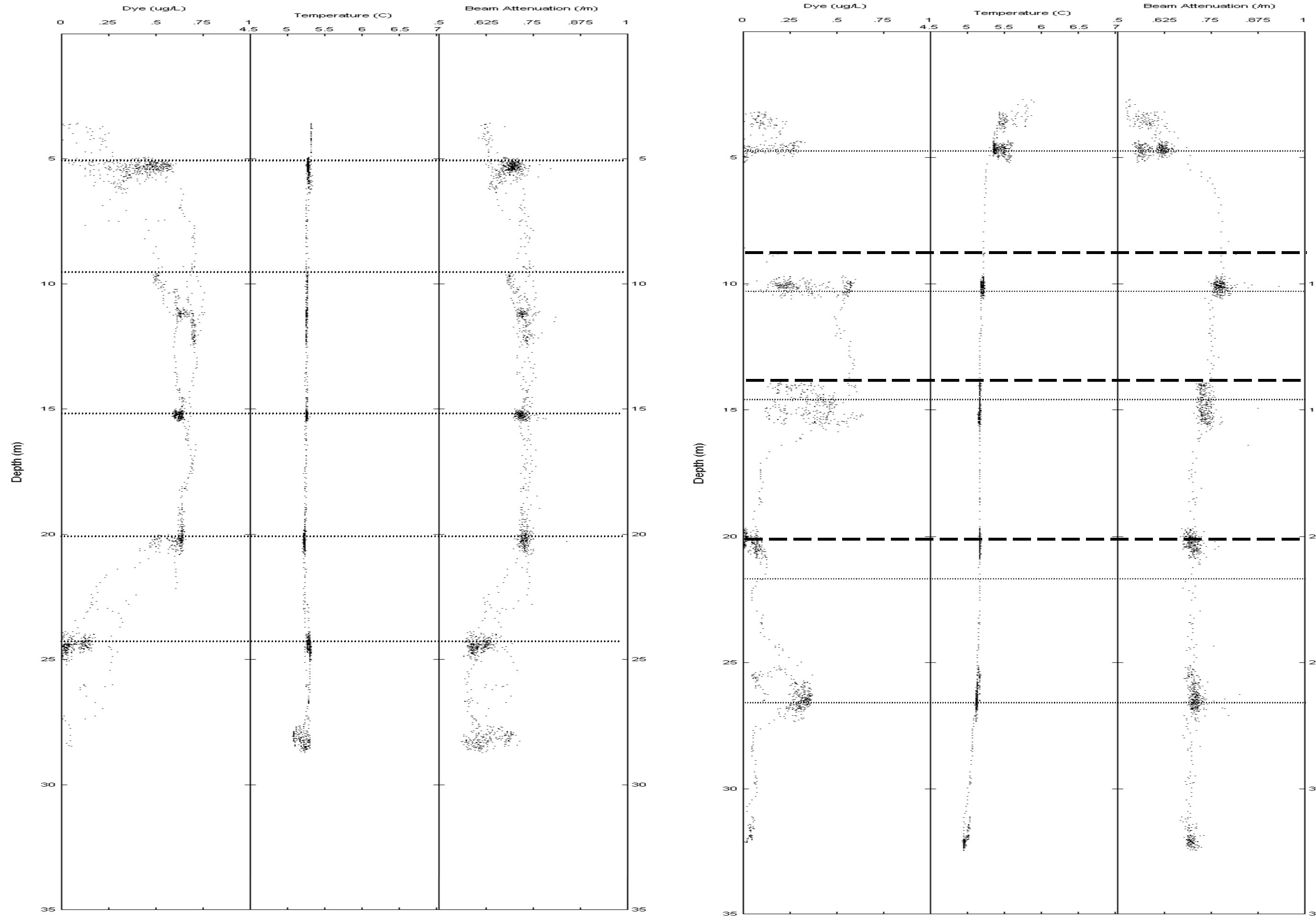

Figure 3-23. Depths where discrete samples were collected on HMZ1 (left) and HMZ2 (right) on April 19, 2002. Sample depths shown by dotted and dashed lines (added bacteria indicator samples). Note: The bacteria indicator sample depths shown with the dashed line were obtained on a second hydrocast that had higher dye concentrations between 15 and 30 meters than shown in this figure (See Figure 4-4 for the combined data).

Table 3-7. HMZ vertical profile discrete sample data summary.

Source	Depth (m)	Dye (ppb)	Ammonia (µM)	Phosphate (µM)	TSS (mg/L)	Copper (µg/L)	Silver (µg/L)	Enteroccus (#/100 mL)[a]	Fecal Coliform (#/100 mL)	Chl *a* (µg/L)	Phaeo. (µg/L)
HMZ1	5.6	0.646	8.8	1.06	0.40			NA	NA	0.369	0.107
	10.2	0.711	11.7	0.95	0.59			NA	NA	0.426	0.165
	15.7	0.689	12.3	0.91	0.57	0.395	0.0208	NA	NA	0.310	0.205
	21.0	0.717	10.9	0.84	0.55			NA	NA	0.251	0.148
	24.9	0.211	2.92	0.60	0.27	0.436	0.0162	NA	NA	0.292	0.105
HMZ2	5.27	0.394	6.68	0.67	0.48			4	0	0.309	0.107
	10.2	NA[b]						2	0		
	10.7	0.375	15.1	0.93	0.56			8	0	0.479	0.298
	14.6	NA[b]						9	2		
	14.9	0.355	11.1	0.81	0.76	0.389	0.018	3	0	0.400	0.254
	20.7	NA[b]						2	0		
	21.1	0.150	9.37	0.78	0.69			8	0	0.360	0.230
	27.3	0.430	10.6	0.78	0.63	0.408	0.018	4	0	0.278	0.186

[a] EC24 Method. [b]Only bacteria samples collected at this depth.

Another way to evaluate the observed changes in the plume is to predict the expected contribution of the effluent to the measured concentrations based on the dye results. The dye data indicate the effluent was diluted at least 85 fold within 25 to 50 m from the diffuser. Based on the data in Table 3-8, the expected increase at this level of dilution in the effluent plume at locations sampled and assuming no biological or other interactions is approximately 8.5 µM for ammonia, 0.20 µM for phosphate, 0.11 mg/L for TSS, 0.08 µg/L for Cu and 0.0047 µg/L for Ag. These estimates agree generally with the measured values, especially ammonia. The estimated phosphate increase was about one-half the observed increase, while the estimated Cu increase was slightly higher than the measured (probably the same considering measurement errors). Of note is the apparent increase in TSS relative to that predicted (0.3 mg/L measured versus 0.11 mg/L predicted). This discrepancy could result from formation of particles by flocculation of dissolved organic matter in the effluent as it contacts seawater as flocculation of dissolved organic matter in fresh water entering seawater is relatively well known phenomena that can generate a transition from dissolved to particulate forms. It may also reflect the mixing of the dyed effluent into a higher background (local pre dyed effluent) than provided using the background station data

The correspondence between the discrete data and the concentrations of dye is generally good although not precise. The highest dye concentrations in discrete samples obtained from the HMZ profiles were in the 5 to 20 m depth range (Table 3-7). The correspondence was better for parameters that had larger concentration differences between the effluent and background levels in the receiving waters.

From a water quality perspective, the plume data demonstrate that state standards and federal marine water quality criteria are not exceeded after the initial mixing of the plume is completed. Copper particularly provides evidence that the design of the diffuser and achieved dilutions effectively reduce the already low levels of contaminants in the secondary treated effluent levels to well below those considered harmful. The highest measured copper concentration in the effluent plume was 0.44 µg/L. This compares to a marine water quality criterion of 3.3 µg/L. Thus, after initial dilution this metal is about eight fold lower than the applicable marine water quality criteria.

The fecal coliform and *Enteroccus* are at acceptable levels immediately after initial dilution is completed. Fecal coliform were found at two colonies per 100 mL in one samples (MDL = 1 colony per 100 mL) and were not detected in any of the other seven samples collected. *Enteroccus* colonies were measurable at 2 to 9 colonies per 100mL (MDL = 2 colonies/100 mL). Detection of these indicators at or slightly above the detection limit is expected and are not considered consequential to water quality. These values compare to the state water quality standards for contact recreation of 200 fecal coliform colonies/100 mL and 35 *Enteroccus*/100 mL of sample.

3.4.3 Dilution estimates from discrete samples

The data from the discrete sample collection effort were used to prepare estimates of the effluent dilution (Table 3-8) for comparison to that determined by from the dye itself as well as the dilution modeling (see Section 4). For the calculations, the average concentration of each parameter measured in the effluent was calculated. The dye concentration used for the effluent was that developed in Section 3.2. For ammonia, phosphate and TSS the mean of all samples taken by both laboratories was calculated for the effluent. The dye, ammonia and phosphate concentrations in the plumes were based on the highest values in the plume (e.g., some samples were not included as the data indicate the samples were outside of the core of the plume). Because the parameters have a natural background in Massachusetts Bay, the measured concentrations in the effluent plume offshore must be adjusted to reflect the "new" input. This was done by taking the average of each measurement made in at the background station. Except for metals, four values were included in the mean. The silver and copper averages are based on only two samples. Mean values for the HMZ studies were based on the highest values in the profile (discrete dye values <0.2 ppb were excluded). This gave an estimated dilution from these samples of 93 and 204 for HMZ1 and HMZ2, respectively Table 3-8). The apparently high dilution estimated from the HMZ2 discrete dye data maybe related to the actual location of the sampling station. The estimates for HMZ1 are consistent with results from the *in situ* study (Section 3.3.3) and the dilution modeling (Section 4). However, the results from HMZ2 are not. In Section 3.3.3.2 it was suggested (based on the relationship between *in situ* dye and beam attenuation) that samples at this station may have been collected in the interface between the predye and dyed effluent or been influenced by predye effluents in the immediate background near the diffuser. Obtaining samples outside of the initial mixing zone at this station would result in overestimates of dilution based on the dye but under estimates on the basis of TSS or other parameters influenced significantly by background values (e.g., for nutrients, metals, and TSS a background correction has to be taken and if too low dilution is underestimated).

Table 3-8. Estimates of effluent dilution based on discrete data results from the April plume tracking survey.

Parameter	Concentration Units	Effluent	Seawater Background	HMZ1	HMZ2	Initial Dilution	
						HMZ1	HMZ2
Dye	ppb	59.7	0.049	0.69	0.34	93	204
Ammonia	µM	1022	1.45	10.95	10.56	108	112
Phosphate	µM	23.6	0.48	0.94	0.79	51	74
TSS	mg/L	12.1	0.32	0.52	0.62	60	40
Copper	µg/L	9.65	0.34	0.42	0.40	136	178
Silver	µg/L	0.557	0.015	0.019	0.018	159	195

Comparison of the initial dilution based on the discrete data provides information on the ability of a given parameter to be a tracer of initial dilution and whether the factors other than dilution may be affecting the concentrations upon discharge offshore. Of the five parameters in Table 3-8, ammonia gives the closest estimate of dilution to that measured with the dye, particularly for HMZ1. The dilution estimate based on ammonia from the HMZ2 does not agree as well with the dye-based estimate, but does agree with the overall modeling results (see Section 4.1.2). The cause may relate the selection of the background value for ammonia, which if higher at this part of the diffuser would cause the initial dilution to be underestimated.

Both the phosphate and TSS data tend to substantially underestimate dilution relative to the dye-based dilution. Selection of the wrong background value or creation of particles from the dissolved organic matter would increase the amount of particles in the plume, thus causing an underestimate of the initial dilution. Based on the data from the *in situ* measurements selection of the wrong background value may be the reason. However, if this were the case one would expect that the ammonia would also be in poor agreement; this is not apparent in the data. It is also not clear why the phosphate is underestimated in both HMZ data sets, unless the particle formation speculated above transfers particulate phosphate to the dissolved phase, thereby increasing the dissolved levels measured in the plume. Measuring total phosphate in the effluent and offshore might help evaluate the legitimacy of this hypothesis. The other more likely factor is related to the accuracy of the dissolved phosphate estimate in the plume. If the mean value for this HMZ is reduced to 0.70 µM, the dilution estimate increases to 106. This change is within the variability of the data. All of these comparisons point to the need to collection more samples in the offshore plume in very accurately known dye fields to better evaluate the causes and gain a clear understanding of the ability of other tracers to represent the initial dilution.

The poor prediction of the dilution using the metals is most likely due to analytical variability and the very small changes that occur relative to the background levels after initial dilution, although for HMZ2 the selection of background becomes more important if the dye is mixing into a previously discharged plume. The silver is even more problematic in that the background and plume values do not agree with silver concentrations measure in the mid-1990's. The only way to increase the level of confidence in these dilution estimates is to collect more samples in the plume at known dye levels as suggested for the phosphate.

3.5 Oceanographic Conditions at the Offshore Study Area

3.5.1 External Forcing Variables

The principal external forcing variables affecting the dye trajectory are the tides and winds. Tidal conditions were determined by predicted tidal heights at Boston, as shown in Figure 3-24. The tides were just past the neap part of the fortnightly cycle during the dye release, thus the advection and mixing associated with the tides was relatively weak. The two surveys (indicated in shading) started close to high tide, continued through the ebb, and finished during the rising tide.

Wind conditions (shown in Figure 3-25) were weak and from the west or southwest during the actual surveys, but there was a strong wind event from the north the day before the dye release. This strong event appeared to influence the currents on the first day of the dye study, as discussed below.

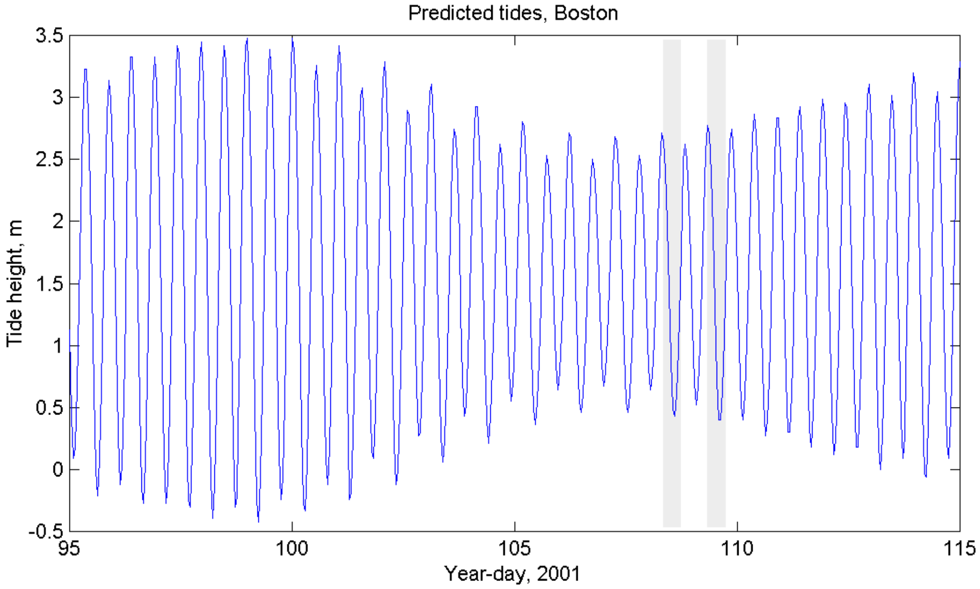

Figure 3-24. **Tidal height at Boston Harbor, based on NOAA predictions. The shaded bands indicate the periods of shipboard measurements. The observations occurred just after the neap phase of the fortnightly cycle.**

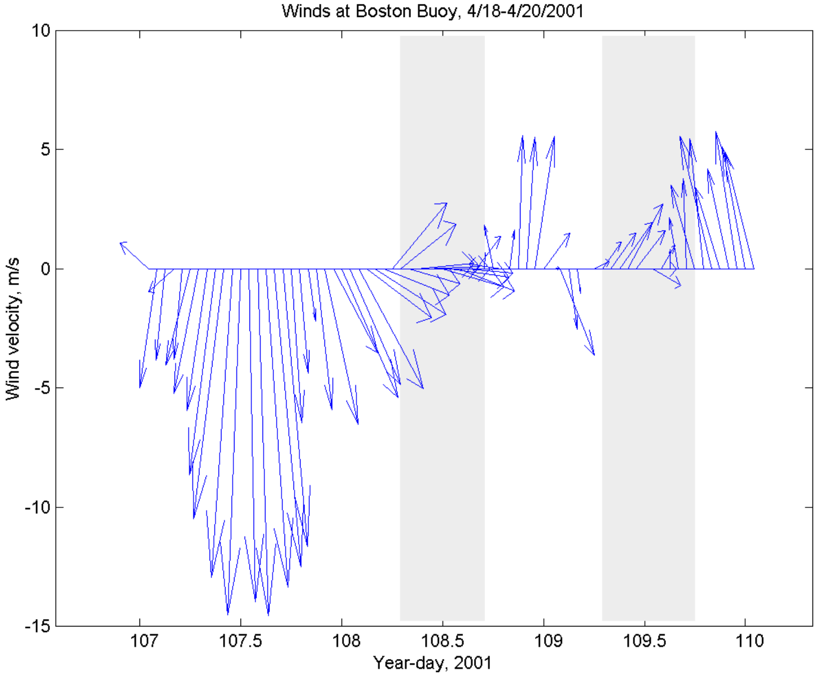

Figure 3-25. Wind vectors during the April dye study measured from the Boston meteorological Buoy in western Massachusetts Bay. The shaded bands indicate the intervals of shipboard measurements.

3.5.2 Oceanographic Conditions

Vertical profiles of water properties (temperature, salinity and density) are shown Figure 3-26, obtained during the "far-field" observations on April 20, 2001. The density data show that seasonal stratification had been established, mostly due to the vertical salinity gradient. Stratification by salinity is typical at this time of year, based on previous observations at the Outfall Site. The density gradient extended through the entire water column, with no evidence of a bottom mixed layer. The variability of the density from one profile to another was due in part to internal waves and in part to spatial variability of the water properties.

Vertical profiles of velocity are shown in Figure 3-27 and Figure 3-28. These profiles were constructed from harmonic analysis of the raw ADCP data, in order to obtain a temporally continuous representation of the raw observations, which had numerous time gaps in them. The east-west component of velocity showed the barotropic (depth-independent) variability due to the tides, as well as vertical variations associated with internal tidal motions and other processes. The north-south component showed strong shears on 4/19, reaching a maximum of 0.2 m/s at the surface in the middle of the day, whereas the bottom current was always close to zero. This strong northward current is likely a "relaxation" response to the strong winds from the north on the previous day. A response on this timescale (approximately 24 hours after the main forcing event) and with a strong vertical shear is consistent with the relaxation of an internal pressure gradient, i.e., a north-south tilt of the pycnocline that had been induced by the winds. This large baroclinic shear had vanished by 4/20, and all that remained in the north-south component were internal tide/wave fluctuations.

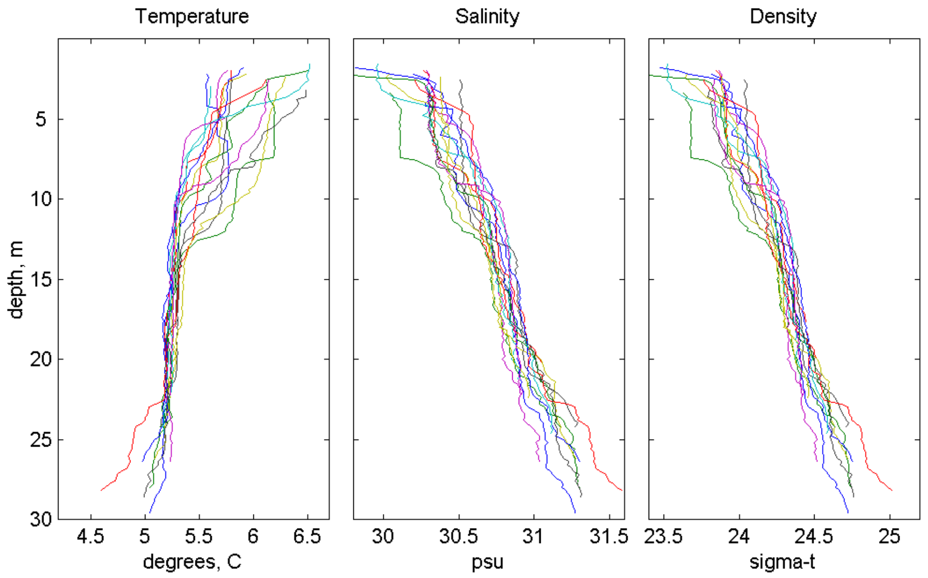

Figure 3-26. Temperature, salinity and density profiles from the far-field observations using the BOSS profiler on 4/20/2001. Every 5th downcast through the 8-hour survey is plotted.

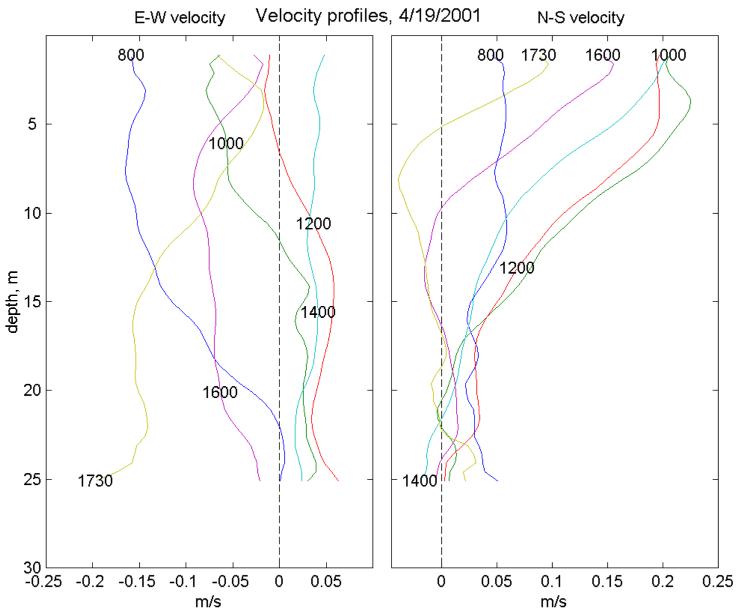

Figure 3-27. East-west and north-south velocity profiles from the shipboard ADCP at 2-hour intervals on 4/19/2001. (EDT)

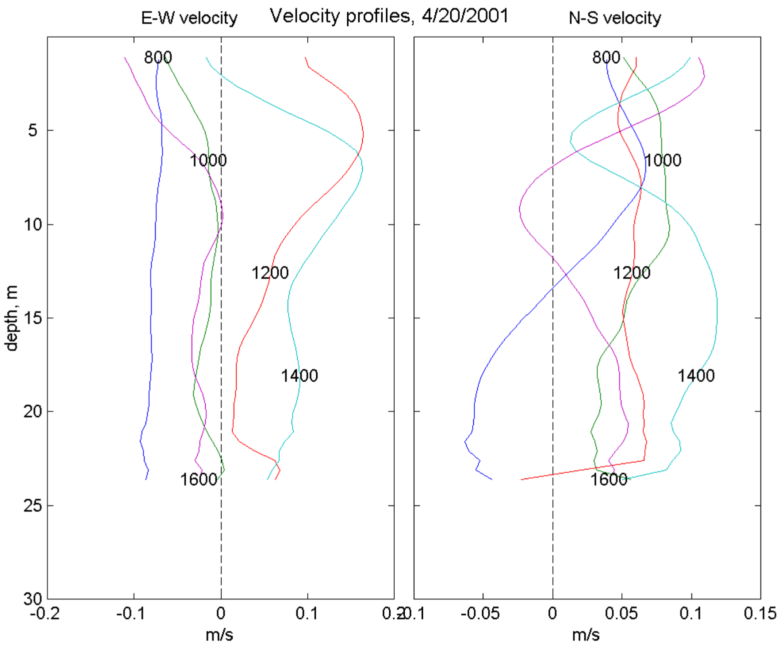

Figure 3-28. East-west and north-south velocity profiles from the shipboard ADCP at 2-hour intervals on 4/20/2001. (EDT)

The net influence of these currents on the displacement of water parcels was estimated by constructing progressive vector plots in Figure 3-29 and Figure 3-30. The displacements of near-surface (1-5 m) and "dye-depth" (19-24 m) water parcels were determined by integrating the harmonically analyzed velocity data in time. The resulting displacements would correspond to actual water displacements if there were no spatial variations in the currents. They should be a reasonable approximation of actual displacements for timescales of several hours. The most striking feature of these displacements is the northward trajectory of the near-surface waters on 4/19, amounting to 5 km in 8 hours. At the dye depth, the displacements were much smaller, on the order of several hundred meters. On 4/20, there was much less mean shear, and the trajectory at the dye depth was more similar to the surface trajectory.

3.5.3 Overall Assessment of Physical Oceanographic Conditions

Although the near-surface shears were strong on April 19, these did not have a strong influence on the conditions at the level of the dye (cf. Figure 3-27 and Figure 3-29). The neap tide conditions provided a minimal amount of energy for vertical mixing, thus this period probably had less than average mixing energy. The presence of vertical stratification is the most important variable influencing the vertical spreading of the dye, explaining why the dye did not extend to the water surface. The vertical stratification is also related to the large vertical shears, both mean and fluctuating. These vertical shears may contribute to more horizontal spreading of the patch during stratified conditions than during vertically well-mixed conditions, although the overall dilution of the dye is likely to be less than in well-mixed conditions.

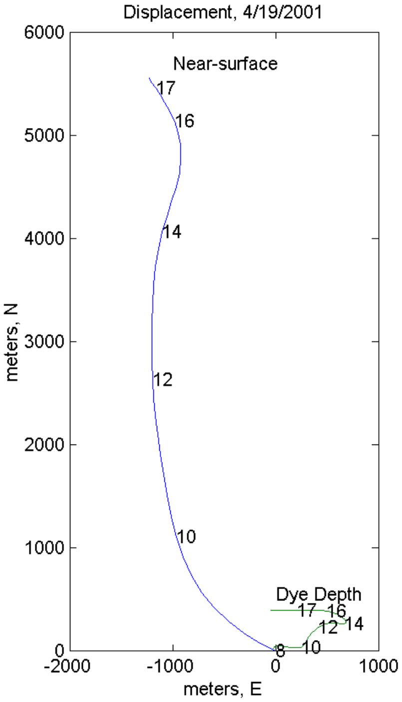

Figure 3-29. Progressive vector plot of or near-surface and "dye depth" water parcels on 4/19/2001. The numbers indicate hours (local time) during the day.

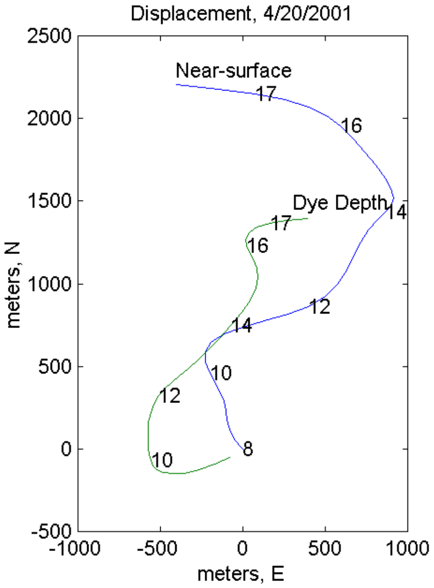

Figure 3-30. Progressive vector plot of or near-surface and "dye depth" water parcels on 4/20/2001. The numbers indicate hours (local time) during the day.

4.0 MODELING

The field results described in the preceding sections were also evaluated through modeling of the effluent dilution. The measurements and the modeling were partly conducted to satisfy the conditions of the Boston MWRA NPDES permit that requires comparison of the field operation of the diffuser with the physical model studies on which the riser and diffuser design were based (Roberts and Snyder, 1993a,b). A summer certification survey conducted under stratified conditions will constitute the permit-required survey.

In this section, the results of the field observations are compared to the original physical model studies (Roberts and Snyder, 1993a,b). In addition, more recent physical model studies have been done using sophisticated laboratory techniques for conditions designed to replicate those actually observed in the field tests. The field data are compared to these new results and to the predictions of mathematical models.

Fluorescent dye was added at the Deer Island Treatment Plant at a variable rate to match the wastewater flow rate so that the final effluent concentration remained approximately constant (Section 2.1.2). The wastewater flow variation is shown in Figure 3-1 and the effluent dye concentration in Figure 3-2. The dye concentration was effectively constant at 59.7 μppb for the duration of the tests.

