Water quality monitoring in Massachusetts and Cape Cod Bays: August and September 1994

Massachusetts Water Resources Authority

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WATER QUALITY MONITORING
IN
MASSACHUSETTS AND CAPE COD BAYS:
AUGUST AND SEPTEMBER 1994

by

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EXECUTIVE SUMMARY

This report is the fourth 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 two surveys conducted during August and two surveys conducted during September 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 late August 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 inter-relationships 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.

August through September 1994 was a period during which the normal strong summer stratification of the water column was generally found at most locations in the Bays, and one in which fall mixing of the water column was initiated in shallow coastal areas. Accompanying stratification was a set of expected conditions: low nutrient and chlorophyll concentrations in surface layers, with the presence of a modest subsurface chlorophyll maximum and nutrient concentrations that rose with increasing depth as DO levels decreased. The most striking finding for the period was a depletion of DO in subpycnocline bottom waters of the nearfield to lowest levels yet noted during MWRA baseline monitoring studies. DO concentrations near, and even below, the state minimum standard of 6.0 mg L$^{-1}$ were measured throughout much of the nearfield in late September. At the regional scale, the most pronounced difference in water quality existed between stations in Boston Harbor and the Bays. Boston Harbor was well mixed and, compared to the Bays, was high in turbidity and in nutrients. The commonly observed nutrient concentration gradient from the Harbor to the Bay was acute during this period. However, chlorophyll was not elevated in the Harbor; rather, it was most enriched (3-6 μg L$^{-1}$) in the Bays at a group of stations south of Boston Harbor, between Cohasset and Marshfield. A secondary, more modest regional difference related to plankton communities: those detected at Cape Cod Bay stations were distinct from those at Massachusetts Bay and Harbor-edge stations. Several key monitoring parameters — nutrients, dissolved oxygen (DO), chlorophyll, and phytoplankton (at the surface of one station, N10P) — were measured on each of the four surveys. During the farfield surveys in late August, additional key parameters — phytoplankton, zooplankton, and water column metabolism (production and respiration) — were measured at 10 “BioProductivity” stations. Specific findings for each of the key parameters are summarized below:

- **Nutrients** — In Boston Harbor, DIN concentrations were ≥20 μM and TN concentrations were as high as 30 μM. In contrast, surface waters in the Bay were depleted in DIN (generally <0.5-1.0 μM) and TN ranged between ~5 and 20 μM. Below the thermocline (10-20 m), dissolved nutrients characteristically increased as a function of increasing water depth. For DIN, concentrations at depths >45 m were often 10-14 μM and were thus not as
high as DIN concentrations measured at some locations within Boston Harbor. Dissolved nutrient concentration showed patterns in relation to salinity over time and distributions over space and time that reflected tidal mixing and export from the Harbor to the Bay, as well as the concomitant increase of nutrients and salinity with depth under stratified conditions.

- **DO** — A decline in DO concentrations in bottom waters of the nearfield, which started in June 1994, continued during August and September. The decline in bottom water DO, while surface waters were regularly supersaturated, defines a distinct partitioning of metabolism of upper and lower layers of the water column during stratification. As stated above, DO concentrations, especially in deepwater locations of the nearfield where fall mixing had not yet completely reached the bottom sediments, reached unprecedented (for the MWRA monitoring program) low concentrations.

- **Chlorophyll** — In late August, the most striking chlorophyll enrichment (3-6 μg L⁻¹) was found in the surface layer at a group of Massachusetts Bay stations within an apparent coastal plume south of Boston Harbor. At the time, lower chlorophyll concentrations were found in the Harbor. In general, chlorophyll concentrations were not very high (often 2-3 μg L⁻¹) for most of the period, either at the surface or mid-depth of the Bays. By the end of the period, a broad chlorophyll enrichment appeared in the surface layer throughout much of the nearfield. This increase in average chlorophyll concentrations signals the start of a fall bloom. Although this event (chlorophyll concentrations of ~6 μg L⁻¹) had not yet attained particularly high concentrations, a broad spatial extent was involved and the average concentrations equaled or exceeded those during the winter-spring bloom in 1994.

- **Phytoplankton** — Total phytoplankton counts illustrated some of the same trends observed for chlorophyll. The phytoplankton community in late August was generally dominated by microflagellates, cryptomonads, and, to a lesser extent, a variety of diatom species. Temporal trends at station N10P (a sentinel monitoring station examined every survey) in Massachusetts Bay indicated usual dominance by microflagellates, low dinoflagellate presence, some minor fluctuations in species, and indications of an increasing diatom component by the end of September.

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

- **Zooplankton** — Zooplankton counts were lower in Cape Cod Bay than in Massachusetts Bay, in absolute terms as well as relative to phytoplankton. The reduction in zooplankton was due to a pronounced absence of copepods. We speculate that copepods were being preyed upon by carnivorous zooplankton forms that were present at this time. Reduced copepod abundance was accompanied by a relatively enhanced diatom component at the Cape Cod Bay stations.

- **Metabolism** — Primary production measurements were made in late August at two stations, one at the edge of Boston Harbor (station F23P) and another in the middle of the nearfield (station N16P). Integrated ^14C primary production rates were relatively low and averaged
0.78 g C m$^{-2}$ d$^{-1}$ ($n=2$) and 0.88 g C m$^{-2}$ d$^{-1}$ ($n=2$) at stations F23P and N16P, respectively. Considering variability and uncertainty in these estimates, as discussed, the integrated production rates at these stations were not different. An extended discussion is provided for this case example in which similar integrated production was attained under very different environmental conditions. In addition to production measurements, dark respiration (by oxygen decline in bottle incubations) was estimated for samples from three depths at three stations (F24, N20P, and F19). A time-series approach was successful, with samples incubated at near ambient (in-situ) temperatures for periods of several hours to seven days. Slopes of linear regressions of DO concentration over time revealed low rates of respiration that tended to decrease with depth, reaching bottom-water rates near 0.001 mg O$_2$ L$^{-1}$ h$^{-1}$.

Using this rate, projections of DO decline in bottom waters from early August to late September produced results similar to the observed decline in the nearfield region.

Finally, a brief discussion emphasizes some of the interannual variations that have been observed for this season from 1992 to 1994. As emphasized above, the striking and perhaps defining feature of 1994 to date has been the extent of DO depression in bottom waters.
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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: AUGUST AND SEPTEMBER 1994”.
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1.0 INTRODUCTION

This report is the fourth 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 four surveys conducted during August and September; each of these surveys included sampling at 21 stations in the nearfield area. The late August 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 (early August nearfield survey, late August farfield/nearfield survey, early September nearfield survey, late September nearfield survey).

Section 6. Discussion of the summer 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 environmental impact of effluent discharge into Massachusetts Bay. A detailed description of the monitoring and its rationale is provided in the Effluent Outfall Monitoring Plan (MWRA, 1991).
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). Periodic reports covering surveys from February to July 1994 have been submitted (Kelly et al., 1994e,f; 1995).

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 four surveys discussed in this periodic report describe actual survey tracks, samples collected, and other survey details (Dragos, 1994a,b; Hansen, 1994; West, 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 August and September 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 August 10 (W9410; early), August 23-27 (W9411; late), September 7-8 (W9412; early), and September 28-29 (W9413; late).

1.4 Summary of Accomplishments:
August and September 1994

For the combined farfield/nearfield surveys in late August (W9411), 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 (¹⁴C) vs. irradiance from shipboard incubations.

For the nearfield surveys (W9410, W9412, W9413), 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 late August farfield/nearfield survey (W9411) and a second day of both the September nearfield surveys (W9412, W9413) were 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 4-7 kt along the nearfield tracks between the vertical stations.

Samples collected for analysis (rather than for 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 August and September.

<table>
<thead>
<tr>
<th>SURVEY</th>
<th>DATES</th>
</tr>
</thead>
<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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<td>W9403 (Nearfield)</td>
<td>March 22-23</td>
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<td>W9404 (Combined Farfield/Nearfield)</td>
<td>April 5-10</td>
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<tr>
<td>W9405 (Nearfield)</td>
<td>April 27-28</td>
</tr>
<tr>
<td>W9406 (Nearfield)</td>
<td>May 22</td>
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<tr>
<td>W9407 (Combined Farfield/Nearfield)</td>
<td>June 21-25</td>
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<tr>
<td>W9408 (Nearfield)</td>
<td>July 7</td>
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<tr>
<td>W9409 (Nearfield)</td>
<td>July 27-28</td>
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<tr>
<td>W9410 (Nearfield)</td>
<td>August 11</td>
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<tr>
<td>W9411 (Combined Farfield/Nearfield)</td>
<td>August 23-27</td>
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<tr>
<td>W9412 (Nearfield)</td>
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<td>W9413 (Nearfield)</td>
<td>September 28-29</td>
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<tr>
<td>W9414 (Combined Farfield/Nearfield)</td>
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<tr>
<td>W9415 (Nearfield)</td>
<td>November 2-3</td>
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<tr>
<td>W9416 (Nearfield)</td>
<td>November 30 - December 1</td>
</tr>
</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, several sampling design modifications were made, in part, 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 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 vertical profiling day of 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 the methods 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 $\sim$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 late August, a time-series incubation approach to measure water column respiration rates, used first in April 1994 and again in June 1994 (Kelly et al., 1994a; 1995), was continued. At the same time initial samples were taken a number of 300-mL BOD bottles were also filled. These bottles were then incubated at constant temperature near in-situ conditions, with replicate bottles serially fixed at set time periods, normally up to 48 hours but up to 7 days for deepest water. 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 mercury 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% (̄x ± 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% (̄x ± 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 D).

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

\[ X_\text{L} = \frac{(X_2 - X_i)}{(X_3 - X_i)} \]

These calculated values are compared to a tabled value. For example, if \( X_3 \) or \( X_\text{L} \) exceed 0.941, then there is a 95\% chance that the value in question is an outlier.

\( X_3 \) and \( X_\text{L} \) are calculated for each set of three dark-bottle replicates. When \( X_3 \) or \( X_\text{L} \) 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 W9411.

The P-I curve modeling for \(^{14}\text{C}\) differed slightly from that described for oxygen in the CW/QAPP. A sequence of two models was used to fit data from \(^{14}\text{C}\) 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

\[ P_n = P_{sb} (1 - e^{-a}) e^{-b} \]

where

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

Here, $$P_B = P_{max} \left[ 1 - e \left( -\alpha \frac{I}{P_{max}} \right) \right]$$

$P_{max}$ = 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 mid-day (1000-1400 h) period was used to standardize conditions. Then, for each
station, an extinction coefficient \((k)\) was determined by regressing \(\ln (I_z/I_o)\) 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 \(I_z = I_o e^{xz}\) 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 \((\mu g \text{ C} / \mu g \text{ Chl} \cdot \text{h}^{-1})\) 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 \(Z_{0.5\% I_o}\). The values were then appropriately summed over depth and units were converted to \(m^2\) from a volumetric basis.

The above procedure estimated hourly mid-day rates \((\mu g \text{ C} \cdot m^{-2} \cdot \text{h}^{-1})\). 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 \(g \text{ C} \cdot m^{-2} \cdot d^{-1}\).

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 station occupation, 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

2-7
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 day-time 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><strong>Following samples are subsampled from water collected with Poly Vinyl Chloride Niskin GO-FLO Bottles</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<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 3 Farfield</td>
<td>300 mL</td>
<td>300 mL Glass BOD</td>
<td>Fix per Oudot et al. (1988). Titrage 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/ Pheopigments</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% MgCO3 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 NA2^14CO3 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>
<tr>
<td><strong>The following measurements are collected by the Battelle Ocean Sampling System</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Conductivity</td>
<td>All</td>
<td>---</td>
<td>Floppy disk</td>
<td>0.01 mS/cm</td>
</tr>
<tr>
<td>Temperature</td>
<td>All</td>
<td>---</td>
<td>Floppy disk</td>
<td>0.001 °C</td>
</tr>
<tr>
<td>Pressure</td>
<td>All</td>
<td>---</td>
<td>Floppy disk</td>
<td>0.01 decibars</td>
</tr>
<tr>
<td>Dissolved Oxygen</td>
<td>All</td>
<td>---</td>
<td>Floppy disk</td>
<td>0.05 mg/L</td>
</tr>
<tr>
<td>Chlorophyll a Fluorescence</td>
<td>All</td>
<td>---</td>
<td>Floppy disk</td>
<td>0.01 μg/L</td>
</tr>
<tr>
<td>Transmissometry</td>
<td>All</td>
<td>---</td>
<td>Floppy disk</td>
<td>0.01 m⁻¹</td>
</tr>
<tr>
<td>In situ Irradiance</td>
<td>All</td>
<td>---</td>
<td>Floppy disk</td>
<td>1 μE m⁻² s⁻¹</td>
</tr>
<tr>
<td>Surface Irradiance</td>
<td>All</td>
<td>---</td>
<td>Floppy disk</td>
<td>1 μE m⁻² s⁻¹</td>
</tr>
<tr>
<td>Bottom Depth</td>
<td>All</td>
<td>---</td>
<td>Floppy disk</td>
<td>1 m</td>
</tr>
<tr>
<td>Navigational Position</td>
<td>All</td>
<td>---</td>
<td>Floppy disk</td>
<td>0.000017 deg</td>
</tr>
<tr>
<td>Parameter</td>
<td>Units</td>
<td>Method</td>
<td>Reference</td>
<td>Maximum Holding Time</td>
</tr>
<tr>
<td>----------------------------</td>
<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>
<td>3 mo.</td>
</tr>
<tr>
<td>Dissolved Nitrate</td>
<td>μM</td>
<td>Technicon II AutoAnalyzer</td>
<td>Lambert and Oviatt (1986)</td>
<td>3 mo.</td>
</tr>
<tr>
<td>Dissolved Nitrite</td>
<td>μM</td>
<td>Technicon II AutoAnalyzer</td>
<td>Lambert and Oviatt (1986)</td>
<td>3 mo.</td>
</tr>
<tr>
<td>Dissolved Phosphate</td>
<td>μM</td>
<td>Technicon II AutoAnalyzer</td>
<td>Lambert and Oviatt (1986)</td>
<td>3 mo.</td>
</tr>
<tr>
<td>Dissolved Silicate</td>
<td>μM</td>
<td>Technicon II AutoAnalyzer</td>
<td>Lambert and Oviatt (1986)</td>
<td>3 mo.</td>
</tr>
<tr>
<td>Dissolved Oxygen</td>
<td>mg L⁻¹</td>
<td>Autotitrator</td>
<td>Oudot et al. (1998)</td>
<td>24 h</td>
</tr>
<tr>
<td>Dissolved Organic Carbon</td>
<td>μM</td>
<td>O.I. Model 700 TOC Analyzer</td>
<td>Menzel and Vaccaro (1984)</td>
<td>3 mo.</td>
</tr>
<tr>
<td>Dissolved Organic Nitrogen</td>
<td>μM</td>
<td>Technicon II AutoAnalyzer</td>
<td>Valderrama (1981)</td>
<td>3 mo.</td>
</tr>
<tr>
<td>Dissolved Organic Phosphorus</td>
<td>μM</td>
<td>Technicon II AutoAnalyzer</td>
<td>Valderrama (1981)</td>
<td>3 mo.</td>
</tr>
<tr>
<td>Total Suspended Solids</td>
<td>mg L⁻¹</td>
<td>Cahn Electrobalance</td>
<td>See Section 12.7.7</td>
<td>6 mo.</td>
</tr>
<tr>
<td>Chlorophyll a/ Phaeopigments</td>
<td>μg L⁻¹</td>
<td>Model 111 Turner Fluorometer</td>
<td>Lorenzen (1966)</td>
<td>2 wk</td>
</tr>
<tr>
<td>Phytoplankton (Whole Water)</td>
<td>Cells L⁻¹</td>
<td>Sedgewick-Rafter counting chambers</td>
<td>Turner et al. (1989)</td>
<td>3 y</td>
</tr>
<tr>
<td>Phytoplankton (Screened Water)</td>
<td>Cells L⁻¹</td>
<td>Sedgewick-Rafter counting chambers</td>
<td>Turner et al. (1989)</td>
<td>3 y</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>
<td>2 wk</td>
</tr>
<tr>
<td>Zooplankton</td>
<td>Cells L⁻¹</td>
<td>Dissecting Microscope</td>
<td>Turner et al. (1989)</td>
<td>3 y</td>
</tr>
</tbody>
</table>

