Water quality monitoring in Massachusetts and Cape Cod Bays: October - December 1994

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FINAL

WATER QUALITY MONITORING
IN
MASSACHUSETTS AND CAPE COD BAYS:
OCTOBER – DECEMBER 1994

by

P. Scott Libby
John R. Kelly
Carl S. Albro
John T. Hennessy
Battelle Ocean Sciences

Jeff Turner
David Borkman
University of Massachusetts — Dartmouth

Laura Reed
Robert Vaillancourt
Cynthia Heil
University of Rhode Island

prepared for:

Massachusetts Water Resources Authority
Charlestown Navy Yard
100 First Avenue
Boston, MA 02129
(617) 242-6000

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EXECUTIVE SUMMARY

This report is the last of five periodic water column reports for water quality monitoring conducted in 1994 by Battelle Ocean Sciences for the Massachusetts Water Resources Authority (MWRA) Harbor and Outfall Monitoring Project. The report includes results from three surveys conducted during October, November, and December of 1994. Each of these surveys included sampling at 21 stations in the nearfield area surrounding the future MWRA outfall diffuser about 15 km offshore in western Massachusetts Bay. The October survey was a combined farfield/nearfield survey that included sampling at an additional 25 stations throughout Massachusetts Bay and Cape Cod Bay, including two stations in Boston Harbor and three stations along the northeastern boundary with the Gulf of Maine that were new for 1994 water column monitoring. In this report, data on physical, chemical, and biological measurements at the stations are presented and interrelationships among parameters are examined for standard hydrographic surveys. Unlike past periodic water quality reports for 1992 and 1993, the additional high-resolution studies conducted using towed in-situ instrumentation during 1994 surveys will be discussed in a separate report.

October - December 1994 was a period of transition from summer to winter conditions in Massachusetts and Cape Cod Bays. During this period, the extent of seasonal stratification decreased and the water column became well mixed throughout much of the region. Accompanying this physical transition in the nearfield from October to December were expected chemical and biological changes: surface nutrient concentrations increased, chlorophyll concentrations and phytoplankton counts decreased, and dissolved oxygen (DO) concentrations became more homogenous. At the regional scale (in October), physical, chemical, and biological parameters were relatively constant within and between the Bays. The commonly observed inshore-offshore nitrate and ammonium gradients were exceptionally strong between Boston Harbor and the nearby coastal and nearfield waters. This sharp decrease in nutrients was associated with a "band" of high chlorophyll concentrations.

Several key monitoring parameters — nutrients, DO, chlorophyll, and phytoplankton (at the surface of one station, N10P) — were measured on each of the three surveys. During the farfield survey in October, phytoplankton and zooplankton were measured at 10 "BioProductivity" stations and water column metabolism measurements (production and respiration) were made at stations F23P and N16P. Specific findings for each of the key parameters are summarized below:

- Nutrients — Aside from Boston Harbor and its adjacent Bay receiving waters, nutrient concentrations generally were low in the surface layer above the thermocline. Below the thermocline, nutrients characteristically increased as a function of increasing water depth. There was a significant increase in surface nutrient concentrations over the course of the three surveys. In October, surface layer DIN was depleted throughout most of the nearfield due to high biological demand. Surface phosphate and silicate concentrations were low but elevated in comparison to nitrate and ammonium. Due to an extended period of significant phytoplankton biomass, these nutrient trends were also observed in
November. By December, the onset of winter mixing and the decline in biological activity had led to higher surface nutrient concentrations throughout the nearfield.

- **DO** — As observed during the summer of 1994, DO concentrations in nearfield bottom waters continued to decline into October. There was a distinct partitioning between the surface layer, where DO was usually supersaturated, and the bottom waters, where DO concentrations had achieved values less than 6 mg L\(^{-1}\) along the western and northern nearfield region (<5 mg L\(^{-1}\) at station N10P). By October, however, the range of bottom-water DO concentrations had increased, and the data indicated that communication between the two layers was increasing with the onset of winter mixing. The homogenization of DO values in surface (decreased) and bottom waters (increased) continued throughout the fall/early winter period.

- **Chlorophyll** — In October, a “band” of high chlorophyll concentrations (6 to 8.5 µg L\(^{-1}\)) was observed along the western nearfield region and coastal stations to the north and south of Boston Harbor. This band coincided with the strong DIN gradient observed from the Harbor seaward. Although chlorophyll concentrations were significantly lower in October 1994 compared to October 1993, the period of elevated chlorophyll concentrations extended to the November survey in 1994. By December, chlorophyll concentrations had declined to more seasonal levels (<2 µg L\(^{-1}\)).

- **Phytoplankton** — The phytoplankton community in October was dominated by microflagellates, cryptomonads, and a variety of diatom species. This assemblage was present from early August to November. Due to the consistency of the phytoplankton community, there was a strong correlation between phytoplankton and zooplankton, which suggests a closely matched ecosystem. Temporal trends in Massachusetts Bay at station N10P (a sentinel monitoring station examined during each survey) generally indicated relatively low and decreasing cell counts, some minor fluctuations in species, and low dinoflagellate presence throughout the October-December period.

Zooplankton and primary production data were collected only on the farfield survey in October, and they provided the following specific results:

- **Zooplankton** — Zooplankton counts were lowest near the Harbor (station F23P) and highest in the near-Harbor coastal and nearfield region. The Harbor was dominated by *Acartia tonsa* and polychaete larvae. Excluding the Harbor station, the Bays showed little compositional variability. Bivalve veliger were numerically dominant at most stations, and *Oithona similis* and *Centropages typicus* were the dominant copepods throughout the Bays.

- **Metabolism** — Primary production measurements were made in October at two stations, one at the edge of Boston Harbor (station F23P) and another in the middle of the nearfield (station N16P). Integrated \(^{14}\)C primary production rates averaged 1.31 g C m\(^{-2}\) d\(^{-1}\) \((n=2)\) and 2.18 g C m\(^{-2}\) d\(^{-1}\) \((n=2)\) at stations F23P and N16P, respectively. The differences in integrated production at these stations were a consequence of different turbidity levels,
photic zone depths, and chlorophyll concentrations. In addition to production measurements, dark respiration (by oxygen decline in bottle incubations) was estimated for samples from three depths at stations N20P and F19, and the surface water at station F24. A time-series approach was successful, with samples incubated at near ambient \textit{(in situ)} temperatures for periods of several hours to about 7 days. Slopes of linear regressions of DO concentration over time revealed respiration rates of 0.001 to 0.015 mg O$_2$ L$^{-1}$ h$^{-1}$. There was a steady decrease in respiration rates seaward from station F24 to F19 and with depth at stations N20P and F19.

Finally, a brief discussion emphasizes some of the interannual variations that have been observed for this season from 1992 to 1994. There have been differences in both the timing and intensity of the fall bloom in Massachusetts Bay. The principal constant observed over the three years for the October - December period has been the occurrence of a fall phytoplankton bloom that generally attains higher peak chlorophyll levels than the winter/spring bloom.
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Note to reader: Appendices A-F are bound separately from this technical report. To request the Appendices, contact the MWRA and ask for one of the MWRA Miscellaneous Publications entitled “APPENDICES TO WATER QUALITY MONITORING IN MASSACHUSETTS AND CAPE COD BAYS: OCTOBER - DECEMBER 1994”.

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1.0 INTRODUCTION

This report is the last of five periodic water column reports for water quality monitoring conducted in 1994 for the Massachusetts Water Resources Authority (MWRA) Harbor and Outfall Monitoring Project. The report includes results from three surveys conducted during October, November, and December; each of these surveys included sampling at 21 stations in the nearfield area. The October survey was a combined farfield/nearfield survey that covered 25 additional stations throughout Boston Harbor and Massachusetts and Cape Cod Bays. Data on physical, chemical, and biological measurements at the stations are presented and interrelationships of these measurements are examined.

The structure of this report is as follows:

Section 1. Background information on the water quality surveys conducted in 1994.

Section 2. Field, laboratory, and data analysis methods.

Sections 3-5. Results of surveys, in chronological order (October farfield/nearfield survey, November nearfield survey, December nearfield survey).

Section 6. Discussion of the fall/early winter surveys.

All tables and figures are presented at the end of each section. An extensive set of appendices is bound separately. The appendices provide supporting tables and plots that represent the data stored in the MWRA database.

1.1 Background

The MWRA is implementing a long-term monitoring plan for the future MWRA effluent outfall that will be located in Massachusetts Bay (Figure 1-1). The purpose of the monitoring is to verify compliance with the conditions of the NPDES discharge permit and to assess the potential

To help establish the present conditions with respect to water properties, nutrients, and other important parameters of eutrophication, the MWRA contracted with Battelle Ocean Sciences to conduct baseline water-quality surveys throughout Massachusetts Bay during 1992 to 1994. Results of the 1992 surveys were presented in a series of three periodic reports (Kelly et al., 1992; Kelly et al., 1993a,b), summarized in an annual report (Kelly et al., 1993c), and used to examine nutrient issues related to the offshore outfall (Kelly, 1994). The results of the 1993 surveys were presented in a series of five periodic reports (Kelly et al., 1994a,b,c,d; Libby et al., 1994). The first four periodic reports for 1994 have been submitted (Kelly et al., 1994e,f; 1995a,b).

Serving the MWRA's need for rapid dissemination of data and information, the periodic report series also provides a preliminary synthesis of monitoring results. The technical approach used in 1994 to implement the water quality portion of this monitoring plan is presented in a combined work/quality assurance project plan (CW/QAPP) (Albro et al., 1993) that was developed specifically for water quality monitoring. The CW/QAPP describes the technical activities performed at sea and in the laboratory, as well as the data quality requirements and assessments, project management, and a schedule of activities and deliverables. In addition, individual survey plans were submitted to MWRA for each survey to provide important operational details. The survey reports submitted for the three surveys discussed in this periodic report describe actual survey tracks, samples collected, and other survey details (Albro, 1994; West, 1994; Dragos, 1994). The survey plans and reports should be consulted for pertinent information concerning each of the surveys. Data reports on nutrients, plankton, and pelagic metabolism have been submitted to MWRA for the surveys conducted during October, November, and December 1994; these data are included in the appendices to this report.
1.2 Survey Objectives

The objectives of the water quality surveys are discussed in detail in the MWRA Effluent Outfall Monitoring Plan (MWRA, 1991) and are summarized as follows:

Physical Oceanography

- Obtain high-resolution measurements of water properties throughout Massachusetts Bay.

- Use vertical-profile data at selected sites in Massachusetts and Cape Cod Bays for analysis of large-scale spatial (tens of kilometers) and temporal (seasonal) variability in water properties, and to provide supporting data to help interpret biological and chemical data.

- Use high-resolution, near-synoptic, water-property measurements along transects within the nearfield area for analysis of smaller-scale spatial (kilometers) and temporal (semi-monthly) variability in water properties, and develop a three-dimensional picture of water properties near the future outfall.

Nutrients

- Obtain nutrient measurements in water that is representative of Massachusetts and Cape Cod Bays.

- Use vertical-profile data at selected sites in Massachusetts and Cape Cod Bays for analysis of large-scale spatial (tens of kilometers) and temporal (seasonal) variability in nutrient concentrations, and to provide supporting data to help to interpret biological data.

- Use vertical-profile data along transects of closely spaced stations within the nearfield area for analysis of smaller-scale spatial (kilometers) and temporal (semi-monthly) variability in nutrient concentrations, and develop a three-dimensional understanding of the nutrient field near the future outfall.

Plankton

- Obtain high-quality identification and enumeration of phytoplankton and zooplankton in water that is representative of Massachusetts and Cape Cod Bays.

- Use vertical-profile data at selected sites in Massachusetts and Cape Cod Bays for analysis of large-scale spatial (tens of kilometers) and temporal (seasonal) variability in plankton distribution.
Water Column Respiration and Production

- Using water that is representative of Massachusetts and Cape Cod Bays, obtain a reasonable estimate of the rates of water-column respiration and production as a function of irradiance.

General

- Evaluate the utility of various measurements to detect change or to help explain observed change.

- Provide data to help modify the monitoring program to allow a more efficient means of attaining monitoring objectives.

- Use the data appropriately to describe the water-quality conditions (over space and time) in Massachusetts and Cape Cod Bays.

1.3 Survey Schedule for 1994 Baseline
Water Quality Monitoring Program

Throughout 1993 and 1994, Battelle and its subcontractors, the University of Rhode Island (URI) and the University of Massachusetts at Dartmouth (UMD), have been conducting surveys similar to those initiated in 1992. The schedule of surveys conducted in 1994 is given in Table 1-1. The survey schedule was designed to match the 1992 and 1993 schedules. The surveys discussed in this report were conducted during October 11-15 (W9414), November 4 (W9415), and December 1 (W9416).

1.4 Summary of Accomplishments:
October to December 1994

For the combined farfield/nearfield surveys in October (W9414), in-situ measurements were taken and samples were collected at the stations shown in Figure 1-1. Samples for laboratory analyses were collected to obtain the following types of data:

- Dissolved inorganic nutrients: nitrate, nitrite, ammonium, phosphate, and silicate.
- Chlorophyll $a$ and phaeopigments in extracts of filtered water.
- *In-situ* fluorometric measurements of chlorophyll, optical-beam transmittance (attenuation), light irradiance, salinity, temperature, and dissolved oxygen.
- Total suspended solids and dissolved oxygen in discrete water samples.
- Organic nutrients: dissolved carbon, nitrogen, and phosphorus; particulate carbon and nitrogen.
- Phytoplankton and zooplankton identification and enumeration.
- Rates of water-column production ($^{14}$C) vs. irradiance from shipboard incubations.

For the nearfield surveys (W9415, W9416), one day was dedicated to vertical profiling, including collection of the following data:

- Dissolved inorganic nutrients: nitrate, nitrite, ammonium, phosphate, and silicate.
- *In-situ* fluorometric measurements of chlorophyll, optical-beam transmittance (attenuation), light irradiance, salinity, temperature, and dissolved oxygen.
- Chlorophyll $a$ and phaeopigments in extracts of filtered water, as well as oxygen samples for titration, all to be used to calibrate *in-situ* readings.
- Phytoplankton samples for analysis and archival purposes.

The last day of the October (W9414) farfield/nearfield survey was dedicated to high-resolution "tow-yo" profiling with an *in-situ* sensor array (as described above, minus irradiance). The towfish was used to obtain the profiles by oscillating from near surface to near bottom as the ship progressed at 4 to 7 kt along the tracks from stations F23P to F26, F26 to F28, and F28 to F25.

Samples collected for analysis (rather than archival) have been analyzed, and *in-situ* sensor measurements have been calibrated and processed. Both types of data are presented in this report and all are summarized in accompanying Appendices A through F.
Table 1-1 Schedule of water quality surveys for calendar year 1994. This report provides data from the surveys conducted in October, November, and December.