The offshore survey activities are described in Section 2.1.3. The survey included measurements of ocean currents with a downward-looking Acoustic-Doppler Current Profiler (ADCP) attached to the survey boat (Section 2.2) and a drogue was released at the end of the near field sampling day at about the depth of the observed wastefield to track the net drift of the dye plume.

Additional figures presenting the ADCP current data are included in Section 3.5. Shear is evident in the current records. The surface waters, down to about 10 m deep, move generally to the North at speeds up to 20 cm/s; the deeper currents are slower, with speeds generally between 1 to 5 cm/s, and move towards the NE. Towards the end of the sampling period, around 16:00 hours (EDT), the bottom currents sped up to about 10 cm/s and shifted to an onshore direction, W to NW. Because the plume behavior and dilution are mostly affected by the deeper currents, the depth-averaged currents (below 10 m) are shown as vectors and by speed magnitudes in Figure 4-2. During the near field surveys when dye was detected (about 12:00 to 17:00 EDT), speeds were mostly in the range of 3–6 cm/s to the NW. At the end of the sampling period, from 16:00 to 17:00 (EDT), the current speed gradually increased to about 10 cm/s, and the direction shifted to onshore, due west.

The drogue trajectory is shown in Figure 3-19. The mean speed of the drogue over the 24 hours following the end of the near field tests was 9.8 cm/s with a mean direction approximately to the NW.

Density profiles were to be measured by CTD (Conductivity-Temperature-Depth) profiling. Unfortunately, the conductivity probe failed for the day of the near field tests. CTD Profiles were obtained on the second (far-field) day, however, and the measurements of temperature, salinity, and density that were obtained in the vicinity of the diffuser are shown in Figure 4-3. Comparison of the temperature profiles on the two days implies that the stratification was similar on both days. The water column was stratified, mostly due to salinity variations. The total difference in density over the water column was about 0.9 sigma-t units. Below about 10 m depth (the region of the profile that most affects the plume behavior), the density profile is approximately linear,

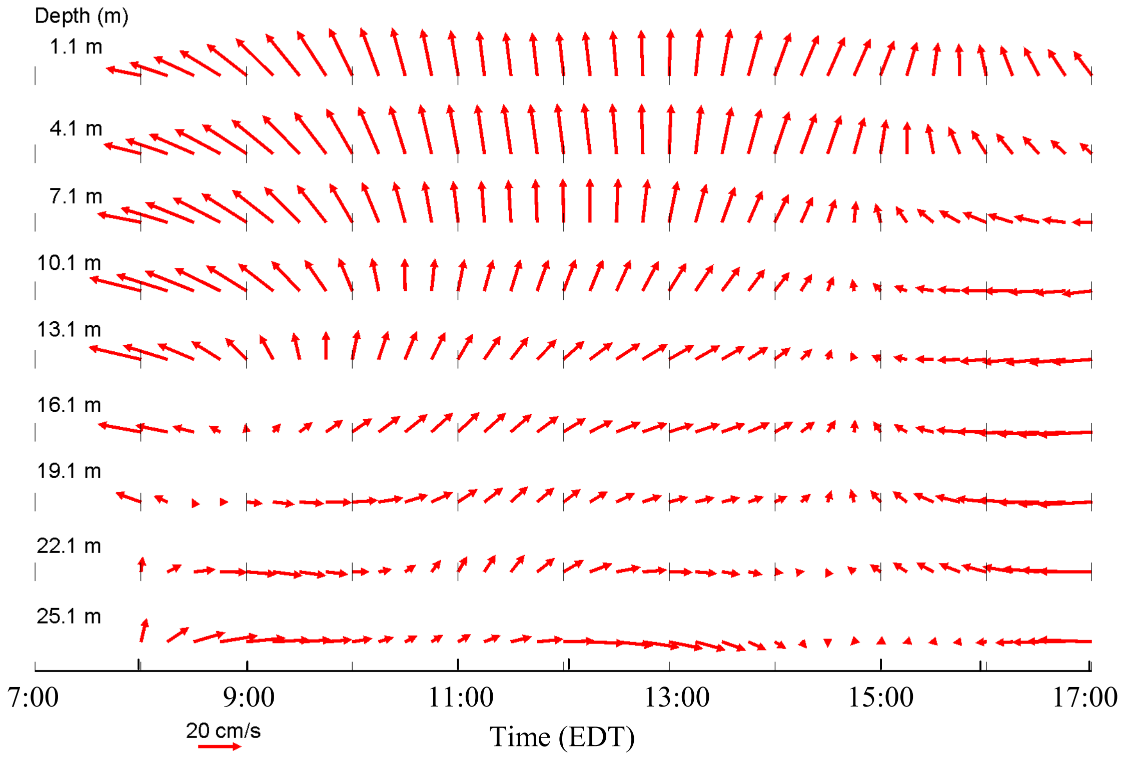

Figure 4-1. Variation of current speed and directions over depth measured by the ADCP on 4/19/01

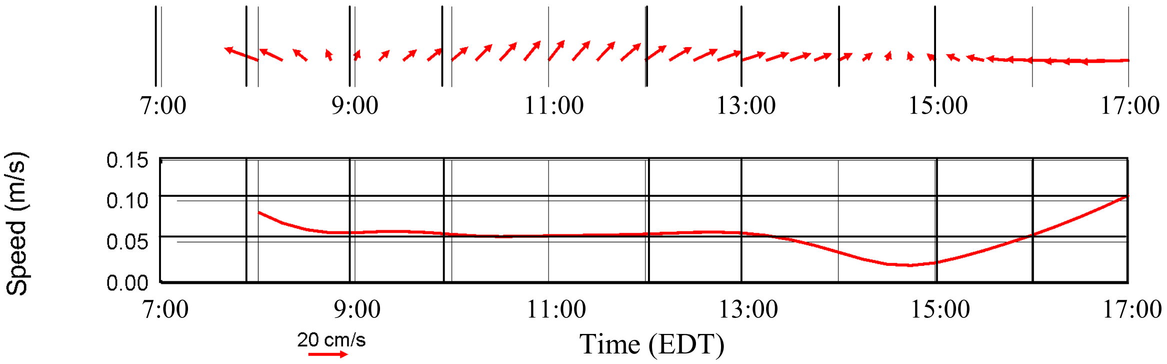

Figure 4-2. Depth averaged (below 10 m) currents on 4/19/01

with a buoyancy frequency, $N = \sqrt{\frac{-g}{\rho_o}\frac{d\rho}{dz}}$ =0.0157 s^{-1}, where g is the acceleration due to gravity, ρ the seawater density at height z above the bottom, $\rho_o \approx 1.0$ g/cc is a reference density. At a depth of about 10 m there is an inflection point in the density profile with a sharp density change of around 0.3 sigma-t units over about 2 m depth. The field test conditions are summarized in Table 4-1.

Table 4-1. Summary of Field Test Conditions, April 2001.

Effluent dye concentration	59.7 ppb (μg/l)
Wastewater flow rate	420 – 470 mgd
Current speed	1 – 20 cm/s
Current direction	Variable, but generally to North
Stratification	About 0.9 sigma-t units over water column

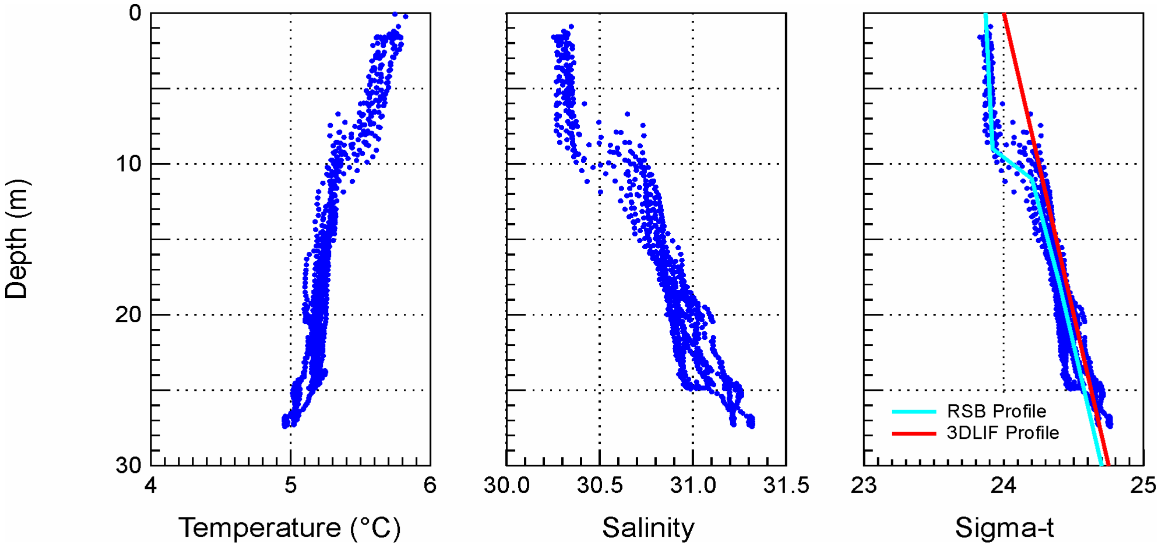

Figure 4-3. Vertical CTD profiles measured on Day 2 near the diffuser.

The dye concentration profiles measured at the HMZ (Hydraulic Mixing Zone) locations are shown in Figure 4-4. HMZ1 is located about 125 m north of riser #40, and HMZ2 is located about 80 m north of riser #10. In these plots the background concentration, c_b, estimated as 0.0035 ppb has been subtracted from all readings.

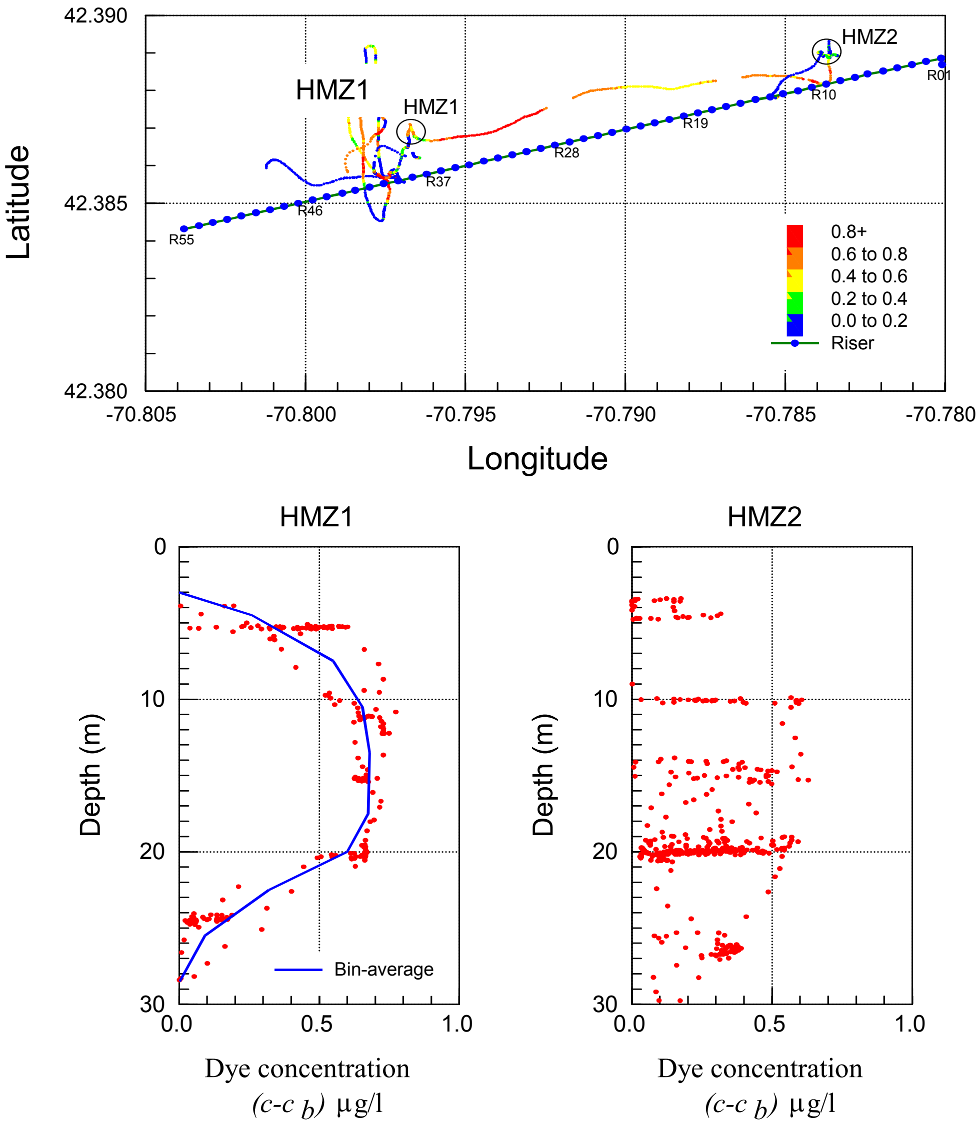

Figure 4-4. Dye Profiles Measurements Measured in the HMZ.

The data show fluctuations at each depth. These are probably due to internal waves, nearfield mixing, and advection of patches of water at different concentrations past the sampling instrument (see Roberts *et al*., 2001, for further discussion of this phenomenon). The field measurements are instantaneous values but the physical model results and mathematical model predictions are time-averaged. Therefore, to facilitate comparisons between field and model values, the field concentrations were "bin-averaged" into bins of height 3 m. The averaged curve for HMZ1 is shown in Figure 4-4. The maximum bin-averaged concentration is 0.68 μg/l, which implies a near-field dilution of about 88:1 for a source concentration of 59.7 μg/l. The highest concentration observed at HMZ2 was 0.63 μg/l[3], which implies a near-field dilution of about 95:1. The near field dilution is therefore probably in the range 88 to 95. Defining the wastefield extent as the depth where the local concentration is 10% of the maximum, the top of the wastefield is at about 4 m depth, the bottom is 26 m depth, and the depth of minimum dilution about 15 m. The port depths around Riser 38 (near HMZ1) are about 32.0 m. Therefore in terms of rise height above the ports, the top of the wastefield is at about 28 m, the bottom is at 6 m, and the height of minimum dilution about 17 m. The wastefield thickness is 22 m.

Dye concentrations measured during the HMZ survey along a track roughly parallel to the diffuser and about 90 m to the north of it are shown in Figure 4-5. These are discussed further in comparison with the new laboratory model studies in the following section.

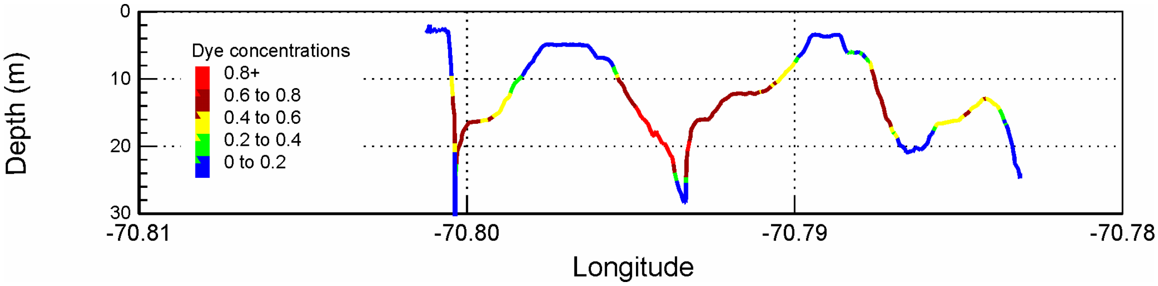

Figure 4-5. Dye Profiles Measured During Lateral Transect Parallel to the Diffuser

4.1 Physical Modeling Studies

4.1.1 Original Physical Model Studies

The original physical model studies (Roberts and Snyder, 1993a,b) were carried out in a large density-stratified towing tank at scales of 52:1 to 87:1. The modeling laws are described in Appendix B. Various conditions were tested. Flows were 17.1, 27.2, and 55.6 m^3/s (390, 620, and 1270 mgd). Current speeds were zero, 12, and 25 cm/s, mostly perpendicular, but some parallel to the diffuser. Density stratifications were "Winter" (homogeneous), "Late summer" (total density difference of 3.7 sigma-t units over the water column), and "Early summer" (total density difference of 3.3 sigma-t units over the water column). For the shapes of these profiles, see Figure 6 of Roberts and Snyder (1993a). These modeled summer stratifications are stronger than observed in the field during April.

Because the conditions in the original physical model do not correspond exactly to those observed in the April field study, direct comparisons between the two are not possible. Some approximate comparisons

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[3] Maximum value used to estimate the initial dilution for HMZ2 due to the large amount scatter in the data from this profile.

are possible, however, by bracketing the results of the physical model studies (see Table 3 of Roberts and Snyder, 1993b).

The physical model tests closest to the April field conditions are those with flowrate = 17.1 m^3/s (390 mgd) and zero current speed. The flowrate during the near field sampling at HMZ1 and HMZ2 (16:33 and 17:12 EDT) varied from 431 to 432 mgd, with an average of 436 mgd (19.1 m^3/s). The current speed was about 6 cm/s, which, as discussed later, would not be expected to significantly increase dilution , thus the results should be similar to zero current speed. The relevant tests are: 9-01-03, late summer stratification; 9-29-03, early summer stratification; and 9-22-03, unstratified. The respective dilutions and heights to level of minimum dilutions for these experiments were: 81 and 12 m; 112 and 15 m; and 180 and 31 m (Roberts, 1989). The results are best compared by the rise heights to level of minimum dilution. For the field tests, the dilution was 88 – 95 and height to level of minimum dilution was 17 m. This lies between the rise height of experiments 9-29-03 (early summer stratification) and 9-22-03 (unstratified), for which the dilutions are 112 and 180. It is closest to the early summer experiment, which had a rise height of 15 m, but the field measured dilution is lower than the value of 112 measured in that experiment. Although this might suggest that the outfall dilutions are lower than the physical model, the difference is probably because of the very different shapes of the density profiles. The field profiles were close to linear. The physical model profiles were uniform with a very sharp thermocline, however, which results in increased mixing in the spreading layer. The dilution at the same rise height for very nonlinear profiles is at least 20% higher (Daviero, 1998) than for a plume at the same rise height with a linear profile. Accounting for this effect, the field dilutions fall into the range measured in the physical model studies.

It is concluded that the field results are consistent with those observed in the original physical model studies (Roberts and Snyder, 1993a,b). To address the question of the effect of density profile shape, further physical modeling was done with linear stratifications as discussed below.

4.1.2 New Physical Model Studies

The original physical model tests were done in a towing tank with the dilution measured by extraction of samples at 100 points. Only time-averaged concentrations could be measured, and measurements could only be obtained at one distance downstream from the diffuser. Since this time, much more sophisticated techniques for the measurement of dilution in similar laboratory experiments have been developed. In particular, laser-induced fluorescence is now capable of measuring tracer concentrations at hundreds of thousands of points simultaneously. Long time records can be obtained, enabling the gathering of information on the temporal variation of concentration fluctuations and therefore expected length of the mixing zone. Finally, refractive index matching enables use in density stratified environments, and laser scanning enables fully three-dimensional views to be obtained.

A newly developed three-dimensional Laser Induced Fluorescence system (3DLIF) was used to measure the spatial evolution of the mixing processes induced by the diffuser and the spatial variation of dilution of the discharge. The scale model experiments were performed in the Environmental Fluid Mechanics Laboratory at the Georgia Institute of Technology.

The modeling laws and experimental methods are described in the Appendix B. A stratified experiment was done for conditions similar to those of the field test of April 19 and 20, 2001. The model conditions corresponded to a flowrate of 390 mgd (17.1 m^3/s), a current speed 9 cm/s perpendicular to the diffuser, and a density profile that was linear over the water column with a density difference of 0.75 σ_t from surface to bottom over the water depth of 30 m. The average current speed (computed from the drogue movement) was 9.8 cm/s, although the subsequent analyses of the ADCP data suggest that the actual currents during the near field surveys were slower, less than 6 cm/s. The model density profile is compared with the field profile in Figure 4-2. The profiles match closely in the most important linear region over the plume rise. All eight ports on each riser were assumed to be flowing, compared to the actual diffuser in which only five or six ports on each riser are discharging.

4.1.3 Results

LIF images were obtained in forty vertical planes between two model risers. The fields extend slightly beyond the risers, for a prototype distance of about 40 m (the riser spacing is 37.2 m, or 122 ft). The horizontal extent of the images, and therefore of the dilution measurements, is about 90 m downstream from the risers. Refractive index matching was used to minimize refraction of the laser sheets due to density variations.

The complex three-dimensional concentration distributions are shown in various ways in Figure 4-6 through Figure 4-8. In Figure 4-6, the outer surface of the plumes and spreading layer are shown; the flow is seen from various perspectives. The eight plumes from each riser merge as they are swept downstream by the current. The resulting plume then merges with those from the adjacent risers. This merging occurs about 17 m from the risers. The plumes then continue to mix laterally, forming a uniform horizontal layer. For these conditions, the plumes overshoot their terminal rise height, and then fall back before leveling off. This flow is similar to an internal wave. The top of the layer is just below the water surface; the eventual thickness of the layer is about 25 m.

Variations in tracer concentrations (and therefore dilution) are shown in Figure 4-7. In these figures, the outer surface is semi-transparent. Tracer concentrations are shown as contour plots in vertical planes that are parallel (lateral profiles) or perpendicular (longitudinal profiles) to the diffuser axis. The concentration levels are shown color-coded and are normalized as c/c_o where c_o is the source concentration. The local dilution is the inverse of the normalized concentration: $S = c_o/c$.

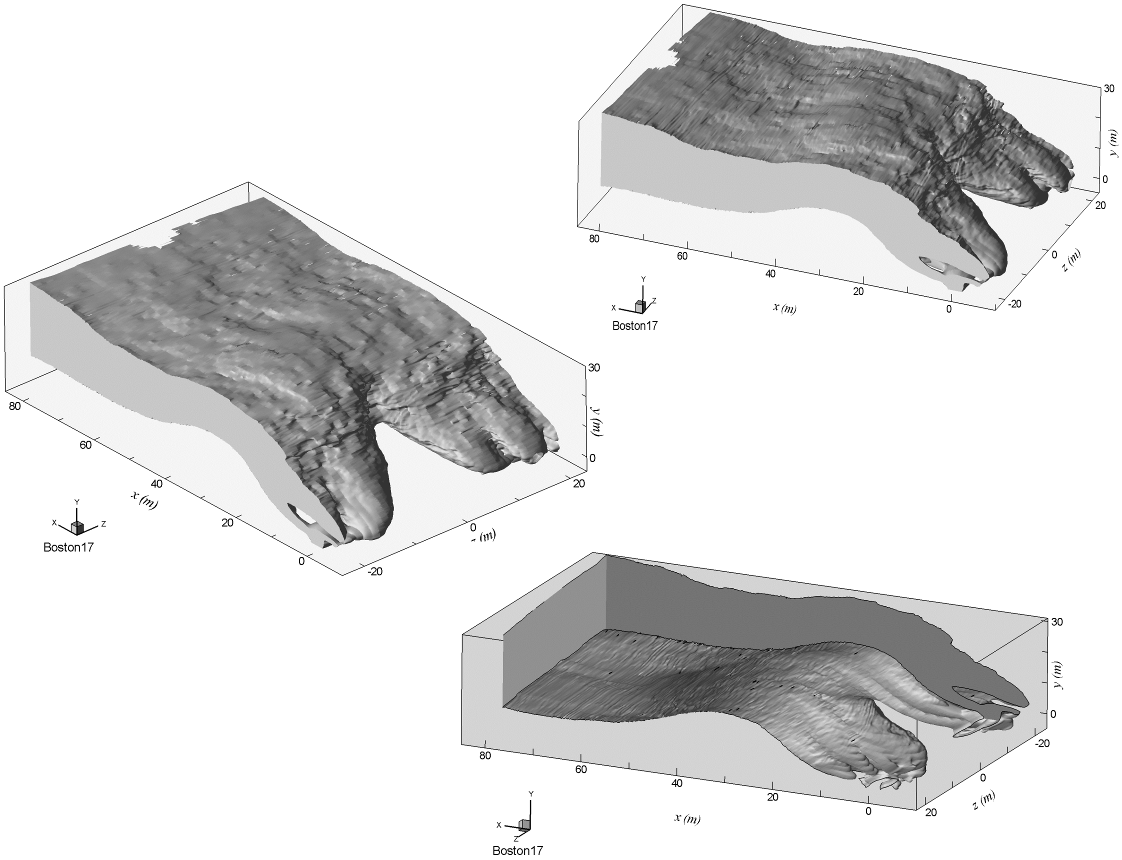

Figure 4-6. Renderings of outer surfaces of plumes and spreading layer from 3DLIF experiments.

The cores of the individual plumes are still apparent as high tracer concentrations in the lateral profile (Figure 4-7a) through the risers ($x = 0$). Farther downstream, at $x \cong 13$ m, the plumes from the individual ports have partially merged. At $x \cong 26$ m, however, lateral mixing has erased these cores, and the layer is fairly homogeneous laterally. Some mixing continues beyond this point, and the layer thickens somewhat up until about 80 m from the risers. Two longitudinal profiles are shown in Figure 4-7b. These are at the midpoint between two risers, and through the center of one of the risers. Again, high concentrations are apparent in the merging plumes near to the riser.

These lateral variations in concentration are shown differently in Figure 4-8 as three-dimensional plots of the concentration distributions in vertical planes at various distances downstream from the risers (the same lateral profiles as shown in Figure 4-7a). Close to the risers, at $x \cong 13$ m, the high local peaks in the cores of the individual plumes are evident. At $x \cong 26$ m, the plumes from adjacent risers are essentially fully merged laterally with only very slight evidence of them left. At $x \cong 40$ m and beyond, the layer is homogeneous horizontally. The dilution increases with distance from the diffuser until it approximately levels off at around 100:1 about 25 m from the risers. This leveling off marks the end of the near field and beyond this point the dilution changes slowly. The lateral variations in Figure 4-8 are consistent with the lateral variations in the field transect, Figure 4-5, although the low horizontal spatial resolution in the field precludes detailed comparison. The vertical profiles are compared directly to the field observations at HMZ1 in Figure 4-9. The field concentrations have been normalized to the source concentration, c_o, to facilitate the comparison.

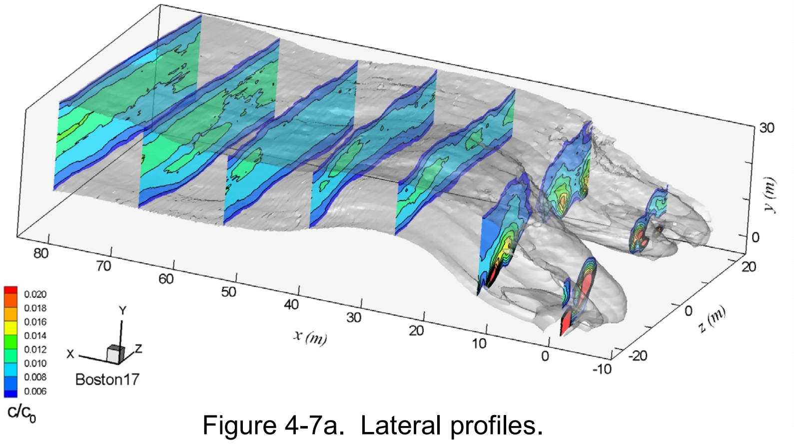

Figure 4-7a. Lateral profiles.

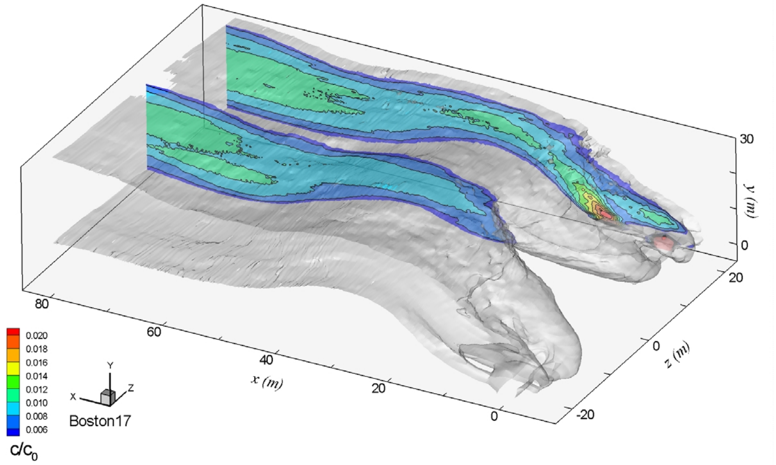

Figure 4-7b. Longitudinal profiles.

