# MYSTIC RIVER: RECONNAISSANCE SURVEY RESULTS

Judith Pederson

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# Prepared by

Judith Pederson, Ph.D., MIT Sea Grant College Program

Data Collection and Laboratory Analysis performed by

Joan Beskinis, DEP/OWM
Bill Clark, MAPC/MBP
Linda Domizio, DEP/OWM
Kathleen Keohane, DEP/OWM
Michael Marsh, EPA/New England
Leslie O'Shea, DEP/OWM
Rick Zeroka, CZM

Bruce Carlisle, MCZM
Renee Purdy DeShazo, DEP/OWM
Brian Friedman, DEP/OWM
Lealdon Langley, DEP/OWM
Beth McCann, DEP/OWM
Mary Crain Penniman, DEP/OWM

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Please direct comments and revisions to Judith Pederson, MIT Sea Grant College Program, 292 Main Street, E-38-300, Cambridge, MA 02139.

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# Related MIT Sea Grant Publications

94-9

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## MYSTIC RIVER: RECONNAISSANCE SURVEY RESULTS

#### ABSTRACT

The Mystic River watershed empties into Boston Harbor, Massachusetts with the Amelia Earhart Dam acting as a barrier between the upstream freshwater portion and the marine portion of which a large segment serves as an industrial port. The river exceeds water quality criteria for bacteria, but few measurements have been made on nutrients, dissolved oxygen or other water quality variables. The results from this study, which were the product of a Water Quality Training Course, have indicated that nitrogen concentrations in water from above the dam is in excess of what is found in the marine portion of the river, although for ammonia there appears to be a downstream source as well. Concentrations of ammonia above the dam were recorded as 0.32 mg N-NH<sub>2</sub>/L compared to 0.21 mg N-NH<sub>4</sub>/L below the dam and nitrate and nitrite are recorded as 0.29 mg N-NO<sub>3</sub>/L above and 0.092 mg N-NO<sub>3</sub>/L below the dam whereas phosphorus was approximately 2.0 mg P-PO/L above and below the dam. Phosphorous concentrations in this study were an order of magnitude higher than is reported elsewhere (0.08-0.19 mg P-PO<sub>2</sub>/L), whereas nitrogen as either ammonia or nitrate and nitrite were within the ranges reported elsewhere. There was one recorded dissolved oxygen (D.O.) violation using oxygen electrodes (i.e. D.O. was not measured as less than 5.0 mg O<sub>2</sub>(L) during the period of study. The difference between the paired Winkler test results and instrumentation readings for D.O. exceeded 10% which is considered be acceptable by working scientists. Differences between surface and bottom D.O. measurements varied between 5% to 34% with 4 of 8 bottom samples measuring D.O. below water quality criteria (based on Winkler analyses of 5 mg O2/L for SB waters. This is consistent with other data that indicate these waters are polluted.

# INTRODUCTION

The data presented and discussed in this report were collected during the Massachusetts Institute of Technology (MIT) Sea Grant Water Quality Training Course, held from 10/10/95 to 10/12/95. The purpose of the Training Program was to evaluate water quality in the marine portion of the Mystic River which empties into Boston Harbor. The Mystic River was chosen because there are few water quality data, other than coliform bacteria, for upper and lower segments of the river e.g. data used for calculating loading estimates in the baseline assessment report (MWRA 1994) are based on values from the Charles River (A. Rex, MWRA, pers. comm.) For the Mystic River, the Amelia Earhart Dam serves as a barrier between the upper fresh water portion and the lower more saline portion (MWRA 1994). There are several segments of the River (upper and lower) that are impacted by storm water, combined sewer overflows, and general runoff from urban and industrial areas, although above the dam, open space (parkland) abuts the river. The area below the dam is a working port and heavily industrialized. For more information see the Manual (MITSG 1996), Boston Harbor Navigation Improvement Project Environmental Impact Statement/Report (Massport and USACOE 1995) and Water Quality Baseline Assessment (MWRA 1994).

Specific activities for the Training Course included:

- develop a reconnaissance sampling design for the estuarine portion of the Mystic River
- evaluate field instrumentation and probes

- analyze nutrients and dissolved oxygen (D.O.) in field collected samples, and
- evaluate data relative to the initial questions posed.

This report summarizes data collected from the reconnaissance study of selected water quality variables (specifically, temperature, salinity, dissolved oxygen, ammonia, nitrates and nitrites, phosphorus, turbidity, and pH) for an area of the Mystic River above and below the Amelia Earhart Dam (Fig.1) using available instrumentation and sampling devices. Laboratory analyses of dissolved oxygen were designed to verify field measurements, and ammonia, nitrate and nitrite and phosphorus analysis were conducted to examine ambient variability and determine if there was a signal that was related to fresh water inflow. A secondary purpose was to evaluate the accuracy, reliability and comparability of instruments to each other, and, for dissolved oxygen, to laboratory analyses.

As part of the reconnaissance study, the following questions were posed.

- Q.1. What are the relative concentrations of pollutants or pollution indicators at different segments of the river?
- Q.2. Are water quality criteria being met throughout the river?
- Q.3. Are there diurnal differences in pollution or pollution indicators?
- Q.4. Can tidal influences be detected in the long-term data?

In addition, the following are also examined:

- Is there a good correlation between dissolved oxygen as measured by different instruments and laboratory analyses?
- How well do the various instruments compare to each other?
- Q.5. Can estimated loading values for the nutrients be determined? How much confidence does one have in these values? How does it relate to published loading estimates?

A Water Quality Training Course Manual (hereafter referred to as the Manual) provides background information on what is known about water quality in the Mystic River, estuarine characteristics, general theory and operating procedures for the various instrumentation and probes used, and an overview of sampling design approach (MITSG 1996).

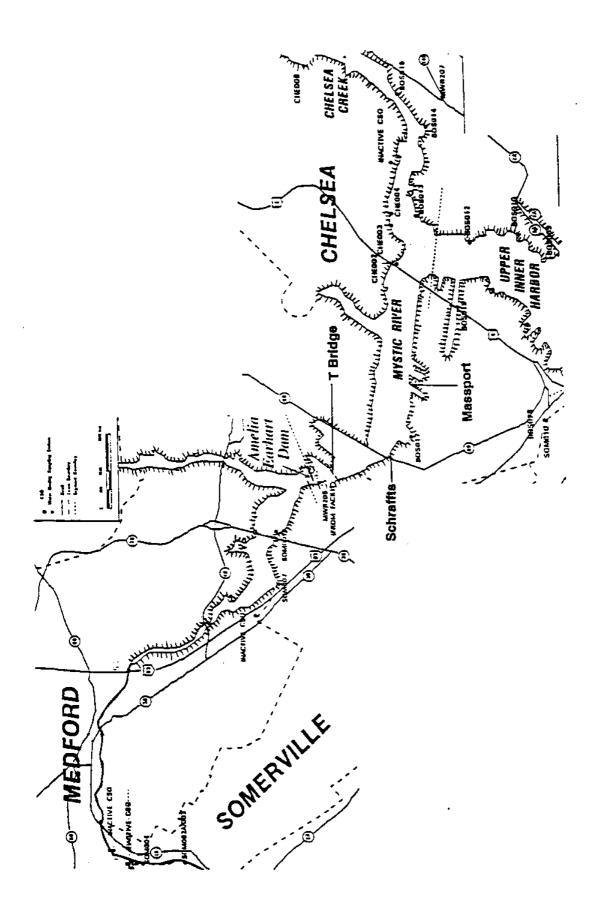


Figure 1. Map of the Mystic River showing station locations; base map adapted from MWRA 1994.

The following discussion is intended to provide insight into the methods and meaning of the data collected by the participants of the Water Quality Training Course. In so doing, the discussion includes topics and details that are generally not part of scientific reports and papers. The purpose of the additional discussion is to provide insights into approaches of analyzing data, interpreting results, and presenting data and to provide several different examples of how data might be presented. As always, the results, analyses and interpretation are only as good as the data. Quality control/quality assurance is an essential part of any field/laboratory study.

#### Methods:

The methods used for the field and laboratory collection and analysis are described in detail in the accompanying Manual (MITSG 1996). For measuring dissolved oxygen, polargraphic electrodes (e.g. YSI PC 6000, YSI PC 600, Hydrolab and a portable hand held Beckman D.O. meter) were used at varying depths and stations throughout the Mystic (Fig. 1). For selected depths and on each of two separate days, water samples were collected in BOD bottles and returned to the laboratory for further D.O. analysis using a modified Winkler test (see MITSG 1996).

Temperature, salinity, turbidity and pH were also measured using a variety of instruments at different depths. Nutrient samples were taken using 5 L Niskin bottles at two depths, 1 meter from the surface and 1 meter from the bottom. These depths corresponded to other measurements and the depths of dissolved oxygen samples.

Sites were chosen to represent a gradient away from the Amelia Earhart Dam which is a physical barrier to low salinity waters from the upper Mystic River and more saline waters from the lower Mystic (Fig. 1). A long-term deployment of a YSI PC6000 series instrumentation at Massport terminal, Revere Sugar (hereafter referred to as Massport), was the downstream station. In addition, samples were taken at the Schraffts public landing dock which was halfway between the two. A closed storm drain was near the Massport site; an open Combined Sewer Overflow (CSO) was below the Amelia Earhart Dam; a scrap metal plant was directly across from the Massport site, and a Boston Edison plant was across from Schraffts.

Samples were refrigerated, returned to the laboratory, frozen overnight, and thawed prior to analysis. Data are reported as µg-at nutrient/L and converted to mg elemental-nutrient/L by multiplying by molecular weights as appropriate. Note that "at" refers to atomic and is used to indicate molarity which is also referred to as concentration, however, concentration is also the term used by wastewater treatment facilities who report data as mg of the elemental-nutrient of interest e.g. nitrogen and phosphorus per liter. The mg elemental-nutrient/L conversions were used to estimate loading rates to be consistent with the literature.

Data were entered into a Microsoft Excel program to facilitate analyzing with different statistical programs or graphing two or more variables. A Data Appendix A with raw

data, statistical analyses, regression plots and bar graphs are attached to this document for reference. In addition, raw data and Reference Data Appendices B.1.-5. are available at the Massachusetts Department of Environmental Protection, Office of Watershed Management at Boston and Grafton offices and at the MIT Sea Grant Office. These are available upon request.

#### Results and Discussion

The results section is arranged following the sequence of questions listed above. As pertinent, comparisons between instrumentation and between instrumentation and laboratory analyses are also indicated in each section.

Q.I. What are the relative concentrations of pollutants or pollution indicators at different segments of the river?

