Water quality monitoring in Massachusetts and Cape Cod Bays: June and July 1994

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FINAL

WATER QUALITY MONITORING
IN
MASSACHUSETTS AND CAPE COD BAYS:
JUNE AND JULY 1994

by

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EXECUTIVE SUMMARY

This report is the third 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 one survey conducted during June and from two surveys conducted during July 1994. Each of these surveys included sampling at 17-21 stations in the nearfield area surrounding the future MWRA outfall diffuser about 15 km offshore in western Massachusetts Bay. The June survey was a combined farfield/nearfield survey that included sampling at 25 additional stations throughout Massachusetts Bay and Cape Cod Bay, including 2 new water column monitoring stations in Boston Harbor and 3 new water column monitoring stations along the northeastern boundary with the Gulf of Maine. In this report, data on physical, chemical, and biological measurements at the stations are presented, and interrelationships among parameters are examined for standard hydrographic surveys. Unlike past periodic water quality reports for 1992 and 1993, the additional high-resolution studies conducted using towed *in-situ* instrumentation during the 1994 surveys will be discussed in a separate report.

Between June and July 1994, the water column was thermally stratified in the Bays. Accompanying stratification was the normal set of conditions expected during early to mid-summer: low concentrations of nutrients and chlorophyll in the surface layers, the presence of a subsurface chlorophyll maximum and higher nutrient concentrations in deep water.

Concentrations of surface chlorophyll and nutrients were higher at selected stations, primarily in Boston Harbor and adjacent shallower areas in western Massachusetts Bay. Thus, an inshore-offshore gradient, now a typical and expected trend in MWRA monitoring results, was observed and was particularly evident in parameters reflecting particulate organic matter (e.g., chlorophyll, fluorescence, and turbidity).

Several key monitoring parameters — nutrients, dissolved oxygen (DO), chlorophyll, and phytoplankton (at the surface of one station, N10P) — were measured on each of the three surveys. During the farfield surveys in June, 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 — Except for Boston Harbor and its receiving waters in the Bay, nutrient concentrations were low in the warm surface layers above the thermocline. Below the thermocline, nutrients characteristically increased as a function of increasing water depth. For DIN, concentrations at depths >45 m generally reached 8-10 μM and were slightly higher than DIN concentrations measured within Boston Harbor (up to 6 μM in June). Dissolved nutrient concentrations of different forms, particularly PO_4, showed variability across different regions, and N/P ratios varied accordingly. Also, an unusual enrichment of silicate in mid-depth water within Cape Cod Bay was a distinctive feature that has been noticed in June of previous years.

■ DO — A decline in DO concentrations in bottom waters of the nearfield was observed from June through July. The bottom-water DO minimum in late July was 8.06 mg L^{-1}, a value considerably lower than what was observed in 1992-1993 when similar monitoring had been conducted. Surface

layer DO was frequently supersaturated, indicating a productive surface layer and a heterotrophic bottom layer, as expected during strong stratification.

■ Chlorophyll — Peak chlorophyll concentrations were typically found within the surface layer at nearshore stations but, at offshore stations, a subsurface chlorophyll maximum was uniform across stations and over surveys. This subsurface layer was generally located near 20 m, which is within the photic zone throughout most of the Bay. The highest chlorophyll concentration (about 11 μg L^{-1}) noted during the farfield survey was found in Boston Harbor. Chlorophyll trends in nearfield surface waters generally followed temporal patterns and concentrations observed during the same early summer period in 1992 and 1993.

■ Phytoplankton — Total phytoplankton counts illustrated some of the same trends noted for chlorophyll concentrations. Total cell counts exceeded 1 x 10^6 cells L^{-1} at a few scattered locations in the Bays. In areas around Boston Harbor, the diatom component of the phytoplankton was higher than in other areas and this occurrence generally coincided with higher nutrients and chlorophyll concentrations. Where the diatom component was higher, the phytoplankton community was a mixture of microflagellates, cryptomonads, and diatoms. The principal diatoms included *Chaetoceros* species and *Skeletonema costatum*. In other areas of the Bays, the mixture emphasized the microflagellate-cryptomonad component. Dinoflagellates were omnipresent, but never attained counts >10^3 cells L^{-1}.

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

■ Zooplankton — High zooplankton counts often coincided with high chlorophyll concentrations and phytoplankton cell counts. The exception, as often noted, was the edge of Boston Harbor where zooplankton counts were unusually low relative to the chlorophyll concentration. There appeared to be some geographic patterns in the composition of the zooplankton community; to an extent these patterns may also coincide with variations in the mixture of phytoplankton species. Zooplankton counts were often >60,000 m^3 and, in general, the abundance of zooplankton was high compared to earlier in the year. At some stations, larval forms (meroplankton) of bivalves and echinoderms were significant components of the zooplankton, but copepods and their nauplii were the principal components. Dominant copepod taxa across stations included both large and small forms, including forms like *Calanus* and *Temora* along with the usual dominants like *Oithona* and *Paracalanus*.

■ Metabolism — In June, primary production measurements were made at two locations: at station F23P at the edge of Boston Harbor and at station N16P in the middle of the nearfield. At station N16P, significant net production was occurring at the depth of the subsurface chlorophyll maximum (20 m). Integrated ^{14}C primary production rates averaged 1.1 g C m^{-2} d^{-1} (n=2) and 1.6 g C m^{-2} d^{-1} (n=2) at stations F23P and N16P, respectively. ^{14}C production, expressed in terms of volumetric rates, were highest at station F23P but, because of higher turbidity, production decreased rapidly over depth compared to station N16P. In addition to production measurements, dark respiration (by oxygen decline in bottle incubations) was estimated for samples at three stations (F24, N20P and F19). A time-series approach produced significant regressions of concentration over time, and rates generally appeared to decrease with distance from shore and with greater water depth. Slopes of

linear regressions of DO concentration over time revealed respiration rates of ~0.004-
0.029 mg O_2 L^{-1} h^{-1}. A brief analysis compares production and respiration rates as estimated over a
water column typical of the nearfield region.

Finally, a brief discussion emphasizes some of the interannual variations that have been observed during
the June-July period from 1992 to 1994. The June-July period over the three years has had a number of
markedly similar geographic and temporal trends. The exact patterns have not been repeated each year,
but often a similar feature has been pronounced in two of the three years. As noted above, perhaps the
most remarkable feature in 1994 was the concentration of DO in nearfield bottom waters approaching 8
mg L^{-1} by the end of July.

CONTENTS

Appendix   A   Station Data Tables and Instrument Calibration Data
              B   Vertical Profile Data from Farfield and Nearfield Stations
              C   Comparison of Vertical Profile Data: Scatter Plots
              D   Metabolism Data and Productivity—Irradiance Modeling
              E   Phytoplankton Species Data Tables
              F   Zooplankton Species Data Tables

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: JUNE AND JULY 1994".

LIST OF TABLES

LIST OF FIGURES

1.0 INTRODUCTION

This report is the third of five periodic water column reports for water quality monitoring conducted in 1994 for the Massachusetts Water Resources Authority (MWRA) Harbor and Outfall Monitoring Project. The report includes results from three surveys conducted during June and July; each of these surveys included sampling at 21 stations in the nearfield area. The June 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 (June farfield/nearfield survey, early July nearfield survey, late July nearfield survey).

Section 6.   Discussion of the early 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). Two periodic reports for 1994 have been submitted (Kelly *et al.*, 1994e,f).

Serving the MWRA's need for rapid dissemination of data and information, the periodic report series also provides a preliminary synthesis of monitoring results. The technical approach used in 1994 to implement the water quality portion of this monitoring plan is presented in a combined work/quality assurance project plan (CW/QAPP) (Albro *et al.*, 1993) that was developed specifically for water quality monitoring. The CW/QAPP describes the technical activities performed at sea and in the laboratory, as well as the data quality requirements and assessments, project management, and a schedule of activities and deliverables. In addition, individual survey plans were submitted to MWRA for each survey to provide important operational details. The survey reports submitted for the three surveys discussed in this periodic report describe actual survey tracks, samples collected, and other survey details (Dragos, 1994; West, 1994; Albro, 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 June and July 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 June 21-25 (W9407), (early) July 7 (W9408), and (late) July 27-28 (W9409).

1.4 Summary of Accomplishments: June and July 1994

For the combined farfield/nearfield surveys in June (W9407), *in-situ* measurements were taken and samples were collected at the stations shown in Figure 1-1. Samples for laboratory analyses were collected to obtain the following types of data:

■ Dissolved inorganic nutrients: nitrate, nitrite, ammonium, phosphate, and silicate.

■ Chlorophyll *a* and phaeopigments in extracts of filtered water.

■ *In-situ* fluorometric measurements of chlorophyll, optical beam transmittance (attenuation), light irradiance, salinity, temperature, and dissolved oxygen.

■ Total suspended solids and dissolved oxygen in discrete water samples.

■ Organic nutrients: dissolved carbon, nitrogen, and phosphorus; particulate carbon and nitrogen.

■ Phytoplankton and zooplankton identification and enumeration.

■ Rates of water column production (^{14}C) vs. irradiance from shipboard incubations.

For the July nearfield surveys (W9408, W9409), 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.

In early July (survey W9408), impending severe weather curtailed sampling after 17 of the planned 21 stations had been completed (West, 1994). The last day of the June (W9407) farfield/nearfield survey and a second day of the late July nearfield survey 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 between Boston Harbor and the nearfield by oscillating from near surface to near bottom as the ship progressed at 4 to 7 kt.

Samples collected for analysis (rather than archival) have been analyzed, and *in-situ* sensor measurements have been calibrated and processed. Both types of data are presented in this report and all are summarized in accompanying Appendices A through F.

Table 1-1 Schedule of water quality surveys for calendar year 1994. This report provides data from the surveys conducted in June and July.

SURVEY	DATES
W9401 (Combined Farfield/Nearfield)	February 8 and 15-18
W9402 (Combined Farfield/Nearfield)	March 1-2 and 5-7
W9403 (Nearfield)	March 22-23
W9404 (Combined Farfield/Nearfield)	April 5-10
W9405 (Nearfield)	April 27-28
W9406 (Nearfield)	May 22
W9407 (Combined Farfield/Nearfield)	June 21-25
W9408 (Nearfield)	July 7
W9409 (Nearfield)	July 27-28
W9410 (Nearfield)	August 11
W9411 (Combined Farfield/Nearfield)	August 23-27
W9412 (Nearfield)	September 7
W9413 (Nearfield)	September 28-29
W9414 (Combined Farfield/Nearfield)	October 11-15
W9415 (Nearfield)	November 4
W9416 (Nearfield)	December 1
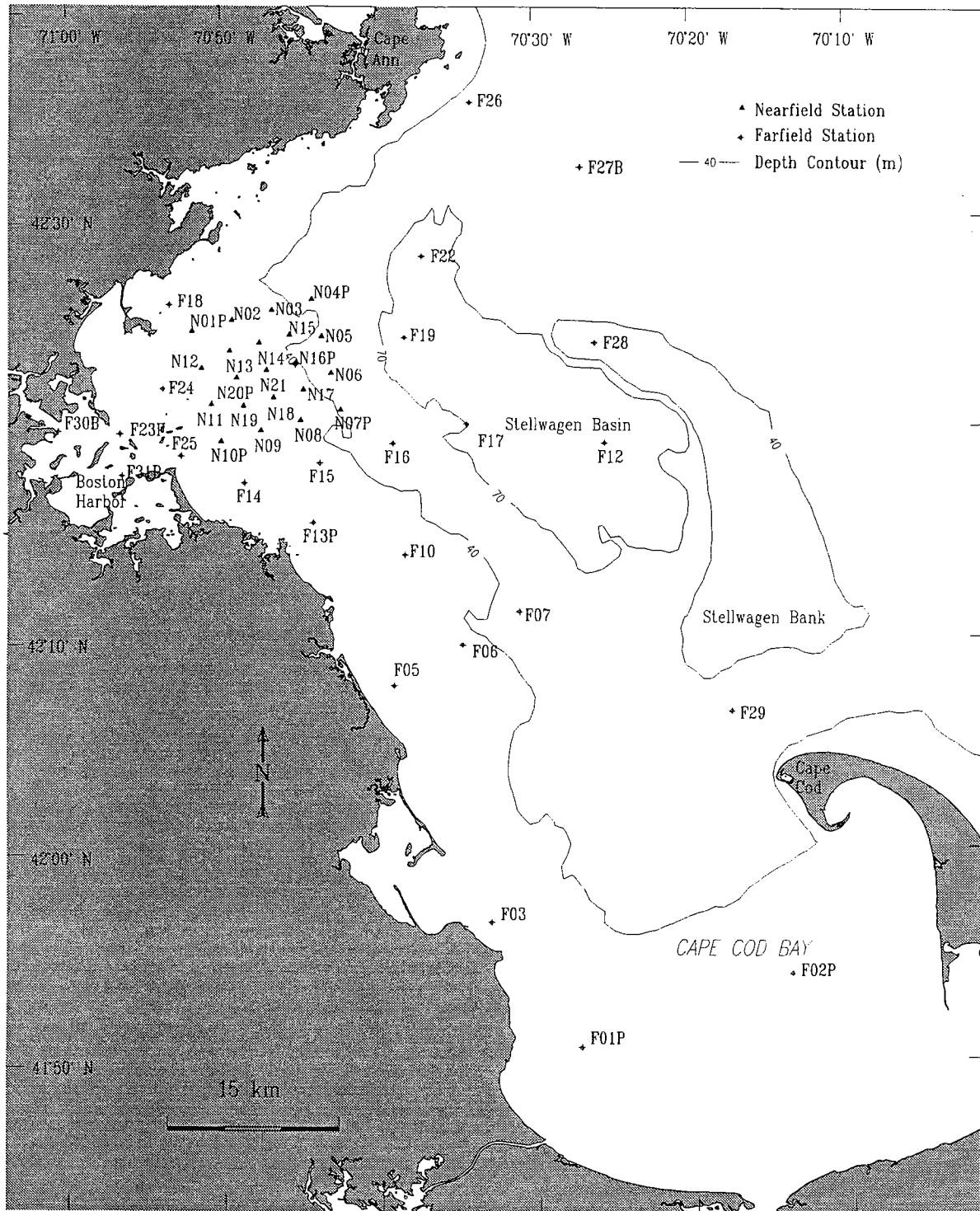
Figure 1-1. Water quality sampling stations in Massachusetts and Cape Cod Bays. Depth contours are in meters. Station codes - F: Farfield, N: Nearfield, B: Biology (1994), P: Biology/Productivity (1992-1994). Station F06 was a B station during 1994.

2.0 METHODS

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

2.1 Field Procedures

2.1.1 Hydrographic and Water Sampling Stations

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

tide/Harbor-nearfield transect. The results of high-resolution profiling will be discussed in a separate report covering all 1994 high-resolution surveys.

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

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

On the 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 those described in the CW/QAPP. At the request of MWRA and due to the preference of the Outfall Monitoring Task Force, only the ^{14}C method was used to estimate primary production; the oxygen light-dark method was not used. At four depths during each occupation of stations F23P and N10P, ^{14}C primary production was measured by exposing samples to a light gradient as described by Albro *et al.* (1993) for the oxygen method. Fifteen 300-mL BOD bottles were inoculated with 2.5 μCi of ^{14}C-sodium bicarbonate. Three bottles were incubated in the dark. The remaining 12 bottles were exposed to irradiance levels ranging from about 20 to 2000 μE m^{-2} sec^{-1}, with several bottles exposed in the range of 200-600 μE 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 June, a time-series incubation approach to measure water column respiration rates, first used in April 1994 (Kelly *et al.*, 1994f), was continued. Initial samples were taken and a number of 300-mL BOD bottles were incubated at constant temperature near *in-situ* conditions, with replicate bottles serially fixed at set time periods, normally up to 48 hours as long as 6 days for samples from the deepest waters. Results of these measurements are presented in Appendix D. Samples were collected from three depths (surface, mid-depth, and mid-bottom) at stations N20P and F19, and from the surface at 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 (N_2) and the carbon dioxide (CO_2) in the gas stream is trapped on a molecular sieve. The sieve is heated to $200\,^{\circ}C$, releasing the CO_2 into a new stream of N_2, the carrier gas that transports the CO_2 to an IR detector where the CO_2 content is measured.

The difference between analytical replicates, estimated from samples reported in Kelly *et al.* (1994a), averaged <1% ($\bar{x}\pm\sigma = 0.47\% \pm 0.73\%$, range = 0.08-2.68%, $n = 12$). The average difference between sample replicates from a GO-FLO bottle was <1% ($\bar{x} \pm \sigma = 0.25\% \pm 0.31\%$, 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 ($X_1, X_2,$ and X_3) are arranged from lowest to highest, the criterion for the *highest* value being an outlier is

$$X\_3 = (X_3 - X_2)/(X_3 - X_1)$$

The criterion for the *lowest* value being an outlier is

$$X\_1 = (X_2 - X_1)/(X_3 - X_1)$$

These calculated values are compared to a tabled value. For example, if X_3 or X_1 exceed 0.941, then there is a 95% chance that the value in question is an outlier.

X_3 and X_1 are calculated for each set of three dark-bottle replicates. When X_3 or X_1 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 W9407.

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

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

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

where

P_B = production (chlorophyll-normalized)

P_{SB} = theoretical maximum production (chlorophyll-normalized) without photoinhibition

a = $\alpha\ I/P_{SB}$

b = $\beta I/P_{SB}$

α = initial slope of the rise in net production with light increasing from zero irradiance [units of $(\mu gC\ \mu gChl^{-1}\ hr^{-1})/(\mu E\ m^{-2}\ sec^{-1})$], calculated from I (light irradiance level, $\mu E\ m^{-2}\ sec^{-1}$) 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 α 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 = $P_{max} \left[1 - e\left(-\alpha\ I/P_{max}\right)\right]$

P_{max} = light-saturated maximal productivity and

α =   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 to 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 $I_z = I_o\, e^{-kz}$ and to determine $Z_{0.5\% \, Io}$, the depth where photosynthetically active radiation equals 0.5% I_o. Estimated rates were expressed per square meter of surface and integrated to $Z_{0.5\% \, Io}$. 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 (μg C μg Chl^{-1} h^{-1}) at 0.5-m intervals to coincide with 0.5-m BIN-averaged chlorophyll values generated from a vertical downcast. To calculate depth-integrated rates, the predicted hourly chlorophyll-normalized rate was then multiplied by the chlorophyll fluorescence at each depth interval from the surface to the $Z_{0.5\% Io}$. The values were then appropriately summed over depth and units were converted to m^{-2} from a volumetric basis.

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

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

Also, for each occupation of each station, an estimate of integrated water column production was calculated based on a composite of the four independent estimates. The composite estimate was calculated by combining model results from incubations, where the results from a given incubation were applied over a depth above and below the incubation sample's collection depth half-way to the next sample's collection depth. Thus, by using different P-I curves to extrapolate over appropriate portions of the water column, a composite production profile (by 0.5-m intervals) was developed. The rates over the composite profile were then appropriately summed over depth. Units were converted to m^{-2} from a volumetric basis, and a conversion to full 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]

Parameter	Stations	Sample Volume	Sample Containers	Shipboard Processing/ Preservation
Following samples are subsampled from water collected with Poly Vinyl Chloride Niskin GO-FLO Bottles				
Dissolved Inorganic Nutrients	All	60 mL	100 mL Polyethylene bottle	Pass through a filter. Fix with chloroform.
Dissolved Oxygen	14 Biology/ Productivity and 3 Farfield	300 mL	300 mL Glass BOD	Fix per Oudot *et. al.* (1988). Titrate within 24 hours.
Dissolved Organic Carbon	14 Biology/ Productivity and F25	50 mL	100 mL amber glass bottle	Pass through a pre-ashed glass fiber filter. Fix with 0.5 mL of phosphoric acid.
Dissolved Organic Nitrogen	14 Biology/ Productivity and F25	20 mL	50 mL glass digestion tube	Pass through a filter. Digest within 8 hours.
Dissolved Organic Phosphorus	14 Biology/ Productivity and F25	20 mL	50 mL glass digestion tube	Pass through a filter. Digest within 8 hours.
Particulate Organic Carbon	14 Biology/ Productivity and F25	50 mL	Whatman GF/F glass fiber filter	Pass through a pre-ashed glass fiber filter. Freeze (-5°C).
Particulate Organic Nitrogen	14 Biology/ Productivity and F25	50 mL	Whatman GF/F glass fiber filter	Pass through a pre-ashed glass fiber filter. Freeze (-5°C).
Total Suspended Solids	14 Biology/ Productivity	200 mL	Petri dish	Pass through a filter. Freeze (-5°C)
Chlorophyll *a*/ Phaeopigments	14 Biology/ Productivity	2 x 10 mL	Whatman GF/F glass fiber filter	Pass through filter. Fix with 1% $MgCO_3$ solution, wrap in foil, store over desiccant, and refrigerate.
Phytoplankton (Whole Water)	14 Biology/ Productivity	800 mL	1000 mL glass bottle	Preserve with Utermohl's solution.
Phytoplankton (Screened Water)	14 Biology/ Productivity	2000 mL	100 mL Polyethylene bottle	Strain through a 20 μm mesh; wash retained organism into a jar. Fix with Utermohl's solution.
^{14}C Production	2 Biology/ Productivity	300 mL	300 mL Glass BOD	Inoculate with 2.5 μCi of $NA_2^{14}CO_3$ and incubate.
Following sample is collected with a vertically towed net				
Zooplankton	14 Biology/ Productivity	800 mL	1000 mL glass bottle	Wash into jar. Fix with a 5-10% Formalin solution.
The following measurements are collected by the Battelle Ocean Sampling System				Precision
Conductivity	All	---	Floppy disk	0.01 mS/cm
Temperature	All	---	Floppy disk	0.001 °C
Pressure	All	---	Floppy disk	0.01 decibars
Dissolved Oxygen	All	---	Floppy disk	0.05 mg/L
Chlorophyll *a* Fluorescence	All	---	Floppy disk	0.01 μg/L
Transmissometry	All	---	Floppy disk	0.01 m⁻¹
In situ Irradiance	All	---	Floppy disk	1 μE m⁻² s⁻¹
Surface Irradiance	All	---	Floppy disk	1 μE m⁻² s⁻¹
Bottom Depth	All	---	Floppy disk	1 m
Navigational Position	All	---	Floppy disk	0.00017 deg

Table 2-2. Laboratory analyses and methods [from Albro *et al.*, 1993]

Parameter	Units	Method	Reference[1]	Maximum Holding Time	Preservation
Dissolved Ammonia	μM	Technicon II AutoAnalyzer	Lambert and Oviatt (1986)	3 mo.	Chloroform
Dissolved Nitrate	μM	Technicon II AutoAnalyzer	Lambert and Oviatt (1986)	3 mo.	Chloroform
Dissolved Nitrite	μM	Technicon II AutoAnalyzer	Lambert and Oviatt (1986)	3 mo.	Chloroform
Dissolved Phosphate	μM	Technicon II AutoAnalyzer	Lambert and Oviatt (1986)	3 mo.	Chloroform
Dissolved Silicate	μM	Technicon II AutoAnalyzer	Lambert and Oviatt (1986)	3 mo.	Chloroform
Dissolved Oxygen	mg L^{-1}	Autotitrator	Oudot *et al.* (1988)	24 h	dark/cool
Dissolved Organic Carbon	μM	O.I. Model 700 TOC Analyzer	Menzel and Vaccaro (1964)	3 mo.	Fix with 0.5 mL of phosphoric acid.
Dissolved Organic Nitrogen	μM	Technicon II AutoAnalyzer	Valderrama (1981)	3 mo.	Add reagents immediately, heat to 100°C within 8 hours.
Dissolved Organic Phosphorus	μM	Technicon II AutoAnalyzer	Valderrama (1981)	3 mo.	Add reagents immediately, heat to 100°C within 8 hours.
Particulate Organic Carbon	μM	Carlo Erba Model 1106 CHN elemental analyzer	Lambert and Oviatt (1986)	3 mo.	Dry over desiccant.
Particulate Organic Nitrogen	μM	Carlo Erba Model 1106 CHN elemental analyzer	Lambert and Oviatt (1986)	3 mo.	Dry over desiccant.
Total Suspended Solids	mg L^{-1}	Cahn Electrobalance	See Section 12.7.7	6 mo.	Dry over desiccant.
Chlorophyll a/ Phaeopigments	μg L^{-1}	Model 111 Turner Fluorometer	Lorenzen (1966)	2 wk	Fix with 1% MgCO$_3$ solution, wrap in foil, store over desiccant, and refrigerate.
Phytoplankton (Whole Water)	Cells L^{-1}	Sedgwick-Rafter counting chambers	Turner *et al.* (1989)	3 y	Preserved with Utermohl's solution, store at room temperature.
Phytoplankton (Screened Water)	Cells L^{-1}	Sedgwick-Rafter counting chambers	Turner *et al.* (1989)	3 y	Fix with Utermohl's solution, store at room temperature.
[14]C Production	[14]C hr^{-1}	Liquid Scintillation Counter (Bechman LS-3801)	Strickland and Parsons (1972)	2 wk	Scintillation fluid
Zooplankton	Cells L^{-1}	Dissecting Microscope	Turner *et al.* (1989)	3 y	Fix with a 5-10% Formalin solution, store at room temperature.

[1]See Section 20 of Albro *et al.*, 1993 for literature references.

3.0 RESULTS OF JUNE 1994
COMBINED FARFIELD/NEARFIELD SURVEY (W9407)

3.1 Farfield Survey

3.1.1 Horizontal Distribution of Surface Water Properties

Surface temperatures were between 11 and 18.3°C in the study area in June 1994 (Figure 3-1). Isolated cool-water locations (near 11°C) were detected at the edge of Plymouth Bay and off Cape Ann. There were warm spots ($\geq$15°C) off Nahant, in Boston Harbor, and in a body of offshore water over Stellwagen Basin and Stellwagen Bank; the warmest surface water was detected in eastern Cape Cod Bay (station F02P), where the temperature exceeded 18°C. The temperature at station F02P was not anomalously high due to diurnal heating; this station was sampled early in the morning, shortly after 0700h (Appendix B). At station F02P, a 10-m-thick surface layer of near-constant warm temperature was indicated, with a sharp thermocline to 15 m and a bottom layer near 5°C. Throughout the rest of the sampling area, including stations at water depths between 15 and 45 m, the surface temperature ranged from 12 to 15°C. This result essentially suggested a broad arc of water with intermediate temperature that extended down the axis of the Bays between the Harbor, offshore, and eastern Cape Cod Bay areas (Figure 3-1).

Surface salinity varied narrowly throughout the Bays (Figure 3-2). Surface water in Boston Harbor, as well as station F02P in eastern Cape Cod Bay, dipped to $\leq$31 PSU and the highest values were ~31.8 PSU. Most values were near 31.5 PSU. Salinity at the northern boundary of the Bay was slightly lower (~31.2-31.3 PSU).

Beam attenuation, which is an indicator of water turbidity, ranged between 0.6 and 1.0 m^{-1} throughout most of the Bays' offshore surface water (Figure 3-3). The striking feature in Figure 3-3, as often noted in MWRA monitoring surveys, is a gradient of decreasing turbidity extending from Boston Harbor seaward to the nearfield area and slightly southward along the coast. Beam attenuation in the Harbor was characteristically >2 m^{-1}. Interestingly, a broad area outside the Harbor, about 10-15 km in length, seemed to be a uniform buffer zone (1.7-1.9 m^{-1}) representing the tidal mixing zone between the turbid

Harbor and clear offshore water (cf. Kelly and Albro, 1993). A sharp change in turbidity was suggested at both the seaward and shoreward edges of this zone of intermediate turbidity. The pattern for chlorophyll (Figure 3-4) was similar to turbidity. High concentrations of chlorophyll (6-10 μg L^{-1}) were detected in the Harbor, intermediate concentrations (mostly 4-6 μg L^{-1}) were apparent throughout the intermediate buffer zone, and concentrations <1 μg L^{-1} were detected in virtually all offshore water, including all of Cape Cod Bay. This sharp turbidity-chlorophyll gradient, noted from Boston Harbor seaward in June 1994, has been observed in June in each year of recent MWRA monitoring.

The patterns for dissolved inorganic nitrogen (DIN) concentrations in surface water had similarities to those for turbidity and chlorophyll (Figure 3-5). Concentrations of DIN were very low everywhere, but slightly enriched (~1-4 μM) in some parts of the Harbor and in the intermediate area just outside of the Harbor. A gradient away from the Harbor was not apparent for nitrate (NO$_3$; Figure 3-6); the DIN gradient was due to enriched ammonium (NH$_4$) concentrations.

Surface water phosphate (PO$_4$) concentrations were low (e.g., >0.18 μM but <0.4 μM) in most of the study area (Figure 3-7), but were slightly enriched in most of the Harbor and Harbor-Bay mixing area. Silicate (SiO$_4$) also showed an enrichment pattern in surface waters that was similar to DIN and PO$_4$ (Figure 3-8). However, unlike DIN and PO$_4$, SiO$_4$ concentrations were also enriched in surface waters of all Cape Cod Bay stations. In Cape Cod Bay, SiO$_4$ concentrations were as high as those found at the Boston Harbor-Bay enrichment plume stations.

3.1.2 Water Properties Along Selected Vertical Sections

A set of standard transects for examining vertical sections was established for the 1994 series of water column periodic reports (Kelly *et al.*, 1994e). The Nahant Transect, Boston-Nearfield Transect, Boston-Cohasset Transect, and Marshfield Transect all run from nearshore to deep water in Stellwagen Basin (Figure 3-9). As a roughly parallel series from north to south, these four transects characterize a large portion of Massachusetts Bay. First, sections for temperature, salinity, chlorophyll, and DIN are described for this series of transects. The same parameters are then presented for the fifth section, the Cape Ann-Stellwagen Transect (Figure 3-9). This line of stations prescribes an arc near an imaginary

boundary between Massachusetts Bay and Gulf of Maine waters — from Stellwagen Basin in mid-Massachusetts Bay, crossing Stellwagen Bank to station F27B in the deep basin outside the Bay, and terminating in shallower water near Cape Ann.

Waters were sharply thermally stratified at all locations, except within Boston Harbor (stations F30B and F31B, Figure 3-10a). At the coastal stations, where water depth was about 20 m, water was usually partially mixed. Beyond depths of 20 m, a 5-10 m warm surface layer with a 10-15 m thermocline, overlay a cold bottom-water layer with temperature $\leq 7\,^\circ C$. At Stellwagen Basin stations (F22, F19, and F17), temperatures of near-bottom water (>50-60 m deep) were $<5\,^\circ C$. Salinity (Figure 3-10b) also showed vertical layering and more vertically mixed conditions in Boston Harbor. The surface layer throughout the Bay was near 31.5 PSU. A salinity >32.2 PSU was characteristic of Stellwagen Basin deep water.

Contoured chlorophyll concentrations across the sections (Figure 3-10c) displayed a regular subsurface layer of chlorophyll with a concentration >1.5 μg Chl a L^{-1}. This subsurface layer was found at nearly all non-coastal stations and generally graded to deeper depths offshore. The layer was characteristically found at the base of the thermocline, but was occasionally evident well below the thermocline and into the bottom water layer (e.g., stations N01P and N04P of the Nahant Transect, Figure 3-10c). As noted from the surface distribution (Figure 3-4), chlorophyll was high in Boston Harbor. At the edge of the northern and southern Harbor (stations F23P and F25, respectively), a local chlorophyll minimum was noted; this may result from active tidal mixing. Just offshore from both the northern and southern edges of the Harbor, patches (several kilometers in length) of chlorophyll-enriched (>4.5 μg Chl a L^{-1}) surface water were detected. At this juncture of inshore and offshore waters, a chlorophyll-enriched surface layer began to grade into the subsurface maximum layer that was characteristic of deeper water.

Except for a relative enrichment of DIN in Boston Harbor (evident in section plots shown in Figure 3-10d), a surface layer low in DIN was omnipresent. Concentrations of DIN increased at the base of the thermocline (near 20 m) and a vertical gradient from there to the bottom was very distinct. The maximum DIN concentrations (> 9 μM) were detected in the two southern stations of Stellwagen Basin (F19 and F17, rather than at station F22).

For the Boundary Transect (Figure 3-11), south (station F12, Stellwagen Basin) is positioned to the left and north (station F26, Cape Ann) is positioned to the right on the sections. Note that station F28 is positioned on Stellwagen Bank and station F27B is located in the deepwater basin seaward of a 40-50-m sill that forms a boundary between the northern tip of Stellwagen Bank and Cape Ann. The vertical thermal patterns were similar at stations across this section, and it is noticeable that Stellwagen Bank interrupts two deepwater cells of cold (<5°C) water in the two basins inside and outside the Bay. Both salinity and the range of DIN concentration were similar in the deepest waters of the two basin stations, although an intermediate depth maximum rather than a deepwater maximum in DIN was suggested at the Stellwagen Basin station (F12). DIN increased sharply at the base of the thermocline and the subsurface maximum layer of chlorophyll, typical of all sampled offshore waters, was uniformly found around the base of or below the thermocline, along the 5-7°C isotherm.

3.1.3 Analysis of Water Quality Characteristics Throughout the Bays

Scatter plots using all *in-situ* sensor data from vertical profiles are shown in Figures 3-12a and b. Individual station profiles are provided in Appendix C. Appendix C also includes separate scatter plots for groups of stations clustered by regions defined in Figure 3-13.

Figure 3-12a shows some dispersion in the temperature-salinity (T-S) relationship, especially at higher temperature and lower salinity and also at highest salinity. The pattern may suggest some variability in water mass history at different places in the Bay. Variability was found across the boundary stations alone, where slightly different T-S relationships were apparent (Appendix C). At high salinity (>32.25 PSU), scattered data points collected in the nearfield region were associated with temperature >5°C (Figure 3-12a; see also Appendix C). This scatter is a curious feature that could indicate some local mixing across the pycnocline (internal waves?).

Figure 3-12a also shows patterns of beam attenuation vs. salinity and beam attenuation vs. chlorophyll for all regions and depths. There is little general relationship between beam attenuation and salinity and, from about 30.6 to ~33 PSU, a central body of points suggests nearly a flat band of beam attenuation readings ranging from ~0.5 to 1 m^{-1}. Some diagnostic Bay-area patterns were revealed by the regional

plots (see Appendix C). For example, two nearly vertical strings of data points (at salinity >32 PSU in Figure 3-12a) were from two northernmost stations in the boundary region. At station F26 off Cape Ann, a sharp increase in turbidity characterized a 12- to 15-m-thick bottom layer, suggesting an active nepheloid layer perhaps associated with bottom turbulence in this area. At station F27 in the deep basin outside the Bays, rather than a sharp increase suggesting a distinct bottom layer, a nearly linear increase in turbidity from 1 to 2 m^{-1} was noted over the depth interval from ~40 to 95 m. The regular increase over depth would be a pattern consistent with a process of settling and gradual accumulation of suspended matter in a relatively stagnant deepwater system. In the Harbor, high turbidity was found at the lowest salinities (the data points >3 m^{-1} near 31 PSU) and, in part, the Harbor data couple with the data of the coastal region, where a linear decrease in turbidity with increasing salinity was apparent. In general, this relationship is consistent with the concentration gradient described above for turbidity and for chlorophyll (Figures 3-3, and 3-4). Interestingly, the lowest salinity was detected in Cape Cod Bay (see also Figure 3-2), although neither high turbidity nor high chlorophyll concentrations characterized this region.

A broad general linear relationship was noted between increasing turbidity and increasing chlorophyll concentrations (Figure 3-12a). Anomalous data points of high turbidity at low chlorophyll concentrations signal bottom nepheloid layers, such as described above. Highest values for both parameters were found in Harbor and coastal waters, but the trend between parameters in those regions was not markedly different from the trend in other regions. Figure 3-12b shows the overall distribution of chlorophyll with depth in all regions. High values in the surface 10 m represent data collected at Harbor, coastal, and two nearfield stations (N10P and N20P). In addition to these high values, the noteworthy feature is a subsurface chlorophyll maximum centered at 20 m depth; this feature is remarkably consistent with and distinctive for most nearfield stations, and for all offshore and boundary stations.

Coincident with the subsurface chlorophyll maximum, a depth of 20 m marked the point at which dissolved oxygen (DO) saturation levels began to decrease with depth (Figure 3-12b). Near-surface layers were often supersaturated, but ranged from about 90 to 125% of saturation. The range only slightly shifted at 20 m, where values from about 85 to 120% were apparent. Below 20 m, saturation levels fell linearly or exponentially in most vertical profiles to minima near 80-85% in some deepwater locations. At depths ~40-90 m, the mean was ~90% of saturation.

Dissolved inorganic nitrogen (DIN) was usually depleted in surface waters, except for locations in the Harbor, and selected locations in the nearfield and coastal regions (Figure 3-14a). Otherwise, there was broad similarity in the distribution of DIN with depth. Concentrations began to increase in the 10- to 20- m depth range, increased to ~40-50 m depth, and began to level off to highest concentrations (10 μM) in the deepest water sampled. Concentrations of NO_3, which ranged between 0 μM at the surface and 6-8 μM at depth, increased nearly linearly with depth (Figure 3-14b). The enrichment in surface water DIN was primarily due to NH_4 (Figure 3-14b). Concentrations for most samples showed a smaller increase in NH_4 with depth (to ~4 μM), but many deepwater samples from the boundary and offshore stations were very low in NH_4.

PO_4 concentrations showed some similarity to DIN concentrations in their distributions with depth (Figure 3-14c). For example, characteristically higher surface water concentrations were found in Harbor and coastal waters. At most of the nearfield stations, PO_4 showed a very tight, coherent pattern of increasing concentration with water depth. However, in contrast to DIN or NO_3, there was also a regional component to the PO_4 distribution. Concentrations of PO_4 at many of the offshore and some of the boundary stations were ~0.2-0.3 μM lower than concentrations at comparable depths in the nearfield region. SiO_4 concentrations over depth showed a pattern similar to that for NO_3 and, thus, a general linear increase with increasing depth (cf. Figure 3-14c and 3-14b). At mid-depth locations, a set of samples from Cape Cod Bay had anomalously high silicate concentrations.

Surface waters were uniformly depleted in DIN, but concentrations of PO_4 were measurable (Figure 3-15a). At depths below the near-surface layer, a Harbor-coastal enrichment in P relative to N (i.e., a lower N/P ratio) was apparent in comparison to most of the nearfield. Sub-thermocline waters in the offshore/boundary regions were generally more enriched in DIN at a given P concentration than water samples from nearfield and Harbor-coastal regions. Interestingly, however, each regional cluster of points (Harbor/coastal, nearfield, and offshore/boundary) had similar implied slopes of N/P trend lines and differed primarily in their implied intercepts, with the Harbor/coastal region being the highest positive intercept for PO_4 (near 0.5 μM) and the offshore/boundary region being the lowest (about 0.2 μM). These regional distinctions were more apparent with DIN, which includes NH_4, than with NO_3 alone (Figure 3-15a).

Harbor, coastal, and nearfield DIN concentrations relative to Si concentrations, had similarity (Figure 3-15b). The N/Si ratios for these regions (~2:1) were slightly higher than for offshore and boundary region samples (1:2 to <2:1). Cape Cod Bay samples, along with a few other samples, were distinct for a low N/Si ratio (~1:2). Using NO_3 rather than DIN distributions, the distinction between regions was only maintained for Cape Cod Bay, which was alone in the relatively high silicate concentrations. Discussion later will examine the identified differences in nutrient concentrations and ratios, and possible diagnostic use of nutrients relative to plankton trends.

Plotted as a function of salinity (Figure 3-16a), DIN data reveal two principal regional trends. The main body of nearfield and some deepwater stations shows a generally sigmoid pattern with increasing salinity: low at low salinity, hitting an inflection point at 32 PSU, and starting to level off at 32.25 PSU. The inflection coincides with the pycnocline separating the distinct surface and bottom layers that were present at this time. A few additional offshore and boundary stations fell to the right of the curve on the plot in Figure 3-16. The second group of data included samples of salinity <32 PSU (i.e., surface-layer samples); these illustrate the surface layer and shallow-water enrichment in DIN within the Harbor/coastal and select nearfield stations, relative to other parts of the Massachusetts and Cape Cod Bay sampling area. The pattern for DIN and salinity is driven more by NH_4 than by NO_3 (Figure 3-16b), but is also apparent for PO_4 and SiO_4 relative to salinity (Figure 3-16c). For silicate, the relative enrichment of Cape Cod Bay is again indicated, in this case relative to its salinity, and likely suggests that the mid-water silicate concentration increase at Cape Cod Bay stations is related to differences in the balance of internal uptake and regeneration processes rather than to advection of high-silicate water.

Plots of combined forms of N (DIN + PON) and total N (TN) compared to salinity are given in Figure 3-17. Concentrations in Boston Harbor were generally high. PON concentrations in a number of Harbor water samples were between 5 and 10 μM, in contrast to PON concentrations ranging from 1.5 to 4 μM elsewhere (Appendix A, Table A-2). In contrast to Boston Harbor, concentrations in Cape Cod Bay were generally low, but they fell within the range measured in the other regions. There were surface-water samples with salinity <31.5 PSU and DIN + PON concentrations <5 μM in nearly every region (Figure 3-17). Except for the set of low-concentration samples, the data suggest a decreasing concentration of DIN + PON, from high concentrations at low salinity in the Harbor to low concentrations at high salinity in mid-waters of nearfield, offshore, and boundary stations. Approximately the same trends described for

DIN + PON apply to total N (TN), except that concentrations of TN are higher because they include ~6-10 µM as dissolved organic nitrogen (DON) (see Appendix A). Viewing only the Harbor and coastal data shown in Figure 3-17, a linear decrease in TN with increasing salinity is evident; these regions are proximal and strongly linked by tidal hydrodynamics. The fact that this trend is not defined as clearly for the set of nearfield stations may either reflect a less-specific association of inshore water with some regions of the nearfield or the influence of additional water flows in some regions of the nearfield. The scatter in nearfield data may also indicate some local imbalances in the exchange of TN between surface and bottom layers in some locations of the nearfield. Such internal exchanges may exert a stronger influence on the water column in more highly stratified, less nutrient-enriched offshore areas, compared to weakly stratified coastal waters that often appear to transport nutrients from the strong Harbor source in a nearly conservative manner (cf. Kelly, 1993).

3.1.4 Distribution of Chlorophyll and Phytoplankton

At stations that were sampled, phytoplankton abundance was in the range of 0.1-1.5 million cells L^{-1} (Figure 3-18); higher counts are indicative of significant phytoplankton populations but not strong bloom conditions. Cell counts were directly related to chlorophyll concentrations; with respect to cell count-chlorophyll ratios (Figure 3-18), no anomalous regions were suggested. Each region had a sample with counts >1 million cells L^{-1}, but the Harbor and coastal samples were all above this value. Nearfield locations with high counts included stations N10P and N20P (surface only) in the southwestern and mid-nearfield regions. Low counts (<0.5 million cells L^{-1}) were found at most nearfield and Cape Cod Bay stations.

A comparison of surface and subsurface (chlorophyll maximum) counts (Figures 3-19, 3-20) indicates that there is neither a consistent nor marked difference between total cell counts as a function of depth. Phytoplankton communities were generally a mix of microflagellates, diatoms, and dinoflagellates. Where total cell counts were higher, diatoms were more abundant, both in absolute terms and relative to groups at other stations. Thus, at stations F23P, F13P, N10P, and N20P, all within the prime area of higher chlorophyll and turbidity and also representing the apparent receiving areas for nutrients potentially exported from the Harbor to the Bay, the data showed noticeable enrichment of the diatom

group. At these stations, microflagellates and dinoflagellates were also more abundant than elsewhere, but the prime difference at these stations (compared to the others) was a substantial enhancement of the diatom component of the community (Figures 3-19 and 3-20).