Figure 4-7. Tracer concentration variations downstream from the risers.

The agreement between the field and 3DLIF measurements (Figure 4-9) is quite remarkable. The field measurement of 85:1 is about 15% lower than the measured minimum dilution of 100:1. The length of the near field, i.e. the region of intense turbulent mixing, is about 25 m for these conditions. The ultimate layer is quite thick, extending from the water surface to about 25 m depth. The field and 3DLIF measurements diverge near the water surface because of the non-linearity of the field density profile at 10 m depth (Figure 4-3). This inflection traps the plume, whereas the linear profile in the laboratory experiments allows the plume to continue to the water surface. Beyond the near field region, the self-induced turbulence decays, and tracer concentrations in the wastefield become essentially constant in the horizontal (lateral) direction.

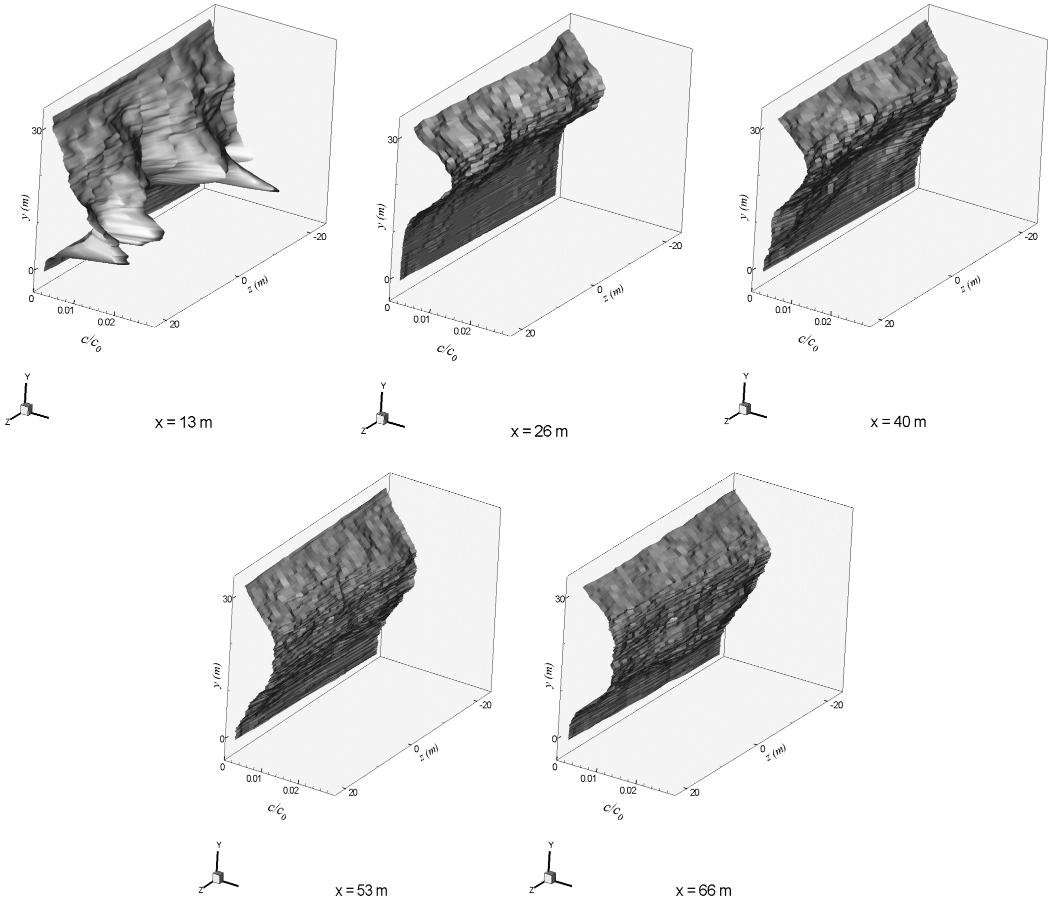

Figure 4-8. Lateral Concentration Variations Downstream from the Risers.

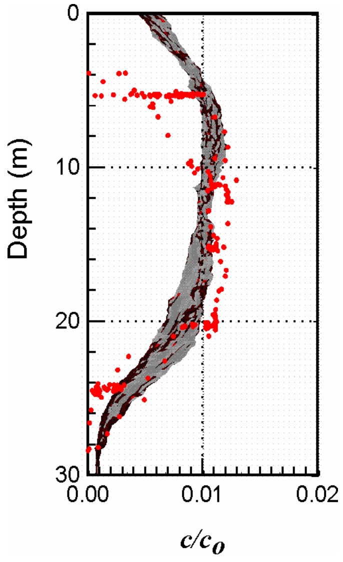

Figure 4-9. Comparison of field and 3DLIF measurements.

4.2 Mathematical Modeling

The field and laboratory results were also compared with the mathematical model RSB, as discussed below. RSB is available in the U.S. EPA Visual PLUMES interface (Frick *et al*., 2001) and also as a separate Windows program RSBWIN. The model is described in Roberts (1999), where a version (called NRFIELD) that was recoded to use long time series of oceanographic data was used. RSB is based on the extensive experiments on multiport diffusers in density-stratified currents of arbitrary direction of Roberts *et al*. (1989). It is a length scale model that uses semi-empirical formulations based on the relative magnitudes of the dominant length scales of the problem. The model output consists of the plume characteristics (dilution, rise height, and wastefield thickness) at the end of the near field. Predictions of RSB were also compared to the original physical model study results (Roberts and Snyder, 1993b, Table 5), with generally good agreement.

As previously discussed, the oceanic conditions were variable during the near field sampling. The depth-averaged currents (below 10 m) were in the range of 3 to 6 cm/s (Figure 4-2) with a direction varying from NE to NW. The wastewater flow rate was fairly constant, ranging from 430 to 470 mgd (18.8 to 20.6 m^3/s).

The most important dynamical parameter governing the dynamics of the diffuser flow in the near field in the ocean is a type of Froude number, *F* (Roberts, et al., 1993):

$$F = \frac{u^3}{b} \qquad (1)$$

where *u* is the current speed and *b* is the buoyancy flux per unit length equal to $g\frac{\Delta\rho}{\rho}\frac{Q}{L}$ where *g* is the acceleration due to gravity, $\Delta\rho$ is the density difference between the wastewater and seawater at the port level, ρ the seawater density at the port level, *Q* the total wastewater flow, and *L* the diffuser length. According to the experiments of Roberts et al (1993), the current exerts little or no effect on the mixing and dilution for $F < 0.1$. For a flow of 450 mgd (19.7 m^3/s) and a diffuser length of 6600 ft (2012 m), this corresponds to a current speed of 6.4 cm/s. As the currents were generally slower than this, it can be concluded that the current had little effect on the initial dilution process.

RSB was run for the assumed conditions of the near field sampling. The flow was taken as 450 mgd (19.7 m^3/s), the current speed as 6 cm/s, and the port depth as 32.0 m. The assumed density profile is non-linear and is shown in Figure 4-3. The diffuser has 440 ports (55 risers each with 8 ports); however, only about 275 of these ports are presently open. The 3DLIF studies were done assuming 440 ports open. The RSB predictions were performed for both 440 and 275 port scenarios. The predictions and comparisons with the field and 3DLIF data are shown in Table 4-2. With fewer ports open, the predicted dilution is about 8% higher. This is because of the increase in momentum flux resulting from discharge of the same flowrate through fewer ports. The agreement is generally very close. The RSB overestimates dilution, but by less than 20%. Uncertainty in the shape of the density stratification profile and current speeds in the field could account for this difference. Also, RSB assumes the ports to be clustered in Tee-shaped risers; this configuration may result in slightly higher dilutions than the 8-port riser configurations on the Boston outfall. The rise height and thickness are closely simulated.

Table 4-2. Comparison of Field Measurements and RSB Predictions

Characteristic	Measurements		RSB predictions	
	Field	3DLIF	440 ports	275 ports
Near field dilution	88-95	100	101	109
Thickness of wastefield (m)	22	25	18	21
Height to top of wastefield (m)	28	30	24	28
Height of minimum dilution (m)	17	21	16	19
Length of near field (m)	-	~26	15	16

4.3 Conclusions

Comparisons of the near field measurements of the plume behavior of April 19, 2001, with results from physical and mathematical models are reported. The field measurements were compared with the original physical model and RSB mathematical model studies on which the diffuser design was based (Roberts and Snyder, 1993a,b). The RSB model closely simulated the plume rise height and wastefield thickness. Although the field conditions were not identical to those of the model studies, the results were generally consistent. The field results are also compared to more recent physical model experiments using three-dimensional laser-induced florescence (3DLIF) to measure dilution. An experiment was run for conditions designed to simulate those actually observed during the field experiment. The results were very close to the field observations.

The 3DLIF results provide more insight into the mixing processes. They show that the plumes from each riser merge, forming a plume that then merges with those from the neighboring risers. This merging begins about 17 m downstream from the risers. After merging, transverse internal mixing erases lateral concentration gradients, and the wastefield becomes essentially laterally homogeneous about 26 m from the risers. At this distance the ultimate dilution of about 100:1 is reached. This marks the end of the near field, and little further dilution occurs beyond this point. The wastefield resembles an internal wave-like pattern and overshoots its ultimate rise height. The wastefield is more than 20 m thick in the vertical direction. Field sampling within the near field, i.e. less than about 26 m from the risers, would probably result in widely fluctuating results that would be difficult to interpret. Beyond this distance, however, wastefield characteristics do not vary rapidly so field sampling positioning is not critical.

The results were also compared to predictions of the mathematical model RSB. The plume rise height and wastefield thickness were closely simulated. Dilution was overestimated by about 20% (105 versus 85), possibly because of uncertainty in the density profiles on the day of the near field measurements.

It is concluded that the outfall is behaving as expected. Measured dilutions and other wastefield characteristics show good agreement with results from both the original and new physical model studies and also with predictions of the mathematical model RSB.

5.0 DISCUSSION AND CONCLUSIONS

The winter survey was designed to ensure the planned approach to the plume tracking described in the *Combined Work/Quality Assurance Project Plan for Plume Tracking: 2001* (Bruce *et al*. 2000) would result in effective data collection methods and to obtain information on the dilution characteristics of the plume under unstratified conditions. All aspects of the technical approach, including methods and equipment employed, data quality objectives, and quality assurance activities were further elaborated in the survey plan prepared for the survey (Battelle 2001a). As described in the survey report (Mansfield *et al*. 2001a), the overall the approach proved successful. Dye additions were complete and Deer Island effluent measured and sampled with minimal data loss. The offshore survey effort was successful in identifying and obtaining *in situ* data from a background area outside of the influence of the diffusers using the study approach, and *in situ* data within the effluent plume were successfully obtained and the dye field characterized spatially and temporally. Moreover, discrete samples were successfully obtained from immediately outside of the Hydraulic Mixing Zone although the position relative to the actual initial mixing zone could not be identified until the data were fully processed and modeled.

In addition, the flexibility built into the offshore component of the study provided the ability to adjust the measurement program in response to changing environmental conditions. As a result a clear picture of the dye behavior was developed.

The April 2001 plume tracking study was also conducted under treatment plant flows that are typical of low rainfall periods. The flows while the Rhodamine WT dye was added to the effluent ranged from 470 to 320 mgd early morning increasing to ~410 mgd as dye addition was completed. Flow remained steady over the period the dye exited the diffuser system in Massachusetts Bay (~12 pM through 6PM (EDT)). The effluent was high quality with total suspended solids averaging 13 mg/L during the dye addition. Representative metals concentrations were measured at low levels (Cu < 10 µg/l and Ag < 0.56 µg/L). Nutrient levels during the addition were also constant and typical for this time of year (ammonia ~1020 µM, phosphate ~24 µM). Bacterial indictors in the effluent varied in abundance over the dye addition but were within the range expected at the sampling point in the west disinfection basin.

Offshore, the dyed effluent exited from the diffusers into a water column that was slightly stratified with a weak pycnocline at about five meters depth. The water column in Massachusetts Bay was transported to the north at about 6 cm/s during the period dye was exiting the diffuser. The northerly set as tracked by a satellite track surface drogue continued through the next day as the dyed effluent was found north and west of the diffuser line. The current velocities were stronger in the upper water column decreasing from ~20 cm/s in the upper 10 meters to 1-5 cm/s at below 20 meters depth.

The evaluation of near-surface shears showed that they were strong on April 19, but did not have a strong influence on the conditions at the depth of the dye during the plume tracking. The survey was conducted near neap tide conditions, which resulted a minimal amount of energy for vertical mixing, thus there was lower than average mixing energy during the study. The vertical stratification observed during the study is also related to large vertical shears, both mean and fluctuating, which may have contributed to more horizontal spreading of the patch than might have been encountered under during vertically well-mixed conditions.

The current direction and velocities provided a good condition for comparing the initial dilution measurements against a dilution scenario modeled during the design of the diffuser (i.e., currents perpendicular to the diffuser). Although a typical non-stratified winter condition was not present during the study, the weak stratification provided sufficient conditions against which the model predictions could be performed and compared to the engineering study results.

The effluent dilutions measured based on the initial dye concentration in the effluent (59.7 ppb Rhodamine) and in the receiving waters (0 to ~0.8 ppb) found initial mixing of the effluent was completed very close to the diffuser line. The lowest dilution measured during the survey was ~56 measured within 20 meters of a riser. Intensive high-resolution *in situ* measurement of dye concentrations near the diffuser line generally found the effluent dilution was at least 85 fold by the time the effluent was ~50 m from the risers. Measured dilution increased from 85 to ~110 as the effluent was transported ~300 m from the diffusers.

The plume dilution measured in Massachusetts Bay was compared to dilution results derived using the original RSB model using current velocities and direction observed during the plume tracking and under scenarios with all 440 diffuser ports open and the present configuration of 275 ports open. The model closely simulated the plume rise height and wastefield thickness. Modeled dilution overestimated measured dilution by about 20% (109 modeled using 275 open diffuser ports versus 88 to 95 measured within 100 m of the diffusers). Although the field conditions were not identical to those of the original model studies, the results from the modeling were generally consistent with expected results. Thus, the results of this RSB model run and field results compared well with the physical model studies on which the diffuser design was based.

A more sophisticated three-dimensional laser-induced florescence (3DLIF) measurement approach for determining dilution was also run at Georgia Institute of Technology. This physical simulation was completed under conditions that more closely match those actually observed during the field experiment. The dilution results compared very closely to the field observations (101 modeled versus 88 to 95 measured). The modeling results using this new model estimated the initial dilution at 100 with the momentum induced initial mixing complete. The 3DLIF results also provided more insight into the mixing processes and show that plumes from the individual ports on each riser merge quickly forming a riser plume that then merges with those from the neighboring risers. This merging begins about 17 m downstream from the risers. After merging, transverse internal mixing erases lateral concentration gradients. The wastefield under the conditions evaluated during the survey becomes laterally homogeneous about 26 m from the risers. The model results indicate that field sampling within less than ~26 m from the risers, would probably result in widely fluctuating results that would be difficult to interpret. Beyond this distance, however, wastefield characteristics do not vary rapidly so field sampling positioning for confirming the initial mixing is not as critical.

The initial dilution resulted in acceptable water quality characteristics within the plume as measured from discrete samples collected from within the dye field after initial dilution is complete. Copper concentrations after initial mixing were slightly higher (~25%) than background levels obtained approximately 1,000 meters south of the diffuser system. Bacterial indictors were near or below the detection limits of the methods. The metals and bacterial indicators were well below applicable water quality standards. In contrast, nutrient measurements of the diluted effluent found relatively high levels of ammonia and phosphate. The levels were consistent with dilution of the concentrations measured in the effluent upon entry to the discharge tunnel on Deer Island.

The discrete sample data were also used to estimate the dilution achieved in the samples. Only ammonia showed reasonably good agreement with the dye results and suggests it can provide an excellent short-term measure (minutes to a few hours) of the dilution near the diffuser. However, because it is biologically active and not conserved over longer time scales, it is less effective as a long-term measure of dilution in the bays. The other discrete parameters either over or underestimated the dilution relative to the dye, possibly due to any of three factors: 1) inappropriate assumed background concentrations due to neglecting mixing of dyed effluent into previous plume, 2) loss or of a gain of a chemical through non conservative processes, and 3) poor precision on the data that was obtained. The data from the survey are inadequate to differentiate any of the three possible causes, although the data make it clear that additional samples are required on future surveys if the first two causes are to be addressed.

One additional observation from the discrete samples is an apparent increase in total suspended solids in the plume relative to increases expected based on the dilution and concentration in the effluent. The data from the discrete samples suggest an increase of about ~0.3 mg/L versus an estimated increase if the TSS was conservative of 0.11 mg/L. Results from the *in situ* tracking also demonstrate an increase in the concentrations of the particle field near the diffuser as measured with a transmissometer. The correspondence converged with background beam attenuation values at dilutions of about 300 to 400 and did not show evidence of particle settling or other loss relative to the dispersion of the dye, either during the HMZ surveys nor 24 hours after the dyed effluent entered the offshore environment. Thus, particles within the precision of these measurements appear to be behaving conservatively after discharge. Further studied are required to better understand this potential loss of effluent derived particles from the water column on the time scales of the plume dilutions studied.

Conclusions

Both the field and modeling results show the outfall is performing as expected. Measured dilutions and other wastefield characteristics from the model are consistent with results from the original RSB model, analysis with the RSB model using field data from this plume tracking study, and a new physical model study. A dilution of ~85 was observed within ~50 meters of the diffuser line which slowly increased to ~105 three hundred meters from the diffusers. Oceanographic mixing and dispersion further increased the dilution in after the dye had exited the outfall system. Dilutions of 200 to 400 were measured 24 hours following discharge.

It is concluded that the outfall is behaving as expected and that acceptable water quality is being achieved at the outfall. Ammonia appears to be an excellent short-term tracer of the effluent and may serve as a check on initial dilution in the future.

Particle settling on time scales of 24 hours is not apparent in the data, thus rapid loss of particles to the seafloor is not occurring.

The survey met its goals of validating the data collection methods while obtaining quality information on the dilution characteristics of the plume. The modifications recommended in Mansfield *et al*. (2001a) will substantially improve the certification survey in July 2001.

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Appendix A

Results of Special Studies

Attachment 1

EFFECTS OF TEMPERATURE AND INSTRUMENTATION ON RHODAMINE WT DYE FLUORESCENCE READINGS

INTRODUCTION

Under Part I, Section 18.e of the National Pollutant Discharge Elimination System (NPDES) permit issued by the U.S. Environmental Protection Agency (EPA) and the Massachusetts Department of Environmental Protection (EPA/MADEP 1999) for the new sewage outfall discharging in Massachusetts Bay, the Massachusetts Water Resources Authority (MWRA) is required to "field test and certify whether the outfall's minimum dilution is equal to, or greater than, the predicted minimum dilution" specified in a hydraulic study. To meet this requirement, Battelle conducted two plume-tracking studies, in the Winter and Summer of 2001. The Winter 2001 survey was intended as a shakedown survey and its purpose was to test protocols planned for the Summer 2001 survey and to develop information on effluent dilution under unstratified conditions. The Summer 2001 survey was the "certification" survey, intended to monitor dilution under strongly stratified water column conditions. During both surveys, the monitoring of effluent plume dilution characteristics and transport was conducted using in situ fluorometers monitoring Rhodamine WT dye as a tracer.

Previous studies have shown that fluorescence intensity increases with decreasing temperature (Feuerstein and Selleck 1963, Wilson *et al*. 1986) and also varies with total suspended solids concentrations in natural samples (Feuerstein and Selleck 1963). Further, Wilson et al (1986) state that fluorescence measurements are instrument-specific. To address these issues, a series of experiments were performed to obtain a robust calibration of the specific instruments used in the field during the Winter and Summer 2001 plume tracking surveys. The objectives of these experiments were

> To assess the effect of temperature on Rhodamine WT fluorescence across the concentrations and media used during the 2001 MWRA plume tracking surveys.
>
> To develop a temperature compensation equation for each instrument package used during the 2001 plume tracking surveys and compare the equation with that previously reported (Feuerstein and Selleck 1963).

METHODS

The data used to develop the temperature -fluorescence relationship equation were developed from three separate sets of experiments:

1. Temperature dye experiments performed in de-ionized (Milli-Q) water only. These experiments were performed on April 13, 2001.
2. Temperature dye experiments performed in filtered seawater and in effluent performed between July 25 and August 1, 2001.
3. Sensor calibrations performed on August 2 and 6, 2001 for the analysis of discrete water samples collected during the Summer 2001 plume tracking survey.

The study performed on filtered seawater and effluent (2 and 3 above) provided the base of data used in this report. The methods used for this study are presented in detail. However, because data are presented from all three sets of experiments, all three sets of conditions and methods are reported.

Equipment

The two Rhodamine fluorometers that were used in the field on the plume tracking surveys were also used for conducting all three sets of experiments. The data from each fluorometer were processed through the analog channel of a conductivity/temperature/depth (CTD) sonde to the Battelle NavSam© computer system. The CTD also provided temperature data used in the experiment. The fluorometer/CTD combinations used in the experiments are shown in Table 1.

Table 1. Sensor systems used for the fluorescence temperature calibration experiments.

			Seapoint *in situ* rhodamine fluorometer Serial # and range setting (ppb)		**Ocean Sensors CTD Model OS200 serial #**
Measurement type	**Water type**	**Dye Concentration**	**# 4125 (Seapoint A)**	**# 4126 (Seapoint B)**	
			DYE	**DYE2**	
Temperature compensation experiments	Deionized water	50 ppb	0-150	0-150	465
		25 ppb	0-150	0-150	465
		2.5 ppb	0-150	0-5	465
	Filtered Seawater	1.0 ppb	0-150	0-5	521*
	DITP Effluent	60 ppb	0-150	NA	521*
Discrete sample analysis	DITP Samples		0-150	NA	464
	Offshore Samples		NA	0-5	407

* OS200 #521 determined to have incorrect calibration coefficients. Results post-processed with correct coefficients.

The manufacturer calibrated each Seapoint fluorometer for Rhodamine WT; that is, the voltage output was calibrated to correspond directly to Rhodamine WT dye concentrations in ppb. In both the Winter and Summer 2001 MWRA plume tracking surveys, Seapoint A fluorometer (Seapoint # 4125) in the 0 – 150 ppb range was used to measure fluorescence in the effluent, whereas Seapoint B fluorometer (# 4126) in the 0 – 5 ppb range was used to measure fluorescence of the diluted effluent in Massachusetts Bay. The fluorometer and range settings used during the actual dye studies were the same as those used in the laboratory studies to determine the fluorescence/temperature response and conduct the discrete sample calibrations and measurements. The only exceptions were when the fluorometer responses were being cross-calibrated. During these studies the range settings were varied.

While the fluorometers used in the temperature calibration experiments were the same as used for the field studies, the CTD units differed. To ensure the CTD electronics did not affect the dye signal, an independent calibration of the analog channels was performed. The calibration verified that the analog signals processed through the different CTD units were the same.

DI Water Study

Three, 2-liter solutions of Rhodamine WT dye were prepared by weighing Milli-Q water and adding dye to the known mass of water. Dye was added volumetrically to give a final concentration (of active ingredient) of 2.5, 25, and 50 uppb in the three solutions. These concentrations were selected to test the instrument across a range of gain settings. The 2.5 μppb solution was measured with both fluorometers, one in the 0 – 5 ppb range and one in the 0 – 150 ppb range. The 25 and 50 μppb solutions were measured with both fluorometers in the 0 – 150 ppb range. Each test solution was measured independently.

Each test solution was transferred to a clean 3-liter glass container, which was placed in a temperature controlled water bath. A stirring rod was placed in the test solution to keep the sample well mixed. Both fluorometers and the temperature sensor of the CTD were placed in the test solution to monitor temperature of the sample. Throughout the experiment, fluorescence in each solution was measured by both Seapoint A and B systems. The tandem testing was used to intercalibrate the sensors, as well as verify their response to temperature. Water temperatures in this experiment ranged from 8 °C to at least 20°C. for each concentration. In each case, the fluorescence was measured as the temperature was rising. Data were also recorded when temperatures extended beyond this range. All sensors and glassware were thoroughly cleaned between experiments.

Filtered Seawater and Effluent Study

The effects of temperature on Rhodamine WT fluorometric readings in effluent and filtered seawater were studied in a laboratory experiment similar to the ones conducted on de-ionized water.

Filtered Seawater

The seawater experiments were conducted on filtered seawater from Nantasket Roads, Massachusetts Bay. The seawater was collected surface waters during the Summer 2001 MWRA plume tracking survey (July 19, 2001). The seawater was transported to the laboratory and stored in a cold room at 4°C until use. Prior to the experiment, the seawater was filtered through Whatman GF/F glass fiber filters with mean pore size of 0.45 μm. Triplicate solutions of 1ppb Rhodamine WT (weight/weight of active ingredient) were independently prepared in filtered seawater. A blank filtered seawater sample was also prepared and processed along with the dilute dye solutions. These seawater dye solutions were intended to represent the matrix and dye conditions of samples collected during the offshore plume tracking surveys.

Effluent

The effluent experiments were conducted in whole (unfiltered) effluent that was collected from the west disinfection basin at the Deer Island Treatment Plant (DITP) on July 23, 2001. The effluent was transported to Battelle facilities and stored at 4°C until needed. Triplicate solutions of 60 ppb active ingredient (weight/weight) in effluent were independently prepared. An effluent blank solution was also prepared and processed along with the dilute dye solutions. These effluent solutions were intended to represent the DITP samples that were collected during the Winter and Summer 2001 MWRA plume tracking surveys.

The temperature response in each of the eight test solutions (3 x 1 ppb seawater plus seawater blank; 3 x 60 ppb effluent plus effluent blank) was analyzed independently. Approximately, 500 mL of each solution was poured into a clean 1-liter opaque plastic container, which was placed in a temperature controlled water bath. Temperature of the test solution was monitored with a temperature sensor from the OS200 CTD unit, which was immersed in the solution. For the 1 ppb solutions, both Seapoint A and B fluorometers, the units that monitored fluorescence in effluent at DITP and in seawater at the diffuser, respectively, were placed in the solution. Seapoint B was operated on the 0 – 5 range and Seapoint A on the 0 – 150 range setting. For the 60 ppb solutions, only the Seapoint A fluorometer was placed in the test solution (see Table 1). This unit was operated on the 0 – 150 range setting. Battelle NavSam© software was used to record the fluorescence and temperature data.

The sample solution was cooled to approximately 5°C and sensors placed in sample. The water bath temperature was then slowly raised to ~ 20°C for each solution. When the peak temperature was reached, the sample temperature was allowed to cool to approximately 10°C, when the sample run was terminated. All sensors and glassware were thoroughly cleaned between experiments.

Calibrations Performed for the Discrete Water Sample Analysis

A set of calibration standards was prepared for each media (Rhodamine WT in either seawater or effluent) for which discrete samples were collected during the Summer 2001 MWRA plume tracking survey. These included:

Seawater: Blank, 0.25 ppb, 0.50 ppb, 1.00 ppb, 1.25 ppb, 2.5 ppb
Effluent: Blank, 50 ppb, 60 ppb, 80 ppb, 90 ppb, 100 ppb

The seawater for these calibrations was the same as collected from Nantasket Roads, Massachusetts Bay on July 19, 2001. It was maintained cold throughout its storage. Prior to the experiment, the seawater was filtered through Whatman GF/F glass fiber filters with mean poresize of 0.45 µm as above. The effluent calibration solutions were prepared in whole (unfiltered) effluent that was collected from both the east and west disinfection basin at the DITP on July 23, 2001. The effluent was stored at 4°C as above.