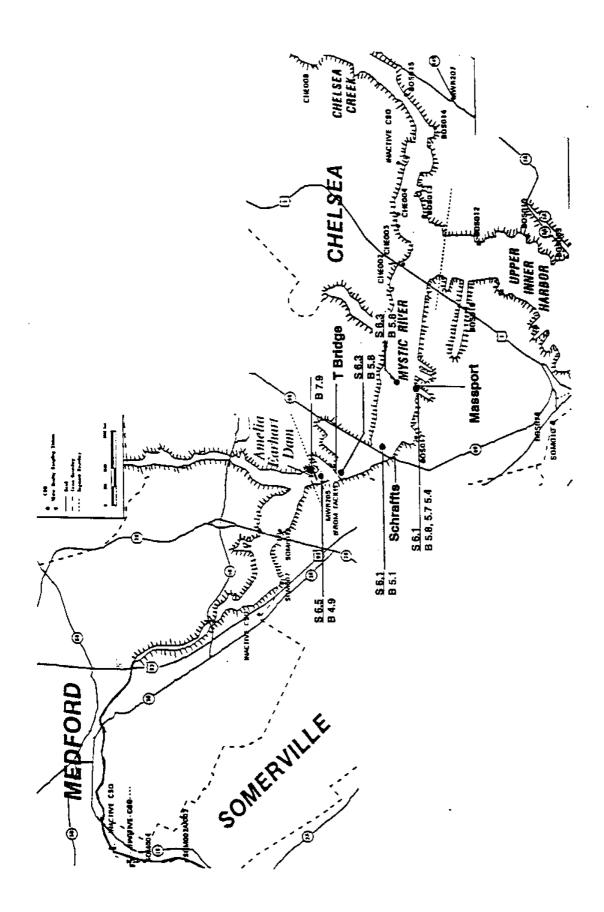
Figures 2 through 5 show the concentrations of dissolved oxygen and nutrients at different stations for the October 11, 1995 sampling period at one meter below the surface (S) and 1 meter above the bottom (B). It is difficult to determine whether there are significant differences between different segments or between the surface and bottom samples by visual inspection alone without applying statistical analyses. By way of example, the D.O. data were statistically analyzed to see if there were significant differences between surface and bottom measurements, to examine the relationships between D.O. and salinity, temperature and depth, and evaluate the relationship between results from the Winkler test (laboratory) and field-deployed probes. We might expect to see lower D.O. in bottom layers if there is a density separation between the surface and bottom (e.g. thermocline or pynocline) and if the Mystic River has high organic loading which would deplete oxygen from bottom layers.

One issue posed during the Sampling Design discussion (see Manual) was: Were the concentrations of D.O. in surface waters different than bottom waters? This can be further broken down into the following questions.

Q.1.a. Did the D.O. in the surface waters differ significantly from that in the bottom waters? Were there significant differences in the D.O. content between the two days for surface samples? bottom samples? or surface and bottom combined?

These questions hint at the level of variability, but, in general, only two days of sampling would not address this question throughout the year or provide diurnal differences without additional sampling.

Figure 6 is a histogram of dissolved oxygen values of surface samples for the first day, second day and both days combined, of bottom samples for the first day, second day and both days combined and surface and bottom (all) of each day. The error bars are  $\pm$ -standard errors of the means. Based on the student "t" test, none of the means are significantly different from each other at the P = 0.05 level where T = 0.318 < t<sub>crit</sub> = 2.36



depths of 1 m below the surface (S) and 1 meter above the bottom (B) at each station for Figure 2. Dissolved oxygen (mg O<sub>2</sub>/L) as measured using a modified Winkler test at dates of 10/10/95 and 10/11/95, base map adapted from MWRA 1994.

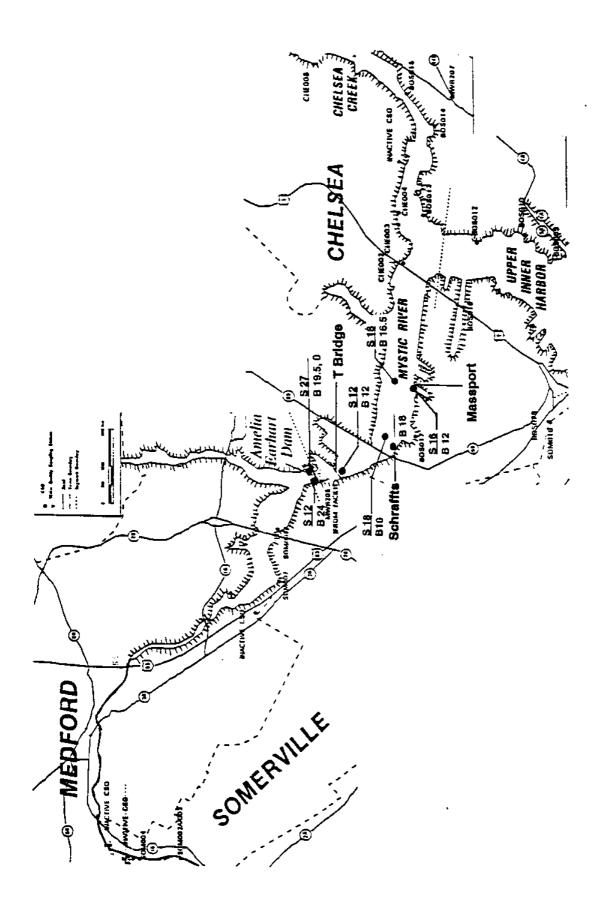


Figure 3. Ammonia concentrations (µg-at N/L) at depths of 1 m below the surface (S) and 1 m above the bottom (B) at each station for 10/11/95; base map adapted from MWRA 1994.

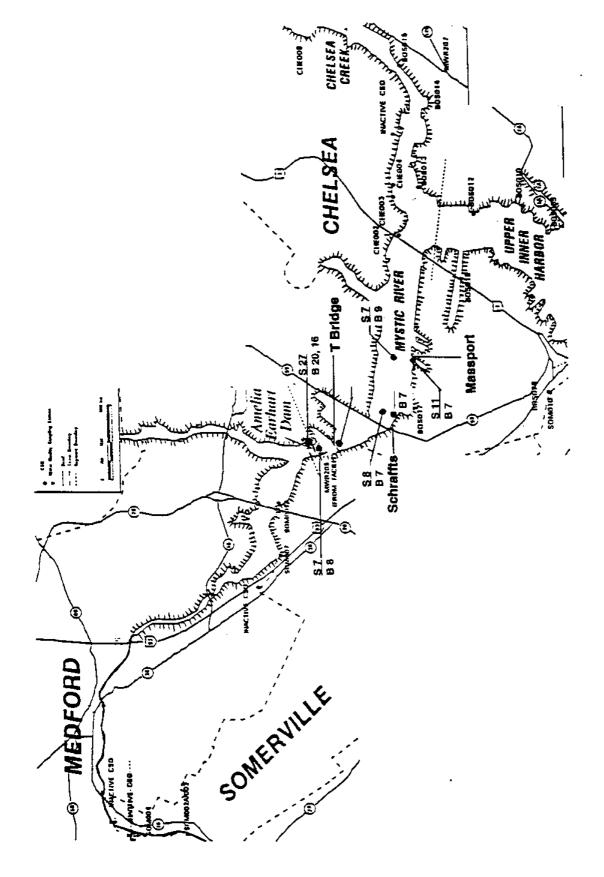


Figure 4. Nitrate and nitrite concentrations (μg-at N/L) at depths of 1 meter below the surface (S) and 1 meter above the bottom (B) at each station for 10/11/95; base map adapted from MWRA 1994.

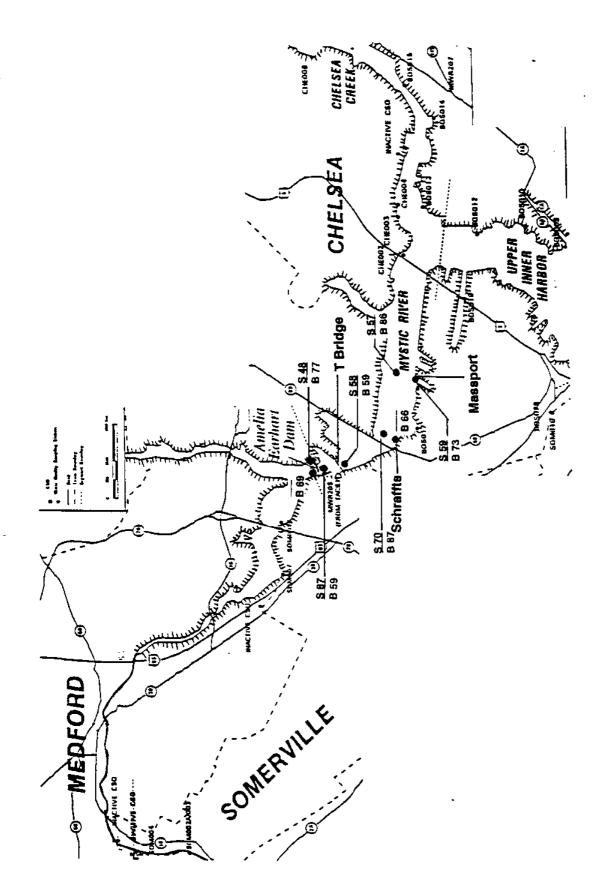


Figure 5. Reactive phosphorus (µg-at P/L) at depths of 1 meter below the surface (S) and I meter above the bottom (B) at each stations for 10/11/95; base map adapted from MWRA 1994.

for surface and bottom sample comparisons on 10/11/95 and  $T = 0.17 < t_{crit} = 2.45$  for surface and bottom samples on 10/10/95. (See Data Appendix A.1.a., p.6).

Two other questions that could be asked are:

Q.1.b. Were there differences in paired values of surface to bottom data at the same site? A statistical comparison was not performed on the data, a non-parametric test would be appropriate. Table 1 shows paired readings, i.e. surface and bottom readings from same location for each day. All but one paired reading shows a high D.O. value in surface waters than bottom waters. Differences ranged greater than 1 mg O<sub>2</sub>/L and ranged from -5 to 34% difference between surface and bottom.

Table 1. Paired dissolved oxygen (mg  $O_2/L$ ) readings from depths of 1 m below the surface (S) and 1 m above the bottom (B) at different locations and sampling dates.

Date	Location	DO (mg O <sub>2</sub> /L)	DO (Mg O <sub>2</sub> /L	S to B differences
		at S	at B	(%)
10/10/95	Massport	7.0	4.6	2.4 (34)
10/10/95	Massport	5.1	4.8	0.3 (6)
10/10/95	Massport	5.0	5.3	-0.3 (-6)
10/10/95	Massport	5.5	4.9	0.6 (11)
10/11/95	Below Dam	6.5	4.8	1.7 (26)
10/11/95	T Bridge	6.1	5.5	0.6 (10)
10/11/95	Schraffts	6.1	5.8	0.3 (5)
10/11/95	Massport	6.3	5.8	0.6 (8)

Q.1.c. By visual inspection, there appears to be a tendency for the surface waters to be consistently higher in D.O. than the bottom waters? Are there other reasons than high organic matter or bacterial metabolism that might explain these differences? Does this tendency correlate with other variables, e.g. temperature and salinity?

Additional comparisons can be made, e.g. D.O. against salinity (Fig. 7) and temperature (Figs. 8a & b) and analyzing for the relationship by calculating regression (data using only the means and for temperature paired data point are given in Fig. 8b). The YSI 600 series data are in the Reference Data Appendix B.2. which is available upon request.

In addition, Figure 9 shows the relationship of D.O. with depth and Figures 10, 11, and 12 show the relationship of depth with salinity (Fig. 10) and temperature (Fig. 11) and salinity plotted against temperature (Fig. 12).

Taken together these plots can be used to evaluate the data (or in the absence of other information) indicate future studies for evaluating the condition of the Mystic River, enforcement of regulations and assessment of the impacts of effort to improve water

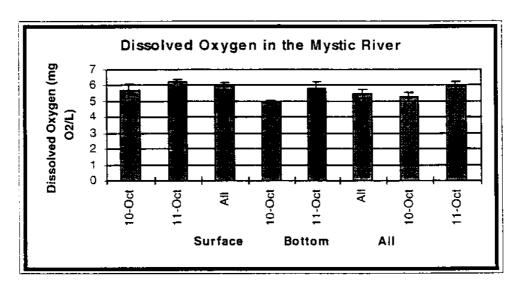


Figure 6. Bar graph showing mean dissolved oxygen (mg  $O_2/L$ ) concentrations with +/-standard error bars at depths of 1 m below the surface and 1 m above the bottom for each day separately (10/10/95 and 10/11/95), surface and bottom combined for each day and for all surface and bottom for both days. See Data Appendix A.1.a.