Tables 3-1a and 3-1b respectively identify the dominant taxa in both surface and subsurface samples. A full taxonomic listing of samples is included in Appendix E. Microflagellates, a multi-species grouping, were always dominant organisms; cryptomonads, another multi-species grouping, were always among the lesser dominants. Dominant individual species included diatoms and dinoflagellates. Of the diatoms, species of *Chaetoceros* were common and nearly ubiquitous. *Ceratium longipes* and *Dinophsysis norvegica* were principal forms of dinoflagellates. Other than *S. costatum*, no noteworthy geographic or depth-related taxonomic patterns were evident among dominant taxa.

Screened phytoplankton samples (Tables 3-2a and 3-2b) confirmed the occasional abundance of *Ceratium* and *Dinophysis* at concentrations as high as 10^3 cells L^{-1}. In general, it was not evident that individual dinoflagellate species or other screened taxa were more or less numerous at any particular region of the study area. Overall, there were a few more total species identified in screened samples from the subsurface chlorophyll maximum, but there were not necessarily more species or greater abundance at the chlorophyll maximum at a given station. However, at stations F01P and F02P in Cape Cod Bay, the numbers of *Ceratium longipes*, *Dinophysis norvegica*, and several *Protoperidinium* species were much higher at depth and almost twice the number of taxa were present there compared to surface samples.

3.1.5 Distribution of Zooplankton

Total zooplankton abundance was correlated with chlorophyll (Figure 3-21), especially if the Boston Harbor data point is omitted. At station F23P at the northern edge of Boston Harbor, MWRA monitoring between 1992 and 1994 has often detected low zooplankton abundance relative to chlorophyll. Coastal (F13P) and nearfield stations (N10P and N20P), which had similar high average chlorophyll concentrations (>3 μg L^{-1}, see Figure 3-21), had double or more the number of zooplankton organisms that were measured at station F23P (Figure 3-22).

Compositionally, copepods and their nauplii comprised about 66% or more of the total numbers of zooplankton. Copepods and nauplii comprised nearly 100% of the total abundance at station F02P. Barnacle nauplii were present at some stations; they were a notable fraction (Figure 3-22) at the same stations that also had significant counts of the diatom *Skeletonema*. The simultaneous presence of barnacle nauplii and *Skeletonema* may indicate the presence of Boston Harbor water.

A full taxonomic listing of the zooplankton in all samples is provided in Appendix F. The fraction of the community classified as the "other" category and significant at some stations (Figure 3-22) was often comprised of meroplanktonic larval forms, including bivalve veligers and echinoderm plutei and, in some cases, the marine cladoceran *Evadne normani*. *Oithona similis* and *Paracalanus parvus*, both small-sized species that are usual dominants in samples from the Bays, and *Calanus finmarchicus*, a large form which can be prey for whales, were also numerically dominant.

For the zooplankton communities sampled across the study area, there were geographic distinctions. For example, *O. similis* was particularly important at both stations in Cape Cod Bay and dominated the total counts at station F02P. In contrast, samples from the edge of Boston Harbor were low abundance of *O. similis* and sometimes was less abundant than *P. Parvus* at Massachusetts Bay stations. The community at the eastern nearfield stations (N16P, N07P, and N04P) was similar and included high numbers (>4000 m^{-3}) of *C. finmarchicus* as one of the most dominant taxa. Stations on the western side and south of the nearfield (N01P, N10P, N20P and F13P) had similar (and mixed) communities that included, as dominants, *P. parvus, O. similis,* and larger copepods, such as *Pseudocalanus newmani, Temora longicornis*, and sometimes *C. finmarchicus*. *Acartia tonsa* was the dominant copepod species (>6000 m^{-3}) at station F23P; this species has often been noted as characteristic of the Harbor. *A. tonsa* was found at highest numbers within the Bay at station N10P (~1300 m^{-3}), which receives tidal export from the Harbor, and at station F13P (almost 500 m^{-3}), which is southward along the coast and in the path of most southward flow of surface water that exits the Harbor.

3.1.6 ^{14}C Production Measurements

Appendix D contains many details of the ^{14}C incubation measurements and P-I curve modeling, but results of modeling and calculations for integrated water column production are summarized in Table 3-3. Note that all calculations used a survey-specific (rather than station- or day-specific) incident irradiance level so that variations in calculated production rates do not result from day-to-day fluctuations in irradiance. Calculations are presented for incubations of four samples from station F23P (at the edge of the Harbor) and station N16P (in the middle of the nearfield); incubations were performed on successive days (June 21 and 22).

The photic zone was deeper at station N16P (31.5-38 m) than at station F23P (12.5-15.5 m), a common finding. P_{max} or P_{sb} values ranged between 2.6 and 17.7 µg C (µg Chl)$^{-1}$ hr^{-1} and, with two exceptions, curves were fit without a photoinhibition term in the model. The surfacemost incubation consistently yielded the highest estimate of integrated water column production at station N16P in deeper water because P_{max} (or P_{sb}) and/or α were often the highest of a given series. In contrast, at station F23P, there was little consistent difference in modeled production rates as a function of the sampling depth of the water used in incubations. The difference in depth-related patterns for stations N16P and F23P is consistent with the presence of a strong vertical stratification at station N16P, compared to somewhat mixed conditions throughout the water column at station F23P. Thus, the phytoplankton communities at station N16P have more likely adapted to a set of environmental conditions (e.g., light, nutrients) and perhaps are somewhat different physiologically, if not distinctly different in populations (see Section 3.1.4). The decreasing P_{max} with depth at station N16P may thus indicate shade adaptation of deeper-water communities that exist at lower light.

The range of integrated production rates, based on individual samples, was 421-3067 mg C m^{-2} d^{-1} at station N16P, the highest value recorded with the surface sample collected on June 21. The range of integrated production rates at station F23P was 553-1751 mg C m^{-2} d^{-1}, also the highest value recorded with the surface sample collected on June 21.

Using the calculation scheme described previously in Section 2 (methods) to combine results of the four incubations into a single estimate, rates of 1440 and 846 mg C m^{-2} d^{-1} were calculated for station F23P on

June 21 and 22, respectively. From the composite profile for station N16P, rates of 2246 and 968 mg C $m^{-2} d^{-1}$ were calculated on June 21 and 22, respectively. Station comparisons and metabolism in general are additionally discussed in Section 6.

3.1.7 Dark Respiration Measurements

Dissolved oxygen (DO) dark-bottle-incubation time series were performed at three depths (surface, mid-depth at the subsurface chlorophyll maximum, and mid-bottom in the bottom water layer). Successful incubations were obtained for samples from stations N20P (middle of the nearfield) and F19 (east of the nearfield). A successful surface water incubation was also performed at station F24 in the coastal zone between the northern Harbor (station F23P) and the nearfield. All time series data and plots are presented in Appendix D. The time series approach produced, in the case of each incubation, decreases in DO and significant (95%) linear regression slopes of DO vs. time. In some cases, regressions for data over 0-48 hours were not significant even though regressions for the 0-24 hour data set were significant (Appendix D). Slopes from all regressions indicated dark respiration rates ranging from ~0.004 to 0.029 mg $O_2 L^{-1} h^{-1}$. A pattern of decline in dark respiration with depth was suggested. At station F19, for example, the rates (as determined by the regression slope) declined from 0.009 to 0.006 to 0.004 mg $O_2 L^{-1} h^{-1}$ with increasing depth. At station N20P, the surface rate was ~0.019 to 0.029 mg $O_2 L^{-1} h^{-1}$ over the 0-48 and 0-24 hour time frames, whereas the mid-depth and mid-bottom rates were lower, 0.005 and 0.004 mg $O_2 L^{-1} h^{-1}$, respectively. The surface water rate at station F24 was 0.018 mg $O_2 L^{-1} h^{-1}$.

3.2 Nearfield Survey

3.2.1 Distribution of Water Properties from Vertical Profiling

Scatter plots for a variety of parameters for the nearfield survey alone (June 24) are shown in Figure 3-23. Patterns and ranges may be compared to all stations (Figure 3-12) as well as to separate regions (Appendix C). Results from the nearfield survey of 21 stations show strong coherence among stations

with respect to T-S characteristics, a feature that reflects the general physical uniformity across the field. The range in T is broad (about 10°C) and the salinity range is from ~30.9 to 32.2 PSU; a decrease in temperature and concomitant increase in salinity represent increasing depth of the sample. Vertical patterns of temperature and salinity at all locations suggest a uniformly present surface layer (warm and less saline) about 15-20 m thick (Figures 3-24a and 3-24b). The thermocline is sharp and extends near the bottom at shallower inshore stations (see Outer Western Transect, Figure 3-24a) and even reaches the bottom at station N10P in the southwestern corner of the nearfield.

As for the farfield data set, beam attenuation was essentially flat across the salinity range (Figure 3-23a). A slight increase in turbidity was noted in near-bottom water and at the minor subsurface chlorophyll maximum layer at a number of stations (Figure 3-23b), but the spikes in beam attenuation (up to 2 m^{-1}) noted at intermediate salinity in Figure 3-23a was primarily associated with higher levels of chlorophyll at stations N10P (particularly), N11, and N12. Those spikes created the apparent correlation between beam attenuation and chlorophyll (Figure 3-23a). DO profiles generally showed conditions near 100% saturation in the upper 20 m, with percent saturation often peaking at the mid-depth maximum and always decreasing below that depth.

The spatial distribution of chlorophyll is illustrated in Figure 3-24c. Highest concentrations (>2 $\mu g\ L^{-1}$) are found at the stations mentioned above: stations N10P, N11, and in a mid-water maximum at station N12. At each transect in deeper water east of those stations, a subsurface chlorophyll maximum layer (1.2-1.6 $\mu g\ L^{-1}$) is noted. Generally this layer occurs near 20 m, but at stations of the Outer Eastern Transect it is apparent at 30-40 m.

DIN concentrations were higher in surface waters where higher chlorophyll was noted (e.g., the same stations N10P, N11, and N12; Figure 3-24d). Offshore, surface layers were depleted in DIN and concentrations increased with depth, starting at the thermocline and continuing to the bottom.

3.2.2 Water Quality Variability in the Nearfield

As a rule, the presence of strong vertical stratification and similar vertical patterns across stations indicated that physical uniformity characterized most of the nearfield. Associated with stratification were notable vertical gradients in chlorophyll, DO, and DIN. Spatially, noteworthy variability to the relatively homogeneous field was found only along the shallow western side of the region, in particular centered at station N10P in the southwestern corner. Here, stratification was weaker, and both nutrients and chlorophyll were enriched relative to other stations. The enrichment must, in part, relate to outflow from Boston Harbor and has frequently been noted in the past, but it may also be fostered by more vertical mixing that is suggested from profiles at this location, where the mixing itself may also be from Harbor-Bay tidal exchange processes.

Table 3-1a. Abundance of the top five dominant phytoplankton taxa in samples collected near the surface in June 1994.

	Coastal Stations		Nearfield Stations						Cape Cod Bay Stations	
	F13P	F23P	N01P	N04P	N07P	N10P	N16P	N20P	F01P	F02P
	June 23	June 21	June 22	June 22	June 21	June 21	June 21	June 21	June 23	June 23
AMPHIDINIUM SPP.										0.002 (5)
CERATIUM FUSUS			0.001 (5)							
CERATIUM LONGIPES							0.002 (5)			
CHAETOCEROS COMPRESSUS	0.365 (2)	0.077 (4)				0.277 (2)		0.564 (1)		
CHAETOCEROS SPP. (10-20UM)		0.030 (5)			0.001 (3)			0.033 (5)		
CHAETOCEROS SPP.(<10UM)	0.018 (5)		0.003 (3)		0.001 (3)	0.080 (5)	0.005 (3)	0.054 (3)	0.014 (4)	0.006 (4)
CRYPTOMONADS	0.121 (3)	0.134 (3)	0.011 (2)	0.049 (2)	0.008 (2)	0.259 (3)	0.012 (2)	0.048 (4)	0.151 (2)	0.063 (2)
DINOPHYSIS NORVEGICA				0.001 (5)						
GYRODINIUM (CF) AUREOLUM										0.013 (3)
KATODINIUM ROTUNDATUM			0.001 (5)	0.002 (4)						
MICROFLAGELLATES	0.652 (1)	0.487 (2)	0.186 (1)	0.242 (1)	0.132 (1)	0.634 (1)	0.189 (1)	0.423 (2)	0.690 (1)	0.316 (1)
NAVICULOID DIATOMS			0.001 (5)							0.002 (5)
PYRAMIMONAS/TETRASELMIS SPP.			0.002 (4)							
RHIZOSOLENIA DELICATULA									0.016 (3)	
SKELETONEMA COSTATUM	0.026 (4)	0.649 (1)				0.175 (4)				
THALASSIONEMA NITZSCHOIDES									0.013 (5)	
THALASSIOSIRA SPP.							0.002 (5)			
UNID. ATHECATE DINOFLAGELLATE			0.001 (5)	0.003 (3)			0.003 (4)		0.014 (4)	0.013 (3)

Units are millions of cells/L and rankings are given in parentheses.

Table 3-1b. Abundance of the top five dominant phytoplankton taxa in samples collected near the chlorophyll maximum in June 1994.

	Coastal Stations		Nearfield Stations						Cape Cod Bay Stations	
	F13P	F23P	N01P	N04P	N07P	N10P	N16P	N20P	F01P	F02P
	June 23	June 21	June 22	June 22	June 21	June 21	June 21	June 21	June 23	June 23
CERATIUM LONGIPES			0.004 (4)		0.003 (4)		0.004 (4)			0.003 (5)
CHAETOCEROS COMPRESSUS	0.394 (2)	0.057 (5)		0.037 (2)		0.304 (2)		0.201 (2)	0.033 (4)	
CHAETOCEROS DECIPIENS				0.003 (5)						
CHAETOCEROS SPP. (10-20UM)		0.073 (4)			0.003 (3)	0.039 (5)	0.003 (5)	0.049 (4)		
CHAETOCEROS SPP.(<10UM)	0.070 (4)			0.010 (3)			0.008 (3)		0.010 (5)	0.003 (5)
CRYPTOMONADS	0.110 (3)	0.148 (3)	0.010 (2)	0.006 (4)	0.162 (2)	0.181 (3)	0.117 (2)	0.051 (3)	0.313 (2)	0.050 (2)
DINOPHYSIS NORVEGICA			0.006 (3)		0.001 (5)					
KATODINIUM ROTUNDATUM	0.028 (5)		0.001 (5)		0.003 (4)				0.043 (3)	
MICROFLAGELLATES	0.706 (1)	0.385 (2)	0.136 (1)	0.128 (1)	0.325 (1)	0.493 (1)	0.319 (1)	0.338 (1)	0.916 (1)	0.298 (1)
PYRAMIMONAS/TETRASELMIS SPP.				0.003 (5)				0.013 (5)		
SKELETONEMA COSTATUM	0.028 (5)	0.448 (1)				0.120 (4)				
THALASSIONEMA NITZSCHOIDES										0.007 (3)
UNID. ATHECATE DINOFLAGELLATE			0.001 (5)	0.006 (4)	0.001 (5)		0.003 (5)			0.004 (4)

Units are millions of cells/L and rankings are given in parentheses.

Table 3-2a. Abundance of all identified taxa in screened (20um) samples collected near the surface in June 1994.

	Coastal Stations		Nearfield Stations						Cape Cod Bay Stations	
	F13P	F23P	N01P	N04P	N07P	N10P	N16P	N20P	F01P	F02P
	Jun. 23	Jun. 21	Jun. 22	Jun. 22	Jun. 21	Jun. 21	Jun. 21	Jun. 21	Jun. 23	Jun. 23
ALORICATE CILIATES	45	13	8	3	3	33	23	33	45	5
CERATIUM FUSUS				8	10		5		15	73
CERATIUM LINEATUM			3	3		3		3		
CERATIUM LONGIPES	55		25	108	113	23	113	38	175	318
CERATIUM TRIPOS					5					
DICTYOCHA FIBULA										
DICTYOCHA SPECULUM	3	10				3				
DINOPHYSIS ACUMINATA	20									
DINOPHYSIS NORVEGICA	413	265	10	293	13	718	38	130	23	5
DINOPHYSIS OVUM	8	3	5	5		10		15		
DIPLOPSALIS SPP.	13									
GYRODINIUM SPIRALE						3				
GYRODINIUM SPP.	5							3		
HETEROCAPSA TRIQUETRA										
MESODINIUM RUBRUM	5					13		10	5	
PROTOPERIDINIUM BREVE	48	23		5		15		28		
PROTOPERIDINIUM DEPRESSUM	43	10		5		8		20		
PROTOPERIDINIUM SPP.	155	28	8	3	5	140		38		5
SCENEDESMUS SPP.							3	3		
TINTINNIDS	13	350	5	5		110	3	10		
UNID. ATHECATE DINOFLAGELLATE	3									
UNID. THECATE DINOFLAGELLATES	20			5				3	3	8

Units are cells/L

Table 3-2b. Abundance of all identified taxa in screened (20um) samples collected near the chlorophyll maximum in June 1994.

	Coastal Stations		Nearfield Stations						Cape Cod Bay Stations	
	F13P	F23P	N01P	N04P	N07P	N10P	N16P	N20P	F01P	F02P
	Jun. 23	Jun. 21	Jun. 22	Jun. 22	Jun. 21	Jun. 21	Jun. 21	Jun. 21	Jun. 23	Jun. 23
ALORICATE CILIATES	13	5	15	3		3	13	18	15	5
CERATIUM FUSUS									13	3
CERATIUM LINEATUM	3		3			3			5	3
CERATIUM LONGIPES	68	5	611	20	1001	13	473	28	1456	448
CERATIUM TRIPOS							3		3	5
DICTYOCHA FIBULA										
DICTYOCHA SPECULUM		25				5			10	5
DINOPHYSIS ACUMINATA	10									
DINOPHYSIS NORVEGICA	1954	523	1034	853	103	1071	138	1509	1481	10
DINOPHYSIS OVUM	20			3		18		35	5	
DIPLOPSALIS SPP.	28									
EBRIA TRIPARTITIA		3								
GYRODINIUM SPIRALE							3	3		
GYRODINIUM SPP.										
MESODINIUM RUBRUM	5	5	3	3				18	3	
PROTOPERIDINIUM BIPES	10									
PROTOPERIDINIUM BREVE	50	10	8	60		38		25	68	5
PROTOPERIDINIUM DENTICULATUM				3						
PROTOPERIDINIUM DEPRESSUM	43	13	8	78	18	10	5	53	90	5
PROTOPERIDINIUM PALLIDUM				3				3		
PROTOPERIDINIUM PELLUCIDUM										
PROTOPERIDINIUM SPP.	80	38	20	178	15	125	5	158	58	10
STAURASTRUM SPP.										
TINTINNIDS	8	460	3	5	5	108	13	50	3	8
UNID. ATHECATE DINOFLAGELLATE	3	8						3		
UNID. THECATE DINOFLAGELLATES	8		5	15	3	3		15	3	

Units are cells/L

Table 3-3. ^{14}C production (mg C m^{-2} d^{-1}) estimated for euphotic layer at BioProductivity stations F23P and N16P in June 1994.

	F23P 21-June-94				F23P 22-June-94				N16P 21-June-94				N16P 22-June-94			
Water depth (m)	24.5				23.0				44.0				42.5			
Z$_{(0.5\%Io)}$ (m)	15.5				12.5				38.0				31.5			
Sample depth (m)	1.6	4.1	9.8	20.5	1.4	4.9	7.5	11.6	1.5	7.8	16.9	28.3	1.4	7.4	21.0	28.3
Rate (mg C m^{-2} d^{-1})	1751	1185	1449	1572	553	1000	928	604	3067	2524	2192	511	1551	1134	472	421
Model[1]	W	W	W	W	W	W	W	W	W	W	W	W	W	W	P	P
P$_{SB}$ or P$_{MAX}$[2]	10.50	8.00	8.50	9.32	5.80	7.40	6.60	5.60	17.10	17.70	9.07	2.60	14.00	8.85	2.79	2.60
α[3]	0.070	0.040	0.060	0.064	0.024	0.070	0.070	0.030	0.240	0.130	0.470	0.050	0.090	0.075	0.050	0.049
β[4]	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.001	0.002