Three separate primary stock solutions of the active ingredient (weight/weight) in each seawater and effluent matrix were prepared independently. Each stock solution was then diluted volumetrically (volume/volume) to achieve the concentrations shown above, which were intended to bracket the dye values observed during the survey. Seawater and effluent blank solutions were also prepared and processed along with the dilute dye solutions.

Each of the calibration solutions was analyzed independently in the following manner. Approximately, 500 mL of each solution were poured into a clean 1-liter opaque plastic container, which was placed in a water bath to minimize temperature excursions of the solution. The fluorescence of the calibration solutions (as well as the discrete samples) was measured at approximately the same temperature that the respective matrices were measured in the field. The seawater calibration solutions and samples were measured within a range of 6 to 8 C; effluent between 18 and 20 °C. The temperature of each test solution was monitored with a temperature sensor from the OS200 CTD unit, which was immersed in the solution. The Seapoint A fluorometer (range 0-150) was calibrated in effluent and the Seapoint B fluorometer (range 0 – 5 ppb) was calibrated in seawater. Battelle NavSam© software was used to record the fluorescence and temperature data. Once the sample and sensors were placed in the water bath and the temperature stabilized, the fluorescence measurement was recorded. All sensors and glassware were thoroughly cleaned between experiments.

Once the calibration curve was established discrete samples were analyzed using the above measurement procedure. After each 5 discrete unknown samples were measured, one or more of the standards was rerun to check the stability of the standard curve and the measurement system response. This was continued until each unknown had been measured. This provided a set of replicate results for each standard concentration.

RESULTS

De-ionized Water

The fluorescence of the 2.5 ppb solution was measured with both Seapoint fluorometers, one in the 0 – 5 ppb range and one in the 0 – 150 ppb range using an uncompensated temperature output signal. Both measured a small uncorrected fluorescence signal that decreased with increasing temperature across a temperature range of approximately 7 to 34 °C (Figure 1). The fluorescence signal from Seapoint A fluorometer operating in the 0 – 150 ppb range showed a slightly lower dye concentration compared to the Seapoint B fluorometer in the 0 – 5 ppb range across all temperatures. The uncorrected fluorescence of the 25 and 50 ppb Rhodamine WT in seawater solutions are presented in Figures 2 and 3, respectively. In both cases, the two fluorometers were set in the 0 – 150 ppb range. Both sets of data show decreasing dye concentration as measured by fluorescence with increasing temperature.

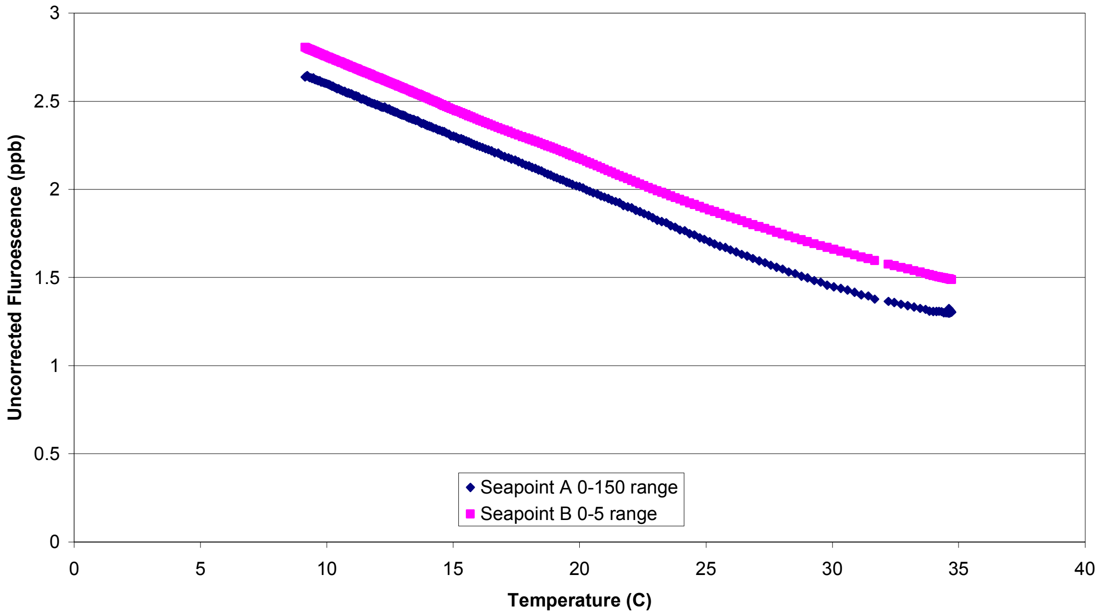

Figure 1. Uncorrected fluorescence of 2.5 ppb Rhodamine WT in de-ionized water.

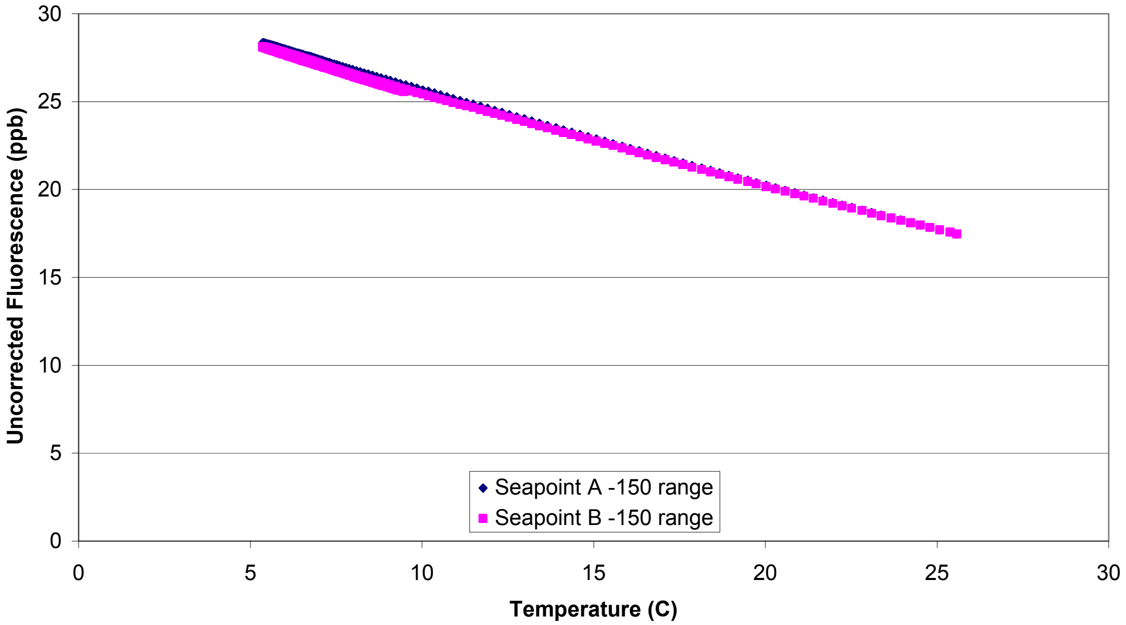

Figure 2. Uncorrected fluorescence of 25 ppb Rhodamine WT in de-ionized water.

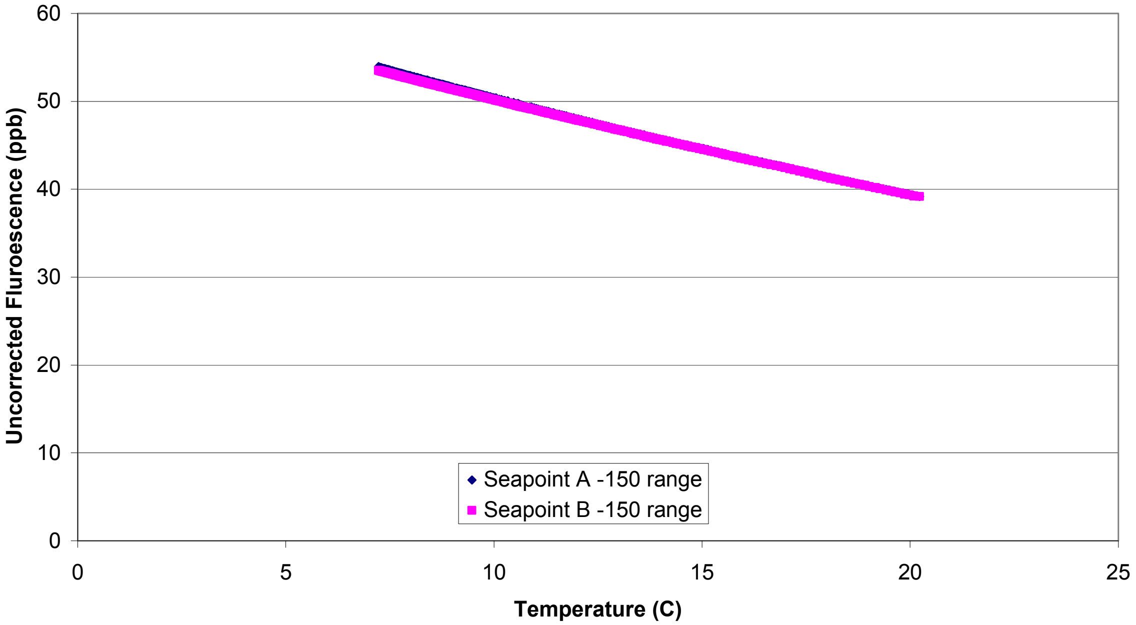

Figure 3. Uncorrected fluorescence of 50 ppb Rhodamine WT in de-ionized water.

Feuerstein and Selleck (1963) report that the effect of temperature on fluorescence intensity can be described with the following relationship:

$$F_c = F_r\, e^{d(T - To)}$$

Where, F_c is the temperature corrected fluorescence concentration
F_r is the uncorrected fluorescence concentration
d is a constant for a given fluorescent dye
T is the temperature at which the fluorescence is measured
T_o is the temperature at which F_c/F_r is unity

The above equation was rearranged as follows to regress the data from the de-ionized water temperature series experiments.

$$T = (1/d)*\ln(F_c/F_r) + T_o$$

Figure 4 presents the transformed temperature series data from the 2.5 ppb experiment, in which the two fluorometers were measuring at different range settings. Plotted in this fashion, the slope of the regression equals 1/d and the regression intercept equals T_o. Similar data transformations were performed on the other temperature series. The calculated slope (d) and T_o for each of the experiments are presented in Table 2. The fluorescence/temperature relationship as observed as d and T_o values for the 25 ppb and 50 ppb solutions are similar to each other (d = ~0.231 versus 0.243 and T_o = 10.22 to 10.72 as the mean of each test solution concentration). Note the full range across the 5 and 50 ppb test solutions measured by the two instruments is 0.0229 to 0.245 and 10.13 to 10.88 for d and T_o, respectively. However, for the 2.5 ppb solution, the slope d was larger than found for the other two solutions and were not the same (0.0285 versus 0.0252 for instruments in the 0 – 5 ppb and 0 – 150 ppb ranges, respectively). T_o values also differed significantly (values 11.6 °C versus 14.1 °C, respectively) from those determined for the high dye concentrations.

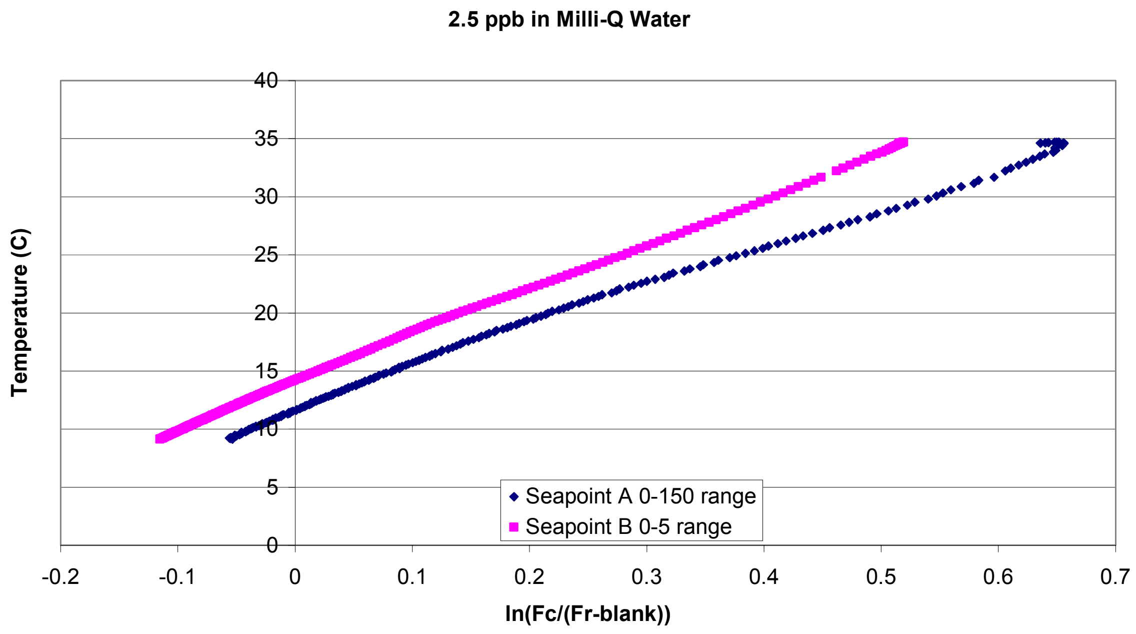

Figure 4. Transformed temperature response data: 2.5ppb Rhodamine WT in Deionized Water (blank in Deionized water assume to be 0).

Table 2. Regression coefficients d and T_o derived for De-Ionized Water Solutions using the transformed sensor data.

Test Solution	Fluorometer	Range	d	To
50 ppb	4126	0 - 150	0.0245	10.31
50 ppb	4125	0 - 150	0.0240	10.13
25 ppb	4126	0 - 150	0.0233	10.88
25 ppb	4125	0 - 150	0.0229	10.56
2.5 ppb	4126	0 – 5	0.0285	11.56
2.5 ppb	4125	0 - 150	0.0252	14.06

These data indicate relatively consistent temperature compensation coefficients (d and T_o) at the higher dye concentrations (that is at lower instrument sensitivity) but suggest different temperature versus dye response regression coefficients for lower dye concentrations measured under different sensitivity scales. The differences among the coefficients raised questions about which regression coefficients should be used and whether “sensor specific” or “sensor scale specific” sensitivity response should be used to in the temperature compensation calibrations. Also identified as a concern was a potential response difference in non-DI water media and whether the coefficients derived in DI water could be applied to seawater and effluent. These concerns were further evaluated using the seawater and effluent temperature series and calibration standards experiments described above.

Filtered Seawater Temperature Compensation Experiment

Seawater Blank

The uncompensated fluorescence of the seawater blank was measured simultaneously with both fluorometers. Each sensor measured a small fluorescence signal that did not show a consistent function to temperature across a temperature range of 5.5° to 19.8 °C (Figure 5). However, the fluorescence signal from Seapoint A fluorometer operating in the 0 – 150 ppb range showed more noise than the Seapoint B fluorometer operating in the 0 – 5 ppb range and also recorded a higher average fluorescence reading. Because there was no apparent function in the background response with temperature, the average fluorescence of the filtered seawater was calculated. The average background in the sample measured with Seapoint A was 0.0876 ppb, whereas the background fluorescence measured with Seapoint B was 0.0663 ppb. These data suggested as in the DI water experiments that there is a sensor or sensor scale specific calibration response.

Given that a background response in the seawater was measured, it was recognized that the signal should be removed from any temperature response curves so that a true dye response could be determined. For the seawater the background response was very small and did not show any functionality with temperature. Thus, the average values calculated above were subtracted from the respective uncorrected fluorescence values in the subsequent 1 ppb Rhodamine WT experiment prior to evaluating the relationship between dye response and temperature.

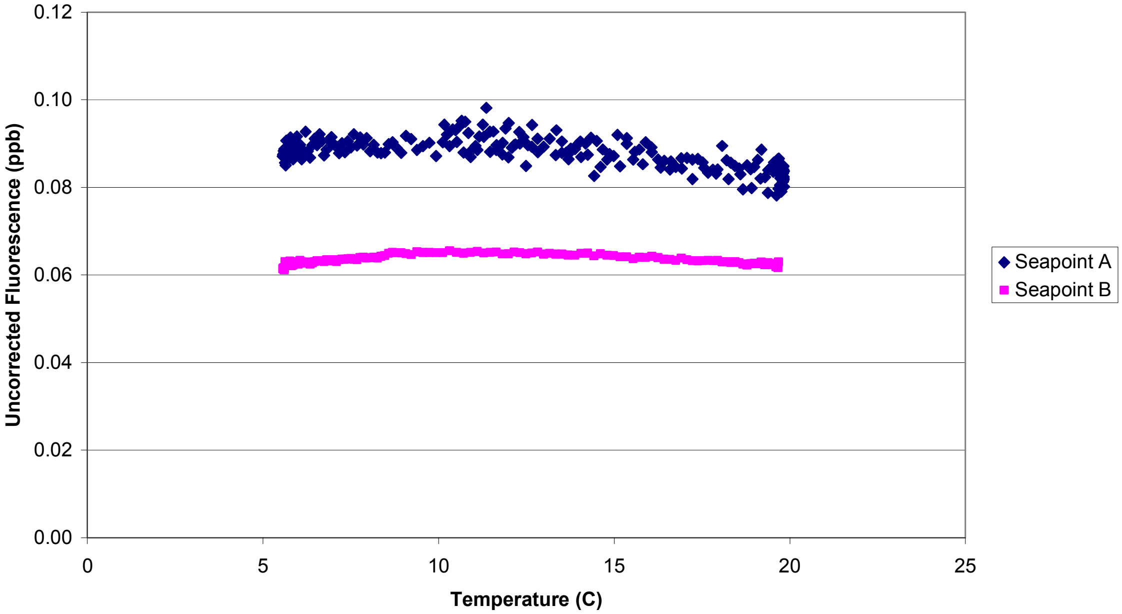

Figure 5. Fluorescence of filtered seawater blank monitored with Seapoint A (range 0-150 ppb) and Seapoint B (range 0 – 5 ppb).

<u>1ppb Rhodamine WT in Seawater</u>
The uncorrected fluorescence signal of the 1 ppb Rhodamine WT solution in seawater was found to decrease with increasing temperature (Figure 6). As with the blank seawater fluorescence, the Seapoint A fluorometer (range 0 – 150 ppb) consistently recorded higher fluorescence at all temperatures compared to the Seapoint B fluorometer operating in the 0 – 5 ppb range. These data add further credence to the

supposition from the DI water study that there is a sensitivity scale specific response when measuring dye using these instruments.

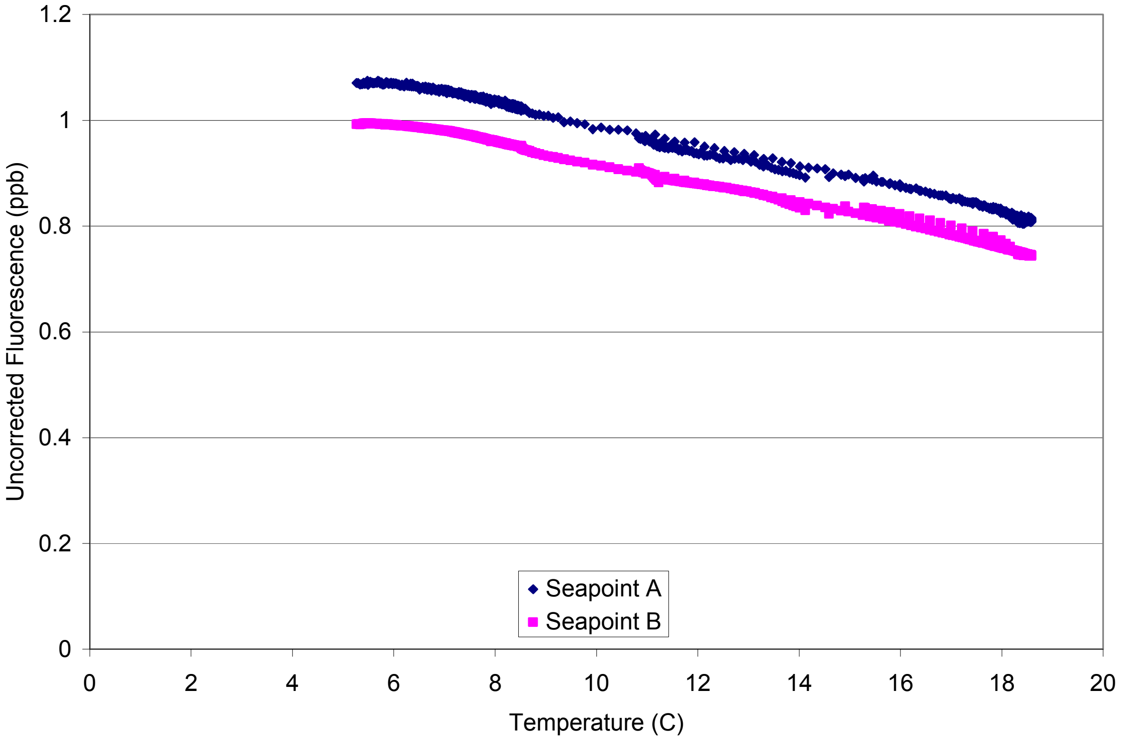

Figure 6. Uncorrected fluorescence data from temperature experiment, 1 ppb Rhodamine WT in filtered seawater.

To develop the temperature compensation coefficients, the fluorescence data for each of the three ppb dye solutions were transformed as described previously (Figure 7). The figure presents the transformed temperature series data from the two fluorometers for all three replicates. To perform the regression analysis, the mean background fluorescence of the filtered seawater blank (0.0876 and 0.0663 ppb for Seapoint A and B, respectively) was first subtracted from the uncorrected fluorescence readings and the regression coefficients calculated as previously described. The calculated d and T_o for each of the replicate series are presented in Table 3 along with the mean and standard deviation derived the three solutions measured by each sensor. For the 1 ppb Rhodamine WT in seawater, the calculated constant d was nearly the same for the two fluorometers (mean values 0.0256 versus 0.0250 for Seapoint A and Seapoint B, respectively) with the standard deviations from the triplicate runs overlapping. Thus, no significant difference in the slope was found. Moreover, the mean regression slope is close to the published literature value. The slope measured for this solution (Seapoint B) was selected as the sea water temperature compensation coefficient as it best represents the seawater conditions and is the instrument used in the plume tracking in the winter and summer plume tracking surveys.

In contrast, the T_o values differed substantially (mean values 8.478 °C versus 4.927 °C, respectively). Each of these means also had a large standard deviation that was 26 to 40 percent of the mean. A convergence of the interception or reference temperature for these solutions was not apparent nor did the T_o converge with that from the DI water measurements. Thus, further evaluation of the T_o was required. The resolution to this issue is described under the discussion of the analysis of the standard solution.

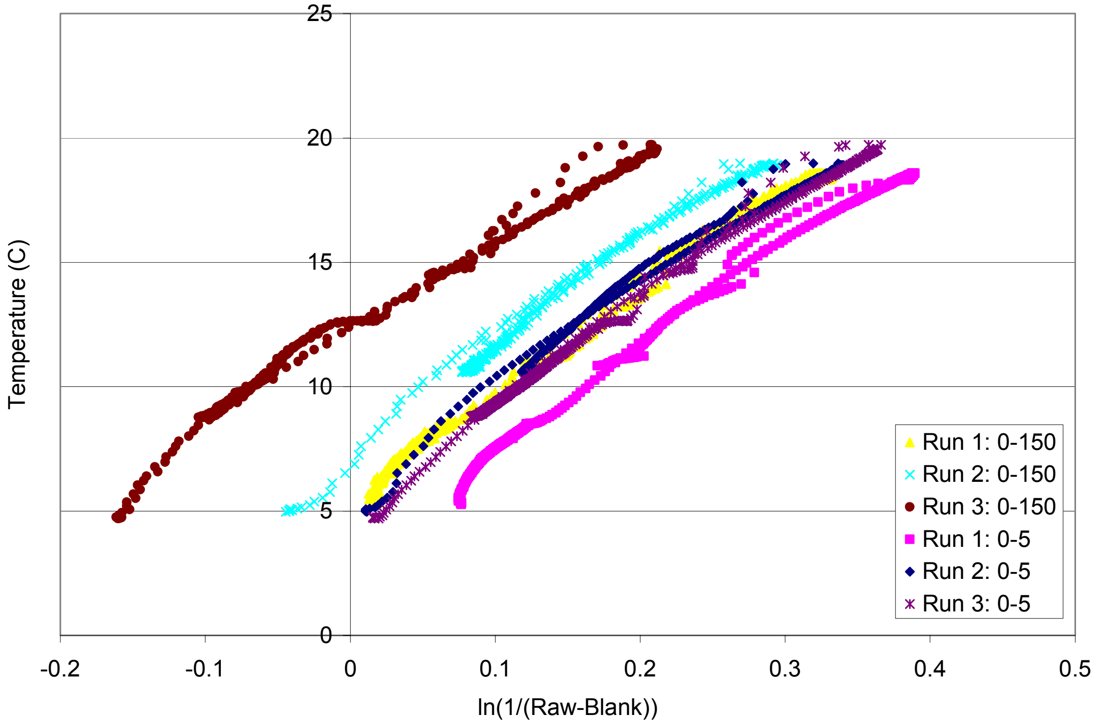

Figure 7. Transformed temperature response data for triplicate 1ppb Rhodamine in Filtered Seawater, measured by Seapoint A (0-150 ppb range) and Seapoint B (0–5 ppb range).

Table 3. Regression analysis of transformed 1 ppb Rhodamine WT temperature response in filtered seawater.

Temperature series	D	T_o
Seapoint A Rep 1	0.0251	5.732
Seapoint A Rep 2	0.0237	7.397
Seapoint A Rep 3	0.0280	12.304
Mean	0.0256	8.478
Std. Dev.	0.002189	3.416566
CV	0.08554	0.402997
Seapoint B Rep 1	0.0255	3.537
Seapoint B Rep 2	0.0250	5.986
Seapoint B Rep 3	0.0246	5.257
Mean	0.0250	4.927
Std. Dev.	0.00043	1.257445
CV	0.017199	0.255236

Effluent

Effluent Blank

The uncorrected fluorescence signal in the background fluorescence of the effluent was found to have a decreasing response as a function of increasing temperature (Figure 8). The uncompensated fluorescence readings ranged from 0.413 to 0.330. The decreasing response posed a small dilemma with respect to application of any background corrections (see rationale under seawater for applying background corrections to the dye readings prior to performing regression analysis). The dilemma is simply whether to correct for a specific background reading at each small temperature increment, or to base the correction on the average, or to develop a customized correction value at the temperature typical of the effluent. Because the change in fluorescence was small compared to the expected fluorescence of the dye in effluent (~ 0.35 versus over 80 ppb), an average blank value was calculated (0.343 ppb) and applied to the experimental data prior to performing transformations and regressions.