*See Section 20 of Albro et al., 1993 for literature references.*
3.0 RESULTS OF EARLY AUGUST 1994 NEARFIELD SURVEY (W9410)

3.1 Distribution of Water Properties from Vertical Profiles

Vertical profiles were obtained at all 21 nearfield stations on August 10 (Appendix B). Scatter plots of the in-situ sensor data are presented in Figure 3-1, which shows that temperature in early August ranged from \( \sim 7.6^\circ \text{C} \) in deeper bottom water to as high as \( 18.4^\circ \text{C} \) in surface water. Salinity ranged narrowly from \( \sim 31.5 \) PSU near the surface to 32.2 PSU near the bottom. Review of temperature, salinity, and density vertical profiles in Appendix B indicated that there was usually a distinct, but thin (5-10 m) surface layer and a relatively homogeneous bottom water layer that began at \( \sim 20-25 \) m. The region of transition between these layers (i.e., the pycnocline) often showed complex layering rather than a smooth gradient between layers, and the degree of layering structure as well as the sharpness and thickness of the pycnocline varied slightly across stations. At a few locations, such as stations N10P and N12, vertical layering was essentially absent except for a thin layer near the bottom.

Beam attenuation, a measure of turbidity of the water, was generally related to chlorophyll concentrations (Figure 3-1a), although neither parameter had a large dynamic range and each generally had low mean values. Beam attenuation readings varied from \( \sim 0.7 \) to 1.65 m\(^{-1}\) and exhibited only a weak correlation to salinity (Figure 3-1a). Chlorophyll ranged from \( \sim 0.3 \) to 4 \( \mu \text{g L}^{-1} \), with a handful of individual readings \( >4 \mu \text{g L}^{-1} \). As indicated in Figure 3-1b, there were several cases where the highest chlorophyll concentrations (2-3 \( \mu \text{g L}^{-1} \)) within a vertical profile were in the surface layer and these cases occurred mostly at stations along the western edge of the nearfield. Characteristically, though, the surface chlorophyll concentrations were low (\(<1 \mu \text{g L}^{-1}\)) and a subsurface chlorophyll maximum (2-5 \( \mu \text{g L}^{-1} \)) was present within the pycnocline at 15-20 m.

Dissolved oxygen (DO) profiles, with few exceptions, indicated a productive surface layer that was supersaturated (\( \geq 110\% \)). Starting within the pycnocline or at its base (15-20 m), DO declined
sharply in percent saturation with greater depth. From 30-50 m, DO was generally 90% saturated and the minimum value was $\sim$ 82% saturation (Appendix A).

Dissolved nutrient concentrations reflected the generally stratified conditions and thus increased with water depth. DIN concentrations were routinely low ($< 0.5$ $\mu$M) at the surface and a peak value near 10 $\mu$M was recorded at the deepest sampling depth (Figure 3-2a). As has been characteristic of the nearfield, NH$_4$ concentrations did not increase as much as NO$_3$ over depth (Figure 3-2b).

The distribution of phosphate and silicate throughout the water column was similar to DIN except that surface waters were less depleted (Figure 3-2c). Consequently, N/P and N/Si ratios were lowest at the surface and increased with depth. Concentrations of phosphate ranged from 0.19 to 1.0 $\mu$M. Concentrations of silicate ranged from 1.8 to 10.1 $\mu$M.

The nutrient-salinity plots (Figure 3-3) all showed considerable scatter. Both nutrients and salinity generally increased with depth, a pattern that is evident in Figures 3-3a, b, and c. However, the lack of a strong correspondence between nutrients and salinity must be interpreted as due to (1) the lack of strong sources of nutrients to the nearfield at this time and (2) slight variations in vertical structure and its resultant effects on spatial variability in biological use of nutrients across the nearfield.

### 3.2 Water Quality Variability in the Nearfield

Vertical contours of temperature, salinity, chlorophyll (as measured by fluorescence), and dissolved inorganic N are presented in Figure 3-4. Temperature showed uniform thermal stratification (Figure 3-4a). The surface layer was $\sim$ 10 m throughout the nearfield but the temperature at the surface was slightly warmer offshore from the Outer Western Transect. The thermocline extended to the bottom sediments in much of the field, so that a distinct bottom-water layer (7-9°C) only appeared below 30 m, at deeper stations on the eastern side of the field. Salinity profiles (Figure 3-4b) typically showed a mild stratification. A surface layer of slightly fresher water ($< 31.6$ PSU) was present across the
entire Outer Western Transect nearest Boston Harbor. This same type of water was found at much of the Inner Western Transect, but was absent eastward of the middle of the nearfield.

For most of the field, the vertical distribution of chlorophyll related strongly to the physical stratification and a subsurface maximum was found within the thermocline at about 20 m (Figure 3-4c). Along the Outer Western Transect, however, the highest chlorophyll concentration was near the surface, but even there concentrations were never particularly high. The pattern across this transect did not suggest a strong correspondence between chlorophyll and salinity, and, by inference, did not suggest an outwelling of chlorophyll in lower salinity water typical of the Harbor. In contrast, the distributional pattern of DIN (Figure 3-4d) did show slightly higher DIN in much of the area with lower surface salinity and perhaps does suggest an outwelling of nutrients from the inshore area. DIN was not higher at station N01P where enhanced chlorophyll probably had already assimilated DIN enrichment. Note that the semi-overlapping spatial patterns of higher DIN and lower salinity in western nearfield surface water were both subtle and complicated by biological assimilation; therefore the feature was indistinct in the DIN-salinity plot (Figure 3-3).
Figure 3-1a. Scatter plots of data acquired by *in situ* sensor package during vertical casts for nearfield survey in early August 1994. Chlorophyll is estimated from *in situ* fluorescence.
Figure 3-1b. Scatter plots of data acquired by in situ sensor package during vertical casts for nearfield survey in early August 1994. Chlorophyll is estimated from in situ fluorescence.
Early August (W9410)

Figure 3-2a. DIN vs. depth in early August 1994.
Figure 3-2b. NH4 and NO3 vs. depth in early August 1994.
Figure 3-2c. PO₄ and SiO₄ vs. depth in early August 1994.
Figure 3-3a. DIN vs. salinity in early August 1994.
Figure 3-3b. NH₄ and NO₃ vs. salinity in early August 1994.
Figure 3-3c. PO$_4$ and SiO$_4$ vs. salinity in early August 1994.
Figure 3-4a. Vertical section contours for nearfield standard transects (view towards Boston Harbor) on Survey W9410. 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 3-4b. Vertical section contours for nearfield standard transects (view towards Boston Harbor) on Survey W9410. 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 3-4c. Vertical section contours for nearfield standard transects (view towards Boston Harbor) on Survey W9410. 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 3-4d. Vertical section contours for nearfield standard transects (view towards Boston Harbor) on Survey W9410. 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 LATE AUGUST 1994
COMBINED FARFIELD/NEARFIELD SURVEY (W9411)

4.1 Farfield Survey

4.1.1 Horizontal Distribution of Surface Water Properties

Surface temperatures varied by several degrees in the study area in late August 1994 (Figure 4-1). Although Inner Boston Harbor was warm (18.7°C) and the nearfield was generally 16-17°C, stations in the tidal mixing zone between the Harbor and the nearfield were cooler (15-15.9°C). This cooler surface water may arise from enhanced vertical mixing and/or upwelling of water from depth within this zone. With the exception of two stations in Stellwagen Basin (F17 and F12), surface temperatures in the remaining parts of the Bays were >16°C. Consistently warm surface waters (>17.5°C) characterized the Cape Cod Bay stations.

Surface salinity at most of the Bay stations was between 31 and 32 PSU (Figure 4-2). The freshest water was detected in Boston Harbor and the surface salinity at stations within the zone of tidal mixing immediately outside the Harbor was ≤31 PSU. Despite the narrow salinity range, two aspects of the spatial distribution of surface salinity are of interest. First, the offshore stations were uniformly the most saline and every transect from shore revealed increasing salinity with distance from the coastline. Values of 32 PSU were noted on Stellwagen Bank (station F28) and over the basin east of the Bank (station F27B). Second, at the most northern station (off Cape Ann, station F26), salinity was as low as in the western nearfield (31.1 PSU), despite the fact that the highest salinity was recorded near this location. In late August, a near-coastal water mass flowing from the north may have been detected at station F26. Perhaps more significantly, a southward flow along the coast outside of Boston Harbor could be inferred from the surface-water salinity contours (Figure 4-2), as well as the seawater density contours (not shown), which both showed streamlines parallel to the coastline.
Beam attenuation in the Bays was generally $\geq 1$ m$^{-1}$ (Figure 4-3). The waters in and surrounding Boston Harbor were more turbid, with beam attenuation generally $\geq 2$ m$^{-3}$. Chlorophyll concentrations (Figure 4-4) were also generally low ($< 1$ $\mu$g L$^{-1}$) in offshore waters and slightly enhanced ($\sim 2-3$ $\mu$g L$^{-1}$) in Boston Harbor. Interestingly, however, the highest surface water chlorophyll concentrations (4-5.5 $\mu$g L$^{-1}$) were observed for a group of stations south of Boston Harbor, off Cohasset within $\sim 10$ km of the coast (stations F14, F15, and F13P). Relatively high surface chlorophyll (3.87 $\mu$g L$^{-1}$) was also measured further south at station F06.

Review of the vertical profiles (Appendix B) at this group of stations revealed that the water column at these stations was weakly stratified, in contrast to the well-mixed and vertically uniform profiles within the Harbor. It was also noted that turbidity at these stations was lower than in the Harbor area and, moreover, that nutrient concentrations were usually elevated in the surface waters along the coast south of Boston. For example, the DIN concentration gradient from Boston Harbor to the Bay appeared to stretch southward at this time (Figure 4-5). DIN concentrations were very high in the Harbor and at the Harbor's edge (10-20 $\mu$M). The concentration gradient between the Harbor and Bay was very sharp but, as noted, stretched south along the coast. In the main group of Bay stations, including all nearfield stations other than the southwestern corner (station N10P), surface water DIN concentrations were very low. Reflecting on the spatial distribution of nitrate concentrations ($\text{NO}_3$; Figure 4-6), it is evident that the Harbor was enriched in $\text{NO}_3$. But the differences in DIN and $\text{NO}_3$ concentrations (cf. Figures 4-5 and 4-6) illustrate that most of the Harbor's enrichment in DIN was in the form of ammonium ($\text{NH}_4$), which is readily assimilated by phytoplankton. Patterns for concentrations of phosphate ($\text{PO}_4$; Figure 4-7) and silicate ($\text{SiO}_4$; Figure 4-8) resemble DIN and nitrate in their enrichment within the Harbor, and in a relative enrichment that extends southward along the south shore coast off Cohasset.

The observation of sufficient DIN (and other nutrients) for phytoplankton growth suggests a hypothesis. Enhanced chlorophyll concentrations at the group of stations indicated above might have arisen if, as water were flowing southward, turbidity was diluted to enhance light availability to a level sufficient for greater phytoplankton growth. Possibly aiding chlorophyll development was a mild water column stratification. Stratification can enhance light availability because it can have the
effect of keeping a phytoplankton population at higher ambient light levels near the surface, and inhibit mixing to depths below the photic zone where light levels are insufficient to maintain a bloom.

4.1.2 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 4-9). 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 4-9). 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.