[1] P: Platt *et al.* (1980).
  W: Webb *et al.* (1974).
[2] P$_{SB}$: Production parameter for Platt *et al.* model.
  P$_{MAX}$: Production parameter for Webb *et al.* model.
[3] Parameter for both models.
[4] Parameter for Platt *et al.* model.
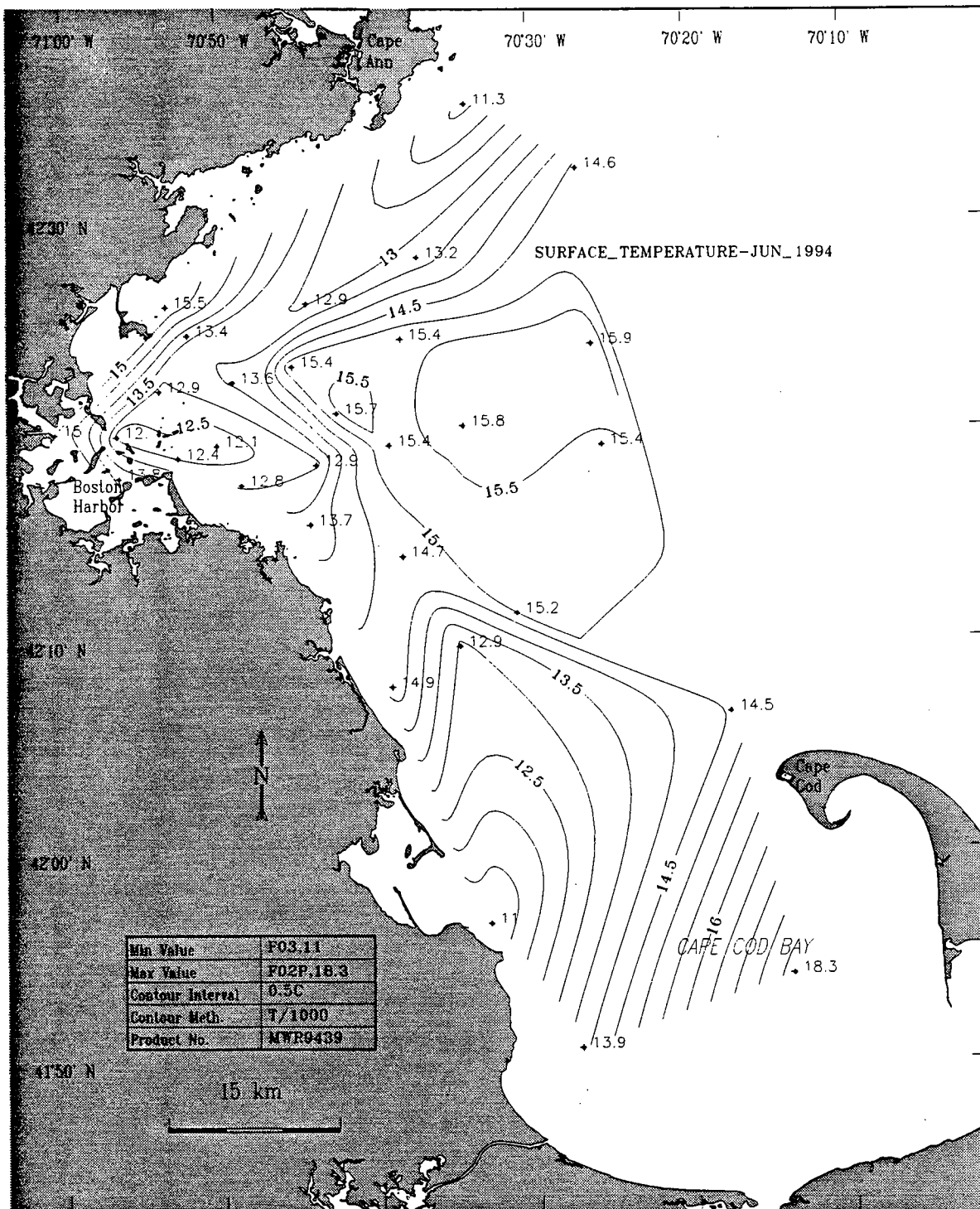
Figure 3-1. Surface temperature (°C) in the study area in June 1994. Data are from the surfacemost sample at all farfield survey stations, including the P stations within the nearfield grid (Appendix A).
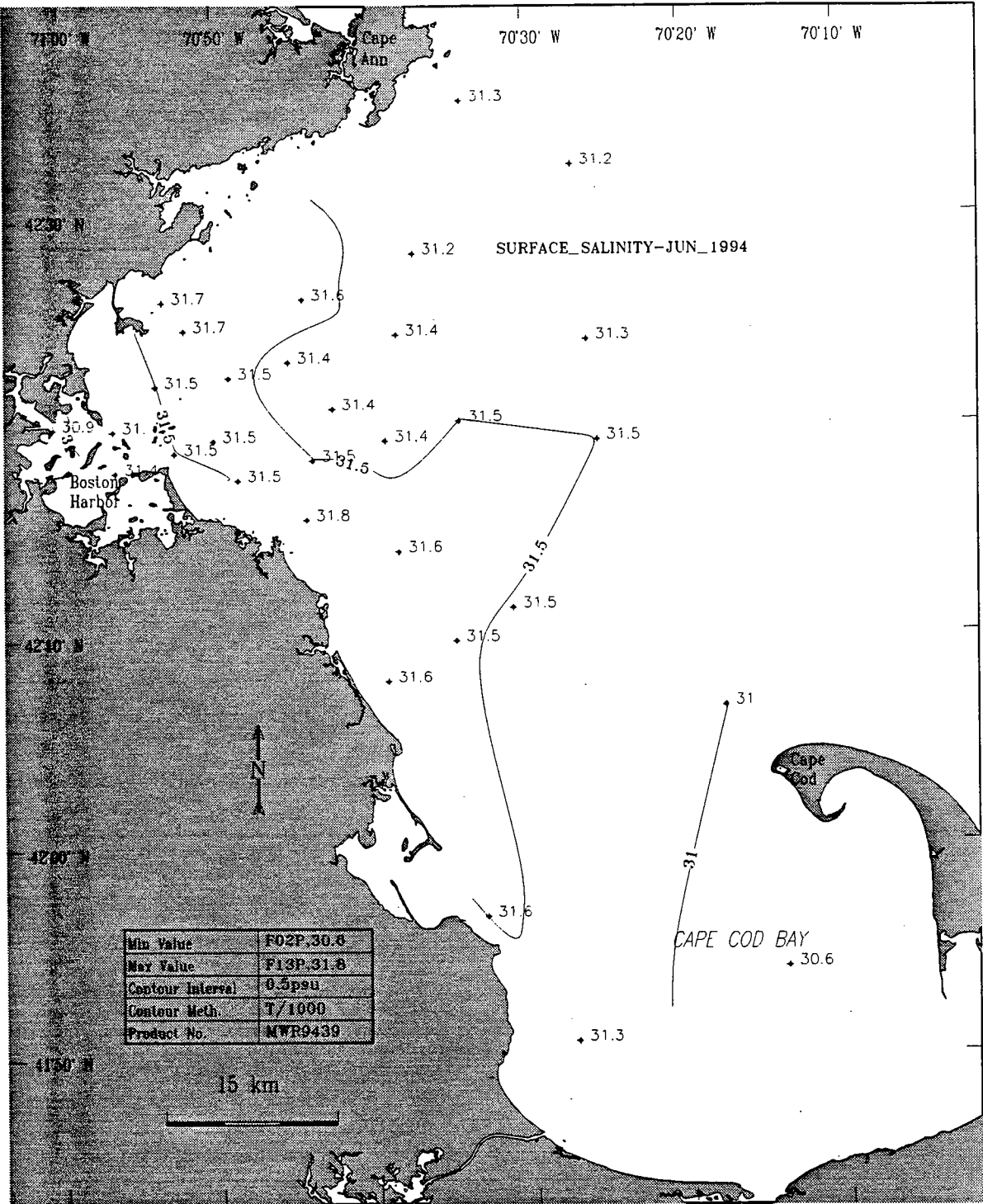
Figure 3-2. Surface salinity (PSU) in the study area in June 1994. Data are from the surfacemost sample at all farfield survey stations, including the P stations within the nearfield grid (Appendix A).
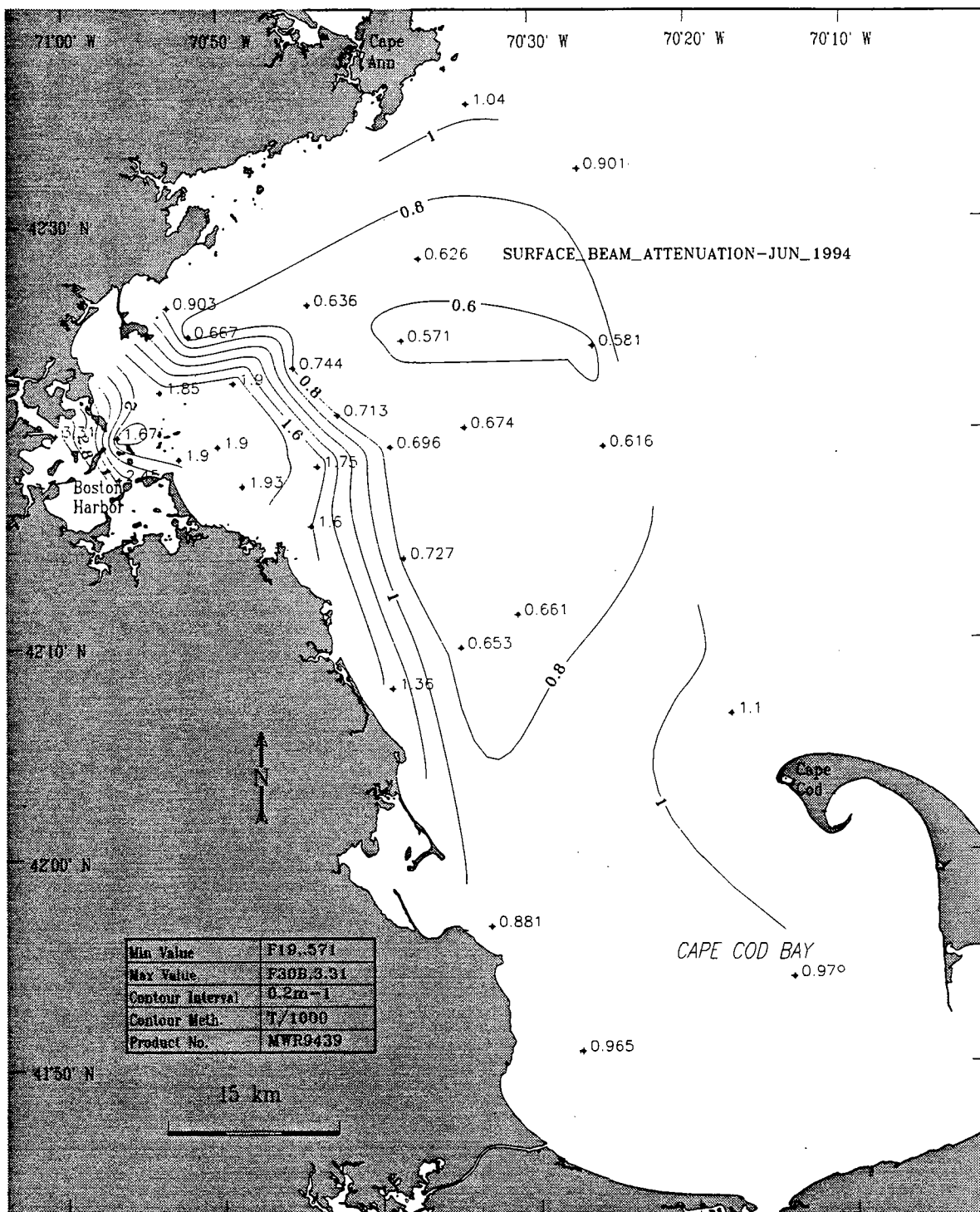
Figure 3-3. Surface beam attenuation (m⁻¹) in the study area in June 1994. Data are from the surfacemost sample at all farfield survey stations, including the P stations within the nearfield grid (Appendix A).
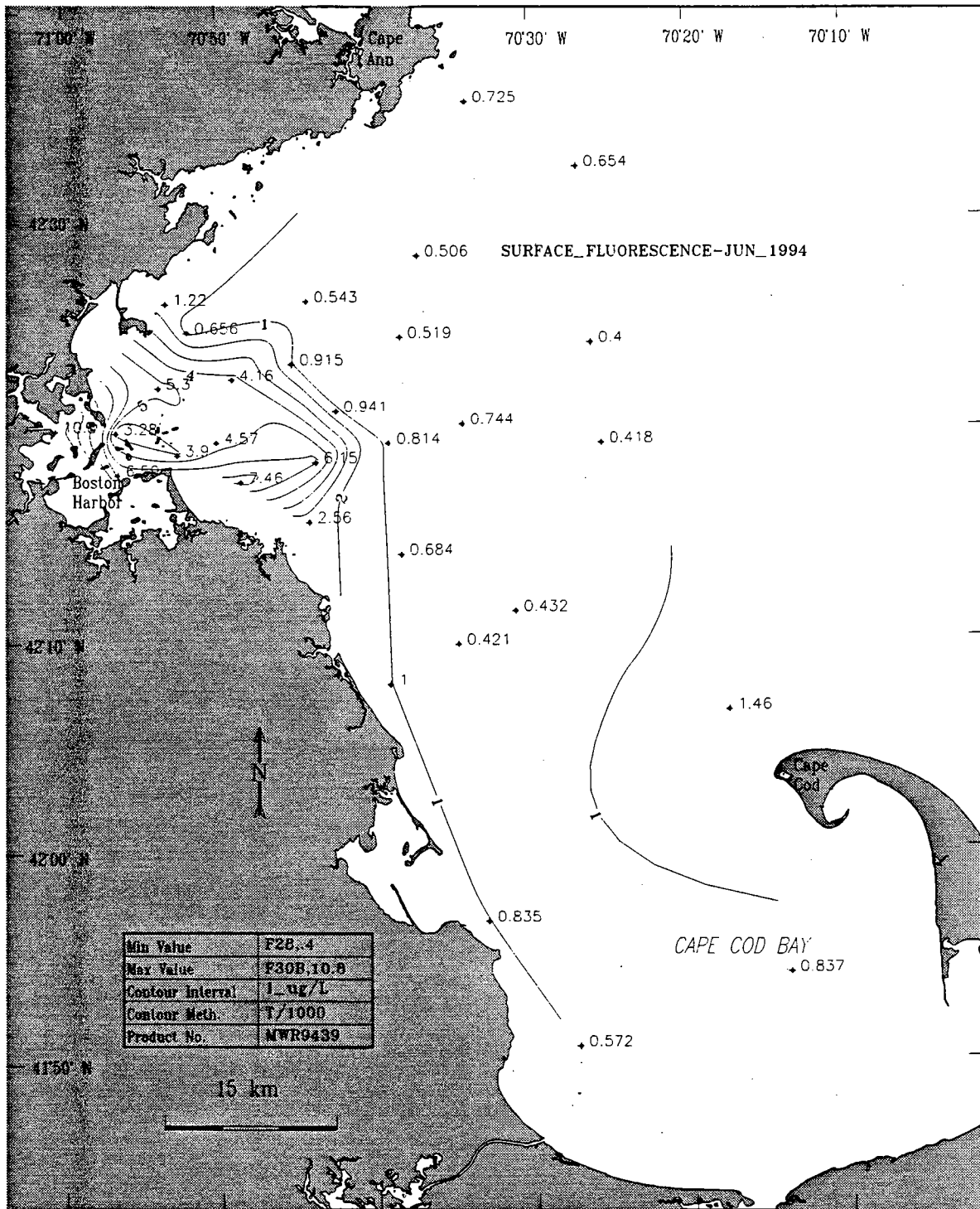
Figure 3-4. Surface *in situ* fluorescence (as μg Chl L⁻¹) in the study area in June 1994. Data are from the surfacemost sample at all farfield survey stations, including the P stations within the nearfield grid (Appendix A).
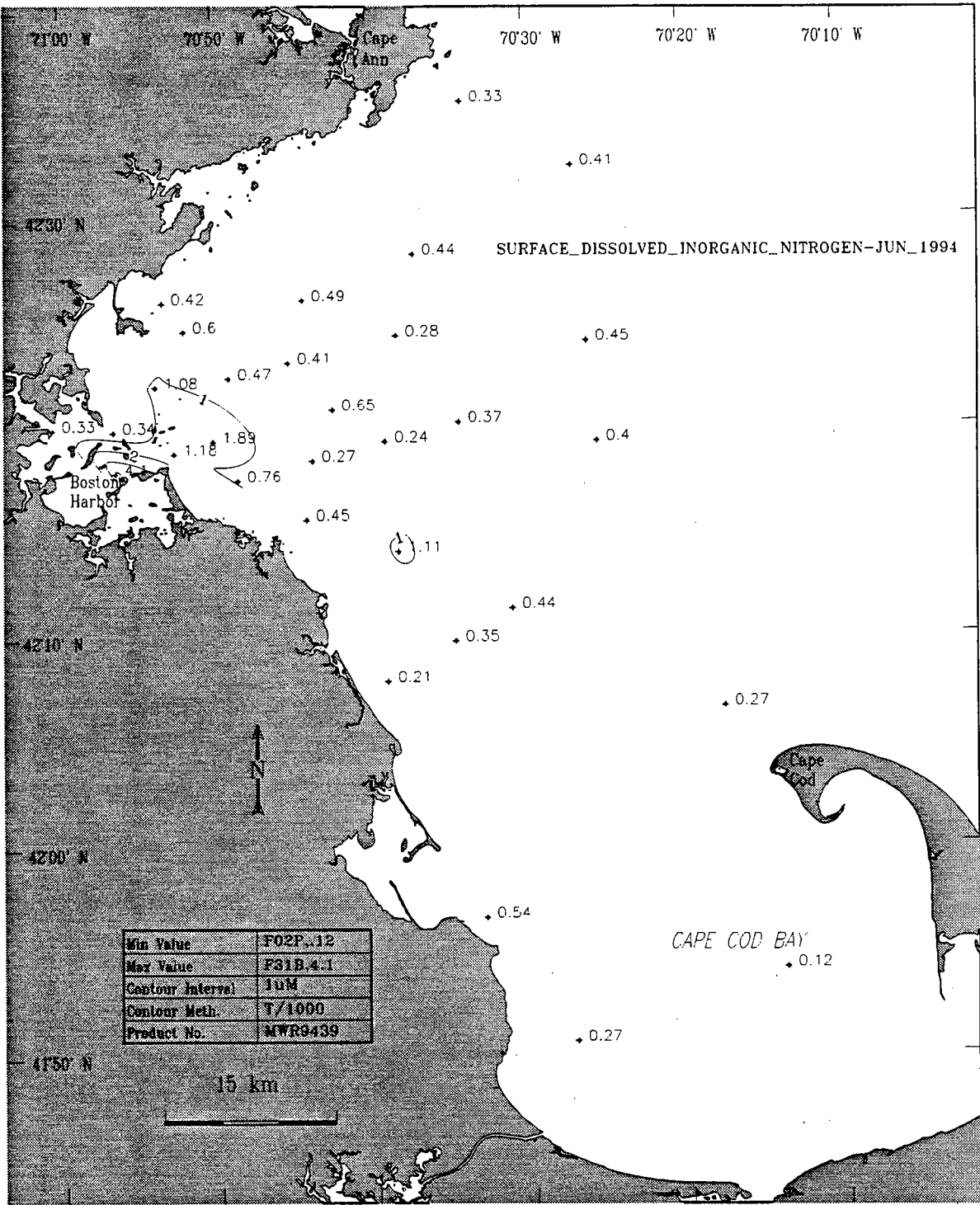
Figure 3-5. Surface dissolved inorganic nitrogen (DIN, μM) in the study area in June 1994. Data are from the surfacemost sample at all farfield survey stations, including the P stations within the nearfield grid (Appendix A).
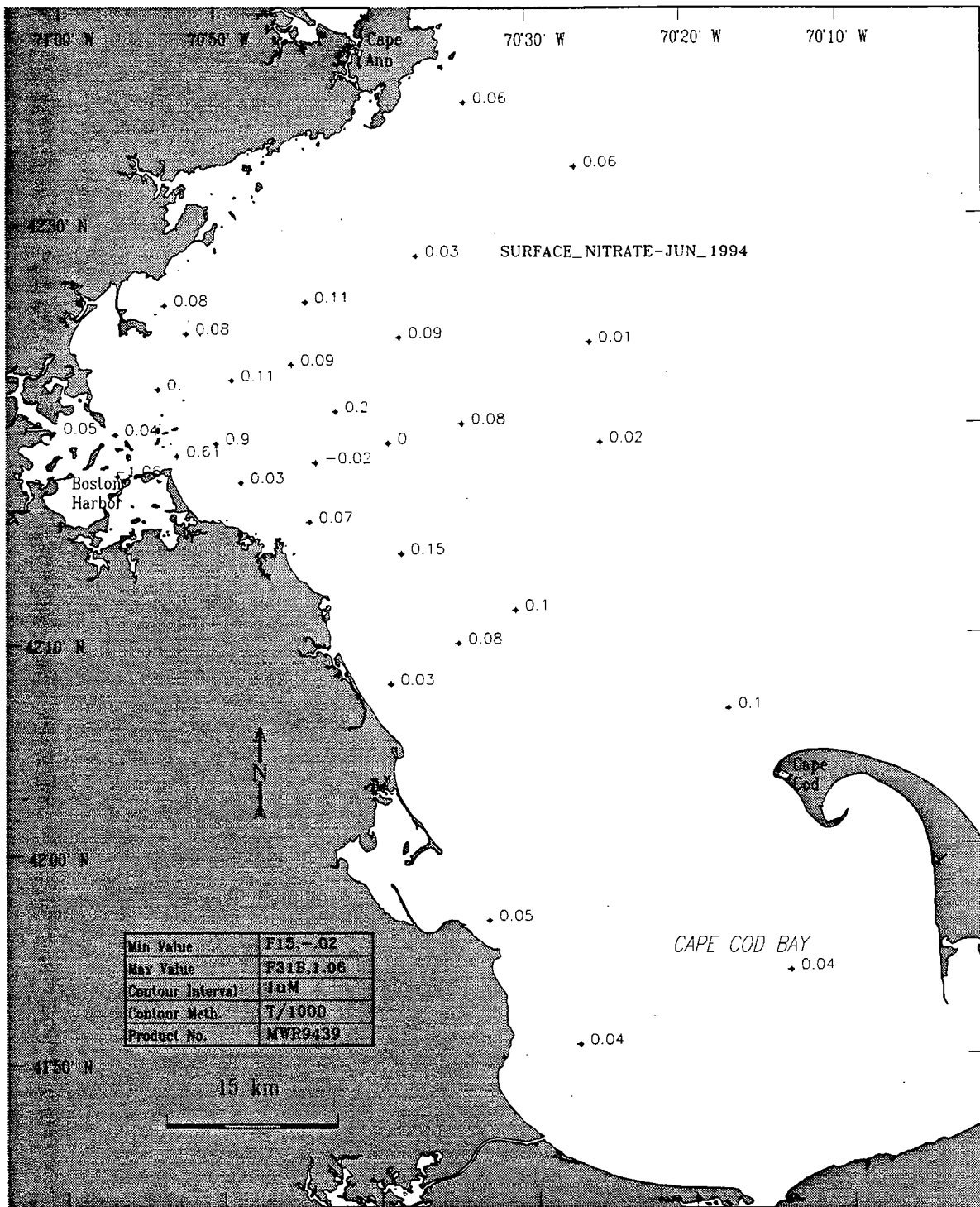
Figure 3-6. Surface nitrate (NO$_3$, μM) in the study area in June 1994. Data are from the surfacemost sample at all farfield survey stations, including the P stations within the nearfield grid (Appendix A).
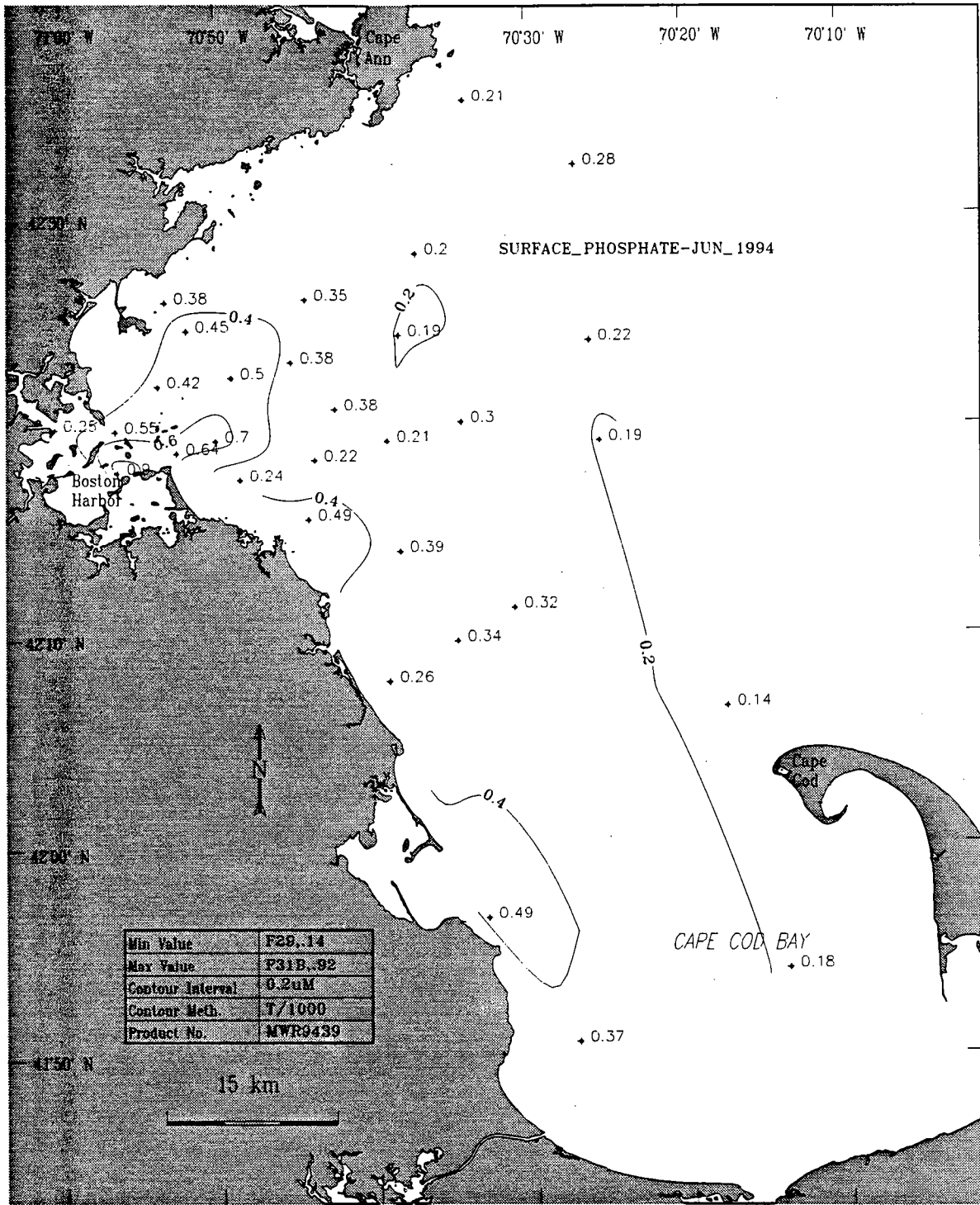
Figure 3-7. Surface phosphate (PO₄, μM) in the study area in June 1994. Data are from the surfacemost sample at all farfield survey stations, including the P stations within the nearfield grid (Appendix A).
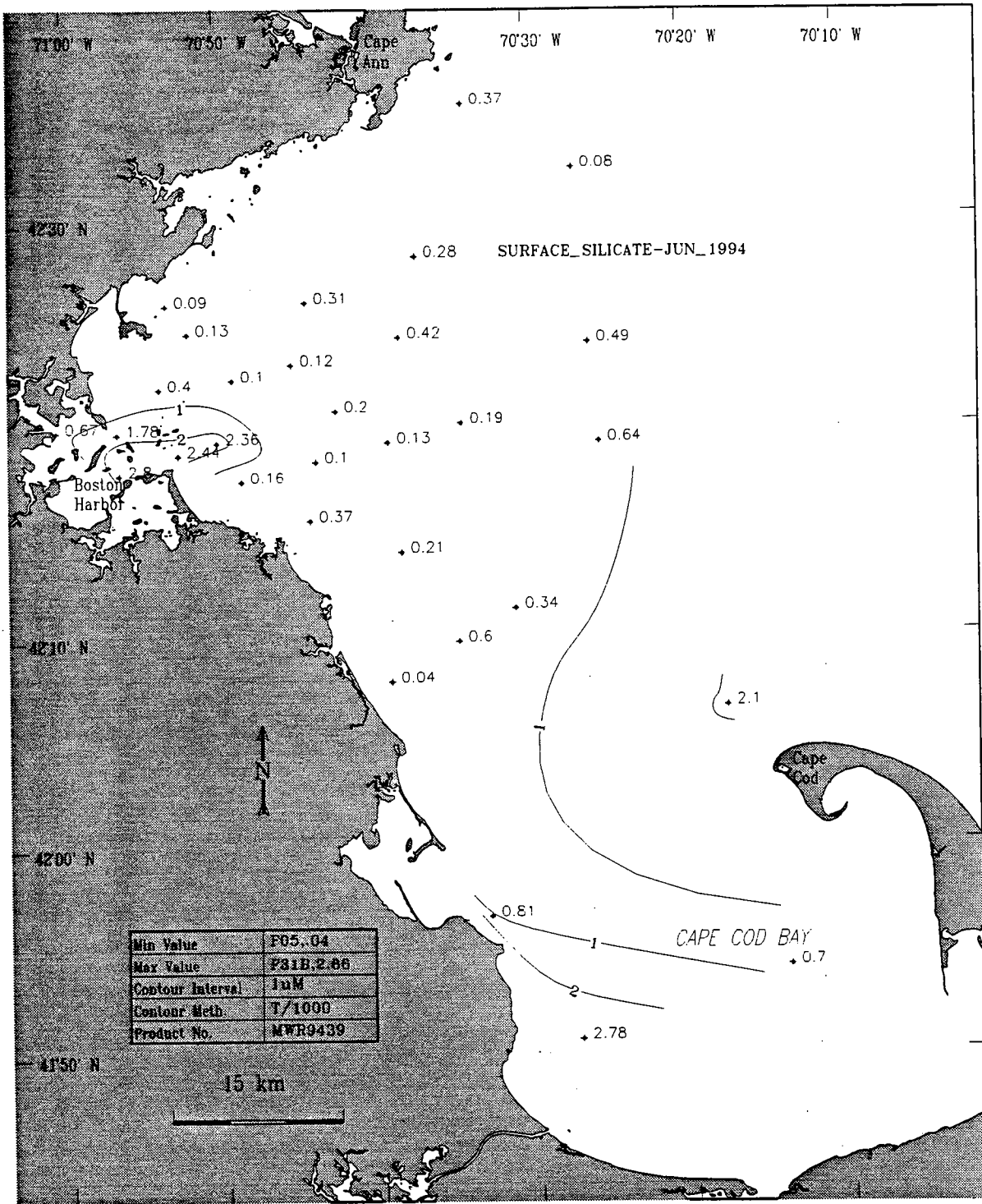
Figure 3-8. Surface silicate (SiO₄, μM) in the study area in June 1994. Data are from the surfacemost sample at all farfield survey stations, including the P stations within the nearfield grid (Appendix A).
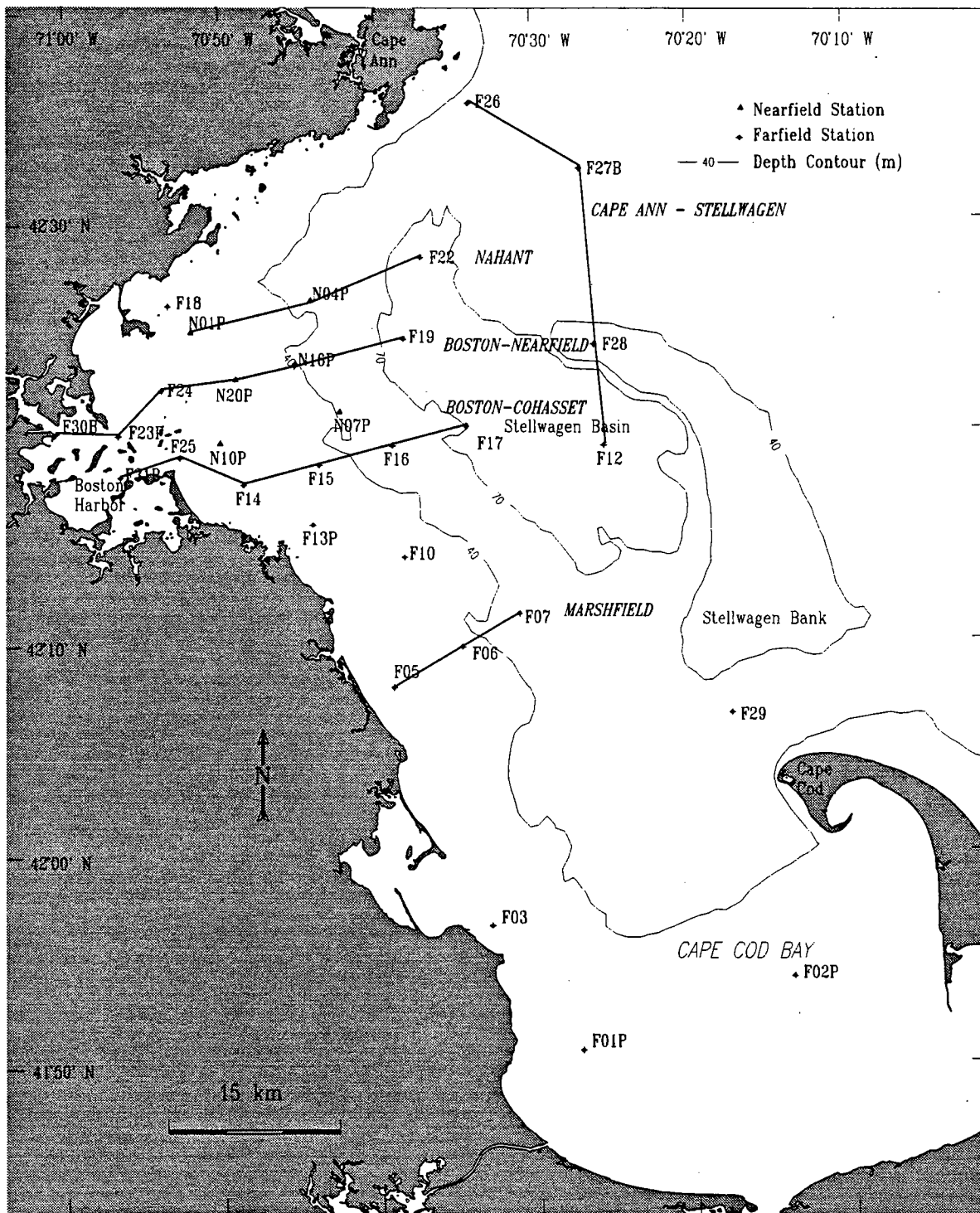
Figure 3-9. Map showing position of five standard transects for which vertical contour plots were produced in Figures 3-10 and 3-11.
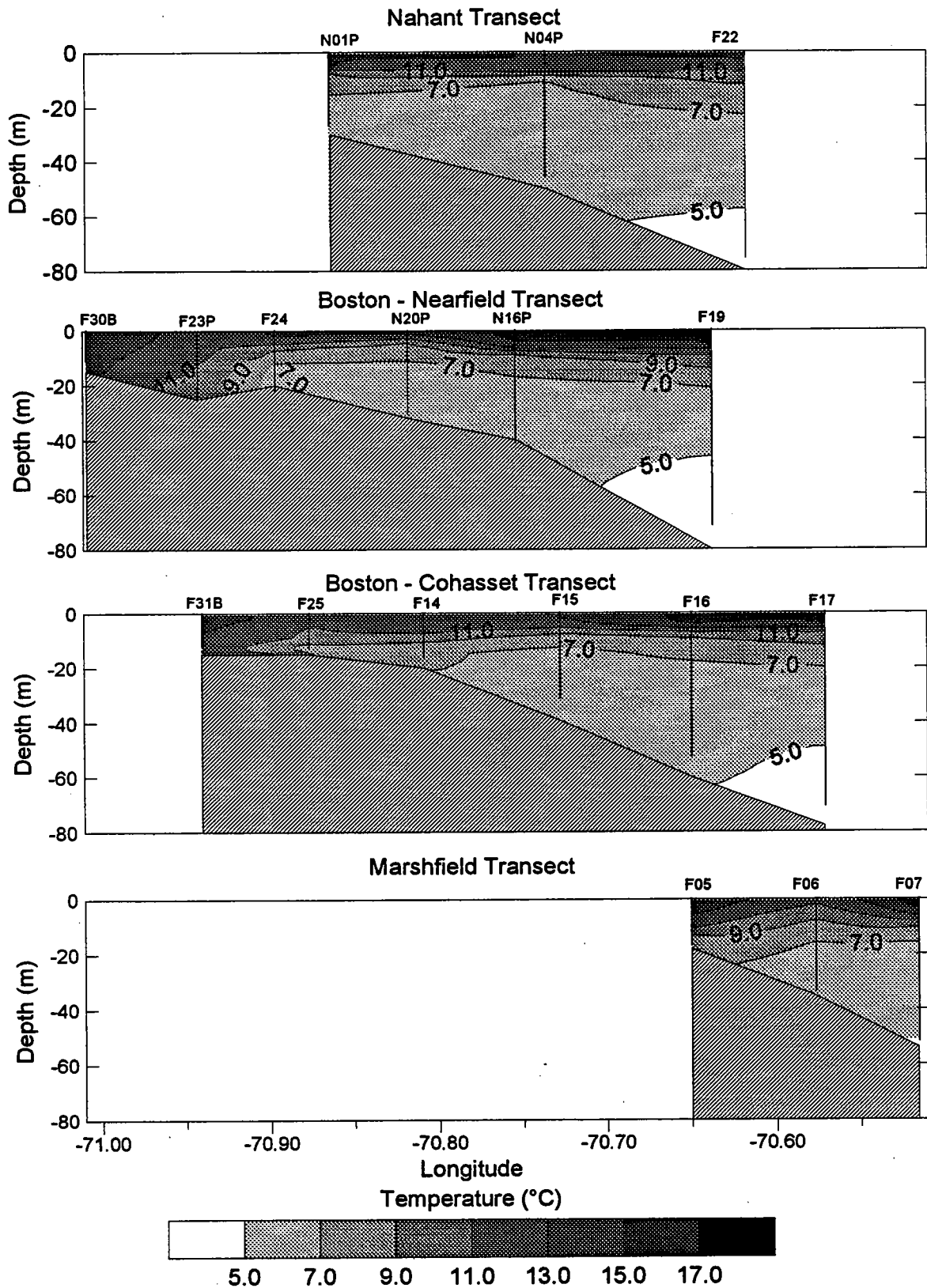
Figure 3-10a. Vertical section contours for standard transects (see Figure 3-9) on Survey W9407. The data used to produce the contours are from high-resolution continuous vertical profiles taken from the downcast at each station.
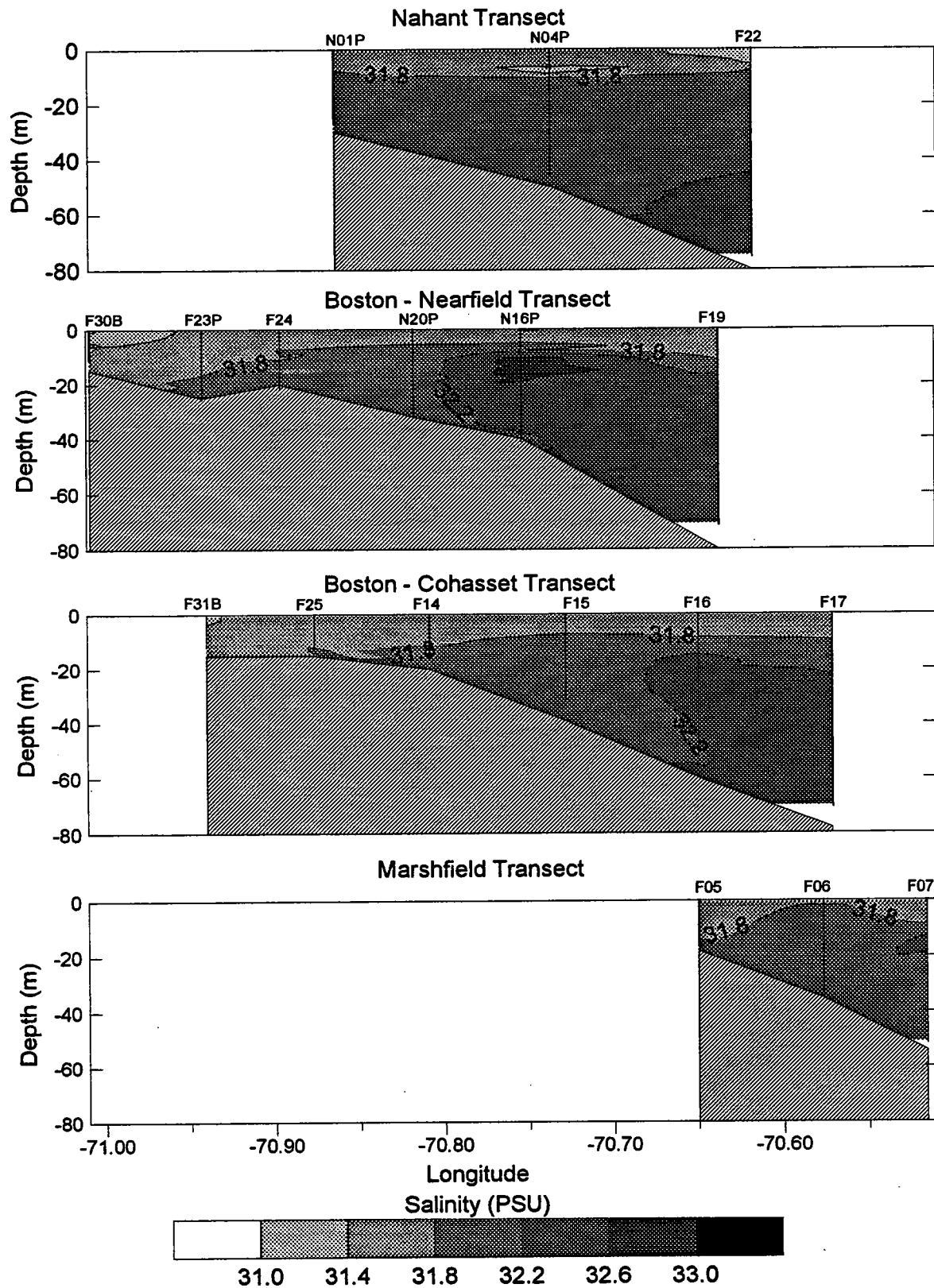
Figure 3-10b. Vertical section contours for standard transects (see Figure 3-9) on Survey W9407. The data used to produce the contours are from high-resolution continuous vertical profiles taken from the downcast at each station.
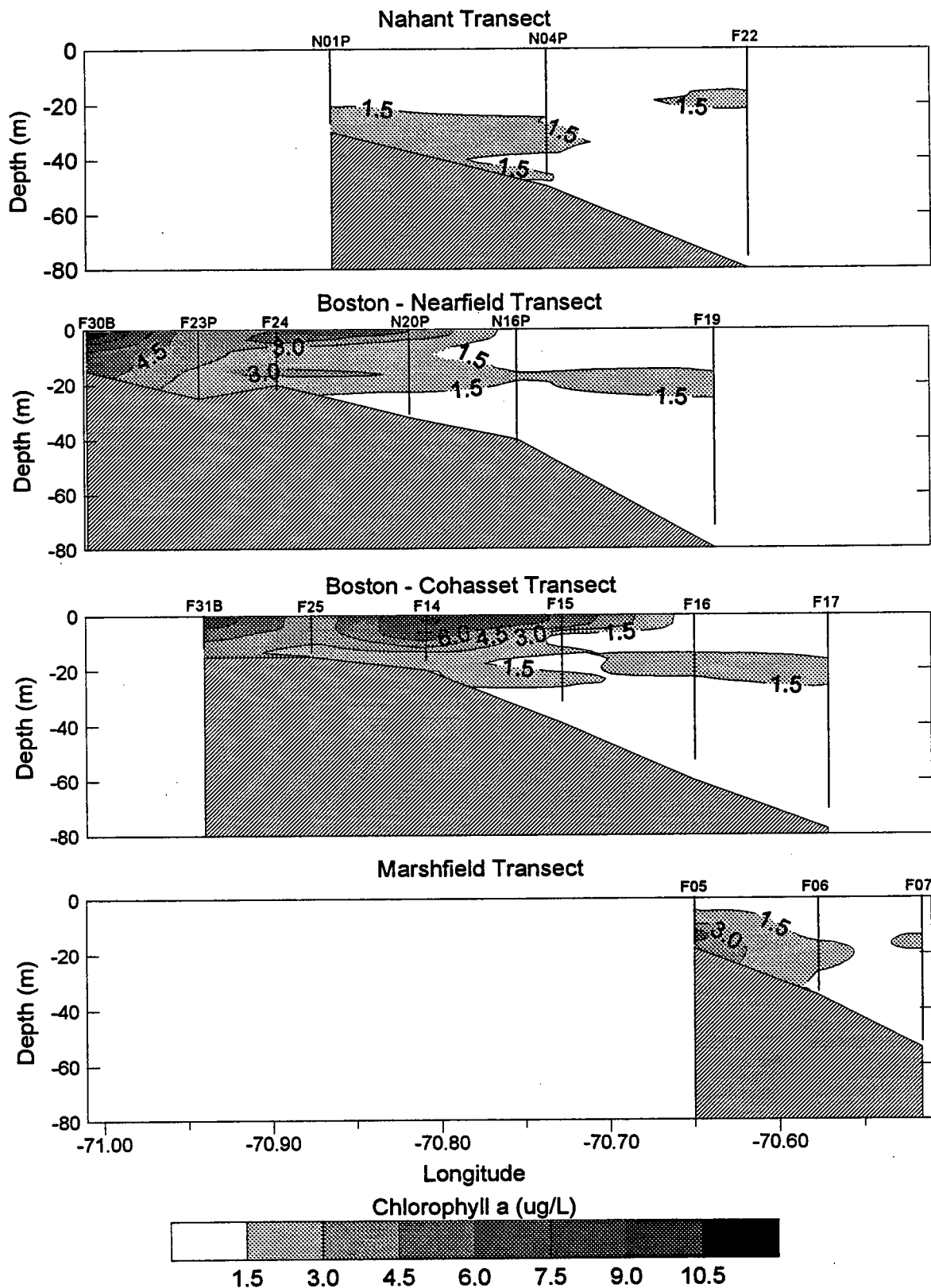
Figure 3-10c. Vertical section contours for standard transects (see Figure 3-9) on Survey W9407. The data used to produce the contours are from high-resolution continuous vertical profiles taken from the downcast at each station.
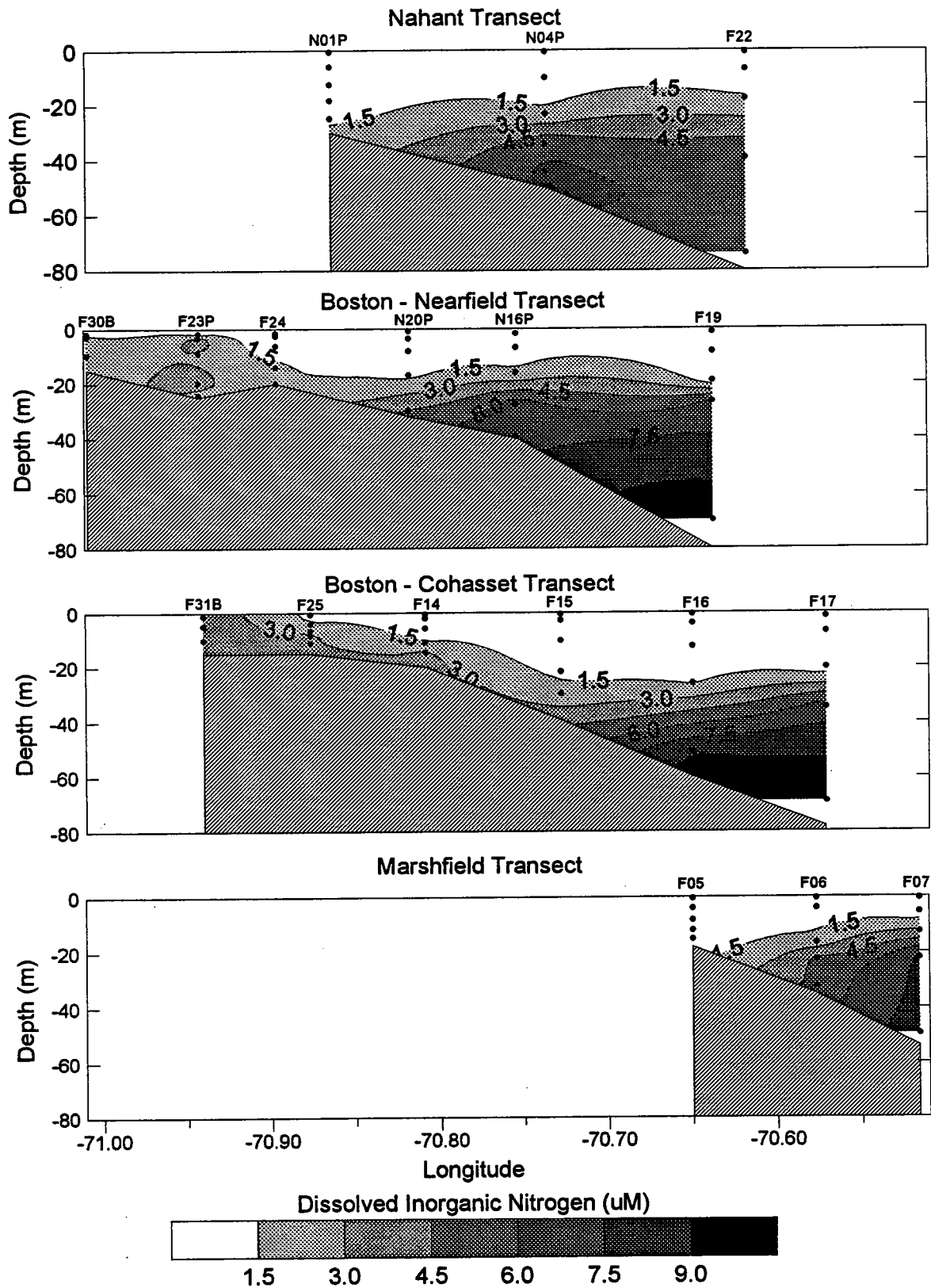
Figure 3-10d. Vertical section contours for standard transects (see Figure 3-9) on Survey W9407. The data used to produce the contours are from discrete bottle samples (Appendix A).

Cape Ann - Stellwagen Transect

Temperature (°C)

5.0 7.0 9.0 11.0 13.0 15.0 17.0

Salinity (PSU)

31.0 31.4 31.8 32.2 32.6 33.0

Chlorophyll a (ug L^{-1})

1.5 3.0 4.5 6.0 7.5 9.0 10.5

DIN (uM)

1.5 3.0 4.5 6.0 7.5 9.0

42.35   42.40   42.45   42.50   42.55   42.60

F12   F28   Latitude   F27B   F26
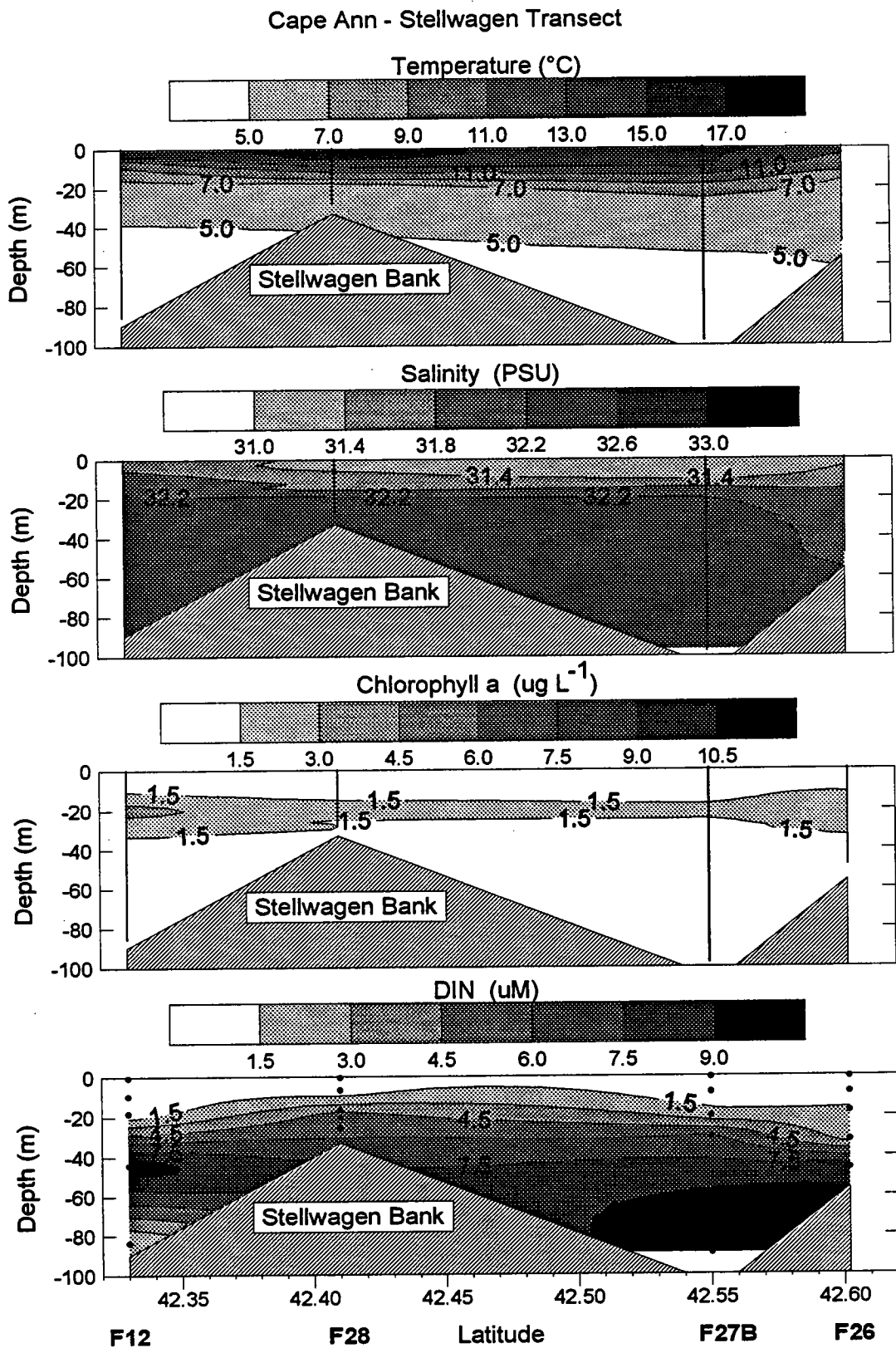
Figure 3-11.   Vertical section contours for the Cape Ann - Stellwagen transect (see Figure 3-9) on Survey W9407. The data used to produce the contours are from high-resolution continuous vertical profiles taken from the downcast at each station (temperature, salinity, and chlorophyll) and discrete bottle samples (DIN; Appendix A).

Salinity (PSU)

Salinity (PSU)

Chlorophyll a (ug/L)

All Stations (W9407)
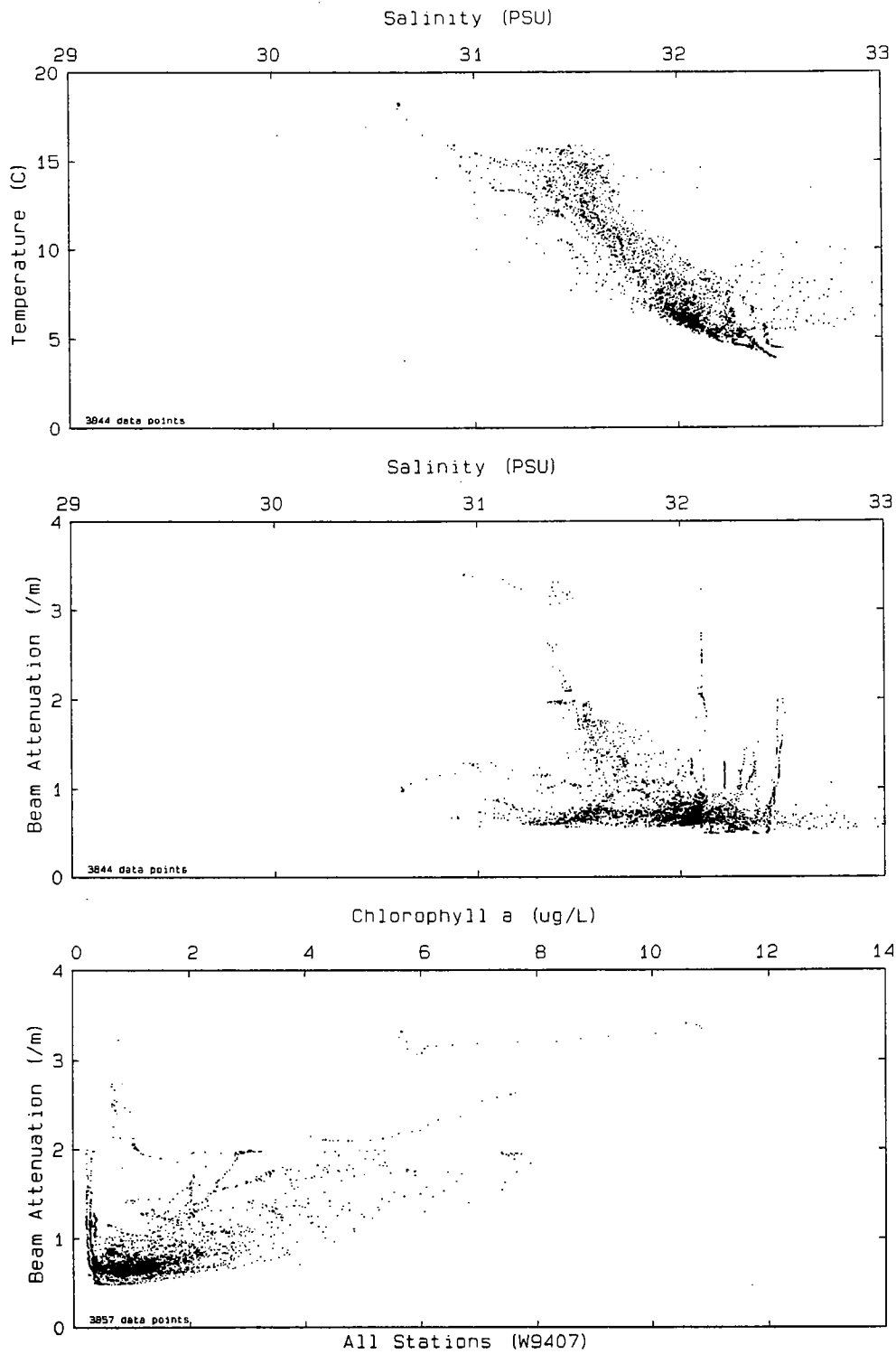
Figure 3-12a. Scatter plots of data acquired by *in situ* sensor package during vertical casts at all farfield and nearfield stations occupied in June 1994. Chlorophyll is estimated from *in situ* fluorescence.
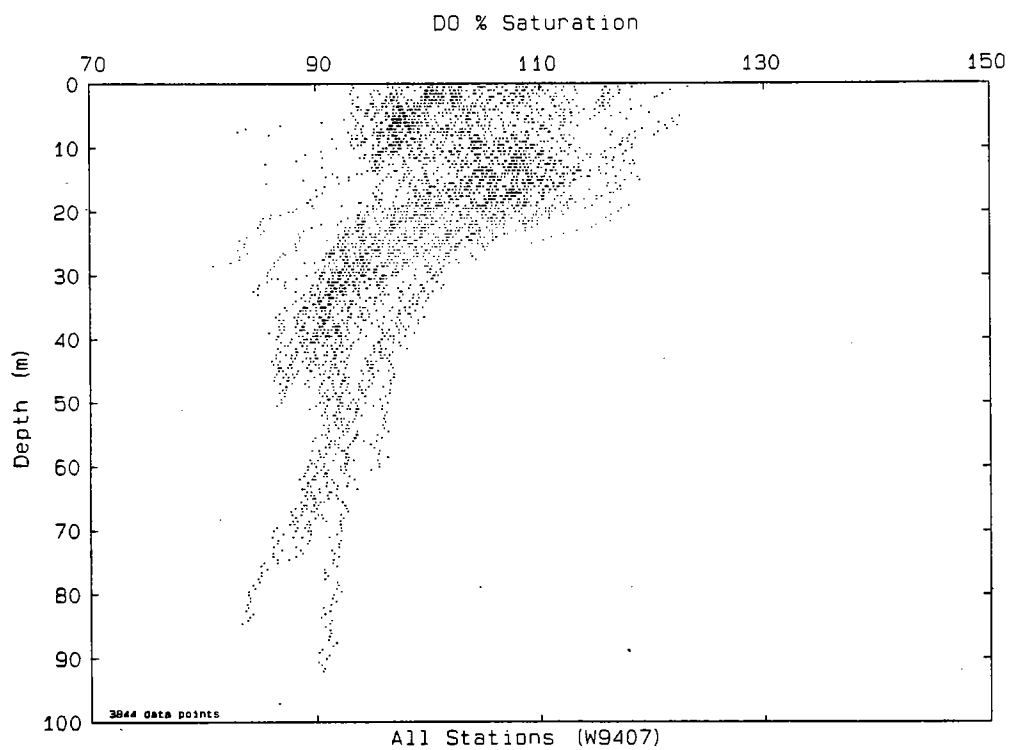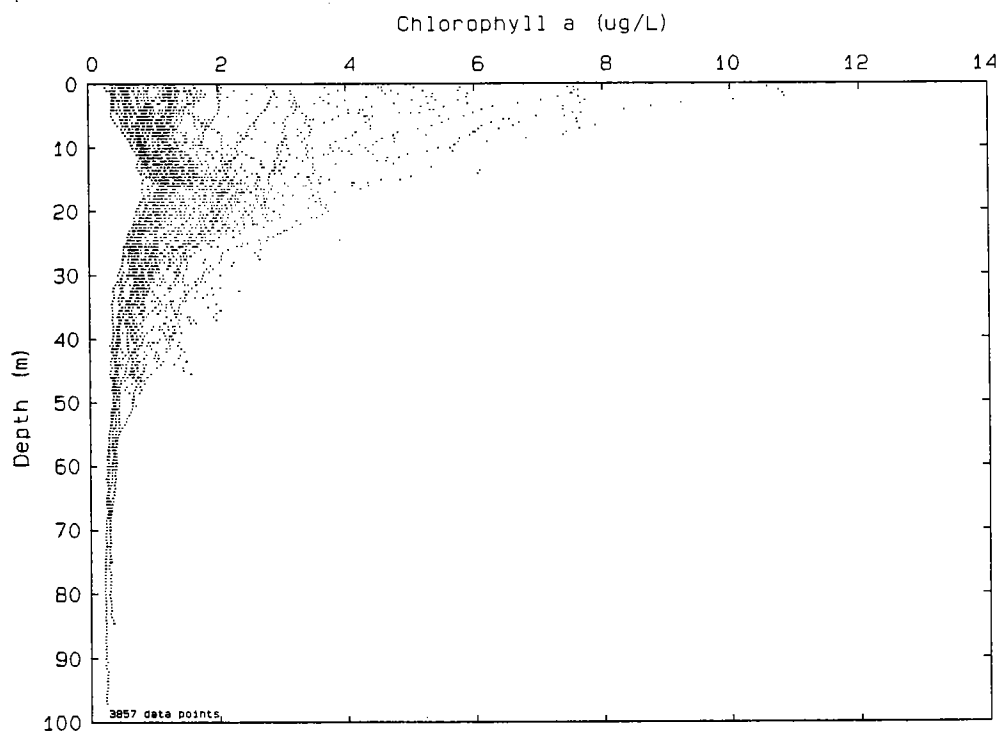
Figure 3-12b. Scatter plots of data acquired by *in situ* sensor package during vertical casts at all farfield and nearfield stations occupied in June 1994. Chlorophyll is estimated from *in situ* fluorescence.
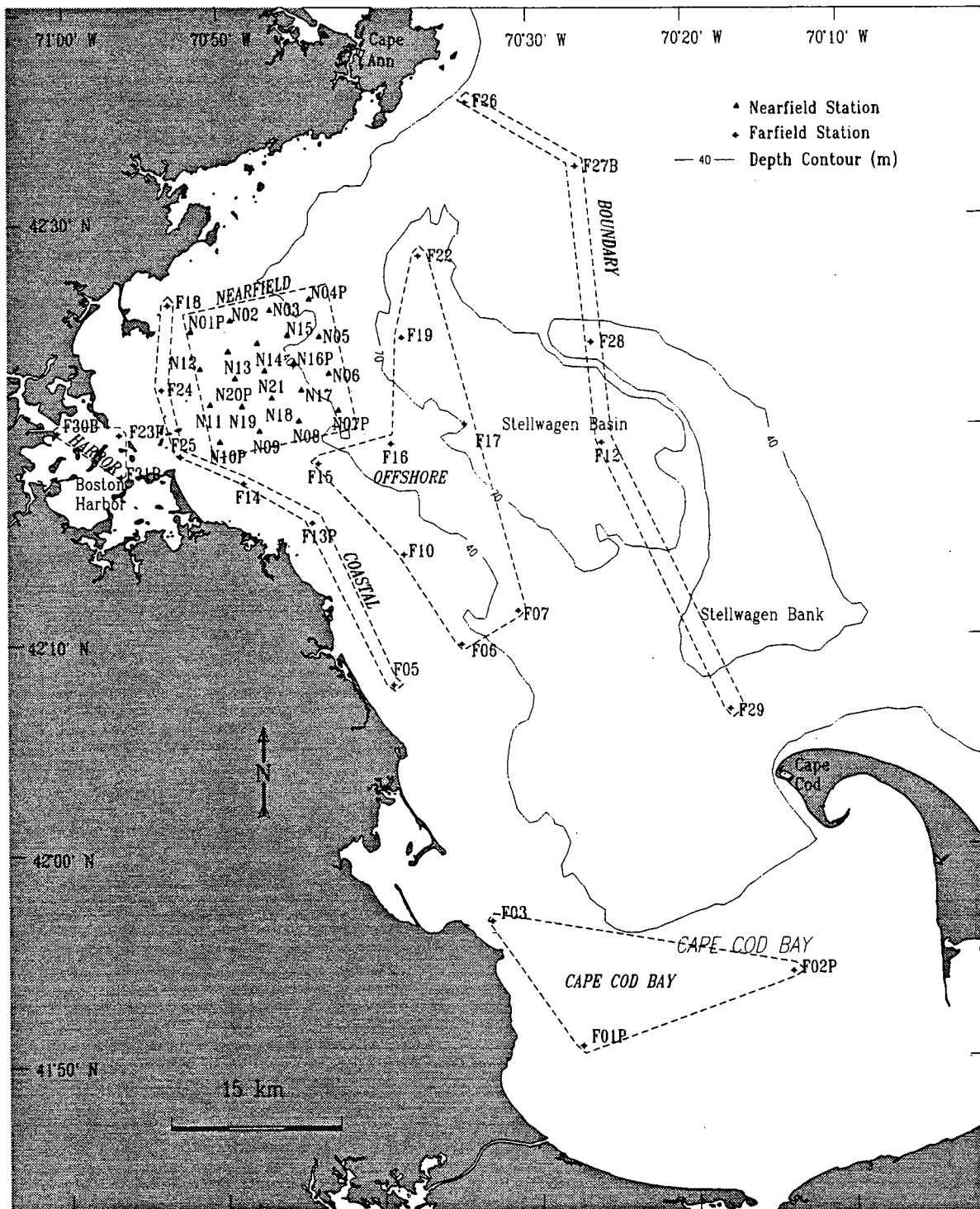
Figure 3-13. **Map to show regional station groups designated in Figures 3-14 through 3-21.**