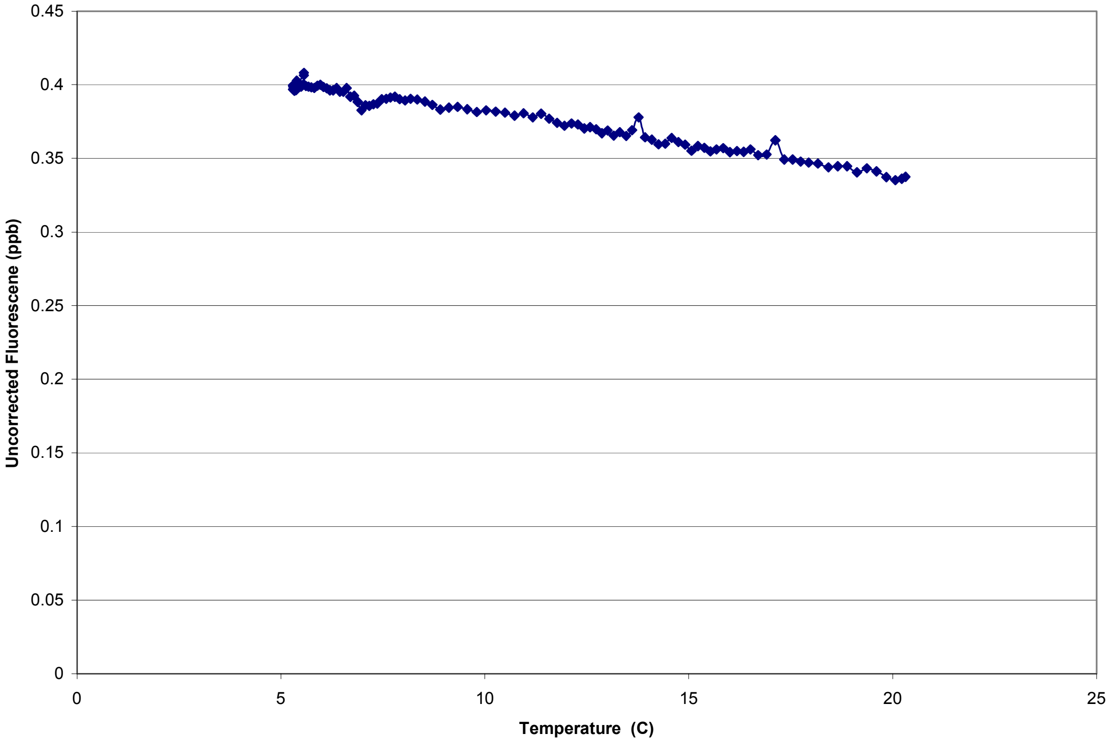

Figure 8. Uncorrected fluorescence of DITP Effluent (Effluent Blank)

60ppb Rhodamine WT in Effluent

The fluorescence signal of the 60 ppb Rhodamine WT solution in the whole effluent was observed to decrease with increasing temperature, with uncompensated Rhodamine WT fluorescence values ranging from approximately 63 ppb at 4°C to 47 ppb at 20°C (Figure 9). Following the analysis procedure described previously, the 0.343 ppb background fluorescence was first subtracted and the uncompensated fluorescence results transformed for each of the three effluent replicates (Figure 10) prior to performing a regression analysis.

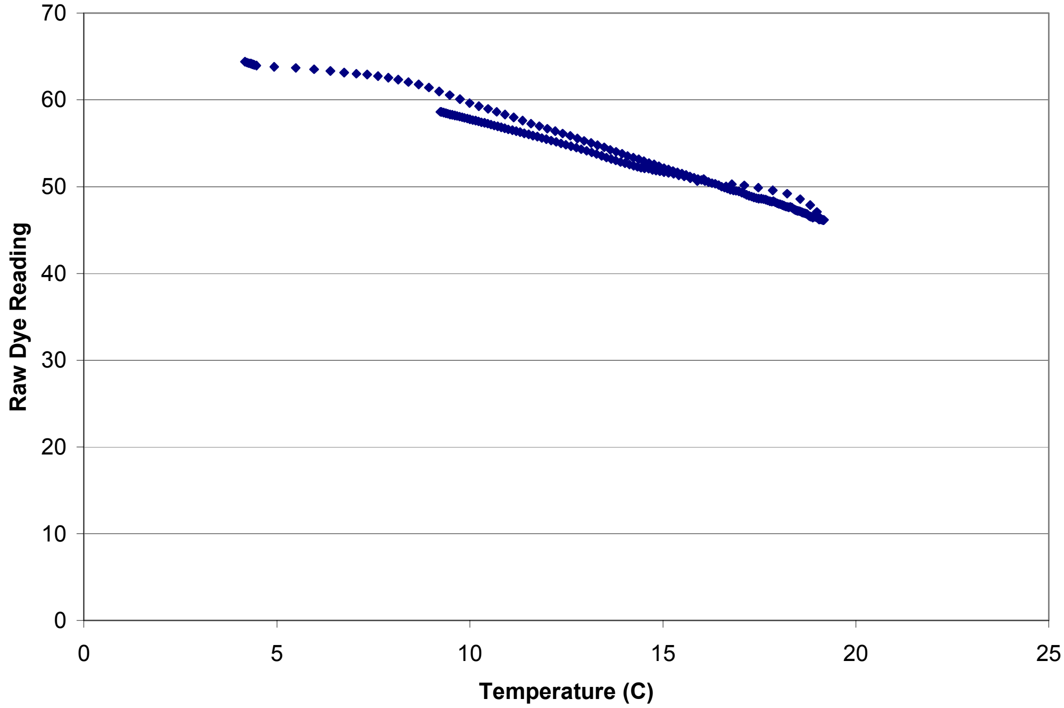

Figure 9. Uncorrected fluorescence of 60 ppb Rhodamine WT in Effluent uncorrected fluorescence concentration ranged from approximately 63 ppb at 4 °C to 47 ppb at 20 °C.

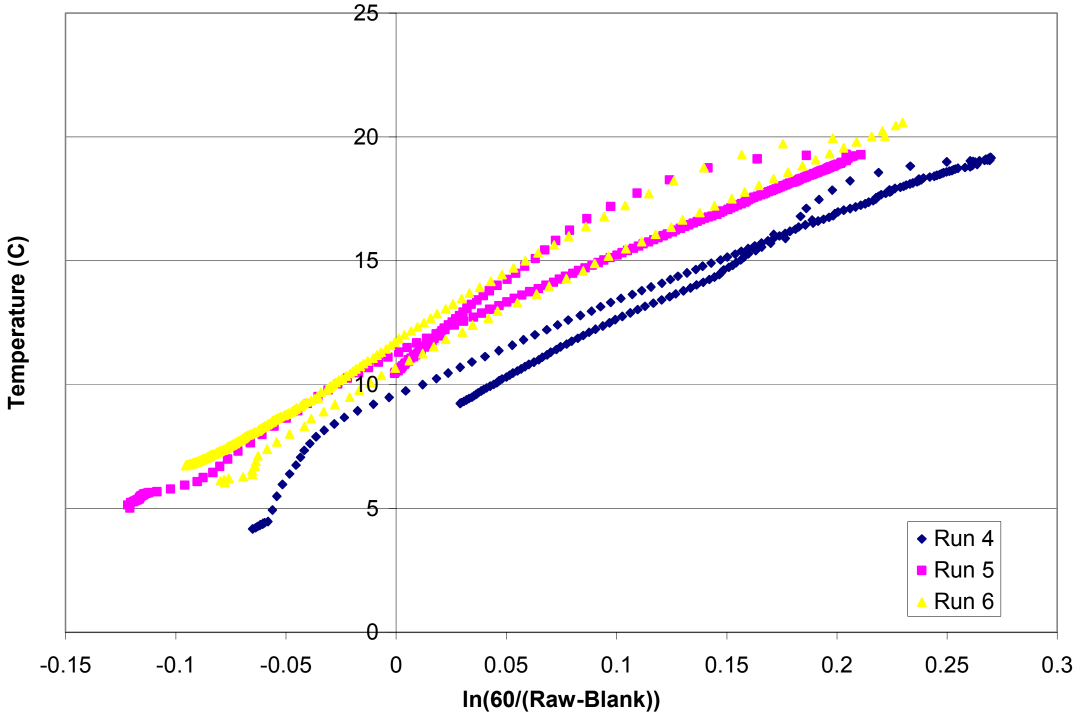

Figure 10. Transformed temperature response data for triplicate samples of 60ppb Rhodamine in DITP Effluent as measured by the Seapoint A fluorometer (0-150 ppb range).

The results of the regression analysis are presented in Table 4. The mean slope (d) was 0.0231 (σ 0.001) and the mean T_o was 10.132 (σ 1.410). The mean slope is slightly less that that observed for the 1ppb seawater standard and the mean T_o was clearly not similar to those measured in the seawater temperature study. The derived slope suggests that a media specific temperature function is present as the sensor used in this measurement set (Seapoint A) provided similar slopes to the Seapoint B sensor in the seawater 1 ppb study (see Table 3). The data indicated that the slope derived from this effluent study should be used to perform temperature compensation calculations on the effluent data. A slope of 0.0231 was thus selected.

The observed differences in T_o were also problematic in that they did not converge with the values found under the seawater study (5 and 8°C), although they did correspond reasonably close with values determined for the DI water study (10 to 11°C). As with the seawater T_o, further evaluations were conducted to develop an appropriate reference temperature (see next section).

Table 4. Regression analysis, 60 ppb Rhodamine WT in Effluent.

Temperature series	D	T_o
Replicate 4	0.0240	8.507
Replicate 5	0.0234	10.852
Replicate 6	0.0218	11.037
Mean	0.0231	10.132
Std. Dev.	0.001177	1.409967
CV	0.051042	0.139161

Calibrations Performed for the Discrete Water Sample Analysis

The fluorescence measurements of the calibration solutions provided an additional opportunity to determine Feuerstein and Selleck (1963) fluorescence/temperature relationship values for slope (d) and reference temperature (T_o). Specifically, the known concentrations in the prepared standards can be used to estimate T_o if it is assumed that the standards are correctly prepared and reflect the true concentration of the Rhodamine WT in the solution. Moreover, the slope media/instrument specific temperature compensation relationship is assumed to be that derived from the above experiments and is independent of concentration. Using these assumptions and data, a T_o for each solution can be calculated using the following data treatment:

$$F_c = F_r e^{d(T - To)}$$

Where, F_c is the temperature corrected fluorescence concentration
F_r is the uncorrected (after applications of a solution specific blank corrections to the raw data fluorescence concentration
d is a constant (slope) for a given fluorescent dye
T is the temperature at which the fluorescence is measured
T_o is the temperature at which F_c/F_r is unity

In the rearranged equation, $T = (1/d)*\ln(F_c/F_r) + T_o$, F_c, the temperature corrected fluorescence, is defined as the concentration of the solution, and F_r, is the fluorescence concentration after correcting for background fluorescence. T_o for the solution is then calculated. The results of these calculations for the seawater standards and effluent standards are shown in Tables 5 and 6, respectively.

Examination of the calculated T_o shows a mean and standard deviation of 6.022 ± 1.66 and 5.535 ± 2.02 °C, for the seawater and effluent, respectively. These values are relatively close and more similar to the T_o developed for the triplicate measurements of the 1ppb seawater solution. Comparison of the calculated results to the prepared standard concentrations show differences in dye concentration on the order of 1 to 10 percent for the seawater and less than 0.02 percent for the effluent (see Tables 5 and 6). However, because the differences between assumed correct concentrations and calculated concentrations for each standard were variable and relatively high for the seawater, one additional step was taken to finalize the reference temperature for calculation of temperature compensated in situ dye readings. It was decided that the best approach would be to use the standards data and replicate measurements to force the regression of the measured and known standard values to a slope of one. This best fit approach forced the data to a single reference temperature value for each media. Reference or T_o values of 4.876 and 5.365 °C were derived using this procedure for the seawater and effluent respectively. The effluent reference temperature is within 0.2 °C of that developed from the mean of the standards while the seawater best fit value is ~1.1 °C of the mean of the derived seawater reference temperatures.

These values along with the slopes derived above were selected for the final temperature compensation curves for the two media. The media specific temperature compensation coefficients were applied to both the summer plume tracking survey and the winter plume tracking surveys. Comparisons of the in situ data collected at the time discrete sample bottle data were collected showed a strong correspondence in the results. Thus, it was also concluded that no further calibrations of the sensor data using the discrete samples were required.

Table 5. Calculated Fluorescence/Temperature Relationship Values Derived from Seawater Calibration Data from Discrete Sample Analysis.

Std. Concentration (ppb)	Temp. (°C)	Fluorescence (ppb)	Fluorescence Bkgd-corrected (ppb)	ln(Std/(Raw-Bkgd))	To=T-F/0.0250	Calculated	% Difference from standard
0	6.986	-0.0039	-0.0019			-0.002006184	
0	5.413	-0.0036	-0.0015			-0.0015671	
0	7.262	0.0014	0.0034			0.003661305	
0.25	6.877	0.2445	0.2465	0.013950622	6.319023134	0.25918355	4%
0.25	6.664	0.2433	0.2454	0.018721929	5.915453825	0.256581734	3%
0.5	6.862	0.5002	0.5023	-0.004551146	7.044108859	0.527849297	6%
0.5	6.658	0.4903	0.4923	0.015473785	6.038590591	0.514745634	3%
0.5	7.233	0.4964	0.4984	0.003160671	7.10676816	0.528676811	6%
1	6.629	1.0353	1.0374	-0.036693734	8.096870357	1.08385243	8%
1	7.165	1.0345	1.0365	-0.035840255	8.598485208	1.097529923	10%
1.25	6.769	1.1829	1.1849	0.053445285	4.631652616	1.242387419	-1%
1.25	6.223	1.1764	1.1784	0.05898914	3.863760419	1.218764404	-2%
2.5	6.878	2.3977	2.3997	0.04094106	5.239961591	2.522851405	1%
2.5	6.329	2.3206	2.3226	0.073593039	3.385039432	2.408530276	-4%
				Selected To for best fit =	**4.876**		
	Background	-0.0020		Average To =	6.022		
	stdev	0.002993		stdev =	1.655		
	CV	-1.47178		CV =	0.2710		

Table 6. Calculated Fluorescence/Temperature Relationship Values Derived from Effluent Calibration Data from Discrete Sample Analysis.

Std. Concentration (ppb)	Temp (°C)	Fluorescence (ppb)	Fluorescence Bkgd-corrected (ppb)	ln(Std/(F-Bkgd))	To=T-F/0.0231	Calculated	% Difference from standard
0	22.26049	0.899189	-0.01858			-0.02744	
0	21.70285	0.911831	-0.00593			-0.00865	
0	22.10168	0.942275	0.02451			0.036079	
50	21.67666	34.69036	33.7726	0.392373	4.690802	49.22733	-1.55
50	21.14667	35.54801	34.63025	0.367296	5.246429	49.86324	-2.74
60	21.66049	45.45025	44.53249	0.298126	8.754618	64.88683	8.14
60	21.25097	46.26981	45.35205	0.279889	9.13455	65.45882	09.1
80	21.36352	54.54201	53.62425	0.400025	4.046406	77.59998	-3.0
80	21.74809	54.62286	53.7051	0.398519	4.496196	78.41045	-1.99
80	19.88635	56.96732	56.04956	0.35579	4.484167	78.38867	-2.01
90	21.01702	61.01218	60.09442	0.403893	3.532485	86.26971	-4.15
90	19.09692	63.32697	62.40921	0.366097	3.24857	85.70577	-4.77
100	20.56192	72.35518	71.43742	0.336348	6.001382	101.4809	1.48
100	21.0604	73.60349	72.68573	0.319025	7.249786	104.45	4.45
				Selected To for best fit =	**5.365**		
	Background	0.917765		Average To =	5.535		
	stdev	0.022148		Stdev	2.023		
	CV	0.024132		CV	0.365		

CONCLUSIONS

The objectives of these experiments were to assess the effect of temperature on Rhodamine WT fluorescence across the concentrations and media used during the 2001 MWRA plume tracking surveys and to develop a temperature compensation equation for each instrument package used during the 2001 plume tracking surveys and compare the equation with that previously reported (Feuerstein *et al.* 1963). These objectives were met and several conclusions can be derived from this study as well as recommendations.

The temperature compensation calibration coefficients developed from the study are summarized in Table 7.

Table 7. Final calibration coefficients developed for temperature compensation under the MWRA plume tracking study.

Media	Slope	T_0 (Intercept) °C
Seawater	0.0250	4.876
Effluent	0.0231	5.365

The conclusions include:

- Temperature effect on the Rhodamine dye is curvilinear
- Rhodamine dye temperature calibration coefficients require sensor specific calibrations for high precision measurements
- Media specific temperature calibration coefficients may also be required
- The slope of the temperature calibrations are close to but do not precisely align with the theoretical slope
- The reference temperature is difficult to derive and requires extensive analysis.

Future evaluation of the slope and reference temperature of this dye is recommend for high precision dye studies. These evaluations should be conducted under rigid laboratory conditions and should evaluate the causes for the discrepancies in sensor specific and media specific differences in the coefficients.

REFERENCES

Feuerstein, D.L. and Selleck, R.E. Fluorescent tracers for dispersion measurements *J. Sanit. Eng. Dic. Amer. Soc. Civil. Eng.* 89(5A4).

Wilson, JF, Cobb, ED & Kilpatrick, FA. 1968. Fluorometric procedures for dye tracing., *USGS TWRI*, Bk3 ChapA12*,* Revised.

Attachment 2

EFFECTS OF TURBIDITY ON FLUOROMETRIC DYE READINGS

INTRODUCTION

Under Part I, Section 18e of the National Pollutant Discharge Elimination System (NPDES) permit issued by the U.S. Environmental Protection Agency (EPA) and the Massachusetts Department of Environmental Protection (EPA/MADEP 1999) for the new sewage outfall discharging in Massachusetts Bay, the Massachusetts Water Resources Authority (MWRA), responsible for the operation and monitoring of the new sewage effluent outfall from the Deer Island Treatment Plant (DITP), is required to "field test and certify whether the outfall's minimum dilution is equal to, or greater than, the predicted minimum dilution" specified in a hydraulic study. To meet this requirement, Battelle conducted two plume-tracking studies, in the winter and summer of 2001. The winter 2001 survey was intended as a shakedown survey and its purpose was to test protocols planned for the summer 2001 survey and to develop information on effluent dilution under unstratified conditions. The summer 2001 survey was the "certification" survey, intended to monitor dilution under strongly stratified water column conditions. During both surveys, the monitoring of effluent plume dilution characteristics and transport was conducted using in situ fluorometers monitoring Rhodamine WT dye as a tracer.

The turbidity study described in this report is one of several ancillary studies conducted in support of the plume tracking surveys. Each of the ancillary studies is intended to address a specific technical issue associated with the use of rhodamine dye for dispersion studies. Feuerstein and Selleck (1963), in a seminal manuscript on the use of fluorescent dyes for dispersion monitoring, noted that the background fluorescence of natural waters increased with increasing concentrations of suspended solids, and demonstrated that dye fluorescence decreased with increasing suspended solids concentrations. They attributed the former phenomenon to the light scattering effect of suspended solids and the latter to optical quenching resulting from the absorption and scattering fluorescent light.

This report describes the tests conducted to address the influence of turbidity in the effluent on dye fluorescence and to determine the background fluorescence in the DITP effluent. The objectives of these experiments were

> To determine if turbidity in the effluent could interfere with the Rhodamine WT dye fluorescence readings
>
> To determine if there is a substantial background fluorescence in the effluent at the Rhodamine WT dye measurement wavelength.

Potential turbidity interference on the dye signal in the offshore environment of Massachusetts Bay is addressed during the background surveys of the plume tracking exercise, the results of which are reported in Mansfield et al. (2001a, 2001b)

METHODS

Data to determine the background fluorescence of DITP effluent and evaluate turbidity effects on Rhodamine dye fluorescence measurements were derived from experiments conducted on March 15, 2001, prior to the Winter 2001 MWRA Plume Tracking Survey. The equipment and experimental design are presented below.

Equipment

The turbidity experiments were conducted with the following equipment:

- Seapoint Rhodamine Fluorometer, Serial # 4125
- Seapoint Turbidity Sensor, Serial # 1342

The Seapoint fluorometer uses a modulated green LED lamp and a narrow band filter to excite Rhodamine WT (540 nm ± 20 nm). The fluorescent light emitted by the Rhodamine WT passes through an orange filter and is detected by a photodiode (610 nm ± 40 nm). The Seapoint fluorometer is calibrated by the manufacturer for Rhodamine WT; that is, the voltage output is calibrated to correspond directly to Rhodamine WT dye concentrations in parts per billion (ppb). For this set of experiments, the data were collected with the fluorometer set in the 0 – 150 ppb range, the same range that was used to measure fluorescence in the DITP effluent during the Winter and Summer 2001 MWRA Plume Tracking Surveys (Mansfield *et al*. 2001a, 2001b). The analog signals from both the fluorometer and the turbidity sensor were processed through analog channels of an Ocean Surveys OS200 conductivity/temperature/depth (CTD) sonde (serial # 465), which was also used to monitor the temperature of the test solutions.

Experimental Design

The turbidity experiments were conducted on dilutions of three separate test solutions: 1) undiluted DITP effluent with no dye added (EFF) was used to establish turbidity levels of the effluent, 2) de-ionized water at a dye concentration of 100 μppb (MQDYE) was used to represent true fluorescence of the dye without the effects of turbidity or other factors attributable to the effluent, and 3) DITP effluent with a dye concentration of 100 μppb (EFFDYE). Each solution was diluted with de-ionized water as shown in Figure 1. The fluorescence response from the test solution was compared to the other solutions to determine the influence of turbidity on Rhodamine WT dye fluorometric readings.

Effluent was collected from the effluent channel immediately downstream from the secondary clarifiers at Battery A at the DITP in early March, 2001, transported to the laboratory, and stored at 4 °C until needed for the study. The effluent at this plant location has not yet been chlorinated, eliminating potential confounding factors that chlorine might have on fluorescence or on the stability of Rhodamine WT (note this effect was studied under a separate special study completed for this plume tracking program). Before the preparation of EFF and EFFDYE, and before all subsequent dilutions of these solutions, the effluent was vigorously stirred. This was done to reduce effects of small-scale effluent variability in a grab sample. Procedures for the preparation of standard solutions and subsequent use in the test solutions followed Turner Designs protocols (Turner Designs, 2001).

A standard solution of 1 mg/L Rhodamine WT dye in de-ionized water (v/v) was prepared. Each dilution series test was conducted in 10 liters of test solution. MQDYE and EFFDYE were prepared at 100% concentration by the standard dye to 10 liters of de-ionized water or effluent, respectively, to achieve an authentic dye concentration of 100 μppb. Each solution was then serially diluted (quantitatively) with de-ionized water to decrease turbidity; i.e., serial dilution (Figure 1). The dilutions were measured volumetrically using a 4-liter graduated cylinder. Fluorescence (μg/L) and turbidity (FTU) were recorded for each of the 100% concentration solutions and subsequent dilutions. The measurements were made by placing the turbidity sensor, rhodamine fluorometer, and the CTD temperature sensor in the test solution. Thorough mixing was achieved in each solution by constant stirring with an electric stirrer. Once the measurements for each solution were completed (a single point data acquisition), the appropriate volume of the test solution was added to a volume of de-ionized water to prepare the subsequent test solution. The turbidity experiments were conducted on the bench top at room temperature. Temperatures, recorded for each solution at the time of data collection, ranged from 18 to 20 °C. Fluorescence measurements were not corrected for temperature.

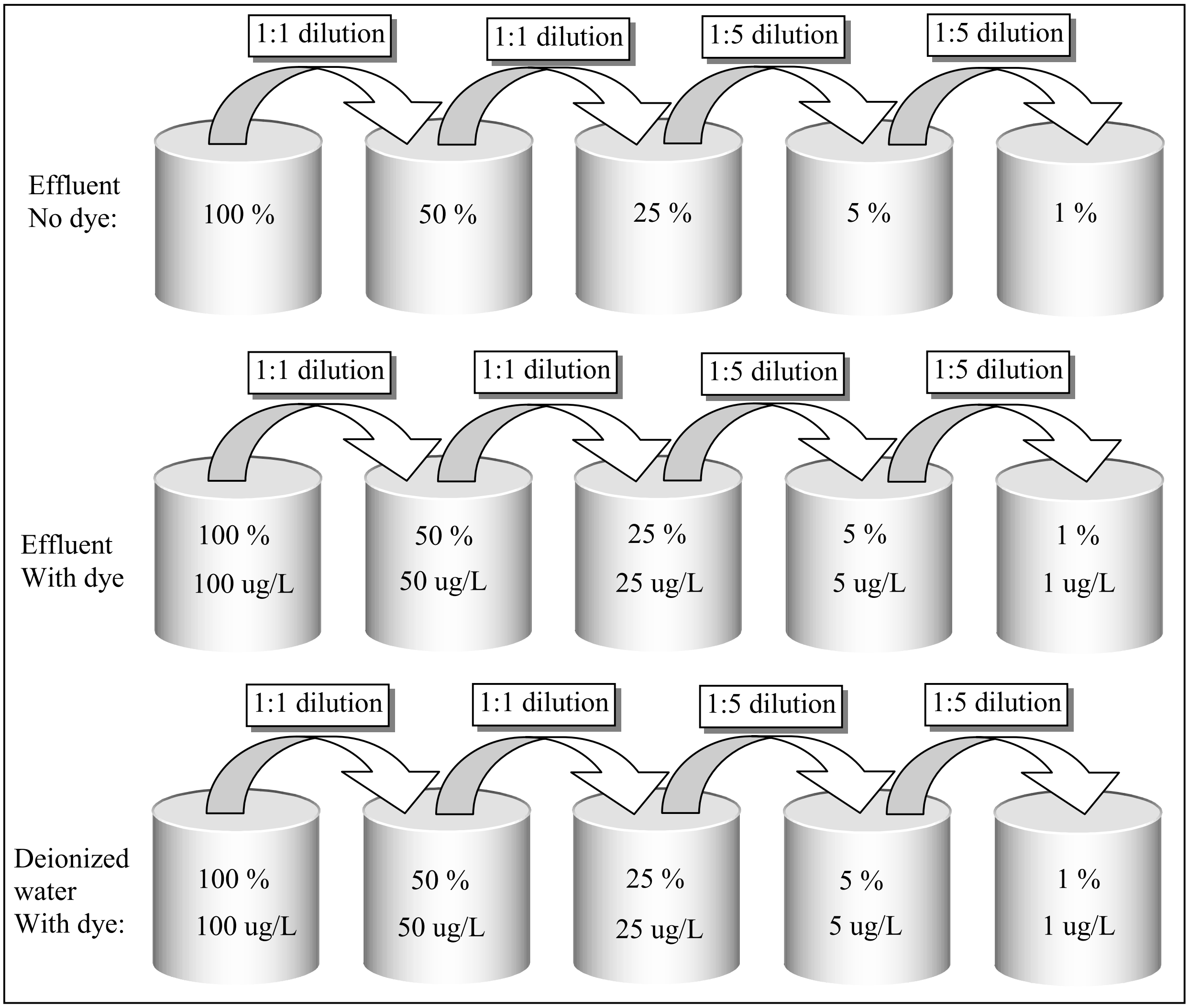

Figure 1: Turbidity experimental setup.

Results

Table 1 lists the measured turbidity (FTU) and relative (%) turbidity in the three test solutions at each of the five dilutions. Relative turbidity was calculated as percent of turbidity value in the 100% test condition (value at 100% concentration/new value). The turbidity of de-ionized water with 100 ppb Rhodamine WT measured 0.6 FTU, dropped to 0.05 FTU in the 25% dye solution, and dropped to –0.1 FTU in the 1% solution, indicating that the dye has a small but measurable turbidity signal in de-ionized water. A similar small dye turbidity signal was observed in the effluent (0.4 FTU higher in 100 ppb EFFDYE versus EFF). As expected, the relative turbidity decreased proportionally with solution concentration (Figure 2). However, a small but significant turbidity signal could still be observed in both

EFF and EFFDYE at 100x dilution. Although the turbidity of 100% de-ionized water with no dye was not measured in this series of experiments, it is expected that it would be the same as that recorded for 1% dye in de-ionized water (-0.1 FTU).

Table 1. Turbidity and relative change in turbidity with dilution.

	Effluent with no dye (EFF)		**Effluent with dye (EFFDYE)**		**Milli-Q with dye (MQDYE)**	
Concentration	**Turbidity (FTU)**	**Relative Turbidity**	**Turbidity (FTU)**	**Relative Turbidity**	**Turbidity (FTU)**	**Relative Turbidity**
100%	15.1	100.0%	15.5	100.0%	0.6	100.0%
50%	7.6	50.3%	6.9	44.5%	0.2	33.3%
25%	3.7	24.5%	3.8	24.5%	0.05	8.3%
5%	0.9	6.0%	0.7	4.5%	-0.6	<0%
1%	0.2	1.3%	0.23	1.5%	-0.1	<0%

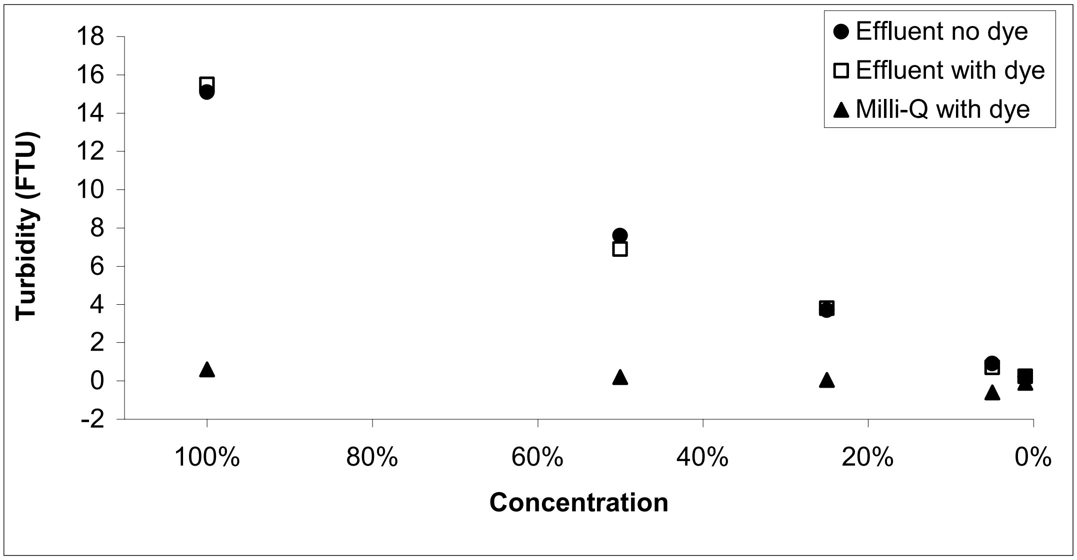

Figure 2. Response of turbidity in the effluent to serial dilution.