There was relatively consistent thermal layering of the water in Massachusetts Bay when water depths exceeded ~30 m (Figure 4-10a). A sharp thermocline was generally found between ~20 and 30 m. In contrast, the Harbor stations (F30B and F31B) and the region of active Harbor-Bay tidal exchange in western Massachusetts Bay (stations F23P, F24, and F25) were well mixed. Note, as described above, the mild thermal stratification beginning at stations F14 and F15 along the Boston-Cohasset Transect as water depth grades from ~20 to 40 m. The deepest water within the Bay, at stations F22 and F19 in Stellwagen Basin, was <7°C during this survey in late August 1994. Salinity also showed vertical layering throughout the Bay, although the salinity range from top to bottom was slight (Figure 4-10b). Within Boston Harbor, vertical layering of salinity was indicated and some horizontal spread of fresher water was suggested for both Boston-Bay transects in Figure 4-10b.

Chlorophyll concentrations contoured across the sections (Figure 4-10c) revealed three main features. First, as discussed above, surface water concentrations were often highest in a near-coastal zone south
of Boston Harbor. At stations in this zone, the sections illustrate that higher chlorophyll concentrations generally extended through most of the surface water layer (∼ 8-12 m) and enhanced chlorophyll was found as far south as the Marshfield Transect (stations F05 and F06). Second, Boston Harbor chlorophyll concentrations were fairly uniform over depth and were higher (1-3 µg Chl a L⁻¹) than the offshore surface concentrations (often < 1 µg Chl a L⁻¹). Third, at Bay stations with water depths > 40 m, a subsurface chlorophyll maximum typically occurred near the top of the thermocline, and peak concentrations (> 2 µg Chl a L⁻¹) within a 5- to 10-m-thick subsurface layer were similar to the chlorophyll concentrations in the Harbor.

Enrichment of DIN in Boston Harbor was evident throughout the water column (Figure 4-10d). DIN appeared to be elevated throughout the surface layer at station F14 to the south, where elevated chlorophyll was noted, but DIN was not elevated further downstream of the presumed source at stations F15, F05, or F06, where chlorophyll enhancements were also observed. DIN had most likely been assimilated by phytoplankton by the time Harbor water could be advected to this location. Thus, surface water DIN concentrations, like elsewhere in the Bay, were essentially depleted even though chlorophyll was enhanced. Starting at water depths near the top of the thermocline (∼ 20 m), DIN concentrations characteristically increased to values > 12 µM in the deepest waters sampled in Stellwagen Basin.

For the Boundary Transect (Figure 4-11), 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 station F27B (outside the Bay), water at depths > 50 m was warmer than water at the same depth in Stellwagen Basin. The 9°C isotherm apparently was interrupted by Stellwagen Bank. Salinity in the deep water of the two basins was similar (Figure 4-11), but review of station profiles in Appendix B shows that the deep water at station F27B was slightly more saline than at station F12 in Stellwagen Basin. Outside the Bay at station F27B, the subsurface chlorophyll maximum was somewhat deeper and was associated with a slight deepening of the DIN-depleted surface layer as judged by the dip in the 3-µM isopleth.
4.1.3 Analysis of Water Quality Characteristics Throughout the Bays

Scatter plots using all *in-situ* sensor data from vertical profiles are shown in Figures 4-12a and b. The temperature-salinity (T-S) plot in Figure 4-12a shows a high degree of scatter. A large portion of the scatter is created by the uniqueness of Boston Harbor relative to the Bays. To illustrate this distinct region with respect to water quality, Boston Harbor data have been identified in Figures 4-12a and b. Appendix C contains a separate display of Boston Harbor (and other regional) data.

As indicated in Figure 4-12a, the Harbor is generally warm (>15°C) and relatively fresh (<31 PSU). Turbidity, as indicated by beam attenuation, is highest in the Harbor. Chlorophyll is at intermediate levels (~1.8 to 3 µg L⁻¹, Figure 4-12b). However, the chlorophyll-beam attenuation relationship in the Harbor is distinctly different from that in the Bay, where higher chlorophyll concentrations are found at turbidity levels lower than found in the Harbor. Finally, the Harbor was distinct for its relatively low percent DO saturation relative to surface waters elsewhere in the Bays (Figure 4-12b). In the rest of the Bay, the percent DO saturation in bottom waters is as low or lower than in the Harbor, but the DO undersaturation occurs from the surface to bottom of the shallow, well-mixed water column in the Harbor.

The data sets for other regions (coastal, nearfield, offshore, boundary, and Cape Cod Bay) tend to overlap in their range for temperature, salinity, beam attenuation, and DO. The T-S patterns generally reflect the normal vertical stratification that exists in the Bays during this season. Surface water temperatures are usually in the 15-17°C range (*i.e.*, similar to the Harbor) but in most of the Bays, the water column is thermally stratified, with as much as a 10°C difference between surface and near-bottom water. Salinity varies more narrowly than temperature, but also systematically with depth; surface values typically between 31-32 PSU grade to >32 PSU in bottom waters below the pycnocline. Although a parameter's regional ranges overlap, there is still significant scatter in parameter-parameter plots. To an extent, this scatter reflects some inter- and intra-regional differences in water depth and the degree of vertical mixing. Coastal stations with little vertical stratification and which are known to be tidally mixed (*e.g.*, station F24) have a less dynamic range in parameters and a T-S pattern different from those stations that are highly stratified. Note that the
deepest stations, which are located in the offshore and boundary regions, concomitantly have the coldest (\(\sim 5.5^\circ{\text{C}}\)) and most saline (\(\sim 32.6\text{ PSU}\)) waters.

Aside from the Harbor region, beam attenuation (turbidity) decreased broadly from lower salinity to higher salinity. However, at many stations, an increase in turbidity was detected near the bottom of a vertical profile (Appendix B). The near-bottom increase in turbidity was noted in deep basins inside and outside the Bay (e.g., stations F27B, F22, and F17), but also occurred in other areas (e.g., shallow coastal station F14). The near-bottom turbidity feature is expressed in Figure 4-12a (middle panel) as vertical strings of points at a near-constant salinity, as well as an increase in beam attenuation without a change in chlorophyll at very low chlorophyll concentrations (Figure 4-12a, bottom panel). Except for the near-bottom spike in turbidity and the unique signature in the Harbor, chlorophyll and turbidity were broadly correlated (Figure 4-12a, bottom panel). Note, however, that a relatively small increase in turbidity is suggested with a \(> 6 \mu{\text{g L}}^{-1}\) increase in chlorophyll.

Typically, chlorophyll profiles with depth (Figure 4-12b) showed: (1) higher chlorophyll (2-7 \(\mu{\text{g L}}^{-1}\)) in the surface 10-15 m or (2) a sharp subsurface maximum (2-4 \(\mu{\text{g L}}^{-1}\)). Regional trends in the profile styles are typical of previous observations and coincident with the physical structure/nutrient status of the water column in different areas. For example, the Harbor and coastal regions (more well-mixed and higher dissolved nutrients in the surface layer; see below) generally displayed the first profile style, with selected stations in the nearfield, offshore, and boundary regions following suit. In contrast, at most of the nearfield region, all Cape Cod Bay stations, and at many offshore/ boundary stations more striking subsurface maxima were found, characteristically at 15-25 m. An unusually deep subsurface maximum approaching 30 m (Figure 4-12b, top panel) was found at station F27B in the boundary region.

As indicated, the Harbor and some coastal stations were undersaturated in DO. Surface waters in all other regions generally were \(\geq 100\%\) saturation; most were near 110\% (Figure 4-12b, bottom panel). The highest degree of supersaturation was found at some offshore and boundary region stations. The degree of saturation declined below \(\sim 10-20\text{ m}\) in the other regions. For deep waters (\(> 30\text{ m}\)) of the nearfield, offshore, and boundary stations, saturation generally reached 80-90\%. Notably, in Cape
Cod Bay, water <20 m (approximately the depth of the subsurface chlorophyll maximum and the bottom of the pycnocline), DO fell very sharply to levels below 80% and reached a low value of about 70% saturation at station F02P.

In late August, DIN concentrations ranged between 0.19 and 20.15 μM (Figure 4-14a). In Harbor and coastal waters, concentrations were typically >10 μM in the surface 10-20 m. In contrast, DIN exceeded 10 μM only in the deep water of other regions. Except for selected nearfield stations, DIN concentrations in those other regions were virtually depleted in the surface layer and increased sharply from the base of the pycnocline into the bottom water layer. Most of the enhanced DIN concentration in Harbor and coastal waters was due to NH₄ rather than to NO₃. NO₃ was slightly elevated in Harbor and coastal waters (Figure 4-14b). In sub- pycnocline bottom water, NO₃ was the dominant form and deep waters throughout the Bay, independent of region, showed a similar NO₃ profile with depth.

A distinct enrichment in PO₄ concentration was also noted in Harbor and coastal surface waters (Figure 4-14c). Surface water PO₄ concentrations in these regions exceeded the highest concentrations measured in deep waters in the Bay; despite this, the trend in PO₄, like DIN, was an increase below the pycnocline through most of the Bays. But unlike DIN, PO₄ concentrations were not depleted in surface water and the overall PO₄ concentration range was 0.15-1.54 μM. Figure 4-14c shows that Cape Cod Bay samples were often lowest in PO₄ at a given depth and this same relative depletion was even more evident for SiO₄. SiO₄ concentrations showed many trends of DIN; however, SiO₄ concentrations (6-10 μM) in Harbor and coastal surface layers were not as high as concentrations noted in bottom water (10-16 μM).

The relationship between DIN and PO₄ was generally similar in all regions (Figure 4-15a). Using all data (n = 264), the relationship was described, by significant (R² = 0.93, Pr>F = 0.0001) linear regression, as DIN = 13.2 (PO₄) - 3.8. As mentioned above and as signified by a significant negative intercept, PO₄ was present in surface water when DIN concentrations were virtually zero. The regression slope near the Redfield ratio of 16:1 suggests that decomposition in bottom waters of
the Bay approximated a normal, expected stoichiometry at this time. Moreover, enrichments within Harbor and coastal waters followed this same stoichiometric trend.

Despite the overall similarity in N/P patterns, some regional distinctions could be made. The deep bottom water in the boundary transect and offshore regions was slightly more enriched in DIN (at a given P concentration) than, for example, the nearfield area (Figure 4-15a). This pattern of relatively high N/P ratios in deep water of the boundary and offshore regions was most pronounced when NO₃ concentrations were compared to PO₄ concentrations (Figure 4-15a). In the shallower areas of the Harbor, coastal, nearfield and Cape Cod Bay regions, NH₄ is usually a principal contributor to DIN and the NO₃/PO₄ ratio is much lower (generally ~4:1) than in deep basin water.

In contrast to a gross regional similarity in DIN/PO₄ ratios, the DIN/SiO₂ pattern illustrated a basic distinction between inshore, Harbor-influenced surface water and subsurface water in the rest of the Bays. Characteristically, the main body of Boston Harbor and coastal data, along with some western nearfield samples, is more enriched in N and thus has a higher N/Si ratio (near 2:1) at higher nutrient concentrations (Figure 4-15b). Independent of this trend are the data from deeper water in the nearfield, offshore, and boundary regions, which follow a trend approximated by a N/Si ratio of 1:1. When only NO₃ is considered does the regional pattern shift. The deep waters of the nearfield, offshore, and boundary regions are not affected (compared to DIN) and still follow an approximate 1:1 relationship, whereas the shallow Harbor-influenced waters track the 1:2 isopleth. Overall, the stoichiometric observations show that examination of different nutrient forms can provide diagnostic evidence of sharp differences in biogeochemical cycles of different regions of the Bay and, to an extent, indicate strong linkages (and/or similar functioning) across neighboring regions.

Regional linkages may also be examined by nutrient-salinity plots, such as those shown in Figure 4-16a. DIN plotted as a function of salinity (Figure 4-16a) reveals a pattern previously observed in the spring. There is a descending arm of DIN concentration with increasing salinity to intermediate salinities (~31.5 PSU), followed by an ascending arm of DIN concentration rising with higher salinity (>32 PSU), even in the nearfield. The descending arm suggests that the high DIN concentrations observed in the Harbor are diluted with low-nutrient Bay water at coastal and at select
nearfield stations. The ascending arm results from physical and geochemical stratification, with higher nutrients concentrations at higher (deep water) salinity due to nutrient regeneration processes. Between the two “arms” are the data that represents the surface layer throughout most of the Bay, where DIN is relatively depleted. Early in the winter, the descending arm is prominent because there is no stratification and subsequent layering with depth. In contrast, during strong stratification in the summer, when nutrients are rapidly assimilated even in the Harbor 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” during this survey indicates that this late summer period may be a biogeochemical transition point between summer and fall ecosystems; moreover, it signals that the Harbor is not fully assimilating its DIN input (see also Kelly, 1994).

In light of this understanding of the two-arm DIN-salinity pattern, the differences between NH₄, NO₃, PO₄, and SiO₄ patterns with salinity (Figure 4-16b) reveal differences in their sources, dynamics, and confirm their potential as water mass diagnostics. For example, the Harbor is a strong source of NH₄, while there is most a small increase in NH₄ in stratified bottom layers. In contrast, the Harbor is a modest source of NO₃, while a sharp increase with depth is indicated. The PO₄ relationship with salinity (Figure 4-16c) was generally similar to that for DIN and, thus, the pattern indicates that the Harbor is a fairly strong source of PO₄. In contrast, the SiO₄-salinity pattern was more similar to the NO₃-salinity pattern, and indicative of a modest Harbor source of SiO₄ to the Bay and nutrient recycling in deep waters.