<table>
<thead>
<tr>
<th>SURVEY</th>
<th>DATES</th>
</tr>
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<tbody>
<tr>
<td>W9401 (Combined Farfield/Nearfield)</td>
<td>February 8 and 15-18</td>
</tr>
<tr>
<td>W9402 (Combined Farfield/Nearfield)</td>
<td>March 1-2 and 5-7</td>
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<tr>
<td>W9403 (Nearfield)</td>
<td>March 22-23</td>
</tr>
<tr>
<td>W9404 (Combined Farfield/Nearfield)</td>
<td>April 5-10</td>
</tr>
<tr>
<td>W9405 (Nearfield)</td>
<td>April 27-28</td>
</tr>
<tr>
<td>W9406 (Nearfield)</td>
<td>May 22</td>
</tr>
<tr>
<td>W9407 (Combined Farfield/Nearfield)</td>
<td>June 21-25</td>
</tr>
<tr>
<td>W9408 (Nearfield)</td>
<td>July 7</td>
</tr>
<tr>
<td>W9409 (Nearfield)</td>
<td>July 27-28</td>
</tr>
<tr>
<td>W9410 (Nearfield)</td>
<td>August 11</td>
</tr>
<tr>
<td>W9411 (Combined Farfield/Nearfield)</td>
<td>August 23-27</td>
</tr>
<tr>
<td>W9412 (Nearfield)</td>
<td>September 7</td>
</tr>
<tr>
<td>W9413 (Nearfield)</td>
<td>September 28-29</td>
</tr>
<tr>
<td>W9414 (Combined Farfield/Nearfield)</td>
<td>October 11-15</td>
</tr>
<tr>
<td>W9415 (Nearfield)</td>
<td>November 4</td>
</tr>
<tr>
<td>W9416 (Nearfield)</td>
<td>December 1</td>
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</tbody>
</table>
2.0 METHODS

Field sampling equipment and procedures, sample handling and custody, sample processing and laboratory analysis, and instrument performance specifications and data quality objectives are discussed in the water quality monitoring CW/QAPP (Albro et al., 1993). The plan is detailed and should be consulted for standard survey methods. In general, only deviations from the CW/QAPP are described in this report. Stations, samples, and other survey-specific information are given in detail in the individual survey reports.

2.1 Field Procedures

2.1.1 Hydrographic and Water Sampling Stations

The combined farfield/nearfield surveys for 1994 represent a continuation of the baseline water quality monitoring conducted in 1992 and 1993 for the MWRA Harbor and Outfall Monitoring Project. However, relative to 1992-1993, there were several sampling design modifications. These were, in part, made in response to discussions at a January 1994 Nutrient Workshop (see Hunt and Steinhauer, 1994). Six new stations, located in Boston Harbor (F30B and F31B) and Massachusetts Bay (F26, F27B, F28, and F29), were added and six previous farfield stations (F04, F08, F09, F11, F20, and F21) were eliminated. In addition, the number of stations where biological measurements are made was increased from 10 stations to 14 stations. For the four new biology stations, samples from 1994 have been archived; thus, 1994 biology data presented in this report are for the same stations described for 1992-1993. Productivity measurements are now being made at only two stations (F23P and N16P). These two stations are being sampled twice, once on each of two separate days during the farfield survey. Productivity is estimated from samples taken at four, rather than the previous two depths; these include all hydrocast bottle depths, except the bottom bottle, and are characterized as surface, mid-surface, chlorophyll maximum (or mid-depth), and mid-bottom. The high-resolution tow-yo sampling frequency was modified. Also, several survey designs were planned, the principal one being a repeated ebb-
flood tide/ Harbor-nearfield transect. The results of high-resolution profiling will be discussed in a separate report covering all 1994 high-resolution surveys.

Table 2-1 summarizes the planned sampling, and indicates the types of measurements and samples taken at nearfield and farfield stations. For a combined farfield/nearfield survey, additional measurements were made at a subset of 14 biology/productivity stations (8 farfield and 6 nearfield); 10 of these stations were termed “BioProductivity” stations during the 1992 and 1993 surveys and are labeled with a “P” (see Figure 1-1). This nomenclature has been retained for these stations even though productivity measurements are only being made at stations F23P and N16P. The four newly designated “Biology” stations are sampled during the farfield surveys, and include station F06 and three new stations that are labeled with a “B” (F27B, F30B, and F31B; see Figure 1-1). The six “P” stations in the nearfield were sampled for a broad suite of parameters as part of the farfield survey and again during hydrographic profiling (dissolved nutrient stations on the vertical sampling day of the nearfield survey).

During the farfield survey, in-situ measurements and dissolved inorganic nutrient samples were obtained at 31 stations plus the 2 repeated productivity stations. At the biology/productivity stations, additional samples were taken for the analyses of dissolved and particulate organic nutrients, total suspended solids, chlorophyll, and plankton identification and enumeration. In addition to this suite of measurements, water column production was estimated during two separate occupations of stations F23P and N16P. At stations F25 and F24, additional samples were collected for the determination of dissolved and particulate organic nutrients.

On the nearfield survey, in-situ measurements and dissolved inorganic nutrient samples were obtained from 21 nearfield stations. Surface phytoplankton samples were taken at the six biology/productivity stations. During both the farfield and nearfield surveys, additional discrete seawater samples were obtained to calibrate the in-situ oxygen and fluorescence sensors. Principal deviations from these planned stations and samples have been reported in the survey report prepared after the completion of each survey.
2.1.2 Productivity Measurements

Productivity measurements differed slightly from those described in the CW/QAPP. At the request of MWRA and due to the preference of the Outfall Monitoring Task Force, only the \(^{14}\)C method was used to estimate primary production; the oxygen light-dark method was not used. At four depths during each occupation of stations F23P and N10P, \(^{14}\)C primary production was measured by exposing samples to a light gradient as described by Albro et al. (1993) for the oxygen method. Fifteen 300-mL BOD bottles were inoculated with 2.5 \(\mu\)Ci of \(^{14}\)C-sodium bicarbonate. Three bottles were incubated in the dark. The remaining 12 bottles were exposed to irradiance levels ranging from about 20 to 2000 \(\mu\)E m\(^{-2}\) sec\(^{-1}\), with several bottles exposed in the range of 200-600 \(\mu\)E m\(^{-2}\) sec\(^{-1}\). Samples for dissolved inorganic carbon (DIC) were taken from the same GO-FLO bottle as samples used for productivity incubations. DIC was analyzed as described in the next section and was used in calculating primary production rates (Section 2.3).

2.1.3 Respiration Measurements

In October, a time-series incubation was used to measure water column respiration rates. This approach had been used previously during the April, June, and August surveys (Kelly et al., 1994f; 1995a,b). Replicate samples were taken in 300-mL BOD bottles. Initial samples were fixed in triplicate, and the remaining bottles were incubated and serially fixed at time periods of up to 7 days. Results are presented in Appendix D. Sampling occurred at three depths (surface, mid-depth, and mid-bottom) at stations N20P and F19, and at the surface of station F24.

2.2 Laboratory Procedures

Table 2-2 summarizes laboratory methods for chemistry and biology samples as detailed in the CW/QAPP. The DIC method used by URI is a “purge-and-trap” method (I.O. Corp., 1984) and was not described in the CW/QAPP. Samples are collected in a 40-mL screw-cap VOC vial with
a septum. The bottle is filled and overflown, the sample is then “killed” with mercuric chloride, and the bottle is sealed. In the laboratory, the vial is placed in a total carbon analyzer where the vial septum is pierced. A sample is then withdrawn, acidified, bubbled with nitrogen (N₂) and the carbon dioxide (CO₂) in the gas stream is trapped on a molecular sieve. The sieve is heated to 200°C, releasing the CO₂ into a new stream of N₂, the carrier gas that transports the CO₂ to an IR detector where the CO₂ content is measured.

The difference between analytical replicates, estimated from samples reported in Kelly et al. (1994a), averaged less than 1% (±σ = 0.47% ± 0.73%, range = 0.08-2.68%, n = 12). The average difference between sample replicates from a GO-FLO bottle was less than 1% (±σ = 0.25% ± 0.31%, range = 0.01-0.81%, n = 6).

2.3 Data Analyses

To calculate production rates, the data for light bottles were first corrected by subtracting uptake measured in dark bottles. Volumetric production rates were then calculated, as described in the CW/QAPP (Albro et al., 1993). The dark-bottle uptake was calculated as the mean of the three dark bottles, excluding samples where a value was an outlier, as determined by statistical testing using the Dixon Criterion (Appendix E).

The Dixon Criterion (Natrella, 1963) evaluates the relative range between values in an ordered set. Thus, if three values (X₁, X₂, and X₃) are arranged from lowest to highest, the criterion for the highest value being an outlier is

\[ X_{-3} = \frac{(X_3 - X_2)}{(X_3 - X_1)} \]

The criterion for the lowest value being an outlier is

\[ X_{-1} = \frac{(X_2 - X_1)}{(X_3 - X_1)} \]
These calculated values are compared to a tabled value. For example, if $X_3$ or $X_I$ exceed 0.941, then there is a 95% chance that the value in question is an outlier.

$X_3$ and $X_I$ are calculated for each set of three dark-bottle replicates. When $X_3$ or $X_I$ exceeds the tabled value of 0.941 for $n=3$, the outlier is rejected and not used in calculations. Appendix D provides results of testing for data collected on survey W9414.

The P-I curve modeling for $^{14}$C differed slightly from that described for oxygen in the CW/QAPP. A sequence of two models was used to fit data from $^{14}$C incubations. Dark-corrected values were normalized to chlorophyll determined for the sample depth being measured. Following this, a sequence of two models was used to fit the data.

The first model fit three parameters, including a photoinhibition term, and followed the Platt et al. (1980) model to predict net production

$$P_B = P_{SB} \left(1 - e^{-a}\right) e^{-b}$$

where

- $P_B$ = production (chlorophyll-normalized)
- $P_{SB}$ = theoretical maximum production (chlorophyll-normalized) without photoinhibition
- $a = \alpha I/P_{SB}$
- $b = \beta I/P_{SB}$
- $\alpha = \text{initial slope of the rise in net production with light increasing from zero irradiance [units of (\mu gC \mu gChl^{-1} \text{ hr}^{-1})/(\mu E \text{ m}^2 \text{ sec}^{-1})], calculated from } I$ (light irradiance level, $\mu E \text{ m}^2 \text{ sec}^{-1}$) and $P_{SB}$.

In the CW/QAPP and in the first periodic report for 1993 (Kelly et al., 1994a), the second model used was a hyperbolic tangent function (Platt and Jassby, 1976). Although Platt et al. (1980) claim equivalence of the two models in terms of $\alpha$ and $P_{max}$, Frenette et al. (1993) have shown that this is not the case. For the second model, following the suggestion of Frenette et al. (1993), the negative exponential formulation given by Webb et al. (1974) was used.

2-5
Here,
\[ P_B = P_{\text{max}} [1 - e (-\alpha I/P_{\text{max}})] \]
\[ P_{\text{max}} \] = light-saturated maximal productivity and
\[ \alpha \] = the initial slope for the curve where productivity is proportional to light intensity (I).

The two models are equivalent where the photoinhibition term (b) is zero. Note that use of this second model marks a return to that used in initial modeling for 1992, minus only a respiration term (cf. Kelly et al., 1992).

The parameters in each model were fit simultaneously by least squares using the NLIN procedure in SAS (1985) for each incubation series that measured paired \( P_B \) and irradiance. Fitting was accomplished where parameters were estimated if, within 50 iterations, the model converged on a suitable simultaneous fit (SAS, 1985). A derivative-free method was used that compares favorably with methods using partial derivatives (Frenette et al., 1993). If the three-parameter model (Platt et al., 1980) fitting did not converge on a fit, the two-parameter model (Webb et al., 1974) was used.

Volumetric production rates, chlorophyll-normalized P-I curves, and model coefficients (Appendix D) were used to calculate integrated water column rates of production. These were expressed as a rate per square meter of surface following the procedure described by Kelly et al. (1993c) which is briefly described in the following text.

Because irradiance varies throughout the day and stations are sampled at different times, the light conditions were standardized. Within a survey, the average incident irradiance \( (I_o) \) measured by the deck cell during a midday (1000 to 1400 h) period was used to standardize conditions. Then, for each station, an extinction coefficient \( (k) \) was determined by regressing \( \ln(I/I_o) \) vs. depth, where \( I_z \) is the irradiance at depth \( z \) and the slope of the resultant line estimates \( k \). The coefficient \( (k) \) was then used with the survey \( I_o \) to generate the standardized light profile using the model \( I_z = I_o e^{-kz} \) and to determine \( Z_{0.5\% I_o} \), the depth where photosynthetically active radiation equals 0.5% \( I_o \). Estimated rates were expressed per square meter of surface and integrated to \( Z_{0.5\% I_o} \).
A 1% to 0.5% isolume is commonly accepted as the level to which net production (in excess of respiration) is achieved by plankton.

Next, for each station and each incubation series ("surface", "intermediate-surface", "intermediate-bottom", or "bottom" sample), the fitted P-I model was combined with the standardized light profile to yield chlorophyll-normalized production rates ($\mu g$ C $\mu g$ Chl$^{-1}$ h$^{-1}$) at 0.5-m intervals to coincide with 0.5-m BIN-averaged chlorophyll values generated from a vertical downcast. To calculate depth-integrated rates, the predicted hourly chlorophyll-normalized rate was then multiplied by the chlorophyll fluorescence at each depth interval from the surface to the $Z_{0.5\%}$ level. The values were then appropriately summed over depth and units were converted to m$^2$ from a volumetric basis.

The above procedure estimated hourly midday rates ($\mu g$ C m$^2$ h$^{-1}$). Conversion to full day-time rates was made by multiplying by a factor of 7 which recognizes that about 55-60% of the production generally occurs during the 4-h period (1000-1400 h) when the irradiance is highest (Vollenweider, 1966). Final modeled rates provide an estimate of day-time primary production as g C m$^2$ d$^{-1}$.

The same procedure was applied to data for each incubation from the set of four samples incubated at a station, yielding independent estimates of production at each station occupation. For each survey that included productivity measurements, all independent estimates are listed in a table that summarizes P-I modeling results (provided in detail in Appendix D).