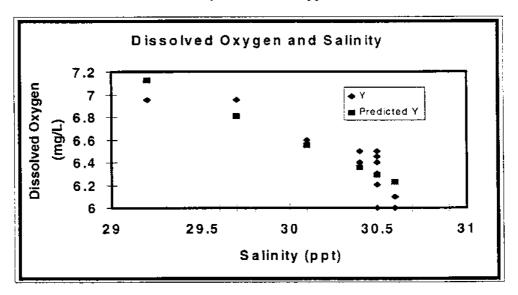


Figure 7. Regression plot ( $R^2 = 0.85$ ) of mean dissolved oxygen ( $O_2/L$ ) and mean salinity as parts per thousand (ppt) measured at the Massport station using daytime measurements of the YSI 600 series on 10/3/95. See Reference Data Appendix B.2, Sheet 6.

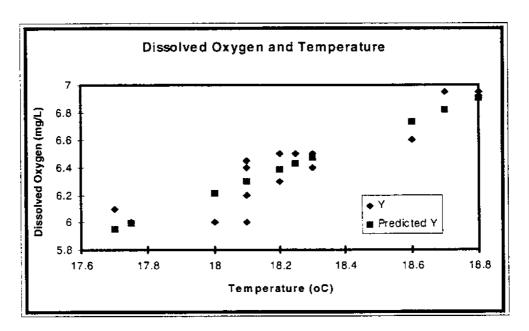


Figure 8a. Regression plot of ( $R^2 = 0.78$ ) of dissolved oxygen (mg O<sub>2</sub>/L) against temperature (°C) measured at the Massport station using mean values from the daytime measurement of the YSI 600 series probe on 10/3/95. See Reference Data Appendix B.2., Sheet 4.

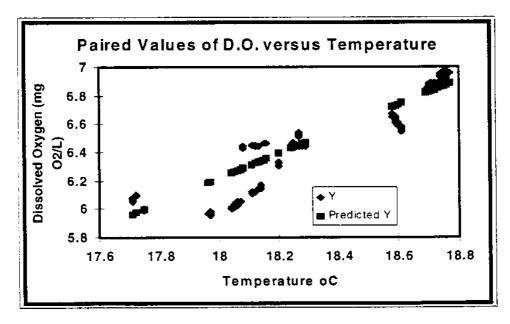


Figure 8b. Regression plot ( $R^2 = 0.85$ ) of paired dissolved oxygen (mg  $O_2/L$ ) and temperature (°C) data measured at the Massport station using daytime measurement of the YSI 600 series probe on 3/13/95. See Reference Data Appendix B.2., Sheet 10.

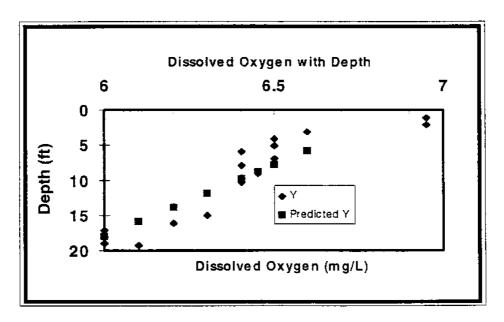


Figure 9. Regression plot ( $R^2 = 0.85$ ) of dissolved oxygen (mg  $O_2/L$ ) against depth (ft) showing an increase in dissolved oxygen with decreasing depth. See Reference Data Appendix B.2., Sheet 5.

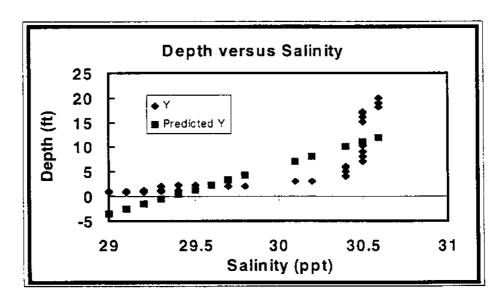


Figure 10. Regression plot ( $R^2 = 0.48$ ) of salinity (ppt) against depth as ft (note surface is at the bottom of the graph) showing increasing salinity with depth. See Reference Data Appendix B.2., Sheet 2.

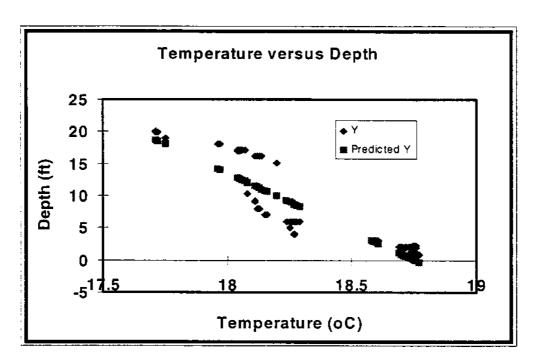


Figure 11. Regression plot  $(R_2 = 0.81)$  of temperature (°C) against depth as ft (note surface is at the bottom of the graph) demonstrating an increase in temperature at the surface. See Reference Data Appendix B.2., Sheet 9.

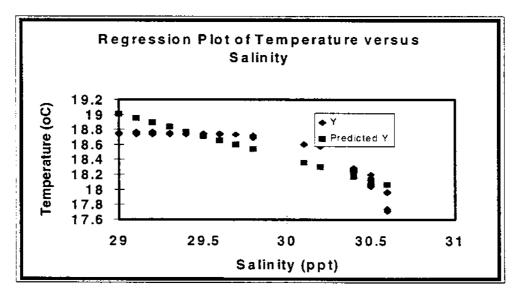


Figure 12. Regression plot ( $R^2 = 0.72$ ) of temperature (°C) versus salinity (ppt) with the predicted and measured data not well correlated graphically. See Reference Data Appendix B.2., Sheet 8.

quality statewide. The data demonstrate a positive relationship between D.O. and temperature which is the opposite of what one expects; i.e. with increasing temperatures D.O. should decrease (see Manual, MITSG 1996). Why don't we see this decrease?

One explanation is that the measurements were taken during daylight hours which means there is increased photosynthesis in the euphotic zone. Although we didn't take Secchi disk readings on both days, the average depth at Massport on 10/11/95 was between 2 to 3 meters, suggesting active photosynthesis>>respiration at the surface and respiration>>production of oxygen (resulting in lower D.O.) near the bottom. There may be other explanations.

The D.O. values decrease with increasing salinity as we would predict. Comparison of salinity, temperature, and depth show salinity increasing with depth, temperature decreasing with depth and higher temperatures with lower salinity. A weak pycnocline (density difference) appears to exist, probably reflecting the fresh water input from the upper Mystic above the dam. Salinity differences appear to occur at about 2 meters (going from 0 parts per thousand, ppt to near 30 ppt within a meter) above the dam and showing only a difference of approximately 1 ppt at about the same depth below the dam. Note that there is a reasonably good correlation ( $R^2 = 0.72$ ) between paired values of salinity and temperature (Fig. 12), however, visual inspection of the graph shows a rather sharp break in the temperature data between 6 and 18 feet (Fig. 11). The high correlation is, in part, due to the large number of data points used (345, Reference Data Appendix B. 2., Sheet 1). There may be other explanations.

The questions raised regarding surface and bottom distributions of dissolved oxygen can be asked for each nutrient. The following is a brief description of the findings for reactive phosphorus, nitrates and nitrites, and ammonia and includes reference to the surface and bottom comparisons for the nutrients. These were plotted and are available in the Data Appendices as indicated in the text.

# Phosphorus

The concentrations of reactive phosphorus that we measured in the Mystic River water samples (Figs. 13a & b) were an order of magnitude higher than the values in the Chan and Alber (1994) report and the CSO report (Table 2-7, MWRA 1994). The values in the two MWRA reports are reported as mg/L (which are mg N-NO<sub>3</sub>/L, mg P-PO<sub>4</sub>/L, and mg N-NH<sub>3</sub>/L) should be divided by the appropriate molecular weight, e.g. N = 14 and P = 31 to obtain concentrations as µg-at P/L. Tables 2 and 3 compare these data calculated both as molarity and concentration expressed as weight per liter. In examining the data, the values are sometimes higher in the surface samples than in the bottom samples, but not consistently (see Data Appendix). Because phosphorus is more likely to be released from sediments in low oxygen conditions we might postulate higher P values in bottom samples than surface samples. However, the oxygen concentrations that we measured in the bottom (1-meter above the sediment) samples were not below the

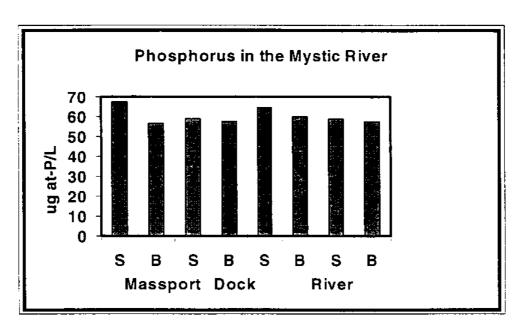


Figure 13a. Bar graph plot of reactive phosphorus (ug-at P/L) in surface and bottom waters at the Massport station on 10/10/95 where S refers to surface and B refers to Bottom. See Data Appendix A.2.c.

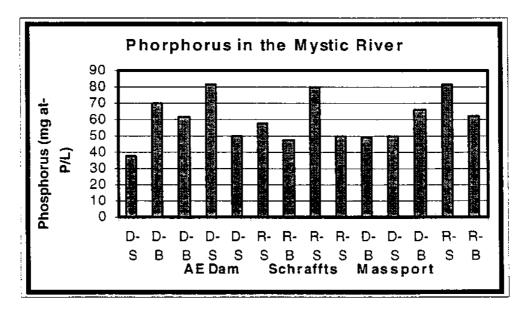


Figure 13 b. Bar graph plot of reactive phosphorus ( $\mu$ g-at P/L) in surface and bottom waters at the Massport station on 10/11/95. D refers to dock, R refers to river, S refers to surface and B refers to bottom. See Data Appendix A.2.c.

water quality criteria and not near hypoxic or anoxic conditions during the fall season and daylight time period. Unfortunately, the data are too variable to draw any conclusions about potential sources, e.g. riverine inputs compared to release from sediments. Similarly, the difference in measured phosphorus in this study compared to others indicates the need for investigative studies to determine whether the differences are real, laboratory artefact or due to another cause. One possible source of error is high suspended solids in the samples which would inflate P concentrations detected in the laboratory procedure. Although a cursory check did not reveal a problem with suspended solids, this is one area where further studies should be done. There may be other possible sources of error.

Table 2. Pollutant loading estimates for above and below the Amelia Earhart Dambased on MWRA data (1994) and this study. Numbers in parentheses are standard error of the means, an=2, n=11, n=3, n=19.

Pollutant		Above Dam (MWRA)	Below Dam (MWRA)	Above Dam (This Study)	Below Dam (This Study)
Ammonia (mg N-NH,/L)		0.1	0.1	0.322(nd) <sup>a</sup>	0.21(0.16) <sup>b</sup>
Nitrate + Nitrite N-NO <sub>3</sub> +NO <sub>4</sub> /L)	(mg	0.48	0.48	0.291(.048) <sup>e</sup>	0.092(.008) <sup>d</sup>
Phosphorus (mg P-PO <sub>4</sub> /L)	·	0.08	0.08	2.0(0.27) <sup>c</sup>	2.13(.068) <sup>d</sup>

Table 3. Ranges of nutrient concentrations used to evaluate water quality in rivers and estuaries (from MWRA 1994) and compared to values from this study. Values are in mg elemental nutrient/L, e.g. mg P-PO<sub>4</sub>/L; <sup>a</sup> refers to values from this study.

Condition	River		Estuarine		River <sup>a</sup>		Estuarine	
	DIN	P	DIN	P	DIN	P	DIN	P
"healthy"	<0.15	<0.01	<0.6	<0.08			0.31	
"fair"	0.15-0.3	0.01-0.05	0.6-1.8	0.08-0.20				
"poor"	>0.3	>0.5	>1.8	>0.2	0.6	2.0		2.13

No further analyses were done, e.g. to compare P with temperature or salinity, however the values were used to estimate loading despite the discrepancy between these values and expected values.