Measurements of organic forms of nitrogen (Figure 4-17) are made only at the surface and at the depth of subsurface chlorophyll maximum. Because deeper water was not sampled, high salinity samples are missing, so that an ascending arm as displayed on dissolved nutrient-salinity plots is neither expected nor observed. In general, concentrations of the combined forms of N (DIN + PON) and total N (TN) were highest in Boston Harbor. Note that most of the combined N was DIN (cf. Figure 4-16a), a finding which also indicates inefficient N assimilation. TN concentrations in Cape Cod Bay were intermediate; the lowest TN concentrations were noted in the nearfield. The TN concentrations at the boundary station (F27B) were also low and within the range measured for nearfield samples. The broad relationship between TN and salinity suggests that there may be semi-
conservative mixing of surface waters from the Harbor to the Bay; there is, however, a considerable amount of scatter in Figure 4-17. Some scatter may arise because local events and processes other than horizontal mixing are significant in controlling nutrient concentrations. Additionally, much of the variability from a strictly linear trend is created by nearfield data and, in particular, many nearfield samples appear to be relatively low in TN and below the principal, quasi-linear trend of TN with salinity. The low TN values could suggest removal of nitrogen from nearfield surface waters. Alternatively, because potential southward coastal flow is indicated by physical data, an interpretation that assumes mixing of endmembers would be misleading if some nearfield stations were hydrodynamically isolated from the Harbor export at this time.

4.1.4 Distribution of Chlorophyll and Phytoplankton

Over an approximate range in phytoplankton abundance of 0.3 to 1.75 million cells L\(^{-1}\), there was a correlation between chlorophyll concentration and total cell counts (Figure 4-18). One general pattern between chlorophyll and cell counts was broadly applicable over each region of the Bays for which this type of sampling was conducted.

In most surface samples, except station F13P, counts were near 0.5-1 million cells L\(^{-1}\). A comparison of surface and subsurface (chlorophyll maximum) counts (Figures 4-19 and 4-20) indicates that, for many stations, there is not a consistent or striking difference between total cell counts as a function of depth. However, for both stations in Cape Cod Bay (F01P and F02P), the sample from the chlorophyll maximum had substantially higher phytoplankton abundance than the surface sample. In most samples from either depth, the community was numerically dominated by microflagellates. However, in this respect, the chlorophyll maximum samples from Cape Cod Bay again stood out as different; the diatom component was enhanced and was the dominant group. Cryptomonads, the main contributors to the “Other” group in Figures 4-19 and 4-20, were a secondary dominant at all stations, but were relatively less significant at the two Cape Cod Bay stations (Tables 4-1a,b). Dinoflagellates were minor components of the total cell count at all locations except station F13P where they were the most abundant.
Tables 4-1a and 4-1b identify the dominant taxa in both surface and subsurface samples, respectively. A full taxonomic listing of samples is included in Appendix E. Though less numerous than the multi-species taxonomic groupings of microflagellates and cryptomonads, the dominant individual species characteristically were diatoms. The diatoms were an amalgam of species, none with especially high abundance nor with especially noteworthy geographic groupings. The diatoms found in late August 1994 have typically been observed in late summer and included *Cerataulina pelagica*, *Cylindrotheca closterium*, *Rhizosolenia delicatula*, *Skeletonema costatum*, *Leptocylindrus minimus*, and *Thalassionema nitzschoides*. *Asterionellopsis glacialis*, the diatom that was responsible for an enormous fall bloom in September/October 1993 (Kelly and Turner, 1995), was noted in the nearfield. Also included, notably at Cape Cod Bay stations, were two species of the pennate diatom *Nitzschia*, one of which reached ~0.3 million cells L⁻¹ at the chlorophyll maximum. Using standard microscopic methods, the abundant taxon of the genus was not identifiable to species (*Nitzschia* spp.). There are varieties of *Nitzschia* (*e.g.*, one form of *pungens*) that cause toxicity (*e.g.*, domoic acid). A more comprehensive analysis based on morphometric criteria using scanning electronmicroscopy determined the *Nitzschia* spp. to be a nontoxic form (Turner, pers. communication).

In addition to the diatoms, one dinoflagellate (*Gymnodinium* spp.) was among dominants and was present at low abundance, generally 10⁴ cells L⁻¹ (Table 4-1a,b). Species of *Gymnodinium* are responsible for “red tides” in Florida and elsewhere, but such phenomena are not known for this genus in the Massachusetts Bay area. This dinoflagellate was among dominants at almost all nearfield stations as well as at station F13P along the coast south of the nearfield. Although typical among the dominants in western Massachusetts Bay stations, *Gymnodinium* was not among dominants and was only present at low abundance (10³ cells L⁻¹) in some samples at station F23P near the Harbor edge and station F02P in Cape Cod Bay (Appendix E). The genus was not detected at station F01P in Cape Cod Bay. In summary, the stated differences in diatom species and in the pattern of depth-related abundance, as well as the lesser abundance of a dinoflagellate *Gymnodinium*, portray a Cape Cod Bay phytoplankton community distributionally (vertically) and taxonomically different in from that found in western Massachusetts Bay and Boston Harbor in late August 1994.
Screened phytoplankton samples (Tables 4-2a and 4-2b) confirmed that there were small numbers (1s to 100s of cells L⁻¹) of dinoflagellates, although nearly two dozen species were represented. Overall, the taxon list for screened organisms (not all dinoflagellates) was more extensive for the set of chlorophyll-maximum samples than for the set of surface-water samples (Table 4-2b vs. 4-2a). The principal dinoflagellate genera, each with multiple species present, were *Ceratium*, *Dinophysis*, and *Protoperidinium*. Interestingly, *Gymnodinium* was not found in screened samples; being a smaller form, it was probably not retained on the 20-μm screen. Highest counts for an individual taxon in screened samples were for a *Protoperidinium* spp. at station F13P.

### 4.1.5 Distribution of Zooplankton

Across all stations, there was no consistent relation between zooplankton abundance and phytoplankton abundance or chlorophyll concentration (Figure 4-21). A noteworthy feature evident in Figure 4-21 is that Cape Cod Bay zooplankton counts were markedly lower than the Massachusetts Bay station counts, although the chlorophyll concentration at Cape Cod Bay stations was similar to many other stations and regions. For the coastal and nearfield stations in western Massachusetts Bay, zooplankton abundance typically ranged from ~30,000 to 60,000 individuals m⁻³ (Figure 4-22). The highest abundance was recorded at station N01P, but there were no distinct geographic trends in total abundance within Massachusetts Bay. In contrast, a Bay-to-Bay geographic trend was pronounced due to a low abundance (11,000 to 16,000 individuals m⁻³) at stations F01P and F02P in Cape Cod Bay (Figure 4-22). Very few copepods and their nauplii were found in Cape Cod Bay, whereas virtually the entire community at all other sampling stations was made up of copepods. Were it not for "Other" forms in Cape Cod Bay, there would be virtually no zooplankton. On the other hand, precisely for the presence of the "Other" forms there may have been virtually no copepods, as next described.

Compositionally, the "Other" forms in Cape Cod Bay were primarily the appendicularian *Oikopleura dioica*, meroplanktonic bivalve veligers, and small medusa (Appendix F). In Cape Cod Bay, *O. dioica* reached abundances of 1102 to 2012 m⁻³, compared to an approximate range of 50 to 200 m⁻³.
elsewhere. *O. dioica* filter feeds on phytoplankton, but the coelenterate medusa and bivalve veligers are carnivores that likely feed on copepods. Medusa, only detected at a few other stations, were an order of magnitude lower in abundance compared to Cape Cod Bay samples (838-1102 m\(^3\) at stations F01P and F02P, respectively). In addition to the stations in Cape Cod Bay, bivalve veligers were abundant at a few other stations, notably station N10P.

Among Massachusetts Bay stations, the principal distinction in zooplankton distribution was between the Harbor-edge station F23P and all the other stations. At station F23P, *Acartia tonsa* and *Eurytemora herdmani* were the dominant taxa (>10,000 m\(^3\) for adults and juveniles). Elsewhere, *Oithona similis*, a small-sized species, was the numerical dominant, with combined adult and juvenile abundances ranging from ~8000 to 30,000 m\(^3\). Differences in *O. similis* abundance largely produced the variability in total abundance across Massachusetts Bay stations shown in Figure 4-22. Additional copepod taxa that were ubiquitous and numerically significant (generally 1500-3000 m\(^3\)) in Massachusetts Bay (excluding station F23P) included *Paracalanus parvus* and *Centropages* spp. (Appendix F).

### 4.1.6 \(^{14}\text{C} \) Production Measurements

Appendix D contains many details of the \(^{14}\text{C} \) incubation measurements and P-I curve modeling, but results of modeling and calculations for integrated water column production are summarized in Table 4-3. 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 (August 23 and 24).

As commonly found, the photic zone was deeper at station N16P (about 28 m) than at station F23P (8.5-10.5 m). Most incubation data were not fit by the model with a photoinhibition term (Platt et al., 1980). However, at station N16P on each day, incubations using the two samples near or in the
pycnocline (~18-28 m) consistently indicated photoinhibition. Under the strongly stratified conditions maintained throughout the summer at station N16P, though taxonomically similar to the near-surface community (Tables 4-1a,b), the phytoplankton community at depth was probably adapted to constantly lower irradiance, thereby being inhibited when exposed to irradiance levels more typical of near-surface water. In contrast to station N16P, the community from depth at station F23P was taken from a well-mixed water column. Thus, the deep station F23P community does not represent populations constrained to lower light regimes or light maxima over time, and photoinhibition is less expected.

There were three cases where the Webb et al. (1974) model fit the data, but where R² values were not high (<0.8, Appendix D). For two of these, the 2.2-m and 5.8-m depths on August 23 (Table 4-3), the model fit to the data was poor in the irradiance range of the initial rise of P with I, or where I = 0-200 \( \mu \text{E m}^{-2} \text{sec}^{-1} \). In these cases, the model appeared to overestimate the rates indicated by the data in this irradiance range. The \( \alpha \) term of the model in these cases was unreliable and was high compared to expected values from the literature. An overestimate of the \( \alpha \) term would result in an overestimate of the integrated water column rate. Thus, the pattern for station F23P on August 23 (Table 4-3 showing near-surface rates much higher than deep-water rates) may be an artifact. Note that the error in the \( \alpha \) term in Appendix D for the two samples examined here suggests high uncertainty in the model that is not captured in the calculations shown in Table 4-3. Other samples with scatter in the initial rise of P-I curve and substantial uncertainty in model parameter estimates include station N16P at 2.2 m and 8.4 m on August 24.

In general, and in comparison to the \( \alpha \) term, the production rate \( (P_{\text{max}} \text{ or } P_{\text{ab}}) \) at light saturation was more adequately characterized and fit by the data of the incubation series. \( P_{\text{max}} \) or \( P_{\text{ab}} \) values ranged between 3.1 and 14 \( \mu \text{g C (\mu g Chl)}^{-1} \) hr\(^{-1} \) (Table 4-3).

At station F23P, \( P_{\text{max}} \) was similar over depth within a day, as expected for a water column that was well-mixed with respect to phytoplankton. For station F23P, \( P_{\text{max}} \) was slightly higher on August 24, when integrated \(^{14}\text{C} \) production rate estimates ranged from 657 to 843 mg C m\(^{-2} \) d\(^{-1} \). Previously, we stated that integrated estimates for the upper two depths at station F23P on August 23 were uncertain.
and likely high; disregarding this, the calculated rates on August 23 ranged from 327 to 950 mg C m$^{-2}$ d$^{-1}$. Because station F23P is well-mixed, the separate incubations may be considered replicate measurements, to some extent. In this case, on August 23, the minimum and maximum of the four estimates were 56 and 164%, respectively, of the mean (580 mg C m$^{-2}$ d$^{-1}$). On August 24, the minimum and maximum of the four estimates were 83 and 107%, respectively, of the mean (790 mg C m$^{-2}$ d$^{-1}$). On August 23 and 24, the vertical distributions of chlorophyll at station F23P were very similar and the average chlorophyll concentration in the photic zone was exactly the same, 1.83 $\mu$g L$^{-1}$, on both days. Remembering that the same incident irradiance was used in calculations for both days, the variability in integrated production, even over the two days, may largely represent variability inherent with the technique and thus should provide a quantitative sense of the certainty.

For the eight separate incubations over the two days, the mean was 685 mg C m$^{-2}$ d$^{-1}$; the minimum and maximum respective estimates were 48 and 139% of the mean.

The range in integrated water column production for incubations at station N16P was 567 to 2377 mg C m$^{-2}$ d$^{-1}$ over the two days. The highest value is associated with a surface incubation with an uncertain $\alpha$ term, but the surface incubation on both August 23 and 24 yielded the highest estimate for each depth series. For the two days, the average photic zone chlorophyll concentration was similar, ranging between 1.42 and 1.39 $\mu$g L$^{-1}$.

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 687 and 880 mg C m$^{-2}$ d$^{-1}$ for station F23P on August 23 and 24, respectively. From the composite profile for station N16P, we calculated rates of 781 and 976 mg C m$^{-2}$ d$^{-1}$ on August 23 and 24, respectively. Of the two stations, station N16P had slightly lower average chlorophyll concentrations but, because of a deeper photic zone, it had double or more the photic zone biomass of station F23P. Despite these underlying differences, on average, the integrated production rates at the two stations in late August were similar, especially considering the uncertainty in the estimates.
4.1.7 Dark Respiration Measurements

Results of dark-bottle-incubation time series at station F24 (in the tidal mixing region between the Boston Harbor and the nearfield), station N20P (middle of the nearfield), and station F19 (east of the nearfield in Stellwagen Basin) are presented in Appendix D. The time series approach was successful over periods of 0-48 h, as well as incubations that extended to about 7 days, and significant (95% level) regressions were indicated. Slopes from all regressions indicated that rates ranged from \(~0.01\) to \(0.0008\) mg O\(_2\) L\(^{-1}\) h\(^{-1}\). In a number of cases, O\(_2\) decline over the time series appeared non-linear; the decline may have been fastest at first and then slowed over time. This was not, however, uniformly the case and where 0-2 day and 0-7 day incubations were performed, rates from regression analyses were similar. The highest implied respiration rate, \(0.01\) mg O\(_2\) L\(^{-1}\) h\(^{-1}\), was found at the surface of station F24. The lowest rate was at depth (almost 47 m) at station F19 in Stellwagen Basin. At both stations N20P and F19, the rates in surface water and mid-depth (chlorophyll maximum) incubations (\(~0.005-0.009\) mg O\(_2\) L\(^{-1}\) h\(^{-1}\)) were higher than the deep-water incubations (0.0008-0.003 mg O\(_2\) L\(^{-1}\) h\(^{-1}\)).