Also, for each occupation of each station, an estimate of integrated water column production was calculated based on a composite of the four independent estimates. The composite estimate was calculated by combining model results from incubations, where the results from a given incubation were applied over a depth above and below the incubation sample's collection depth half-way to the next sample's collection depth. Thus, by using different P-I curves to extrapolate over appropriate portions of the water column, a composite production profile (by 0.5-m intervals) was developed. The rates over the composite profile were then appropriately summed.
over depth. Units were converted to m$^2$ from a volumetric basis, and a conversion to full daytime primary production rates (g C m$^2$ d$^{-1}$) was made as described above for the individual incubation depth samples.
Table 2-1. Field samples and measurements [cf. Albro et al., 1993]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Stations</th>
<th>Sample Volume</th>
<th>Sample Containers</th>
<th>Shipboard Processing/Preservation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissolved Inorganic Nutrients</td>
<td>All</td>
<td>60 mL</td>
<td>100 mL Polyethylene bottle</td>
<td>Pass through a filter. Fix with chloroform.</td>
</tr>
<tr>
<td>Dissolved Oxygen</td>
<td>14 Biology/ Productivity and Farfield</td>
<td>300 mL</td>
<td>300 mL Glass BOD</td>
<td>Fix per Oudot et al. (1988). Titrate within 24 hours.</td>
</tr>
<tr>
<td>Dissolved Organic Carbon</td>
<td>14 Biology/ Productivity and F25</td>
<td>50 mL</td>
<td>100 mL amber glass bottle</td>
<td>Pass through a pre-ashed glass fiber filter. Fix with 0.5 mL of phosphoric acid.</td>
</tr>
<tr>
<td>Dissolved Organic Nitrogen</td>
<td>14 Biology/ Productivity and F25</td>
<td>20 mL</td>
<td>50 mL glass digestion tube</td>
<td>Pass through a filter. Digest within 8 hours.</td>
</tr>
<tr>
<td>Dissolved Organic Phosphorus</td>
<td>14 Biology/ Productivity and F25</td>
<td>20 mL</td>
<td>50 mL glass digestion tube</td>
<td>Pass through a filter. Digest within 8 hours.</td>
</tr>
<tr>
<td>Particulate Organic Carbon</td>
<td>14 Biology/ Productivity and F25</td>
<td>50 mL</td>
<td>Whatman GF/F glass fiber filter</td>
<td>Pass through a pre-ashed glass fiber filter. Freeze (-5°C).</td>
</tr>
<tr>
<td>Particulate Organic Nitrogen</td>
<td>14 Biology/ Productivity and F25</td>
<td>50 mL</td>
<td>Whatman GF/F glass fiber filter</td>
<td>Pass through a pre-ashed glass fiber filter. Freeze (-5°C).</td>
</tr>
<tr>
<td>Total Suspended Solids</td>
<td>14 Biology/ Productivity</td>
<td>200 mL</td>
<td>Petri dish</td>
<td>Pass through a filter. Freeze (-5°C)</td>
</tr>
<tr>
<td>Chlorophyll a/Phaeopigments</td>
<td>14 Biology/ Productivity</td>
<td>2 x 10 mL</td>
<td>Whatman GF/F glass fiber filter</td>
<td>Pass through filter. Fix with 1% MgCO_3 solution, wrap in foil, store over desiccant, and refrigerate.</td>
</tr>
<tr>
<td>Phytoplankton (Whole Water)</td>
<td>14 Biology/ Productivity</td>
<td>800 mL</td>
<td>1000 mL glass bottle</td>
<td>Preserve with Utermohl's solution.</td>
</tr>
<tr>
<td>Phytoplankton (Screened Water)</td>
<td>14 Biology/ Productivity</td>
<td>2000 mL</td>
<td>100 mL Polyethylene bottle</td>
<td>Strain through a 20 μm mesh; wash retained organism into a jar. Fix with Utermohl's solution.</td>
</tr>
<tr>
<td>^14C Production</td>
<td>2 Biology/ Productivity</td>
<td>300 mL</td>
<td>300 mL Glass BOD</td>
<td>Inoculate with 2.5 μCi of NA_1^14CO_2 and incubate.</td>
</tr>
<tr>
<td><strong>Following sample is collected with a vertically towed net</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zooplankton</td>
<td>14 Biology/ Productivity</td>
<td>800 mL</td>
<td>1000 mL glass bottle</td>
<td>Wash into jar. Fix with a 5-10% Formalin solution.</td>
</tr>
</tbody>
</table>

The following measurements are collected by the Battelle Ocean Sampling System

<table>
<thead>
<tr>
<th>Parameter</th>
<th>All</th>
<th>Floppy disk</th>
<th>Precision</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductivity</td>
<td></td>
<td></td>
<td>0.01 mS/cm</td>
</tr>
<tr>
<td>Temperature</td>
<td></td>
<td>Floppy disk</td>
<td>0.001 °C</td>
</tr>
<tr>
<td>Pressure</td>
<td></td>
<td>Floppy disk</td>
<td>0.01 decibars</td>
</tr>
<tr>
<td>Dissolved Oxygen</td>
<td></td>
<td>Floppy disk</td>
<td>0.05 mg/L</td>
</tr>
<tr>
<td>Chlorophyll a Fluorescence</td>
<td></td>
<td>Floppy disk</td>
<td>0.01 μg/L</td>
</tr>
<tr>
<td>Transmission</td>
<td></td>
<td>Floppy disk</td>
<td>0.01 m^-1</td>
</tr>
<tr>
<td>In situ Irradiance</td>
<td></td>
<td>Floppy disk</td>
<td>1 μE m^-2 s^-1</td>
</tr>
<tr>
<td>Surface Irradiance</td>
<td></td>
<td>Floppy disk</td>
<td>1 μE m^-2 s^-1</td>
</tr>
<tr>
<td>Bottom Depth</td>
<td></td>
<td>Floppy disk</td>
<td>1 m</td>
</tr>
<tr>
<td>Navigational Position</td>
<td></td>
<td>Floppy disk</td>
<td>0.00017 deg</td>
</tr>
<tr>
<td>Parameter</td>
<td>Units</td>
<td>Method</td>
<td>Reference</td>
</tr>
<tr>
<td>-------------------------</td>
<td>-----------</td>
<td>----------------------------</td>
<td>----------------------------</td>
</tr>
<tr>
<td>Dissolved Ammonia</td>
<td>µM</td>
<td>Technicon II AutoAnalyzer</td>
<td>Lambert and Oviatt (1986)</td>
</tr>
<tr>
<td>Dissolved Nitrate</td>
<td>µM</td>
<td>Technicon II AutoAnalyzer</td>
<td>Lambert and Oviatt (1986)</td>
</tr>
<tr>
<td>Dissolved Nitrite</td>
<td>µM</td>
<td>Technicon II AutoAnalyzer</td>
<td>Lambert and Oviatt (1986)</td>
</tr>
<tr>
<td>Dissolved Phosphate</td>
<td>µM</td>
<td>Technicon II AutoAnalyzer</td>
<td>Lambert and Oviatt (1986)</td>
</tr>
<tr>
<td>Dissolved Silicate</td>
<td>µM</td>
<td>Technicon II AutoAnalyzer</td>
<td>Lambert and Oviatt (1986)</td>
</tr>
<tr>
<td>Dissolved Oxygen</td>
<td>mg L⁻¹</td>
<td>Autotitrator</td>
<td>Oudot et al. (1988)</td>
</tr>
<tr>
<td>Dissolved Organic Carbon</td>
<td>µM</td>
<td>O.I. Model 700 TOC Analyzer</td>
<td>Menzel and Varcaro (1964)</td>
</tr>
<tr>
<td>Dissolved Organic Nitrogen</td>
<td>µM</td>
<td>Technicon II AutoAnalyzer</td>
<td>Valderrama (1981)</td>
</tr>
<tr>
<td>Dissolved Organic Phosphorus</td>
<td>µM</td>
<td>Technicon II AutoAnalyzer</td>
<td>Valderrama (1981)</td>
</tr>
<tr>
<td>Total Suspended Solids</td>
<td>mg L⁻¹</td>
<td>Cahn Electrobalance</td>
<td>See Section 12.7.7</td>
</tr>
<tr>
<td>Chlorophyll a/Phaeopigments</td>
<td>µg L⁻¹</td>
<td>Model 111 Turner Fluorometer</td>
<td>Lorenzen (1966)</td>
</tr>
<tr>
<td>Phytoplankton (Whole Water)</td>
<td>Cells L⁻¹</td>
<td>Sedgwick-Rafter counting chambers</td>
<td>Turner et al. (1989)</td>
</tr>
<tr>
<td>Phytoplankton (Screened Water)</td>
<td>Cells L⁻¹</td>
<td>Sedgwick-Rafter counting chambers</td>
<td>Turner et al. (1989)</td>
</tr>
<tr>
<td>¹⁴C Production</td>
<td>¹⁴C hr⁻¹</td>
<td>Liquid Scintillation Counter (Beckman LS-3801)</td>
<td>Strickland and Parsons (1972)</td>
</tr>
<tr>
<td>Zooplankton</td>
<td>Cells L⁻¹</td>
<td>Dissecting Microscope</td>
<td>Turner et al. (1989)</td>
</tr>
</tbody>
</table>

See Section 20 of Albro et al., 1993 for literature references.
3.0 RESULTS OF OCTOBER 1994
COMBINED FARFIELD/NEARFIELD SURVEY (W9414)

3.1 Farfield Survey

3.1.1 Horizontal Distribution of Surface Water Properties

Surface temperatures were between 13.1 and 15.0°C in the study area in October 1994 (Figure 3-1). The coolest temperatures were observed along the north shore. Boston Harbor, northern Massachusetts Bay, and offshore stations exhibited temperatures < 14°C. To the south, much of the surface water was > 14.5°C and this warmer water extended into Cape Cod Bay.

Surface salinity (Figure 3-2) was consistently between 31.8 and 32.1 PSU throughout Massachusetts and Cape Cod Bays. Near Boston Harbor, salinity dropped to < 31.5 PSU. The lowest surface salinity was at the entrance to the Inner Harbor (station F30B) where a value of 30.9 PSU was measured.

Surface water beam attenuation was in the range of 1.1 to 2.1 m\(^{-1}\) (Figure 3-3). Turbidity was high along the coast north and south of Boston Harbor. There was a gradient from high to lower turbidity, extending from the coast seaward. Beam attenuation was lower in the Harbor in comparison to the coastal and western nearfield stations. Surface chlorophyll, as measured by fluorescence (Figure 3-4), was closely correlated with surface turbidity. High concentrations of chlorophyll, > 5 \(\mu g\) L\(^{-1}\), were detected along the coast both north (N01P and F18) and south (N10P, F14, and F15) of the Harbor. Chlorophyll concentrations decreased to < 2.0 \(\mu g\) L\(^{-1}\) towards Boston Harbor and seaward. In Cape Cod Bay, surface chlorophyll ranged from 2.79 to 3.49 \(\mu g\) L\(^{-1}\).

The pattern for surface dissolved inorganic nitrogen (DIN) concentrations showed a very sharp decreasing concentration gradient that radiated seaward from the Harbor (Figure 3-5). At Harbor (F30B, F31B, and F23P) and tidally influenced coastal (F24, F25, and N10P) stations, DIN...
concentrations ranged between 6.9 and 16.4 \( \mu \text{M} \). A sharp decrease in DIN of 6-14 \( \mu \text{M} \) was observed east of these coastal stations, where DIN was usually well below 1 \( \mu \text{M} \). A similar gradient away from the Harbor was observed for nitrate (\( \text{NO}_3^- \); Figure 3-6) and ammonium (\( \text{NH}_4 \)) concentrations, both of which were nearly depleted in the Bays.

Following a pattern similar to DIN, surface water phosphate (\( \text{PO}_4^- \)) concentrations were highest in the Harbor (1.35 \( \mu \text{M} \) at F30B) and decreased to < 1 \( \mu \text{M} \) in the Bays (Figure 3-7). Concentrations for most locations in the Bays were ~ 0.5 \( \mu \text{M} \), with higher concentrations found at some nearshore stations from Boston Harbor southward to western Cape Cod Bay. Silicate (\( \text{SiO}_4 \)) was also enriched in and near Boston Harbor (> 5 \( \mu \text{M} \)) and decreased into western Massachusetts Bay, similar to the gradient noted for DIN (Figure 3-8). Surface concentrations of silicate were somewhat higher in Cape Cod Bay (2.96 to 4.91 \( \mu \text{M} \)) than in Massachusetts Bay (< 3 \( \mu \text{M} \)). Unlike DIN, \( \text{PO}_4^- \) and \( \text{SiO}_4 \) concentrations were not significantly depleted in the surface water throughout Massachusetts and Cape Cod Bays.

### 3.1.2 Water Properties Along Selected Vertical Sections

A set of standard transects for examining vertical sections was established for the 1994 series of water column periodic reports (Kelly et al., 1994e). The Nahant Transect, Boston-Nearfield Transect, Boston-Cohasset Transect, and Marshfield Transect all run from nearshore to deep water in Stellwagen Basin (Figure 3-9). As a roughly parallel series from north to south, these four transects characterize a large portion of Massachusetts Bay. First, sections for temperature, salinity, chlorophyll, and DIN are described for this series of transects. The same parameters are then presented for the fifth section, the Cape Ann-Stellwagen Transect (Figure 3-9). This line of stations prescribes an arc near an imaginary boundary between Massachusetts Bay and Gulf of Maine waters — from Stellwagen Basin in mid-Massachusetts Bay, crossing Stellwagen Bank to station F27B in the deep basin outside the Bay, and terminating in shallower water near Cape Ann. Vertical downcast profile plots for each station are provided in Appendix B. Generally, the profiles show the coastal stations to be well mixed with a seaward increase in stratification. At
the deeper nearfield and offshore stations, the thermocline, halocline, and pycnocline were generally located at \(\sim 25\) m.

The temperature in the upper 20-25 m of the water column was 13-14\(^\circ\)C throughout much of Massachusetts Bay (Figure 3-10a). As noted previously, slightly warmer surface water was observed in southern Massachusetts Bay (>14\(^\circ\)C). At the inshore stations, the water column was well mixed with temperatures >13\(^\circ\)C throughout the water column. The vertical thermal gradient between surface and bottom increased from <1\(^\circ\)C near the coast to >5\(^\circ\)C offshore with the presence of a cool, bottom water mass (<11\(^\circ\)C) below 25 m.

Vertical sections of salinity depict features similar to those discussed above: generally well mixed in the shallow coastal stations, an increase in stratification offshore with a halocline near 25 m, and small vertical gradients (<1 PSU; Figure 3-10b). Salinity (Figure 3-10b) also showed some horizontal spread of fresher water from Boston Harbor (~31 PSU) to the nearfield (~32 PSU). Density layering (\(\sigma_t\), not shown) was similar to that for salinity (see Appendix B).

Chlorophyll concentrations were elevated (>3 \(\mu g\) L\(^{-1}\)) in the upper 20 m of the water column across all transects (Figure 3-10c). A band of high chlorophyll concentration (>4.5 \(\mu g\) L\(^{-1}\)) was observed at the western nearfield and near-Harbor coastal stations. This was noted earlier with the high chlorophyll concentrations and beam attenuations observed in the surface waters at these stations. At the deeper, offshore stations, there was a sharp vertical gradient in chlorophyll associated with the bottom of the joint thermocline-halocline-pycnocline that marked the transition between surface and bottom water layers. Sharp decreases in beam attenuation and dissolved oxygen (as percent saturation) were coincident with the chlorophyll and physical gradients.

The strong horizontal gradient in surface DIN was also observed in the vertical section plots. The relative enrichment of DIN in Boston Harbor was evident throughout the water column (Figure 3-10d) and DIN appeared to be dispersed several kilometers into the Bay, reaching the western side of the nearfield. This gradient is coincident with the band of elevated chlorophyll concentrations and the pattern may have been intensified by biological utilization of the nutrients.
Offshore of this nutrient-enriched zone, the vertical profiles showed strong gradients in DIN. Waters throughout the surface layer to the depth of the thermocline (~25 m) were low in DIN (<2.5 μM) and, in the bottom water layer below the thermocline, DIN concentrations characteristically increased to values >10 μM.