#### Ammonia

Ammonia data from this exercise are difficult to interpret for two reasons. The potential for contamination from the laboratory is extremely high and no standard curve was determined for the first day. The data for both days are given in Figures 14a and b, but only data from 10/11/95 are used for comparison and further calculations of loading rates. There are differences in the average values between the first and second day which are not likely to be "real" differences. The values fall within the range of those reported in for other coastal rivers and estuaries in the literature (see Tables 2 & 3). Because of the uncertainty of the values, the data were plotted by river segment and for the surface and bottom for 10/11/95 data set only (Fig. 4). Refer to Data Appendix A.3. for standard curves, class data and surface and bottom comparisons.

### Nitrates and Nitrites

The nitrate values are consistent between 10/10/95 and 10/11/95 especially for the Massport station (Figs. 15a & b). It is tempting to suggest that the surface waters, which are also less saline and probably reflect the fresh water source from the upper Mystic as the water comes over the dam (see later discussions, Data Appendix A.4.a. and Table 2 & 3). Again, the data are sparse, but experience and comparison with other systems may lead to more robust conclusions. In a later section, the data are used to estimate loadings from the "fresh water" portion, the higher concentrations are found with the lower salinity surface waters, and are slightly lower in the more saline waters in the bottom layers. Although there is only 1 ppt difference in surface to bottom salinity below the dam, the higher nitrate and nitrite concentrations are found in the less saline waters. Above the dam the same distribution holds true, but the salinity differences range from 0 to 30 ppt in surface to bottom waters with a sharp break at 2-3 m.

# Water Quality Criteria

Our second major question is regulatory in nature; Are water quality criteria being met throughout the river? There are water quality criteria (see MITSG 1996, Appendix B) for temperature, generally written for thermal discharge management, and pH of 6.5 to 8.5; for this study both temperature and pH are within acceptable limits. As noted in the Manual, of the water quality data we collected, namely dissolved oxygen, nitrates and nitrites, phosphorus, and ammonia, only dissolved oxygen has numerical water quality criteria. The value of less than 5 mg  $O_2/L$ , the water quality criteria for marine waters classified as SB (see Manual, Appendix B) or unless background values are lower or less than 60% due to a discharge, were not observed during the period of this study. From the data in Table 1, there are 4 values less than 5.0 mg  $O_2/L$ . although levels of less than 3.0 mg  $O_2/L$  were recorded near the bottom (< 0.3 m) were recorded using a hand-held YSI on 10/3/95 when the YSI 6000 probe was deployed. Unfortunately these data were not recorded. This suggests that the observed summer depletion of oxygen (see Massport, 1995 and MWRA, 1993) is not as evident by fall, and is probably a sediment/water

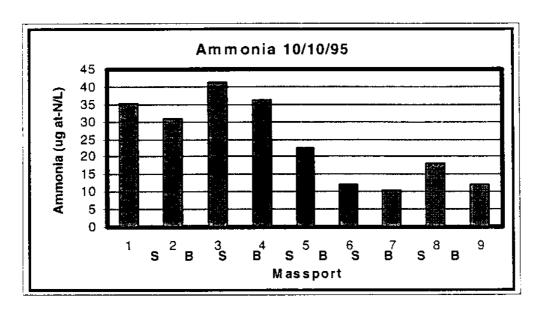


Figure 14a. Bar graph plot of nitrate and nitrite ( $\mu$ g-at N/L) in surface and bottom samples at Massport station for 10/10/95 where S refers to surface and B to bottom samples. See Data Appendix A.4.

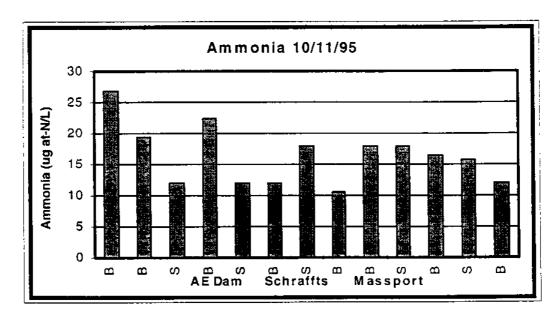


Figure 14b. Bar graph plot of nitrate and nitrite ( $\mu$ g-at N/L) in surface and bottom samples at each station for 10/11/95 where S refers to surface and B to bottom samples. See Data Appendix A.4.

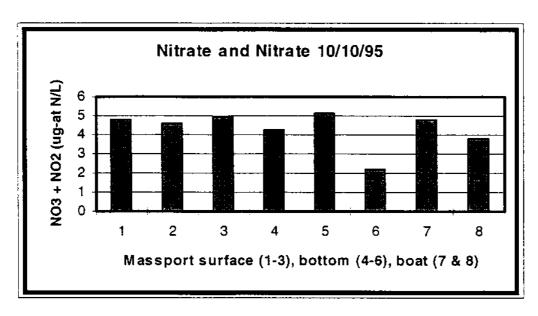


Figure 15a. Bar garph plot of ntirate and nitrite ( $\mu$ g-at N/L) in surface and bottom samples at Massport Station for 10/10/95. See Data Appendix A.4.

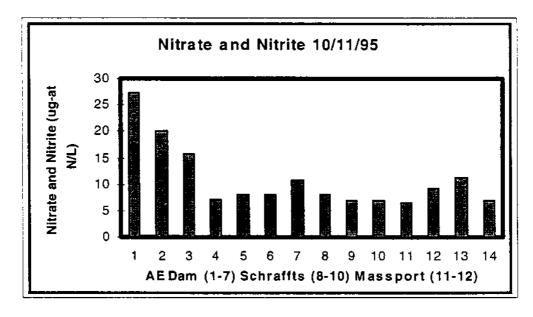


Figure 15b. Bar graph plot of nitrate and nitrite ( $\mu$ g-at N/L) in surface and bottom samples at each station for 10/11/95. See Data Appendix A.4.

interface problem which is more pronounced during warmer, lower flow summer conditions.

Part of our class activity was to compare measurements from instruments and laboratory analyses. Figure 16 is a plot of oxygen data from BOD bottle samples using a modified Winkler test performed on samples from field sites that corresponded to recorded D.O. using field equipment. As a working rule, field scientists accept a 10% difference between D.O. values using electrodes compared to laboratory analysis. Table 4 provides readings for both deployed dissolved oxygen meter readings that correspond to BOD samples analyzed by a modified Winkler test. Only two of 9 readings are below a difference of 10%. In general, the field instruments read higher than the laboratory analyses, which has implications for management of coastal waters if these relationships continue to hold. At a minimum, it suggests that in addition to the calibration of instruments prior to going into the field, BOD samples be taken at the beginning, the end and where it appears that water quality criteria are not being met. It is not sufficient to merely calibrate instruments prior to field collection of data, but it is necessary to verify readings, particularly if enforcement action may be involved.

Table 4. Comparison of dissolved oxygen (mg  $O_{2}/L$ ) using electrodes on field deployed instrumentation and analyzed using a modified Winkler test. Percent differences are calculated by obtaining a difference and dividing by the instrument value.

Station	D.O. Laboratory	D.O. Instrument	% Difference
Massport	7.0	6.1	-14.8
Massport	5.5	6.6	16.7
Massport	5.0	5.9	15.2
Massport	4.6	5.7	19.2
Massport	4.8	5.9	18.6
AE Dam	7.9	9.3	15.1
AE Dam	6.5	7.0	7.0
AE Dam	4.8	4.8	0.0
Massport	5.4	6.1	11.5

# Diurnal Comparisons

The third question we raised at the beginning of the class is: Are there diurnal differences in pollution or pollution indicators? We measured D.O., turbidity, and pH at a depth of 1 m above the bottom at the Massport site. Neither turbidity nor pH showed any discernible fluctuations (Reference Data Appendix B.3.), although these were not further analyzed. A comparison of D.O., temperature and salinity over the seven day deployment of the YSI 6000 are given in Figures 17, 18, and 19 (see Reference Data Appendix B.3.). There appears to be a slight diurnal pattern to D.O. i.e. that D.O. is higher during the daylight hours than at night. We would expect D.O. to be lower in the night because photosynthesis shuts down and plants and animals continue to respire, however, other

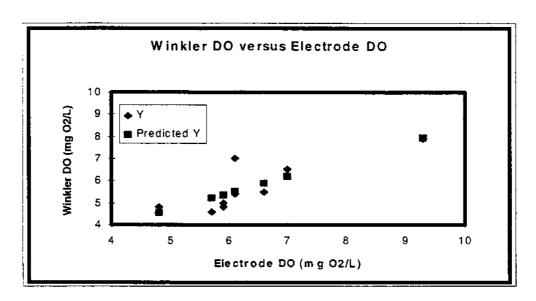


Figure 16. Regression plot ( $R^2 = 0.86$ ) of dissolved oxygen (mg O<sub>2</sub>/L) from BOD samples using a modified Winkler test compared to dissolved oxygen measurements taken with electrodes of a YSI 6000 series probe which had been deployed for 1 week prior to 10/10/95 data at the same depths and times. See Data Appendix A.1.b. and Reference Data Appendix, Sheet 6.

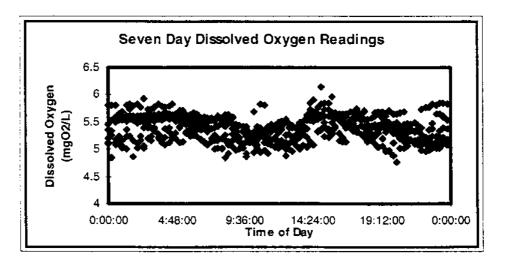


Figure 17. Plot of dissolved oxygen (mg O<sub>2</sub>/L) plotted for the same time each day covering the period from 10/3/95 to 10/10/05 at the Massport station using YSI 6000 series oxygen electrode generated data. See Reference Data Appendix B.3.

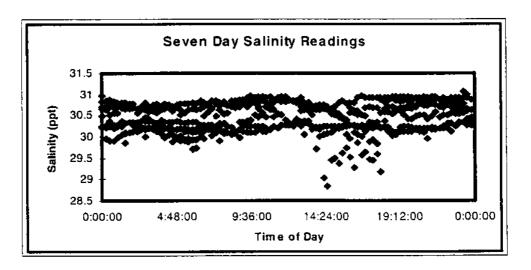


Figure 18. Plot of salinity (ppt) plotted for the same time each day covering the period from 10/3/95 to 10/10/95 at the Massport station using YSI 6000 series generated data. See Reference Data Appendix B.3.

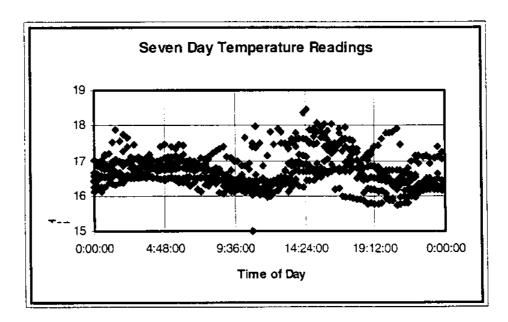


Figure 19. Plot of temperature (°C) plotted for the same time each day covering the period from 10/3/96 to 10/10/95 at the Massport station using the YSI 6000 series generated data. See Reference Data Appendix B.3.

factors appear to influence D.O. readings and the range for any given time of day or night is high and overlaps. If we took our measurements during warmer months when water temperatures are higher we should expect to see a strong diurnal pattern, particularly if stratification exists. In the areas of the Mystic River near the Dam we might also expect to see high (above saturation) levels of D.O. in the surface waters during the day and low D.O. at night which is consistent with observations of low numbers of benthic organisms during summer months (Massport and USACOE 1994). Supersaturated waters are an indicator that the system is stressed. There was no evidence from data collected for this study that D.O. violations of water quality criteria occur, but the highest D.O. reading was taken above the dam in the surface waters and may indicate a night time low that is in violation of the criteria (see Data Appendix A.1.a.).