4.2 Nearfield Survey

4.2.1 Distribution of Water Properties from Vertical Profiling

Scatter plots for a variety of parameters measured on the nearfield survey (August 26) are shown in Figure 4-23. Patterns and ranges may be compared to all stations (Figure 4-12) as well as to separate regions (see Appendix C). Results of the nearfield survey of 21 stations show a strong similarity to results from the 6 “P” stations sampled during the farfield survey and included in Figure 4-12. Coherence among stations with respect to T-S characteristics was not very strong (Figure 4-23a), probably indicating differences in the patterns of physical layering across the nearfield. The temperature of the deepest bottom waters was \(>8^\circ\text{C}\). The temperature range is slightly \(>10^\circ\text{C}\) from surface to bottom and the corresponding salinity range is from \(~31\) to 32.5 PSU. Spatial variations in temperature and salinity portray a T-S gradient from shore to sea, with T and S increasing slightly.
to the eastern side of the field (Figures 4-24a and 4-24b). The pattern for salinity in surface water along the Outer Western Transect suggests fresher water export from the Harbor that was biased towards the south at this time. As expected, bottom waters at the deeper stations along the eastern side of the field were the coldest and most saline.

Beam attenuation displayed the common inverse relationship with salinity and the slight, but direct, relationship with chlorophyll. This has been a typical finding for many nearfield surveys and, for example, resembles results from the early August 1994 survey (Section 3). Relative to early August, the range for nearfield surface water salinity was extended lower by ~0.5 PSU and, concomitantly, beam attenuation was slightly higher (Figure 4-23a).

The two styles of chlorophyll vs. depth profiles that were described previously were apparent within the intensive nearfield survey data set (Figure 4-23b). At a subset of stations, chlorophyll concentrations were highest (2-5 μg L⁻¹) in the surface layer. At the remaining stations, a subsurface chlorophyll peak was generally found at 15-22 m. With two exceptions, DO profiles showed conditions of supersaturation in the upper 20 m. For all stations, the percent saturation decreased below that depth. Lowest undersaturation (<80%) occurred at some of the shallower stations instead of the deepest water and the lowest DO concentration was <7 mg L⁻¹.

From section plots in Figure 4-24c, a change in the vertical distribution of chlorophyll was noted as a function of distance from shore. Nearshore, along much of the Outer Western Transect, chlorophyll concentrations were highest (>3-4 μg L⁻¹) in the surface 10 m. In the midfield and the eastern side of the field, the subsurface peak was more pronounced; at depth, peak concentrations were occasionally >3 μg L⁻¹. Interestingly, there was some correspondence between lower salinity and higher chlorophyll along the Outer Western and Inner Western Transects (Figure 4-24b,c).

Except for the surface layer at stations N10P, N11, and N12 of the Outer Western Track, where DIN concentrations were >4 μM, surface DIN concentrations were generally low throughout the field (Figure 4-24d). It was notable that the location of higher surface DIN concentrations along the southern portion of the Outer Western Transect occurred within the shallow layer of lower salinity.
(<31.3 PSU). DIN concentrations were highest (>10 μM) in bottom water at station N01P in the northwest corner of the nearfield. With subtle variations, the expected increase in DIN with depth below the surface layer — characteristic of stratified conditions — was observed throughout the field.

4.2.2 Water Quality Variability in the Nearfield

There were corresponding spatial trends in physico-chemical and biological parameters, expressed both vertically and horizontally and displayed in Figure 4-24. Perhaps most interesting was the variability in chlorophyll from inshore to offshore. Across this increase in water depth, the vertical position of chlorophyll concentration peaks graded from the surface layer to the bottom layer. Concomitantly, DIN concentrations and salinity were generally higher in surface layers inshore than in surface layers offshore. Moreover, along the inshore transect, the distribution of higher chlorophyll, higher DIN, and lower salinity was biased to the south. The patterns from the farfield survey, where chlorophyll enrichment was noted along the coast south of Boston, suggested that a general southward flow of surface water may have been occurring at this time and the spatial distributions noted from the data of the nearfield survey would be consistent with the concept of southward flow.
Table 4-1a. Abundance of the top five dominant phytoplankton taxa in samples collected near the surface in August 1994.

<table>
<thead>
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<th>Coastal Stations</th>
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<th>Nearfield Stations</th>
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<th>Cape Cod Bay Stations</th>
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<td></td>
<td>F13P</td>
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</tr>
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Units are millions of cells/L and rankings are given in parentheses.
Table 4-1b. Abundance of the top five dominant phytoplankton taxa in samples collected near the chlorophyll maximum in August 1994.

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<th>Coastal Stations</th>
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<th>Nearfield Stations</th>
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<th>Cape Cod Bay Stations</th>
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<td>F23P</td>
<td>N01P</td>
<td>N04P</td>
<td>N07P</td>
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Units are millions of cells/L and rankings are given in parentheses.
Table 4-2a. Abundance of all identified taxa in screened (20 um) samples collected near the surface in late August 1994.

<table>
<thead>
<tr>
<th>Coastal Stations</th>
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Units are cells/L
Table 4-2b. Abundance of all identified taxa in screened (20 um) samples collected near the chlorophyll maximum in late August 1994.

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<td>Dinophysis Acuminata</td>
<td>10</td>
<td>35</td>
</tr>
<tr>
<td>Dinophysis Caudata</td>
<td>18</td>
<td>13</td>
</tr>
<tr>
<td>Dinophysis Norvegica</td>
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</tr>
<tr>
<td>Dinophysis SPP.</td>
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</tr>
<tr>
<td>Diplopsalis SPP.</td>
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</tr>
<tr>
<td>Eutreptia/Euteuptiella SPP.</td>
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<td>3</td>
</tr>
<tr>
<td>Gyrodinium Spirale</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>Gyrodinium SPP.</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Heterosigma Akashiwo</td>
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<td>35</td>
</tr>
<tr>
<td>Pediasstrum Spp. Colony</td>
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<td>3</td>
</tr>
<tr>
<td>Prorocentrum Micans</td>
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</tr>
<tr>
<td>Prorocentrum Triestinum</td>
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</tr>
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<td>Protoperidinium Bipes</td>
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<td>Protoperidinium Breve</td>
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<tr>
<td>Protoperidinium Depressum</td>
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<tr>
<td>Protoperidinium Spp.</td>
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<tr>
<td>Protoperidinium Steinii</td>
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<td>20</td>
</tr>
<tr>
<td>Scripsiella Trochoidea</td>
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<tr>
<td>Staurastrum Spp.</td>
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<td>Tintinnids</td>
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</tr>
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<td>Tintinnids (Hyaline)</td>
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<td>Unid. Athecate Dinoflagellate</td>
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<tr>
<td>Unid. Thecate Dinoflagellates</td>
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<td>8</td>
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Units are cells/L
Table 4-3. $^{14}$C production (mg C m$^{-2}$ d$^{-1}$) estimated for euphotic layer at BioProductivity stations F23P and N16P in late August 1994.

<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>Water depth (m)</td>
<td>24.5</td>
<td>21.5</td>
<td>35.5</td>
<td>38.5</td>
</tr>
<tr>
<td>$Z_{0.5%10}$ (m)</td>
<td>8.5</td>
<td>10.5</td>
<td>27.5</td>
<td>28.0</td>
</tr>
<tr>
<td>Sample depth (m)</td>
<td>2.2  5.8  11.7  17.0</td>
<td>2.5  5.2  8.6  12.7</td>
<td>2.7  7.6  18.4  25.2</td>
<td>2.2  8.4  18.9  28.8</td>
</tr>
<tr>
<td>Rate (mg C m$^{-2}$ d$^{-1}$)</td>
<td>950  663  327  379</td>
<td>837  825  843  657</td>
<td>1004  600  956  787</td>
<td>2377  804  567  946</td>
</tr>
<tr>
<td>Model$^1$</td>
<td>W     W     W     W</td>
<td>W     W     W     W</td>
<td>W     W     P     P</td>
<td>W     W     P     P</td>
</tr>
<tr>
<td>$P_{SB}$ or $P_{MAX}$$^2$</td>
<td>9.24  8.92  5.21  7.31</td>
<td>14.04 12.18 11.58 11.49</td>
<td>5.35  3.87  7.25  4.87</td>
<td>12.05  4.31  3.13  5.26</td>
</tr>
<tr>
<td>$\sigma^2$</td>
<td>1.220  0.160  0.050  0.040</td>
<td>0.054  0.065  0.076  0.040</td>
<td>0.076  0.031  0.050  0.065</td>
<td>0.213  0.063  0.072  0.150</td>
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<tr>
<td>$\beta^4$</td>
<td>-     -     -     -</td>
<td>-     -     -     -</td>
<td>-     -     0.002  0.002</td>
<td>-     -     0.002  0.005</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 4-1. Surface temperature (°C) in the study area in late August 1994. Data are from the surfacemost sample at all farfield survey stations, including the P stations within the nearfield grid (Appendix A).
Figure 4-2. Surface salinity (PSU) in the study area in late August 1994. Data are from the surfacemost sample at all farfield survey stations, including the P stations within the nearfield grid (Appendix A).
Figure 4-3. Surface beam attenuation (m$^{-1}$) in the study area in late August 1994. Data are from the surfacemost sample at all farfield survey stations, including the P stations within the nearfield grid (Appendix A).
Figure 4-4. Surface in situ fluorescence (as µg Chl L⁻¹) in the study area in late August 1994. Data are from the surfacemost sample at all farfield survey stations, including the P stations within the nearfield grid (Appendix A).
Figure 4-5. Surface dissolved inorganic nitrogen (DIN, μM) in the study area in late August 1994. Data are from the surfacemost sample at all farfield survey stations, including the P stations within the nearfield grid (Appendix A).
Figure 4-6. Surface nitrate (NO$_3$, $\mu$M) in the study area in late August 1994. Data are from the surfacemost sample at all farfield survey stations, including the P stations within the nearfield grid (Appendix A).
Figure 4-7. Surface phosphate (PO$_4$, µM) in the study area in late August 1994. Data are from the surfacemost sample at all farfield survey stations, including the P stations within the nearfield grid (Appendix A).
Figure 4-8. Surface silicate (SiO$_4$, µM) in the study area in late August 1994. Data are from the surfacemost sample at all farfield survey stations, including the P stations within the nearfield grid (Appendix A).
Figure 4-9. Map showing position of five standard transects for which vertical contour plots were produced in Figures 4-10 and 4-11.
Figure 4-10a. Vertical section contours for standard transects (see Figure 4-9) on Survey W9411. The data used to produce the contours are from high-resolution continuous vertical profiles taken from the downcast at each station.
Figure 4-10b. Vertical section contours for standard transects (see Figure 4-9) on Survey W9411. The data used to produce the contours are from high-resolution continuous vertical profiles taken from the downcast at each station.
Figure 4-10c. Vertical section contours for standard transects (see Figure 4-9) on Survey W9411. The data used to produce the contours are from high-resolution continuous vertical profiles taken from the downcast at each station.
Figure 4-10d. Vertical section contours for standard transects (see Figure 4-9) on Survey W9411. The data used to produce the contours are from discrete bottle samples (Appendix A).
Figure 4-11. Vertical section contours for the Cape Ann - Stellwagen transect (see Figure 4-9) on Survey W9411. 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 4-12a. Scatter plots of data acquired by in-situ sensor package during vertical casts at all farfield and nearfield stations occupied in late August 1994. Chlorophyll is estimated from in-situ fluorescence. Circled areas are Boston Harbor stations.
Figure 4-12b. Scatter plots of data acquired by *in-situ* sensor package during vertical casts at all farfield and nearfield stations occupied in late August 1994. Chlorophyll is estimated from *in-situ* fluorescence. Circled areas are Boston Harbor stations.
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Figure 4-14c. PO₄ and SiO₄ vs. depth in late August 1994.
Figure 4-15a. Scatter plots of nitrogen forms vs. $\text{PO}_4$ in late August 1994. Lines show constant proportions of nitrogen relative to phosphorus.
Figure 4-15b. Scatter plots of nitrogen forms vs. SiO$_4$ in late August 1994. Lines show constant proportions of nitrogen relative to silicate.
Late August (W9411)

**Figure 4-16a.** DIN vs. salinity in late August 1994.
Figure 4-16b. NH$_4$ and NO$_3$ vs. salinity in late August 1994.
Figure 4-16c. \( PO_4 \) and \( SiO_4 \) vs. salinity in late August 1994.
Figure 4-17. Nitrogen forms vs. salinity in late August 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 4-18. Total phytoplankton abundance vs. chlorophyll (extracted samples) at P stations in late August 1994.
Figure 4-19. Total phytoplankton abundance, by taxonomic group, near the surface of P stations in late August 1994.