For the Boundary Transect (Figure 3-11), south (station F12, Stellwagen Basin) is positioned to the left, and north (station F26, Cape Ann) is positioned to the right on the sections. Note that station F28 is positioned on Stellwagen Bank, and station F27B is located in the deepwater basin seaward of a 40- to 50-m sill that forms a boundary between the northern tip of Stellwagen Bank and Cape Ann. At each station, the water column was weakly stratified. Temperatures ranged from >13°C in the surface layer to <10°C in the deep bottom waters at stations F27B (outside the Bay) and F12. Slightly cooler temperatures were observed in the surface layer at station F26 (12-13°C). Salinity ranged from 31.7 to 33.2 PSU along the transect, and both the highest and lowest salinities were observed at station F27B. The water column was well mixed at station F28 (on Stellwagen Bank). At all four stations of the transect, chlorophyll concentrations were >1.5 μg L⁻¹ in the surface layer above the pycnocline. The subsurface chlorophyll maximum occurred within a shallow layer between 5 and 20 m. The highest chlorophyll concentrations (>6 μg L⁻¹) were found at station F26. At each station, there was a strong correlation between chlorophyll concentrations, beam attenuation, dissolved oxygen, and the thermocline-halocline- pycnocline. DIN concentrations were highly layered, being nearly depleted at the surface and increasing with depth (>10 μM). Bottom water in Stellwagen Basin (station F12) reached slightly higher DIN concentrations than in the deeper basin outside the Bay (station F27B). Over Stellwagen Bank (station F28), DIN concentrations of all samples were <2.5 μM.

3.1.3 Analysis of Water Quality Characteristics Throughout the Bays

Scatter plots using all in-situ sensor data from vertical profiles are shown in Figures 3-12a and b. As suggested above, the physical, biological, and geochemical characteristics defined some distinct regions of the bays. These regions include the Harbor-coastal waters, the nearfield,
offshore, and boundary area in Massachusetts Bay and Cape Cod Bay (cf. Figure 3-13). Appendix C includes separate scatter plots for groups of stations clustered by region. Vertical gradients of the measured parameters were observed to increase with station depth. The water column at the nearshore stations was generally well mixed. At the deeper nearfield, boundary, and offshore stations, the thermocline, halocline, and pycnocline, along with gradients in biological and geochemical parameters, were consistently between 25 and 35 m (Appendix B). Despite weak horizontal gradients for physical measurements, strong horizontal gradients were observed in geochemical parameters between the Harbor and the western nearfield.

The temperature-salinity plot in Figure 3-12a shows that there was a relatively narrow range in temperature and salinity (~5°C and 2 PSU). There were, however, physical distinctions between Harbor, offshore, and Cape Cod Bay waters. The low salinity water observed in the Harbor clearly sets this region apart from the outlying Bays. As mentioned previously, there was little variation in temperature or salinity in the surface waters of Massachusetts Bay. Inspection of regional T-S scatter plots (Appendix C) revealed broad overlap of data points between adjacent regions and, due to increasing station depth, there was a general increase in salinity and decrease in temperature across the coastal, nearfield, offshore, and boundary regions. Unlike the vertical gradients observed to the north, Cape Cod Bay was warm and moderately saline and exhibited little variability in the T-S scatter plot.

In the Harbor, beam attenuation (turbidity) was relatively constant over a small (~1 PSU) range in salinity. Aside from the Harbor region, there was a general decrease in turbidity with increasing salinity and depth (Figure 3-12a). In very deep, high-salinity waters of Stellwagen Basin, beam attenuation often increased near the bottom of the vertical profile. This near-bottom turbidity feature also exhibited low chlorophyll concentrations (Figure 3-12a bottom) and likely represents a bottom nepheloid layer of suspended sediment. The highest beam attenuation measurements (>2 m²) were observed in the high-chlorophyll waters offshore and the near-bottom water at station F19. In Cape Cod Bay, there was little variation in beam attenuation versus salinity or chlorophyll. Except for the Harbor and Cape Cod Bay, there was a relatively tight correlation between beam attenuation and chlorophyll fluorescence (Figure 3-12a).
Chlorophyll, as measured by fluorescence, ranged from 1 to 8 μg L⁻¹ in the upper 20 m of water (Figure 3-12b). The wide range and relatively high chlorophyll concentrations were evident at stations in each of the regions, except for the Harbor stations where concentrations were <3.5 μg L⁻¹. At most stations, high chlorophyll concentrations were observed over much of the surface layer above the thermocline. The general pattern for dissolved oxygen (DO), as percent saturation, was similar to the vertical distribution of chlorophyll (Figure 3-12b). Excluding Cape Cod Bay, Boston Harbor, and near-Harbor coastal (F24 and F25) and nearfield (N10P) stations, DO was generally 100 to 110% in the surface layer. In Massachusetts Bay, there was a very strong gradient in DO associated with the thermocline. Dissolved oxygen ranged from 60 to 80% in the near-bottom waters throughout the Bay. At the stations excluded above, DO ranged between 80 and 100%, and vertical variability was minimal.

There was a significant difference in DIN concentrations near the Harbor in comparison to stations further offshore and to the south (Figure 3-14a). The highest DIN concentrations were found in the Harbor, with surface concentrations up to 19 μM. High surface concentrations (4-15 μM) were also observed at near-Harbor stations F24, F25, N10P, N11, and N12. Ammonium (NH₄) made up a significant fraction of DIN in these surface waters (Figure 3-14b). Though both Harbor and near-Harbor coastal samples were enriched in NH₄ and NO₃, Harbor and station F24 samples were more enriched in NH₄ than were station F25 and western nearfield samples (Figure 3-14b). This geochemical difference may have resulted from a variety of physical (tidal mixing) or biological (preferential NH₄ uptake) factors. At all other stations, DIN concentrations in the upper 10-15 m were <2 μM and NH₄ was essentially depleted. High DIN, primarily consisting of nitrate (NO₃; Figure 3-14b), was observed below ~20 m at the deeper nearfield, offshore, and boundary stations. DIN concentrations were ≤2 μM at each of the Cape Cod Bay stations.

A wide range of phosphate (PO₄) concentrations (0.2 to 1.6 μM) was measured at each depth and a general increase in concentration was observed with depth (Figure 3-14c). A pattern similar to DIN was evident with concentrations higher at the surface near the Harbor and at depth offshore. This pattern was also observed with silicate (SiO₄) concentrations. Deep water SiO₄
concentrations, however, were nearly double those found near the Harbor (Figure 3-14c).
Surface concentrations of PO$_4$ and SiO$_4$ were low throughout the Bays, but neither was depleted to
the same degree as DIN. Phosphate and silicate concentrations were, on average, higher in Cape
Cod Bay compared to Massachusetts Bay.

The relationship between DIN and PO$_4$ was similar for each region at all depths (Figure 3-15a).
At detectable levels of DIN, the N/P ratio generally followed Redfield proportionality (16N:1P)
and this is supported by a linear regression of DIN vs. PO$_4$ \(\text{slope}=14.4, y\text{-intercept}=-6.0, r^2=0.88\).
The N-species driving the relationship, however, was different in the Harbor (NH$_4$) and in
Massachusetts Bay (NO$_3$). Similar stoichiometries were observed for the nutrient source and sink
in the near-Harbor coastal and nearfield region. This suggests that the regional biological
processes (production and decomposition) provide a biogeochemical linkage between the Harbor
and Stellwagen Basin.

Harbor enrichment in N relative to Si was observed when comparing DIN, but not NO$_3$, to SiO$_4$
(Figure 3-15b). The N/Si ratio was high (~2:1) in the Harbor and low (<1:1) in the deep
waters of Massachusetts Bay. The NO$_3$/Si ratio, however, is similar (<1:1) for both the Harbor
and the Bay. DIN and NO$_3$ were depleted relative to SiO$_4$ in Massachusetts Bay surface waters
and Cape Cod Bay. These data suggest that N (primarily as NH$_4$) uptake is enhanced relative to
Si uptake in the near-Harbor coastal and nearfield region. This is characteristic of a
phytoplankton assemblage that is dominated by non-diatom species (see Section 3.1.4). Overall,
these observations show that examination of different nutrient forms can provide details on the
biogeochemical cycles of different regions of the Bay and the linkages (and/or similar functioning)
across neighboring regions.

Nutrient-salinity plots are useful in distinguishing water mass characteristics and in examining
regional linkages. DIN plotted as a function of salinity (Figure 3-16a) reveals a pattern that is
often observed: a descending arm of DIN concentration with increasing salinity (to ~31.8 PSU),
low or depleted DIN at intermediate salinities (31.8-32.0 PSU), and an ascending arm of DIN
concentration rising with higher salinity above 32 PSU. The descending arm suggests the dilution
of Harbor DIN with low-nutrient Bay water at coastal and western nearfield stations. The intermediate depleted DIN and the ascending arm result from biological, physical, and geochemical stratification. The low DIN at intermediate salinity represents the surface waters throughout the Bays where biological activity has consumed DIN from both horizontal (Harbor) and vertical (bottom waters) sources. The higher nutrient concentrations at higher salinity (and increased depth) are due to a combination of biological decomposition and nutrient regeneration processes.

As mentioned in previous reports, the relative prominence of the ascending or descending arm is indicative of the extent of stratification and an indicator of transitions between seasonal ecosystems. Early in the winter, the descending arm is prominent because there is no stratification or subsequent layering with depth. In contrast, during strong stratification in the summer, when nutrients are rapidly assimilated and the Harbor exports organic nitrogen (Kelly, 1994), the descending arm is not prominent but the ascending arm is highly pronounced. The strong presence of both “arms” indicates that this period is a biogeochemical transition point between summer and winter ecosystems.

In light of this understanding of the normal two-arm DIN-salinity pattern, the differences between NH₄, NO₃, PO₄, and SiO₂ patterns with salinity (Figure 3-16b and 3-16c) in October reveal something about differences in their sources, dynamics, and their potential as water mass diagnostics. For example, the Harbor is a strong source of NH₄, while NH₄ is negligible in both the surface and bottom waters of the Bays. In contrast, the Harbor is a more moderate source of NO₃ and, in Massachusetts Bay, a sharp increase with depth is indicated. The PO₄ relationship with salinity was similar to that for DIN and, thus, the pattern indicated that the Harbor is a fairly strong source of PO₄. In contrast, the SiO₂-salinity pattern was more similar to the NO₃-salinity pattern and indicated that the Harbor was only a modest source of SiO₂ to the Bay. Phosphate and silicate, however, were present in surface waters throughout both Bays.

In general, concentrations of the combined forms of N (DIN + PON) and total N (TN) were high in Boston Harbor (Figure 3-17). Concentrations in Cape Cod Bay were low, but they fell within
the range measured in the nearfield. Because sampling for these forms of N is conducted at the surface and subsurface chlorophyll-maximum depths, the samples do not extend to the deepest waters sampled at a station. Because so few deep-water samples were collected, the DIN+PON and TN versus salinity plots generally display only the characteristic descending arm of the DIN-salinity plot. This arm displays decreasing concentrations as a function of increasing salinity — a feature that generally reflects the mixing of Harbor water with Bay water and indicates the importance of the Harbor as a nutrient source to the surface layer in western Massachusetts Bay. It is interesting to note that this Harbor-to-Bay decrease is driven by DIN. Particulate organic nitrogen is relatively constant between the Harbor and Bays, and dissolved organic nitrogen actually increases from the Harbor (~10 μM) to the nearfield region (~13 μM). Overall, the nutrient-salinity plots support the Harbor-Bay linkages reported above: (1) the Harbor serves as a source of dissolved inorganic nutrients (NH₄ more so than NO₃, PO₄, and SiO₄); (2) the nutrients are diluted by Bay waters and removed biologically in the near-Harbor coastal and nearfield region; and (3) the deep waters of the Bays serve as a sink for these nutrients, though a significant portion may be transported out of the region as dissolved organic material.

3.1.4 Distribution of Chlorophyll and Phytoplankton

At the stations that were sampled, phytoplankton abundance was in the range of 0.8 to 2.5 million cells L⁻¹ (Figure 3-18); this range is indicative of significant phytoplankton populations and fall bloom conditions. There was a very strong linear relationship between phytoplankton counts and chlorophyll concentrations. In general, cell counts and chlorophyll concentrations were low at Harbor station F23P, high at the near-Harbor coastal (F13P) and nearfield (N01P) stations, and intermediate in Cape Cod Bay. The variability observed between these regions was also evident in the data for the six nearfield stations, where phytoplankton counts and chlorophyll concentrations ranged from 1.2 to 2.5 million cells L⁻¹.

A comparison of surface and subsurface (chlorophyll maximum) counts (Figures 3-19, 3-20) indicates that there is not a striking difference between total cell counts as a function of depth. At
both depths and at every station except station N10P, microflagellates were the dominant organisms. Except for stations F23P and N10P, the phytoplankton assemblages were relatively similar throughout the Bays. At the Harbor station F23P, the phytoplankton population was evenly divided between diatoms, microflagellates, and cryptomonads. *Thalassiosira spp.* (solitary) was dominant in both the surface and chlorophyll-maximum sample (Table 3-1a and 3-1b). Cryptomonads, the main constituent of the "others" group in Figures 3-19 and 3-20, were a significant part of the phytoplankton population at all stations. Dinoflagellates were a minor component of the total cell count, but were among the lesser dominants at a number of stations.

Tables 3-1a and 3-1b identify the dominant taxa in both surface and subsurface samples, respectively. A full taxonomic listing of samples is included in Appendix E. As mentioned above, the multi-species groups – microflagellates and cryptomonads – were the dominant organisms in October 1994. The dominant individual species were virtually all diatoms, but only at station N10P did any diatoms reach significant numbers. The primary diatoms found were *Rhizosolenia delicatula, Thalassiosira spp.* (solitary), and *Skeletonema costatum*. Interestingly, *Asterionellopsis glacialis*, the dominant diatom during the enormous fall bloom in October 1993, was conspicuously absent from most of the phytoplankton samples in October 1994. There were no distinct differences in the phytoplankton communities of Cape Cod and Massachusetts Bay.

Screened samples (Tables 3-2a and 3-2b) confirmed that there were relatively small numbers (1s to 1000s of cells L\(^{-1}\)) of dinoflagellates, although more than a dozen species were detected. At most stations, the screened samples were dominated by a variety of *Ceratium* species. At stations N10P and F23P, screened samples were dominated by tintinnids and fewer *Ceratium* were present.

### 3.1.5 Distribution of Zooplankton

Total zooplankton abundance showed geographic differences similar to phytoplankton (Figure 3-21). Zooplankton numbers were lowest at Harbor station F23P, highest at coastal station F13P,
and intermediate at the nearfield and Cape Cod Bay stations. Zooplankton abundance was eight times higher at F13P compared to F23P (80,000 vs. 10,000 individuals m\(^{-3}\)). Bivalve veliger made up more than half of the enumerated zooplankton at F13P and were a significant portion of the population at most stations ("others" in Figure 3-22; Appendix F). At all other stations, copepods and their nauplii were numerically dominant. There was an inshore-offshore decrease in zooplankton abundance from F13P to the eastern nearfield (N04P and N07P). Compositionally, there were few other geographic differences. Throughout both Bays, *Oithona similis*, a small copepod, and *Centropages typicus*, a large copepod, were present in relatively high abundances (2,000 to 27,000 individuals m\(^{-3}\)). At station F23P, the copepod fraction (adult and juveniles, as well as nauplii) was much lower and dominated by *Acartia tonsa*. Polychaete larvae were only present in the Harbor. Additional copepod taxa – *Paracalanus parvus*, *Centropages hamatus*, and *A. tonsa* – were ubiquitous and numerically significant (100s to 1000s).