Another noteworthy aspect of the week-long data, particularly noticeable with salinity data at the Massport site, is a group of low salinity readings that probably correspond to the rainfall which occurred during the week (10/3/95-10/10/95) of the YSI 6000 series deployment.

We asked if one could detect differences attributable to tides. These data were not plotted by an appropriate offset of the semidiurnal tidal cycle, however, to make a reasonable analysis it is necessary to do so. Is it likely that tidal differences (40 minutes each 12 hour period) could account for the variability? How would one separate out differences of daylight (especially important for dissolved oxygen measurements) from tidal influences? Tides and/or winds may also contribute to the variability observed if the tidal influence extends spatially and temporally across a low salinity or higher temperature period within the sampling area.

#### Instrumentation comparisons

We asked the question, How well do the instruments compare to each other? The instruments were calibrated, e.g. air calibrated for D.O., and standard calibrated for salinity prior to deployment, but not intercalibrated. Table 5 gives values for D.O., salinity and temperature at selected sites using different instruments. For all data see Data Appendix A.5.

Table 5. Comparison of temperature, salinity and oxygen data using different instrumentation and probes at the same time and place. Portable instruments included a VWR which measured temperature and salinity and a YSI oxygen electrode.

Variable	Hydrolab	Portable
Temperature °C	17.43	18.1
Salinity (ppt)	22.5	27.4
Dissolved Oxygen (mg	6.1	5.7
O <sub>2</sub> /L		

# Estimating nutrient loading

Although we may question how reliable our data are, we can go through the exercise of estimating total loading for the river inputs and even estimate the amount coming from the fresh water portion compared to the marine contribution. Given the caveats associated with the data, the loading estimates for phosphorus are questionable. This exercise is for purposes of how data from your watershed sampling could be used and applied to management questions. As always, one must asses the level of certainty in the data sets (for this exercise, the data are reasonable for D.O. and nitrate and nitrite, probably for ammonia, but not necessarily for phosphorus). We can also note that the data in this report are applicable to October, and maybe even the fall of the year, but not necessarily representative of the total year. There were only one or two data points available for the Alber and Chan (1994) estimates of loadings into Boston Harbor and these are based on Charles River data (A. Rex. MWRA, pers. comm.). How much confidence is there in these values? Does it matter? As coastal managers attempt to estimate loadings from point and nonpoint sources, the relative contributions become important. If loading estimates are off by an order of magnitude (e.g. phosphorus from this study compared to MWRA data), it can bias where enforcement and clean-up efforts should be targeted. In times of limited dollars for clean-up, it is important to focus on minimizing major sources.

### Data conversion

Our nutrient data are expressed as  $\mu$ M-at N or P/L (which is the molarity of the solution) and therefore, if we want to estimate the concentration (e.g. mg N-NH<sub>4</sub>/L) as is usually reported by MWRA and others in the literature, we need to multiply by the molecular weight of nitrogen or phosphorus. This is 14 for nitrogen and 31 for phosphorus. If we wanted to know the weight of nitrate it would be 14 + 3(16) or 52 times the  $\mu$ M-at nitrate nitrogen/L value, but to keep our units equivalent we are only concerned about nitrogen or phosphorus.

For loading estimates we need to know the area of the river and the flow. We measured flow rates at 15 cm/sec in the surface waters (approximately 1 m in depth). A reading of 25 cm/sec at an unknown depth was also recorded by the class, but it is not used because of uncertainties about the number. Specifically, the probe was not necessarily facing the stream flow and may have also been measuring sine boat displacement by tides. Thus, only the 15 cm/sec is assumed accurate for the top meter of the lower Mystic River, but even so, it may also have recorded velocity of the boat in addition to the movement of the water. Flow rates taken near the dock side sampling sites gave no readings at all. Given the uncertainty around the class flow measurements, we will use the MWRA values for low, medium and high flow rates for the Mystic River (MWRA 1994).

Although this information is not used in analyzing the data, the river depth is approximately 10 m deep at low tide throughout the dredged portion of the channel. The depth at which salinities change appears to be around 2 m (see Hydrolab data in Data

Appendix, particularly YSI 6000 series 10/3/95 data, and class Hydrolab data from above the Amelia Earhart Dam).

Some comparisons are given below.

- 1. One can calculate dilution of the fresh water by the more saline lower Mystic River by using the mean nutrient concentrations above the dam and comparing them to below the dam values (note differences in sample analyses are 3 and 11 or 19). For ammonia the dilution factor appears to be 1.5 (= upstream concentrations/downstream concentrations) whereas for nitrate and nitrite the factor is 3. If these differences are real, it would be interesting to explore the possible reasons for the differences observed and compare these to what was expected. For example: Is there another source of ammonia downstream? What is the rate of conversion from ammonia to nitrogen gas? Is there differential uptake of nitrates by phytoplankton?
- 2. Using data from Alber and Chan (1994), who estimated high, medium and low flow rates for the Mystic River as 3.4, 2.4 and 1.3 m<sup>3</sup>/sec, respectively we used our values to estimate loadings for nitrogen (as ammonia, nitrate and nitrite) and phosphorus. Thus, a loading rate is calculated as flow (m<sup>3</sup>/sec) x 60 sec x 60 min x 24 hr x 365.25 da to get an annual flow rate times concentration. The concentration is mg elemental nutrient/L converted to kg/L then to kg/m<sup>3</sup> where 1 L = 0.001 m<sup>3</sup> and multiplied by the annual flow rate. The annual loading rate is expressed as mtons/yr where 1 kg = 0.001 mton.

The estimated loading rates are given in Table 6. The MWRA estimates are from Alber and Chan (1994) and are based on their Table 2-6-6 assuming North Harbor estimates are additive among the three river systems, Mystic, Charles and Neponset (see Table 2-6-2) where the Mystic River values, as given above, are a proportion of the high, low and mean values in proportion to annual flow estimates of each of the three rivers. Using mean values for both concentration and flow rate gives values (see medium river flow rates in Table 6), estimates of loading are 46.4 mton/y nitrogen for the river and 23.1 mton/y for the estuary, whereas average values for phosphorus are 151.9 mton/y for the river loadings and 162 mton/y for the estuary. The loading estimates are an order of magnitude higher than the MWRA values, but it was not possible to reconstruct if there was a systematic error in the laboratory analyses that would account for this discrepancy. However, it is the most likely source of error when compared to a larger base of data from the literature that also report lower phosphorus concentrations. Assuming the validity of the analyses for nitrogen, estimated nitrogen loading from the river is higher than the concentrations in the estuary; hence for October there is more DIN nitrogen entering from the freshwater portion compared to the saline portions of the river.

If the data were more extensive in time and space, conclusions would be robust, with this limited data set they are not. Nonetheless, the purpose of this report is to demonstrate how data can be used and what is needed to ensure reliability, both with field equipment and verification with laboratory analyses. It is difficult to escape the conclusion that data should be collected seasonally, diurnally, and spatially to reflect sources and less

polluted areas, and temporally to evaluate the effects of tides, winds and other factors. This requires a commitment on the part of agencies or others who are collecting data to identify the purpose select wisely what types of data should be collected, and identify the use of the information generated as it applies to the state and federal regulations and mandates. It is also important to recognize the need to include quality control/quality assurance at all levels. It is better to collect less data of high quality than to sample for the sake of sampling.

Table 6. River flow data from MWRA (1994) and estimated loadings for P and N for the riverine and estuarine portion of the Mystic River based on data from MWRA (1994) and this study. The low values are the mean minus the standard error, the higher values are the mean plus the standard error of the mean times the respective flow estimates. Mean values and medium flow rates are given in text. <sup>a</sup> See text, Alber and Chan (1994) and MWRA (1994) for estimates used.

River Flow	Low (m <sup>3</sup> /sec)	Medium (m³/sec)	High (m³/sec)
Mystic River	1.3	2.4	3.4

Nutrient Loads	Total N	Total N	Total P	Total P
	(mton/y)	(mton/y)	(mton/y)	(mton/y)
River	MWRA	This study	MWRA	This study
High	97-193.5	61-71.5	8.5-20	186-243
Mean	68-136	43-50	6-14	131-172
Low	37-74	23-27	3-8	71-93
Estuary				
High		13.5-35		93-244
Mean		12.5-33		82-215
Low		11.5-30		71-186

# **CONCLUSIONS:**

- 1. During the month of October when waters are vertically mixed, the concentration of dissolved inorganic nitrogen (DIN) in riverine waters is approximately twice that in saline waters (approximately 20 mg N/L above the dam compared to 10 mg/L below the dam).
- 2. Ammonia concentrations from this study are higher (0.332 mg N-NH<sub>2</sub>/L above the dam compared to 0.21 mg N-NH<sub>2</sub>/L below the dam) than average values reported by MWRA (1994), which are reported at 0.1 mg N-NH<sub>2</sub>/L for both above and below the dam.

- 3. Phosphorus concentrations are an order of magnitude higher (2 mg P-PO<sub>4</sub>/L) than other reported values (0.08-0.19 mg P-PO<sub>4</sub>/L), suggesting a systematic error in the analysis or some other factor which was not accounted for in this study.
- 4. Dissolved oxygen levels fell below the water quality criteria (5.0 mg O<sub>2</sub>/L) in bottom waters during the sampling period of October 3-11, 1995, with D. O. values being higher in surface waters than at depth. If extrapolated to warmer months, there may be low oxygen events which would be consistent with observations of little or no biota in summer samples (Massport and ACOE 1995).
- 5. Instrumentation and laboratory analyses were rarely (2 out of 9 time) within 10% of each other for dissolved oxygen, and in general, instrumentation probes read higher than chemical analyses.
- 6. Comparison of nitrogen loading estimates from the riverine portion are compared to the condition values of healthy, fair and poor. The loading rates suggest DIN are unacceptable. If phosphorus data generated for this report are within an acceptable level of accuracy, phosphorus levels are also at unacceptable levels.
- 7. Comparison of equipment and laboratory analyses suggest that as part of the field work for monitoring water quality parameters, it is necessary to verify the field equipment even when it has been properly calibrated prior to deployment. This is particularly important if the values are to be used for enforcement purposes.

# References:

Alber, M and A. Chan 1994. Sources of Contaminants to Boston Harbor: Revised Loading Estimates. MWRA Technical Report no. 94-1, March 1994. 93pp.

Massachusetts Water Resources Authority (MWRA) 1994. Baseline Water Quality Assessment: Master Planning and CSO Facility Planning. prepared by Metcalf and Eddy, circa 335 pp + appendix

Massachusetts Institute of Technology Sea Grant College Program 1996. Water Quality Training Course: Field and Laboratory Manual, prepared by Judith Pederson, circa 50 pp + appendices.

Massachusetts Port Authority and U.S. Army Corps of Engineers 1995. Boston Harbor, Massachusetts: Navigation Improvement Project and Berth Dredging Project; Final Environmental Impact Statement/Report. prepared by Normandeau Associates, 3 vols.

# DATA APPENDIX A.

Data sheets with statistical analysis for water quality data collected by the Water Quality Training Course for the Mystic River, Boston, MA.

Data Appendix A.1.a. Dissolved oxygen data, descriptive statistics, and "t" test results comparing surface and bottom dissolved oxygen results from 10/10/95 and 10/11/95 sampling activities.

Data Appendix A.1.b. Regression statistics comparing dissolved oxygen data from YSI 6000 electrode measurements and modified Winkler tests for both sampling days (10/10/95 and 10/11/95).

Data Appendix A.2.a. Standard curve plot for phosphorus solutions from 10/10/95 with regression statistics.