Phytoplankton - August 1994
(Surface)

Millions of Cells per Liter

Station

F01P  F02P  F13P  F23P  N01P  N04P  N07P  N10P  N16P  N20P

Diatoms  Dinoflag  Microflag  Others
Phytoplankton - August 1994
(Chlorophyll Maximum)

Figure 4-20. The total phytoplankton abundance, by taxonomic group, near the chlorophyll maximum of P stations in late August 1994.
Figure 4-21. Zooplankton abundance vs. average chlorophyll concentration (extracted samples; n=4 per station) for late August 1994.
Figure 4.22. Zooplankton abundance, by groups, at P stations in late August 1994.
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Figure 4-23b. Scatter plots of data acquired by in situ sensor package during vertical casts for nearfield survey in late August 1994. Chlorophyll is estimated from in situ fluorescence.
Figure 4-24a. Vertical section contours for nearfield standard transects (view towards Boston Harbor) on Survey W9411. 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 4-24b. Vertical section contours for nearfield standard transects (view towards Boston Harbor) on Survey W9411. 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 4-24c. Vertical section contours for nearfield standard transects (view towards Boston Harbor) on Survey W9411. 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 4-24d. Vertical section contours for nearfield standard transects (view towards Boston Harbor) on Survey W9411. 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 EARLY SEPTEMBER 1994 NEARFIELD SURVEY (W9412)

5.1 Distribution of Water Properties from Vertical Profiles

Vertical profiles were obtained at all 21 nearfield stations on September 8 (Appendix B). Review of vertical profiles revealed that significant cooling and mixing had occurred in the surface layer since August 26. Shallow stations had nearly uniform vertical profiles of temperature, salinity, and density. In general, the surface layer had deepened considerably since the previous survey and a weak pycnocline was now present from >20 to 35-40 m, with a distinct bottom layer present at >40 m depth only at the deepest stations on the eastern side of the nearfield. Scatter plots of the in-situ sensor data show a strong coherence across stations and a small dispersion among the T-S signature of the samples (Figure 5-1a). Salinity at most sampling points was near 31.9 PSU and the temperature was near 15°C. At only a few points, which represented pycnocline and deeper water, was salinity >32 PSU and temperature <11°C. Associated with mixing and deepening of the surface layer, the minimum surface salinity increased relative to late August and values in early September were mostly between 31.5 and 32 PSU. It was interesting to note that the estimated mean salinity in the nearfield in early September (31.91 PSU) was similar to that estimated for early August (31.82 PSU) or late August (31.85 PSU). This relative temporal stability in mean salinity provides evidence that intrinsic processes, such as within-field vertical mixing, are sufficient to explain observed changes in vertical structure and, therefore, secondarily indicates that horizontal advections from outside the nearfield are not necessary to explain the observed profile change, even though such extrinsic processes may have occurred.

Due to the small range in salinity in early September, no pattern of beam attenuation with salinity was discernible (Figure 5-1a). In general, the range for beam attenuation was narrow; some near-bottom increases were once again indicated (Appendix B).

The chlorophyll concentration vs. depth profile displayed a broad mid-depth peak (<3 µg L⁻¹) at 10-20 m. Note that such peaks generally occurred in spite of a physically uniform surface layer.
structure. In contrast to late August data, early September near-surface chlorophyll concentrations were consistently lower than those observed in the subsurface maximum. Chlorophyll concentrations decreased below ~20 m, a depth coinciding with the top of a weak pycnocline.

DO saturation was very uniform and generally near 100% between the surface and 20 m. Undersaturation in surface waters was only noted at stations N10P and N11 (Figure 5-1b and Appendix B); these stations receive tidally exchanged water from the Harbor inshore, but without a measurement from a Harbor station, one can only speculate on an inshore source for lower DO water. As for other parameters, DO saturation decreased below 20 m into pycnocline and bottom-layer waters. Lowest saturation was detected in the deepest bottom water on the eastern side of the nearfield, where values such as 65% saturation and DO concentrations < 6 mg L\(^{-1}\) were recorded.

With two exceptions, DIN concentrations were very low in the surface water layer and then increased almost linearly with depth (Figure 5-2). From ~20 m to 50 m, DIN concentrations increased from ~0.5 to 10 \(\mu\)M. The exceptional stations were in the southwestern corner of the nearfield (stations N10P and N11), the same area in which surface water undersaturation of DO occurred (see above). Most of the enrichment in surface water at these stations was due to \(\text{NH}_4\), but slight elevation of NO\(_3\) was also noted (Figure 5-2b). As with DO undersaturation, a predominance of \(\text{NH}_4\) is generally indicative of Harbor water. The increase in DIN concentration with depth was virtually all due to an increase in NO\(_3\) (Figure 5-2b).

Although salinity across the nearfield was within a fairly narrow range, nutrient-salinity plots nevertheless revealed expected patterns (Figure 5-3). The main feature is the ascending “arm” of nutrient concentrations as salinity increases, a pattern that reflects the concomitant increase in salinity and nutrients in the pycnocline within bottom water (DIN, NO\(_3\), PO\(_4\), and SiO\(_4\), but not NH\(_4\); Figures 5-3a,b,c). The higher nutrient concentrations observed at stations N10P and N11 were found at lower salinity and thus there appears a fragment of the typical descending “arm” of nutrients at low to intermediate salinity, an appearance that provides further confirmatory evidence of Harbor export in the southwestern corner of the nearfield where tidal interactions are strong (Kelly and Albro, 1994; Kelly, 1994).
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. A uniform surface layer, about 20 m thick (~15-16°C), covered the entire nearfield (Figure 5-4a). The thermocline generally extended to the bottom so that, except for the eastern side of the field, most of the water column was within the surface mixed layer. Contoured sections of salinity (Figure 5-4b) showed less uniform layering and more patchiness, but the variations in salinity were very slight and most of the readings were near 31.9 PSU. Deepwater salinity (>40 m) along the Outer Eastern Transect was >32.2 PSU. The lowest salinity, <31.6 PSU throughout the water column, was measured at station N10P.

Chlorophyll concentrations were relatively low and geographic trends were largely lacking (Figure 5-4c). At most stations, a subsurface peak (>2 µg L⁻¹) was detected at ~5-10 m to the base of the surface mixed layer (20 m). The 1% light level, one definition of the bottom limit of the photic zone (see Appendix B), generally was in the 10-20 m range, more commonly shallower on the western side of the field and grading to 20 m or more at most eastern stations. The photic zone was particularly shallow (~5 m) at station N10P, which had relatively high turbidity, as indicated by beam attenuation values approaching 2 m⁻¹, compared to other stations where beam attenuation was typically near 1 m⁻¹. No subsurface chlorophyll peak was detected at stations N10P, N11, and N12 along the Outer Western Transect and chlorophyll concentrations never reached 2 µg L⁻¹.

Except for station N10P, surface layers throughout the nearfield were depleted in DIN to 20 m, the depth of the 15°C isotherm that marked the bottom of the surface mixed layer, as well as the extent of the photic zone (Figure 5-4d). Below 20 m, DIN increased and reached peak values in high salinity water near the bottom of deepwater, eastern stations. The patterns shown in Figures 5-4c and 5-4d confirm that water at station N10P was primarily responsible for the appearance of the descending arm on the DIN vs. salinity plot (Figure 5-3) and, furthermore, once again lead to the suggestion that there is export of fresher water and nutrients from inshore to the southwest corner of the nearfield. Interestingly, at this early September 1994 survey, higher DIN (and other nutrients) in the southwest corner was not accompanied by elevated chlorophyll concentrations. As suggested by
observations on turbidity and light above, there may be a strong connection between reduced light availability and low chlorophyll at station N10P, with turbidity creating a limitation on chlorophyll growth even though nutrients were relatively available.
Figure 5-1a. Scatter plots of data acquired by *in situ* sensor package during vertical casts for nearfield survey in early September 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 early September 1994. Chlorophyll is estimated from in situ fluorescence.
Figure 5-2a. DIN vs. depth in early September 1994.
Figure 5-2b.  $\text{NH}_4$ and $\text{NO}_3$ vs. depth in early September 1994.
Figure 5-2c.  PO₄ and SiO₄ vs. depth in early September 1994.
Early September (W9412)

Figure 5-3a. DIN vs. salinity in early September 1994.
Figure 5-3b. NH₄ and NO₃ vs. salinity in early September 1994.
Figure 5-3c. $PO_4$ and $SiO_4$ vs. salinity in early September 1994.
Figure 5-4a. Vertical section contours for nearfield standard transects (view towards Boston Harbor) on Survey W94I2. 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 W9412. 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 W9412. 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 W9412. 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 RESULTS OF LATE SEPTEMBER 1994 NEARFIELD SURVEY (W9413)

6.1 Distribution of Water Properties from Vertical Profiles

Vertical profiles were obtained at all 21 nearfield stations on September 28, almost three weeks after the early September survey (Appendix B). Many vertical profiles showed no distinct layering of temperature (T), salinity (S), or density (σT); rather, there was a gradual increase in S and (σT) and a gradual decrease in T. At all of the deepwater stations on the eastern track of the nearfield, however, a remnant of the summer two-layer stratified system was detected, with a pycnocline found at about ~20-35 m. Moreover, scattered throughout the field, there were near-bottom changes in profiles that revealed a weak bottom water layer intermittently present in late September.

Scatter plots of the in-situ sensor data show fairly strong coherence across stations in the T-S signature (Figure 6-1a). Relative to early September, the surface temperatures remained stable and the deepest bottom water warmed slightly; the minimum bottom water temperature was 10.5°C compared to 9.7°C in early September. The mean salinity in late September (31.9 PSU) was the same as in early September; the range had expanded only slightly at both the maximum and minimum ends of the distribution.

Beam attenuation (turbidity) was regularly higher in surface water; thus, the pattern with salinity approximated an exponential decrease in beam attenuation with increasing salinity (Figure 6-1a). Turbidity was, in part, a function of chlorophyll concentration (Figure 6-1a); in general, turbidity doubled across a chlorophyll range of about 0.5-7 μg L⁻¹. Peak chlorophyll concentrations were often found below the surface; but rather than being concentrated at 15-25 m, as was noted for most of the late summer stratified period, the chlorophyll maximum was usually within the top 10 m. The concentration of chlorophyll was generally high (>4 μg L⁻¹) throughout the upper 15 m.

DO was generally 100-110% of saturation near the surface (Figure 6-1b). The fact that more frequent DO supersaturation occurred in late September, rather than in early September (cf. Figure
5-1b), is consistent with a finding of elevated near-surface chlorophyll concentrations in late September compared to early September. Enhanced chlorophyll and supersaturation, even mild (5-10%), suggest an enhanced net production and accumulation of phytoplankton biomass in the nearfield during September 1995. As found in early September, DO undersaturation in surface water occurred at stations in the southwestern corner (stations N10P, N11, and N12). In early September, a deep surface layer (0-20 m) was uniformly near 100% DO saturation. In contrast, in late September, DO often began its decline with depth near a shallow chlorophyll maximum (10 m). Thus, many DO profiles decline almost as a linear function of depth. Characteristically, DO measurements below 30 m were <80% of saturation. A number of readings were <70% saturation and the lowest DO reading (5.4 mg L⁻¹) was well below 6 mg L⁻¹, the state standard.

Nutrient patterns over depth resembled those for DO; between ~10 m and the bottom, nutrient concentrations always increased linearly with increasing depth. For example, only a thin surface layer with depleted DIN was evident (Figure 6-2a). As in September, several near-surface samples (the southwestern corner stations) were enriched in DIN and other nutrients (Figure 6-2b,c). Maximum bottom water DIN concentrations were 10.9 μM, and maximum PO₄ and SiO₂ concentrations were 1.08 and 12.5 μM, respectively. These maximum bottom-water concentrations in late September were similar to or slightly greater than concentrations measured in early September (9.6 μM DIN, 1.08 μM PO₄, and 11.4 μM SiO₂), suggesting that subpycnocline bottom waters were only slowly accumulating nutrients from bottom-layer and sediment regeneration processes during September.

The late September nutrient-salinity plots (Figure 6-3a,b,c) showed more scatter than plots of early September data. All other nutrient trends noted in early September (Section 5) were the same in late September.
6.2 Water Quality Variability in the Nearfield

Vertical contours of temperature, salinity, chlorophyll (as measured by fluorescence), and dissolved inorganic N are presented in Figure 6-4. The temperature sections are remarkably similar to those generated for the previous survey in early September (cf. Figure 6-4a and 5-4a). The only subtle difference between early and late September was that the deepest water (> 40 m) was slightly warmer in late September. The surface layer again was generally defined by the 15°C isotherm, which was located at about 20 m throughout the field. In late September, salinity layering appeared to be more consistent than in early September and, once again, the lowest salinity (< 31.6 PSU) was observed at station N10P (Figure 6-4b).

In late September, chlorophyll concentrations were higher (> 4 μg L⁻¹) at station N10P than in early September, but concentrations were more elevated (> 5 μg L⁻¹, sometimes > 6 μg L⁻¹) within the surface 10 m at virtually all other stations. A concentrated chlorophyll layer, several meters thick, appeared to grade from the surface at station N01P (northwest corner) to about 5-10 m depth down the entire center of the field along the eastern edge (e.g., stations N05 and N06). This field-wide enhancement of chlorophyll marked a fall bloom phenomenon in 1994; whether the survey captured initiation, mid-bloom, or late-bloom conditions may become clearer as the data for the next survey in mid-October are examined.

Surface layers throughout most of the nearfield remained low in DIN (Figure 6-4d) since early September and the sections for DIN in late September were similar to early September (cf. Figure 6-4d vs. Figure 5-4d). DIN in late September was again elevated at the southwestern corner of the nearfield, particularly at station N10P, but also at stations N11 and N09. In late September, bottom water was typically more enriched in DIN than in early September.
Figure 6-1a. Scatter plots of data acquired by *in situ* sensor package during vertical casts for nearfield survey in late September 1994. Chlorophyll is estimated from *in situ* fluorescence.
Figure 6-1b. Scatter plots of data acquired by *in situ* sensor package during vertical casts for nearfield survey in late September 1994. Chlorophyll is estimated from *in situ* fluorescence.
Figure 6-2a. DIN vs. depth in late September 1994.
Figure 6-2b. NH$_4$ and NO$_3$ vs. depth in late September 1994.
Figure 6-2c. $\text{PO}_4$ and $\text{SiO}_4$ vs. depth in late September 1994.
Figure 6-3a. DIN vs. salinity in late September 1994.
Figure 6-3b. NH₄ and NO₃ vs. salinity in late September 1994.
Figure 6-3c. PO$_4$ and SiO$_4$ vs. salinity in late September 1994.
Figure 6-4a. Vertical section contours for nearfield standard transects (view towards Boston Harbor) on Survey W9413. 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 6-4b. Vertical section contours for nearfield standard transects (view towards Boston Harbor) on Survey W9413. 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 6-4c. Vertical section contours for nearfield standard transects (view towards Boston Harbor) on Survey W9413. 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 6-4d. Vertical section contours for nearfield standard transects (view towards Boston Harbor) on Survey W9413. The data used to produce the contours are from discrete bottle samples taken at each station during the nearfield sampling day (Appendix A).
7.0 DISCUSSION OF THE LATE SUMMER/EARLY FALL
PERIOD OF SURVEYS

7.1 Water Properties

7.1.1 Variability at the Regional Scale

During the months covered by this report, the regional scale was surveyed only once in late August (see Section 4), so temporal variability on the Bay-wide scale was not assessed within the late summer period. Comments here relate to spatial variability.