Table 2 presents the fluorescence data for each of the test solutions. The measured dye fluorescence in the effluent was similar to that in the Milli-Q water at each concentration, indicating that the presence of effluent did not have a significant effect on the fluorescence signal. At 100% concentration, the fluorescence in the EFFDYE measured 102.1 ppb versus 96.4 ppb for the MQDYE. Because the background fluorescence in effluent was only 0.4 µppb, it is unlikely that the difference between the EFFDYE and MQDYE is related to properties of the effluent. It is also unlikely that the effluent properties could enhance fluorescence. The significant property of the effluent that could affect fluorescence is suspended solids content (here measured as turbidity), which, according to Feuerstein and Selleck (1963), should decrease apparent dye fluorescence, not increase it. Thus, the small difference between the two 100% solutions is attributed to inaccuracies in the initial preparation of the respective 100% solutions. As the serial dilutions were made, the measured difference in concentration between the effluent and de-ionized water decreased (Figure 3).

The background fluorescence of the effluent at the Rhodamine WT wavelength was low (0.4 µppb at 100% effluent) but did not decrease significantly upon dilution (0.37 µppb at 5% effluent and 0.3 at 1% effluent). The reasons for this small relative decrease are not clear. Further evaluation of the causes would require an expanded research effort. Because the response does not impact the interpretation of these data against the study objectives, further evaluation was not conducted.

Table 2. Fluorescence and relative change in fluorescence with dilution.

	Effluent no dye (EFF)		Effluent with dye (EFFDYE)		Milli-Q with dye (MQDYE)	
Concentration	**Fluorescence (µg/L)**	**Relative Fluorescence**	**Fluorescence (µg /L)**	**Relative Fluorescence**	**Fluorescence (µg/L)**	**Relative Fluorescence**
100%	0.4	100.0%	102.1	100.0%	96.4	100.0%
50%	0.4	100.0%	51.6	50.5%	47.6	49.4%
25%	0.35	87.5%	25.9	25.4%	23	23.9%
5%	0.37	92.5%	5.4	5.3%	4.8	5.0%
1%	0.3	75.0%	1.3	1.3%	1.1	1.1%

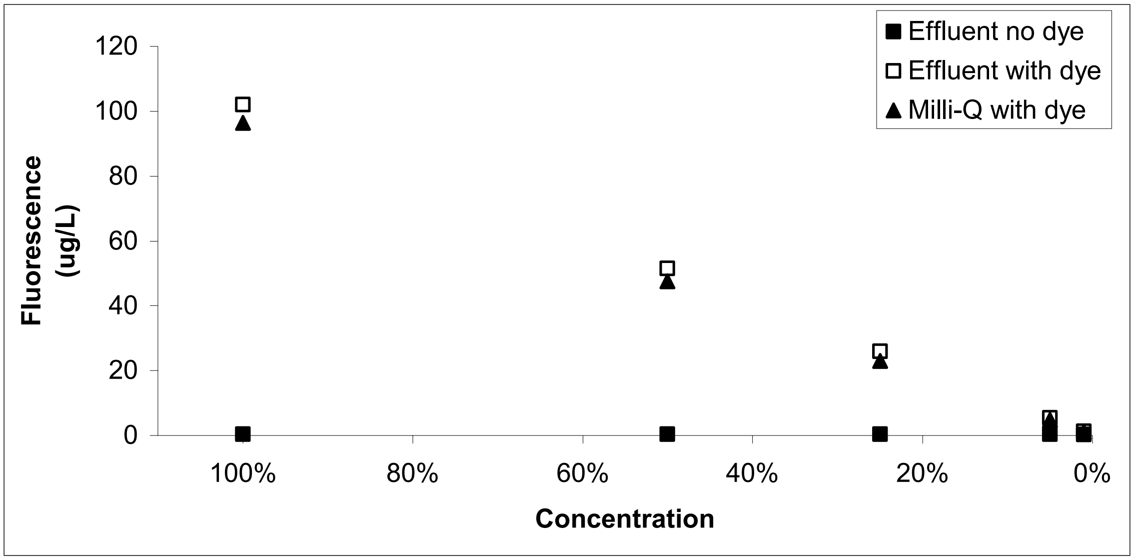

Figure 3. Fluorescence response in serial dilutions of effluent.

DISCUSSION

The background turbidity and fluorescence of the effluent measured in this experiment is consistent with values measured at the DITP west disinfection basin during the Winter 2001 MWRA Plume Tracking Survey. Figure 4 presents a scatter plot of turbidity and fluorescence measured *in situ* prior to addition of dye to the effluent stream. The majority of the effluent turbidity values ranged from 9 to 12 FTU and effluent fluorescence ranged from 0.35 to 0.45 ppb. No correlation between fluorescence and turbidity was observed. Figure 5 presents a complete set of turbidity and fluorescence data measured in the effluent throughout the dye addition for the winter survey (i.e., before, during, and after the addition of dye to the effluent stream). Although the turbidity signal displays considerable scatter, the plot shows a generally constant response in turbidity with possibly a very slight increase in turbidity measurements resulting from dye addition (the dye concentration in the effluent stream during the dye addition period averaged 54 µppb). A similar slight increase was also observed in the bench top study.

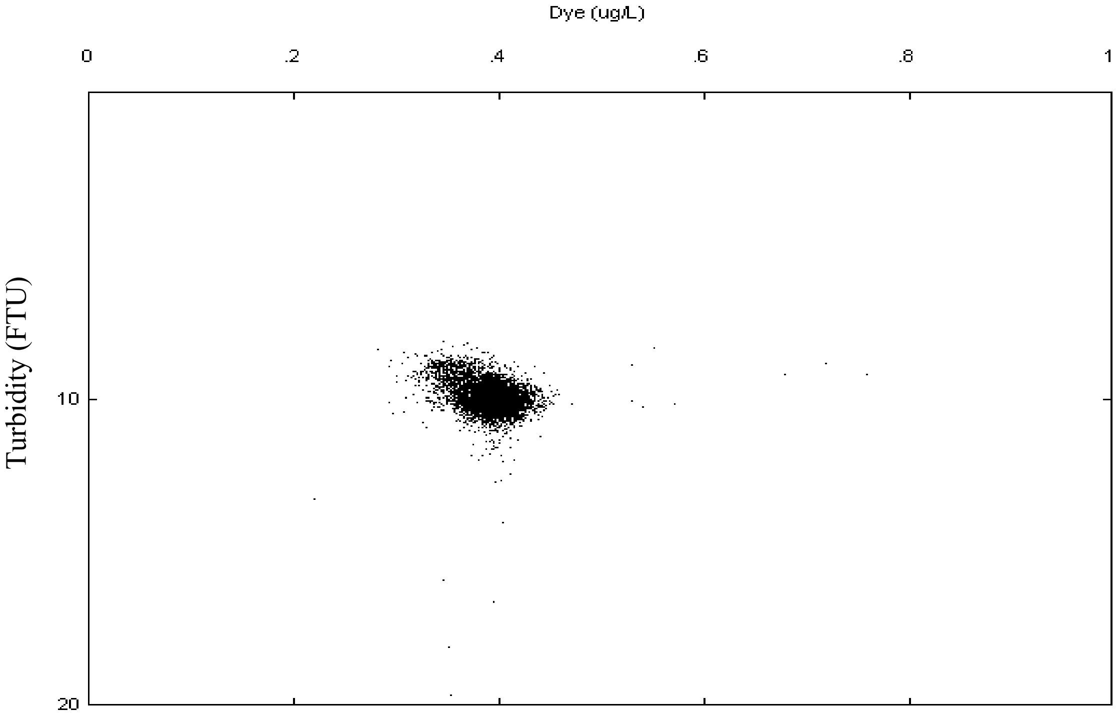

Figure 4. Turbidity versus Fluorescence Basin Prior to Dye Addition in the West Disinfection..

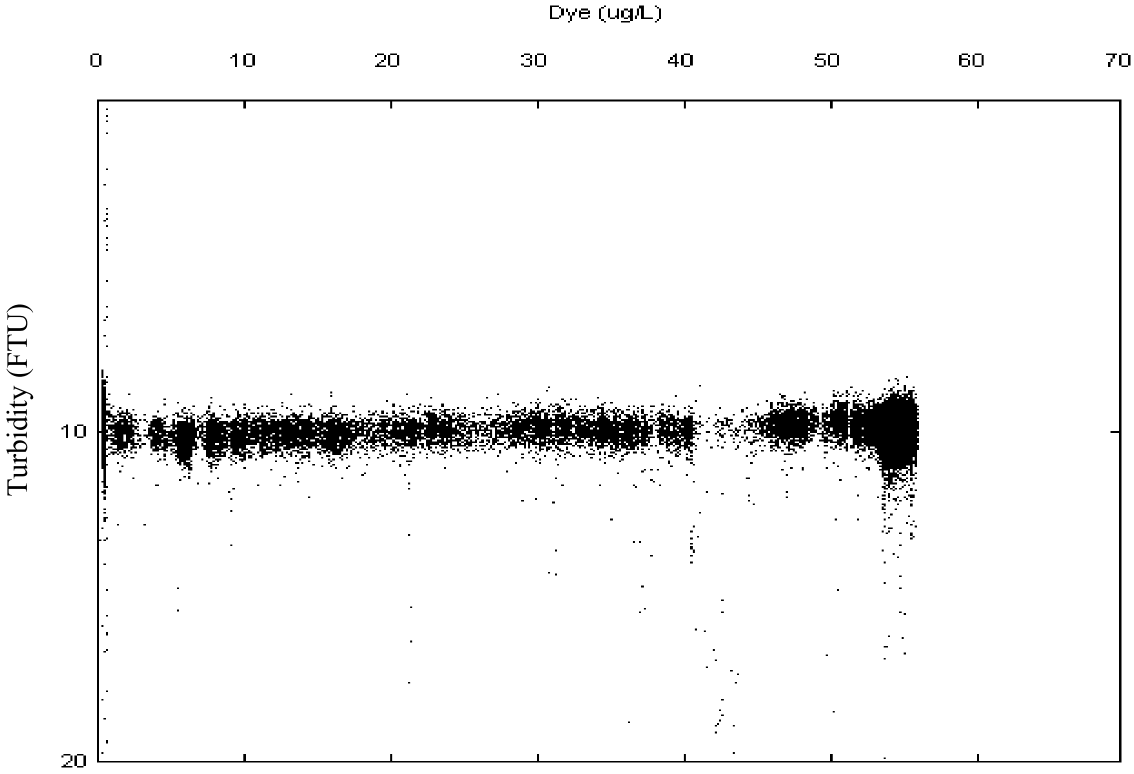

Figure 5. Turbidity versus Fluorescence in the West Disinfection Basin Prior before, during, and after dye addition to the effluent for the Winter 2001 MWRA Plume Tracking Survey.

CONCLUSIONS

This study demonstrated that while the effluent from the DITP has a measurable fluorescence signal (~0.4 ppb) at the Rhodamine WT wavelength, the signal is small relative to the signal from the dye added to the effluent (>50 ppb). The small signal is not expected to contribute significantly to the measured dye concentrations in effluent.

Further, the measured concentrations of equivalent concentrations of dye in the effluent sample and de-ionized water were the same when volumetric measurement errors were considered. Thus, this experiment does not substantiate the findings of Feuerstein and Selleck (1963) who reported increases in suspended solids concentration decreases observed fluorescence measurements. One explanation is advances in fluorometer technology, including the use of narrow bandwidth LED lamps for excitation and improvements in photodiode detection.

The fundamental conclusion from this evaluation is that correction factors to adjust the response of the dye relative to turbidity are not required for the quantification of dye in effluent.

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Attachment 3

EFFECTS OF CHLORINE AND OTHER PHYSICAL OR CHEMICAL CONDITIONS IN EFFLUENT ON RHODAMINE WT DYE FLUORESCENCE

INTRODUCTION

Under Part I, Section 18e of the National Pollutant Discharge Elimination System (NPDES) permit issued by the U.S. Environmental Protection Agency (EPA) and the Massachusetts Department of Environmental Protection (EPA/MADEP 1999) for the new sewage outfall discharging in Massachusetts Bay, the Massachusetts Water Resources Authority (MWRA), responsible for the operation and monitoring of the new sewage effluent outfall from the Deer Island Treatment Plant (DITP), is required to "field test and certify whether the outfall's minimum dilution is equal to, or greater than, the predicted minimum dilution" specified in a hydraulic study. To meet this requirement, Battelle conducted two plume-tracking studies, in the winter and summer of 2001. The winter 2001 survey was intended as a shakedown survey and its purpose was to test protocols planned for the summer 2001 survey and to develop information on effluent dilution under unstratified conditions. The summer 2001 survey was the "certification" survey, intended to monitor dilution under strongly stratified water column conditions. During both surveys, the monitoring of effluent plume dilution characteristics and transport was conducted using in situ fluorometers monitoring Rhodamine WT dye as a tracer.

The chlorine study described in this report is one of several ancillary studies conducted in support of the plume tracking surveys. Each of the ancillary studies is intended to address a specific technical issue associated with the use of rhodamine dye for dispersion studies. The rhodamine dye injected into the effluent stream is subjected to a number of factors, which may affect its fluorescent signature. These factors include agitation, biological degradation, adsorption onto particles, variable and extreme pH, and contact with (NaOCl). The degradation of rhodamine or rhodamine fluorescence by chlorine and the effects of biodegradation, agitation, and adsorption in a biologically active environment are difficult to separate (Smart and Laidlaw, 1977). For the purposes of this experiment, it was not necessary to know the specific proportions of each of these effects. Consequently, this report describes a study conducted to determine if combined conditions in the effluent stream after dye addition until discharge to Massachusetts Bay could impact dye measurements.

The chlorine concentration in the MWRA effluent immediately downstream from the hypochlorite mixers; i.e., the location where dye will be added for the plume tracking surveys, is typically less than 7 mg/L (MWRA 2000, MWRA 2001). Deaner (1973) reported that chlorine concentrations of 2 to 9 mg/L in an effluent should not significantly alter the fluorescent properties of the dye. However, Turner Designs (2001) reports that chlorine in any amount appears to destroy rhodamine WT within a few minutes, and Wilson et al. (1968) also report that chlorine is known to quench the fluorescence of rhodamine dyes. This report describes the tests conducted to address the influence of chlorine in the effluent on dye fluorescence, as well as determine if the conditions in the DITP effluent stream could affect either dye fluorescence or dye concentrations before discharge to Massachusetts Bay. No study of the potential impact of chlorine in the offshore environment, such as reaction with bromine and subsequent reaction of bromine with Rhodamine, has yet been conducted. The potential of reactive bromine interfering with Rhodamine will be addressed in a separate study. The objectives of this experiment were

To determine whether chlorine added to the MWRA effluent causes degradation of rhodamine WT dye.

To determine if biodegradation, adsorption, and agitation could have a net effect on rhodamine dye fluorescence

METHODS

The laboratory study to determine the effects of chlorine on Rhodamine WT was conducted at Battelle on March 14 and 15, 2001. The study, performed on unfiltered effluent, provided the base of data used in this report. The methods used for this study are presented in detail below.

Equipment

The chlorine experiments were conducted with the following equipment:

- Seapoint Rhodamine Fluorometer, Serial # 4125.
- Ocean Sensors OS200 CTD, Serial #465, factory calibrated
- Seabird SBE 18 pH sensor.

The Seapoint fluorometer uses a modulated green LED lamp and a narrow band filter to excite Rhodamine WT (540 nm ± 20 nm). The fluorescent light emitted by the Rhodamine WT passes through an orange filter and is detected by a photodiode (610 nm ± 40 nm). The Seapoint fluorometer is calibrated by the manufacturer for Rhodamine WT; that is, the voltage output is calibrated to correspond directly to Rhodamine WT dye concentrations in parts per billion (ppb). For this set of experiments, the data were collected with the fluorometer set in the 0 – 150 ppb range, the same range that was used to measure fluorescence in the DITP effluent during the Winter and Summer 2001 MWRA Plume Tracking Surveys. Fluorescence data were temperature corrected following data acquisition as follows:

$$F_c = F_r e^{d(T - To)}$$

Where, F_c is the temperature corrected fluorescence concentration
F_r is the uncorrected fluorescence concentration
d is a constant for a given fluorescent dye
T is the temperature at which the fluorescence is measured
T_o is the temperature at which F_c/F_r is unity
and d = 0.0231 and T_o = 6.974 (See Temperature calibration letter report, Battelle 2001).

The analog signals from the fluorometer, pH meter, and temperature sensors were processed through analog channels of an Ocean Surveys OS200 conductivity/temperature/depth (CTD) sonde (serial # 465) and Battelle Navsam© software. The glass electrode/Ag/AgCl-reference pH probe was factory calibrated. The raw pH data were temperature compensated within NavSam© following temperature and depth correction algorithms provided by the manufacturer.

Residual chlorine was measured with a HACH colorimeter-based test kit, No. 4670000, approved for the analysis of chlorine residual in wastewater. The colorimetric analysis of chlorine produces a similar color to that of rhodamine, which could confound the chlorine measurement by this method. This potential interference was addressed in the study design

Experimental Design

A 30-liter effluent sample was collected from the DITP effluent channel immediately downstream of the secondary clarifiers on March 12, 2001. This collection point is before the chlorine addition system at DITP. At the time of collection, the residual chlorine in the disinfection basins measured at 2.4 mg/L. The effluent sample was transported to the laboratory and stored at 4°C until the needed for the study, which began on March 14, 2001 and ended on March 15, 2001.

The chlorine study was conducted on 10-liters of effluent contained in a 15-liter fiberglass tank. The fluorescence, pH, and temperature sensors and an electric stirrer were immersed in the effluent and the container was then covered and maintained in the dark in an air-conditioned laboratory and continuously stirred as the temperature slowly rose to room temperature. During this period, and subsequently throughout the experiment, the sample was continuously monitored for rhodamine WT fluorescence, pH, and temperature. Over the first 4-hour period before the addition of dye, the temperature rose from 7.5 ° to 15.8 °C.

Because of the concern that rhodamine dye would produce a false chlorine residual measurement with the HACH colorimetric chlorine analysis, a second test solution was prepared and run parallel to the primary test solution for the purposes of chlorine measurement. This test solution was of the same volume and was maintained under the same conditions as the primary test solution. Equivalent amounts of chlorine were added to both tanks, however, no dye was added to the secondary tank. Chlorine residual was determined periodically in the secondary tank and recorded in a laboratory notebook.

Once background fluorescence and pH conditions and effluent temperature stabilized (at t = 4 h), Rhodamine WT was added drop-wise until an elevated fluorescence reading was achieved. (The actual initial Rhodamine concentration achieved was ~62 ug/L.) At this time the effluent was rapidly mixed for 1 h while data were continuously collected. The data collected during this period were used to address any biodegradation, adsorption, and agitation effects that the dye may be subjected to in the channel from the point of injection up the hypochlorite addition and mixers.

At t = 5 h, approximately 60 minutes after rhodamine addition, chlorine (as NaOCl[4]) was added to the tank to simulate the DITP hypochlorite dosing point. The chlorine was added as a single injection to achieve a chlorine residual in the test tank of ~4.0 mg/L. After this time, chlorine residual (in the secondary tank) was measured approximately every half-hour for 7.5 hours (t – 12.5 h).

After 10:15 PM, March 14, 2001 (t = 13h), the test tank was left unattended in the laboratory while continuous measurements continued through the night. Chlorine residual measurements resumed at 7:45 AM on March 15, 2001, at which time it was discovered that a software error had stopped the continuous monitoring at 12:08 AM. The program was restarted and continuous monitoring resumed. At 9:45 AM, t = 24.4 h, a second chlorine dose (NaOCl) was added to the test tank to bring the chlorine residual up to ~10 mg/L. At 2:22 PM, t = 29 h, the experiment was discontinued.

During the post-chlorination portion of the experiment, the recorded temperature in the test tank fluctuated with room temperature (from 15.2° to 18.8°C). All fluorescence data presented in the results section below have been corrected to fluorescence at T_o using the temperature/fluorescence relationship established in a separate experiment (Battelle 2001).

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[4] Commercial sodium hypochlorite solution used at DITP for the purpose of effluent disinfection was provided by MWRA.

RESULTS

Figure 1 shows the results of all measured parameters over the 29-hour test period. The gap between 890 and 1350 minutes is the overnight period during which time the data acquisition program had malfunctioned.

Rhodamine WT fluorescence. Following dye addition, the temperature corrected rhodamine fluorescence was stable at 62.46 ug/L (Std. Dev. = 0.059) throughout the course of the 29-h experiment. No immediate drop in rhodamine concentration was observed upon initial chlorine addition (at residual chlorine levels of 4.0 mg/L), nor was any rhodamine concentration decrease observed when the residual chlorine levels were increased to 10 mg/L toward the end of the experiment. The slight dip then recovery of fluorescence seen in the figure is most likely a product of the initial mixing of the added chlorine into the test solution.

Chlorine residual. Chlorine residual in DITP effluent at the time and point of collection measured 2.4 mg/L. At the start of the experiment a day later, this concentration had decreased to 0.04 mg/L. At t = 5 h, chlorine was added to achieve a concentration of residual chlorine of 4.0 mg/L and over the next 19.3 h (until t = 24.3 h) this concentration slowly decreased to 2.1 mg/L. At 24.3 h, hypochlorite was again added to increase residual chlorine to 10 mg/L at which time no additional chlorine measurements were taken.

Measurement of pH. Over the first 3.6 h of the study, the pH of the effluent slowly increased from 6.5 to 8.0 as the temperature increased from 7.4 to 15.3 °C. Over the next 2 hours, the pH continued to rise slowly to 8.2 (at 17.0 °C), where it remained throughout most of the study. The highest pH (8.4 at 16.2 °C) was observed t= 29.0 h.

DISCUSSION

At the DITP, the amount of chlorine added to the effluent stream is metered and excess chlorine is removed such that such that chlorine residual in effluent exiting the basin averages less than 0.45 mg/L. This dechlorination point is just downstream of the monitoring point established for the winter and summer plume tracking programs. Thus, while concentrations in portions of the basin are roughly equivalent to the levels used in the experiment, these elevated but decreasing concentrations only exist for approximately 60 minutes, the residence time of effluent in the disinfection basin. The chlorine residual concentrations used in this experiment are approximately 130x higher than those monitored in April 2001 as effluent exited the disinfection basin (Mickelson, personal communication 2001) and 40x higher than the average residual chlorine after the disinfection/dechlorination process reported for April 2001 (residual chlorine averaged 0.1 mg/L in April 2001, MWRA 2001). At a flow of 350 MGD, the combined residence time of effluent in the DITP disinfection basin and outfall tunnel is 10.8 h to diffuser no. 55 and 13.1 h to diffuser no. 2. Thus, with no observed rhodamine decrease in this experiment at much higher chlorine concentration levels and longer exposure periods, no loss of rhodamine dosed into the effluent stream during either the winter or summer MWRA 2001 plume tracking surveys is anticipated

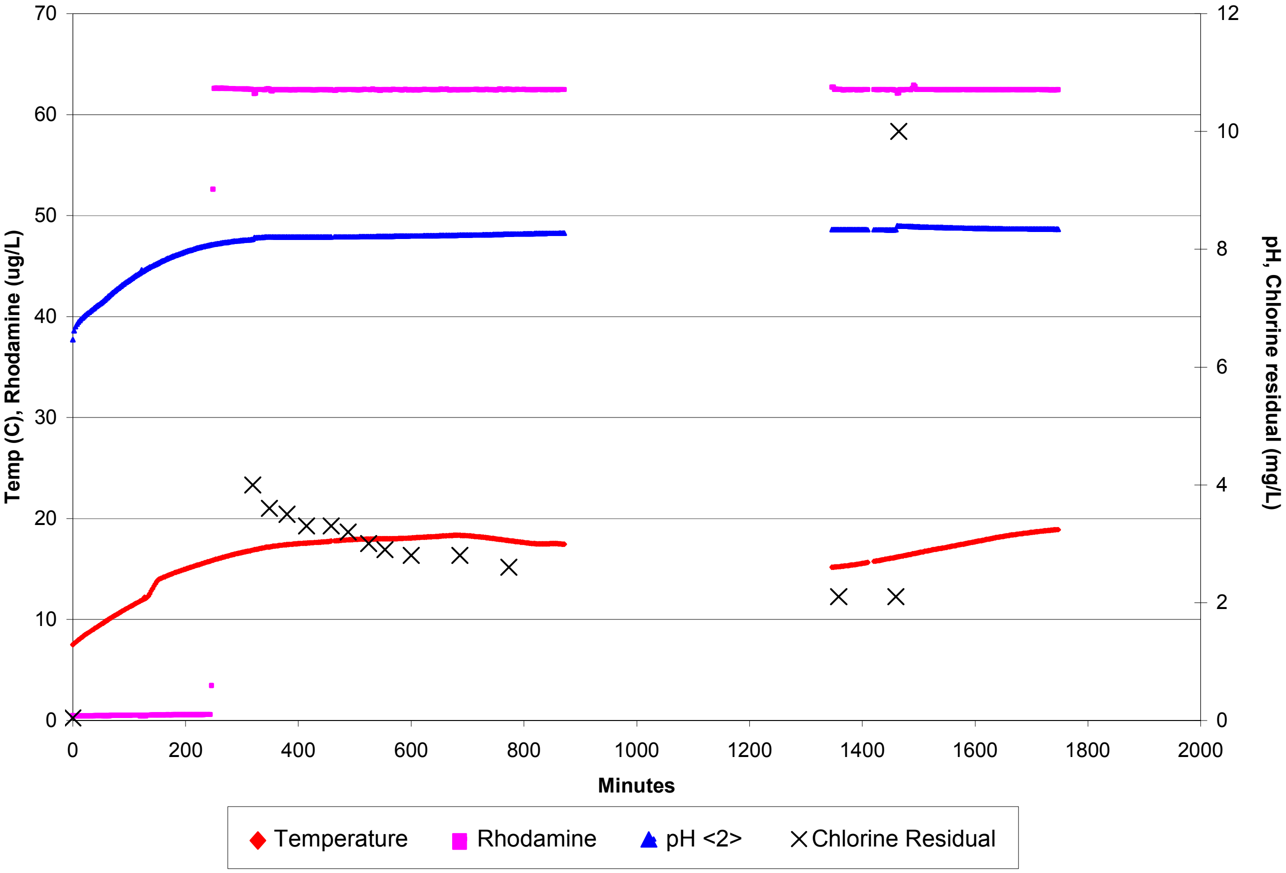

Figure 1. Rhodamine Fluorescence, Temperature, pH, and Chlorine Residual in DITP Effluent Chlorine Experiment.

A similar increase in effluent pH was observed by MWRA in a separate study (Delaney 2001). In the MWRA experiment, the pH in raw unfiltered effluent increased from 7.2 to 8.1 over a period of 15 minutes as the effluent temperature rose from 10.0 to 19.7 °C while the sample was vigorously shaken. The increase in pH was attributed to carbon dioxide degassing resulting from the decrease in carbon dioxide solubility with increased temperature.