Data Appendix A.2.b. Standard curve plot for phosphorus solutions from 10/11/95 with regression statistics.

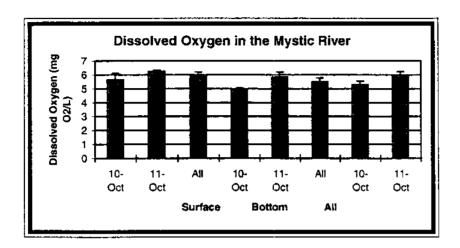
Data Appendix A.2.c. Data from class analyses used to generate bar graphs of phosphorus concentrations at each station and depth for each day.

Data Appendix A.2.d. Statistical analyses of surface and bottom concentrations of phosphsour for each day.

Data Appendix A.3. Ammonia standard curve used to estimate ammonia concentrations and class generated ammonia data and plots of concentrations for each day.

Data Appendix A.4. Nitrate and nitrite data standard curves used to estimate concentrations in samples.

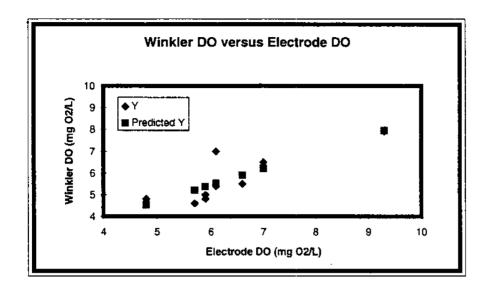
station id	sample id	date	time	finish	start	do	do corr	sort
				mm(ml)	mm(mi)	mgO2/L	mgO2/L	
MRMA	a1dos	101095				6.8	. 7	
MRMA	a1dob	101095		34.3	29.8	4.5	4.6	
MRMA	b1dos	101095		39.4	34.4	5	5.1	
MRMA	b1dob	101095		45.6	40.9	4.7	4.8	
MRMA	c1dos	101095	·	33.5	28.6	4.9		
MRMA	c1dob	101095				5.2	5.3	
MRMA	b1cos	101095		<b>38</b> .9	33.5	5.4	5.5	
MRMA	b1cob	101095		40.9	36.1	4.8	4.9	
mrae	a1dos-ab	101195						
mrae	a2dos-ab	101195						
mrae	a1dob-ab	101195		39.5			7.9	
mrae	a1dos	101195		31.3	25.7	<b>5</b> .6	6.5	
mrae	a1dob	101195		25.7	21.5	4.2	4.8	
mrae	a1cos-T	101195		45.4	40.2	5.3	6.1	
mrae	a1cob-T	101195		40.2	35.4	4.8	5.5	
mrsh	a1cos	101195		21.5	16.2	5.3	6.1	,
mrsh	a1cob	101195		46.7	41.7	7 5	5.8	
mrsh	a1dob	101195		41.7	36.8	3 4.9	5.7	
mrma	a1dob	101195	<del></del>	50.1	45.4	4.7	7 5.4	
mrma	a1cos	101195		36.8	31.3	5.5	6.3	
mrma	atcob	101195		44.5	39.5	5 5	5.8	
corr		101095		ml reading	g/ml expect	ed	10/10/95	19.5/20
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			101095 101095 101095 101095	5.1 5.1 5.5	7 4.6 1 4.8 5 5.3 5 4.9	3 10-0c 3 11-0c 9 All	t 5.65 t 6.25 5.95	0.46 0.1 0.25
			101095 101095 101095	5.1 5.5 5.5 6.5	7 4.6 1 4.8 5 5.5 5 4.9 5 7.9	3 10-0c 3 11-0c 3 All 9 10-0c	t 5.65 t 6.25 5.95 t 4.9	0.46 0.1 0.25 0.15
			101095 101095 101095 101095 101195	5.1 5.5 5.6 6.5	7 4.6 1 4.8 5 5.0 5 4.9 6 7.9	3 10-0c 3 11-0c 9 All 9 10-0c 3 11-0c	t 5.65 t 6.25 5.95 t 4.9	0.46 0.1 0.25 0.15 0.37
			101095 101095 101095 101095 101195 101195	5.1 5.5 5.6 6.1 6.1	7 4.6 1 4.8 5 5.0 5 4.9 6 7.9 1 4.8	3 10-0c 3 11-0c 3 All 9 10-0c 3 11-0c	t 5.65 t 6.25 5.95 t 4.9 t 5.84	0.46 0.1 0.25 0.15 0.37 0.27
			101095 101095 101095 101095 101195 101195 101195	5.1 5.5 5.5 6.1 6.1 6.1	7 4.6 1 4.8 5 5.0 5 4.9 6 7.9 1 4.8 1 5.0 3 5.0	3 10-Oc 3 11-Oc 9 All 9 10-Oc 3 11-Oc 5 All 3 10-Oc	t 5.65 t 6.25 5.95 t 4.9 t 5.84 5.5 t 5.28	0.46 0.1 0.25 0.15 0.37 0.27
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			101095 101095 101095 101095 101195 101195 101195 101195 101195	5.1 5.5 5.5 6.5 6.7 6.7	7 4.6 4.8 5 5.6 5 4.9 6 7.9 1 4.8 1 5.9 5 5.	3 10-Oc 3 11-Oc 9 All 9 10-Oc 3 11-Oc 5 All 3 10-Oc 7 11-Oc 4	t 5.65 t 6.25 5.95 t 4.9 t 5.84 5.5 t 5.28	0.46 0.1 0.25 0.15 0.37 0.27
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			101095 101095 101095 101095 101195 101195 101195 101195 101195	5.1 5.5 5.5 6.5 6.7 6.7	7 4.6 4.8 5 5.6 5 4.9 6 7.9 1 4.8 1 5.9 5 5.	3 10-Oc 3 11-Oc 9 All 9 10-Oc 3 11-Oc 5 All 3 10-Oc 7 11-Oc 4	t 5.65 t 6.25 5.95 t 4.9 t 5.84 5.5 t 5.28	0.46 0.1 0.25 0.15 0.37 0.27
			101095 101095 101095 101095 101195 101195 101195 101195 101195	5.1 5.5 5.5 6.5 6.7 6.7	7 4.6 4.8 5 5.6 5 4.9 6 7.9 1 4.8 1 5.9 5 5.	3 10-Oc 3 11-Oc 9 All 9 10-Oc 3 11-Oc 5 All 3 10-Oc 7 11-Oc 4	t 5.65 t 6.25 5.95 t 4.9 t 5.84 5.5 t 5.28	0.46 0.1 0.25 0.15 0.37 0.27
			101095 101095 101095 101095 101195 101195 101195 101195 101195	5.1 5.5 5.5 6.5 6.7 6.7	7 4.6 4.8 5 5.6 5 4.9 6 7.9 1 4.8 1 5.9 5 5.	3 10-Oc 3 11-Oc 9 All 9 10-Oc 3 11-Oc 5 All 3 10-Oc 7 11-Oc 4	t 5.65 t 6.25 5.95 t 4.9 t 5.84 5.5 t 5.28	0.46 0.1 0.25 0.15 0.37 0.27
			101095 101095 101095 101095 101195 101195 101195 101195 101195	5.1 5.5 5.5 6.5 6.7 6.7	7 4.6 4.8 5 5.6 5 4.9 6 7.9 1 4.8 1 5.9 5 5.	3 10-Oc 3 11-Oc 9 All 9 10-Oc 3 11-Oc 5 All 3 10-Oc 7 11-Oc 4	t 5.65 t 6.25 5.95 t 4.9 t 5.84 5.5 t 5.28	0.46 0.1 0.25 0.15 0.37 0.27
			101095 101095 101095 101095 101195 101195 101195 101195 101195	5.1 5.5 5.5 6.5 6.7 6.7	7 4.6 4.8 5 5.6 5 4.9 6 7.9 1 4.8 1 5.9 5 5.	3 10-Oc 3 11-Oc 9 All 9 10-Oc 3 11-Oc 5 All 3 10-Oc 7 11-Oc 4	t 5.65 t 6.25 5.95 t 4.9 t 5.84 5.5 t 5.28	0.46 0.1 0.25 0.15 0.37 0.27
			101095 101095 101095 101095 101195 101195 101195 101195 101195	5.1 5.5 5.5 6.5 6.7 6.7	7 4.6 4.8 5 5.6 5 4.9 6 7.9 1 4.8 1 5.9 5 5.	3 10-Oc 3 11-Oc 9 All 9 10-Oc 3 11-Oc 5 All 3 10-Oc 7 11-Oc 4	t 5.65 t 6.25 5.95 t 4.9 t 5.84 5.5 t 5.28	0.46 0.1 0.25 0.15 0.37 0.27
			101095 101095 101095 101095 101195 101195 101195 101195 101195	5.1 5.5 5.5 6.5 6.7 6.7	7 4.6 4.8 5 5.6 5 4.9 6 7.9 1 4.8 1 5.9 5 5.	3 10-Oc 3 11-Oc 9 All 9 10-Oc 3 11-Oc 5 All 3 10-Oc 7 11-Oc 4	t 5.65 t 6.25 5.95 t 4.9 t 5.84 5.5 t 5.28	0.46 0.1 0.25 0.15 0.37 0.27
			101095 101095 101095 101095 101195 101195 101195 101195 101195	5.1 5.5 5.5 6.5 6.7 6.7	7 4.6 4.8 5 5.6 5 4.9 6 7.9 1 4.8 1 5.9 5 5.	3 10-Oc 3 11-Oc 9 All 9 10-Oc 3 11-Oc 5 All 3 10-Oc 7 11-Oc 4	t 5.65 t 6.25 5.95 t 4.9 t 5.84 5.5 t 5.28	0.46 0.1 0.25 0.15 0.37 0.27
			101095 101095 101095 101095 101195 101195 101195 101195 101195	5.1 5.5 5.5 6.5 6.7 6.7	7 4.6 4.8 5 5.6 5 4.9 6 7.9 1 4.8 1 5.9 5 5.	3 10-Oc 3 11-Oc 9 All 9 10-Oc 3 11-Oc 5 All 3 10-Oc 7 11-Oc 4	t 5.65 t 6.25 5.95 t 4.9 t 5.84 5.5 t 5.28	0.46 0.1 0.25 0.15 0.37 0.27
			101095 101095 101095 101095 101195 101195 101195 101195 101195	5.1 5.5 5.5 6.5 6.7 6.7	7 4.6 4.8 5 5.6 5 4.9 6 7.9 1 4.8 1 5.9 5 5.	3 10-Oc 3 11-Oc 9 All 9 10-Oc 3 11-Oc 5 All 3 10-Oc 7 11-Oc 4	t 5.65 t 6.25 5.95 t 4.9 t 5.84 5.5 t 5.28	0.46 0.1 0.25 0.15 0.37 0.27