Because of continued strong stratification, the main variations in physical properties at stations in the Bays were in the vertical dimension. However, there were also strong gradients in temperature, salinity, and turbidity from Boston Harbor to the nearshore coastal zone. There were noticeable, but less defined, geographic trends in physical properties from the coastal zone to offshore waters. In terms of surface water properties, Massachusetts Bay and Cape Cod Bay were similar.

Isopleths of surface water turbidity and chlorophyll extended southward along the coast from Boston Harbor to Marshfield; these isopleths essentially followed the surface water density isopleths, which paralleled the shoreline throughout Massachusetts Bay. The spatial distribution of surface water density, salinity, and turbidity is consistent with the concept of export of nutrient-enriched water from Boston Harbor; this water mixes with Bay water and is transported southward. One hypothesis proposed is that, as turbidity is diluted and water is constrained within the surface layer by strong thermal stratification, elevated chlorophyll concentrations may develop. This may explain the maximum chlorophyll concentrations observed at some stations (i.e., those within 10-15 km of the coast and >10 km south of the Harbor).

With the inclusion of new monitoring stations (stations F30B and F31B) within Boston Harbor in 1994 monitoring surveys, differences in Harbor and Bay water quality and seasonal cycles have
become more evident. For example, in late August, consistently higher levels of turbidity were detected at all Harbor and Harbor-edge stations than at stations in the Bay. The Harbor's salinity range was distinctly lower than in the Bay, and it was apparent that temperatures were often cooler in the Harbor than in surface water in most Bay locations. Attributable in part to stratification (Bay) vs. active mixing in the Harbor, the observation on temperature may illustrate a basic difference in the response of the two water bodies to shorter days and cooler air temperatures that signal the start of the fall season.

The 1994 surveys also included new water column monitoring stations across the northeastern boundary between Massachusetts Bay and the Gulf of Maine. Boundary conditions will briefly be mentioned here. Previously, the most seaward stations were in deep offshore water within Stellwagen Basin; the new 1994 stations (F26, F27B, and F28) were established to provide more data to describe the open northern boundary of the Bay, particularly for use in setting boundary conditions for the Bays Eutrophication Model being developed for the MWRA (HydroQual and Normandeau, 1995). During the late summer survey in August 1994, the temperature and salinity signature at station F26 near Cape Ann resembled other coastal stations in Massachusetts Bay, including those just outside Boston Harbor. In general, turbidity and chlorophyll were slightly lower than at most coastal stations and the western edge of the nearfield, but similar to much of the eastern side of the nearfield. As was characteristic for most of the Bay stations, dissolved nutrient concentrations in surface layers were generally depleted. In contrast to station F26, stations F27B (outside the Bay) and F28 (on Stellwagen Bank), although low in surface water nutrients, were characterized more by “oceanic” conditions of higher salinity, clearer water, and low chlorophyll concentrations. Compared to previous data (1992-1993) from the most northeastern MWRA monitoring station, in late August 1994, surface water conditions at stations F27B and F28 were characteristically similar to conditions at station F22, whereas station F26 was more typical of coastal conditions. With respect to deep water (>50 m), comparison of water characteristics in basins inside (e.g., stations F22 and F12 in Stellwagen Basin) and outside (station F27B east of Stellwagen Bank) of the Bay revealed that deep water in Stellwagen Basin typically was colder and less saline, but similar to or higher in DIN concentrations than the basin water east of Stellwagen Bank.
7.1.2 Variability in the Nearfield

Over the period of surveys in August and September, there was a high degree of consistency in the vertical and geographic patterns of physical properties of the water column in the nearfield. The 15°C isotherm often marked the top of the sharp pycnocline separating surface and bottom layers, and this consistently was found at about 10-20 m. Between August and September, the pycnocline deepened. In September, the shallower western side of the nearfield was almost completely mixed, with only a vestige of the warm season two-layer system remaining. The eastern half of the nearfield was still thermally stratified in late September. Surface water at the western edge of the nearfield was cooler than other parts of the field during August, but not in September. This pattern partially illustrates a difference and the time lag in temperature cycles mentioned above for the Harbor relative to the Bay. During this season, the geographic pattern for temperature in bottom water is the reverse of that for surface water; bottom water at the shallow western stations was consistently warmer (2-4°C) than at the eastern stations. The cross-nearfield bottom water temperature gradient was most marked in late September as stratification began to deteriorate at the shallower side of the field. With respect to salinity, there was a consistent pattern of vertical layering, though not as acute as thermal layering (which established the density layering). A similar average salinity was maintained in the field over the course of the four surveys. The maximum salinity (>32.2 PSU) was relatively invariant and always found in the deepest water. Geographically, the other striking and constant feature was relatively low salinity in surface water on the western side of the nearfield. Salinity minima were always observed at station N10P in the southwestern corner of the nearfield. A “lens” of low-salinity water was often found extending from station N10P to stations N11 and N12, but rarely to station N01P in the northwest corner of the field. In general, a lower-salinity surface water mass was biased to the south outside of Boston Harbor. However, it cannot be determined whether this consistent pattern reflects a general southward drift of surface water throughout the period or whether it is just a feature that emerges due to each station’s relative distance to the neighboring shoreline.
7.1.3 Special Features: Comparison of 1994 with Previous Years

Figure 7-1 shows the surface temperature in the nearfield for all of 1993 and for 1994 through September. Interannual differences for winter-spring-early summer have been discussed in the three previous periodic water column reports for 1994 and comments here focus on the late summer period. Relative to 1993, the temperature in nearfield surface waters was apparently more restricted in each survey during August and September 1994. A seasonal surface water maximum regularly has been detected in August (1992-1993) and this was again noted in 1994. In September of each year during the 1992-1994 period, the average and maximum surface water temperature was lower than in August. In 1994, the feature that is distinct from 1992 and 1993 is that, in addition to the extremely narrow temperature range in both early and late September, the average surface temperature was near 16°C. Compared to 1993 (Figure 7-1), when temperatures were generally 14°C or less, the nearfield surface layer in late September 1994 was uniformly very warm. The seasonal changes in surface water temperature are regulated by climate and the interannual patterns are subject to interannual variations in climate as well as local weather. Nevertheless, as noted above, the surface mixed layer was deeper in September than in August. The vertical profiles for late September were similar to early September and indicate little overall change in physical structure during the month, but minor horizontal and vertical mixing during September could have homogenized the surface layer across the field.

Concomitant with higher surface layer temperatures and more defined two-layer stratification, was a continued decline of DO concentrations in nearfield bottom waters that had been initiated in early summer (Figure 7-2a). The commonly observed progressive and uninterrupted summer decline in bottom water DO began earlier in the summer of 1994 than in previous years; Kelly et al. (1995) suggested that uncharacteristically low June 1994 bottom waters might be a harbinger of late-season DO concentrations and they forecast that the state standard of 6 mg L⁻¹ could be exceeded before fall mixing vented the bottom water. By late September, the DO concentrations of a number of bottom water samples were at or below 6 mg L⁻¹. The DO concentration minimum in late September 1994 was more than 1 mg L⁻¹ below readings that were made in 1993. We reexamined the calibration between Winkler titration and DO sensor reading, the latter being the basis for data in Figure 7-1.
Appendix A shows the calibration for late September (survey W9413) and confirms that it was highly significant ($R^2 > 0.9$, $n=29$). Using a regression with the intercept set to zero, the slope indicate that the uncalibrated sensor and Winkler readings were, on average, within 10% of each other. Some sensor readings across the field were lower ($< 6 \text{ mg L}^{-1}$) than the lowest Winkler determination ($6.24 \text{ mg L}^{-1}$), but low readings were also made where Winkler determinations were not performed; this creates the uncomfortable situation where the calibration regression is being used beyond the range of values on which it is based. Even with a strong regression, the regression residuals illustrate significant uncertainty in the predictability of individual points. Some variability in individual points may relate to differences in sampling (retrieved Niskin bottom sample and subsequent Winkler titration vs. time-averaged value of the in-situ sensor at a time interval bracketing the closing of the Niskin bottle) and can not necessarily be attributed solely to the method of DO determination. In general, one may assume an uncertainty, on average, of $< \pm 10\%$ in the sensor-derived values which, at lowest DO concentrations measured, translate to about $\pm 0.5 \text{ mg L}^{-1}$. Considering this uncertainty, the DO concentrations in late September are still markedly low compared to previous years and are near, if not below, the state standard.

The range in bottom layer DO concentrations across the nearfield in late September 1994 was broad, about $2 \text{ mg L}^{-1}$. It was noted that the ranges, but not the minima, for late September 1993 and 1994 overlapped (Figure 7-2a). In part, the scatter and range could be a result of a deep pycnocline and a consequence of using depths $> 20 \text{ m}$ in Figure 7-2a, thus including some late September 1994 samples collected between 20 and 30 m; the DO concentrations for these samples were higher because they were not strictly within the bottom layer. We examine the possibility of such an artifact in Figure 7-2b, where DO data for late September 1994 are shown for each station, but only for the near-bottom sample (characteristically $\sim 5 \text{ m}$ above bottom). The range for these near-bottom DO concentrations remained broad and included values between 5.4 and 7.3 $\text{ mg L}^{-1}$.

In addition to suggesting that DO throughout most of the field was $< 6.5 \text{ mg L}^{-1}$, Figure 7-2b suggests some small-scale geographic variability in near-bottom DO that surpasses variability in thermal stratification regimes (Figure 7-2b). For example, the temperature trend from shore shows essentially progressively lower temperatures in bottom waters as the water column deepens, a trend
that reflects the continuum across the field from a nearly completely mixed water column inshore to one still strongly stratified offshore. Bottom water DO shows a tendency to be higher where higher temperatures were recorded (northwest corner at stations N01P and N02, and near the southwest corner at station N19) and low where temperatures were low (eastern side of the field). Of interest is that the highly progressive geographic trend in temperature is not mimicked by DO (as concentration, shown, or as percent saturation, not shown). If real, the mismatch is intriguing; we can only speculate that heterogeneity in near-bottom DO, relative to temperature, might result from undulations in bathymetry that affect water motion and particle deposition, potentially creating patchiness in DO uptake processes such as sediment oxygen demand.

7.2 Water Column Nutrient Dynamics

7.2.1 Vertical Structure

Bay stations were strongly stratified in August but, by late September, shallow water areas began to mix as indicated by profiles at western nearfield stations. In general, nutrient-depth patterns were distinct throughout the Bay during this period, with relative, if not absolute, depletion of nutrients in surface layers and increasing concentrations with depth from the pycnocline to the bottom.

7.2.2 Inshore-Offshore Gradients

Nutrient concentrations followed typically described inshore-offshore trends, vertically as dictated by stratification and horizontally, especially in the form of a strong nutrient concentration gradient with distance from Boston Harbor. Higher nutrient concentrations (dissolved and total forms) were associated with less saline inshore waters and lower nutrient concentrations were characteristic of more saline offshore waters.
In late August, nutrient concentrations in Boston Harbor were high (∼20 μM DIN). The high concentrations, detected at new 1994 stations located within the Harbor proper (stations F30B and F31B), contrast with negligible concentrations (0.3-4 μM DIN) measured in the Harbor in June 1994 (Kelly et al., 1995) and are comparable to or greater than winter (pre-bloom) concentrations in February 1994 (Kelly et al., 1994a). Compared to early summer, elevated concentrations of DIN in late August are indicative of inefficient use of nutrients by plankton in the Harbor. By late August, with decreasing temperature and light, the Harbor appeared to be entering the biologically unproductive fall-winter season when nutrients become rapidly accumulated in the water because nutrient assimilation and primary production rates decrease while heterotrophic regeneration rates are still high. From this perspective, it is interesting that these unassimilated Harbor nutrients, exported to stratified near-coastal waters, appeared to stimulate chlorophyll in a coastal plume outside the Harbor. These observations suggest that, in some years, annual ecological cycles and annual temperature cycles in the Harbor may be disjunct from cycles in the Bay.

7.2.3 Special Features: Comparison of 1994 with Previous Years

In previous years (1992 and 1993), the range in surface water DIN concentrations has typically decreased in summer when mostly low and often undetectable DIN concentrations are characteristic. In late summer/early fall, the DIN concentration range and mean typically increase (e.g., Figure 7-3). In contrast, from May to late September 1994, although many concentrations were still typically low, surface-layer DIN concentrations in some samples from each nearfield survey were >6 μM. Consequently, the DIN concentration range was typically broader over the 1994 summer than in previous years. To examine the possibility that occasional high concentrations were found because the normal N-depleted surface layer was shallower in 1994 than in previous years, we plotted DIN concentrations for the surface 10-m and 15-m layers. Results did not different greatly from results shown in Figure 7-3, which includes the top 20 m.
7.3 Biology in Relation to Water Properties and Nutrient Dynamics

7.3.1 Phytoplankton-Zooplankton Relationships

Figure 7-4 indicates a poor correspondence between zooplankton and phytoplankton counts. It should be noted that zooplankton counts were low in Cape Cod Bay and at station F13P in the coastal region off Cohasset where chlorophyll and phytoplankton counts were both elevated. Reduced counts in Cape Cod Bay were discussed in Section 4 and may be attributed to the presence of carnivorous meroplankton that prey on copepods. Zooplankton counts at station F13P were not unusually low in the absolute sense, only relative to phytoplankton. Such a condition could arise with an expected lag in the development of zooplankton populations in response to an episodic bloom of phytoplankton.