In summary, it appears that typical chlorine residual levels found in the DITP disinfection basin and at the DITP hypochlorite dosing point will not have a significant effect on the fluorescence of rhodamine WT dye at ~62 ug/L. No other properties of the DITP secondary effluent or conditions at the plant (such as agitation, adsorption onto particulate, and changes in pH) were shown to have an effect on the rhodamine fluorescence. For the dye addition and plume tracking surveys, dye fluorescence measurements will be corrected for temperature (Hunt 2001). However, no other corrections to fluorescence data will be necessary.

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Attachment 4

EFFECTS OF BROMINE ON RHODAMINE WT FLUORESCENCE IN CHLORINATED EFFLUENT

INTRODUCTION

Under Part I, Section 18e of the National Pollutant Discharge Elimination System (NPDES) permit issued by the U.S. Environmental Protection Agency (EPA) and the Massachusetts Department of Environmental Protection (EPA/MADEP 1999) for the new sewage outfall discharging in Massachusetts Bay, the Massachusetts Water Resources Authority (MWRA), responsible for the operation and monitoring of the new sewage effluent outfall from the Deer Island Treatment Plant (DITP), is required to "field test and certify whether the outfall's minimum dilution is equal to, or greater than, the predicted minimum dilution" specified in a hydraulic study. To meet this requirement, Battelle conducted two plume-tracking studies, in the winter and summer of 2001. The winter 2001 survey was intended as a shakedown survey and its purpose was to test protocols planned for the summer 2001 survey and to develop information on effluent dilution under unstratified conditions. The summer 2001 survey was the "certification" survey, intended to monitor dilution under strongly stratified water column conditions. During both surveys, the monitoring of effluent plume dilution characteristics and transport was conducted using *in situ* fluorometers monitoring Rhodamine WT dye as a tracer.

The bromine study described in this report is one of several ancillary studies conducted in support of the plume tracking surveys. Each of the ancillary studies is intended to address a specific technical issue associated with the use of rhodamine dye for dispersion studies. The rhodamine dye injected into the effluent stream is subjected to a number of factors which may affect its fluorescent signature. These factors include agitation, biological degradation, adsorption onto particles, variable and extreme pH, and contact with NaOCl. It has been suggested that free chlorine may impact rhodamine fluorescence when bromine is present. Free chlorine may react with the bromine salts found in seawater, which then may react with the rhodamine (Turner Designs, 1995).

The chlorine concentration in the MWRA effluent immediately downstream from the hypochlorite mixers; i.e., the location where dye was added for the plume tracking surveys, is typically less than 7 mg/L (MWRA 2000, MWRA 2001). A separate experiment was conducted to address the direct affects of chlorination on rhodamine dye fluorescence (See Chlorine Effects Letter Report, Battelle 2001a). That study found no significant impact at the dye concentrations used for the plume tracking surveys (Battelle, 2001a). However, as the chlorinated, dyed effluent enters the seawater environment, a bromine/chlorine interaction may be present. This interaction could potentially interfere with rhodamine fluorescence. The objective of this experiment was

> To determine whether bromine in seawater interacts with chlorinated effluent to degrade (bleach) rhodamine WT dye.

METHODS

The laboratory study to determine the effects of a bromine/chlorine interaction on Rhodamine WT was conducted at Battelle on December 18, 20, and 21, 2001. The methods used for this study are presented in detail below.

Equipment

The bromine/chlorine experiments were conducted with the following equipment:

- Two Seapoint Rhodamine Fluorometers, Serial # 4125 and #4126
- Ocean Sensors OS200 CTD, Serial #407, factory calibrated
- HACH total chlorine (TCR) test kit (loaned by MWRA).

For this set of experiments, the data were collected with the fluorometers set in the 0 – 150 ppb or 0 –50 ppb range. Fluorescence data were temperature corrected based on media specific coefficients established in a previous study (Battelle 2001b).

The analog signals from the fluorometer, conductivity and temperature sensors were processed through analog channels of an Ocean Surveys OS200 conductivity/temperature/depth (CTD) sonde (serial # 465) and Battelle Navsam© software.

Residual chlorine was measured with a HACH colorimeter-based test kit, No. 4670000, approved for the analysis of chlorine residual in wastewater.

Experimental Design

This study involved four experiments. Experiments two through four evolved from results of the preceding experiments.

Experiment 1: Seawater
The initial experiment was designed to address the chlorine/bromine/rhodamine interaction by adding known amounts of NaOCl in a 100% seawater medium containing several concentrations of dye. Holding the seawater at 100% while dye concentrations were varied kept the bromine at a constant and high level. Solutions were made at four rhodamine concentrations, approximately 20, 10, 1, and 0 ppb (however, only the 20 ppb solution was used based on the results of the 20 ppb solution, see results below). Dye concentrations were obtained by measuring rhodamine fluorescence in a known volume of seawater and adding rhodamine until the temperature compensated output of the rhodamine sensor equaled the desired concentration.

The experiment was conducted by adding chlorine to the seawater/rhodamine solution. The solution was continuously stirred in a 1-liter test tank and continuously monitored for temperature and salinity with an OS200 CTD unit. The solution was also continuously monitored for rhodamine dye fluorescence with a Seapoint *in situ* rhodamine fluorometer. After baseline readings of temperature, salinity, and rhodamine were established the solution was injected with a quantitative amount of sodium hypochlorite solution to achieve the desired chlorine concentration (~ 0.5 mg/L). However, chlorine concentrations were not measured in this experiment.

Experiment 2: Deionized water
This experiment was designed to address the affects of low bromine levels on the rhodamine fluorescence in a non-seawater chlorinated media. The procedures described in Experiment 1 were repeated in Milli-Q water providing a bromine free control for experiment 1. The design was modified to include addition of 25 ml of seawater after chlorine effects were measured. The experiment indicated that chlorine in Milli-Q water can bleach rhodamine dye and that a bromine interaction that degrades the dye can occur when seawater is added.

Experiment 3: Effluent

Based on the results of Experiment 1 and 2, a third experiment was designed to assess bromine/chlorine/rhodamine interaction in the presence of actual MWRA effluent. Secondary effluent (not chlorinated) was collected on December 20, 2001 by MWRA sampling personnel. The effluent was brought to Battelle on December 21, 2001. During this experiment, total chlorine residual was measured with a HACH TCR test kit provided by MWRA.

The effluent was mixed well and approximately 3 liters added to a 13-liter test tank. The CTD and both rhodamine sensors were placed in the tank. Rhodamine WT dye (from the same lot used during the summer plume tracking survey) was added qualitatively until a rhodamine reading of ~45 ppb was reached. Once a stable concentration was established the solution was spiked with 2.5 ml of a 0.05% NaOCl solution, producing a TCR of 0.28 mg/L in the effluent. The solution was monitored for several minutes to ensure that a stable concentration was maintained. All sensors were then removed from the tank and cleaned thoroughly.

The experimental design consisted of adding a known volume of seawater or Milli-Q water to a known volume of chlorinated effluent at a known dye concentration. The seawater addition served as the experimental test. The Milli-Q water served as the control for dilution effects.

Two, 2-liter experimental tanks were set up side-by-side. One liter of the 45 ppb rhodamine/effluent solution was measured into each of the tanks. A rhodamine fluorometer was placed into each tank. The fluorometers were connected to the same CTD system. This allowed continuous and simultaneous fluorescence measurements of each tank. The conductivity and temperature probes of the CTD were placed into the experimental tank. This allowed salinity readings in this tank as seawater was added. A circulating water pump stirred each tank.

After the effluent with dye was added to the tanks, the data collection file was started. The solutions were monitored for several minutes to verify that each tank was at the same stable concentration. A TCR measurement was also taken from each tank. Total residual chlorine had decreased in each solution to ~0.10 mg/L, apparently consumed by the effluent. Each tank was spiked with 1 ml of the 0.05 NaOCl solution, raising the TCR to 0.39 mg/L in each tank. The solutions were monitored for several minutes to measure any effect of the increased chlorine concentration on the dye concentrations. To verify that each solution was at the same concentration and that the sensors were responding comparably, each sensor was removed from its tank and placed in the opposite solution. Measurements continued for several minutes in this configuration before sensors were switched back to their initial orientation.

500-ml volumes of seawater and Milli-Q water were measured out in graduated cylinders. The seawater was collected from Massachusetts Bay. Quickly and simultaneously, the volumes were added to the test tanks. The seawater was added to the experimental tank and the Milli-Q was added to the control tank. Rhodamine, temperature, salinity, and TCR measurements were continued for approximately 20 minutes following the 500-ml addition.

Experiment 4: Background

Separate measurements were taken to establish the background fluorescence and salinity of each of the three media used in this study (effluent, seawater, and Milli-Q).

RESULTS

Experiment 1: Seawater
The initial seawater experiment was designed such that relatively high chlorine concentrations (~0.5mg/L) would be added to relatively high rhodamine concentrations in a high bromine environment (straight seawater). If no degradation of the dye was measured at these levels, it was assumed that there was no interference on rhodamine caused by a chlorine/bromine interaction. This was not the case. Figure 1 shows the response of rhodamine fluorescence to the addition of chlorine in a high bromine environment. Chlorine was added as 1 ml of a 0.05% NaOCl solution. The immediate decrease in rhodamine fluorescence at the 17-minute mark coincides with the chlorine addition. This experiment was repeated under the same conditions with identical results. Because of the strong affect observed at these levels, no other concentrations were analyzed by these methods. The data clearly document a chlorine/bromide interaction in seawater that degrades the rhodamine dye.

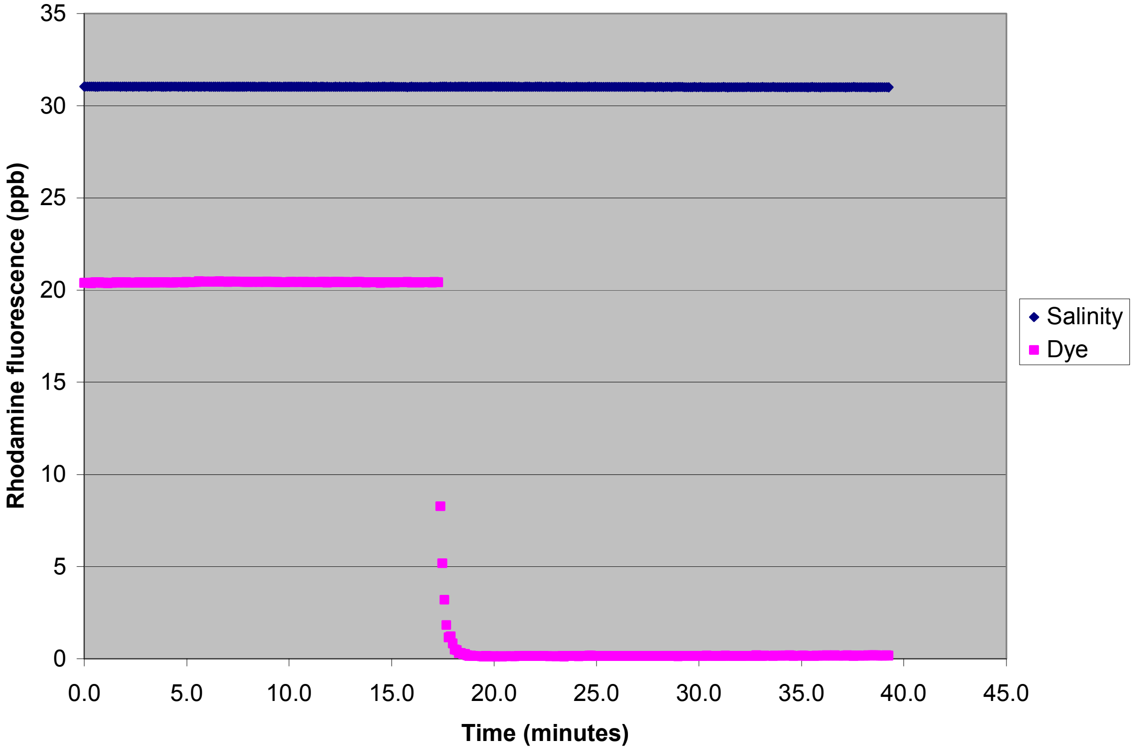

Figure 1. Reaction of Rhodamine Fluorescence to Chlorine Spike in Seawater Media.

Experiment 2: Milli-Q Water.
The second experiment was conducted to address the affect of low bromine levels on the fluorescence of rhodamine in a chlorinated media. Figure 2 shows rhodamine fluorescence and salinity over time. The initial measured rhodamine concentration in the Milli-Q test tank was 19.8 ppb. This concentration was measured for several minutes to verify that the concentration was stable. The solution was then spiked with 1 ml of a 0.05% NaOCl solution (TCR~ 0.5 mg/L). Over the course of 1.5 minutes, rhodamine fluorescence was reduced to 18.4 (~93% of initial fluorescence) as a result of the chlorine addition. At this point the chlorine addition was repeated. In the following 1.5 minutes rhodamine was reduced to 16.2ppb (~82% initial fluorescence). The solution was then spiked a third time with 1 ml of a 5% NaOCl solution (approximate TCR=50 mg/L). The rhodamine fluorescence was reduced to 15.0 ppm (~76%

initial fluorescence) within a few minutes. The tank was then monitored for ~50 minutes. The fluorescence slowly decreased over this period. After 50 minutes, rhodamine fluorescence had been reduced to 9.0 ppb (45% initial fluorescence). At this point, the solution was spiked with 25 ml of Massachusetts Bay seawater (final salinity ~0.6 PSU). Within 6 minutes of the seawater addition, rhodamine fluorescence was reduced to undetectable levels (<0.05ppm).

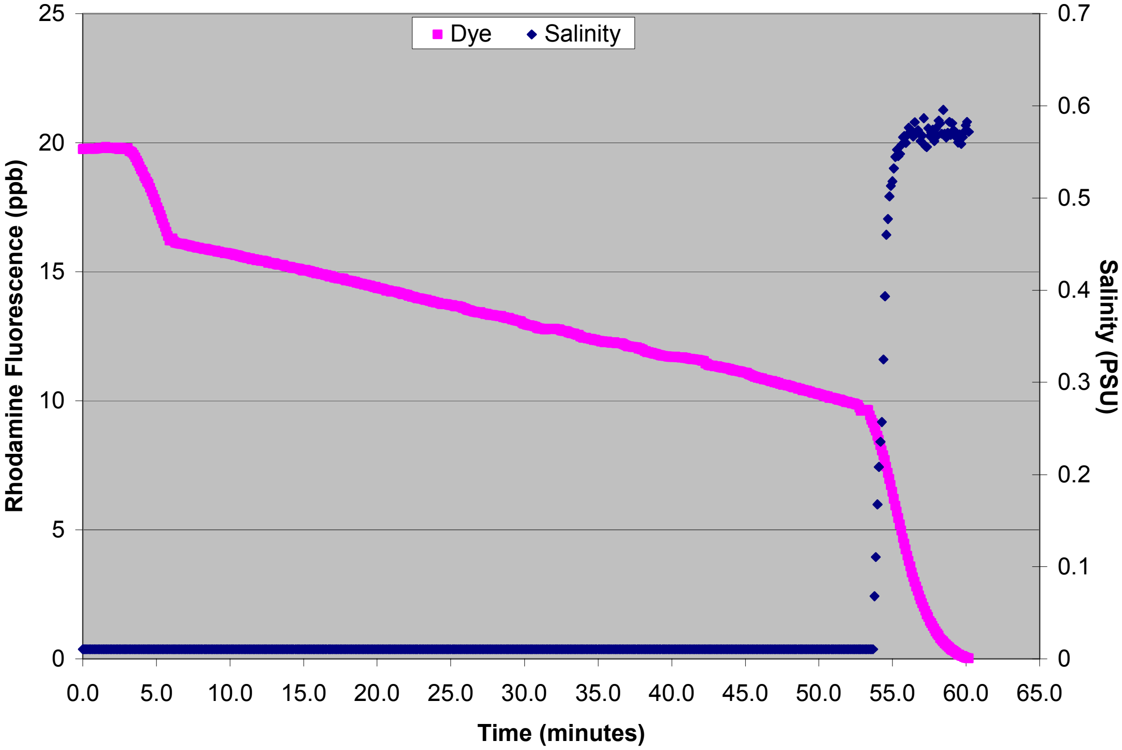

Figure 2. Reaction of Rhodamine Fluorescence to Chlorine and Seawater Additions in Milli-Q Media.

This experiment showed a strong reaction of rhodamine fluorescence in a Milli-Q medium to the addition of chlorine. Instantaneous decreases in fluorescence were seen upon the addition of both low (~0.5 mg/L) and high (~50 mg/L) levels of chlorine. Fluorescence also showed a slow, steady decrease over time in the presence of chlorine. However, the most significant fluorescence reaction occurred when a small amount of seawater was introduced to the chlorinated solution. A clear bromine/chlorine/rhodamine interaction was observed even when only a small amount of bromine was added to the Milli-Q medium.

The influence of chlorine on rhodamine fluorescence has been previously tested in several media, including seawater, drinking water, and wastewater. Rhodamine fluorescence in wastewater has been shown to remain stable in the presence of chlorine (Deaner, 1973, Turner designs, 1995, Battelle 2001a). Because experiments 1 and 2 were not conducted with effluent it was decided to further test the interactions by using effluent.

Experiment 3: Effluent.

This experiment was designed to assess rhodamine fluorescence response when bromine (seawater) is introduced to chlorinated effluent. This scenario simulates the conditions present during the 2001 MWRA plume tracking surveys. During these surveys rhodamine dye was added to the pre-chlorinated effluent stream, the effluent (and dye) were then chlorinated and held in a disinfection basin. After sufficient time was allowed for disinfection, excess chlorine was eliminated by addition of sodium bisulfite resulting in low, if any, total chlorine residual in the final effluent. The effluent was then released into a seawater environment through a series of offshore diffusers.

Figure 3 shows the rhodamine fluorescence, salinity, and TCR over time in this experiment. Rhodamine fluorescence and TCR were measured in both tanks; salinity was measured in the experimental tank only. Rhodamine concentration was stable in the effluent solutions even at TCR levels up to 0.39 mg/L (as previously observed in Battelle 2001a). The addition of 500 ml seawater or Milli-Q each reduced the rhodamine concentration from ~45 ppb to ~30 ppb.

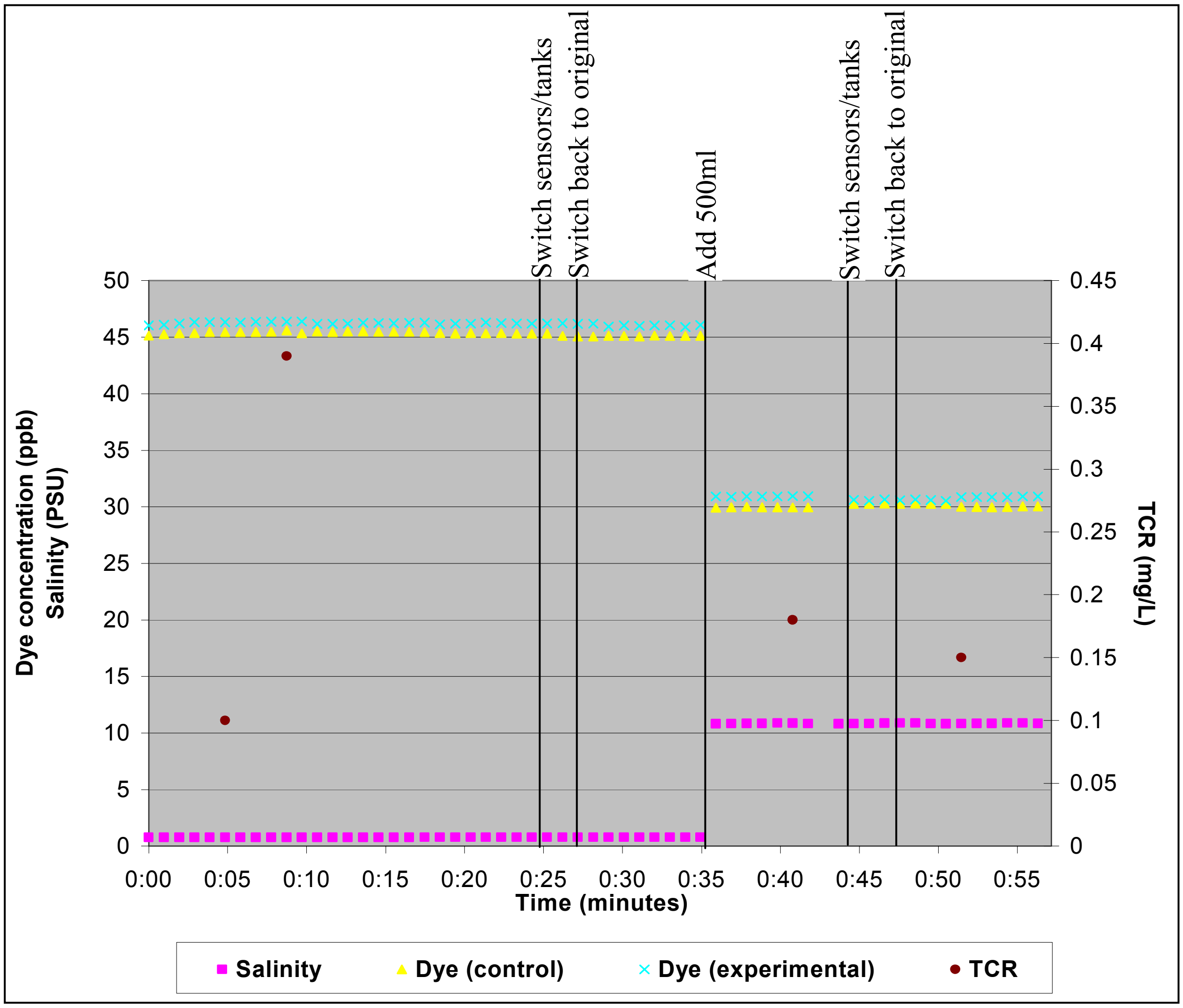

Figure 3. Reaction of Rhodamine Fluorescence to Chlorine, Seawater, and Milli-Q Additions in Effluent Media

This reduction is fully accounted for by the dilution resulting from adding 500 ml to a 1000 ml solution (i.e. 33% reduction). The change in salinity from 0.8 PSU to 10.8 PSU also verifies the addition of 500 ml 31 PSU seawater to 1000 ml of effluent. Other than dilution, no decrease in rhodamine fluoresce was seen at any point either in the control or experimental tanks. Thus unlike the experiments conducted with seawater only and Milli-Q water, the effluent provides protection against dye bleaching both from chlorine and from the chlorine/bromide interaction.

Experiment 4: Background

Separate measurements were taken to establish the background fluorescence and salinity of each of the three media used in this study (effluent, seawater, and Milli-Q). Table 1 lists the background Rhodamine fluorescence and salinities of each of these media. Background values were similar and low relative to the range of dye concentrations measured in these experiments. Therefore no background correction was applied to the any of these data.

Table 1. Background Fluorescence and Salinity

	Rhodamine Fluorescence	Salinity
Effluent	-0.3	0.8
Seawater	-0.7	31.2
Milli-Q	-0.7	0.0

DISCUSSION AND CONCLUSIONS

The experiments conducted here were designed to verify that the rhodamine dye additions performed during the 2001 MWRA plume tracking surveys were not compromised by any interference from a bromine/chlorine interaction. It is important that the initial dye concentration be reliable and that dilution estimates not be complicated by loss of apparent dye concentration to other sources. Chlorine has previously been shown to negatively interfere with rhodamine fluorescence. In addition, the presence of bromine and chlorine together have been shown to increase this affect. However, when placed in an effluent medium, neither chlorine nor a chlorine/bromine interaction appear to affect rhodamine fluorescence. Although it is not clear what the mechanism is (speculation is that the high ammonia or dissolved and particulate or all may act to protect the dye from degradation), the MWRA secondary effluent provides protection from this effect. Thus, with no observed rhodamine decrease in this experiment at rhodamine, chlorine, and bromine concentrations representative of those encountered during the plume tracking surveys, no loss of rhodamine fluorescence either in the effluent or in the seawater is anticipated to have occurred during those surveys.

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Attachment 5

EFFECTS OF PHOTODEGRADATION ON RHODAMINE WT FLUORESCENCE IN SEAWATER

INTRODUCTION

Under Part I, Section 18e of the National Pollutant Discharge Elimination System (NPDES) permit issued by the U.S. Environmental Protection Agency (EPA) and the Massachusetts Department of Environmental Protection (EPA/MADEP 1999) for the new sewage outfall discharging in Massachusetts Bay, the Massachusetts Water Resources Authority (MWRA), responsible for the operation and monitoring of the new sewage effluent outfall from the Deer Island Treatment Plant (DITP), is required to "field test and certify whether the outfall's minimum dilution is equal to, or greater than, the predicted minimum dilution" specified in a hydraulic study. To meet this requirement, Battelle conducted two plume-tracking studies, one in the winter and one in the summer of 2001. The winter 2001 survey was intended as a shakedown survey and its purpose was to test protocols planned for the summer 2001 survey and to develop information on effluent dilution under unstratified conditions. The summer 2001 survey was the "certification" survey, intended to monitor dilution under strongly stratified water column conditions. During both surveys, the monitoring of effluent plume dilution characteristics and transport was conducted using in situ fluorometers monitoring Rhodamine WT dye as a tracer.

The photodegradation study described in this report is one of several ancillary studies conducted in support of the plume tracking surveys. Each of the ancillary studies is intended to address a specific technical issue associated with the use of rhodamine dye for dispersion studies. The rhodamine dye, when injected into the effluent stream, is subjected to a number of factors, which may affect its fluorescent signature. These factors include agitation, biological degradation, adsorption onto particles, variable and extreme pH, and contact with NaOCl. In addition, the offshore environment poses several possible sources of rhodamine interference or destruction, including bromine interactions, temperature changes, and photochemical decay. During the 2001 MWRA plume tracking surveys, a rhodamine plume was monitored for up to three days. During this time, the rhodamine may have been exposed to daytime sunlight levels capable of diminishing its fluorescent strength and detectability.

Photochemical decay of fluorescent dyes has been previously documented (Feuerstein and Selleck, 1963 and Tai and Rathburn, 1988). Rhodamine WT dye has been shown to be more resistant to photodegradation than other tracers such as fluorescein. However, some decay may be expected during prolonged exposure to sunlight. Photochemical decomposition of rhodamine dye is dependent on light intensity. Because sunlight intensity varies substantially from day to day as well as over the course of each day, it is difficult to quantify the rate of decay over a multi-day survey. In addition, sunlight intensity varies from season to season. The experiment presented here was designed to address the photochemical impact on rhodamine WT dye during the specific survey days. Light intensity in the water column is depth dependent. The "tow-yo" sampling method used in the plume tracking surveys followed the plume signature from surface waters to over 20 meters deep. This experiment was designed to address photochemical decay in a "worst-case" situation (i.e. at the surface). Because the results of this experiment compared well with the literature, depth-dependent decay rates based on previous experiments (Tai and Rathburn, 1988) are also presented here.

The Winter Plume Tracking Survey was conducted over the course of two days (offshore) and the Summer Survey over the course of three days. The photodegradation experiment was conducted during the same days as the actual surveys. The objectives of this experiment were to:

To determine whether exposure to sunlight would result in a decreased fluorescent signal from rhodamine WT dye in seawater.

To determine a photochemical decay rate for the specific survey days, which will be applied to the survey data if necessary.

METHODS

The laboratory study to determine the effects of sunlight on rhodamine WT fluorescence was conducted at Battelle on April 18-20 and July 16-19, 2001. The methods used for this study are presented in detail below.

Equipment

The photodegradation experiments were conducted with the following equipment:

- A Seapoint Rhodamine Fluorometers, Serial # 4125
- Ocean Sensors OS200 CTD, Serial #465, factory calibrated

For this set of experiments, the data were collected with the fluorometer set in the 0 – 5 ppb range. Fluorescence data were temperature corrected based on media specific coefficients established in a previous study (Battelle 2001). The temperature compensation was applied through post-processing, as final temperature coefficients had not been established at the time of the analysis.

The analog signals from the fluorometer, conductivity, and temperature sensors were processed through analog channels of an Ocean Surveys OS200 conductivity/temperature/depth (CTD) sonde (serial # 465) and Battelle Navsam© software.