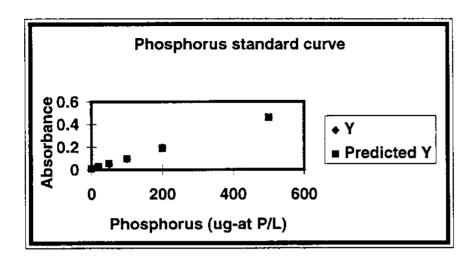
Column1		Column1		СоІи	mn1	Colur	Column1		
Mean	5.65	Mean	6.25	Mean	5.95	Mean	4.9		
Standard E	0.462781	Standard E	0.095743	Standard E	0.246403	Standard E	0.147196		
Median Mode	5.3	Median	6.2	Median	6.1	Median	4.85		
Mode	#N/A	Mode	6.1	Mode	6.1	Mode	#N/A		
		Standard E							
Sample Va	0.856667	Sample Va	0.036667	Sample Va	0.485714	Sample Va	0.086667		
Kurtosis	2.815274	Kurtosis	-1.28926	Kurtosis	-0.97533	Kurtosis	1.5		
Cleaning	4 COEDAG	Charmana	O DEVECO	Champaga	0.10005	Ckournage	0.040001		
Range	2	Range	0.4	Range	2	Range	0.7		
Minimum	5	Minimum	6.1	Minimum	5	Minimum	4.6		
Maximum	7	Maximum	6.5	Maximum		Maximum	5.3		
Sum	22.6	Sum	25	Sum	47.6	Sum	19.6		
Count	4	Count	4	Count	8	Count	4		
Confidence	0.907034	Confidence	0.187652	Confidence	0.48294	Confidence	0.288498		
1010surface		1011surface	3	all surf		1010bottom	<u> </u>		
Range Minimum Maximum Sum Count Confidence 1010surface	nn 1	Coluc	no1	Colu	mn1	colur	<u> </u>		
Mean	5.842857	Mean	5.5	Mean	5.275	Mean	5.990909		
Standard E	0.367007	Standard E	0.272697	Standard E	0.265754	Standard E	0.237201		
Median	5.7	Median Mode	5.4	Median	5.05	Median	5.8		
Mode	5.8	Mode	4.8	Mode	#N/A	Mode	6.1		
Standard E	0.971008	Standard E	0.904434	Standard [	0.751665	Standard [	0.786708		
Sample Va	0.942857	Sample Va	0.818	Sample Va	0.565	Sample Va	0.618909		
Mode Standard E Sample Va Kurtosis Skewness Range Minimum Maximum Sum Count	4.64953	Kurtosis	5.275853	Kurtosis	4.918609	Kurtosis	3.281175		
Skewness	1.896467	Skewness	2.023087	Skewness	2.085888	Skewness	1.272626		
Bange	3.1	Range	3.3	Range	2.4	Range	3.1		
Minimum	4.8	Minimum	4.6	Minimum	4.6	Minimum	4.8		
Maximum	79	Maximum	7.9	Maximum	7	Maximum	7.9	· · · · · · · · · · · · · · · · · · ·	
Sum	40.9	Sum	60.5	Sum	42.2	Sum	65.9		
Count	70.0	Count	11	Count	9 9	Count	11	<del></del>	
Confidence	0.710310	Confidence	0.534475	Confidence	0.520867	Confidence	0.464905		
Calve		all bottom t-test 2 sam		-i		OUAIIIU I 19			
Colur	nn i	t-test ∠ sam	ipies assur	uiud	t-test 2-sar	npie assumi	ng unequal	vanances	
<u> </u>		unequal var		1/- : 0		Maniakia d	1/a-i-bia 0		
Mean	5.275			Variable 2		Variable 1			
Standard E				5.842857		5.65	4.9		
Median		Variance		0.942857		0.856667			
Mode	#N/A	Observatio	. <u>4</u>		Observation		4		
		Hypothesiz	0			0.471667	<del></del>		
Sample Va	0.565		7		Hypothesia				
Kurtosis	4.918609		1.073436		df	<u> 6</u>			
Skewness		P(T<=t) on	0.15934		t Stat	1.544396			
Range		t Critical or			<del> </del>	0.086721			
Minimum		P(T<=t) tw				r 1.943181			
Maximum		t Critical tw			<del>-</del>	0.173443			
Sum	42.2	do surf to d	o bott 10/1			2.446914			
Count		·-·			10/10surf	to bot			
Confidence	0.520867								
		all combined							

## Sheet18

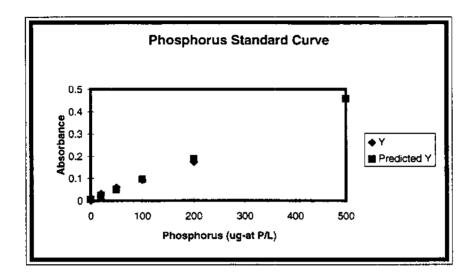
SUMMARY	OUTPUT	Winkler DO	versus Pro	be DO				·
			70.000110			<del>-</del> . ———	<del>-</del>	
Regression	Statistics							
Multiple R	0.826518		<del></del>					
R Square	0.683132					· · · · · · · · · · · · · · · · · · ·		
Adjusted Fi	0.637865							
Standard E	0.693205	i						
Observatio	9						:	
ANOVA			<u> </u>	<del></del>		<del></del> - <del></del> :		
	df	<i>\$\$</i>	MS	F	ignificance i	F ;	!	•
Regressior	1	7.251823	7.251823	15.0912	0.006016		:	· · · · · · · · · · · · · · · · · · ·
Residual	7	3.363732	0.480533					
Total	8	10.61556				!		
			_					
		andard Erri	t Stat				wer 95.00C	
Intercept		1.269903					-2.13151	3.874175
X Variable	0.760592	0.19579	3.884739	0.006016	0.297623	1.223561	0.297623	1.223561
		<u> </u>						
	<del>.</del>						*	
RESIDUAL	OUTPUT						<b>_</b>	
ObservatiorF	Predicted V	Beciduals				·		
1	5.510947	1.489053					·	
2	5.891243	-0.39124						
	5.358828	-0.35883	<del></del>					
4	5.20671	-0.60671	· · ·			·		
5.	5.358828	-0.55883		_ <del>- · · · -</del>				
6	7.944841	-0.04484						
7	6.19548	0.30452		-			<b>_</b>	
<u>-</u> 8	4.522177	0.277823				···		
9	5.510947	-0.11095	<del> </del>		<del></del>			



r <del></del>			······································					
SUMMARY	OUTPUT	Phosphorus	standard o	urve				
				<del>_</del>				
Regression	Statistics							
Multiple R	0.999572					:		
R Square	0.999144						:	
Adjusted R	0.99893							
Standard E	0.005556							
Observatio	6							
ANOVA								
	df	SS	MS	F	ignificance i	F		
Regression	1	0.144195	0.144195	4670.478	2.75E-07			
Residual	4	0.000123	3.09 <b>E-</b> 05					
Total	5	0.144319						
		:			:			
(	Coefficients	andard Err	t Stat	P-value	Lower 95%	Upper 95%	wer 95.00C	per 95.000
Intercept	Coefficients 0.007866	andard Err 0.00297	t Stat 2.648802	<i>P-value</i> 0.057053		<i>Upper 95%</i> 0.016111	wer 95.000 -0.00038	<i>per 95.000</i> 0.016111
Intercept	0.007866	0.00297	2.648802	0.057053	-0.00038	0.016111	-0.00038	0.016111
Intercept	0.007866	0.00297	2.648802	0.057053	-0.00038	0.016111	-0.00038	0.016111
Intercept	0.007866	0.00297	2.648802	0.057053	-0.00038	0.016111	-0.00038	0.016111
Intercept	0.007866 0.000903	0.00297	2.648802	0.057053	-0.00038	0.016111	-0.00038	0.016111
Intercept X Variable	0.007866 0.000903	0.00297	2.648802	0.057053	-0.00038	0.016111	-0.00038	0.016111
Intercept X Variable	0.007866 0.000903	0.00297 1.32E-05	2.648802 68.3409	0.057053 2.75E-07	-0.00038	0.016111	-0.00038	0.016111
Intercept X Variable RESIDUAL	0.007866 0.000903	0.00297 1.32E-05	2.648802 68.3409	0.057053 2.75E-07	-0.00038	0.016111	-0.00038	0.016111
Intercept X Variable RESIDUAL	0.007866 0.000903 OUTPUT	0.00297 1.32E-05	2.648802 68.3409 dard Resid	0.057053 2.75E-07	-0.00038	0.016111	-0.00038	0.016111
Intercept X Variable RESIDUAL Dbservations	0.007866 0.000903 OUTPUT Predicted Y 0.007866	0.00297 1.32E-05 	2.648802 68.3409 dard Resid 0.204138	0.057053 2.75E-07	-0.00038	0.016111	-0.00038	0.016111
Intercept X Variable RESIDUAL Dbservation 1 2	0.007866 0.000903 OUTPUT Predicted Y 0.007866 0.02593	0.00297 1.32E-05 	2.648802 68.3409 dard Resid 0.204138 0.552474	0.057053 2.75E-07	-0.00038	0.016111	-0.00038	0.016111
Intercept X Variable  RESIDUAL  Observation 1 2 3	0.007866 0.000903 OUTPUT Predicted Y 0.007866 0.02593 0.053027	0.00297 1.32E-05 Residuals 3 0.001134 0.00307 -0.00403 -0.00619	2.648802 68.3409 dard Resid 0.204138 0.552474 -0.72474	0.057053 2.75E-07	-0.00038	0.016111	-0.00038	0.016111

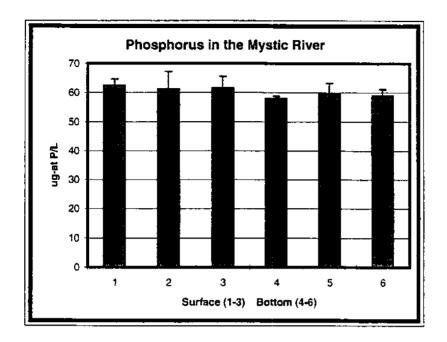


	<u> </u>							
SUMMARY	OUTPUT							
	<b>O</b> 1 11 11							
Regression				·				
Multiple R	0.998887	· <del></del>					<del></del> . <del> </del>	<del> </del>
R Square	0.997776				<u> </u>			
<del></del>	0.99722		<u> </u>				<del>-</del>	
Standard E	0.008957	·						
Observatio	6-				1			-
ANOVA	•		•	· · · · · · · · · · · · · · · · · · ·	:		<u>.</u>	
	df	SS	MS	F	ignificance l	-	_	
Regression	1	0.143961	0.143961	1794.434	1.86E-06			
Residual	4.	0.000321	8.02E-05	:			:	
Total	5	0.144282						
								<u> </u>
	Coefficients	andard Ern	t Stat	P-value	Lower 95%	Upper 95%	wer 95.00C	per 95.000
Intercept	0.005639	0.004787	1.17802	0.304087	-0.00765	0.01893	-0.00765	0.01893
X Variable	0.000902	2.13E-05	42.36077	1.86E-06	0.000843	0.000962	0.000843	0.000962
RESIDUAL	OUTPUT							
ObservatiorF	Predicted V	Residuals 1	dard Resid	uale		<del></del>		
1	0.005639	-0.00564	-0.62957					
2	0.023689	0.007311	0.816261			<del></del>		
3	0.023069	0.007311	0.919569					<del>_</del>
4	0.035764	-0.00189	-0.21078			<del></del>		
l <u> </u>			- <del> </del>	<u>i</u>		<b></b>		
	N 106107	ለ ሲተባተላ						
5	0.186137 0.456884	-0.01214 0.004116	-1.35503 0.459563	i				