June (W9407)

REGION

+ + + Boundary	● ● ●	Nearfield
□ □ □ Coastal	△ △ △	Offshore
* * * Cape Cod Bay	○ ○ ○	Boston Harbor
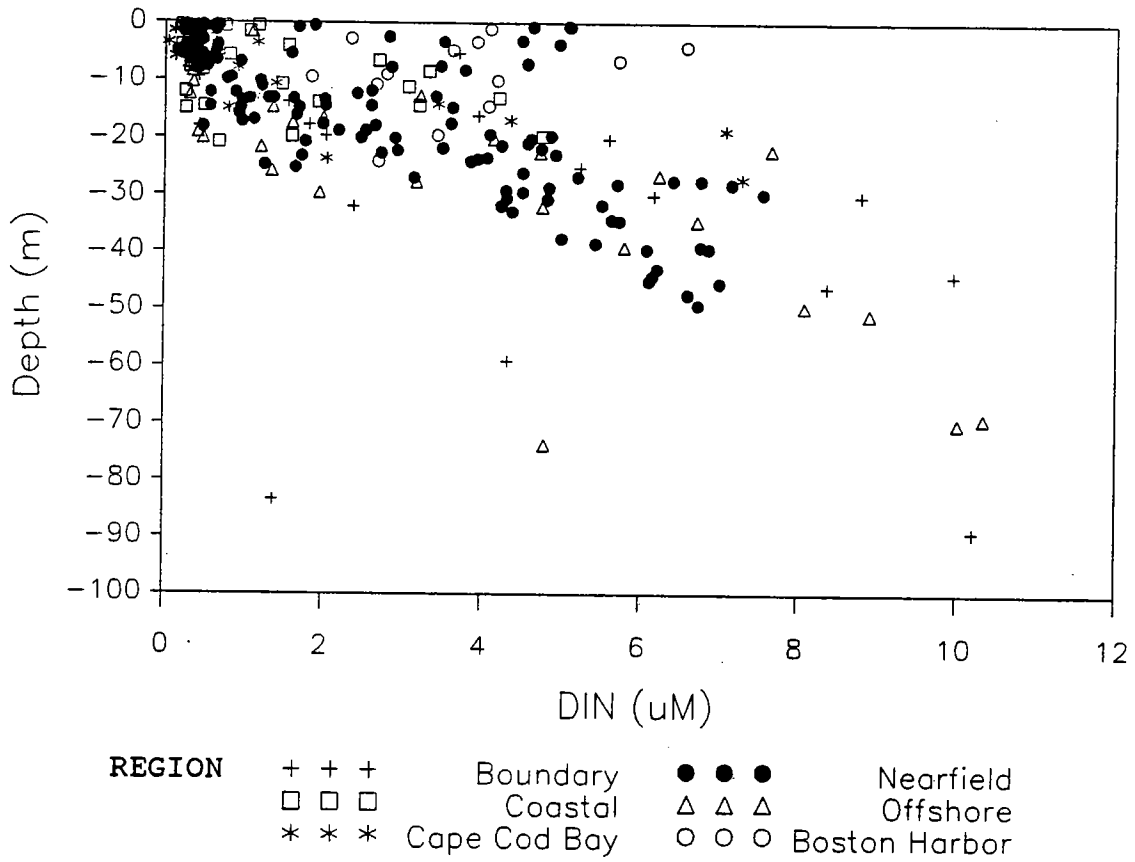
Figure 3-14a.   DIN vs. depth in June 1994.
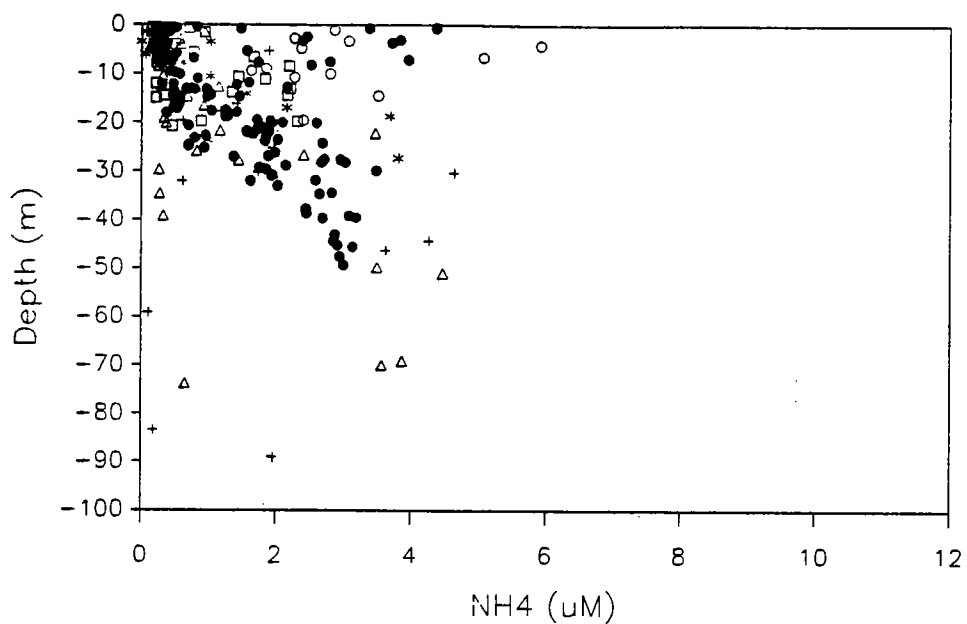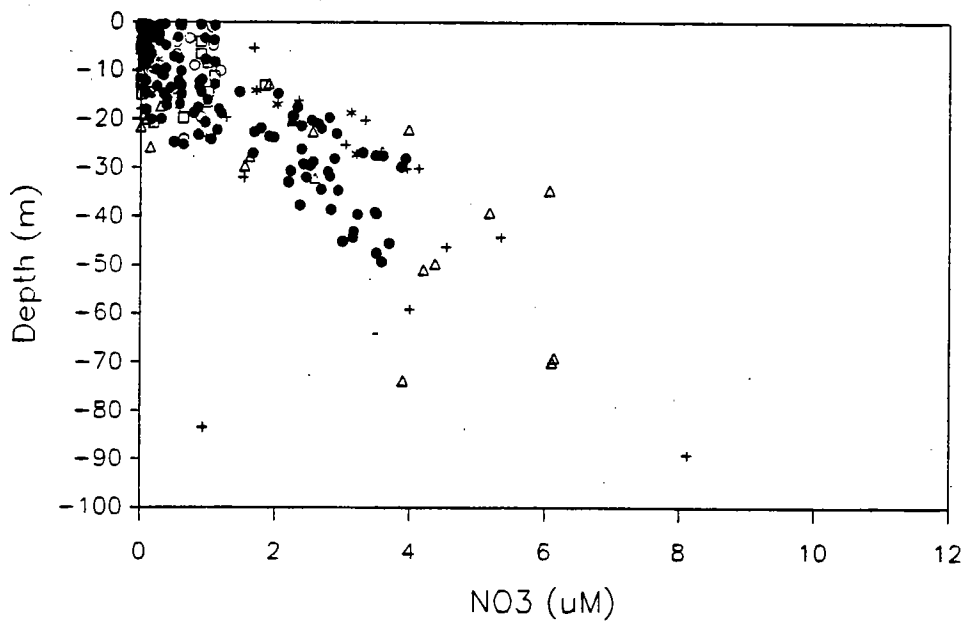
June (W9407)

June (W9407)

Figure 3-14b.   NH₄ and NO₃ vs. depth in June 1994.
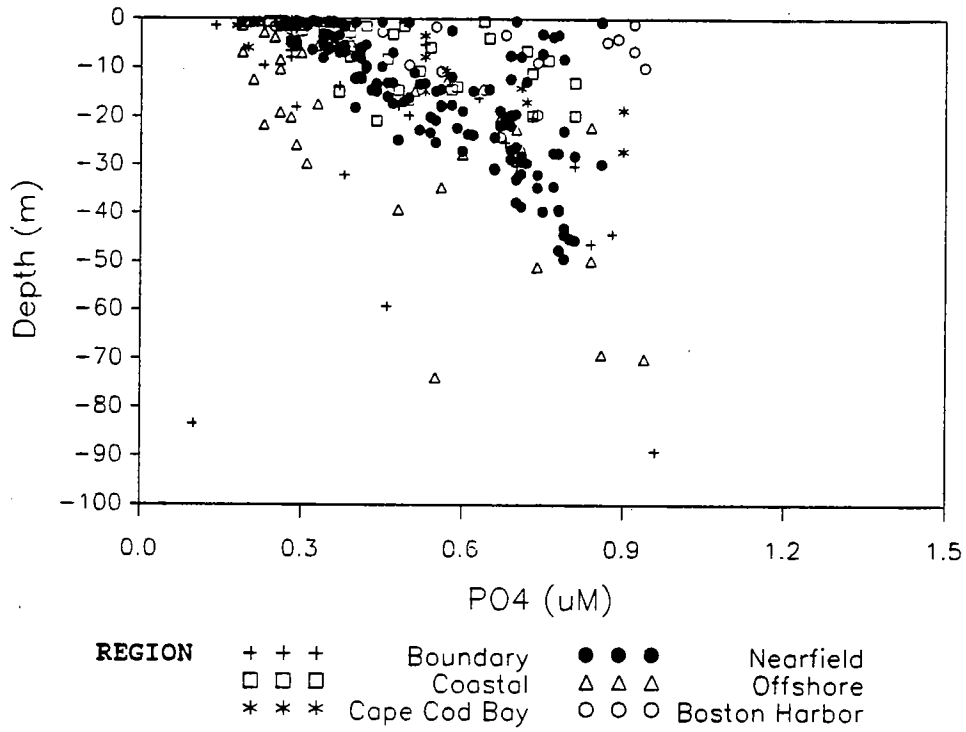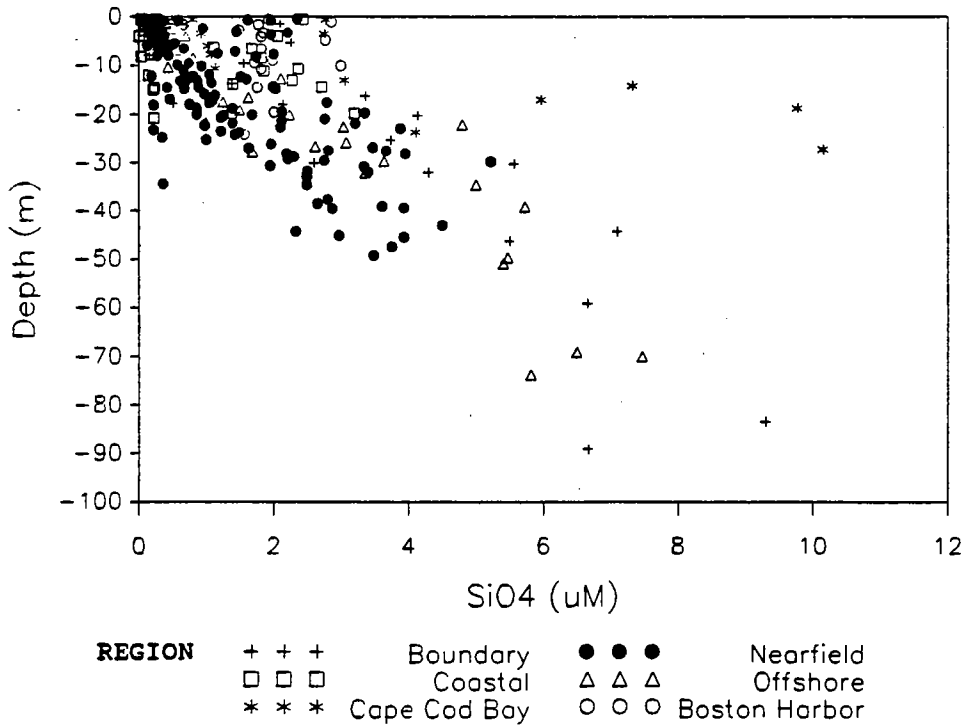
Figure 3-14c.   PO₄ and SiO₄ vs. depth in June 1994.

June (W9407)

REGION   + + +   Boundary   ● ● ●   Nearfield
         □ □ □   Coastal   △ △ △   Offshore
         * * *   Cape Cod Bay   ○ ○ ○   Boston Harbor

June (W9407)

REGION   + + +   Boundary   ● ● ●   Nearfield
         □ □ □   Coastal   △ △ △   Offshore
         * * *   Cape Cod Bay   ○ ○ ○   Boston Harbor
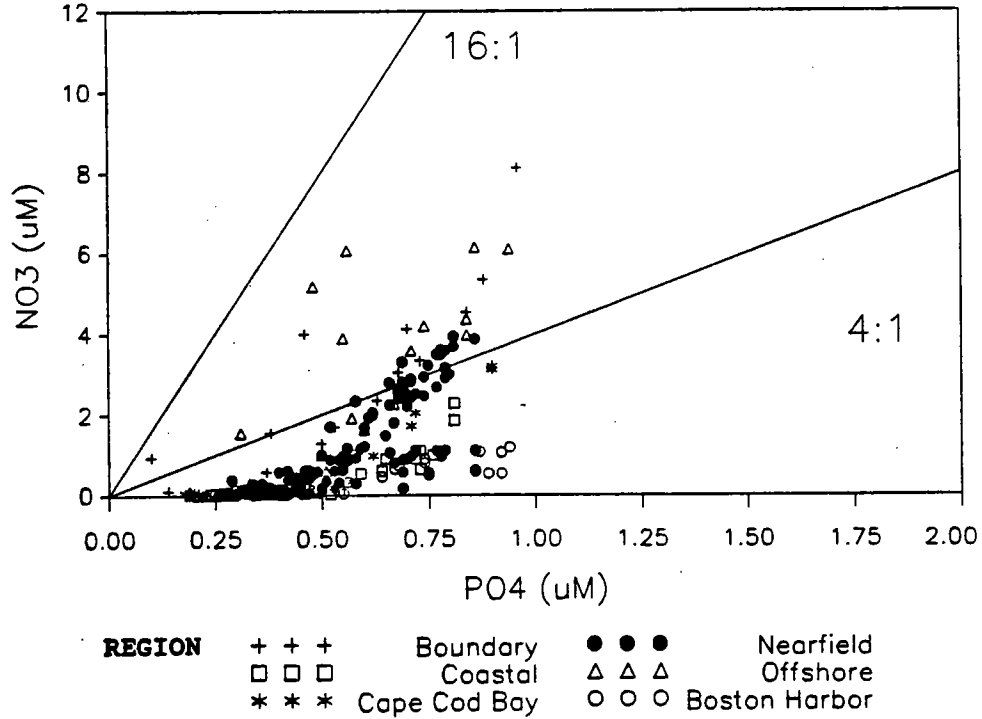
Figure 3-15a.   Scatter plots of nitrogen forms vs. PO$_4$ in June 1994.   Lines show constant proportions of nitrogen relative to phosphorus.

June (W9407)
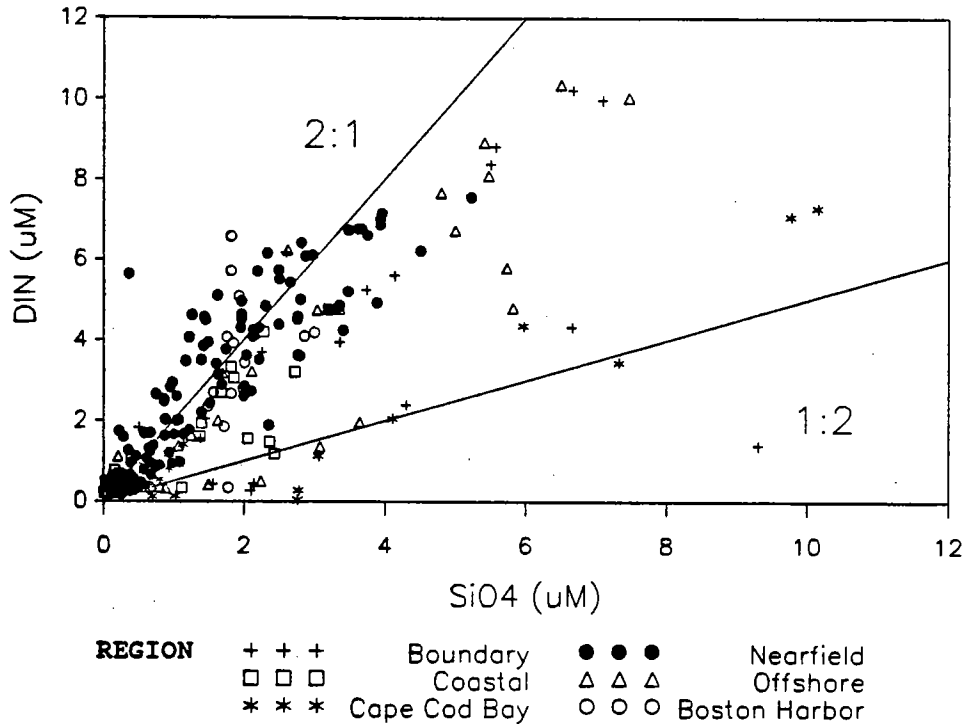
June (W9407)
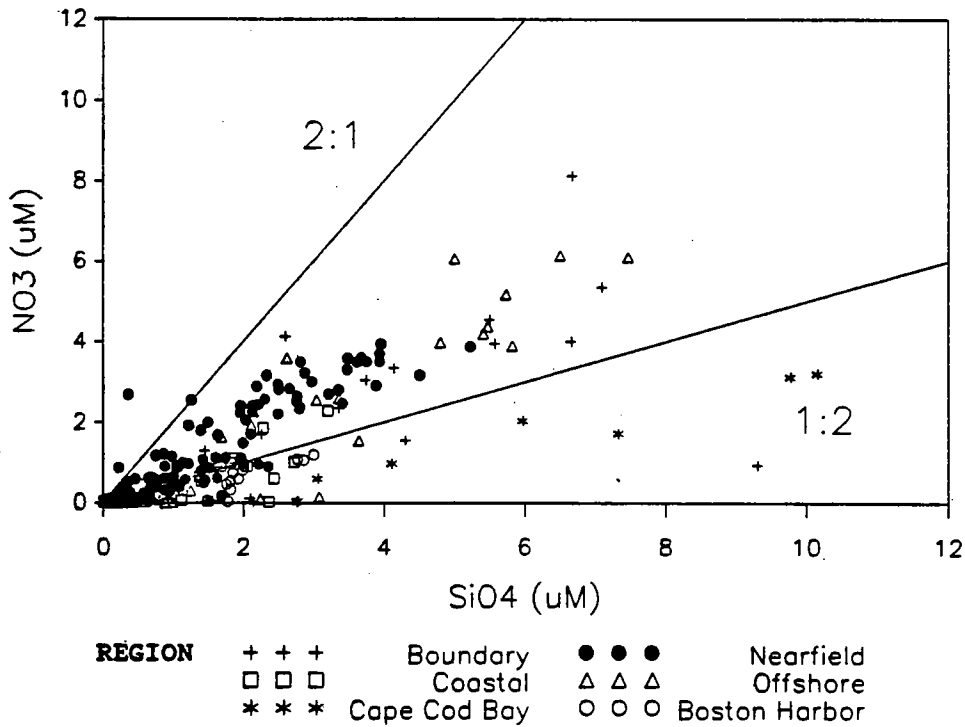
Figure 3-15b. Scatter plots of nitrogen forms vs. SiO$_4$ in June 1994. Lines show constant proportions of nitrogen relative to silicate.

June (W9407)
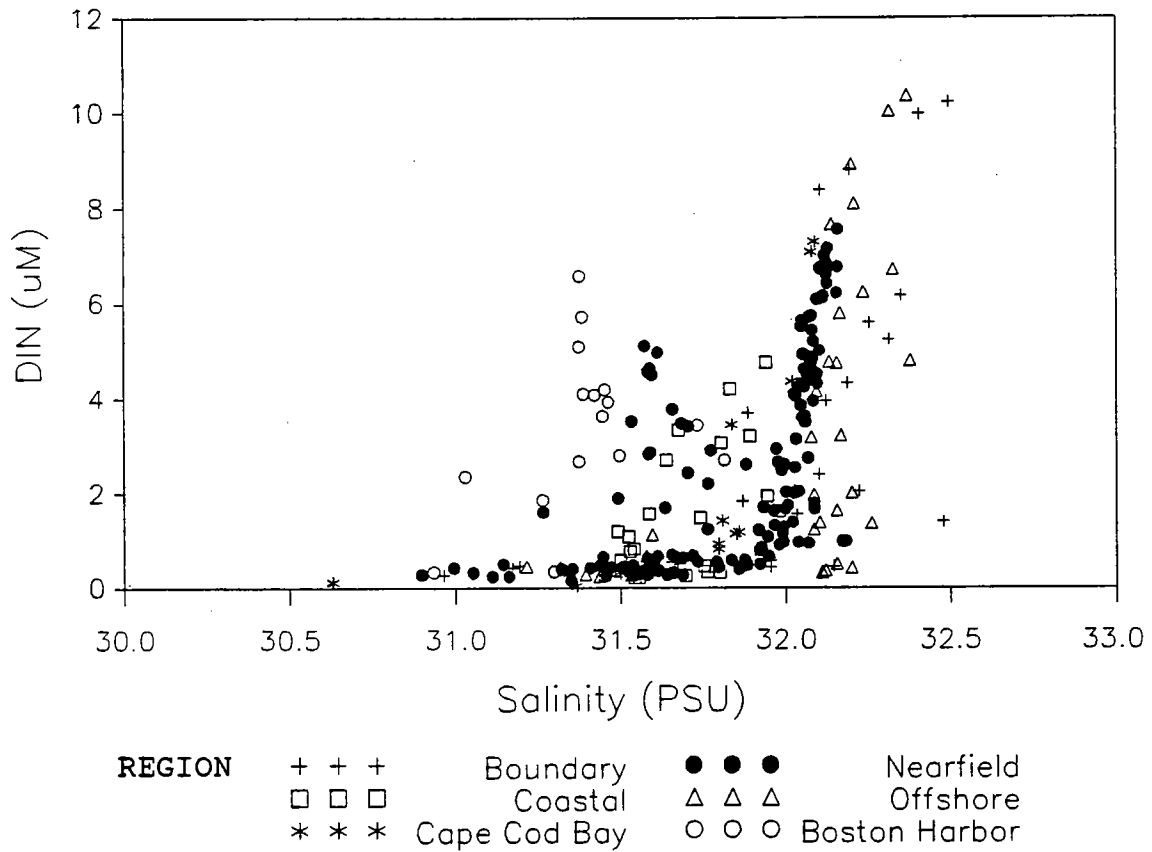
Figure 3-16a.   DIN vs. salinity in June 1994.

June (W9407)

REGION + + + Boundary   ● ● ● Nearfield
        □ □ □ Coastal   △ △ △ Offshore
        * * * Cape Cod Bay O O O Boston Harbor

June (W9407)

REGION + + + Boundary   ● ● ● Nearfield
        □ □ □ Coastal   △ △ △ Offshore
        * * * Cape Cod Bay O O O Boston Harbor
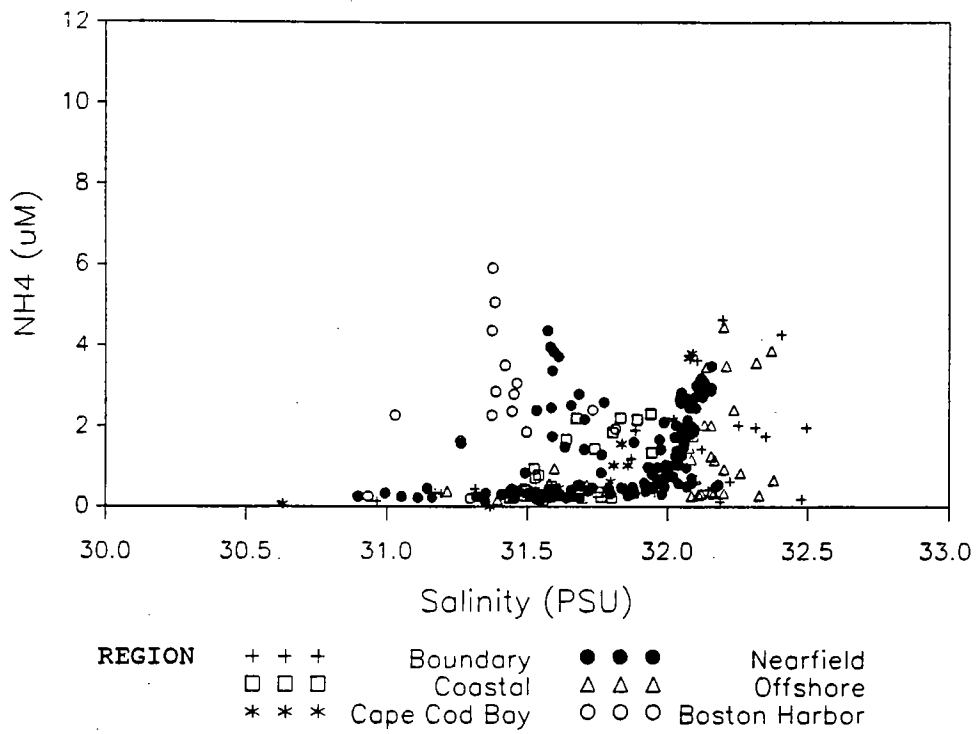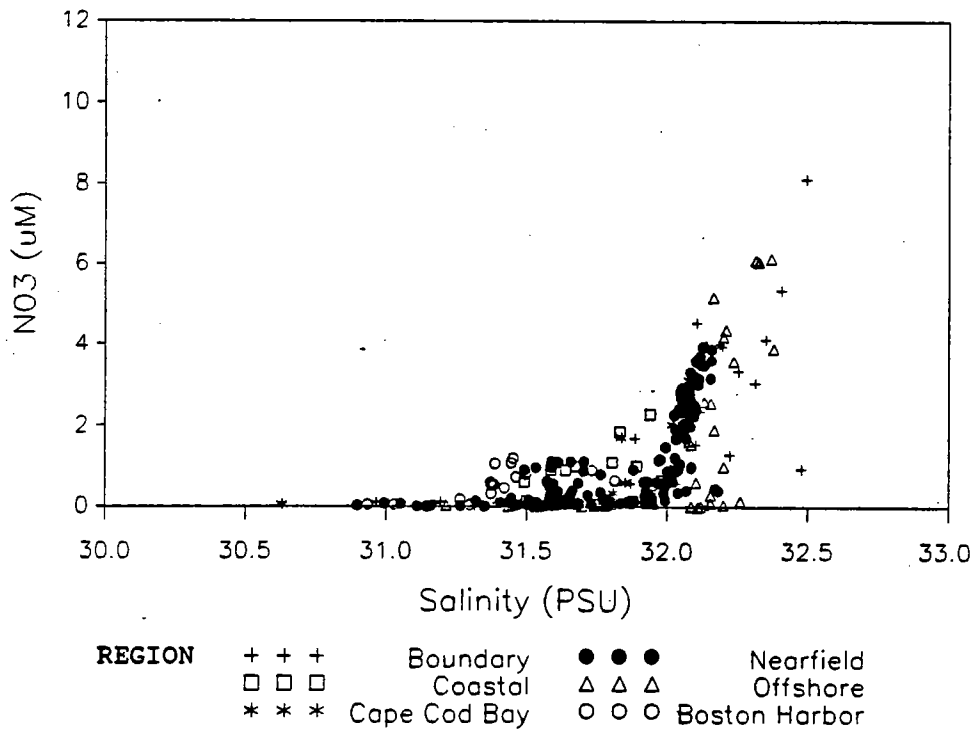
Figure 3-16b. NH$_4$ and NO$_3$ vs. salinity in June 1994.
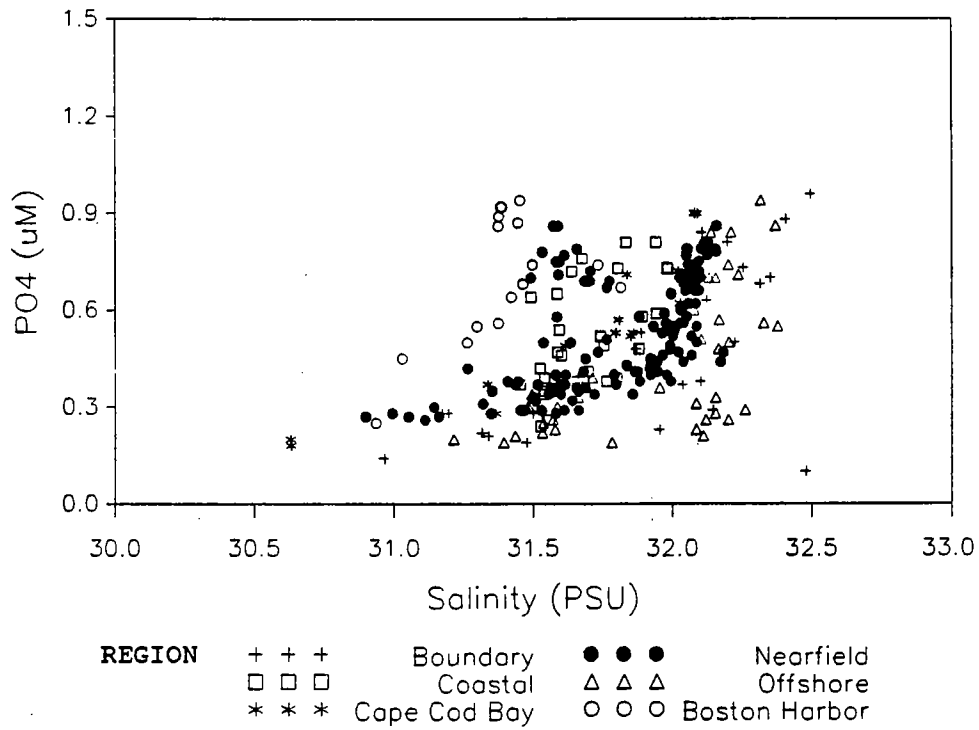
June (W9407)
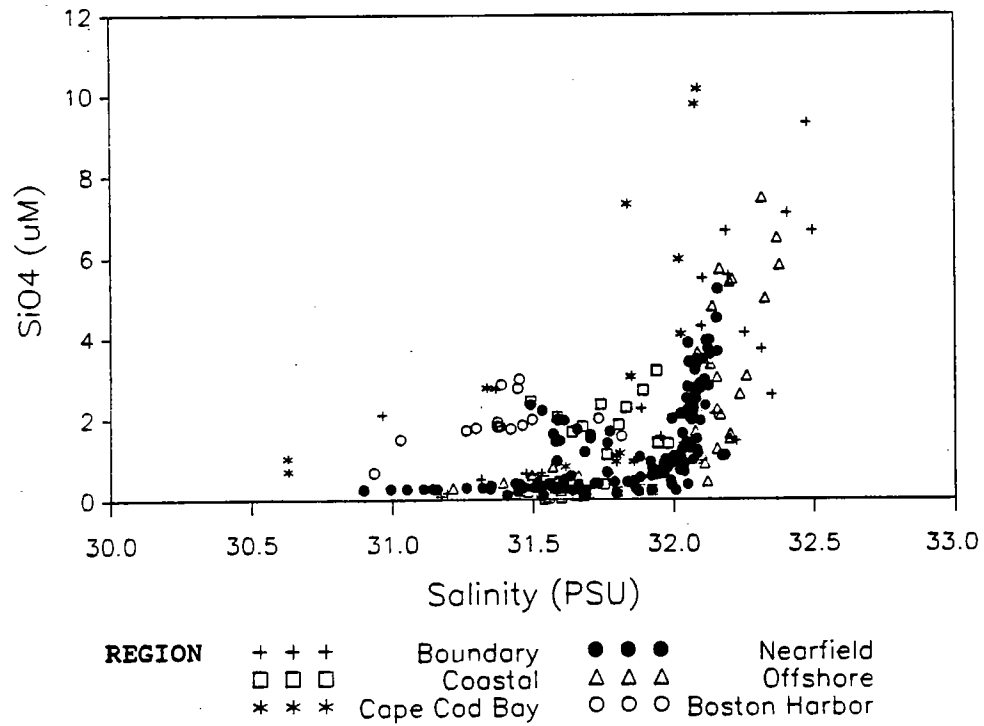
June (W9407)

Figure 3-16c. PO$_4$ and SiO$_4$ vs. salinity in June 1994.

June (W9407)

REGION + + + Boundary   ● ● ● Nearfield
        □ □ □ Coastal   △ △ △ Offshore
        * * * Cape Cod Bay O O O Boston Harbor

June (W9407)

REGION + + + Boundary   ● ● ● Nearfield
        □ □ □ Coastal   △ △ △ Offshore
        * * * Cape Cod Bay O O O Boston Harbor
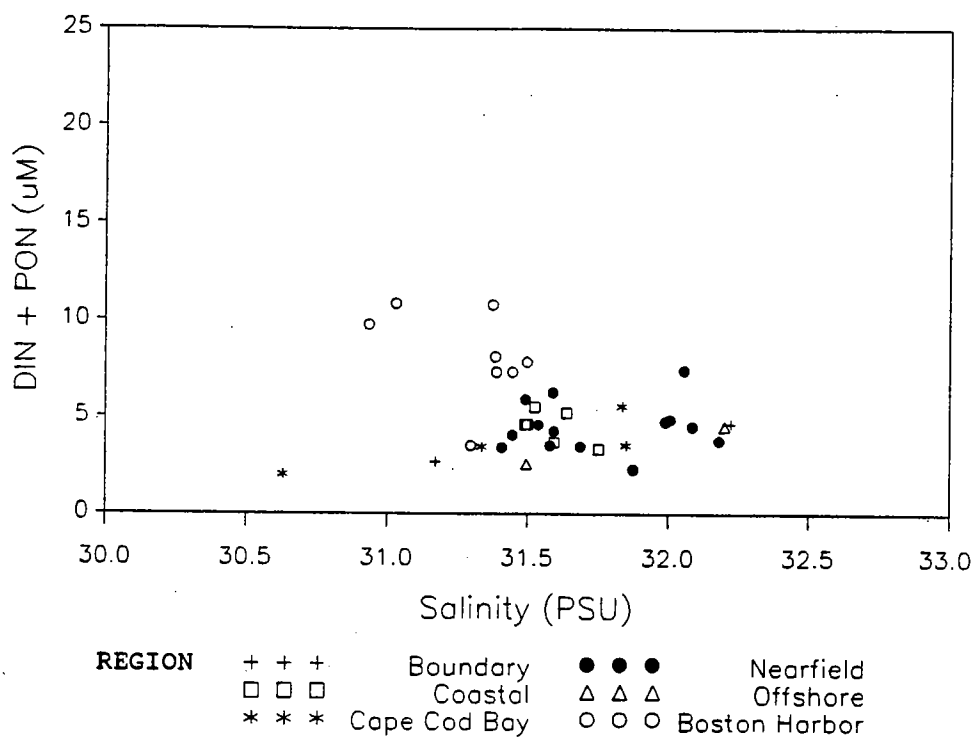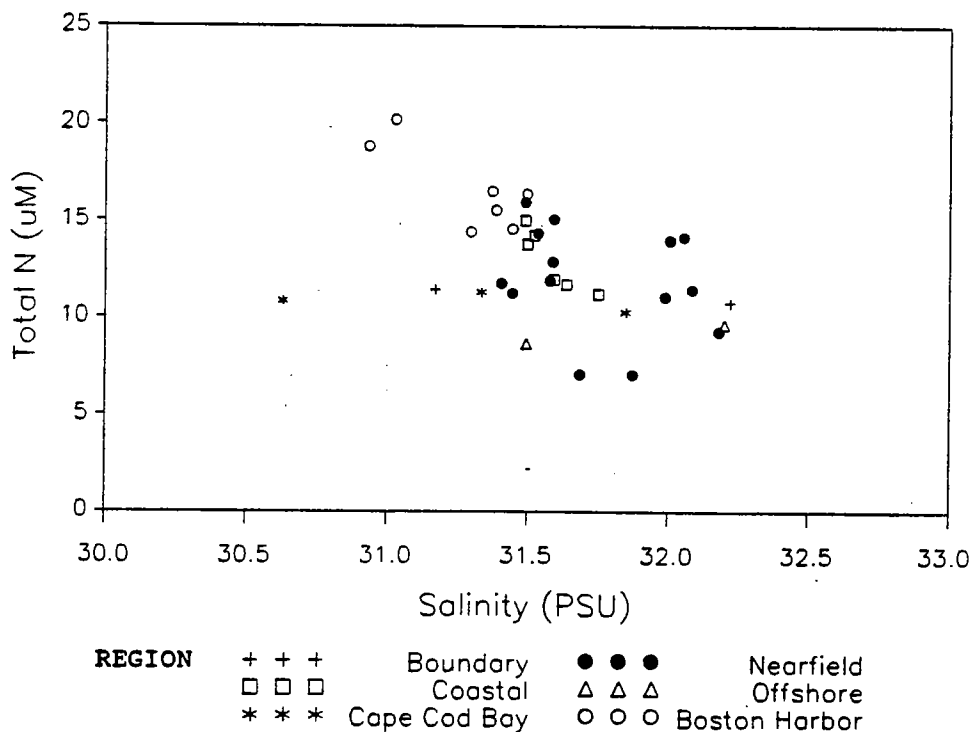
Figure 3-17. Nitrogen forms vs. salinity in June 1994. Data are from P stations and special stations (Appendix A). Dissolved inorganic nitrogen = DIN, Particulate organic nitrogen = PON, Total nitrogen (TN) = Total dissolved nitrogen (TDN) + PON.

June (W9407)
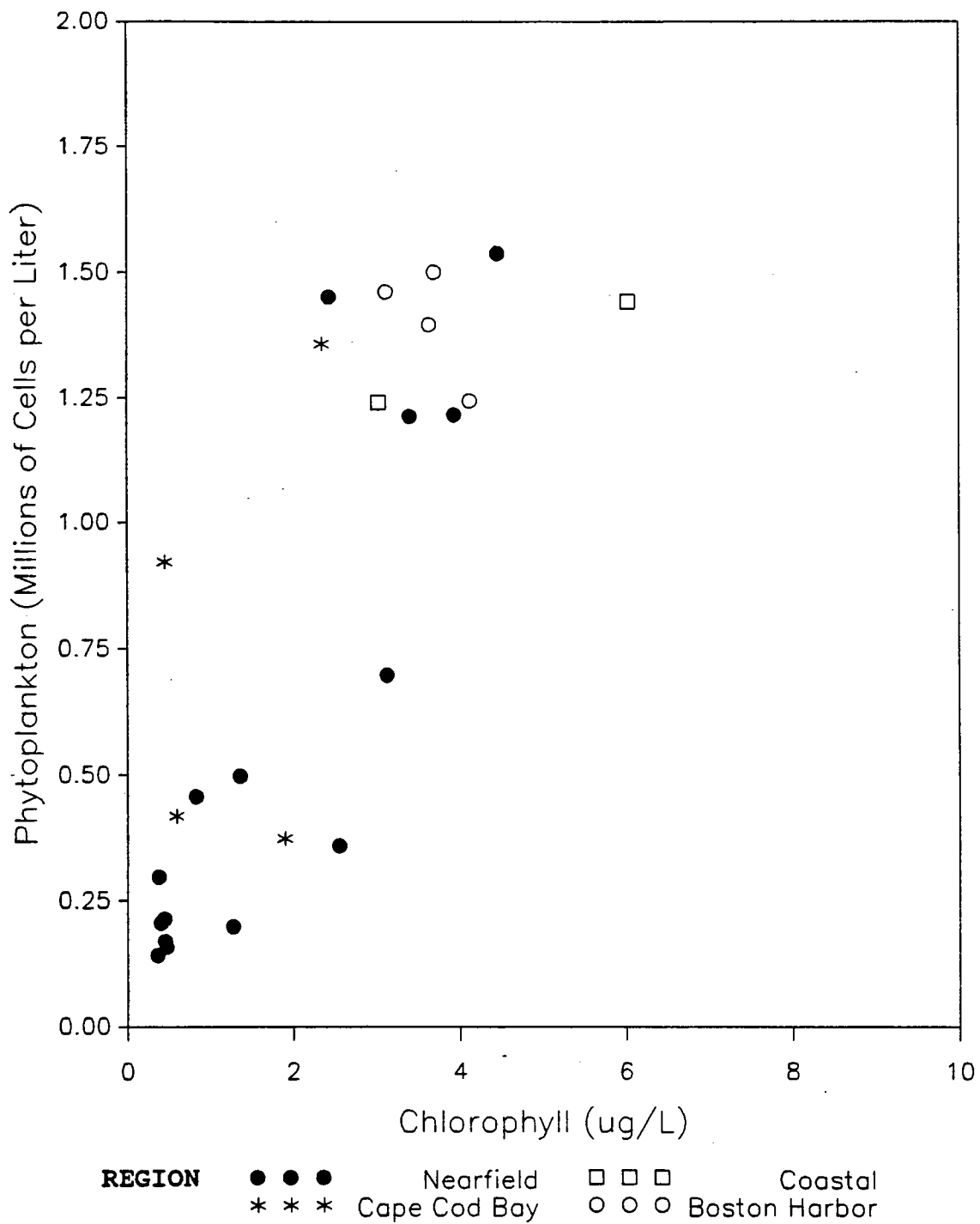
Figure 3-18. Total phytoplankton abundance vs. chlorophyll (extracted samples) at P stations in June 1994.