### 3.1.6 \(^{14}\)C Production Measurements

Appendix D contains many details of the \(^{14}\)C incubation measurements and P-I curve modeling, but results of modeling and calculations for integrated water-column production are summarized in Table 3-3. Note that all calculations used a survey-specific (rather than station- or day-specific) incident irradiance level so that variations in calculated production rates do not result from day-to-day fluctuations in irradiance. Calculations are presented for incubations of four samples from station F23P (at the edge of the Harbor) and station N16P (in the middle of the nearfield); incubations were performed on successive days (October 11 and 12).

The photic zone was deeper at station N16P (21.5-22.5 m) than at station F23P (14.5-15.5 m), a common finding. \(P_{\text{max}}\) or \(P_{\text{sb}}\) values ranged between 5.7 and 17.1 \(\mu\text{g C (\(\mu\text{g Chl})^{-1}\) hr}^{-1}\) and most curves were fit without a photoinhibition term by the negative exponential model (Webb *et al.*, 1974). The range of integrated production rates, based on individual samples, was 1080 to
2406 mg C m\(^{-2}\) d\(^{-1}\). Due to higher biomass, production rates were higher at N16P compared to F23P, even though assimilation rates (\(P_{\text{ass}}\)) were approximately twice as high at F23P.

Using the calculation scheme described previously in Section 2 (methods) to combine results of the four incubations into a single estimate, we calculated rates of 1387 and 1234 mg C m\(^{-2}\) d\(^{-1}\) for station F23P on October 11 and 12, respectively. From the composite profile for station N16P, we calculated rates of 2231 and 2137 mg C m\(^{-2}\) d\(^{-1}\) on October 11 and 12, respectively. There was little temporal variability, but due to photic zone depth differences and spatial variability in chlorophyll, the integrated production rates across stations were ~60% of each other.

3.1.7 Dark Respiration Measurements

Results of dark-bottle-incubation time series at stations F24 (in the tidal mixing region between Boston Harbor and the nearfield), N20P (middle of the nearfield), and F19 (east of the nearfield) are presented in Appendix D. The time series approach was successful over both two- and seven-day periods, and the strongest regressions of DO concentration over time were obtained with the shorter time series. The respiration rates observed in October (0.001 to 0.015 mg O\(_2\) L\(^{-1}\) h\(^{-1}\)) covered the range of values measured in 1994. Unusually low respiration rates were observed in the mid-bottom waters at F19 and N20P (0.001 and 0.002 mg O\(_2\) L\(^{-1}\) h\(^{-1}\)). These samples were taken at depths below the thermocline. In the surface layer, there was a steady inshore-offshore decrease in respiration rates from 0.015 mg O\(_2\) L\(^{-1}\) h\(^{-1}\) at F24 to 0.006 mg O\(_2\) L\(^{-1}\) h\(^{-1}\) at F19. The decrease in surface layer rates was not coincident with a decrease in temperature or chlorophyll. In fact, chlorophyll concentrations were about three times higher at N20P compared to F24. The high rate measured at F24 may have resulted from increased heterotrophic respiration due to higher concentrations of particulate and dissolved organic material (Appendix A).
3.2 Nearfield Survey

3.2.1 Distribution of Water Properties from Vertical Profiling

On October 14, vertical profiling was performed at 21 nearfield stations, repeating 6 BioProductivity stations sampled earlier as part of the farfield survey. Scatter plots for a variety of parameters are shown in Figure 3-23. Patterns and ranges may be compared to all stations in Figure 3-12, as well as to separate regions in Appendix C. Results for the nearfield survey of 21 stations show a strong coherence among stations with respect to T-S characteristics. The range in temperature is narrow (~3°C) and the salinity range is from ~31 to 32.5 PSU. Anomalously low salinities were observed in the surface waters at N05 and N06 (31-31.5 PSU; Appendix B). Otherwise, spatial variations in temperature and salinity were minimal with slightly cooler temperature and lower salinity along the Outer Western Transect (Figures 3-24a and 3-24b). The main trend in the T-S plot showed a decrease in temperature and concomitant increase in salinity with increasing depth below the thermocline-halocline.

Beam attenuation was high at lower salinity (<32 PSU) and decreased with increasing salinity (Figure 3-23a). An increase at high salinity was noted near the bottom of vertical profiles (Appendix B). Beam attenuation and chlorophyll were closely correlated (Figure 3-23a). Chlorophyll concentrations ranged from 2 to 8 µg L⁻¹ in the upper 15-20 m above the thermocline throughout the nearfield (Figure 3-23b). Correspondingly, DO profiles generally showed conditions of supersaturation in the upper 20 m, with percent saturation decreasing below that depth. At the near-Harbor stations N10P, N11, and N12, however, DO was undersaturated throughout the water column (Figure 3-23b). At all stations greater than 25 m deep, DO was greatly undersaturated (60 to 80%) in the near-bottom water.

A band of high chlorophyll concentrations (6 to 8.5 µg L⁻¹), noted during the farfield survey, was observed along the Inner Western Transect (Figure 3-24c). High concentrations were also observed at station N01P. The elevated chlorophyll levels were coincident with a large decrease in DIN concentrations (Figure 3-24-d). The spatial pattern showed high (>4.5 µM) DIN
concentrations at the Harbor-influenced stations (N10P, N11, and N12) and low to depleted DIN throughout the rest of the nearfield region. Similar patterns were observed for PO₄ and SiO₄, although these nutrients were not as depleted as DIN (Appendix A). DIN concentrations increased with depth and were highest (> 10 μM) in deepest water on the eastern side of the nearfield (Figure 3-24d).

3.2.2 Water Quality Variability in the Nearfield

There were corresponding spatial trends in physical, chemical, and biological parameters, expressed both vertically and horizontally, and displayed in Figure 3-24. The most interesting was the correlation between the band of high chlorophyll and the strong horizontal gradient in DIN. This correlation was evident during both the farfield and the nearfield surveys. In previous reports, it was noted that the coastal region adjacent to Boston Harbor (stations F24, F25 and the western nearfield) is an area of intense tidal mixing that reflects the influence of both Harbor and Bay waters. During October 1994, the gradients in physical parameters were small, although Harbor influence of salinity did extend to the nearfield. Sharp gradients, however, were observed in the chemical parameters. DIN concentrations decreased from >15 μM in the Harbor to <1 μM in the western nearfield. Similar, but less extreme, gradients were found for PO₄ and SiO₄. These gradients coincided with an increase in chlorophyll from the Harbor to a band of high chlorophyll concentration in the western nearfield. The ¹⁴C productivity results suggest that the assimilation rates were higher at F23P than at N16P, indicating that there was an actively growing phytoplankton community associated with the nutrient-rich waters flowing out of the Harbor. This suggests that the large change in the nutrient regime is due to biological uptake.

Comparisons of data for nearfield stations, occupied during the farfield survey and again on the nearfield survey, provide some indication of the temporal dynamics in the nearfield. At all stations except N10P, chlorophyll concentrations increased (1-2 μg L⁻¹) in the surface layer and the subsurface chlorophyll maximum generally became more distinct. Station N10P is strongly influenced by tidal dynamics, so it is not necessarily a good indicator for field-wide temporal
trends. The increase in chlorophyll, the general availability of nutrients from Harbor and deep water sources, and the presence of an actively growing phytoplankton assemblage suggest that the peak of the fall bloom may have occurred after the October survey.
Table 3-1a. Abundance of the top five dominant phytoplankton taxa in samples collected near the surface in October 1994.

<table>
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<th>Coastal Stations</th>
<th>Nearfield Stations</th>
<th>Cape Cod Bay Stations</th>
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Units are millions of cells/L and rankings are given in parentheses.
Table 3-1b. Abundance of the top five dominant phytoplankton taxa in samples collected near the chlorophyll maximum in October 1994.

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<tr>
<td>GYRODINUM SPP.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KATODINUM ROTUNDATUM</td>
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</tr>
<tr>
<td>LEPTOCYLINDRUS MINIMUS</td>
<td></td>
<td></td>
<td>0.01 (5)</td>
</tr>
<tr>
<td>CHAETOCEROS SPP. (10-20UM)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GYMNOODINUM SPP.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NITZSCHIA SPP.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LEPTOCYLINDRUS DANIUS</td>
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</tr>
</tbody>
</table>

Units are millions of cells/L and rankings are given in parentheses.
Table 3-2a. Abundance of all identified taxa in screened (20 um) samples collected near the surface in October 1994.

<table>
<thead>
<tr>
<th></th>
<th>Coastal Stations</th>
<th>Nearfield Stations</th>
<th>Cape Cod Bay Stations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>F13P</td>
<td>F23P</td>
<td>N01P</td>
</tr>
<tr>
<td>ALORICATE CILIATES</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>CERATIUM FUSUS</td>
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<td>63</td>
<td>68</td>
</tr>
<tr>
<td>CERATIUM LONGIPES</td>
<td>43</td>
<td>20</td>
<td>28</td>
</tr>
<tr>
<td>CERATIUM MACROCEROS</td>
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<td>80</td>
</tr>
<tr>
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<td>15</td>
<td>3</td>
</tr>
<tr>
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<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DICTYOCHA SPECULUM</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DINOPHYSIS ACUMINATA</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DINOPHYSIS CAUDATA</td>
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<td>23</td>
<td>3</td>
</tr>
<tr>
<td>DINOPHYSIS NORVEGICA</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GYRODINIUM SPP.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PROROCENTRUM MICANS</td>
<td>5</td>
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<td></td>
</tr>
<tr>
<td>PROTOPERIDINIUM DEPRESSUM</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>PROTOPERIDINIUM SPP.</td>
<td>30</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>TINTINNIDS (AGLOMERATE)</td>
<td>10</td>
<td>608</td>
<td>10</td>
</tr>
<tr>
<td>TINTINNIDS (HYALINE)</td>
<td>3</td>
<td>5</td>
<td></td>
</tr>
</tbody>
</table>

Units are cells/L
Table 3-2b. Abundance of all identified taxa in screened (20 um) samples collected near the chlorophyll maximum in October 1994.

<table>
<thead>
<tr>
<th></th>
<th>Coastal Stations</th>
<th>Nearfield Stations</th>
<th>Cape Cod Bay Stations</th>
</tr>
</thead>
<tbody>
<tr>
<td>ALORICATE CILIATES</td>
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<td>5</td>
<td>8</td>
</tr>
<tr>
<td>CERATIUM FUSUS</td>
<td>18</td>
<td>5</td>
<td>100</td>
</tr>
<tr>
<td>CERATIUM LONGIPES</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CERATIUM MACROCEROS</td>
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<tr>
<td>CERATIUM TRIPOS</td>
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<td>DICTYOCHA FIBULA</td>
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</tr>
<tr>
<td>DINOPHYSIS ACUMINATA</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>DINOPHYSIS CAUDATA</td>
<td>8</td>
<td>3</td>
<td>20</td>
</tr>
<tr>
<td>GYMNODINIUM SPP.</td>
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<td></td>
</tr>
<tr>
<td>PROROCENTRUM MICANS</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>PROTOPERIDINIUM DEPRESSUM</td>
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<td></td>
</tr>
<tr>
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<td>18</td>
</tr>
<tr>
<td>TINTINNIDS (HYALINE)</td>
<td>8</td>
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</tr>
</tbody>
</table>

Units are cells/L
Table 3-3. $^{14}$C production (mg C m$^{-2}$ d$^{-1}$) estimated for euphotic layer at BioProductivity stations F23P and N16P in October 1994.

<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>Water depth (m)</td>
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<td>30.0</td>
<td>41.5</td>
<td>39.5</td>
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<tr>
<td>$Z_{0.5%}$ (m)</td>
<td>14.5</td>
<td>15.5</td>
<td>21.5</td>
<td>22.5</td>
</tr>
<tr>
<td>Sample depth (m)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rate (mg C m$^{-2}$d$^{-1}$)</td>
<td>1830 1341 1316 1080</td>
<td>1244 1273 1582 1506</td>
<td>2327 2051 2182 1845</td>
<td>2049 1892 2406 2133</td>
</tr>
<tr>
<td>Model$^1$</td>
<td>W W W W</td>
<td>W P W W</td>
<td>W P W P</td>
<td>W W W W</td>
</tr>
<tr>
<td>$P_{SB}$ or $P_{MAX}^2$</td>
<td>15.03 13.15 13.37 11.23</td>
<td>9.78 17.14 13.80 13.05</td>
<td>6.19 6.83 5.70 7.77</td>
<td>6.55 5.94 7.18 6.12</td>
</tr>
<tr>
<td>$\alpha^3$</td>
<td>0.172 0.082 0.075 0.059</td>
<td>0.095 0.058 0.092 0.089</td>
<td>0.061 0.052 0.060 0.061</td>
<td>0.062 0.060 0.088 0.088</td>
</tr>
<tr>
<td>$\beta^4$</td>
<td></td>
<td>0.005</td>
<td>0.002</td>
<td>0.007</td>
</tr>
</tbody>
</table>