7.3.2 Chlorophyll, Phytoplankton Species, and Water Properties

Chlorophyll was higher in the surface 10 m at stations along the south shore from Cohasset to Marshfield, where extracted measurements were made, including stations from the nearfield (N10P on the nearfield survey), coastal (F13P), and offshore (F06) regions (Figure 7-5). At some locations in the coastal plume, both chlorophyll and total N (TN; ~20 μM) concentrations were relatively high. However, TN concentrations were high in Boston Harbor, where chlorophyll concentrations were not high. Subsequently, no overall relationship between TN and chlorophyll was observed (Figure 7-6).

Minor subsurface chlorophyll peaks were typically found from 10 to 20 m. Subsurface concentrations at the Cape Cod Bay stations were among the highest and deepest encountered (Figure 7-5). In addition to a slight distinction in the vertical distribution of chlorophyll, the phytoplankton community in Cape Cod Bay was identified (see Section 4) as compositionally different from Massachusetts Bay. Cape Cod Bay samples were less dominated by microflagellates, which are typical summer dominants in the Bays and, instead, were enhanced in diatoms. Two samples from the near-bottom layer (~20-27 m) at station F02P, were unusually high in SiO₄, both as absolute concentrations and relative to DIN (cf. Figure 4-15b). As noted in Section 4, SiO₄ was generally depleted in Cape Cod Bay surface
waters and, therefore, a relatively high flux of SiO₄ across the pycnocline could help to maintain diatom populations, especially at the subsurface chlorophyll maximum. Even so, removal of significant numbers of copepod grazers (e.g., Figure 7-4), by veliger and medusa predation or by any other mechanism, could also lead to enhanced diatom presence at Cape Cod Bay stations because many copepod forms feed selectively on diatoms and, thereby, can control their summer population levels. Thus, we postulate that both biological and geochemical mechanisms may be responsible for the noted phytoplankton differences in Massachusetts and Cape Cod Bays in late August 1994.

Table 7-1 summarizes temporal trends at one nearfield station in Massachusetts Bay during August and September 1994. Microflagellates and cryptomonads were consistently dominant. The remaining dominant taxa, excluding Gymnodinium and Prorocentrum (small dinoflagellates), were diatoms. Table 7-2 additionally shows that dinoflagellates were only present in very low numbers throughout the entire period. Diatom taxa varied through the period. They are typically responsible for fall near-coastal blooms in Massachusetts Bay and the taxa listed in Table 7-1 include previously recorded species typical of fall blooms. A wide variety of diatom species was noted in late September, when chlorophyll concentrations throughout much of the nearfield were enhanced relative to the rest of the late summer/early fall period.

7.3.3 Primary Production and Dark Respiration

The sampling strategy was designed to allow 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. Kelly et al. (1994e) presented a comparison of depth integration schemes and recommended that the composite profile scheme, as used in this report, be the standard for 1994.

Using the standard scheme, production rates at stations F23P and N16P in late August averaged 783 and 879 mg C m⁻² d⁻¹, respectively. Note that these rates are relatively low compared to other
rates for 1994 (Kelly et al., 1994b,c) and compared to maximum summer rates calculated from recent measurements (Kelly and Turner, 1995); nevertheless they are in the range of previous late summer measurements and appear to be commensurate with the fairly low levels of chlorophyll that were observed in late August 1994. The ranges for the two measurements at these stations overlapped; considering a discussion of uncertainties in production estimates (Section 4), the stations are not distinct in their integrated production rates, in spite of many differences in their environments. For example, reflecting the high turbidity in the Harbor, the extinction coefficient ($k$, see Section 2) was about 0.5-0.7 m$^{-1}$, compared to 0.18-0.19 m$^{-1}$ at station N16P. Thus, there was a photic zone in the Harbor that was <50% of that at the Bay station. Harbor station F23P is a dynamic, tidally well-mixed and nutrient-rich environment ($\sim 10 \mu$M DIN and 27 $\mu$M TN). In contrast, station N16P is nutrient-poor ($< 1 \mu$M DIN and $\sim 10 \mu$M TN) and stably stratified. The major similarity between these two stations was not environmental but biological — chlorophyll concentrations, total phytoplankton, and zooplankton densities were all slightly higher at station F23P and the gross taxonomic composition of the phytoplankton communities at the two stations was similar. However, the zooplankton community differed. Station F23P was dominated by an estuarine copepod, *Acartia tonsa*, as well as *Eurytemora*; in contrast, station N16P was dominated by small shelf-water copepods (*Oithona similis*, secondarily *Paracalanus parvus*). In the light of a basically similar phytoplankton community being exposed to a distinctly different set of environmental conditions and probably being part of a distinctly different food web, the basic similarity of the integrated water column rates at the two stations seems noteworthy.

How does the general similarity in integrated $^{14}$C production arise? The depth distribution of production was very different at the two stations (Figure 7-7). Most of the production at station F23P is achieved near the surface at high light levels, whereas production rates, though lower at the surface, are more constant from the surface to 15-20 m at station N16P. The difference in maximum surface rates reflects the fact that P-I curves yielded $P_{\text{max}}$ values that were higher, on average, at station F23P (e.g., for $n = 4$ incubations, an average rate of 7.7 and 12.3 on August 23 and 24 at station F23P compared to rates of 5.3 and 6.1 for the same days at station N16P; see Section 4). Note that a higher $P_{\text{max}}$ at a higher nutrient environment is consistent with ecological theory developed from chemostat and nutrient enrichment experiments. Thus, the modeled production
profiles follow trends expected for the differences in light and nutrients at the two stations. Though chlorophyll concentrations were slightly higher at station F23P, the mass of chlorophyll within the photic zone at station N16P was much greater (>2x) and this mass, more than concentration, primarily establishes the integrated rate in this case.

This examination of the modeled vertical profiles provides insight on how some environmental factors influence integrated production and reveals that, in this case, it is essentially coincidental that the integrated rates are similar. But it also illustrates an issue with use, via simple comparisons, of integrated production rates as a monitoring tool—when intended as warning tool, it can potentially produce “false negative” results in the sense that the environment (e.g., light, nutrients, stratification) can change substantially without a change in the integrated rate. It is notable that, in cases such as illustrated here, the underpinnings of the method (e.g., P-I curves, light profiles) that lead to estimates of an integrated value, accompanied by a thorough description of water quality conditions, can provide significant insight and understanding of the ecosystem.

Finally, a comment on respiration, the other component of water column metabolism. Dark respiration was measured at three stations (F24, N20P, and F19). Of prime interest, with respect to the discovery of low DO in September 1994, is how bottom water dark-respiration rates might compare to bottom water DO decline in late summer. This topic will be more fully explored in future reports to the MWRA that summarize annual and interannual results of baseline monitoring (1992-1994). The time-series approach to measuring dark respiration in 1994 has provided the best estimates to date on deep-water DO uptake and, as a monitoring tool, deep-water respiration was originally conceived to be useful in predicting and understanding DO status with the bottom layer during stratification. As described for late August (Section 4), dark respiration rates (2-day and 7-day incubations) tended to decrease with depth and were estimated to be in the range of 0.0008-0.003 mg O₂ L⁻¹ h⁻¹ in bottom water at stations N20P and F19. Assuming a rate of 0.0015 mg O₂ L⁻¹ h⁻¹, the DO decrease from the early August to the late September survey (seven weeks) is projected as 1.76 mg O₂ L⁻¹. To a first approximation, the projected decline is consistent with the average decline indicated from monitoring the nearfield’s bottom water over the same period.
7.3.4 Special Features: Comparison of 1994 with Previous Years

Temporal trends for chlorophyll in nearfield surface waters during 1993 and 1994 are shown in Figure 7-8. Water depths to 20 m are included. A late summer/early fall difference between 1994 and 1993 is clearly visible. In 1993, a spatially extensive fall diatom bloom, bearing local concentrations of 10-20 \( \mu g \) L\(^{-1}\), was a defining feature of the annual chlorophyll cycle (Libby et al., 1994; Kelly and Turner, 1995). In contrast, no such event had occurred by late September 1994. In 1992, sampling was not conducted in late September and the most intense chlorophyll concentrations of the fall bloom period may have been missed. Note that the mean and maximum surface layer chlorophyll concentrations in late September 1994 were higher than the three previous surveys in August and September, but peak concentrations were still < 8 \( \mu g \) L\(^{-1}\). Nevertheless, the late September chlorophyll concentrations are equivalent to any other previous period of the year, including any survey conducted during the winter-spring bloom.

7.4 Summary and Recommendations

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

In the late summer/early fall period, most areas of the Bays remained stratified. A main geographical distinction in water quality was noted between Boston Harbor stations and the Bay. The commonly observed nutrient concentration gradient with distance from the Harbor was strongly evident; moreover, data on physical, chemical, and biological parameters illustrated that the Harbor and Bay have different annual cycles, which were particularly disjunct during this season. Additionally, primary production measurements at a station in Boston Harbor and in the nearfield of Massachusetts Bay provided a case illustration that a similar integrated water column production can arise for different reasons and in very different environments.
With regard to other geographical features, monitoring data have repeatedly emphasized, from year to year, regional differences between Massachusetts and Cape Cod Bays. These differences have been noted during all seasons. In late August 1994, Cape Cod Bay stations were relatively depleted in copepods, possibly resulting from development of a predatory food chain. Regardless of the mechanism, which is unknown, the plankton community (phytoplankton and zooplankton) at stations in Cape Cod Bay was distinct from that observed at Massachusetts Bay and Boston Harbor stations.

The principal water quality feature during the August-September 1994 period is unquestionably the discovery of an uncharacteristically low DO concentration in nearfield bottom waters. DO levels realized by late September in near-bottom water at most of the nearfield stations approached or exceeded the state minimum standard of 6.0 mg L\(^{-1}\), a level not approached in the recent years of MWRA monitoring. This phenomenon had earlier been anticipated from June-July bottom-water DO monitoring data and had been forecast as a potential occurrence by projecting from estimates of the rate of DO decline during summer stratification in 1992 and 1993. Dark respiration rate measurements for bottom water in late August offer an additional means to uptake and project a DO decline for the late summer/early fall season and, to a first approximation, predicted a bottom water DO decline similar to that observed from early August to late September 1994.
Table 7-1. Abundance of top five dominant phytoplankton taxa in samples collected near the surface at station N10P in August and September 1994.

<table>
<thead>
<tr>
<th></th>
<th>Aug. 10</th>
<th>Aug. 23</th>
<th>Aug. 26</th>
<th>Sept. 8</th>
<th>Sept. 28</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASTERIONELLOPSIS GLACIALIS</td>
<td>0.158 (2)</td>
<td></td>
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<td></td>
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<tr>
<td>CERATAULINA PELAGICA</td>
<td></td>
<td>0.051 (3)</td>
<td>0.066 (4)</td>
<td>0.011 (4)</td>
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<td>CRYPTOMONADS</td>
<td>0.130 (3)</td>
<td>0.060 (2)</td>
<td>0.193 (3)</td>
<td>0.054 (2)</td>
<td>0.289 (2)</td>
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<tr>
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<td></td>
<td>0.020 (5)</td>
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</tr>
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<td>GYMNODINIUM SPP.</td>
<td></td>
<td></td>
<td></td>
<td>0.022 (5)</td>
<td>0.011 (4)</td>
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<td>LEPTOCYLINDRUS MINIMUS</td>
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<td></td>
<td></td>
<td>0.026 (3)</td>
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<tr>
<td>LITHODESMIUM (cf) UNDULATUM</td>
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<td></td>
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<td></td>
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<td>MICROFLAGELLATES</td>
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<td>0.534 (1)</td>
<td>0.923 (1)</td>
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<td>0.011 (4)</td>
<td>0.011 (4)</td>
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Units are millions of cells/L and rankings are given in parentheses.
Table 7-2. Abundance of all identified taxa in screened (20 um) samples collected near the surface at station N10P in August and September 1994.

<table>
<thead>
<tr>
<th>Taxa</th>
<th>Aug. 10</th>
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<th>Sept. 8</th>
<th>Sept. 28</th>
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<td>15</td>
<td>8</td>
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</tr>
<tr>
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<td>20</td>
<td>20</td>
<td>3</td>
<td></td>
</tr>
<tr>
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<td></td>
<td></td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>CERATIUM TRIPOS</td>
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<td>8</td>
<td>5</td>
<td>33</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td>15</td>
</tr>
<tr>
<td>DINOPHYYSIS CAUDATA</td>
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<td></td>
<td></td>
<td></td>
<td>13</td>
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<tr>
<td>DINOPHYYSIS NORVEGICA</td>
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</tr>
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<td>DIPLOPSALIS SPP.</td>
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Units are cells/L
Figure 7-1. Comparison of the nearfield region in 1994 to the annual cycle of 1993: temperature (°C).
Figure 7-2a. Comparison of the nearfield region in 1994 to the annual cycle of 1993: dissolved oxygen (mg L⁻¹).
Figure 7-2b. Comparison of near-bottom temperature (°C) and DO (mg L⁻¹) in the nearfield region in late September 1994. The grid shows the location of the twenty-one sampling stations. Near-bottom data are those from the deepest bottle sample at each station (Appendix A).
1993, Nearfield Stations

1994, Nearfield Stations

Figure 7-3. Comparison of the nearfield region in 1994 to the annual cycle of 1993: dissolved inorganic nitrogen (μM).
Late August (W9411)

Figure 7-4. Zooplankton abundance vs. phytoplankton abundance for late August 1994.
Figure 7-5. Chlorophyll (extracted) vs. depth for the study area in late August 1994.
Figure 7-6 Chlorophyll (extracted) vs. total nitrogen concentrations for the study area in late August 1994.
Figure 7-7. $^{14}$C production vs. depth at Bioproductivity stations F23P and N16P in late August 1994.
Figure 7-8.  Comparison of the nearfield region in 1993 to the annual cycle of 1994: chlorophyll (µg L⁻¹) as estimated from in situ fluorescence.
8.0 REFERENCES


8-1