Phytoplankton - June 1994
(Surface)
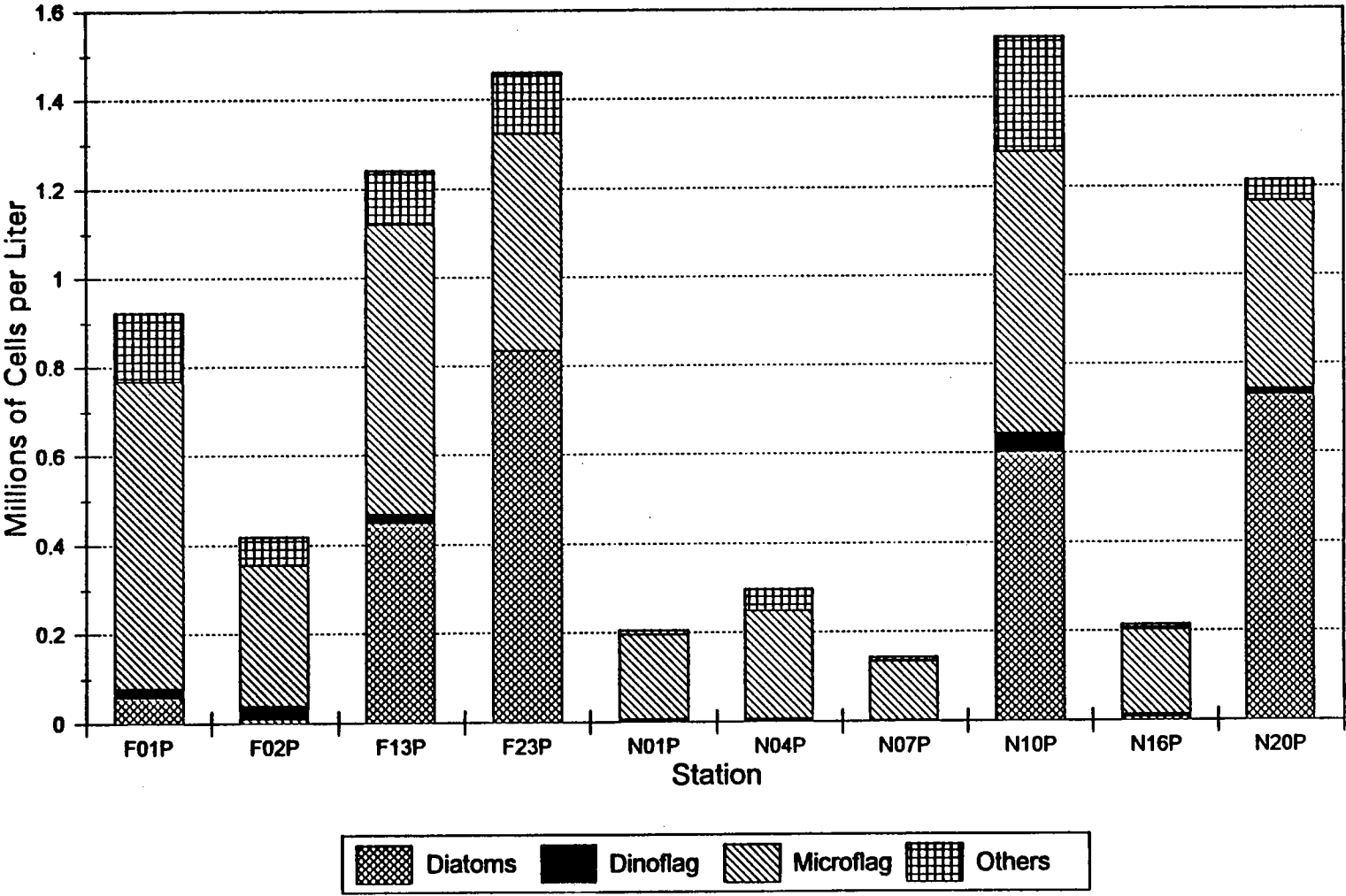
Figure 3-19. Total phytoplankton abundance, by taxonomic group, near the surface of P stations in June 1994.

Phytoplankton - June 1994
(Chlorophyll Maximum)
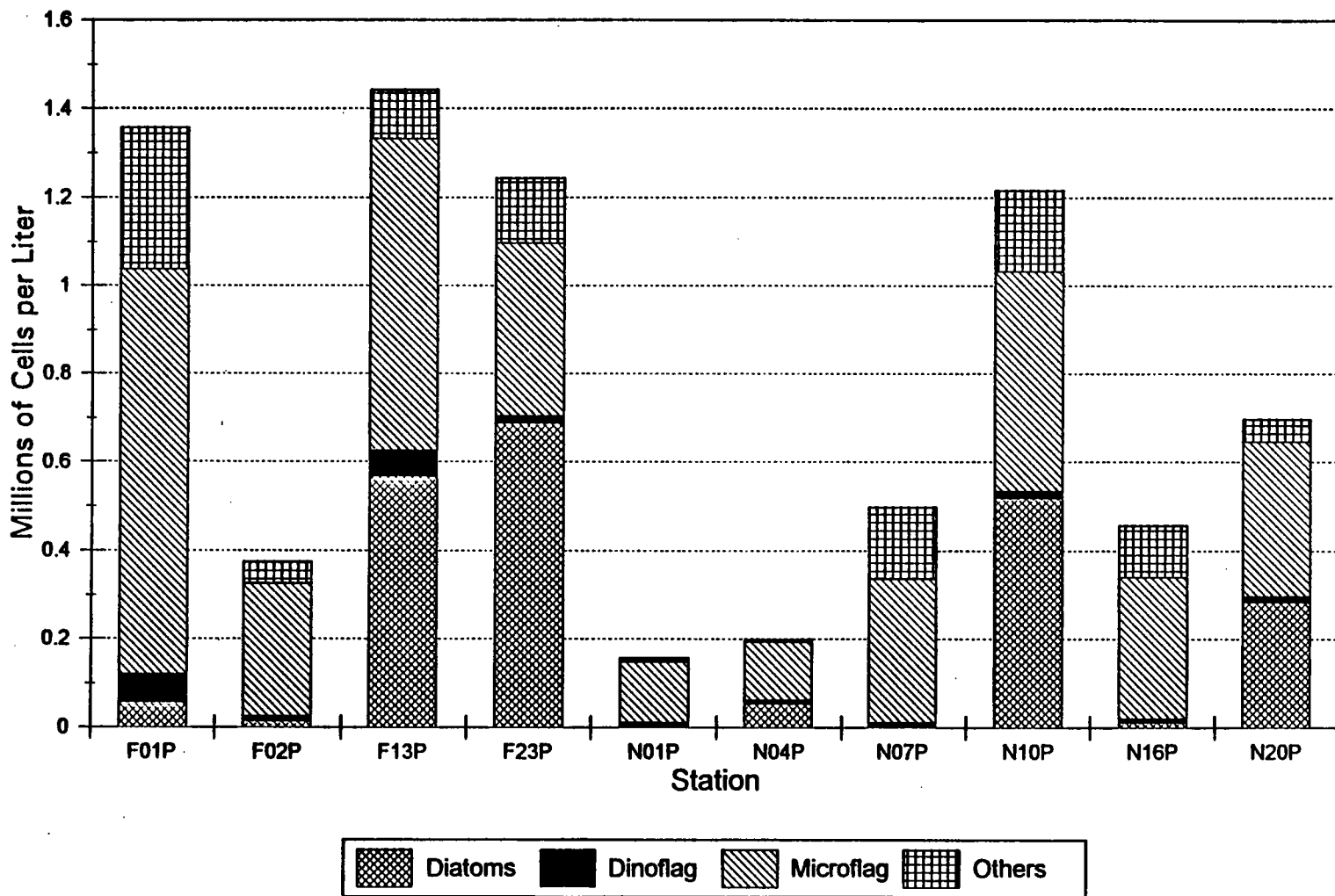
Figure 3-20.   Total phytoplankton abundance, by taxonomic group, near the chlorophyll maximum of P stations in June 1994.
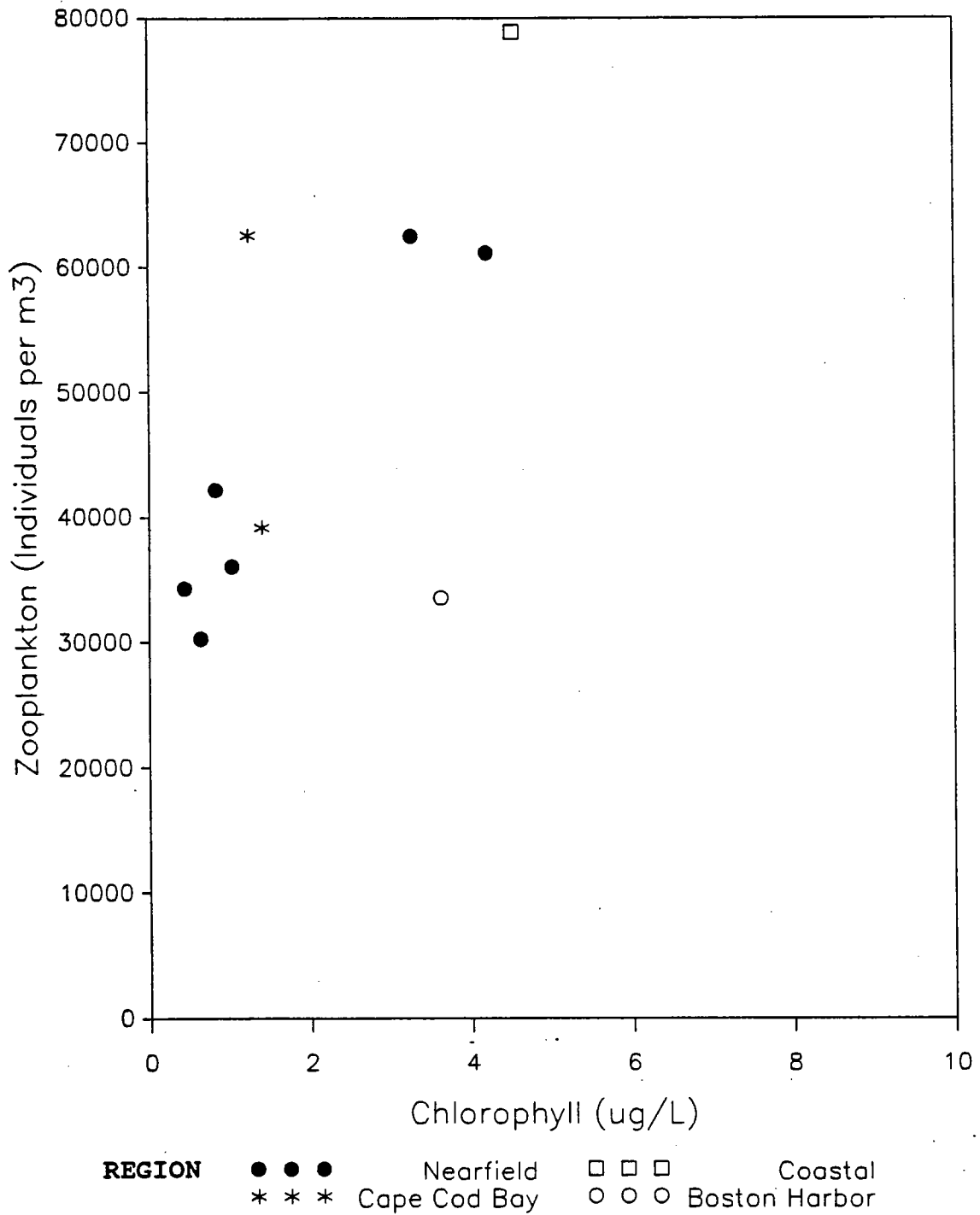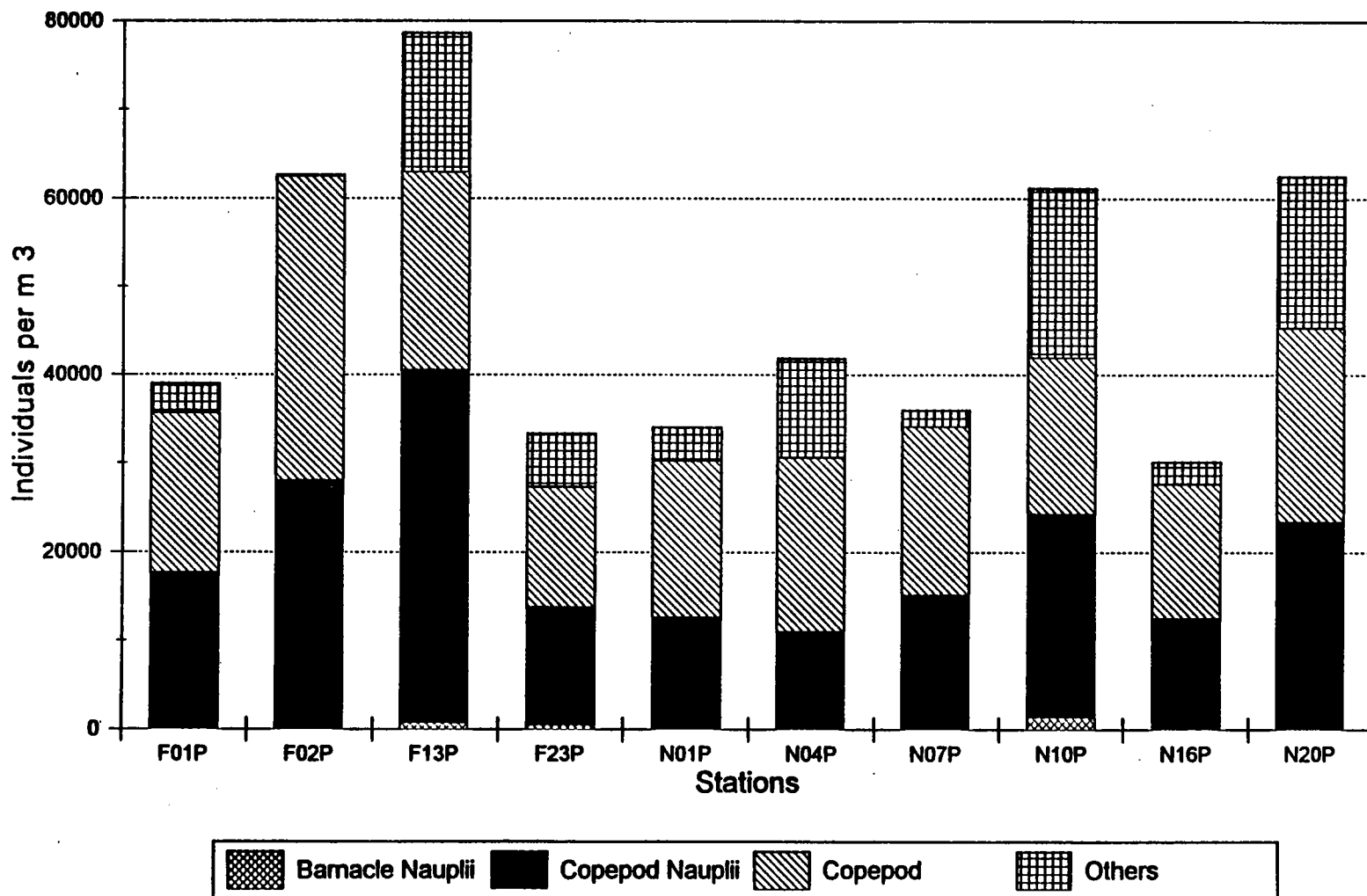
June (W9407)

REGION ● ● ● Nearfield □ □ □ Coastal
* * * Cape Cod Bay O O O Boston Harbor

Figure 3-21. Zooplankton abundance vs. average chlorophyll concentration (extracted samples; n=4 per station) for June 1994.

Zooplankton - June 1994

Figure 3-22. Zooplankton abundance, by groups, at P stations in June 1994.

Salinity (PSU)

Salinity (PSU)

Chlorophyll a (ug/L)

Nearfield Survey (9407)
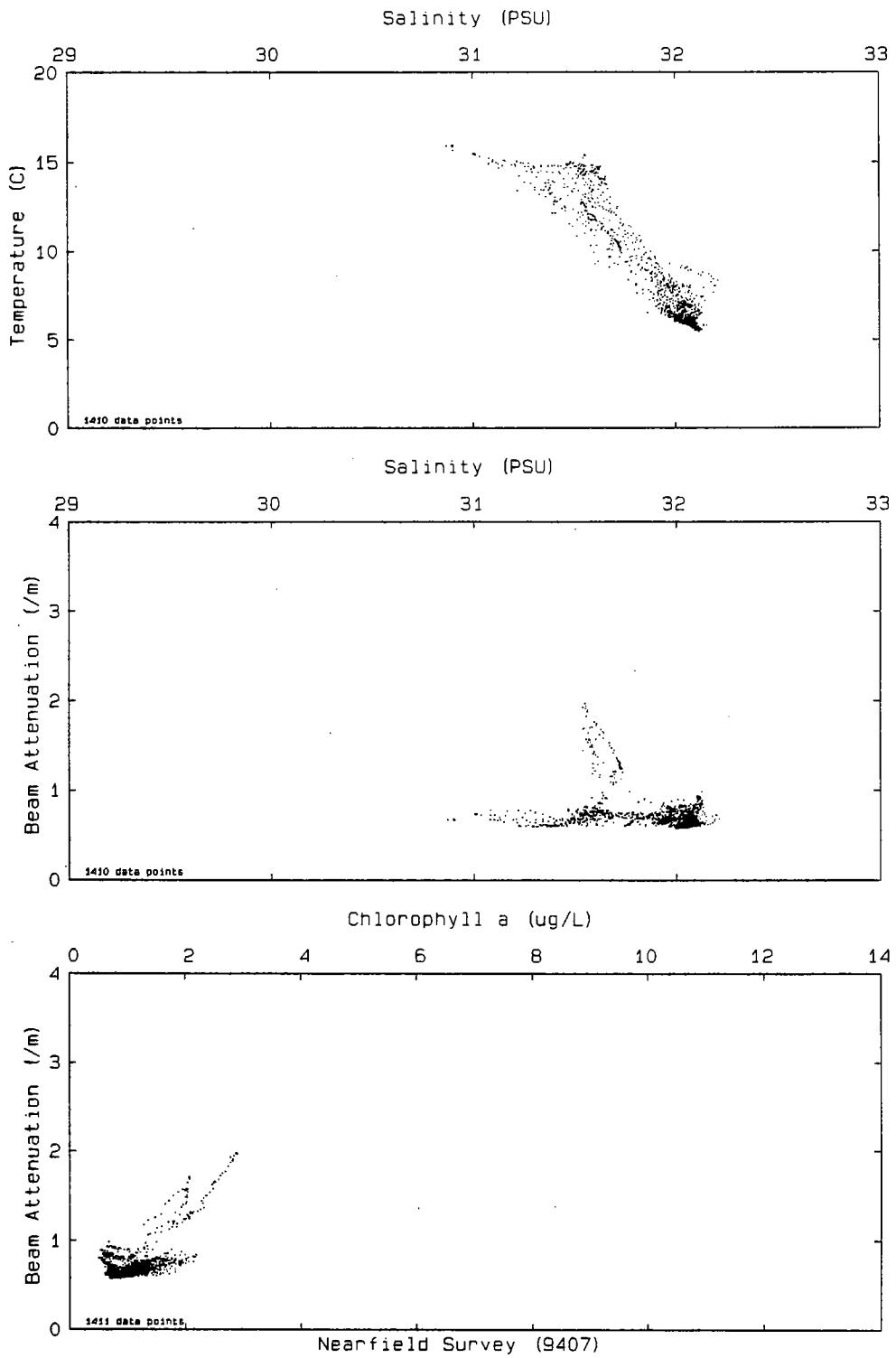
Figure 3-23a. Scatter plots of data acquired by *in situ* sensor package during vertical casts for nearfield survey in June 1994. Chlorophyll is estimated from *in situ* fluorescence.
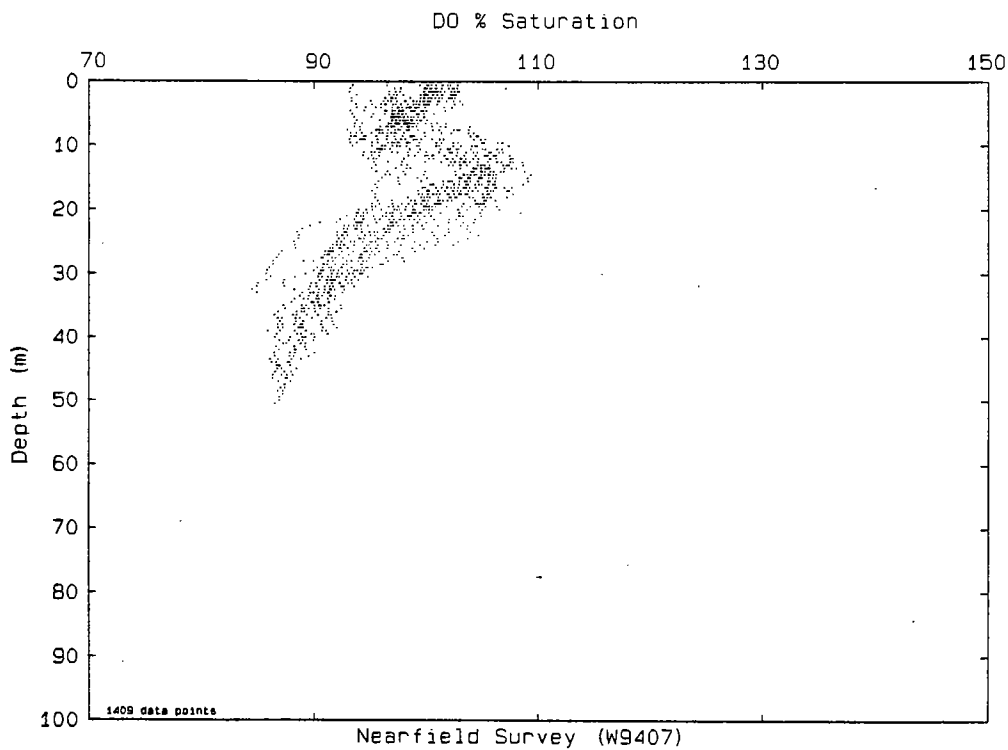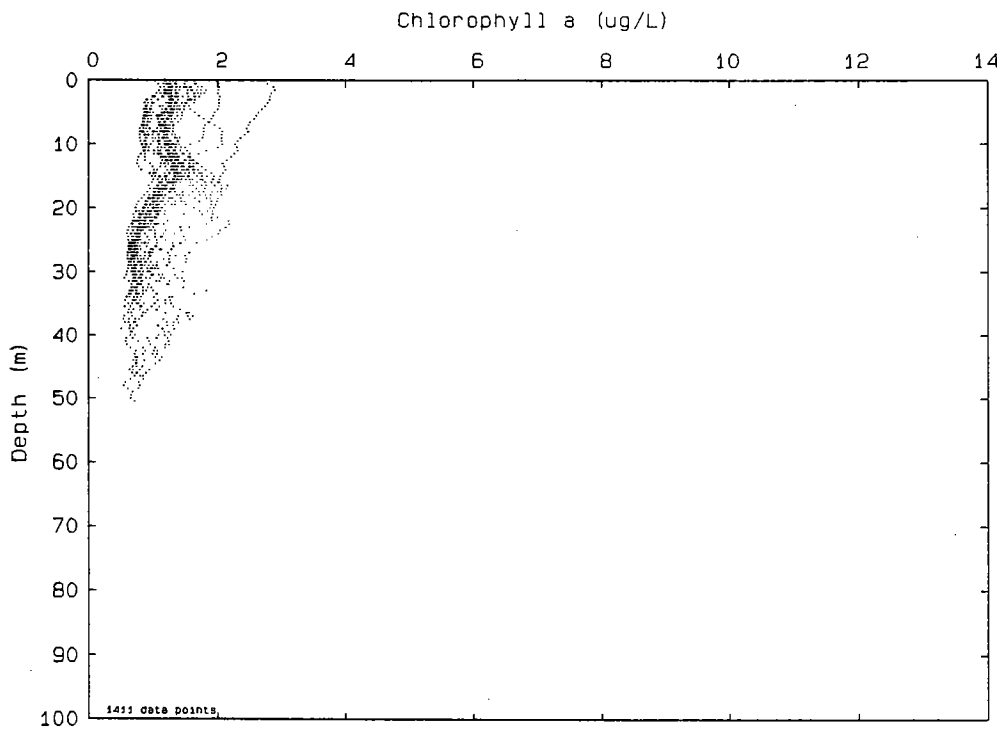
Figure 3-23b. Scatter plots of data acquired by *in situ* sensor package during vertical casts for nearfield survey in June 1994. Chlorophyll is estimated from *in situ* fluorescence.
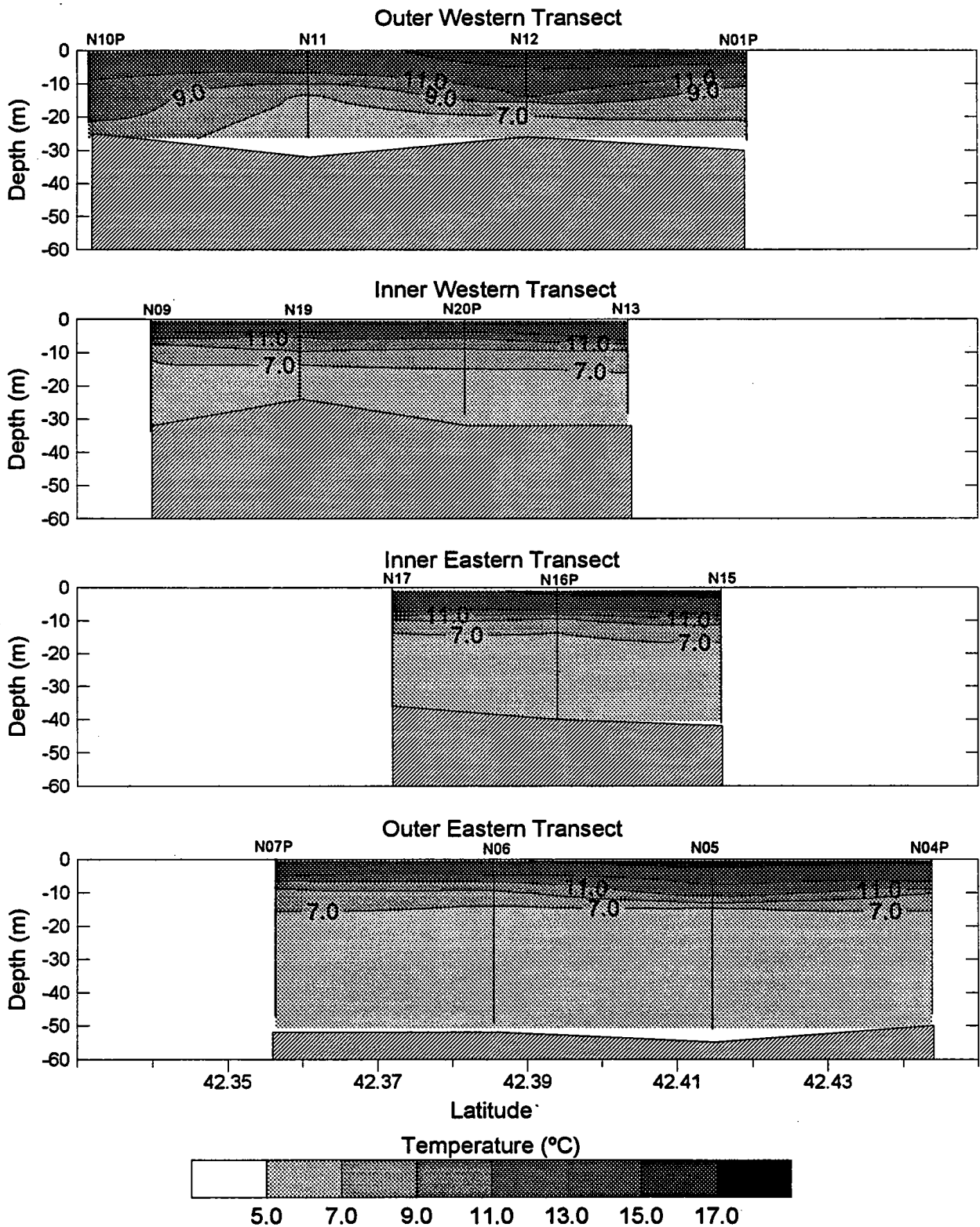
Figure 3-24a. Vertical section contours for nearfield standard transects (view towards Boston Harbor) on Survey W9407. The data used to produce the contours are from high-resolution continuous vertical profiles taken from the downcast at each station during the nearfield sampling day.
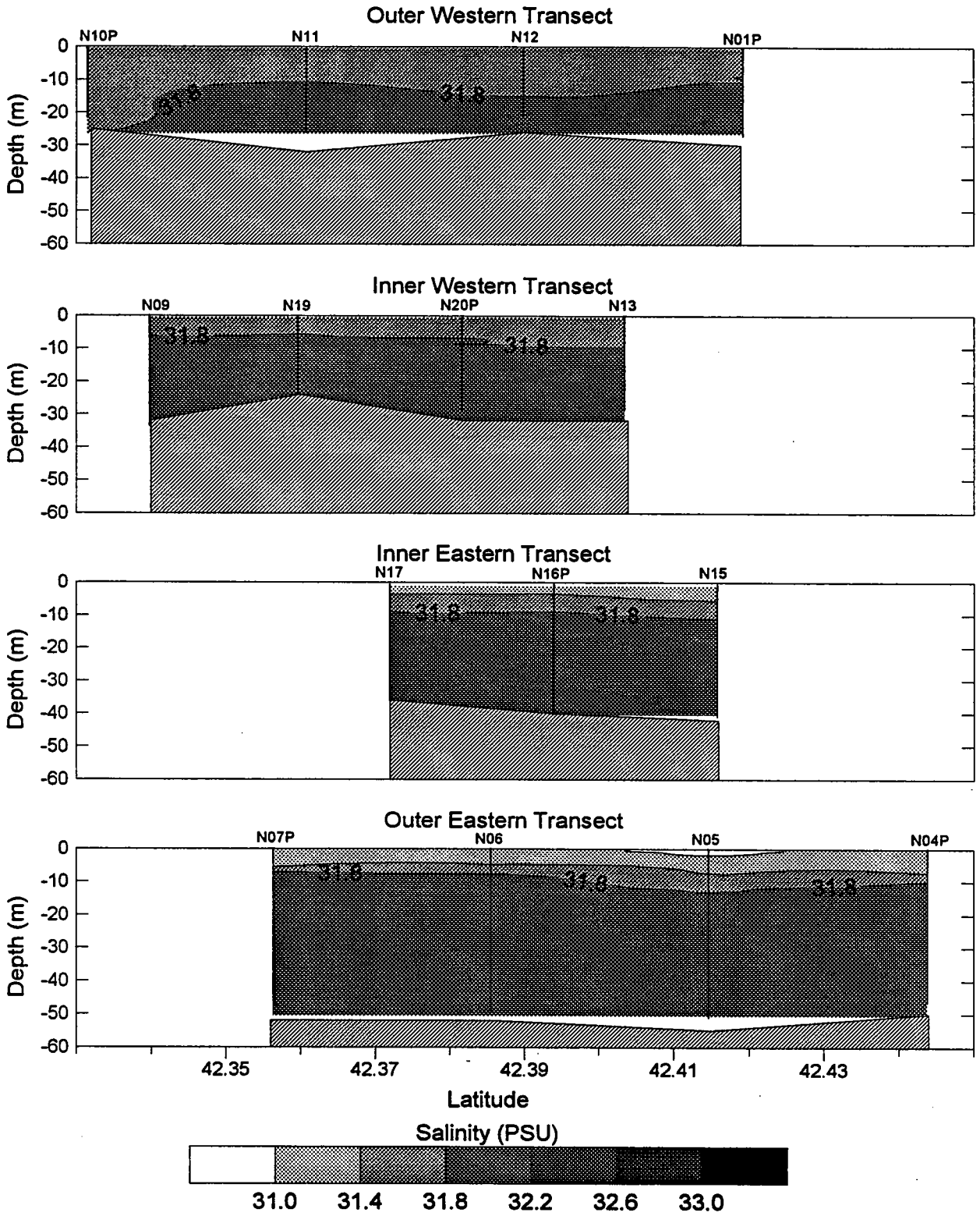
Figure 3-24b. Vertical section contours for nearfield standard transects (view towards Boston Harbor) on Survey W9407. The data used to produce the contours are from high-resolution continuous vertical profiles taken from the downcast at each station during the nearfield sampling day.

Figure 3-24c. Vertical section contours for nearfield standard transects (view towards Boston Harbor) on Survey W9407. The data used to produce the contours are from high-resolution continuous vertical profiles taken from the downcast at each station during the nearfield sampling day.
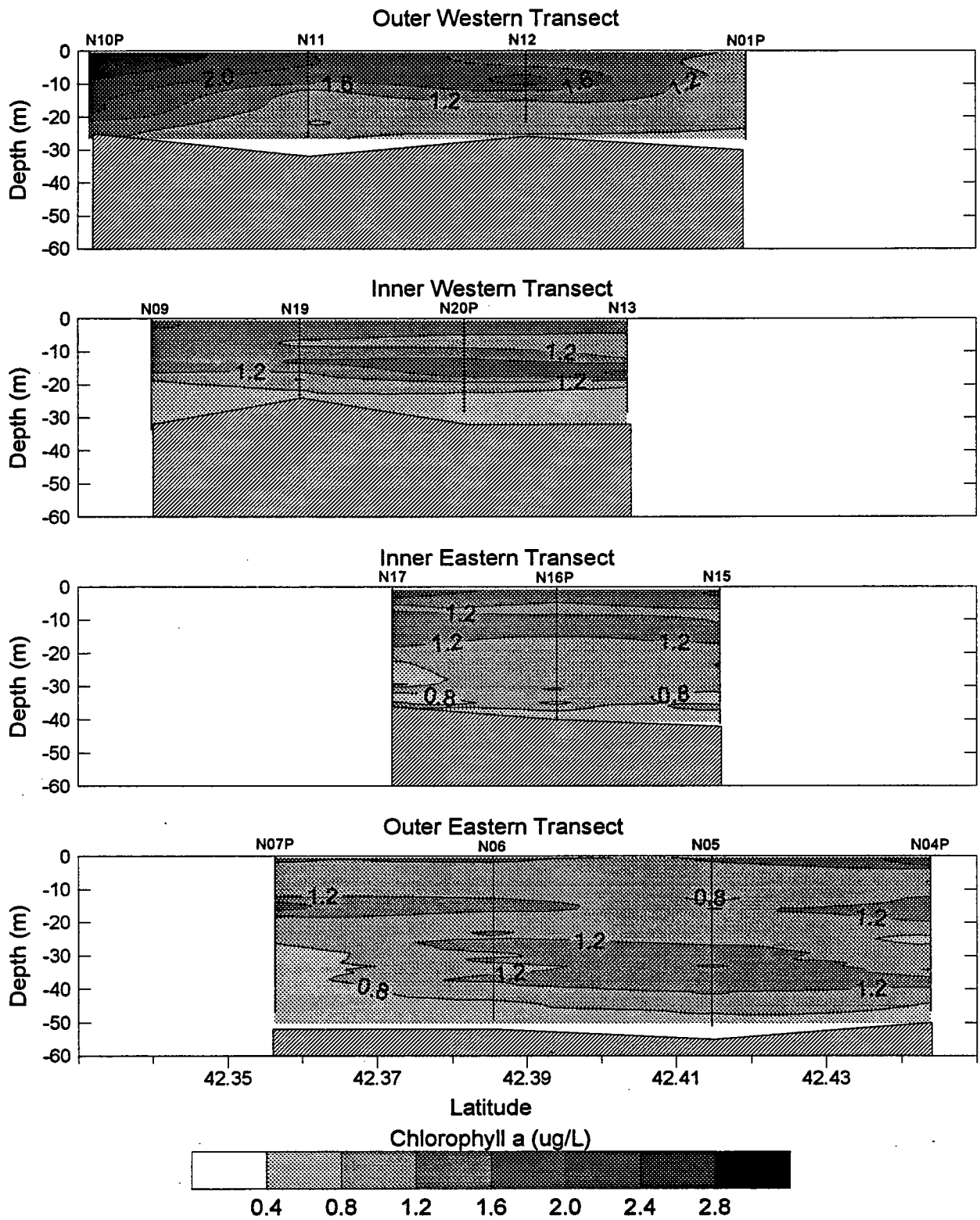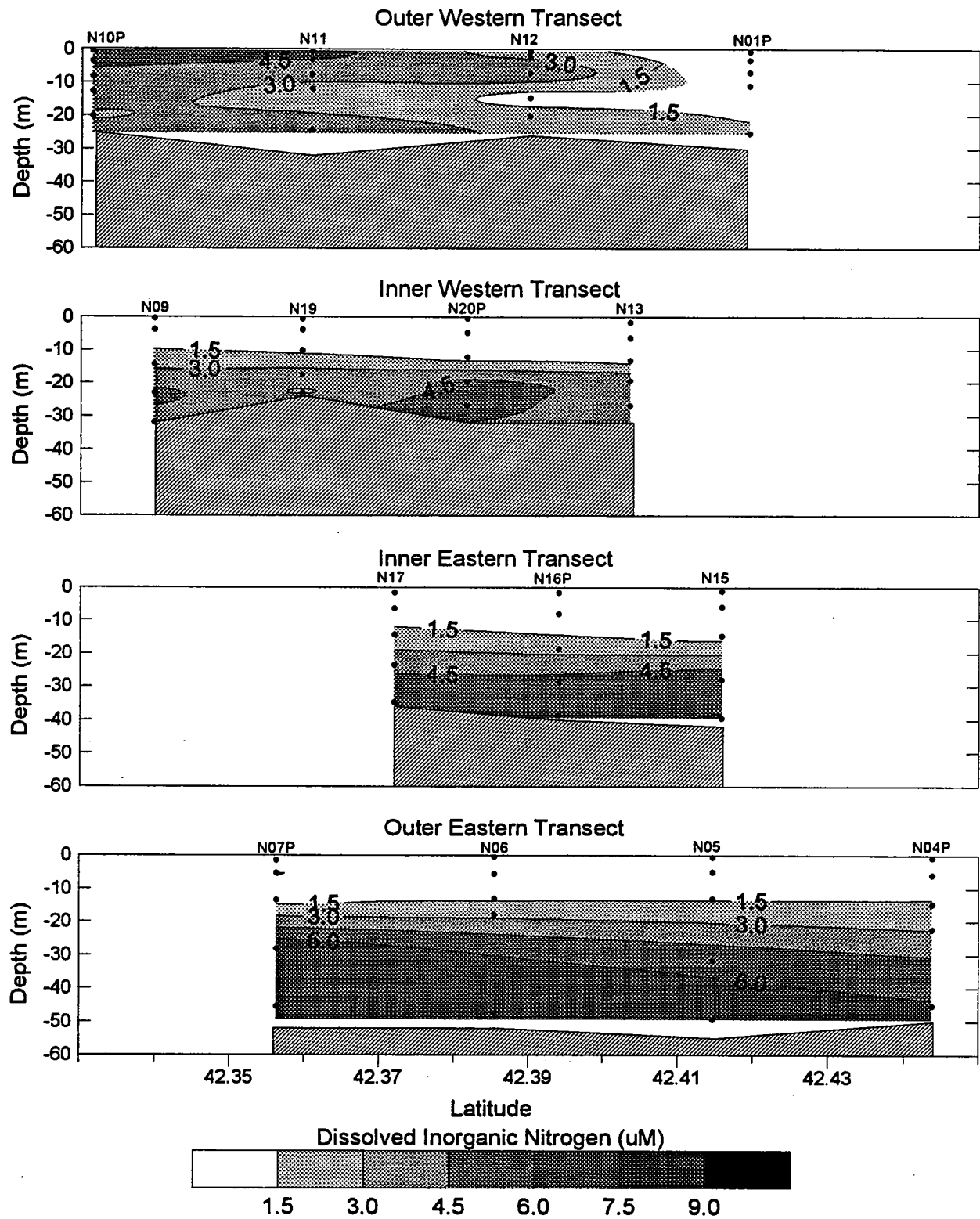
Figure 3-24d. Vertical section contours for nearfield standard transects (view towards Boston Harbor) on Survey W9407. The data used to produce the contours are from discrete bottle samples taken at each station during the nearfield sampling day (Appendix A).

4.0 RESULTS OF EARLY JULY 1994 NEARFIELD SURVEY (W9408)

4.1 Distribution of Water Properties from Vertical Profiles

Due to severe storm warnings on July 7, vertical profiles and bottle samples were obtained at only 17 of the planned 21 nearfield stations (West, 1994 and Appendix B). Scatter plots of the *in-situ* sensor data are presented in Figure 4-1. The temperature range for the nearfield in early July had broadened slightly since the June nearfield survey, while the salinity range had narrowed. Bottom waters were nearly the same as in June (5-6°C), but surface layers had warmed as much as 2°C. Surface water salinity was now ~31.5 PSU and graded to bottom water values (~32.0 to 32.2 PSU) that were similar to those measured in June. A coherent T-S pattern among station profiles was again earmarked by uniform density stratification that was primarily established by thermal, rather than salinity, gradients from surface to bottom. Review of vertical profiles in Appendix B indicates that the thermocline/pycnocline existed as a rapid vertical change within the 5-20 m depth zone and, although the exact thermocline position varied slightly across stations, the profiles all broadly define a two-layer system.

Beam attenuation and chlorophyll covaried, but there was much scatter in the relationship (Figure 4-1a). Low beam attenuation was found at highest salinity (bottom-water) and higher beam attenuation readings were associated with lower salinity within surface layers and, as expected, were usually associated with higher chlorophyll readings (Figure 4-1a, see also vertical profiles in Appendix B). At a number of stations, chlorophyll exceeded 2 μg L^{-1} in the surface 10-12 m; there was also a characteristic subsurface peak at 20 m that exceeded the 2 μg L^{-1} concentration and showed maxima at ~4 μg L^{-1} (Figure 4-1b). DO profiles usually portrayed a supersaturated surface layer (105-130%) that extended to the mid- to low thermocline depth (Figure 4-1b). As in June, profiles below 20 m dipped below 100% saturation and appeared to stabilize at ~90% saturation in bottom waters 30-50 m deep.

Dissolved nutrient concentrations increased with water depth (Figure 4-2). DIN was virtually depleted at the surface and increased over depth to reach maximum concentrations of about 10 μM (Figure 4-2a). In mid-depth waters, the NH_4 and NO_3 components of DIN were approximately equal, but NO_3 was the major component where water depths were >25 m (Figure 4-2b).

4-1

Phosphate concentrations also increased with depth, generally in a linear manner (Figure 4-2c). Interestingly, as with N forms, no distinctive change in the pattern of concentration over depth was evident to mark the thermocline/pycnocline. In contrast to DIN, there was never an undetectable concentration of PO_4 at the surface of nearfield stations in early July. N/P ratios at the surface were thus low and indicative of relative N limitation, as has been characteristic of the region during summer stratification (cf. Kelly and Turner, 1995). Silicate concentrations also increased in direct proportion to depth (Figure 4-2c). Silicate concentrations were ~0.5 µM at the surface and 6-8 µM at depth.

Nutrient-salinity plots (Figure 4-3a, b, c) all showed increasing concentrations as a function of increasing salinity, reflecting the dual increase in nutrients and salinity with increased water depth. The nutrient-salinity plots have a noticeable concave curvature, which may be a consequence of imbalances in relative rates of nutrient regeneration and uptake processes as a function of depth. For example, active removal of nutrients in surface water and in mid-depth waters as chlorophyll biomass accumulates (the subsurface chlorophyll maximum) could alter the nutrient-salinity plot. Because the pycnocline acts as a strong barrier to advective mixing, the nutrient-salinity plot should not be interpreted and used as a mixing diagram (see also Kelly *et al.*, 1994f). Stratification within the nearfield area causes the principal dissolved nutrient concentration gradient to occur in the vertical rather than in the horizontal dimension.

4.2 Water Quality Variability in the Nearfield

Vertical contours of temperature, salinity, chlorophyll (as measured by fluorescence), and DIN are presented in Figure 4-4. Four stations in the middle of the field were not sampled due to weather. As noted on survey W9407 in June, a fairly uniform layering across the field is suggested (Figure 4-4a,b), with the thermocline near the bottom at shallower stations of the Outer Western Transect (Figure 4-4a). Along the Outer Western Transect, high chlorophyll ($>3\mu$g L^{-1}) was observed in surface water (stations N10P and N11, grading to subsurface peaks at station N12. East of this transect, only a subsurface chlorophyll peak was observed again, at ~20 m as noted in June. In relation to June, however, concentrations were higher at this subsurface layer and frequently exceeded 3 μg L^{-1}. Concomitant with surface chlorophyll enrichment around stations N10P and N11 was a slight elevation of DIN

concentrations, relative to other surface water locations where DIN concentrations were essentially depleted. Figure 4-4d shows that DIN concentrations increased in most locations from a depth within the pycnocline (generally 10-15 m) to the bottom and, consequently, greatest concentrations are evident in deepest water (40-50 m) of the Outer Eastern Transect.