$^1$ P: Platt et al. (1980).
$^2$ $P_{SB}$: Production parameter for Platt et al. model.
$P_{MAX}$: Production parameter for Webb et al. model.
$^3$ Parameter for both models.
$^4$ Parameter for Platt et al. model.
Figure 3-1. Surface temperature (°C) in the study area in October 1994. Data are from the surfacemost sample at all farfield survey stations, including the P stations within the nearfield grid (Appendix A).
Figure 3-2. Surface salinity (PSU) in the study area in October 1994. Data are from the surfacemost sample at all farfield survey stations, including the P stations within the nearfield grid (Appendix A).
Figure 3-3. Surface beam attenuation (m$^2$) in the study area in October 1994. Data are from the surfacemost sample at all farfield survey stations, including the P stations within the nearfield grid (Appendix A).
Figure 3-4. Surface *in situ* fluorescence (as μg Chl L⁻¹) in the study area in October 1994. Data are from the surfacemost sample at all farfield survey stations, including the P stations within the nearfield grid (Appendix A).
Figure 3-5. Surface dissolved inorganic nitrogen (DIN, μM) in the study area in October 1994. Data are from the surfacemost sample at all farfield survey stations, including the P stations within the nearfield grid (Appendix A).
Figure 3-6. Surface nitrate (NO$_3$, $\mu$M) in the study area in October 1994. Data are from the surfacemost sample at all farfield survey stations, including the P stations within the nearfield grid (Appendix A).
Figure 3-7. Surface phosphate (PO₄, μM) in the study area in October 1994. Data are from the surfacemost sample at all farfield survey stations, including the P stations within the nearfield grid (Appendix A).
Figure 3-8. Surface silicate ($SiO_2$, $\mu$M) in the study area in October 1994. Data are from the surfacemost sample at all farfield survey stations, including the P stations within the nearfield grid (Appendix A).
Figure 3-9. Map showing position of five standard transects for which vertical contour plots were produced in Figures 3-10 and 3-11.
Figure 3-10a. Vertical section contours for standard transects (see Figure 3-9) on Survey W9414. The data used to produce the contours are from high-resolution continuous vertical profiles taken from the downcast at each station.
Figure 3-10b. Vertical section contours for standard transects (see Figure 3-9) on Survey W9414. The data used to produce the contours are from high-resolution continuous vertical profiles taken from the downcast at each station.
Figure 3-10c. Vertical section contours for standard transects (see Figure 3-9) on Survey W9414. The data used to produce the contours are from high-resolution continuous vertical profiles taken from the downcast at each station.
Figure 3-10d. Vertical section contours for standard transects (see Figure 3-9) on Survey W9414. The data used to produce the contours are from discrete bottle samples (Appendix A).
Figure 3.11. Vertical section contours for the Cape Ann - Stellwagen transect (see Figure 3.9) on Survey W9414. The data used to produce the contours are from high-resolution continuous vertical profiles taken from the downcast at each station (temperature, salinity, and chlorophyll) and discrete bottle samples (DIN; Appendix A).
Figure 3-12a. Scatter plots of data acquired by *in situ* sensor package during vertical casts at all farfield and nearfield stations occupied in October 1994. Chlorophyll is estimated from *in situ* fluorescence.
Figure 3-12b. Scatter plots of data acquired by \textit{in situ} sensor package during vertical casts at all farfield and nearfield stations occupied in October 1994. Chlorophyll is estimated from \textit{in situ} fluorescence.
Figure 3-13. Map to show station groups designated in Figures 3-14 through 3-21.
Figure 3-14a. DIN vs. depth in October 1994.
Figure 3-14b. NH$_4$ and NO$_3$ vs. depth in October 1994.
Figure 3-14c. PO₄ and SiO₄ vs. depth in October 1994.
Figure 3-15a. Scatter plots of nitrogen forms vs. PO₄ in October 1994. Lines show constant proportions of nitrogen relative to phosphorus.
Figure 3-15b. Scatter plots of nitrogen forms vs. SiO$_4$ in October 1994. Lines show constant proportions of nitrogen relative to silicate.
Figure 3-16a. DIN vs. salinity in October 1994.
Figure 3-16b. NH$_4$ and NO$_3$ vs. salinity in October 1994.
Figure 3-16c. PO$_4$ and SiO$_4$ vs. salinity in October 1994.
Figure 3-17. Nitrogen forms vs. salinity in October 1994. Data are from P stations and special stations (Appendix A). Dissolved inorganic nitrogen = DIN, Particulate organic nitrogen = PON, Total nitrogen (TN) = Total dissolved nitrogen (TDN) + PON.
Figure 3-18. Total phytoplankton abundance vs. chlorophyll (extracted samples) at P stations in October 1994.
Figure 3-19. Total phytoplankton abundance, by taxonomic group, near the surface of P stations in October 1994.

Phytoplankton - October 1994
(Surface)

Millions of Cells per Liter

<table>
<thead>
<tr>
<th>Station</th>
<th>Diatoms</th>
<th>Dinoflag</th>
<th>Microflag</th>
<th>Others</th>
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</thead>
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<td></td>
</tr>
<tr>
<td>F02P</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>F13P</td>
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</tr>
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<td>N01P</td>
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<td></td>
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</tr>
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<tr>
<td>N07P</td>
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</tr>
<tr>
<td>N10P</td>
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<td></td>
<td></td>
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</tr>
<tr>
<td>N16P</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>N20P</td>
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</tr>
</tbody>
</table>
Figure 3-20. Total phytoplankton abundance, by taxonomic group, near the chlorophyll maximum of P stations in October 1994.
Figure 3-21. Zooplankton abundance vs. average chlorophyll concentration (extracted samples; n=4 per station) for October 1994.
Figure 3.22. Zooplankton abundance, by groups, at P stations in October 1994.
Figure 3-23a. Scatter plots of data acquired by in situ sensor package during vertical casts for nearfield survey in October 1994. Chlorophyll is estimated from in situ fluorescence.
Figure 3-23b. Scatter plots of data acquired by *in situ* sensor package during vertical casts for nearfield survey in October 1994. Chlorophyll is estimated from *in situ* fluorescence.
Figure 3-24a. Vertical section contours for nearfield standard transects (view towards Boston Harbor) on Survey W9414. The data used to produce the contours are from high-resolution continuous vertical profiles taken from the downcast at each station during the nearfield sampling day.
Figure 3-24b. Vertical section contours for nearfield standard transects (view towards Boston Harbor) on Survey W9414. The data used to produce the contours are from high-resolution continuous vertical profiles taken from the downcast at each station during the nearfield sampling day.
Figure 3-24c. Vertical section contours for nearfield standard transects (view towards Boston Harbor) on Survey W9414. The data used to produce the contours are from high-resolution continuous vertical profiles taken from the downcast at each station during the nearfield sampling day.
Figure 3-24d. Vertical section contours for nearfield standard transects (view towards Boston Harbor) on Survey W9414. The data used to produce the contours are from discrete bottle samples taken at each station during the nearfield sampling day (Appendix A).
4.0 RESULTS OF NOVEMBER 1994 NEARFIELD SURVEY (W9415)

4.1 Distribution of Water Properties from Vertical Profiles

Vertical profiles were obtained at all 21 nearfield stations on November 4 (Appendix B). Scatter plots of the \textit{in-situ} sensor data are presented in Figure 4-1. The temperature range for the nearfield in November (11-12.5°C) had decreased as well as narrowed slightly from the range observed in October (cf. Figure 4-1a and Figure 3-23a) and the salinity increased, ranging from 32 to 33 PSU. The T-S pattern coherence among station profiles that had been noted for the October survey was stronger in November. A review of vertical profiles in Appendix B indicates that temperature, salinity, and density were nearly uniform at shallow nearshore stations and that a thermocline was present at \(\sim30\) m at the deeper stations. Thus, even in early winter, conditions from west to east still represented a transition from well-mixed inshore water to more stratified offshore conditions.

Beam attenuation was low and ranged narrowly from 0.8 to 1.6 m\(^{-1}\) (Figure 4-1a). As in October, there was a slight increase in turbidity near the surface (low salinity water) and a near-bottom increase at deeper stations (more saline water). Chlorophyll concentrations were still generally high and were weakly correlated with turbidity (Figure 4-1a). In the upper 20 m, chlorophyll values ranged from 1 to 6 \(\mu\)g L\(^{-1}\) and the subsurface chlorophyll maximum generally occurred at depths of 5 to 10 m (Figure 4-1b). The lowest chlorophyll concentrations were found at the well-mixed nearshore stations (N10P, N11, and N12).

DO, as percent saturation, showed a clear west-to-east increase in the surface layer (Figure 4-1b). Along the Outer Western Transect, DO ranged between 80 and 90% in the upper 20 m, and only became slightly supersaturated (<105%) at the eastern nearfield stations. DO decreased below the thermocline at deeper stations and near-bottom DO was comparable to the low levels observed in October (70 to 90%).
Surface concentrations of dissolved nutrients had increased in the nearfield since the October survey (Figure 4-2). DIN concentrations ranged from 0.3 to 16 μM, and the highest concentrations were observed in the surface waters at stations N10P and N11 (Figure 4-2a). A strong seaward gradient in surface DIN was observed from the near-Harbor stations (10-16 μM) to the eastern nearfield stations (<1 μM). Except for stations along the western transect, NH₄ concentrations were low over the entire water column throughout the nearfield (Figure 4-2b). NO₃ concentrations showed a pattern similar to DIN, with an inshore-offshore surface gradient and an increase with depth at offshore stations. Comparable NO₃ concentrations were found in the near-Harbor surface water and offshore bottom water.

The distribution of phosphate and silicate throughout the water column was similar to DIN. Concentrations of PO₄ ranged from ~0.35 to 1.5 μM and SiO₄ ranged from 1.5 to 11 μM (Figure 4-2c). As with DIN, the highest concentrations of PO₄ were found at station N10P. The highest SiO₄ concentrations, however, were observed in the deep offshore waters.

The DIN-salinity plot (Figure 4-3a) shows both ascending and descending “arms” (see Section 3), indicating a decrease in DIN (NH₄) concentrations as a function of increasing salinity in the well-mixed surface waters and an increase in DIN (NO₃) as a function of increasing salinity at depth. A similar pattern was observed for NH₄ and PO₄ (Figure 4-2b and 4-2c), as the Harbor continued to be a strong source of both nutrients. Except for a small increase in nutrient concentrations in more saline offshore bottom water, NO₃ and SiO₄ show only a weak correlation with salinity. The descending arm for the DIN-, NH₄-, and PO₄-salinity plots was more pronounced than the ascending arm and, as mentioned earlier, this is indicative of an early winter ecosystem. This is supported by the lack of structure in the NO₃- and SiO₄-salinity plots which also suggests that the region is proceeding towards winter conditions.
4.2 Water Quality Variability in the Nearfield

Vertical contours of temperature, salinity, chlorophyll (as measured by fluorescence), and dissolved inorganic N are presented in Figure 4-4. The vertical profile data used to produce the contours were obtained over the course of a day: stations N10P (0730 EST) to N01P (0830 EST), stations N04P (1000 EST) to N07P (1100 EST), stations N09 (1145 EST) to N13 (1315 EST), and N15 (1400 EST) to N17 (1500 EST). The diurnal warming was suggested by higher temperature in a thin surface layer at stations in the middle of the field that were sampled in mid-afternoon (Figure 4-4a). Inshore waters were generally well mixed, while the offshore waters were weakly stratified.

The influence of Harbor waters was evident in the low salinity (<32 PSU) at N10P and lower salinity surface waters that were present along the Outer Western Transect (Figure 4-4b). There was a slight increase (<0.4 PSU) in salinity from west to east. As with temperature, salinity indicated an increase in stratification at the eastern nearfield stations.

Chlorophyll concentrations and distribution were remarkably similar to those observed during the October 1994 nearfield survey. At most stations, subsurface chlorophyll-maximum concentrations were high (>4.5 µg L⁻¹) and were found in the upper 20 m of the water column (Figure 4-4c). Chlorophyll concentrations were lowest along the Outer Western Transect and increased to the east. Elevated chlorophyll concentrations (>1.5 µg L⁻¹) were present in the mixed layer throughout the region.

Strong spatial gradients were observed for DIN (Figure 4-4d). Surface concentrations of DIN ranged from >15 µM in the western nearfield at N10P to <1.0 µM along most of the Outer Eastern Transect. There was a steady seaward decrease in surface DIN. There was also a west-to-east increase in the strength of vertical DIN gradients. As observed for temperature and salinity, the western nearfield was generally well mixed and showed little vertical variation in DIN. At the deeper eastern stations, there was a strong DIN gradient between the mixed layer (<2.5 µM) and the near-bottom waters (>7.5 µM).
Overall, the November data suggest a continued, yet slow, progression towards winter conditions in the nearfield region. The water column had become more uniform and physically well mixed, but there was still evidence of the Harbor influence and offshore stratification. The Harbor continued to be a source of nutrients to the region, and although physical gradients were weak, there were strong inshore-offshore and vertical nutrient gradients. As in October, these chemical gradients were biologically mediated and maintained by a large phytoplankton population, as indicated by the continued presence of high chlorophyll concentrations throughout the nearfield.
Figure 4-1a. Scatter plots of data acquired by *in situ* sensor package during vertical casts for nearfield survey in November 1994. Chlorophyll is estimated from *in situ* fluorescence.
Figure 4-1b. Scatter plots of data acquired by in situ sensor package during vertical casts for nearfield survey in November 1994. Chlorophyll is estimated from in situ fluorescence.
Figure 4-2a. DIN vs. depth in November 1994.
Figure 4-2b. NH₄ and NO₃ vs. depth in November 1994.
Figure 4-2c.  PO$_4$ and SiO$_4$ vs. depth in November 1994.
Figure 4-3a. DIN vs. salinity in November 1994.
November (W9415)

Figure 4-3b. NH$_4$ and NO$_3$ vs. salinity in November 1994.
Figure 4-3c. PO₄ and SiO₄ vs. salinity in November 1994.
Figure 4-4a. Vertical section contours for nearfield standard transects (view towards Boston Harbor) on Survey W9415. The data used to produce the contours are from high-resolution continuous vertical profiles taken from the downcast at each station during the nearfield sampling day.
Figure 4-4b. Vertical section contours for nearfield standard transects (view towards Boston Harbor) on Survey W9415. The data used to produce the contours are from high-resolution continuous vertical profiles taken from the downcast at each station during the nearfield sampling day.
Figure 4-4c. Vertical section contours for nearfield standard transects (view towards Boston Harbor) on Survey W9415. The data used to produce the contours are from high-resolution continuous vertical profiles taken from the downcast at each station during the nearfield sampling day.
Figure 4.4d. Vertical section contours for nearfield standard transects (view towards Boston Harbor) on Survey W9415. The data used to produce the contours are from discrete bottle samples taken at each station during the nearfield sampling day (Appendix A).
5.0 RESULTS OF DECEMBER 1994 NEARFIELD SURVEY (W9416)

5.1 Distribution of Water Properties from Vertical Profiles

Vertical profiles were obtained at all 21 nearfield stations on December 1 (Appendix B). Bottle data and profile plots are provided in Appendix A and B, respectively. Scatter plots of the in-situ sensor data show a strong coherence across stations in T-S signature (Figure 5-1a). Temperatures ranged from 9 to 10°C and salinity ranged from 32.4 to 32.8 PSU. The coolest temperatures were associated with lower salinity at the northwestern corner of the nearfield (N01P), while the warmest temperatures were found in the southeastern corner (N07P and N06). Generally, there was little variation in the T-S vertical profiles and the water column was well mixed throughout the nearfield (Appendix B). Since the previous survey, temperatures had continued to decrease and were 2-3°C cooler than temperatures observed in November.

Beam attenuation was generally low (~1 m⁻¹) and showed no clear relationship to salinity. Turbidity was highest in the bottom water at offshore station N06. Except for station N06, beam attenuation profiles showed little variation with depth and only a slight offshore decrease. Beam attenuation did not correspond well with chlorophyll (Figure 5-1a). Chlorophyll concentrations were lower (≤2 µg L⁻¹) than those observed in November and profiles were similar throughout the nearfield (Figure 5-1b). At most stations, chlorophyll had a subsurface maximum between 5-20 m.

In October, surface water DO was supersaturated at all but the near-Harbor stations and, in November, DO was undersaturated at all but the most eastern stations. By December, DO was undersaturated throughout the nearfield region, and ranged between 90 and 100% (Figure 5-1b). As with the other parameters, there was little vertical variability in DO.