Experimental Design

Sample preparation and collection

Prior to each of the MWRA 2001 Plume Tracking Surveys, rhodamine dye solutions were made up in seawater collected from Massachusetts Bay. For these experiments, test solutions were made at two rhodamine concentrations for each survey. A blank seawater control also prepared for each survey. Rhodamine solutions were made in two steps. First, straight rhodamine dye was diluted (1 drop into ~1000ml seawater) to make a working solution. A rhodamine fluorometer was then placed in a tank containing 10 liters of seawater and the working solution was added drop-wise until the target concentration was observed on the instrument readout. Because temperature compensation was applied through post-processing, the actual concentrations were higher than targeted. The targeted 1.0 ppb solution had an actual concentration of 1.4 ppb, and is referred to as the "high concentration" solution in this report. The targeted 0.5 ppb solution had an actual concentration of approximately 0.70 – 0.82 ppb, and is referred to as the "low concentration" solution in this report. Test solutions were stored in sealed 13-liter buckets until needed for the experiments.

All experimental activities were conducted exactly the same for both the winter and summer plume tracking surveys unless otherwise noted. All collected samples were stored in sealed HDPE bottles held in the dark at 4° C until analysis following the survey. The test solutions were placed, uncovered, outside at the Battelle laboratory in an area that receives direct sunlight during all daylight hours (behind the boat house). Each 10-liter solution was contained in a white 13-liter polyethylene bucket (diameter = 285 cm, depth = 270 cm, water depth = 175 cm). A 1-liter, pre-survey reference sample was taken from each of the test solutions when they were first placed outside. For the summer survey, the solutions were placed outside at 9 PM on the day before the nearfield survey. Because of forecasted precipitation, the winter solutions were placed outside at 5:00 AM the day of the nearfield survey. At the end of each survey day a 1-liter sample was taken from each of the test solutions. Table 1 lists approximate sample collection and analysis times for each of the surveys.

Table 1. Sample collection and analysis times (approximate).

	Pre-Survey	End of Nearfield Day	End of Farfield Day #1	End of Farfield Day #2	Sample Analysis
Winter Survey	4/19/01 05:00	4/19/01 21:00	4/20/01 21:00	--NA--	4/27/01 18:00
Summer Survey	7/16/01 21:00	7/17/01 21:00	7/18/01 21:00	7/19/01 21:00	8/7/01 09:00

Sample analysis

A 2-liter tank, containing the sensor ends of the Seapoint rhodamine fluorometer and the OS200 CTD served as the test chamber for these experiments. The sample was poured into the test chamber and thoroughly stirred. The chamber was covered with a light shield to prevent any fluorescence interference. The sample was measured for 60 seconds and the average reading calculated. The test chamber and sensors were thoroughly cleaned with Milli-Q then dried between each sample.

Data Processing

In October 2001 final temperature compensation coefficients were developed for rhodamine WT dye in both effluent and seawater media (Battelle, 2001). The temperature compensation coefficients for seawater derived from that experiment were applied to the raw data collected during all of the photodegradation experiments. All data reported in this report is a product of this post-processing

RESULTS

Winter Survey

Table 2 lists the concentrations and the percent of initial concentration for each of the test solutions of the course of the entire survey period. The Blank values are the measured fluorescence in the blank samples each day. The Low and High Concentration values are the measured fluorescence minus the blank value for that sample day. The percent fluorescence is also depicted in Figure 1. A decrease in rhodamine fluorescence was seen at both of the dye concentrations. By the end of the Nearfield day the fluorescence had dropped by as much as 3%. As much as a 4.3% decrease was seen by the end of the Farfield day.

Table 2. Dye Fluorescence and Percentage of Initial Concentration During the Winter Plume Tracking Survey.

		Seawater Blank	Low Concentration	High Concentration
Pre-survey	**Concentration (ppb)**	0.207	0.618	1.220
	Percent of Initial Concentration	100.0%	100.0%	100.0%
After NF (13:37 hours of daylight)	Concentration (ppb)	0.210	0.599	1.191
	Percent of Initial Concentration	101.5%	97.0%	97.6%
	Percent Change From Previous Day	+1.5%	-3.0%	-2.4%
After FF (13:40 hours of daylight)	Concentration (ppb)	0.211	0.591	1.173
	Percent of Initial Concentration	101.9%	95.7%	96.1%
	Percent Change From Previous Day	+0.4%	-1.3%	-1.5%

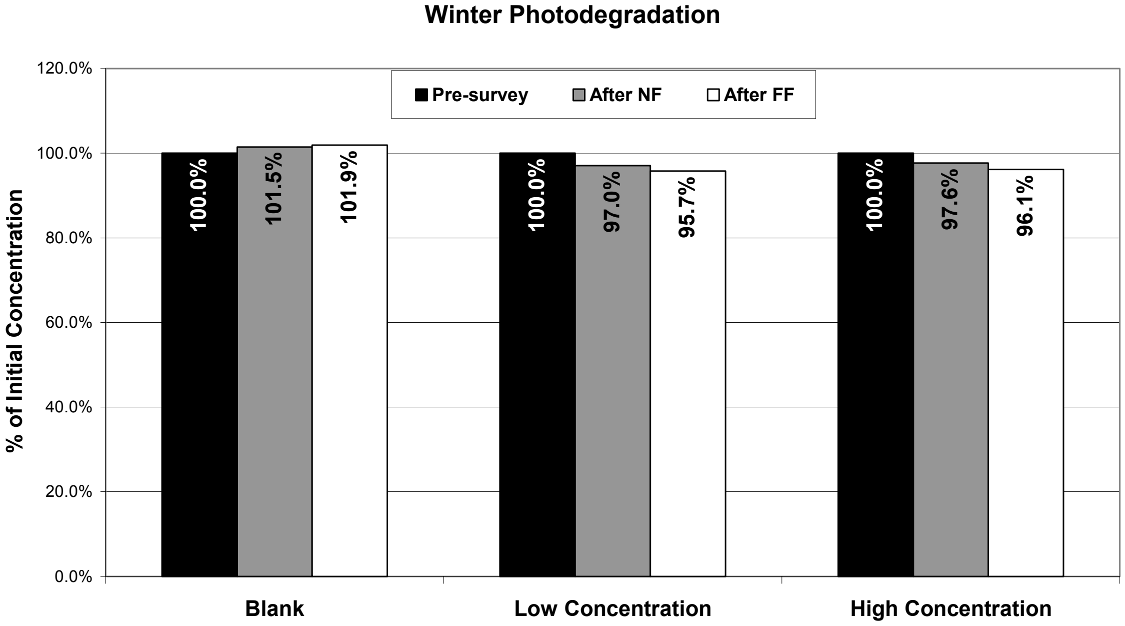

Figure 1. Percentage of Initial Concentration During the Winter Plume Tracking Survey.

Summer Survey

Table 3 lists the concentrations and the percent of initial concentration for each of the test solutions of the course of the entire survey period. The Blank values are the measured fluorescence in each of the blank samples. The Low and High Concentration values are the measured fluorescence minus the blank value for that sample day. The percent fluorescence is also depicted in Figure 2. A decrease in rhodamine fluorescence was seen at both of the dye concentrations. The decrease after the nearfield and first farfield days was not as large as during the winter survey. By the end of the Nearfield day the fluorescence had dropped by 0.7%. By the end of the entire survey the High concentration sample showed a 5.7% decrease, which was only slightly more than observed by the end of the first farfield day in the winter survey.

Table 3. Dye Fluorescence and Percentage of Initial Concentration During the Summer Plume Tracking Survey.

		Blank	**Low Concentration**	**High Concentration**
Pre-survey	**Concentration (ppb)**	0.198	0.504	1.225
	Percent of Initial Concentration	100.0%	100.0%	100.0%
After NF (14:55 hours of daylight)	Concentration (ppb)	0.197	0.500	1.216
	Percent of Initial Concentration	99.8%	99.3%	99.3%
	Percent Change From Previous Day	-0.2%	-0.7%	-0.7%
After FF Day #1 (14:54 hours of daylight)	Concentration (ppb)	0.197	0.487	1.183
	Percent of Initial Concentration	99.6%	96.7%	96.5%
	Percent Change From Previous Day	-0.2%	-2.6%	-2.8%
After FF Day #2 (14:52 hours of daylight)	Concentration (ppb)	0.196	0.477	1.156
	Percent of Initial Concentration	99.3%	94.6%	94.3%
	Percent Change From Previous Day	-0.3%	-2.1%	-2.2%

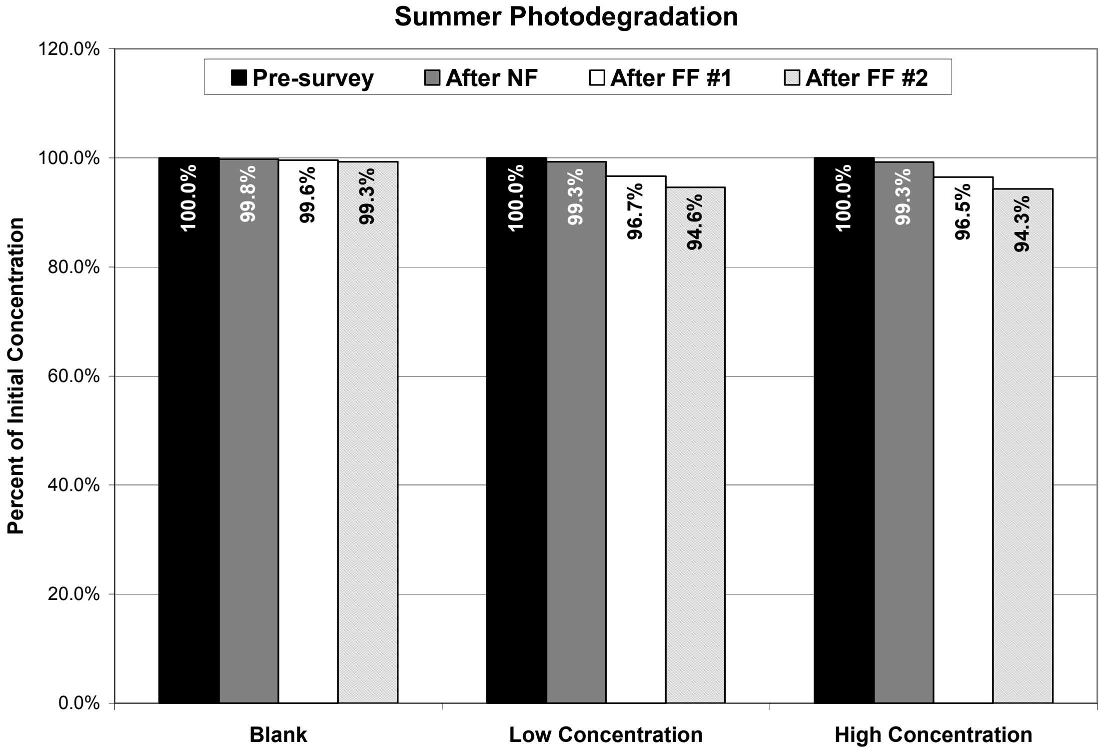

Figure 2. Percentage of Initial Concentration During the Summer Plume Tracking Survey.

DISCUSSION AND CONCLUSIONS

During both the winter and summer surveys a decrease in rhodamine fluorescence was seen in the photodegradation test tanks. Single day decreases ranged from 0.7 % to 3.0%. Overall decreases ranged from 4.3% over 2 days in the winter, to 5.7 % over three days in the summer.

In their 1988 experiment on the Photolysis of Rhodamine-WT Dye, Tai and Rathburn calculated the decay rate of rhodamine when exposed to direct sunlight. These rates were calculated for each of the four seasons. The rates were reported in terms of rate constants and half-life. The results of the MWRA experiments compared well with the results reported by Tai and Rathburn. During the spring the rhodamine half-life was 17.3 days, or approximately a 4% decrease per day. During the summer the rhodamine half-life was 14.8 days, or approximately a 5% decrease per day. The daily decreases seen in the Battelle experiments were somewhat less than those seen by Tai and Rathburn. This is most likely due to less than maximum available sunlight because of partial cloud cover experienced during the actual survey days.

The Tai and Rathburn decay rates listed above were calculated for waters at the very surface. They also calculated the decay rates over a range of water depths (0.5, 1.0, 2.0, and 4.0 meters). Table 4 lists their depth dependent half-life results at 40° North Latitude. Table 4 also lists the photochemical decay terms of % decrease per day for comparison with this study. Because the surface water decay rates are comparable in the two studies, the depth-dependent decay rates reported by Tai and Rathburn should be applicable to the MWRA Plume tracking data.

Table 4. Depth-dependent Photolysis Decay Rates of Rhodamine-WT Dye at 40° Latitude (from Tai and Rathburn, 1988).

Depth (m)	Spring		Summer	
	Half-Life (Tai & Rathburn)	% Decrease Day^{-1} (Converted)	Half-Life (Tai & Rathburn)	% Decrease Day^{-1} (Converted)
0	17.3	4.0	14.8	4.7
0.5	20.7	3.3	17.6	3.9
1.0	24.3	2.9	20.6	3.4
2.0	32.2	2.2	27.2	2.5
4.0	49.9	1.4	41.9	1.7

During the winter plume tracking survey, the dye plume was primarily located between 7 and 20 meters deep. Based on the depth-dependent decay rates listed in Table 4, dye loss due to photodegradation at this depth would be expected to be < 1% per day. During the summer plume tracking survey the dye plume was primarily located below 10m deep although the upper boundaries were occasionally seen up to 5m deep. Again, this would likely represent a photochemical decay rate of < 1% per day at full light. The first day (nearfield) of the summer survey had 87% cloud cover (National Weather Service) resulting in a measured dye loss of only 0.7% in the surface water test tanks. Thus, it is presumed that there would have been a negligible effect at the deeper depths on this day.

Both the present and previous experiments have shown that photochemical breakdown of rhodamine WT dye can occur under natural light settings. The rate of this decay is dependent on the light intensity. A number of factors, including cloud cover and water depth, can decrease sunlight intensity reducing the rate of photodegradation. Comparing the measured loss of fluorescence during the actual MWRA Plume Tracking survey days, with depth-dependent rates from the literature, the photochemical effects on the actual dye plume can be estimated. Each of the dye plumes tracked during the winter and summer surveys were entrained in sub-surface waters. This would have helped to shield the dye from even the small photochemical effects measured in this experiment. The first survey day (nearfield) on each of the surveys was critical for calculations of initial dilution and MWRA's compliance with the NPDES permit. During these nearfield days, it is estimated that the rhodamine would have been subjected to less than a 1% decrease due to photolysis. Even a 1% loss is unlikely as this is based on a full day of exposure to sunlight. During the winter and summer surveys, dye did not begin to emerge from the offshore risers until 12:06 and 10:27 respectively. All measurements used for the initial dilution calculations were completed by approximately 17:00 on each of the surveys. This means that the dye plume was subjected to a maximum of only 7 to 8.5 hours of light while initial dilution measurements were being conducted.

The entire plume tracking effort was conducted over the course of two to three days. During this time, the measured dye loss as a result of photochemical breakdown was as much as 5.7% (by the end of the summer survey). After adjusting this breakdown rate for water depth, it appears that a more realistic loss in the field would be less than 3%. Because the farfield plumes had spread over large areas it is impossible to account for all of the potential sources of dye loss. A photochemical decrease of less than 3% would not significantly impact the detection of the dye in the farfield. Also, because the farfield portions of the survey were designed to map overall movements and dispersion of the plume, a small photochemical loss does not interfere with the objectives of the program.

Based on the results obtained from this survey and from the literature, no correction factor is necessary for photodegradation during the 2001 MWRA Plume Tracking Surveys.

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Attachment 6

INTERCALIBRATION OF RHODAMINE FLUOROMETERS USED AT DEER ISLAND AND MASSACHUSETTS BAY

Under Part I, Section 18.e of the National Pollutant Discharge Elimination System (NPDES) permit issued by the U.S. Environmental Protection Agency (EPA) and the Massachusetts Department of Environmental Protection (EPA/MADEP 1999) for the new sewage outfall discharging in Massachusetts Bay, the Massachusetts Water Resources Authority (MWRA) is required to “field test and certify whether the outfall’s minimum dilution is equal to, or greater than, the predicted minimum dilution” specified in a hydraulic study. To meet this requirement, Battelle conducted two plume-tracking studies, in the Winter and Summer of 2001. The Winter 2001 survey was intended as a shakedown survey and its purpose was to test protocols planned for the Summer 2001 survey and to develop information on effluent dilution under unstratified conditions. The Summer 2001 survey was the “certification” survey, intended to monitor dilution under strongly stratified water column conditions. During both surveys, the monitoring of effluent plume dilution characteristics and transport was conducted using two independent *in situ* fluorometers monitoring Rhodamine WT dye as a tracer. The two separate *in situ* Rhodamine fluorometers manufactured by Seapoint Sensors Inc. were used to measure dye concentration at MWRA’s Deer Island Treatment Plant (DITP) and in Massachusetts Bay and during the laboratory studies conducted to evaluate possible interference with the dye

Since the dye is the primary tracer of the effluent and two sensors were used in the program a potential source of error in dilution calculations could be differences in the response of the sensors. To ensure the comparability of the instrument responses and thus ensure accuracy of the dilution calculation, it is necessary that the instruments be comparable and consistent in the detection and quantification of the Rhodamine WT dye. The outputs of the two instruments under known conditions were intercompared prior to the winter survey and verified during laboratory studies conducted after the Summer survey.

The objectives of this study were:

> To verify that the DITP and offshore rhodamine fluorometers produced comparable rhodamine readings across a range of dye concentrations and gain settings
>
> To determine if any correction factor is necessary when comparing data produced by the separate instruments.
>
> To verify that the instruments comparability was stable through out the plume tracking study.

Methods

The outputs of the Seapoint rhodamine fluorometers were intercalibrated and verified during the temperature correction experiments conducted on April 13, 2001 and again in late July 2001. The results of the temperature correction experiment are reported in a separate letter. However, the following methods describe both the temperature experiment and the intercalibration assessment.

On April 13, 2001 the affects of temperature on Rhodamine fluorometric readings were addressed in the laboratory. Three, 2-liter solutions of Rhodamine WT were made by weighting Milli-Q water and adding a known amount of dye to the known mass of water. Dye was added volumetrically to give a final concentration (active ingredient) of 2.5, 25, and 50 µg/L in the three solutions. These concentrations were selected to test the instruments across a range of gain settings. The 50 µg /L solution was measured at 1X gain, the 25 µg/L at 3X, and the 2.5 µg /L at 30X. Each test solution was measured independently.

Each test solution was poured into a clean 3-liter glass bowl. The bowl was placed in a temperature controlled water bath. A stirring rod was placed in the test solution to keep the sample well mixed. The sensor end of an Ocean Sensors OS200 CTD was placed in the test solution to monitor temperature of the sample. The two Seapoint *in situ* rhodamine fluorometers were also placed in the test solution. This tandem testing was used to intercalibrate the sensors and verify their response to temperature. NavSam© software was used to record the data. The water bath temperature was slowly raised for each concentration. Data was also recorded when temperatures extended beyond this range. All sensors and glassware were thoroughly cleaned between experiments.

The temperature in the experiment ranged from 5 to 34 °C. Temperature compensation was not used by the NavSam© software during the data collection. Thus, three apparent ranges of dye readings used in this experiment were 1.23 - 2.83, 17.24 - 28.11, and 38.65 – 53.43 µg/L. The data were recorded and stored by NavSam© at 4hz. Over 38,000 data points were generated during the experiment.

Similar studies were conducted in the July conditions using effluent and seawater obtained in late July (see temperature correction calibration letter report for details).

Results and Conclusions

The dye data from the two sensors were compared by regression analysis of the non-temperature compensated fluorescence readings. The outputs of the two instruments across the entire range of readings compared very well (Figure 1). The slope of the regression was 1.009 with an intercept of -0.167 and r-square of 0.9999. Based on these data, the two instruments provide highly comparable outputs when operated under similar sensitivity settings. Thus, no intercalibration correction was necessary for these instruments.

Other sensor intercalibration data developed as part of the winter plume tracking study can be found in Section 4.2.1 (Table 4) of the winter plume tracking survey report and confirm the comparability of the instruments under temperature compensated data collection algorithms.

During the July temperature calibration studies, it was found that the sensitivity setting of the instruments and the media caused slightly different responses from the sensors. As a result of the temperature study sensor/media specific temperature compensation curves were developed

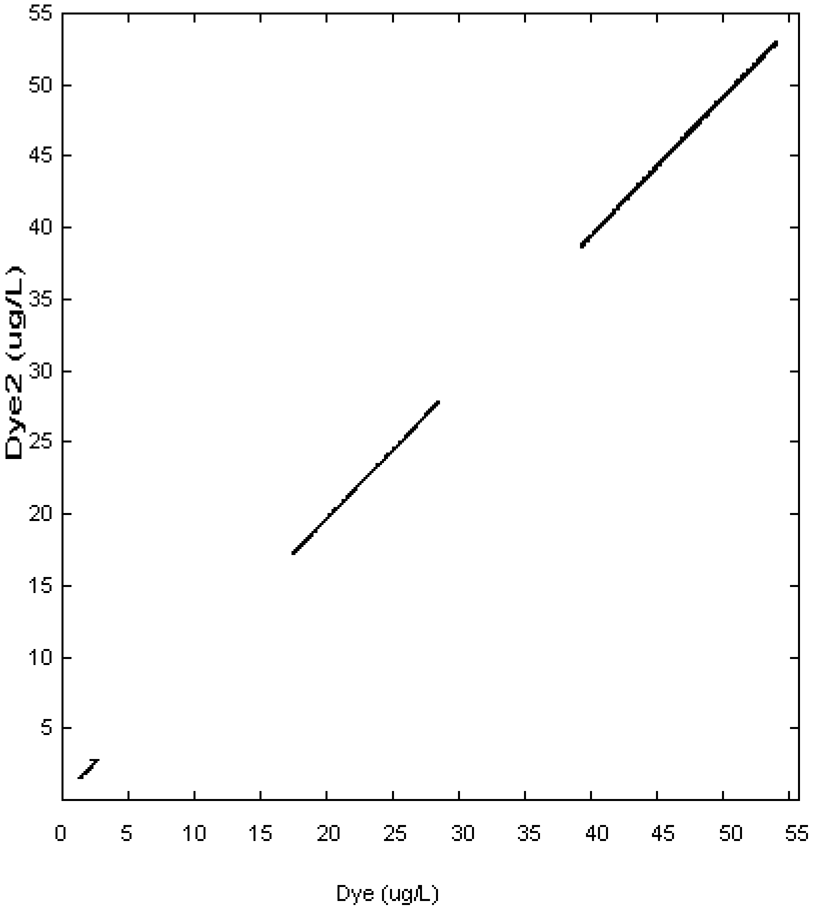

Figure 1. Fluorescence readings from two seapoint rhodamine sensors.

Appendix B

Model Laws and 3DLIF Experimental Methods

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Model Laws and 3DLIF Experimental Methods

The physical models are based on equality of the jet densimetric Froude number between model and prototype. The jet densimetric Froude number is defined as:

$$F_j = \frac{u_j}{\left[g \frac{\Delta\rho}{\rho} d \right]^{1/2}} \qquad \text{(A1)}$$

where u_j is the jet velocity, g the acceleration due to gravity, $\Delta\rho$ the density difference between the effluent and receiving water, ρ the effluent density, and d the nozzle diameter. The jet densimetric Froude number is equal between the model and prototype and the model is undistorted so that all linear dimension ratios are equal to d_r, the ratio between the prototype nozzle diameter and the model nozzle diameter. The source volume, momentum, and buoyancy fluxes are therefore correctly modeled. Jet behavior is also influenced to some extent by viscous effects. These are characterized by the jet Reynolds number, *Re*:

$$\mathrm{Re} = \frac{u_j d}{\nu} \qquad \text{(A2)}$$

where ν is the kinematic viscosity of the jet fluid. The model Reynolds numbers are smaller than in the prototype but were high enough to maintain turbulent flow at the nozzles.

The 3DLIF experiments were conducted in a stratified towing tank as described in Roberts and Tian (2000). The tank is glass-walled 6.10 meters long by 0.91 meters wide by 0.61 meters deep. The LIF system consists of two fast scanning mirrors that drive a laser beam from an Argon-Ion laser through the flow in a programmed pattern. The system is controlled by two computers, one for overall timing control, and one for image capture. A small amount of a fluorescent dye, Rhodamine 6G, is added to the effluent. The laser causes the dye to fluoresce, and the emitted light is captured by a CCD camera. In operation, the vertical mirror sweeps the beam down and back while the camera is exposing (i.e. the shutter is "open"). The horizontal mirror then moves the beam a small distance horizontally, the previous frame is downloaded, the camera buffer cleared, and the next exposure begun. This is repeated so that multiple vertical "slices" through the flow are obtained. After a predetermined number of "slices" the beam returns to the starting point and the cycle starts again. The images are written to hard disc in real time and saved for further processing. For the present experiments, 40 slices at 100 frames per second were captured. Calibration is necessary in order to obtain quantitative scalar dye concentration from the images. The images are corrected pixel-by-pixel for sensor response, lens luminance variation (vignetting), and attenuation due to clear water and dye using the methods of Daviero et al. (2001). The accuracy of the dilution measurements thus obtained is about ±15%. Finally, the multiple slices through the flowfield are regenerated, using image processing techniques, into three-dimensional images of the flow field.

The experimental configuration is shown in Figure C1. For experimental convenience, the model diffuser is inverted with a heavy discharge falling downwards. (This is the same configuration used in the original model studies, Roberts & Snyder, 1993ab, and is allowable because density differences are small compared to absolute densities in the flow field. All images are shown inverted to represent the prototype condition.) The model scale varied from 52 to 81:1 in the original model tests; the 3DLIF tests were done at a smaller scale of 163:1. Despite this smaller scale, the 3DLIF dilution measurements are close to those of the original tests.

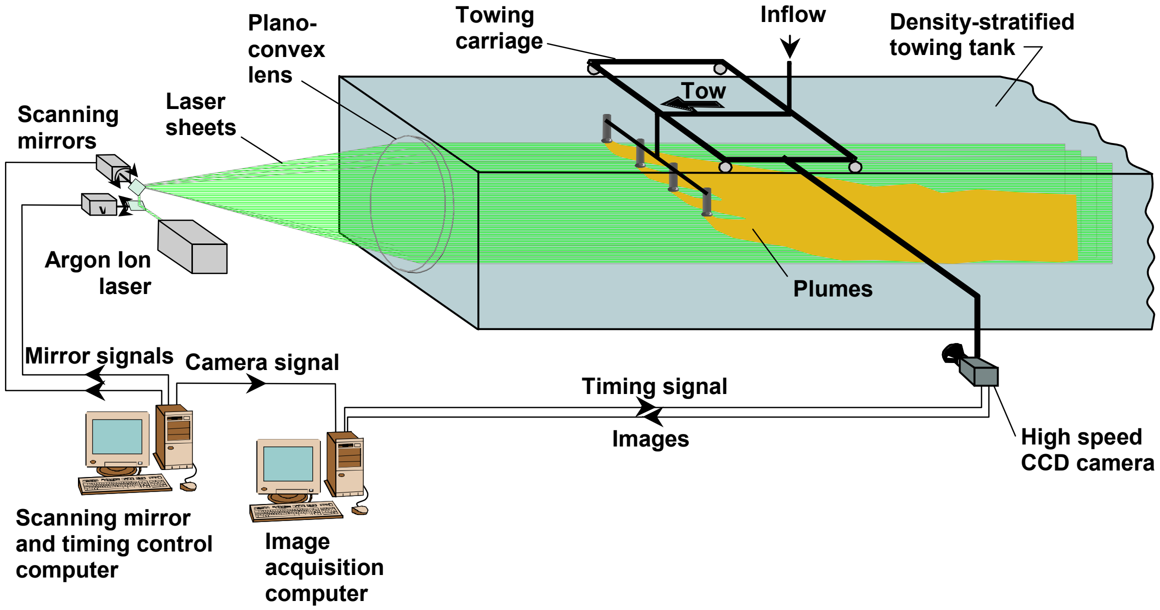

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Figure 1. Schematic Depiction of 3DLIF Experimental Arrangement.

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