In summary, the spatial patterns observed in the nearfield in June were largely repeated in early July. There were minor variations in the intensity of peak concentrations but the prime vertical and horizontal features were unchanged.
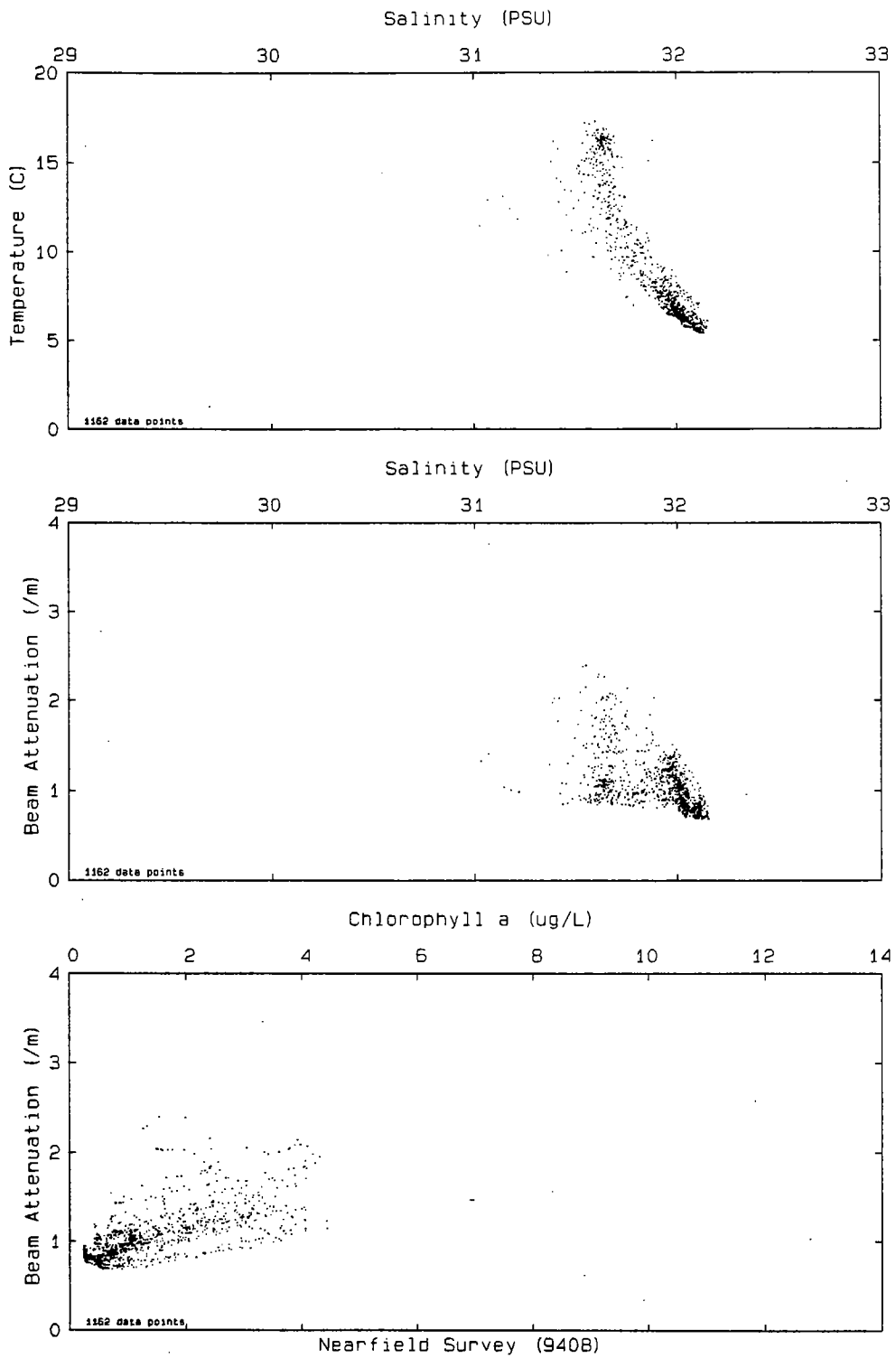
Salinity (PSU)

Chlorophyll a (ug/L)

Nearfield Survey (9408)

Figure 4-1a. Scatter plots of data acquired by *in situ* sensor package during vertical casts for nearfield survey in early July 1994. Chlorophyll is estimated from *in situ* fluorescence.
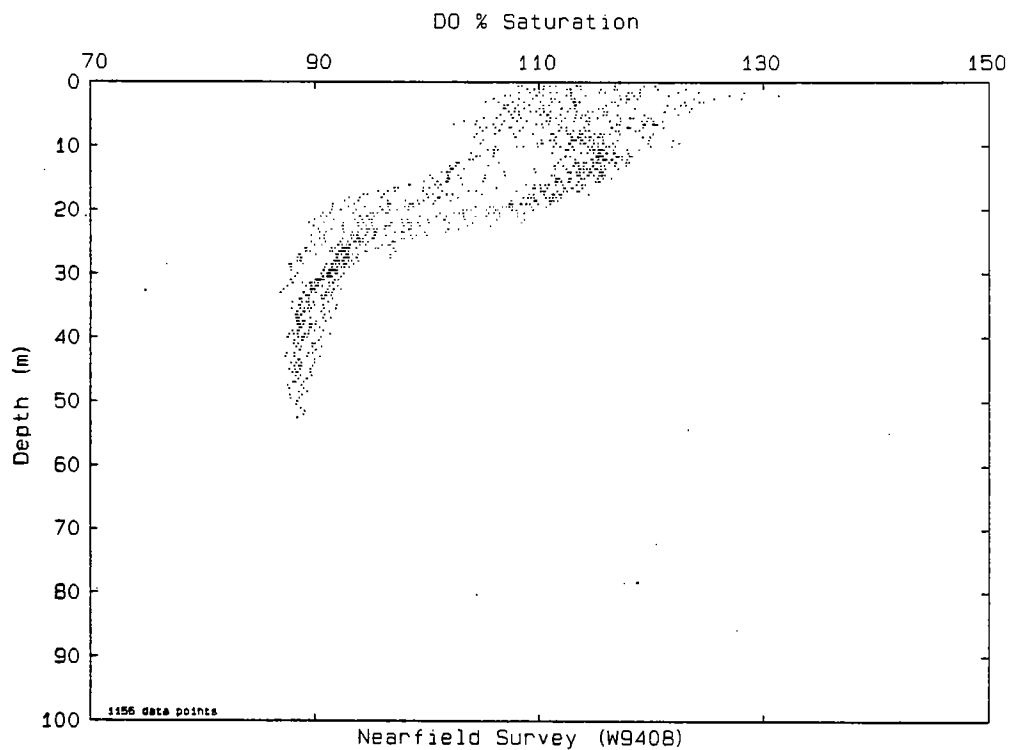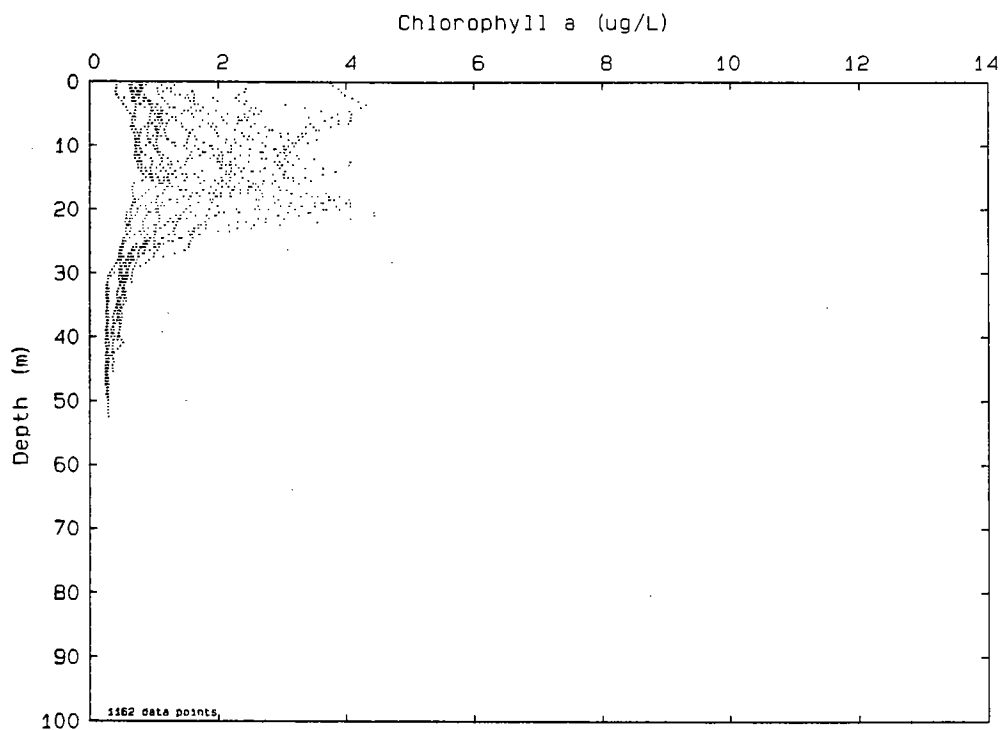
Figure 4-1b. Scatter plots of data acquired by *in situ* sensor package during vertical casts for nearfield survey in early July 1994. Chlorophyll is estimated from *in situ* fluorescence.
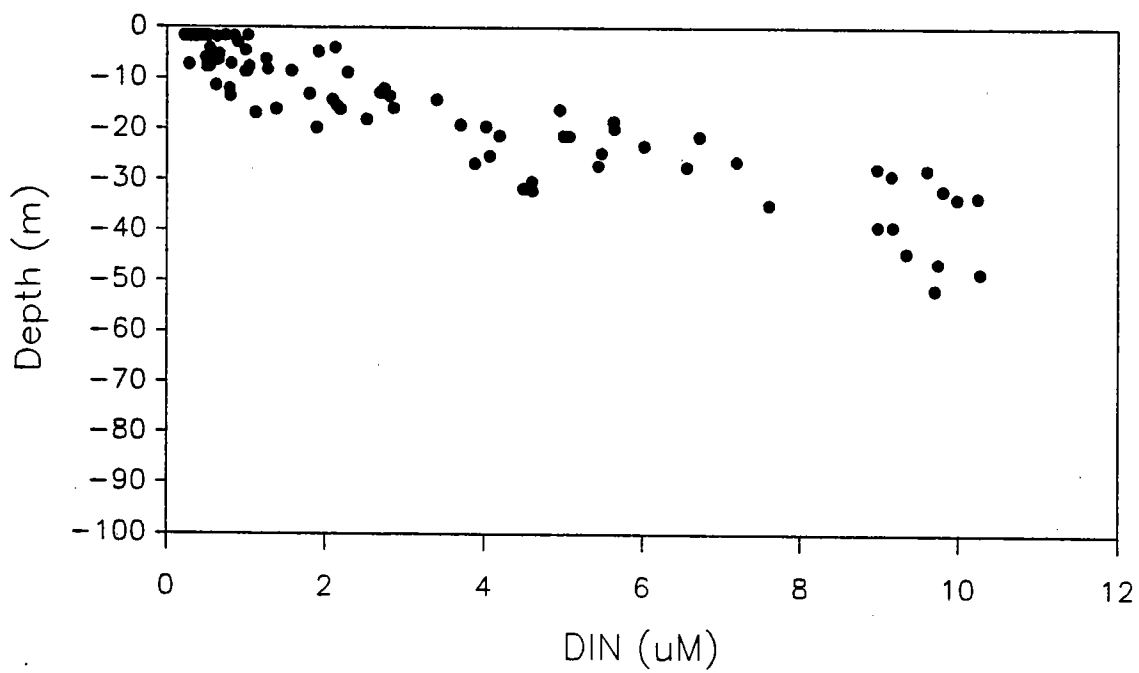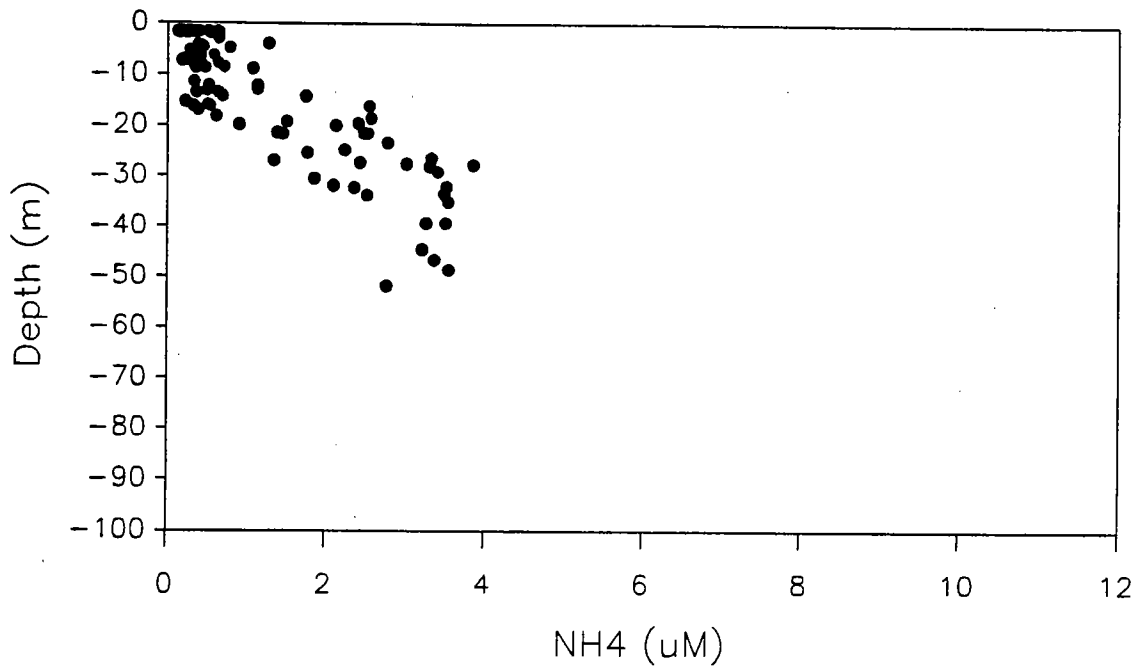
Early July (W9408)

Figure 4-2a.   DIN vs. depth in early July 1994.
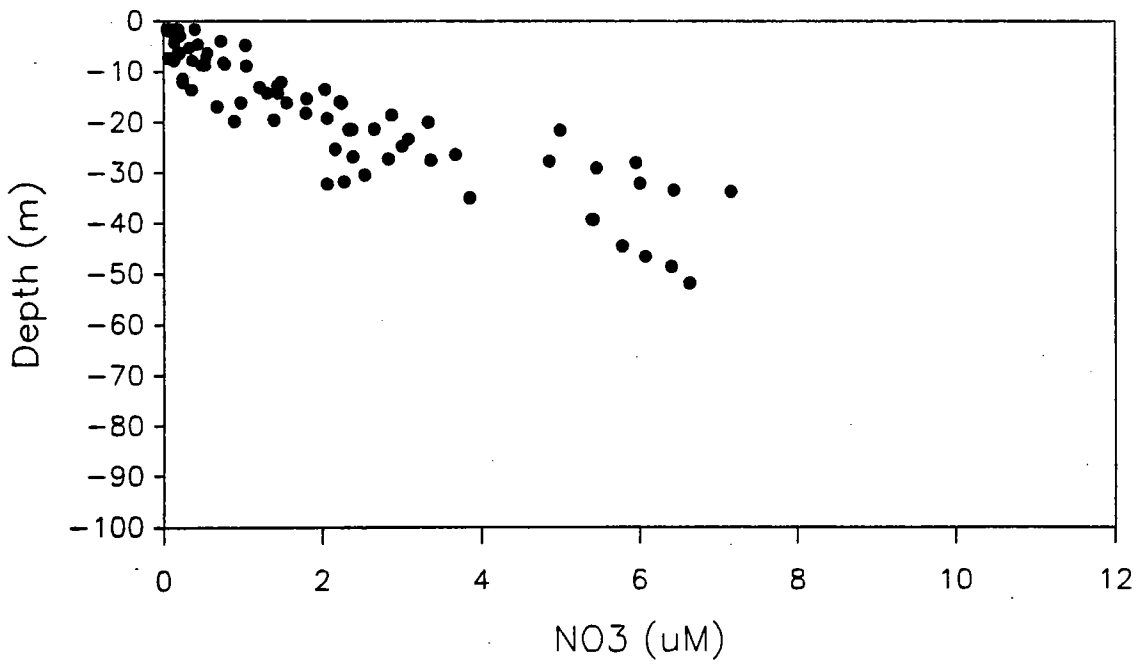
Early July (W9408)

Early July (W9408)

Figure 4-2b.   NH$_4$ and NO$_3$ vs. depth in early July 1994.
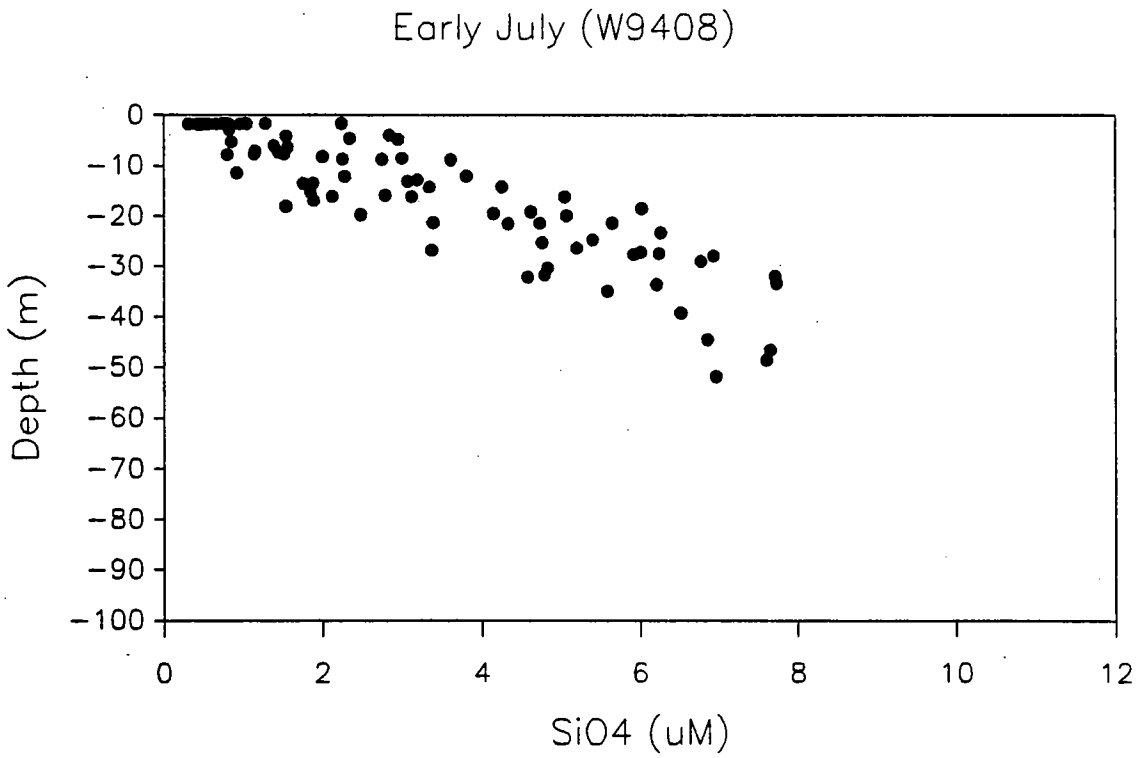
Early July (W9408)

Depth (m) vs PO4 (uM)

Early July (W9408)

Depth (m) vs SiO4 (uM)

Figure 4-2c. PO$_4$ and SiO$_4$ vs. depth in early July 1994.

Early July (W9408)

Figure 4-3a.   DIN vs. salinity in early July 1994.

Early July (W9408)
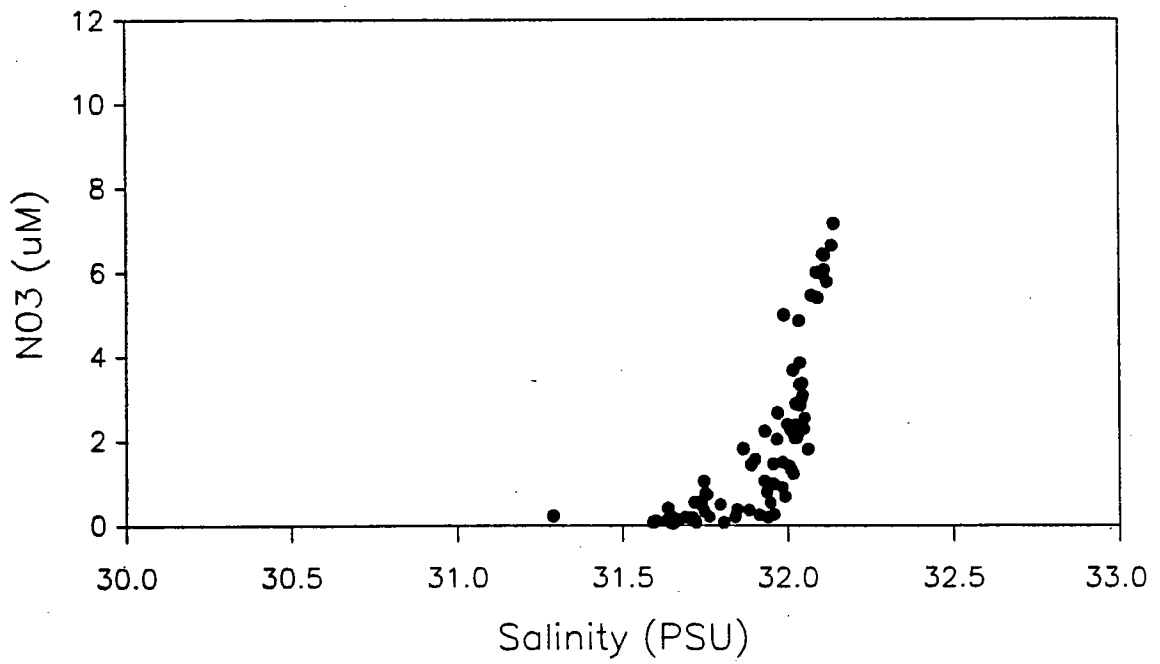
Early July (W9408)

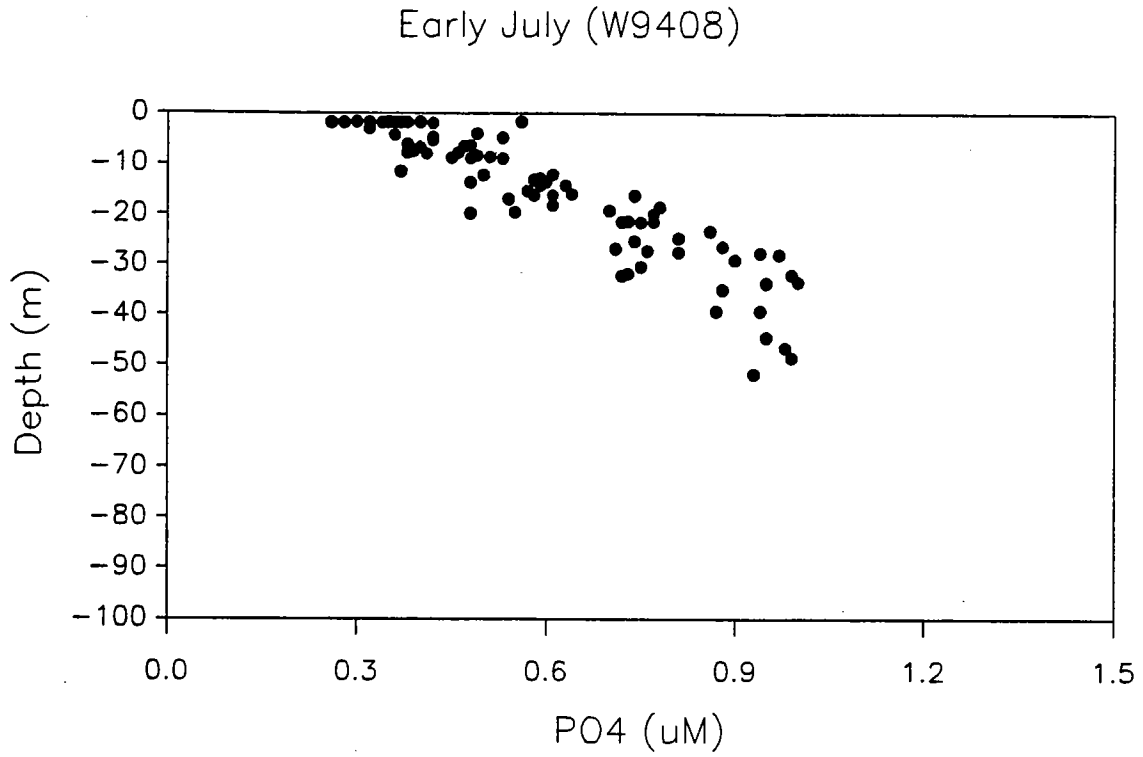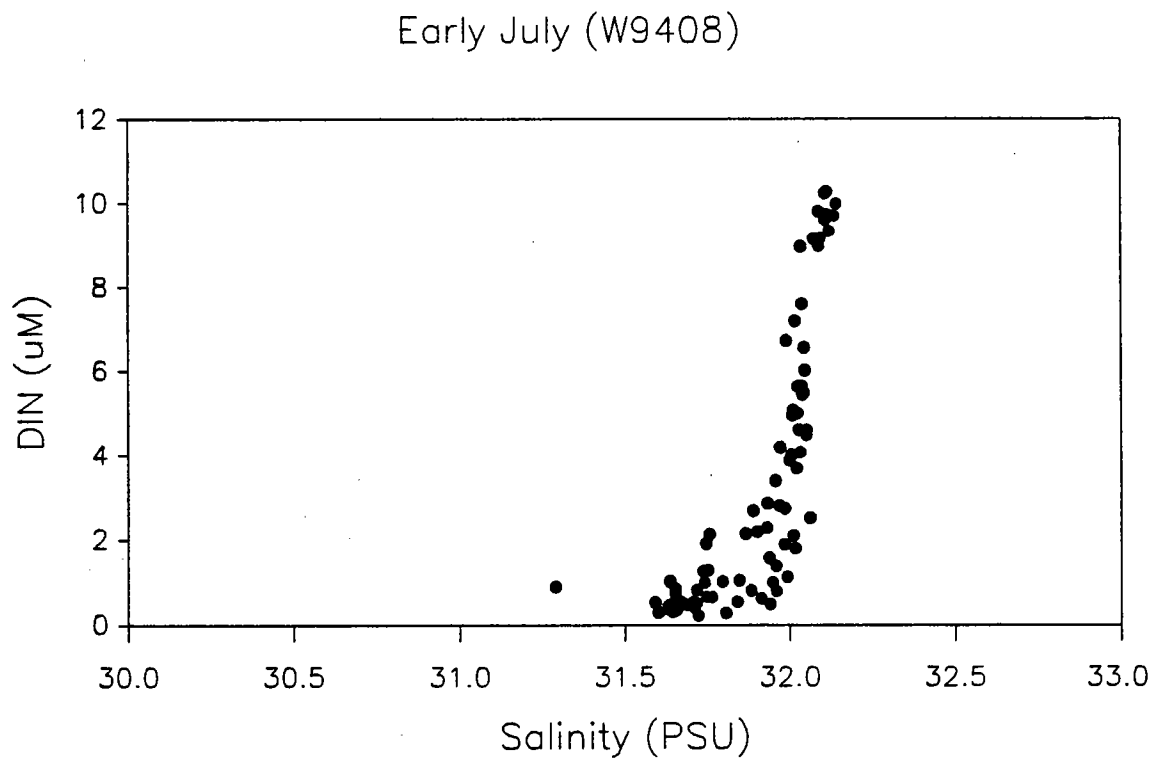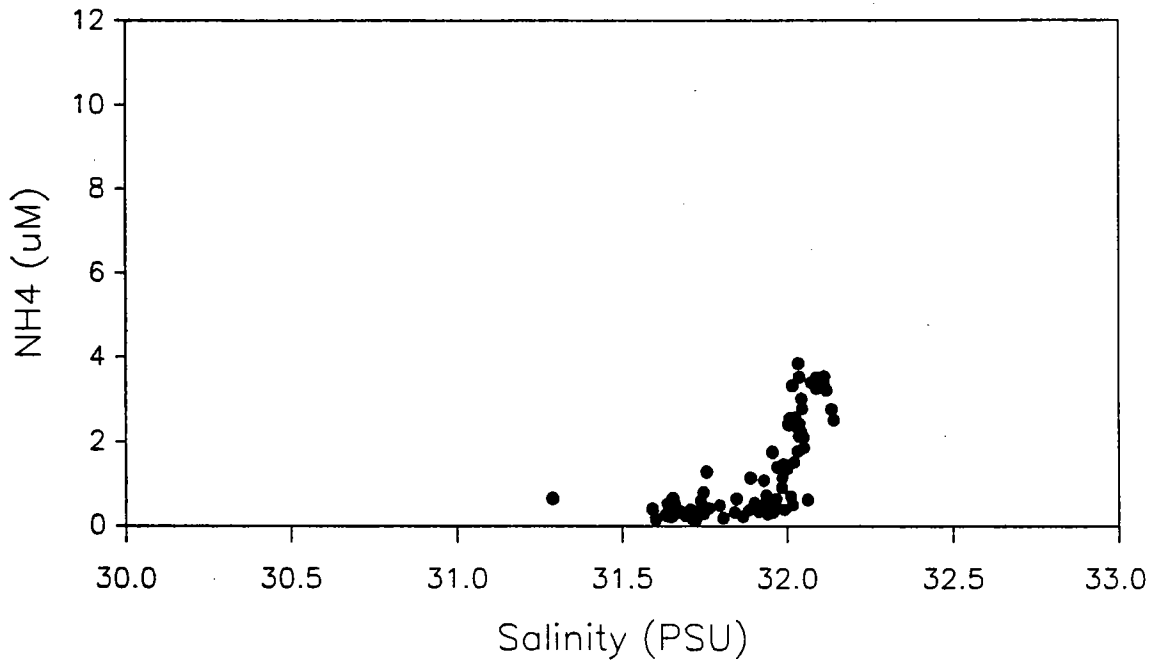**Figure 4-3b.   NH₄ and NO₃ vs. salinity in early July 1994.**
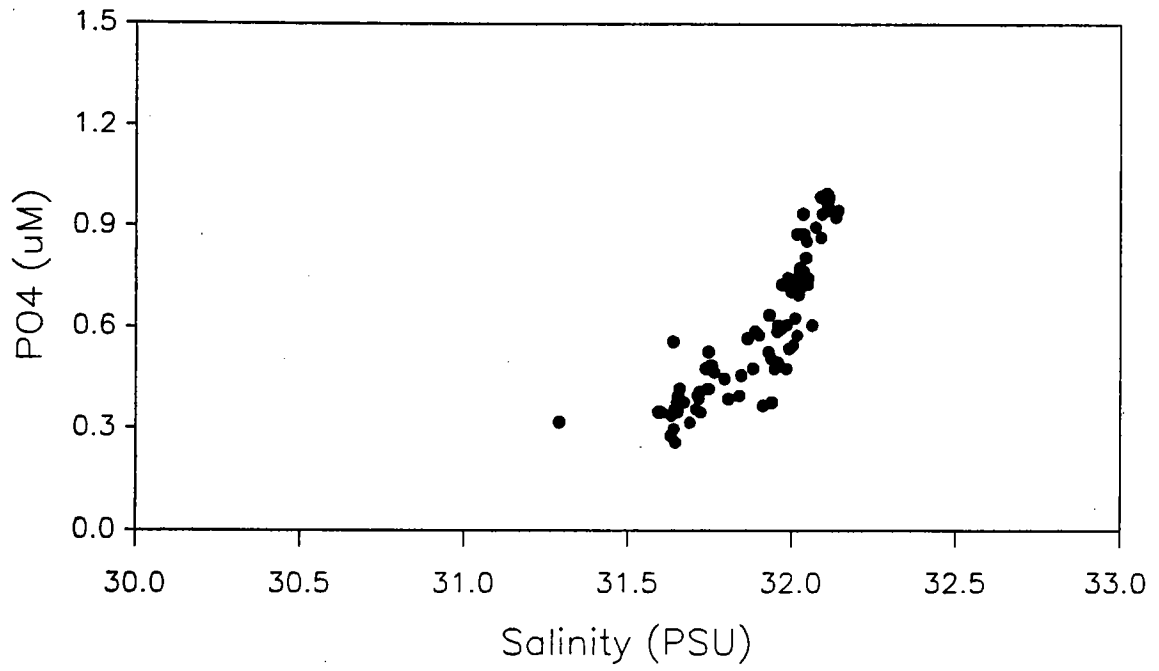
Early July (W9408)
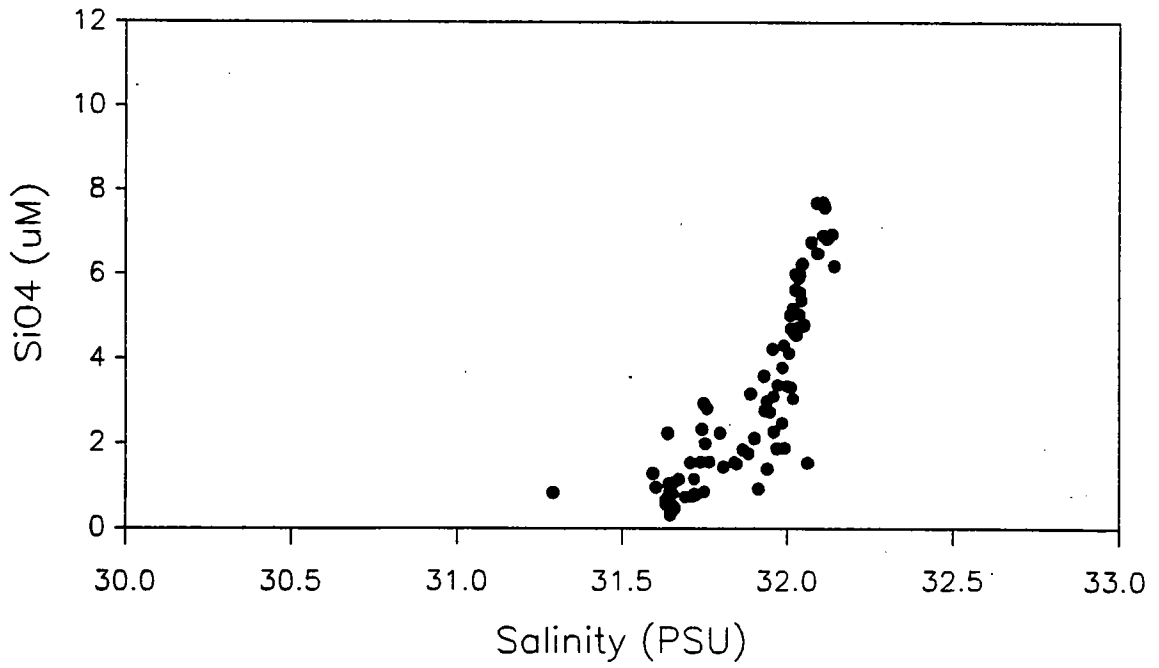
Early July (W9408)

Figure 4-3c.   PO$_4$ and SiO$_4$ vs. salinity in early July 1994.

Figure 4-4a. Vertical section contours for nearfield standard transects (view towards Boston Harbor) on Survey W9408. 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. Due to severe weather warnings, stations N13, N15, and N17 were not sampled.

Figure 4-4b. Vertical section contours for nearfield standard transects (view towards Boston Harbor) on Survey W9408. 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. Due to severe weather warnings, stations N13, N15, and N17 were not sampled.

Figure 4-4c. Vertical section contours for nearfield standard transects (view towards Boston Harbor) on Survey W9408. 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. Due to severe weather warnings, stations N13, N15, and N17 were not sampled.
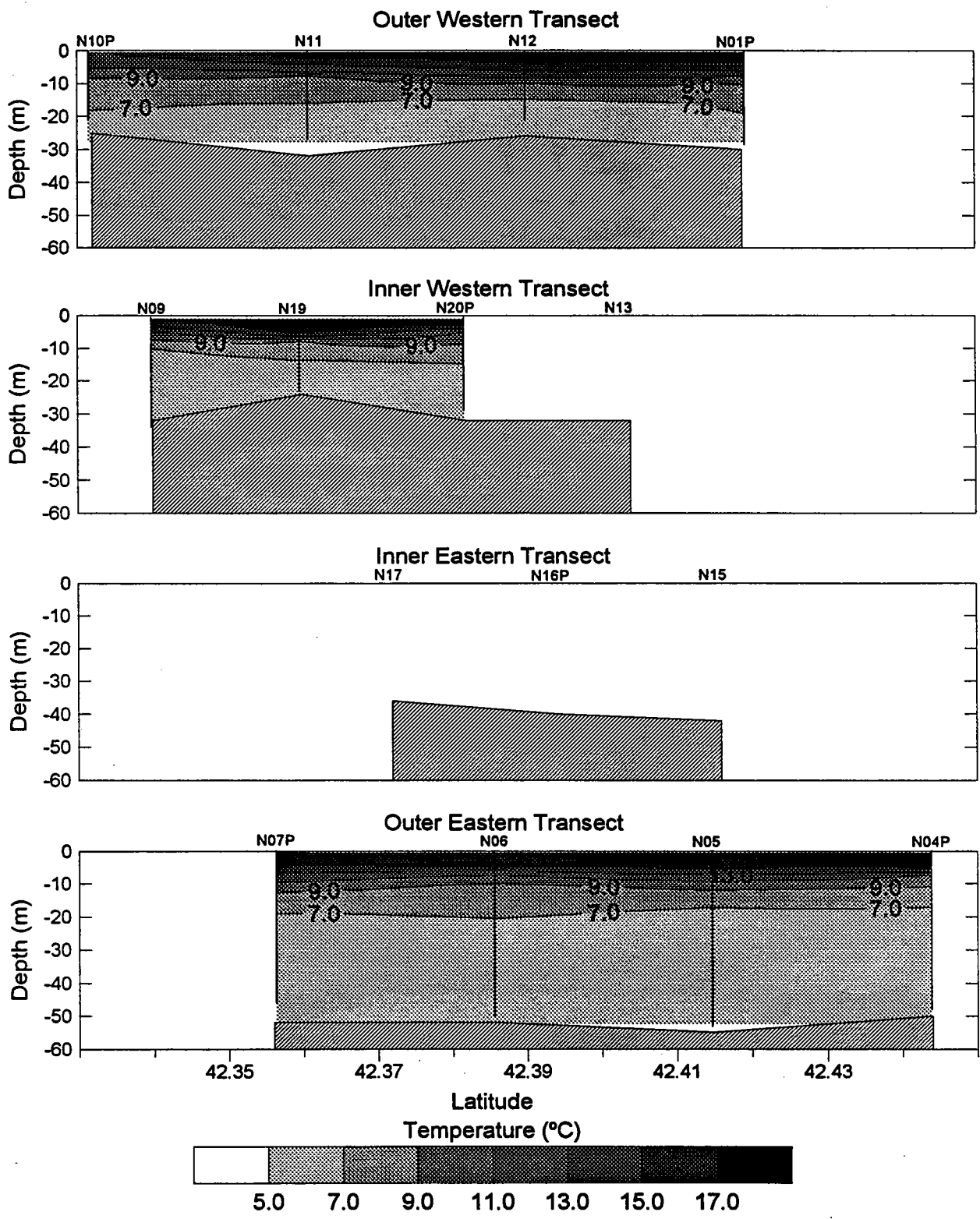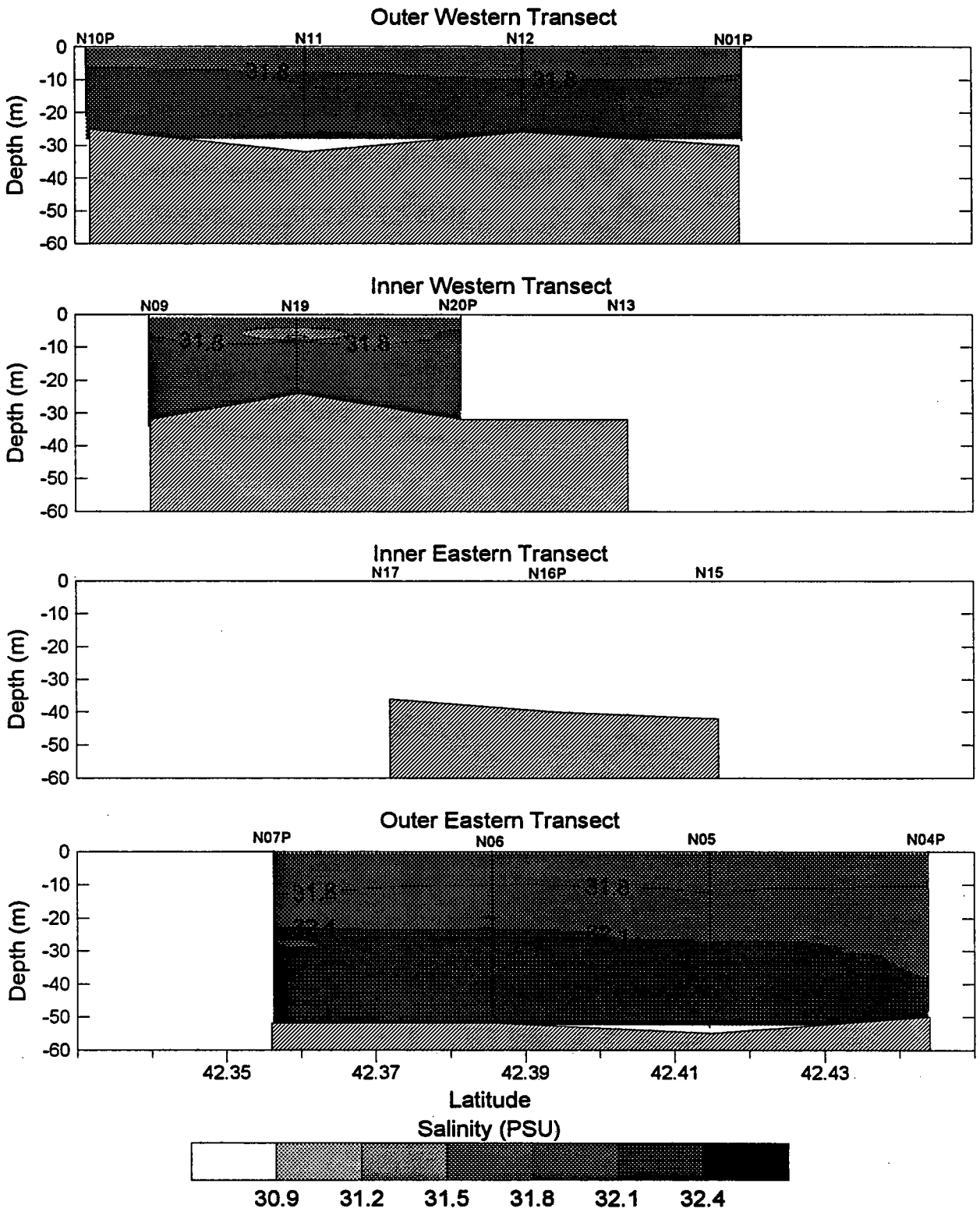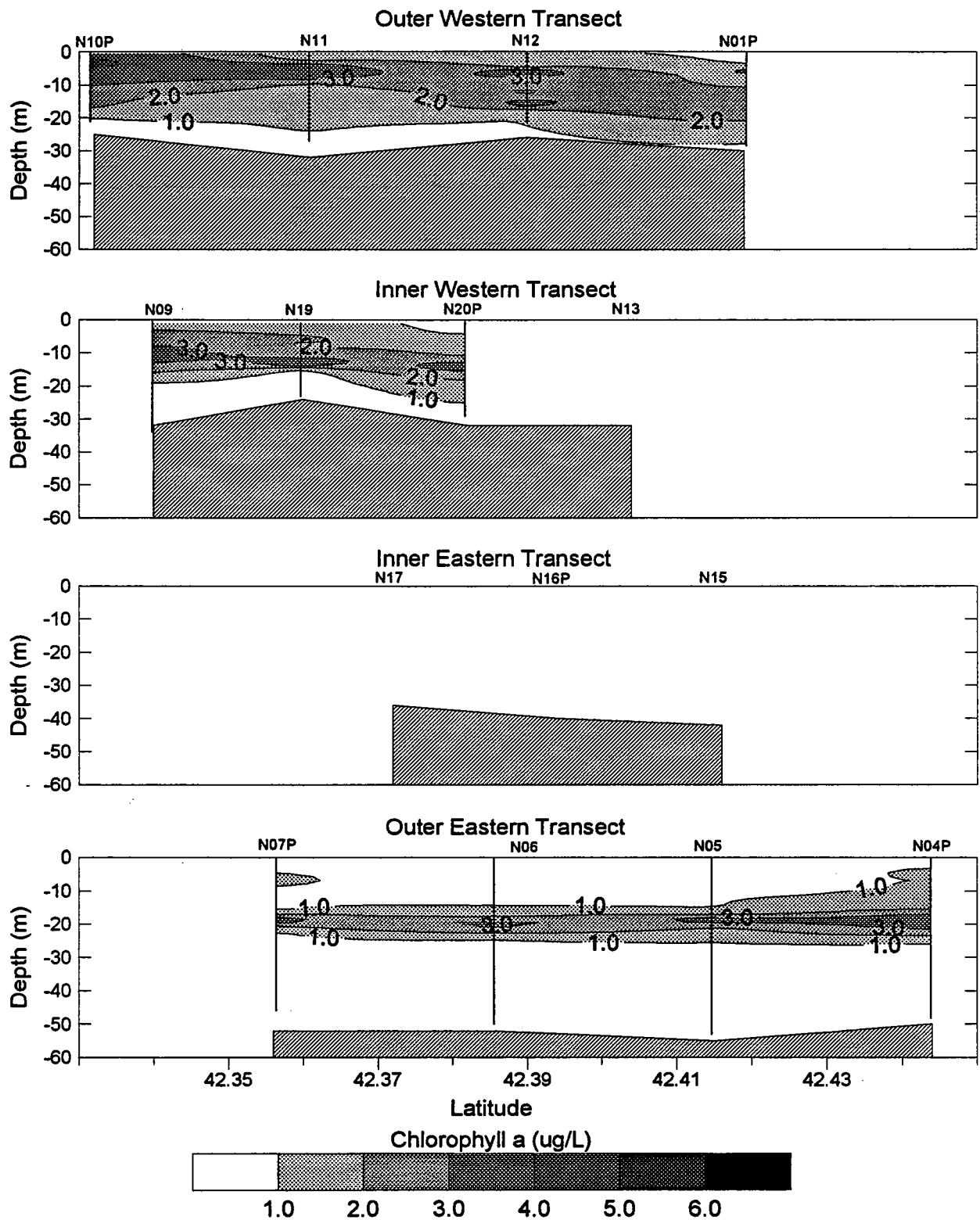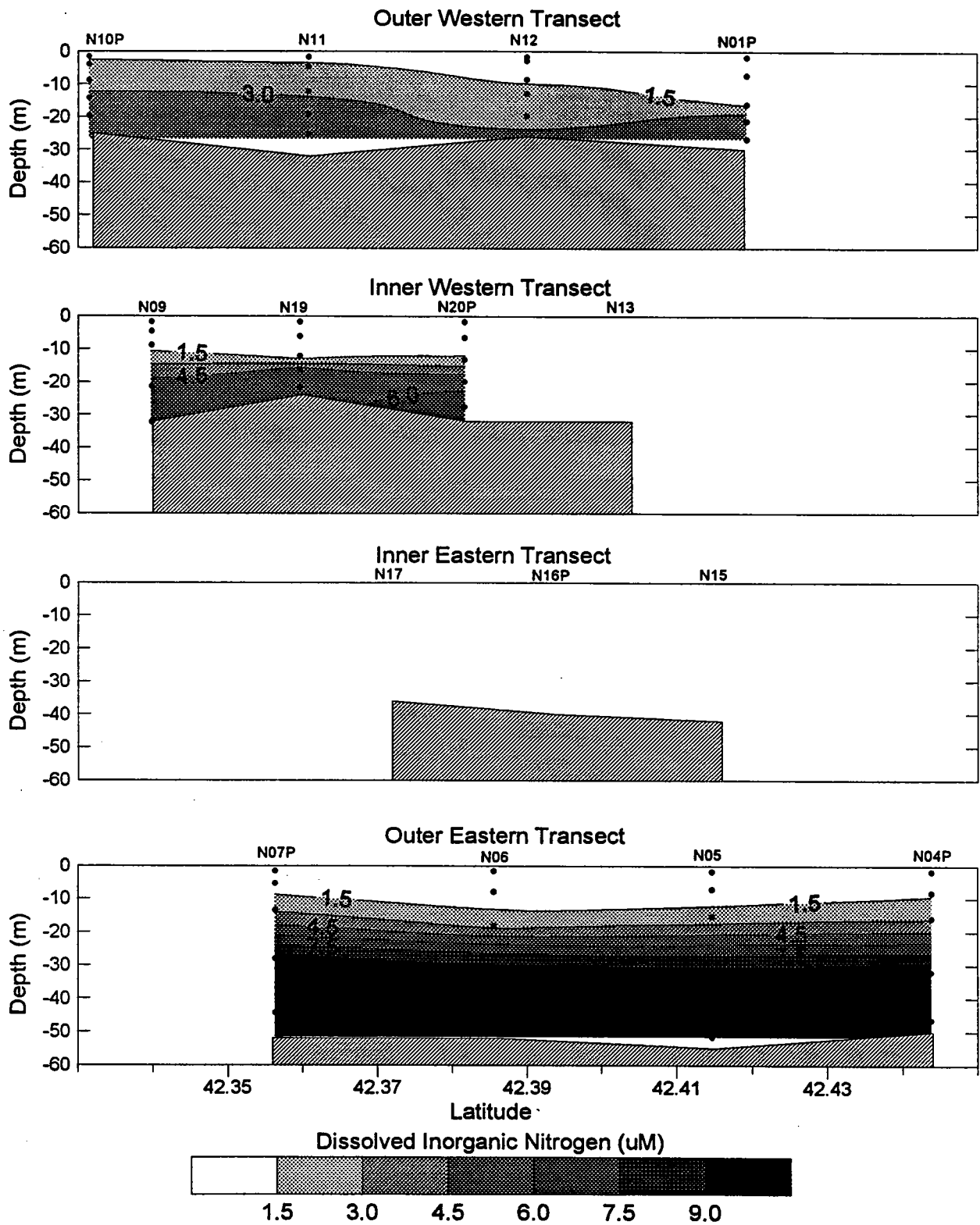
Figure 4-4d. Vertical section contours for nearfield standard transects (view towards Boston Harbor) on Survey W9408. The data used to produce the contours are from discrete bottle samples taken at each station during the nearfield sampling day (Appendix A). Due to severe weather warnings, stations N13, N15, and N17 were not sampled.