Nutrient concentrations continued to increase relative to the October and November surveys, and were consistently high at all depths sampled (Figure 5-2). Three samples gave anomalously high
concentrations for NH$_4$ (N11 bottom sample) and SiO$_4$ (N11 bottom sample, N07P and N14 surface samples). Because there is no analytical reason to question the data, we suspect that the observed data result from localized deviations and not region-wide trends. These three samples are not included in the discussion, but the data have been presented in the figures.

DIN concentrations were $>4\ \mu$M throughout the nearfield and ranged from 1 to 9 $\mu$M at depth (Figure 5-2a). There was a small decrease in DIN from west to east which resulted from slightly higher NH$_4$ concentrations nearshore. Ammonium concentrations were low ($\leq 2\ \mu$M) over the entire water column (Figure 5-2b). During October and November, NH$_4$ served as a very good indicator of Harbor influence at western nearfield stations. The lower NH$_4$ concentrations in December could have resulted from decreased Harbor flow to the nearfield, lower Harbor NH$_4$ concentrations, or increased mixing/dilution of Harbor and Bay waters. Measurements of coincident physical parameters indicate that the nearfield region was well mixed during this period and suggest that dilution of Harbor waters was the main factor controlling NH$_4$ concentrations.

Nitrate was the main constituent of DIN in December, and concentrations were consistently between 4 and 6 $\mu$M (Figure 5-2b). There was little variability in the vertical profiles or spatial distribution in the region. Similarly, PO$_4$ and SiO$_4$ concentrations showed little spatial variability and were high throughout the nearfield, averaging 0.8 and 6 $\mu$M, respectively (Figure 5-2c).

The trends observed in nutrient-salinity plots in October and November indicated a transition between summer and winter ecosystems in the nearfield region. In December, the nutrient-salinity plots (Figure 5-3) showed no definite patterns or relationships between the parameters and are indicative of winter conditions. On average, DIN concentrations were somewhat lower than they were in November, but there were no depleted or nearly depleted samples in December (Figure 5-3a). Unlike the previous fall surveys, ammonium concentrations were low throughout the region and did not clearly trace Harbor outflow (Figure 5-3b). Nitrate, phosphate, and silicate concentrations were high and variable over the range of salinity, indicating no clear relationship between the parameters.
None of the nutrients exhibited an obvious pattern with salinity, as had been observed in October and November (see Sections 3 and 4). The significance of this lack of a relationship in the nutrient-salinity plots for the nearfield is not entirely clear, but the simplest interpretation of the patterns observed in December is that biological activity was reduced and physical mixing was enhanced. This, of course, is also suggested by the generally low chlorophyll concentrations and the nondescript vertical profiles of physical parameters (Appendix B).

5.2 Water Quality Variability in the Nearfield

Vertical contours of temperature, salinity, chlorophyll (as measured by fluorescence), and dissolved inorganic N are presented in Figure 5-4. There was a temperature gradient across the field, with slightly cooler temperatures at the northern inshore edge of the field (station N01P) and warmer temperatures at the southern offshore edge of the field (stations N07P and N06, Figure 5-4a). In the relatively deep water along the Outer Eastern Transect, temperatures decreased in the bottom water (>40 m). The cooler temperatures were coincident with higher salinity (>32.8 PSU; Figure 5-4b). Except for the thin bottom-water layer, salinity was relatively consistent over the region.

Chlorophyll concentrations were <2.5 μg L⁻¹ and tended to decrease from west to east (Figure 5-4c). DIN was replete throughout the nearfield region. The near-Harbor stations had slightly elevated DIN concentrations, but no strong spatial patterns were evident. Overall, the data indicated that winter conditions (i.e., well-mixed, nutrient-replete, and chlorophyll-poor water column) became well established during the month between the November and December surveys.
Figure 5-1a. Scatter plots of data acquired by *in situ* sensor package during vertical casts for nearfield survey in December 1994. Chlorophyll is estimated from *in situ* fluorescence.
Figure 5-1b. Scatter plots of data acquired by *in situ* sensor package during vertical casts for nearfield survey in December 1994. Chlorophyll is estimated from *in situ* fluorescence.
Figure 5-2a. DIN vs. depth in December 1994.
Figure 5-2b. NH$_4$ and NO$_3$ vs. depth in December 1994.
Figure 5-2c. PO₄ and SiO₄ vs. depth in December 1994.
Figure 5-3a. DIN vs. salinity in December 1994.
Figure 5-3b. NH₄ and NO₃ vs. salinity in December 1994.
Figure 5-3c.  PO$_4$ and SiO$_4$ vs. salinity in December 1994.
Figure 5-4a. Vertical section contours for nearfield standard transects (view towards Boston Harbor) on Survey W9416. The data used to produce the contours are from high-resolution continuous vertical profiles taken from the downcast at each station during the nearfield sampling day.
Figure 5-4b. Vertical section contours for nearfield standard transects (view towards Boston Harbor) on Survey W9416. The data used to produce the contours are from high-resolution continuous vertical profiles taken from the downcast at each station during the nearfield sampling day.
Figure 5-4c. Vertical section contours for nearfield standard transects (view towards Boston Harbor) on Survey W9416. The data used to produce the contours are from high-resolution continuous vertical profiles taken from the downcast at each station during the nearfield sampling day.
Figure 5-4d. Vertical section contours for nearfield standard transects (view towards Boston Harbor) on Survey W9416. The data used to produce the contours are from discrete bottle samples taken at each station during the nearfield sampling day (Appendix A).
6.0 DISCUSSION OF THE FALL/EARLY WINTER PERIOD OF SURVEYS

6.1 Water Properties

6.1.1 Variability at the Regional Scale

During the months covered by this report, the regional scale was surveyed only once in October (see Section 3), so temporal variability on the Bay-wide scale was not assessed within the fall/early winter period. Summary comments here relate to spatial variability.

In general, physical and chemical parameters were relatively consistent and the range of values was small throughout the Bays. The principal differences in temperature and salinity occurred between Boston Harbor and Massachusetts Bay rather than between Massachusetts and Cape Cod Bays. There was a slight increase in temperature from the Harbor and northern Massachusetts Bay to southern Massachusetts and Cape Cod Bays. The physical structure of the water column changed from well mixed in the Harbor and nearshore to moderately stratified offshore in the Bays. At the offshore stations, a consistent thermocline, halocline, and pycnocline was observed at ~25 m.

The most striking differences were observed in nutrient measurements between the nutrient-rich Harbor and tidally influenced stations, and the nutrient-poor nearfield region. The large nutrient gradients coincided with a band of high chlorophyll concentrations across the western nearfield. Low nutrient and high chlorophyll conditions were ubiquitous in the surface layer of both Bays. At offshore stations in Massachusetts Bay, the vertical profiles for nutrients showed strong gradients with concentrations increasing below the thermocline. Shallow inshore and Cape Cod Bay stations were well mixed and lacked this feature.

Two new Harbor stations (F30B and F31B) were included in the 1994 surveys to help clarify Harbor-Bay water quality differences and interactions. In October, Harbor waters were cooler,
fresher, and more enriched in nutrients than the Bays. As noted in August 1994 (Kelly et al., 1995b), this is in part attributed to active mixing in the Harbor and mild stratification in the Bays, and the difference in how these two bodies of water respond to the shorter days and cooler air temperatures that signal the start of the fall season. Additionally, there was a difference in the biological activity in the Harbor and Bay waters. Although nutrient concentrations were very high, biologically the Harbor had "shut down", and most of the nutrients were transported to the nearby coastal and nearfield waters where a thriving phytoplankton community was observed. As during other seasonal transitions, the Harbor precedes Massachusetts Bay in shifting from a summer to a winter ecosystem.

The 1994 surveys also included water column monitoring stations across the northeastern boundary between Massachusetts Bay and the Gulf of Maine. Previously, the most seaward stations were in deep offshore water within Stellwagen Basin. During the fall (October) period, only subtle distinctions were noted between boundary waters and their adjacent offshore waters. Physical conditions, as well as water quality, at the new boundary stations were generally within the range observed elsewhere in Massachusetts Bay. In terms of nutrients, the boundary station data were within the range of concentrations observed in surface and deep waters in Stellwagen Basin.

### 6.1.2 Variability in the Nearfield

Over the period of surveys, October to December, the nearfield region underwent a seasonal transition from summer/fall to winter conditions. In October and continuing into November, the nearfield region was generally nutrient depleted, chlorophyll rich, and mildly stratified. By the December survey, the region was nutrient replete, chlorophyll poor, and well mixed. Due to increased mixing and decreased temperatures and productivity, dissolved oxygen saturation in the surface waters decreased steadily from October to December. These changes represent the onset of winter conditions in the nearfield.
Spatial variability was noted during all three nearfield surveys. Generally, the inshore side of the nearfield was well mixed in terms of temperature and salinity, while the offshore waters were moderately stratified. To varying degrees, the Harbor signature of cooler, less-saline, nutrient-rich water was observed along the western edge of the nearfield region. In October and November, strong nutrient gradients were observed across the nearfield from the nutrient-rich western stations to the nutrient-depleted offshore stations (most of the nearfield). On the eastern side of the nearfield, a distinct, colder, and more saline bottom-water layer persisted through October and December, although the thermocline/pycnocline became deeper over the period.

6.1.3 Special Features: Comparison of 1994 with Previous Years

Figure 6-1 shows the surface temperature in the nearfield for all of 1993 and 1994. The thermal progression in summer-fall 1994 in nearfield surface waters was characterized by continual warm temperatures. From August to late September, the average surface temperatures were between 16 and 17°C. The seasonal decline in temperature began by the October 1994 survey (~13°C) but, even into November, the nearfield region continued to be ~3°C warmer compared to 1993. In December, the 1994 surface temperatures were still ~1°C warmer than the previous year. Interannual comparisons of seasonal surface temperature are affected by climatic variations and local weather. It has been suggested (Kelly et al., 1994f) that the mild weather experienced in New England during late winter/early spring of 1994 led to early water column warming and thermocline development. An unseasonably warm fall may have been responsible for the continued presence of warm surface waters into November 1994.

Dissolved oxygen concentrations reached a minimum (<5 mg L⁻¹) in October 1994. As with temperature, the seasonal decline in bottom water DO began earlier, lasted longer, and achieved lower concentrations in 1994 than in previous years. For June 1994, Kelly et al. (1995a) suggested that uncharacteristically low DO in bottom waters in early summer may carry over into late-season measurements. By late September, a number of DO samples were at or below 6 mg L⁻¹ (Kelly et al., 1995b). In October, the DO minima had decreased, but the range of
values was wider, 4.8 to 9.0 mg L\(^{-1}\). The lowest DO values (< 6 mg L\(^{-1}\)) were observed in the bottom waters at N10P, N01P, N02, and N03. The highest DO concentrations (> 8 mg L\(^{-1}\)) were found at depths only a few meters deeper than the 20 m hypothetical bottom water depth. Thus, in October, bottom waters continued to show a decline in DO, but, due to an increase in mixing, communication between the surface and bottom layers increased and the range of DO values also increased. The high DO concentrations overlapped the range observed in October 1993, but the rest of the 1994 values were far lower than in 1993.

6.2 Water Column Nutrient Dynamics

6.2.1 Vertical Structure

Vertical profiles of temperature, salinity, and density are indicators of water column stratification and/or mixing. The profiles demonstrated that stratification intensified with distance from shore and diminished over the period of the three surveys. Nutrient concentrations over depth can also indicate the presence of mixed or stratified conditions. The fall transition from stratified to mixed conditions had begun by October and the nutrient-poor surface layer that is generally typical of Massachusetts Bay during the stratified season was slowly being replaced by nutrient-replete conditions from the Harbor seaward. Except for Harbor and nearby coastal and nearfield stations, nutrient-depth patterns were distinct throughout the Bay in October, with relative, if not absolute, depletion of nutrients in surface layers and increasing concentrations with depth.

6.2.2 Inshore-Offshore Gradients

The data indicated that nutrients followed typically described trends: higher nutrient concentrations (dissolved and total forms) were associated with less-saline inshore waters, and lower nutrient concentrations were characteristic of more-saline offshore surface waters. As discussed in previous sections and above, this period is generally a transition from summer
stratified conditions to winter well-mixed conditions in the nearfield. In October, the Harbor continued to slow biologically (Kelly et al., 1995b), and high concentrations of nutrients were transported to the nearby coastal and nearfield regions. The Harbor influence was expressed in the nutrient-salinity plots as a prominent descending arm. The physical (increased mixing) and biological (decreased productivity) changes resulted in higher nutrient concentrations throughout the nearfield and weaker inshore-offshore nutrient gradients. This progression to winter conditions was expressed in the nutrient-salinity plots examined over the sequence of fall/early winter surveys.

6.2.3 Special Features: Comparison of 1994 with Previous Years

In October 1994, the DIN concentrations were higher and covered a wider range than observed during 1993 (Figure 6-3). A combination of factors, Harbor influence and lack of a strong fall bloom, were responsible for this difference. Although DIN concentrations were elevated at the near-Harbor stations in 1994, concentrations were depleted throughout much of the nearfield. In contrast to 1993, but similar to 1992, PO₄ and SiO₄ remained elevated relative to NH₄ and NO₃. These interannual differences in nutrient regimes may have resulted from the differences in phytoplankton dynamics (or vice versa). The 1992 survey data suggest that the fall bloom occurred before the October survey, and that the breakdown of stratification and the onset of winter mixing was well underway by the survey. In October 1993, there was an enormous Bay-wide diatom bloom of Asterionellopsis glacialis, while in 1994 the fall bloom assemblage was dominated by microflagellates. Unfortunately, we can not adequately address how the nutrient regimes affected the development of the fall bloom, but can only state that the nutrient composition reflects the biological conditions observed in October 1993 and 1994.

As has been the case in previous years (1992 and 1993), a seasonal increase in nutrients was observed in November and December 1994. In November 1994, surface water DIN concentrations were low in the eastern half of the nearfield, resulting in a wide range of
concentrations (0.3 to 16 μM). By December 1994, DIN concentrations were generally >4 μM throughout the nearfield and winter conditions had become established.

6.3 Biology in Relation to Water Properties and Nutrient Dynamics

6.3.1 Phytoplankton-Zooplankton Relationships

Figure 6-4 indicates that there was a strong relationship between phytoplankton and zooplankton counts. Zooplankton numbers were lowest at Harbor station F23P, highest at coastal station F13P, and intermediate at the nearfield and Cape Cod Bay stations. Zooplankton counts at the Harbor-edge station (F23P) have often been relatively low during the 1992-1994 monitoring period, but the reason for a relative impoverishment of zooplankton at station F23P is not known. There was an inshore-offshore decrease in zooplankton abundance from F13P to the eastern nearfield (N04P and N07P) that generally coincided with a decrease in phytoplankton. At station N10P, microflagellates had been dominant since early August (Kelly et al., 1995b). The consistency of the phytoplankton population and the relatively warm temperatures that persisted into October were conducive to a closely matched phytoplankton-zooplankton ecosystem.