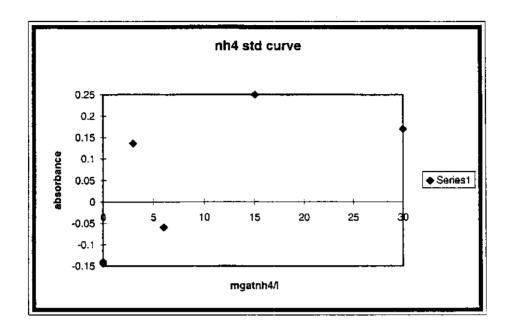


stationid	sample id	date	time	absorb		PO4	PO4surf	PO4bot
						ug-at P/L	ug-at P/L	ug-at P/L
mrma	a1dos	101095		0.069		67.68445	67.68	56.61
mrma	a1dob	101095		0.059 (	3	56.61301	58.83	57.72
mrma	b1dos	101095	i	0.061	S	58.82729	64.36	59.93
mrma	b1dob	101095		0.06	В	57.72015	58.83	57.72
mrma	c1dos	101095	;	0.066	S	64.36301	38.07	70.21
mrma	c1dob	101095	,	0.0621	В	59.93444	81.28	61.34
mrma	b1cos	101095	j.	0.061	S	58.82729	50.26	48.05
mrma	b1cob	101095	)	0.06	B	57.72015	58.02	49.15
mrae	a1dos-ab	101195		0.04	D-S	38.07354	80.18	65.77
mrae	a2dob-ab	101195	i	0.069	D-B	70.20688	50.26	62.45
mrae	a1dob-ab	101195	<u> </u>	0.061	D-B	61.34251	50.26	
mrae	a1dos	101195	i	0.079	D-S	81.28734	81.28	
mrae	a1dob	101195	i	0.051	D-S	50.26204	1	
mrae	a1cos-T	101195	i .	0.058	R-S	58.01837		
mrae	a1cob-T	101195	)	0.049	R-B	48.04595		
mrsh	atcos	101195	;	0.078	R-S	80.17929	-	
mrsh	a1cob	101195	i	0.051	R-S	50.26204		
mrsh	a1dob	101195	i	0.05	D-B	49.154		
mrma	a1dos	101195	i	0.051	D-S	50.26204		
mrma	a1dob	101195	5	0.065	D-B	65.77469		
mrma	a1cos	101195	5	0.079	R-S	81.28734		
mrma	a1cob	101195	5	0.062	R-B	62.45055		
		101095	)	0		0		
	•	101095	5	0.031		20		
		101095	5	0.059		50		
	·	101095	;	0.094		100		
		101095	5	0.174		200		
	•	101095	5	0.461		500		
		101195	5	0.009				
		101195	5	0.029		20	<del>-</del>	
		101195	5	0.049		5C	 	
		101195	5	0.092		100		
		101195	5	0.196	•	200		_
		101195	)	0.458		500	)	

Column1		Colui	mn1	Colu	mn1	Colui	nn1	
Mean	62.425	Mean	61.20125	Mean	61.60917	Mean	57.995	
Standard E	2.183409	Standard E	6.08102	Standard E	4.018908	Standard E	0.696042	
Median	~	Median		Median	58.83	Median	57.72	-
Mode	58.83	Mode	50.26	Mode	50.26	Mode	57.72	-
	4.366818	Standard I	17.19972	Standard E				
Sample Va		Sample Va						
Kurtosis		Kurtosis		Kurtosis			2.219568	
Skewness		Skewness			<del></del>	Skewness		
Range	<del></del>	Range		Range	- · · · ·	Range	3.32	
Minimum		Minimum		Minimum		Minimum	56.61	
Maximum		Maximum		Maximum		Maximum	59.93	
Sum	249.7	<del></del>	489.61		739.31		231.98	
Count		Count		Count		Count	4'	
		Confidence						
							1.304210	
phossurf 10	710	phossurf10	/11	total surf 1	<u> </u>	Pbot 10/10		<del>.</del>
Colur	mn 1		Colu	mn1	Colu	mn 1		
00,01	1077	·		71177		771173	· · · · · · · · · · · · · · · · · ·	
Mean	58.895		Mean	59.495		58.895		
Standard E	2.148756		Standard E	3.671194	Standard E	2.148756		
Median	58.825		Median	61.895	Median	58.825		
Mode	57.72		Mode	#N/A	Mode	57.72		
Standard E	6.794963		Standard E	8.992552	Standard E	6.794963		
Sample Va	46.17152		Sample Va	80.86599	Sample Va	46.17152		
Kurtosis	-0.06958		Kurtosis	-1.60095	Kurtosis	-0.06958		
Skewness	-0.16906	ı	Skewness	-0.45252	Skewness	-0.16906		
Range	22.16		Range	22.16	Range	22.16		
Minimum	48.05		Minimum		Minimum	48.05		
Maximum	70.21		Maximum	70.21	Maximum	70.21		
Sum	588.95		Sum	356.97	Sum	588.95		
Count	10		Count		Count	10		
Confidence	4.211478	<del> </del>	Confidence	7.195397	Confidence	4.211478		
		•··········	Phottom 10		total bottor			
Mean	 se				10101 001101	p.,,oo	···	
62.43	2.18		t-Test: Two	-Sample A	ssumina Ur	equal Varia	nces	
61.2	6.08				Variable 2	<del>`</del>		
61.61	4.01		Mean	61.60917		<del></del>		
58	0.7		Variance	193.8195		<del></del>		
59.5	3.67		Observation					
58.9	2.15		Hypothesia	•				
		,	df	17		· -	· ·	
		·	t Stat	0.595568				
<u> </u>				0.279655				
<u> </u>	<del></del> ·		· ·	1.739606		<del>-</del>		
<u> </u>			P(T<=t) tw					
				2.109819				
I			TORRIGAT W	· Z.103019				



stationid	sample id	date	NH410/10	absorb	nh4	NH4surf	NH4bott	NH410/11
	*	10/10/95	ugatNH4/L	: -	ugatNH4/L	ugatNH4/L	ugatNH4/L	ugatNH4/L
mrma	bidos	S	33.73263	0.246	33.73263	33.73	35.22	
mrma	b1dob	В	35.21818	0.256	35.21818	35.22	31.06	
mrma	c1dos	S	36.70374	0.266	36.70374	36.71	41.46	
mrma	c1dob	В	41.4575	0.298	41.4575	31.5	36.41	
mrma	a1dos	S	35.21818	0.256	35.21818	12.04	22.44	:
mrma	a1dob	В	31.05864	0.228	31.05864	. 12.05	12.05	i
mrma	b1cos	S	31.50431	0.231	31.50431	17.98	10.56	:
mrma	b1cob	В	36.40662	0.264	36.40662	17.98	17.98	1
mrae	1dob-ab	101195		0.2	26.8991	16.51	12.04	:
	2dob-ab	i		0.15	19.47135	15.58	19.47	26.9
<del></del>	1dos-ab			-0.102	. 0	26.47	<del>:</del>	19.47
	1dos			0.1	12.0436	ō		12.0436
•	1dob			0.17	22.44245		•	22.44245
	1cos-T			0.1	12.0436			12.0436
	1cob-T			0.1	12.0436		<u>-</u>	12.0436
mrsh	1cos			0.14				17.9858
	1cob			0.09	10.55805			10.55805
	1dob	•		0.14	17.9858			17.9858
mrma	1cos			0.14	17.9858			17.9858
	1cob			0.13		<del></del>	<u>.</u>	16.50025
	1dos			0.125				15.75748
	1dob			0.1	12.0436			12.0436
calib				-0.14			0	
		•		-0.145	·			
<del></del>	· · · · · · · · · · · · · · · · · · ·		:	-0.145				)
		:		0.17				
	-			0.25				
				-0.06				
	<del>-</del> :			0.136				
AE	В	26.8991	-					
AE	_B	19.47135						····
AE	S	12.0436						
AE	B	22.44245						
AE	S	12.0436				-m·		
AE	В	12.0436						<del></del>
SH	S	17.9858				_		
SH	В	10.55805						
SH	В	17.9858						
MA	S	17.9858						
MA	В	16.50025						
MA	S	15.75748	3		•			



station id	sample id	date inc	3+no2	absorb
mr		ddmmyy ug	at/L	
mrma	aldos	101095	4.79	0.34
mrma	b1dos	101095	4.63	0.33
mrma	¢1dos	101095	4.95	0.35
mrma	a1dob	101095	4.3	0.31
mrma	b1dob	101095	5.11	0.36
mrma	c1dob	101095	2.2	0.18
mrma	b1cos	101095	4.79	0.34
mrma	b1cob	101095	3.82	0.28
mrae	a1dos-ab	101195	27.24	0.95
mrae	aidob-ab	101195	19.97	0.71
mrae	a1dob-ab	101195	15.73	0.27
mrae	a1dos-t	101195	7.2	0.29
mrae	a1dob-t	101195	8.15	0.32
mrae	a1cos-T	101195	8.15	0.32
mrae	a1cos-1	101195	10.88	0.41
mrsh	aicos	101195	8.15	0.32
mrsh	alcob	101195	6.94	0.28
mrsh	a1dob	101195	6.94	0.28
mrma	a1cos	101195	6.64	0.27
	alcob	101195	9.36	0.36
mrma mrma	a1dos	101195	11.18	0.42
ţ	a1dos a1dob	101195	6.94	0.28
mrma	blank	101193	0.43	0.20
	blank	1011	-1.5	0.07
	Didi ik			
	<del></del>			
ugNO3	absorb	<u></u>		
10-00	ot .			
2				
1	0 0.73		•	
	5 0.31	<del></del>		
	2 0.22			
	0 0	<del></del> -		
	<del></del>			
				:
11-00	 :t	1		:
	0! 0.67	,		
1	0 0.47	<del>,</del>		
	5 0.22			
2.				1
	0 0			
			• • • • • • • • • • • • • • • • • • • •	
	<del></del>			<del></del>
<u> </u>				
		<del></del>		
L				<u> </u>

SUMMARY	QUTPUT I	nitrate/nitrite	std curve	10/10		<u> </u>	<u> </u>	
001411411111111			014 04.70				. ,_,	
Regression								
Multiple R	0.993837	<del>-</del>				·		
R Square								<b>.</b>
Adjusted R								
Standard E	0.063352						··	
Observatio	5							
ANOVA	<u> </u>							
ANOVA	alf		MS	F	ianifiaanaa C		<u></u>	
0	<u>df</u>	SS 0.00704		241,1472	ignificance F	<b>.</b> 	:	
Regression		0.96784		241,1472	0.00058		<u>.</u>	
Residual	3.	0.01204	0.004013		- ··· · <del> · · · -</del>			
Total	4	0.97988						
(	Coefficients	andard Err.	t Stat	P-value	Lower 95%l	Jpper 95%i	wer 95.00C	per 95.000
Intercept	0.046285	0.040791	1.134697	0.338965	-0.08353	0.1761	-0.08353	0.1761
X Variable	0.061583	0.003966	15.52892	0.00058	0.048962	0.074204	0.048962	0.074204
					u			
– .–.–								
DEOIDHAI	OUTDUT.		,					
RESIDUAL	OUIPUL	- · ·						
Observation	Predicted Y	Residuals			<u></u>			
1	1.277947	-0.02795						
2	0.662116	0.067884	<del>.</del>					
	0.354201	-0.0442			<del> </del>			
4	0.169451	0.050549			<del>i</del>			-
5	0.046285	-0.04629			<del></del>			
	•							
					+			
SUMMARY	OUTPUT	nitrate/nitrite	e sta curve	10/11	RESIDUAL	OUTBUT		<del></del>
Regression	Statistics	<del>.</del>			RESIDUAL	COIFGI		
<del> </del>					Observation	Prodicted V	Residuals	<del></del>
Multiple R	0.978504					0.715	-0.045	
R Square	0.95747			<del></del>	1 2		0.045	
Adjusted R					3	0.383	0.003	
Standard E	_ ~~~~~~~~	<del></del>			4	0.217 0.134	0.003	
Observatio	5			····	<del>*</del>		-0.051	
ANOVA		·			<u> </u>	0.051	-0.051	
ANOVA	df	SS	MS	F	ignificance			<b></b>
Regression		0.27556	0.27556	67.53922		<u> </u>	· ·	
		0.27336	0.27338	01.00022	. 0.000771		<del></del>	··· <del>···</del>
Residual	3		0.00408		<u> </u>		<del></del>	
Total	4	0.2878			•			
	Coefficients	andard Err	t Stat	P-value	Lower 95%	Upper 95%	wer 95.000	oper 95.00
Intercept	0.051	0.041641	1.224745	0.308068			-0.08152	
X Variable	0.0332		8.218225	0.003771		0.046056		<del></del>
7	0.0002	0.00707	J.L OLLU	J. J		#.0.000	<b>4.5200</b> 11	