5.0 RESULTS OF LATE JULY 1994 NEARFIELD SURVEY (W9409)

5.1 Distribution of Water Properties from Vertical Profiles

Vertical profiles were obtained at all 21 nearfield stations on July 27 (Appendix B). Significant warming had taken place since early July. Surface water temperatures approached $20\,^{\circ}C$ in some cases and bottom water temperature minima were now >6°C (Figure 5-1a). Deep water salinity still was slightly >32 PSU, but the range for the surface layer had broadened on average the surface water salinity had decreased by almost 0.5 PSU and was ~31 to 31.5 PSU relative to early July. Variability in the surface waters across the nearfield is noticeable as scatter in salinity at warmer temperatures compared to the strong coherence of data at high salinity/low temperature (Figure 5-1a). The vertical profiles shown in Appendix B reveal that stratification remained strong, with thermocline/pycnoclines present between ≤5 m and ~15 m (i.e., generally a little higher in the water column than in early July). At station N10P, an unusually sharp pycnocline was noted between ~9 and 11 m depth, and crisply delineated upper and lower water layers. Nearby stations N11 and N12 appeared to have some of the same surface water layer as station N10P, but a complex, multi-layer thermocline was observed at these stations. A complex but subtle vertical layering was also observed at stations N13, N14, N19, and N20P, located east of stations N10P, N11, and N12.

The patterns for beam attenuation vs. salinity and chlorophyll were similar to those detected in early July (Figure 5-1a, cf. Figure 4-1a). However, relative to early July, maximum turbidity and chlorophyll values had respectively increased to ~3.7 m^{-1} and >9 μg L^{-1}. These maximum values were detected near the surface (Figure 5-1b). Higher concentrations were often observed in the surface layer, but a subsurface maximum (>3 μg L^{-1}) was a broadly distinct feature. Compared to early June and July, however, this feature was positioned higher in the water column and, in late July, was centered near 12 m rather than 20 m (Figure 5-1b).

The profiles of DO (as percent saturation) showed a fairly constant decrease from surface to bottom (Figure 5-1b). Surface values were above saturation (generally 110-130%), whereas most of the readings below the 30-m depth were <90% saturated and many were below 85% saturation. The minimum recorded DO at the closing of Niskin bottles was 8.06 mg L^{-1} and 82% saturation; it was noted that there

was excellent agreement between *in-situ* DO sensors and calibration values from Winkler titrations (Appendix A).

As found in June and early July, in late July dissolved nutrient concentrations generally increased with depth. In contrast to the earlier surveys, a subset of surface layer samples was enriched in nutrients (Figure 5-2); this subset created some near-surface scatter in the plots vs. depth for DIN, NH_4, and PO_4 in particular, but was also evident in plots of NO_3 and SiO_4 concentrations (Figure 5-2b,c). DIN concentrations ranged from 0.3 to 9 μM, similar to the range detected in the nearfield since late April. Maximum NH_4 and NO_3 concentrations were similar (6.0 and 5.7 μM respectively); however, the distributions over depth were different. The maximum NH_4 was observed at ~5 m and the maximum NO_3 was detected near 50 m.

Distributions of phosphate and silicate followed the typical pattern for stratified conditions, with the selection of enriched samples in near surface water (Figure 5-2c). As has commonly been found in the summer, neither phosphate nor silicate were as depleted as DIN in the surface waters.

With one exception, the nutrient-salinity plot (Figure 5-3) patterns resembled those from the previous survey in early July. Relative enrichment in DIN, NH_4, PO_4, and SiO_4 (and to a lesser extent, NO_3) concentrations was evident in a number of samples having an intermediate salinity near 31.5 PSU. These data indicate a nutrient-rich external (to the nearfield) source of water; the samples with high nutrient concentrations could not be a result of mixing of other water within the nearfield during either the early or late July survey.

5.2 Water Quality Variability in the Nearfield

Vertical contours of temperature, salinity, chlorophyll (as measured by fluorescence), and DIN are presented in Figure 5-4. Across the field, a uniform vertical thermal layering is suggested; the overall shallowness of stations towards the western side of the field places the thermocline closer to the bottom. Therefore, while the surface layer is approximately the same thickness moving from shore to sea, the

bottom layer expands noticeably into deeper water. Note in Figure 5-4a that the bottom of the pycnocline across the shallow set of stations of the Outer Western Transect tends to rise and fall with the bottom topography; it is likely that bottom turbulence from tidal currents in this area influence the variations in the strength of vertical layering.

Geographic trends for the halocline were similar to those for temperature (Figure 5-4b), but with a slightly higher degree of small-scale spatial variability. Some of this may be an artifact of the choice of contour intervals, but there were evidently some small near-surface patches of lower salinity water (<31.2 PSU) at stations near the center of the field (N16P and N17).

The vertical distribution of chlorophyll allowed a sharp distinction between western and eastern nearfield stations (Figure 5-4c). A surface layer with generally high chlorophyll concentrations (>3.0 μg L^{-1}) and several patches with concentrations >4.5 μg L^{-1} was found along both the Outer and Inner Western Transects. Along the Outer and Inner Eastern Transects, the maximum chlorophyll concentrations was more typically between 1.5 and 3.0 μg L^{-1} and evident as a distinct subsurface layer within the thermocline at about the 8-10°C isotherm. At each transect peak surface-water values tended to occur near the northern end, and a downward tilt in the depth of peak chlorophyll concentrations occurred diagonally across the field from northwest to southeast.

Concentrations of DIN were low in surface layers throughout the eastern nearfield (Figure 5-4d) and the subsurface chlorophyll maximum was at depth where DIN started its noticeable increase with depth. Interestingly, highest DIN concentrations are evident in deep water at the northeastern corner of the field. This relatively deep bottom-water enrichment did not seem to be associated with any physical difference in bottom water characteristics because the vertical profiles for temperature, salinity, and density for all four stations across the Outer Eastern Transect were remarkably similar (Appendix B). Thus, although advection could be hypothesized as one possible explanation of a slightly enriched deep-water nutrient pool, the data apparently do not provide evidence of a bottom water advection of enriched water, such as that from a deeper water source. An alternate explanation would be higher local rates of deep water decomposition, nutrient regeneration, or lower rates of processes that tend to deplete the bottom water nutrients. The plots of DO (percent saturation; see Appendix B) indicate that slightly lower DO occurred in deep water at stations N04P and N06, compared to stations N06 and N07P, a result that is consistent

with the hypothesis of local, rather than advective, control. Lacking hydrodynamic data, however, interesting distributions, such as the apparent deep-water enrichment, are difficult to explain with much confidence.

Figure 5-4d also confirms that the nutrient enrichments identified in the depth and salinity plots occurred at inshore western nearfield stations. Along the western side of the nearfield, the correspondence of DIN and chlorophyll concentrations is not very strong. This most likely results from semi-isolated patches of phytoplankton at different population growth stages, where some populations have depleted local nutrients and other populations have not. Regardless, the patterns suggest that nutrient enrichment and chlorophyll enrichment (or *in-situ* stimulation, cf. Kelly and Albro, 1993) occur as surface water is transported across the western boundary of the nearfield.

Figure 5-1a. Scatter plots of data acquired by *in situ* sensor package during vertical casts for nearfield survey in late July 1994. Chlorophyll is estimated from *in situ* fluorescence.
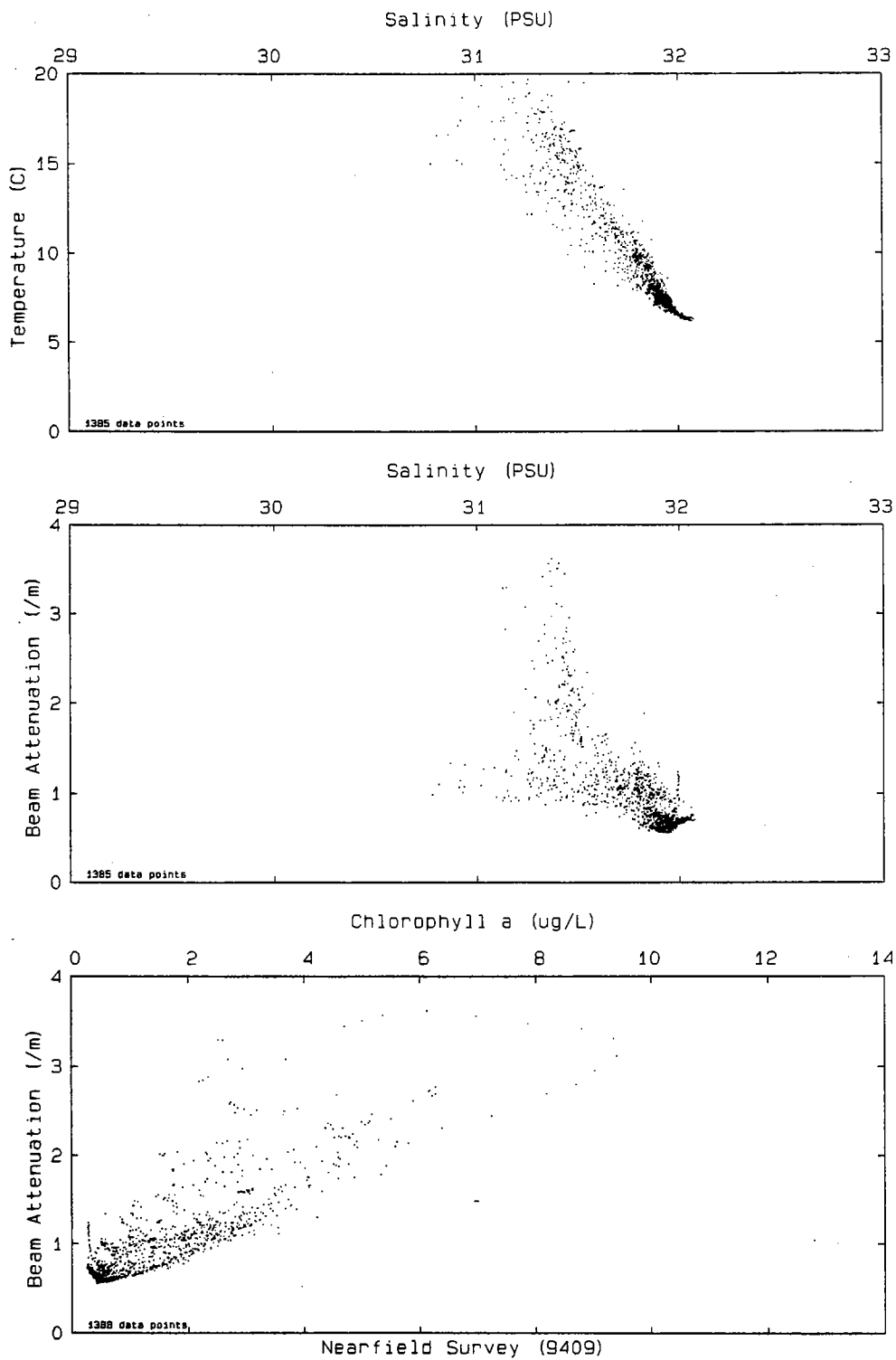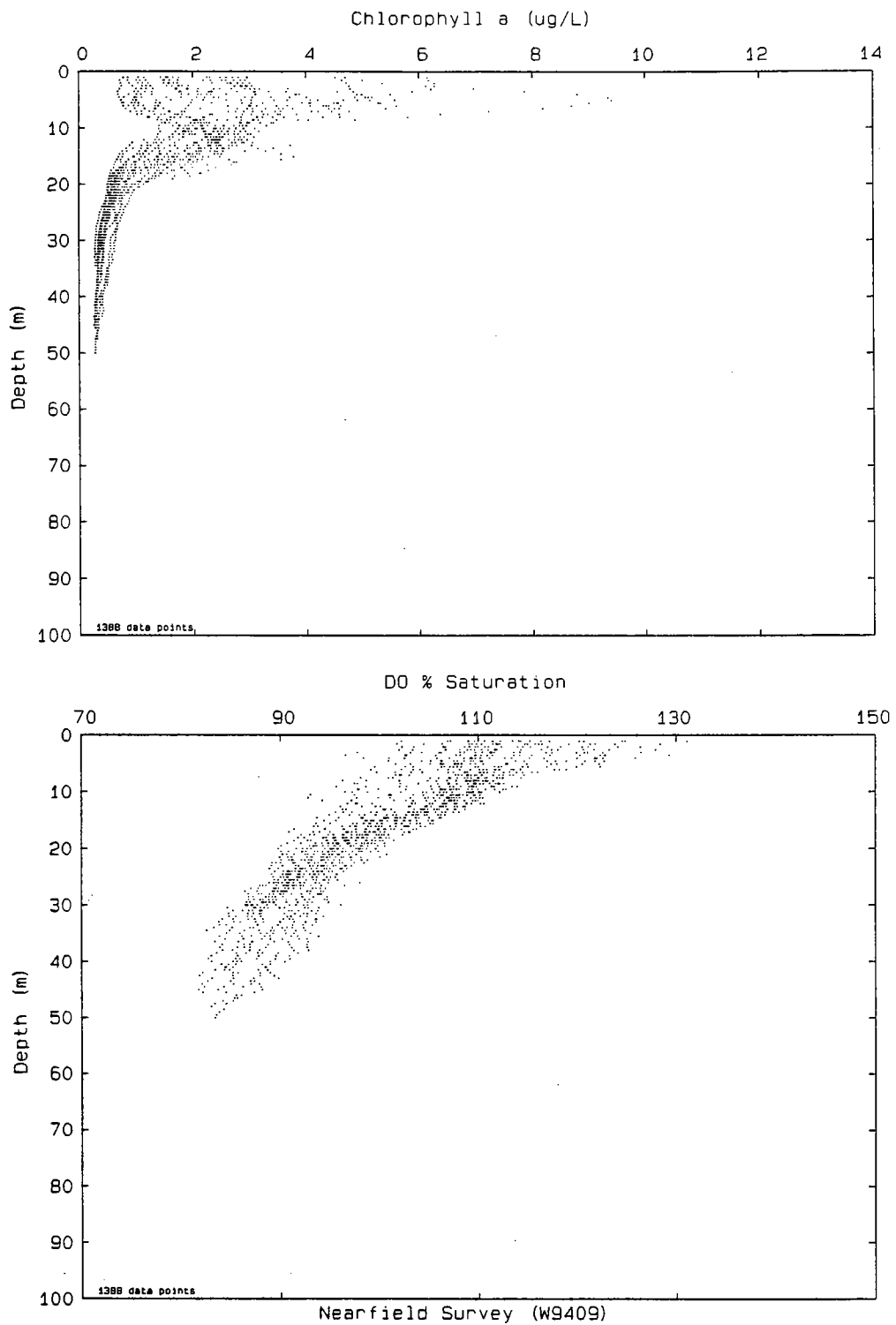
Figure 5-1b. Scatter plots of data acquired by *in situ* sensor package during vertical casts for nearfield survey in late July 1994. Chlorophyll is estimated from *in situ* fluorescence.
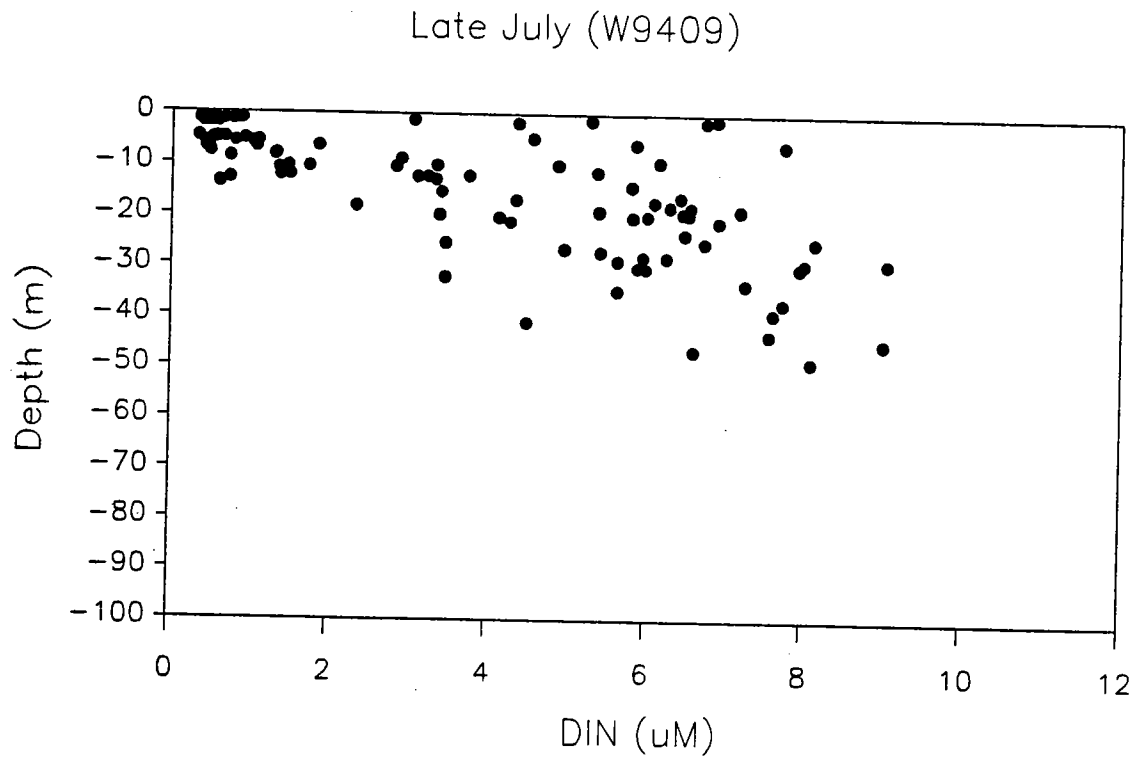
Figure 5-2a.   DIN vs. depth in late July 1994.

Late July (W9409)

NH4 (uM)

Late July (W9409)

NO3 (uM)
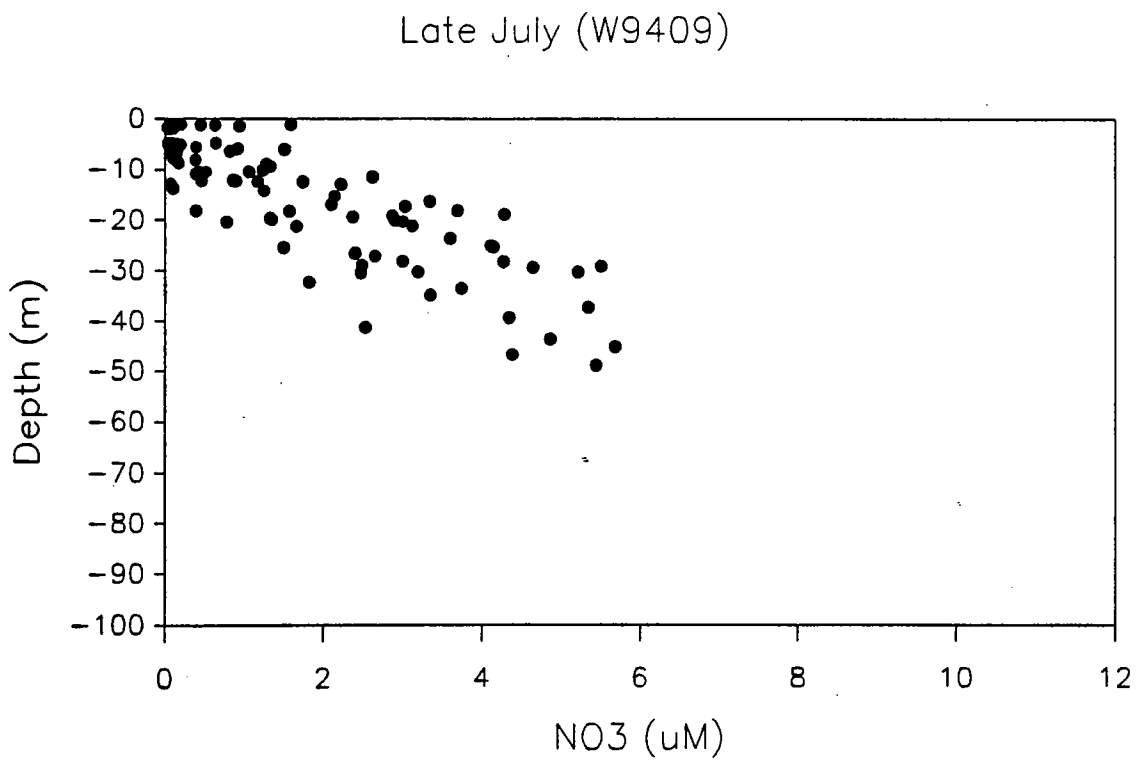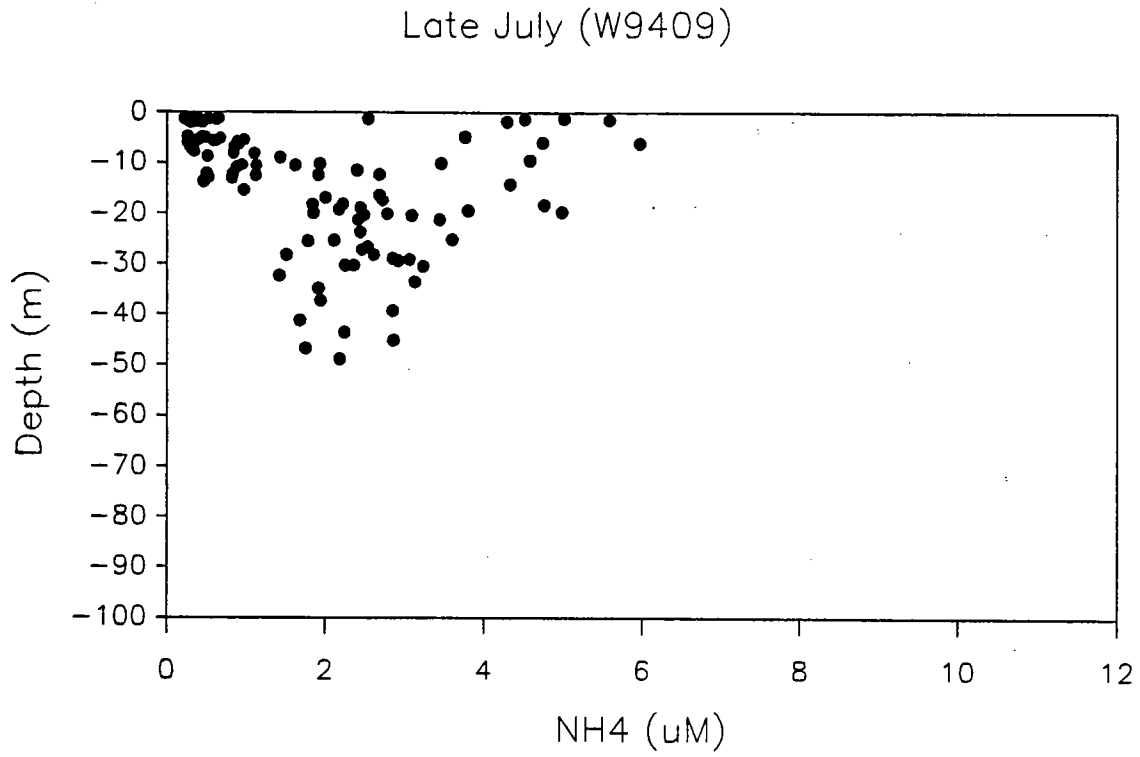
Figure 5-2b.   NH$_4$ and NO$_3$ vs. depth in late July 1994.

Late July (W9409)
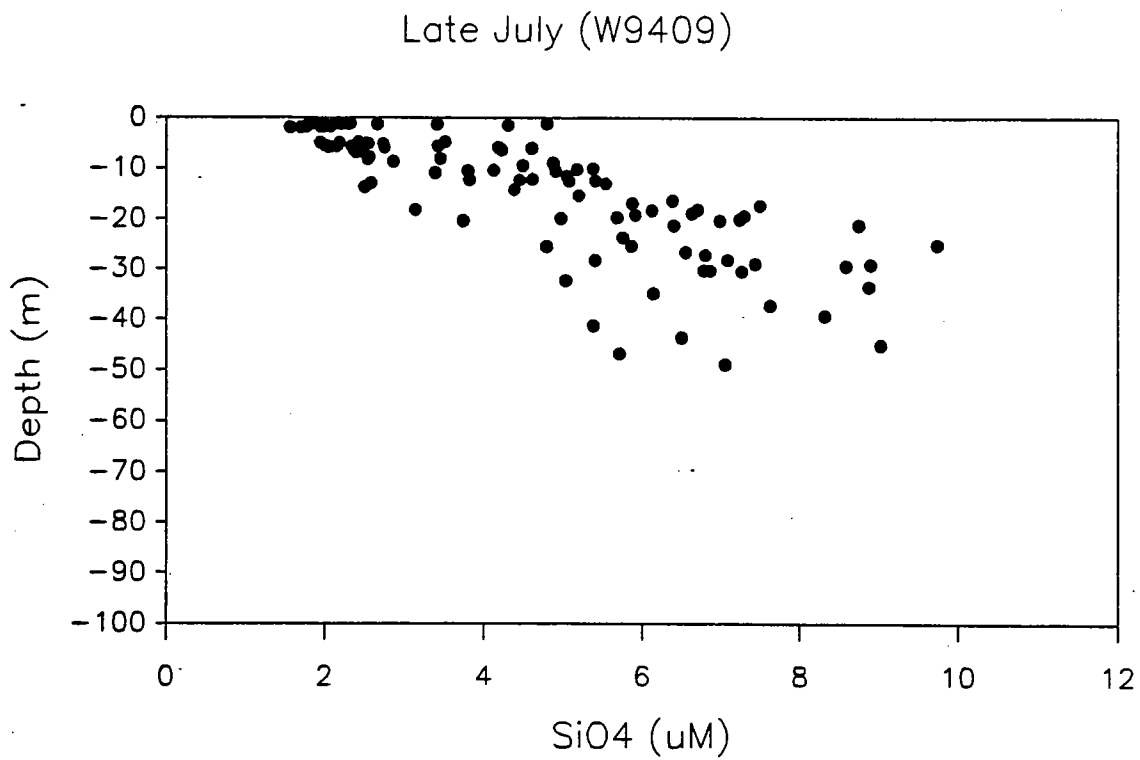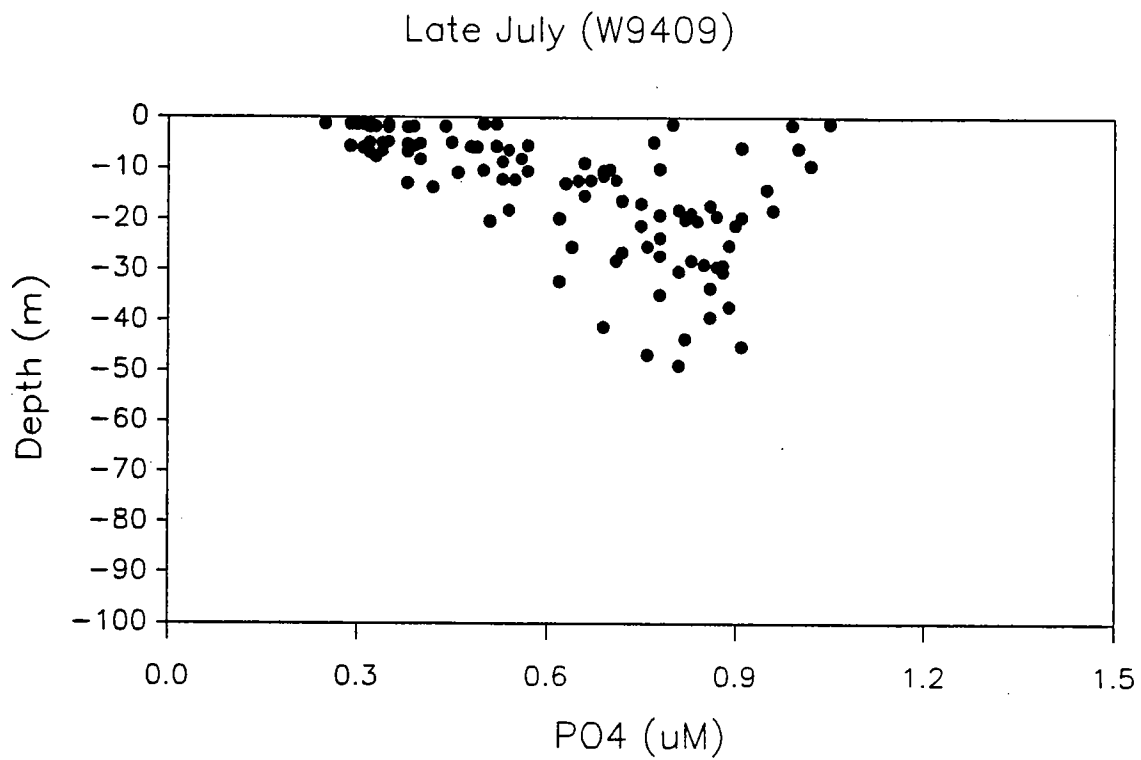
Late July (W9409)

Figure 5-2c.   PO$_4$ and SiO$_4$ vs. depth in late July 1994.
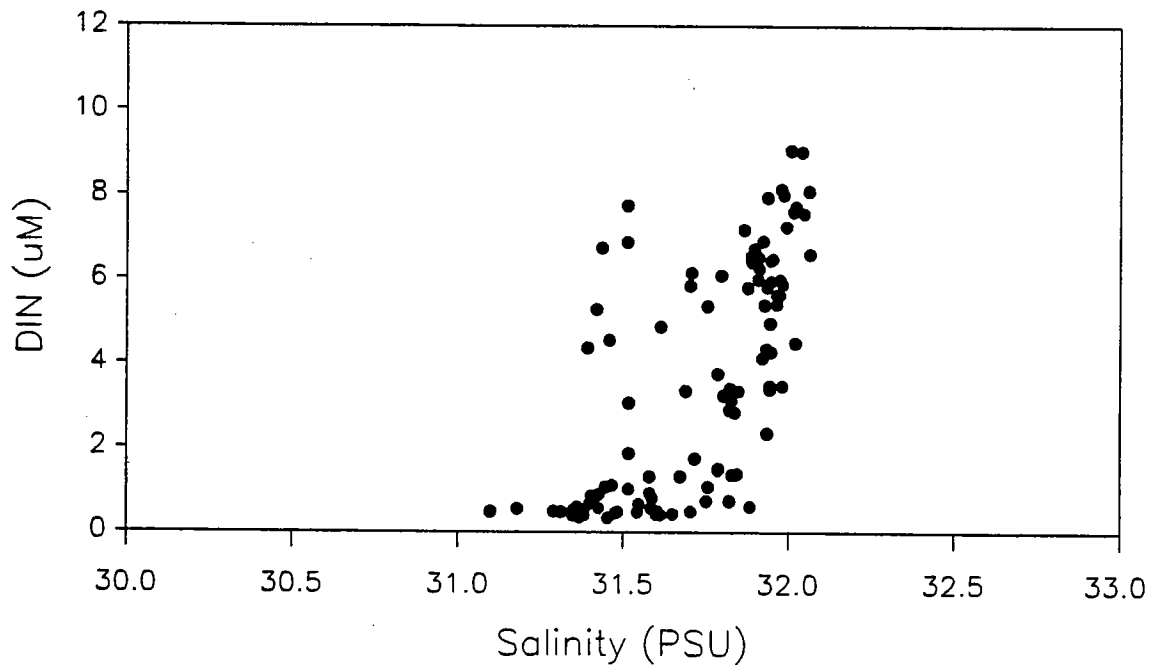
Late July (W9409)

Figure 5-3a.   DIN vs. salinity in late July 1994.
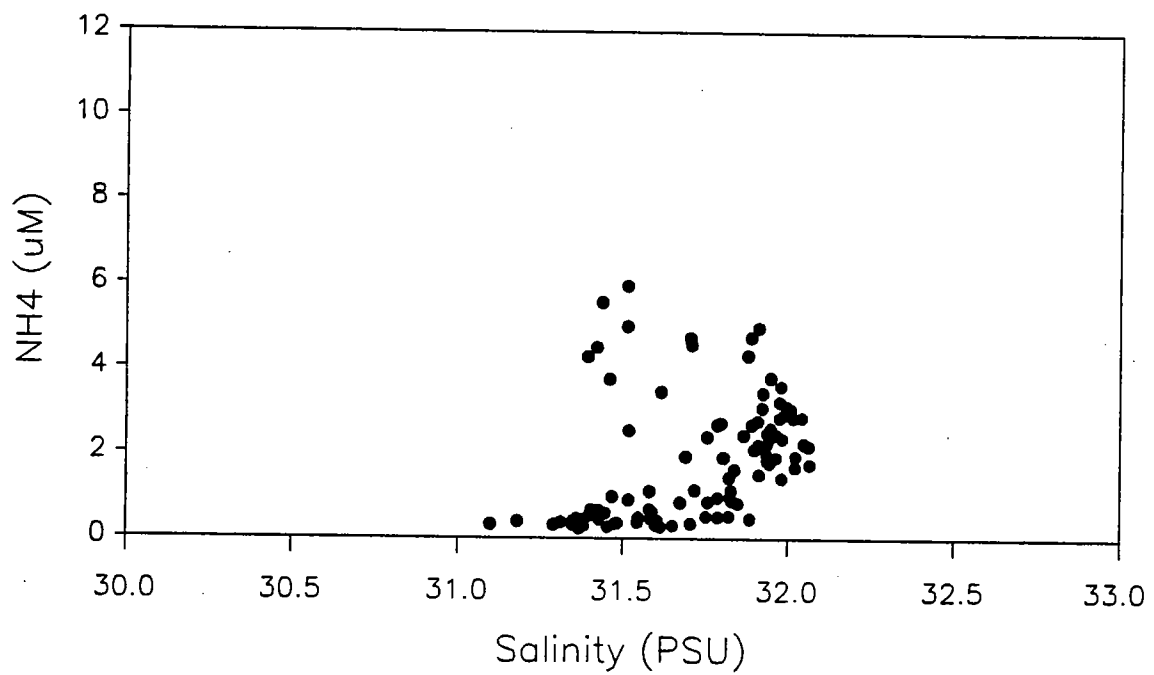
Late July (W9409)
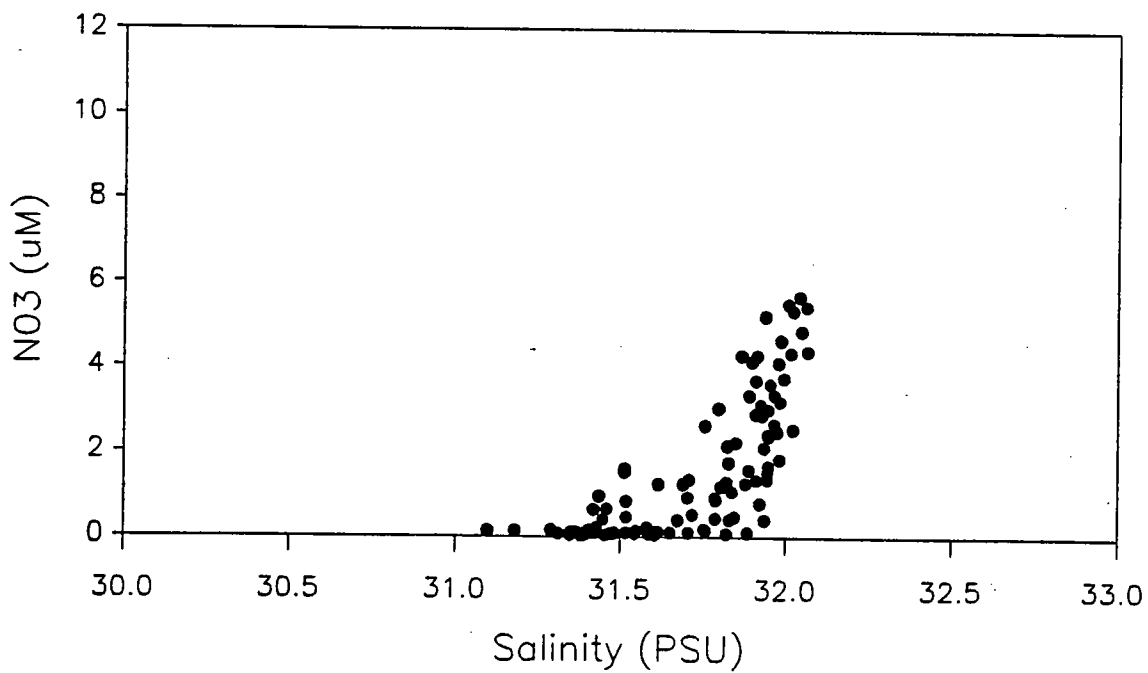
Late July (W9409)