6.3.2 Chlorophyll, Phytoplankton Species, and Water Properties

In October 1994, chlorophyll concentrations ranged from 2 to 8 μg L⁻¹ in the upper 20-m surface layer (Figure 6-5) and decreased below this depth. In general, chlorophyll concentrations were low at Harbor stations (F23P, F30B, and F31B), high in a near-Harbor band of coastal (F13P) and nearfield (N01P, N10P, and N20P) stations, and intermediate seaward of this band and in Cape Cod Bay.

In Cape Cod Bay, Massachusetts Bay, and Boston Harbor, the phytoplankton community in October was dominated by microflagellates and cryptomonads (see Section 3). For the fall/early
winter period, phytoplankton time trends in Massachusetts Bay were analyzed for nearfield station N10P. At this station, there was a decrease in overall abundances between October and December, and microflagellates and cryptomonads remained numerically dominant (Table 6-1). By December, there was an increase in the variety of diatoms present at station N10P. During the October survey, station N10P was sampled on two consecutive days and a major shift in dominant taxa from *Thalassiosira* to microflagellates was observed. Ubiquitous in the nearfield and Harbor, *Thalassiosira* may have been dominant in localized areas closer to shore and/or the Harbor. Previous reports have discussed the water quality fluctuations that have been repeatedly observed at N10P that, in part, reflect tidal events and may have been responsible for the change found in phytoplankton assemblages. A major shift was also observed in the screened samples collected at N10P (Table 6-2). On October 13, the screened sample contained high numbers of tintinnids (as did Harbor station F23P), while on October 14, the sample was similar to others taken in the nearfield region. From October to December, there was an increase in the number of cells and species collected in the screened samples. In December, silico-flagellates, *Dictyocha fibula* and *Dictyocha speculum*, were dominant and significant numbers of tintinnids were present at N10P.

As stated above, a "band" of high chlorophyll concentrations was observed at near-Harbor coastal and nearfield stations. This band coincided with a strong DIN gradient that extended from the Harbor to the western nearfield region. A comparison of total nitrogen (TN) and chlorophyll concentrations (Figure 6-6) in October showed no apparent relationship between the two parameters. Low chlorophyll concentrations (~2 µg L⁻¹) were observed in the Harbor (F23P), coastal (F24), eastern nearfield (N07P), and boundary (F27B) regions, and coincided with TN concentrations ranging from 10 to 40 µM.

### 6.3.3 Primary Production and Dark Respiration

The sampling strategy was designed to make comparisons between primary production rates at the Harbor-edge environment (station F23P) and the middle of the nearfield (station N16P), an
environment that is normally less turbid than the Harbor and that is distant enough to be only weakly influenced by the outflow of Harbor water. Using the depth-composite scheme recommended by Kelly et al. (1994e) as the standard for 1994 MWRA monitoring studies, results of incubation of samples from four different depths have been combined to yield an integrated water column rate of $^{14}$C production.

Using the standard scheme, production rates at stations F23P and N16P in October averaged 1311 and 2184 mg C m$^{-2}$ d$^{-1}$, respectively, and the ranges for the two measurements at these stations were narrow. The depth distribution of production was similar for the two stations, and both had subsurface maxima of $\sim 25 \mu$g C L$^{-1}$ h$^{-1}$ on October 11 and $\sim 20 \mu$g C L$^{-1}$ h$^{-1}$ on October 12 (Figure 6-7). Due to lower turbidity, the photic depth at N16P was $\sim 50\%$ deeper than at F23P. The average photic-zone chlorophyll concentration was higher at N16P (3.8 and 3.1 $\mu$g L$^{-1}$ on the two days) compared to F23P (1.8 $\mu$g L$^{-1}$ on both days). The deeper photic zone and higher biomass resulted in higher integrated production rates at N16P compared to F23P, even though assimilation rates ($P_{max}$) were approximately twice as high at F23P.

In Section 3, based on the high assimilation rates measured at station F23P, we suggested that there was an actively growing phytoplankton community associated with the nutrient-rich waters flowing out of the Harbor. The elevated assimilation rates at F23P compared to N16P may have been due to a number of factors: (1) actual in-situ rates at F23P were higher, (2) different phytoplankton assemblages and a correspondingly different reaction to bottle incubation effects (i.e., diatoms vs. microflagellates), and/or (3) during incubation the effect of turbidity is artificially removed. We expect that these high assimilation rates were not occurring in situ at station F23P, but rather that the phytoplankton in these parcels of water had the potential for high growth rates once optimal conditions were present, as in the nearby coastal and nearfield regions ("band" of high chlorophyll).

Dark respiration was measured at stations F24, N20P, and F19. There was a steady inshore-offshore decrease in surface-layer respiration rates from 0.015 mg O$_2$ L$^{-1}$ h$^{-1}$ at F24 to 0.006 mg O$_2$ L$^{-1}$ h$^{-1}$ at F19. Assuming that the average respiration rate for the five surface-layer
measurements (two-day incubations) is applied to the nearfield, respiration was consuming \( \sim 0.009 \text{ mg O}_2 \text{ L}^{-1} \text{ h}^{-1} \). Converted to carbon, assuming a respiratory quotient (RQ=CO_2/O_2 atoms) of 1.0, implies a consumption of 3.4 \( \mu \text{g C L}^{-1} \text{ h}^{-1} \), which is low compared to production rates (Figure 6-7). Unusually low respiration rates were observed in the mid-bottom waters (below the thermocline) at F19 and N20P (0.001 and 0.002 mg O_2 L^{-1} h^{-1}). Following the calculations above, respiration rates in the bottom waters were very low consuming 0.4 to 0.8 \( \mu \text{g C L}^{-1} \text{ h}^{-1} \). In previous reports, these estimates were used to compare daily production and respiration. At station N16P, a reasonable estimate of respiration in the surface layer could be attained by applying the respiration rate (3.4 \( \mu \text{g C L}^{-1} \text{ h}^{-1} \)) over the photic zone depth (22 m). Respiration has been implicitly included in the net production estimate made during the light. Respiration over the 12-h dark period was approximately 900 mg C m^{-2} d^{-1}. Assuming that the average bottom-water rate (0.6 \( \mu \text{g C L}^{-1} \text{ h}^{-1} \)) applies to the bottom 18 m at station N16P that is heterotrophic over the entire day, integrated subthermocline respiration would be 260 mg C m^{-2} d^{-1}. Thus, the data suggest that \(^{14}\text{C} \) production exceeded respiration at station N16P by a factor of two in October 1994. This finding is supported by observed increases in chlorophyll concentrations (1-2 \( \mu \text{g L}^{-1} \)) over the course of the October farfield and nearfield surveys. As stated earlier, production of an actively growing phytoplankton assemblage, increased chlorophyll concentrations, and the general availability of nutrients from Harbor and deep-water sources suggest that the peak of the fall bloom may have occurred after the October survey.

6.3.4 Special Features: Comparison of 1994 with Previous Years

Temporal trends for chlorophyll in nearfield surface waters during 1993 and 1994 are shown in Figure 6-8. Water depths to 20 m are included, a layer that includes the chlorophyll maxima observed in the nearfield from October to December 1994. There are striking differences between the seasonal trends for 1993 and 1994. In October 1993, a spatially extensive diatom bloom of *A. glacialis* was the defining feature of the annual chlorophyll cycle (Libby et al., 1994; Kelly and Turner, 1995). Due to the bloom, chlorophyll concentrations were much higher in
October 1993 (3 to 20 μg L\(^{-1}\)) compared to both October 1994 (1 to 8 μg L\(^{-1}\)) and 1992 (1 to 6 μg L\(^{-1}\)). In addition to similar chlorophyll concentrations, the phytoplankton communities in October 1992 and 1994 were a diverse mix of microflagellates (dominant both years), diatoms, and cryptomonads. Libby et al. (1994) suggested that the fall bloom in 1992 may have been "missed" because of the timing of surveys (more than a month between September and October 1992 surveys). In this report, we have indicated that the peak of the fall bloom may have occurred after the October survey, but the data do not suggest chlorophyll levels comparable to October 1993.

The data for fall/early winter 1994 do indicate elevated chlorophyll concentrations from late September to early November, an extended fall bloom. The mean and maximum chlorophyll concentrations observed in the photic zone during these three surveys were higher than during any previous period in 1994. During each year of baseline monitoring (1992-1994), fall chlorophyll concentrations in the nearfield have been higher than those occurring during the winter-spring bloom (Figure 6-8). The combination of higher biomass, lower temperatures, and the onset of winter mixing suggests that the fall bloom may constitute a greater carbon sink for the region than the winter-spring bloom.

### 6.4 Summary and Recommendations

The interannual comparisons can emphasize the intensity and regularity of seasonal and annual events in Massachusetts Bay. The data for the entire 1994 sampling year will be summarized in more detail in annual reports and these interannual comparisons will be reinforced.

There was relatively little variation in physical, chemical, or biological parameters within or between Massachusetts and Cape Cod Bays in the October to December 1994 period. An inshore-offshore increase in stratification was evident, but even at the deep stations only moderate stratification was noted. There were, however, strong nutrient gradients from Boston Harbor into
western Massachusetts Bay. The nutrient gradients were associated with a band of high 
chlorophyll concentrations and were intensified by biological utilization.

The Harbor and Bays respond to the shorter days and cooler air temperatures in different ways 
and on a different timetable. The Harbor preceded Massachusetts Bay in moving from a summer 
to a winter ecosystem. In the fall/early winter, Harbor waters were cooler, fresher, well mixed, 
and more enriched in nutrients than the waters of the Bays. There was also a difference in the 
biological activity in the Harbor and Bay waters; although nutrient concentrations were very high, 
biologically the Harbor had "shut down". As noted above, Harbor nutrients were transported to 
and utilized in the nearby coastal and nearfield waters. Moreover, the stoichiometry and 
concentrations of these available nutrients from the Harbor may play a role in controlling the 
magnitude, speciation, and development of the fall bloom observed in the Bay.
Table 6-1. Abundance of top five dominant phytoplankton taxa in samples collected near the surface at station N10P in October, November, and December 1994.

<table>
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<tr>
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<th>Oct. 13</th>
<th>Oct. 14</th>
<th>Nov. 4</th>
<th>Dec. 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>MICROFLAGELLATES</td>
<td>0.45 (2)</td>
<td>1.33 (1)</td>
<td>0.58 (1)</td>
<td>0.30 (1)</td>
</tr>
<tr>
<td>CRYPTOMONADS</td>
<td>0.19 (3)</td>
<td>0.56 (2)</td>
<td>0.24 (2)</td>
<td>0.14 (2)</td>
</tr>
<tr>
<td>THALASSIONEMA NITZSCHOIDES</td>
<td></td>
<td>0.02 (5)</td>
<td>0.03 (3)</td>
<td></td>
</tr>
<tr>
<td>THALASSIOSIRA SPP.(SOLITARY)</td>
<td>0.79 (1)</td>
<td>0.14 (3)</td>
<td></td>
<td>0.02 (4)</td>
</tr>
<tr>
<td>KATODINIUM ROTUNDATUM</td>
<td></td>
<td></td>
<td>0.01 (5)</td>
<td></td>
</tr>
<tr>
<td>NAVICULOID DIATOMS</td>
<td></td>
<td></td>
<td>0.01 (5)</td>
<td></td>
</tr>
<tr>
<td>UNID. CENTRALES</td>
<td></td>
<td></td>
<td>0.01 (5)</td>
<td></td>
</tr>
<tr>
<td>CYLINDRITHECA CLOSTERIUM</td>
<td>0.05 (5)</td>
<td>0.05 (3)</td>
<td>0.01 (5)</td>
<td></td>
</tr>
<tr>
<td>RHIZOSOLENIA SETIGERA</td>
<td></td>
<td></td>
<td></td>
<td>0.01 (5)</td>
</tr>
<tr>
<td>SKELETONEMA COSTATUM</td>
<td>0.05 (5)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>UNID. ATHECATE DINOFLAGELLATE</td>
<td>0.05 (5)</td>
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<td></td>
<td></td>
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<tr>
<td>RHIZOSOLENIA DELICATULA</td>
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<td>0.08 (4)</td>
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<td></td>
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<tr>
<td>NITZSCHIA SPP.</td>
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<td>0.05 (5)</td>
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</tr>
<tr>
<td>LEPTOCYLDINRUS DANIUS</td>
<td>0.18 (4)</td>
<td></td>
<td>0.04 (4)</td>
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</tr>
</tbody>
</table>

Units are millions of cells/L and rankings are given in parentheses.
Table 6-2. Abundance of all identified taxa in screened (20 um) samples collected near the surface at station N10P in October, November, and December 1994.

<table>
<thead>
<tr>
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<th>Oct. 13</th>
<th>Oct. 14</th>
<th>Nov. 04</th>
<th>Dec. 01</th>
</tr>
</thead>
<tbody>
<tr>
<td>CERATIUM FUSUS</td>
<td>5</td>
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<td>5</td>
<td>50</td>
</tr>
<tr>
<td>CERATIUM MACROCEROS</td>
<td>5</td>
<td>15</td>
<td>3</td>
<td>23</td>
</tr>
<tr>
<td>CERATIUM TRIPTOS</td>
<td>10</td>
<td>40</td>
<td></td>
<td>73</td>
</tr>
<tr>
<td>DICTYOCHA FIBULA</td>
<td></td>
<td></td>
<td>5</td>
<td>911</td>
</tr>
<tr>
<td>DICTYOCHA SPECULUM</td>
<td></td>
<td></td>
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<td>210</td>
</tr>
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<td>DYNAMIC PHYSIS CAUDATA</td>
<td></td>
<td>8</td>
<td></td>
<td>13</td>
</tr>
<tr>
<td>PROTOPERIDINIUM DEPRESSUM</td>
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<td></td>
<td></td>
<td>15</td>
</tr>
<tr>
<td>PROTOPERIDINIUM SPP.</td>
<td>5</td>
<td>3</td>
<td>5</td>
<td>13</td>
</tr>
<tr>
<td>TINTINNIDS (AGLOMERATE)</td>
<td>343</td>
<td>10</td>
<td>671</td>
<td>443</td>
</tr>
<tr>
<td>TINTINNIDS (HYALINE)</td>
<td></td>
<td></td>
<td></td>
<td>3</td>
</tr>
</tbody>
</table>

Units are cells/L
Figure 6-1. Comparison of the nearfield region in 1994 to the annual cycle of 1993: temperature (°C).
Figure 6-2. Comparison of the nearfield region in 1994 to the annual cycle of 1993: dissolved oxygen (mg L⁻¹).
Figure 6-3. Comparison of the nearfield region in 1994 to the annual cycle of 1993: dissolved inorganic nitrogen (μM).
Figure 6-4. Zooplankton abundance vs. phytoplankton abundance for October 1994.
Figure 6-5. Chlorophyll (extracted) vs. depth for the study area in October 1994.
Figure 6-6 Chlorophyll (extracted) vs. total nitrogen concentrations for the study area in October 1994.
Figure 6-7. $^{14}$C production vs. depth at Bioproductivity stations F23P and N16P in October 1994.
Figure 6-8. Comparison of the nearfield region in 1993 to the annual cycle of 1994: chlorophyll (μg L⁻¹) as estimated from in situ fluorescence.
7.0 REFERENCES