Figure 5-3b.   NH₄ and NO₃ vs. salinity in late July 1994.
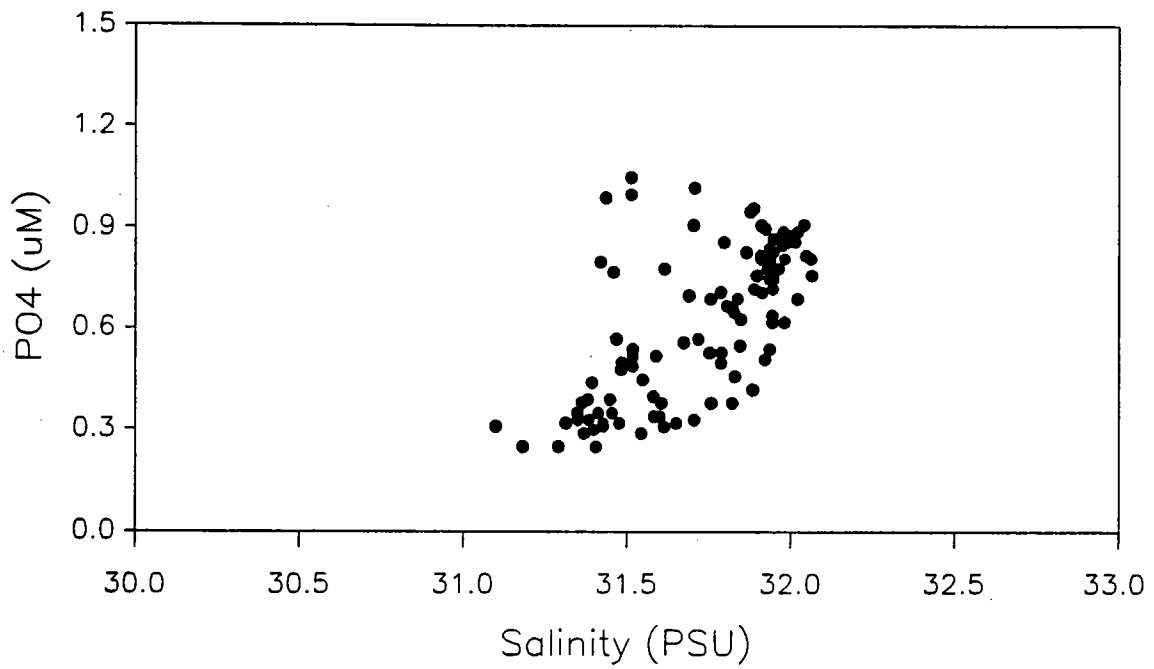
Late July (W9409)
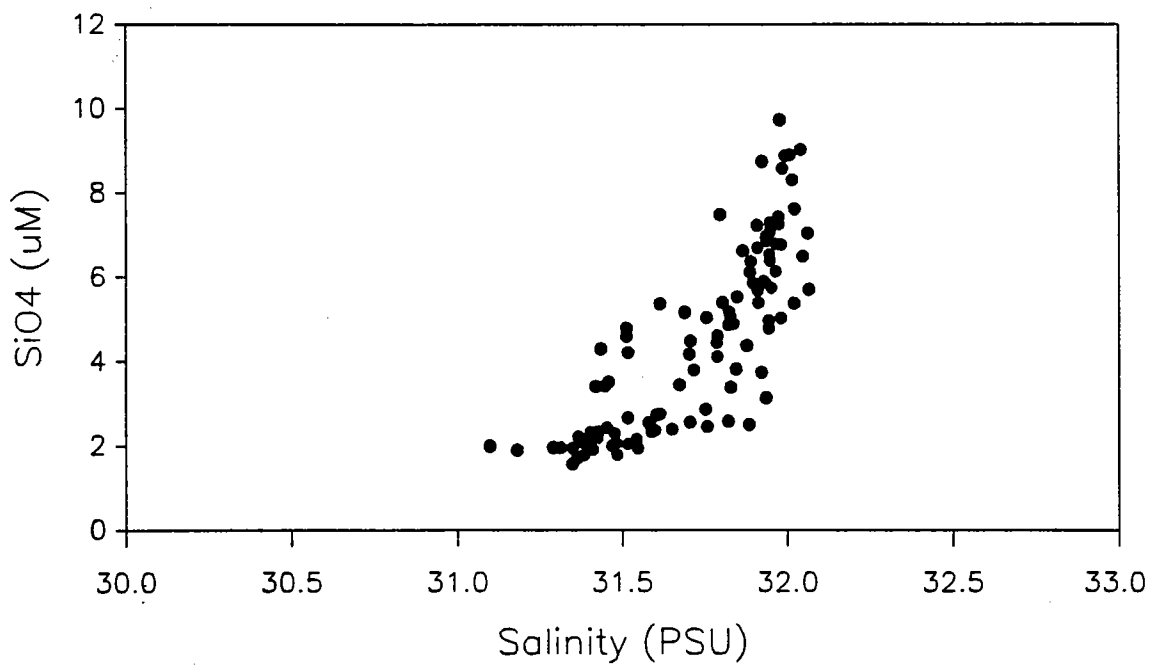
Late July (W9409)

Figure 5-3c. **PO$_4$ and SiO$_4$ vs. salinity in late July 1994.**
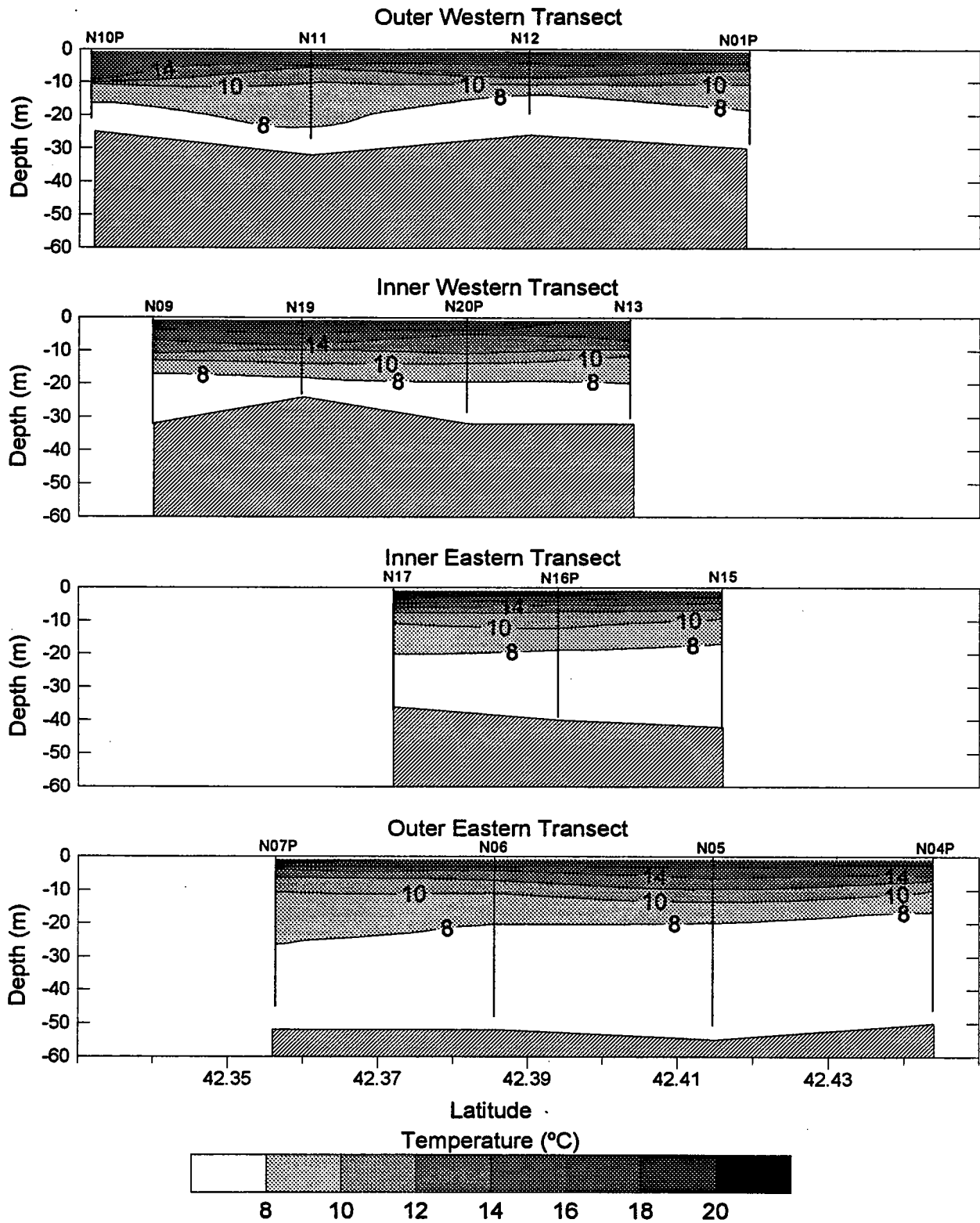
Figure 5-4a. Vertical section contours for nearfield standard transects (view towards Boston Harbor) on Survey W9409. The data used to produce the contours are from high-resolution continuous vertical profiles taken from the downcast at each station during the nearfield sampling day.
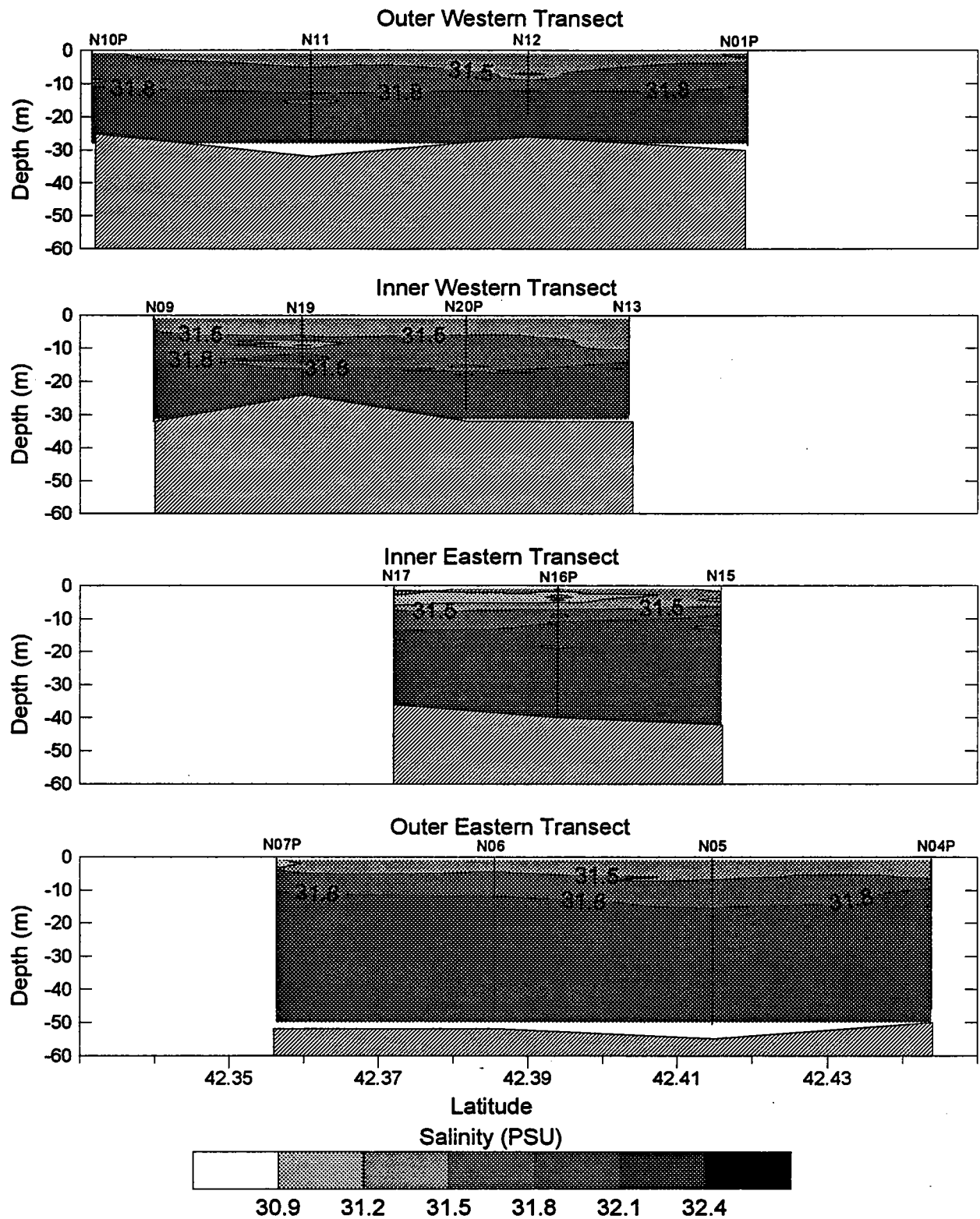
Figure 5-4b. Vertical section contours for nearfield standard transects (view towards Boston Harbor) on Survey W9409. The data used to produce the contours are from high-resolution continuous vertical profiles taken from the downcast at each station during the nearfield sampling day.
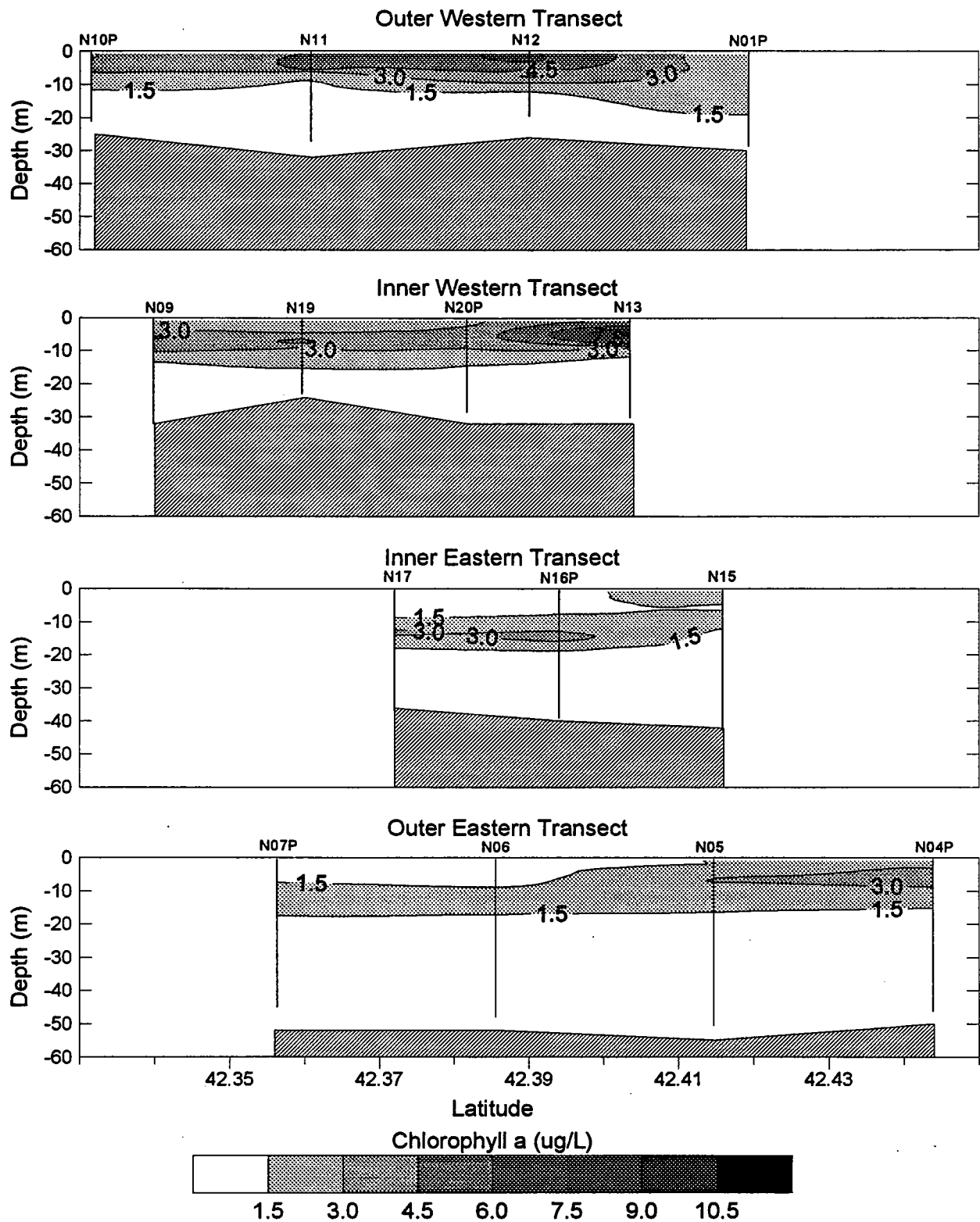
Figure 5-4c. Vertical section contours for nearfield standard transects (view towards Boston Harbor) on Survey W9409. The data used to produce the contours are from high-resolution continuous vertical profiles taken from the downcast at each station during the nearfield sampling day.
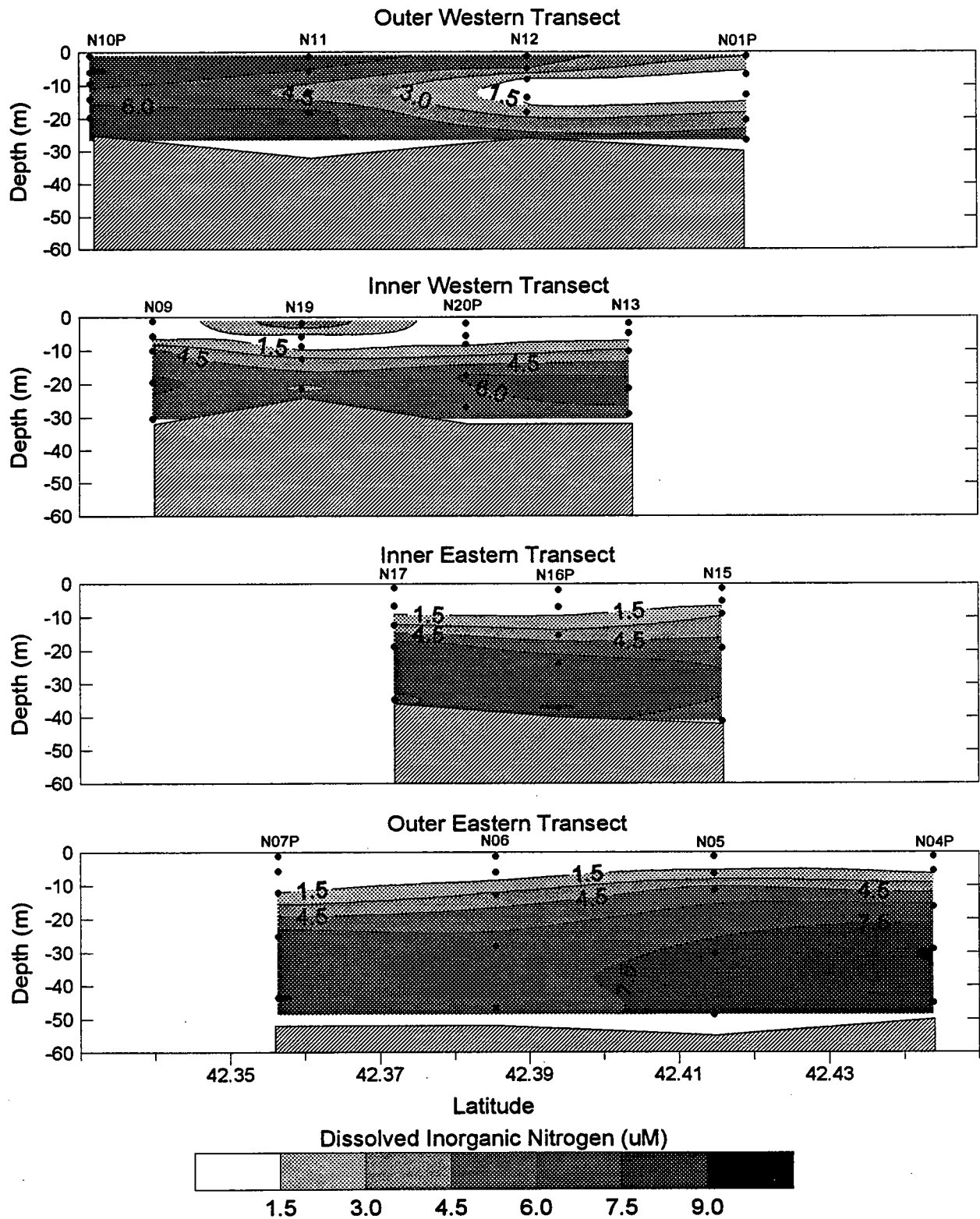
Figure 5-4d. Vertical section contours for nearfield standard transects (view towards Boston Harbor) on Survey W9409. The data used to produce the contours are from discrete bottle samples taken at each station during the nearfield sampling day (Appendix A).

6.0 DISCUSSION OF THE EARLY SUMMER PERIOD OF SURVEYS

6.1 Water Properties

6.1.1 Variability at the Regional Scale

During the months covered by this report, the regional scale was surveyed only once in June (see Section 3), so temporal variability on the Bay-wide scale was not assessed across the period of surveys included in this report. Accordingly, summary comments here relate to spatial variability rather than to temporal variability.

Other than very shallow Harbor and coastal waters, vertical profiles of temperature and salinity showed a typical summer character: basically, a two-layered system with a seasonal thermocline persistent throughout the Bays. As mentioned in Section 3, some minor geographic variations in surface water characteristics were noted. For example, the surface water in eastern Cape Cod Bay was relatively warm and less saline, more like Boston Harbor water than the Bays. The source of fresher water cannot be implied from the limited data. However, local freshwater sources are not large and it seems more likely that the feature could represent a remnant surface layer from a spring freshet (from Boston Harbor and/or north of Cape Ann), trapped and lingering in a hydrodynamically sluggish pocket of Cape Cod Bay.

Compared to regional variations in physical characteristics, turbidity and fluorescence revealed a strong regional feature, the elevation of both parameters in Boston Harbor and radiating outward into western Massachusetts Bay. Based on several years of MWRA water column monitoring studies, this finding has now become expected for this time of the year.

The 1994 surveys included water column monitoring stations across the northeastern boundary between Massachusetts Bay and the Gulf of Maine. Previously, the most seaward stations were in deep offshore water within Stellwagen Basin, so the Cape Ann–Stellwagen Transect deserves brief mention. A suggestion from the data presented for vertical sections across this transect was the isolation of cold deep water in Stellwagen Basin from the similarly cold deep water in the Basin just outside the Bay, lying east

of the northern tip of Stellwagen Bank (station F27B). The 5°C isopleth was interrupted by the Bank, and this isopleth was found at a depth generally lower than the main sill depth between Cape Ann and the Stellwagen Bank, the sill being the area where bottom water communication from the north into Stellwagen Basin could occur. A review of data from stations within Stellwagen Basin suggested that the 5°C isopleth was inclined to the south in Stellwagen Basin. For example, this isopleth was found at 60 m at station F22 at the northern head of Stellwagen Basin and it graded to a depth of 40 m at station F12 (cf. Figures 3-10 and 3-11). Similarly, the 32.2 PSU salinity isopleth also inclined, from about 45 m at the north to 20 m at the southern ends of the Basin. These data imply a possible geostrophic flow to the north in deep water of Stellwagen Basin, rather than a deep bottom-water flow into the northern part of the Basin from deep water outside the Bay to the northeast. The data are hydrographical, not hydrodynamical, so flow of water is, at best, inferred. Even so, the data may suggest a lack of communication of deep Basin water inside and outside the Bay at this time.

6.1.2 Variability in the Nearfield

Physical layering in the nearfield was very uniform in space and relatively constant in time across the early summer surveys. The thermocline approached the bottom only at shallowest stations and only a few examples of mild vertical mixing, probably by tides and their effect on Harbor exchange, were noted near the southwestern corner of the nearfield. Interestingly, the broad physical uniformity emphasizes the geochemical and biological gradient from shore. Moreover, it also highlights a tendency for small-scale heterogeneity (spatial patchiness) in biogeochemical characteristics that is not immediately apparent in physical measurements (i.e. Figure 5-4).

With respect to phytoplankton, Tables 6-1 and 6-2 display dominant taxa found in surface water at station N10P during June and July sampling. Other than a small shift among diatoms, from *Chaetoceros* to other minor dominants (*Rhizosolenia* or *Cylindrotheca*) in July, both the whole-water and screened samples showed fairly constant communities and ordinary trends.

6.1.3 Special Features: Comparison of 1994 with Previous Years

Figure 6-1 shows the surface temperature in the nearfield for all of 1993 and through late July 1994. For reference, Libby *et al.* (1994) and Kelly and Turner (1995) provide additional graphical comparisons of the 1992 and 1993 annual cycles. Characteristically, by June and July of each year (and also 1992), the range in surface temperatures within the nearfield expanded considerably as thermal layering strengthened. In 1994, the warming in June and July, evident in the increase in mean, maximum, and minimum temperatures, extended the general warming progression that started in February and continued each month thereafter. In contrast, the temperature cycle in the entire first half of 1993 was much less smooth and progressive, and the maximum temperature in the early summer period in 1993 was in early July, rather than in late July. However, compared to 1992, *both* 1993 and 1994 surface waters warmed earlier and thus, relative to 1992, were higher by 1-3°C in maxima and the average nearfield surface water during June and early July. For 1994, the progressive and early warming coincided with strong, uniform development and persistence of thermal stratification.

DO concentrations in nearfield bottom waters dropped abruptly between late April and May, reaching ~9 mg L^{-1} in May (Figure 6-2). This seasonal dip in bottom-water DO appears to be a regular feature in the nearfield because it was apparent in 1993 (Figure 6-2) and was also noted in 1992 (see Kelly, 1994). A slight rebound or stabilization of DO concentrations occurred in June 1994, a feature also noted in previous years. In 1994, the June rebound was slight, as in 1993. Through July 1994, DO concentrations in bottom water then continued to decrease. Because of this progressive decline, average DO concentrations in nearfield bottom waters were near 8.5 mg L^{-1} by late July 1994. A progressive decline in July was not noted in 1993 (Figure 6-2) or in 1992. In contrast, in 1993 and 1992, late July DO readings in bottom water were generally ~1 mg L^{-1} higher and, on average, approached 10 mg L^{-1}. The strong, persistent stratification during the first months of summer may have influenced the rate of bottom-water DO decline in 1994, but at mid-summer (late July) the minimum and average DO concentrations in nearfield bottom waters were significantly lower than in the two previous years.

It will be interesting to examine data from the remainder of 1994 to determine whether this early decline in DO translates to lower annual DO minima in the fall before water column overturn. Declines in nearfield bottom-water DO concentrations from June/July to mid-October in 1992 and 1993 were

between 0.023 and 0.037 mg L^{-1} d^{-1} (Kelly, 1994; Kelly and Turner, 1995). Assuming that range of rates, a remaining period of 80 days until breakdown of stratification in mid-October, and a minimum DO in late July of 8.06 mg L^{-1}, then the projected annual nearfield bottom-water minima in 1994 could be between 5.1 and 6.2 mg L^{-1}, values which are lower than those reported in the years since about 1988 (cf. Kelly, 1991).

6.2 Water Column Nutrient Dynamics

6.2.1 Vertical Structure

In general, nutrient-depth patterns were a function of strong stratification. Vertical nutrient profiles were generally similar throughout the Bay in June (exceptions given below) and consistent in the nearfield across surveys during June and July. There was relative, if not absolute, depletion of nutrients in surface layers and increasing concentrations of all nutrient forms (N, P, Si) with depth.

In June, some regional distinctions were noted in the nutrient-depth patterns. For example, Boston Harbor, coastal, and some nearfield stations had higher nutrient concentrations in surface waters. Surface water enrichments varied across nutrient forms; for example, enrichments in NH_4 and PO_4 were pronounced, whereas enrichment in SiO_4 was less apparent and enrichment in NO_3 was not very noticeable. Additionally, vertical profiles of PO_4 differed among regions in that concentrations at similar depths in the nearfield area were much higher than in the offshore and boundary regions. This gradient in PO_4 concentrations created a distinctive pattern of increasing DIN/PO_4 ratios in subsurface waters from nearshore to offshore regions and was accompanied by a similar pattern for surface waters. These patterns may or may not have prominent ecological importance, but they certainly illustrated a diagnostic for water mass characterization.

A final noteworthy feature of nutrient-depth patterns in different regions singled out Cape Cod Bay. Here, some mid-water elevation of SiO_4 was prominent in depth plots and thus emphasized lower N/Si ratios in many samples from this Bay. Possible relationships between phytoplankton composition and

silicate have already been noted and in previous years these relationships have distinguished the ecological dynamics in Cape Cod Bay from those in Massachusetts Bay (cf. Kelly *et al.*, 1993c). This topic is briefly discussed below.

6.2.2 Inshore-Offshore Gradients

Enrichment of Harbor, coastal, and usually surface water at some western nearfield stations during June was described above (Section 6.2.1), and was illustrated by geographic and section plots presented in Sections 3, 4, and 5 above. Description and interpretation of ecological consequences of the broad, persistent gradient of decreasing surface water nutrient concentrations that exists with distance from Boston Harbor has been the focus of recent synthesis efforts and special sampling efforts (e.g., Kelly, 1991, 1994; Kelly and Albro, 1994). These common patterns were again observed in the early summer 1994 data.

6.2.3 Special Features: Comparison of 1994 with Previous Years

By late March and early April 1994, surface water DIN concentrations reached the stratified period's seasonal low in the annual nutrient cycle (Figure 6-3). Thereafter, mean values fluctuated up and down slightly but overall were still low. This pattern generally repeats the pattern observed in 1993 and in 1992. The noteworthy aspect of early summer 1994, compared to 1993 and 1992, however, is the wide range of concentrations observed at each survey in June and July within the top 20 m (Figure 6-3). Maximum concentrations were 6-8 μM in 1994, compared to characteristic peaks of 4 μM in 1993.

The present data do not address fully the reason for the wider range of DIN concentrations observed in 1994, but the detection of a wider range raises interesting notions, as next discussed. Higher concentrations may be related to interannual variations in the nature of vertical stratification, including the thickness of the surface layer and sharpness of the pycnocline. For example, at some locations in the nearfield in 1994, the 20-m depth extends into the bottom layer where nutrient concentrations are already increasing with depth. However, this could only be a partial explanation of the wider range of surface

layer DIN concentrations in 1994 because in late July concentrations >6 μM were detected in the surface-most samples at several western nearfield stations that are regularly influenced by Harbor-Bay tidal exchange. This detection may be a coincidental consequence of the timing of sampling relative to the tidal stage in 1994 vs. other years, or could suggest a degree of interannual variability in Boston Harbor's summer DIN concentrations and nitrogen removal processes within the Harbor. MWRA data on Harbor DIN concentrations across years might clarify the latter possibility.

6.3 Biology in Relation to Water Properties and Nutrient Dynamics

6.3.1 Phytoplankton-Zooplankton Relationships

Some of the geographic variation in the zooplankton community, such as a coastal-western nearfield grouping that was somewhat distinct from eastern nearfield station, may correspond directly to the importance of diatoms at coastal-western nearfield stations. However, Figure 6-4 indicates considerable scatter in the relationship between zooplankton and phytoplankton counts. Some of the scatter is created by low zooplankton counts at the edge of the Harbor (station F23P) and at one Cape Cod Bay station (F01P). Relative to chlorophyll concentrations at station F23P, the zooplankton counts are often low. Omitting the data from these two stations, there is suggestion of a direct relationship between counts of phytoplankton and zooplankton. This is of interest because in April 1994, the data suggested an inverse relationship, a fundamental shift in the pattern. In April, zooplankton counts were generally much lower than in June; in contrast to Figure 6-4, total counts at stations in April ranged from 10,000 to 40,000 m^3. During the seasonal change that occurred between April (characterized by cold water conditions near the end of the winter-spring diatom bloom) and June (characterized by warm surface waters, fully stratified conditions, and a mixed phytoplankton community), a fundamental change in the coupling of phytoplankton and zooplankton is highly plausible. Previous MWRA water column monitoring annual and periodic reports have reported similar intermittent, perhaps seasonal, phasing in the apparent nature of a phytoplankton-zooplankton relationship that may be indicated by total counts of plankton.

6.3.2 Chlorophyll, Phytoplankton Species, and Water Properties

As shown by chlorophyll-calibrated fluorescence profiles, chlorophyll was high in the surface water of some regions and occurred as a subsurface maximum in other regions (Figure 6-5). The highest discrete-sample chlorophyll concentration measured in June ($\sim$11 μg Chl a L^{-1}) was detected near the surface in Boston Harbor. In contrast, peak concentrations of chlorophyll at both Cape Cod Bay stations were subsurface, at about 15 m.

Despite relative enrichment of silicate in mid-depth water of Cape Cod Bay, the diatom community was not enhanced; in theory, diatons could exploit the availability of silicate. However, the diatom community in Cape Cod Bay was actually diminished relative to the community in water surrounding Boston Harbor, where N/Si ratios were broadly higher and relative silicate availability appeared to be lower. A similar anomaly was found in early summer. High silicate concentrations in Cape Cod Bay were described by Kelly et $al.$ (1993c). As hypothesized in 1992, the nutrient composition detected in 1994 may actually reflect biological conditions – a community that does not use much silicate – rather than a geochemical condition that stimulates a certain biological population. In 1992, the anomaly included an intense bloom of the dinoflagellate $Ceratium$. Although $Ceratium$ species and another dinoflagellate, $Dinophysis$ $norvegica$, were present at stations F01P and F02P in Cape Cod Bay in 1994, they were more abundant in the chlorophyll maximum than at the surface; concentrations were in the range of 10^2-10^3 L^{-1}, much lower than the June 1992 bloom concentrations ($>10^5$ L^{-1}) in Cape Cod Bay (cf. Kelly et $al.$, 1993c). On average, the concentrations were higher in Cape Cod Bay than in Massachusetts Bay (cf. Tables 3-2a,b),

Chlorophyll concentrations were highest where total N (TN) concentrations were highest (Figure 6-6). For the entire study area, TN concentrations ranged from $\sim$7 to 20 μM and chlorophyll ranged from <1 to >11 μg Chl a L^{-1}. As mentioned in Section 5, there was not a strong positive and consistent correspondence between high DIN and high chlorophyll concentrations; this lack of a solid relationship is partially due to lags between nutrient transport, assimilation, and regeneration processes. On the other hand, at this time of the year most of the water column nitrogen is packaged in particulate matter (some as plankton tissue) and any available N cycles rapidly through the DIN pool into the particulate pool. A strong correspondence between particulate nitrogen and chlorophyll is expected because plankton

generally produce a constant amount of nitrogen tissue for each unit of chlorophyll. It is precisely due to this correspondence that, as has been commonly found in the study area over annual and summer time frames (Kelly, 1994), TN and chlorophyll concentrations were directly related in June 1994 (Figure 6-6).

6.3.3 Primary Production and Dark Respiration

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

Depth-integrated production rates calculated by the standard scheme for data from stations F23P and N16P averaged 1143 and 1623 mg C m^{-2} d^{-1}, respectively, for the two measurements in June. The maximum rate was calculated for station N16P on June 21 and the minimum rate was calculated for station F23P on June 22. For both stations, rates on June 22 were lower than on June 21, and this difference between days (reason unknown) is apparent in Figure 6-7.

The depth distribution of production is very different in the two environments. At station F23P, where conditions are more turbid, light is attenuated rapidly and production rates are similarly attenuated in the top 10 m. The average photic-zone chlorophyll concentration was higher at station F23P (3.2 and 3.0 μg L^{-1} on the two days) than at station N16P (1.1 and 1.4 μg L^{-1} on the two days). Accordingly, peak volumetric rates near the surface were higher each day at station F23P. However, the photic zone extended deeper than 25 m at station N16P (profiles in Figure 6-7 extend to the 0.5% isolume). At station N16P, substantial production was calculated to >20 m on June 21; on both days, rates in the upper water column were fairly uniform and only gradually decreased with depth, a sharp contrast to profiles at station F23P. Thus, while peak rates were higher at station F23P, integrated rates were roughly equivalent in the

low-turbidity, low-chlorophyll water about 15-20 km offshore. These results reinforce the concept that integrated production rates are, in part, a balance between biomass (chlorophyll) and light availability (e.g., Cole and Cloern, 1987) and that similar rates can be obtained at locations with different chlorophyll concentrations.

Patterns of dark respiration rates suggested that surface layer (volumetric) rates were lower offshore, corresponding to the observed gradient of decreasing chlorophyll and in correspondence with the pattern of volumetric production rates (Figure 6-7). Moreover, dark respiration rates appeared to decline with depth, probably a consequence of both organic matter concentrations and temperature. Respiration estimates for the colder environments of mid-depth and bottom water were approximately 0.004 to 0.006 mg O_2 L^{-1} hr^{-1} and these were similar to rates obtained in April at fairly similar temperatures. Converted to carbon, assuming a respiratory quotient (RQ = CO_2/O_2 atoms) of 1.0, implies a consumption of 1.5-2.2 μg C L^{-1} h^{-1}. Note that this rate is comparable to net production rates in the lower portion of the photic zone (Figure 6-7). In contrast, implied dark respiration in warmer, more organic-rich, near-surface water typical of the nearfield region was approximately 0.02 mg O_2 L^{-1} hr^{-1} or about 7.5 μg C L^{-1} h^{-1}

Assuming that a respiration rate of 1.8 μg C L^{-1} h^{-1} applies to a cool 15-m bottom layer that is heterotrophic throughout the day, then integrated subpycnocline respiration would be 27 mg C m^{-2} h^{-1}. For this deep dark layer, the respiration rate would apply over 24 hours, resulting in a daily rate of 648 mg C m^{-2} d^{-1}. Assuming that an average respiration of 7.5 μg C L^{-1} h^{-1} applies to the top 10 m in the nearfield, then integrated surface layer/pycnocline respiration would be 75 mg C m^{-2} h^{-1}. In calculating a daily rate for comparison to production, this respiration rate should be applied over a 12-h dark period because respiration has been implicitly included in the net production estimate made during the light. Surface-layer respiration in the dark then is calculated as 900 mg C m^{-2} d^{-1}. An additional assumption is that, over the day, the production/respiration processes in the 10-m mid-water layer are approximately balanced. In total, the sum of surface and bottom respiration estimates throughout the day in a hypothetical nearfield region suggests that respiration amounts to ~1548 mg C m^{-2} d^{-1}. This sum compares favorably to an average net production of 1623 mg C m^{-2} d^{-1} measured at nearfield station N16P.

This simplistic analysis, intended only as a guide, has used approximations and rough averages to make calculations that are extremely sensitive to assumptions; the analysis itself illustrates the complexity of comparing monitoring data on short-term autotrophic and heterotrophic rates in a vertically integrated fashion. Heuristically, the calculation suggests the following interesting conclusions:

- The incubation estimates for production and respiration rates appear reasonable when compared against each other.

- An approximate daily balance between production and respiration processes may occur over the whole water column.

- However, over a day, net autotrophy occurs in a surface layer that is distinct from a heterotrophic bottom-water (as would be expected at this time of year, see Kelly and Turner, 1995)

- Notably, integrated dark respiration in a shallow warm surface layer may exceed that in a thicker layer of colder water found at depth, even if the net change over time in bottom water is a DO concentration decrease and the net change in surface-water is a DO concentration increase.

6.3.4 Special Features: Comparison of 1994 with Previous Years

Temporal trends for chlorophyll in nearfield surface waters during 1993 and early 1994 are shown in Figure 6-8. Water depths to 20 m are included. The data thus characterize a layer that reaches into the pycnocline and to the depth of the subsurface chlorophyll maximum noted in vertical profiles. With specific regard to the June and July periods, the two years have similar maximum/minimum ranges and survey-to-survey averages for surface layer chlorophyll concentrations. The only subtle difference appears to be that in 1994 the range appears to be expanding. In 1993, the range and maximum concentrations in the nearfield were observed in June rather than in July and a progressive expansion of the maximum and average chlorophyll concentrations did not begin until late summer.

6-10

6.4 Summary and Recommendations

During each of the last three years, principal patterns have been noted and a number of these patterns, that have become expected, have been repeated in the first half of 1994, as documented in this report. These patterns include concentration gradients, seasonal stratification, Bay-to-Bay variations in timing and intensity of biological events, and range of nutrient concentrations. Each year there are also a few features that reveal how the unfolding of ecological events is peculiar to that year and some of these have also been alluded to in this report. To date, the interannual comparisons (also Kelly and Turner, 1995) emphasize the fundamental regularity of seasonal events and relative constancy of overall water quality conditions over yearly periods in Massachusetts Bay and Cape Cod Bay.

Significant ecological distinctions that last beyond one or two surveys obviously are recognizable only in the context of time series and geographical comparisons over seasonal and annual time frames. As data for the last half of the 1994 sampling year become available and are summarized in annual reports, interannual similarities and differences during this baseline period of MWRA monitoring will be further evaluated. Such evaluation is critical to developing an efficient and effective post-discharge monitoring program for the future outfall in western Massachusetts Bay.

Table 6-1. Abundance of top five dominant phytoplankton taxa in samples collected near the surface at station N10P in June and July 1994.

|	N10P June 21	N10P June 24	N10P July 07	N10P July 27
CHAETOCEROS COMPRESSUS	0.277 (2)	0.164 (3)		
CHAETOCEROS SPP.(<10UM)	0.080 (5)	0.035 (5)	0.034 (5)	0.031 (5)
CRYPTOMONADS	0.259 (3)	0.149 (4)	0.195 (2)	0.329 (2)
CYLINDROTHECA CLOSTERIUM				0.066 (4)
MICROFLAGELLATES	0.634 (1)	0.779 (1)	0.684 (1)	0.708 (1)
RHIZOSOLENIA DELICATULA			0.038 (4)	
SKELETONEMA COSTATUM	0.175 (4)	0.260 (2)	0.157 (3)	0.112 (3)

Units are millions of cells/L and rankings are given in parentheses.

Table 6-2. Abundance of all identified taxa in screened (20um) samples collected near the surface at station N10P in June and July 1994.

	N10P Jun. 21	N10P Jun. 24	N10P Jul. 07	N10P Jul. 27
ALORICATE CILIATES	33	23	90	
CERATIUM FUSUS			3	3
CERATIUM LINEATUM	3			
CERATIUM LONGIPES	23	3	270	65
CERATIUM TRIPOS				8
DICTYOCHA FIBULA			3	
DICTYOCHA SPECULUM	3	5	18	
DINOPHYSIS ACUMINATA		5		
DINOPHYSIS NORVEGICA	718	393	571	3
DINOPHYSIS OVUM	10	18		
DIPLOPSALIS SPP.		3	3	
EBRIA TRIPARTITIA			3	
EUTREPTIA/EUTREPTIELLA SPP.				3
GYRODINIUM SPIRALE	3			
GYRODINIUM SPP.			3	
MESODINIUM RUBRUM	13	10		
PROTOPERIDINIUM BREVE	15	25		
PROTOPERIDINIUM DEPRESSUM	8	8	95	5
PROTOPERIDINIUM SPP.	140	53	18	8
TINTINNIDS	110	58	88	23
UNID. ATHECATE DINOFLAGELLATE				10
UNID. THECATE DINOFLAGELLATES		3		

Units are cells L -1

1993, Nearfield Stations
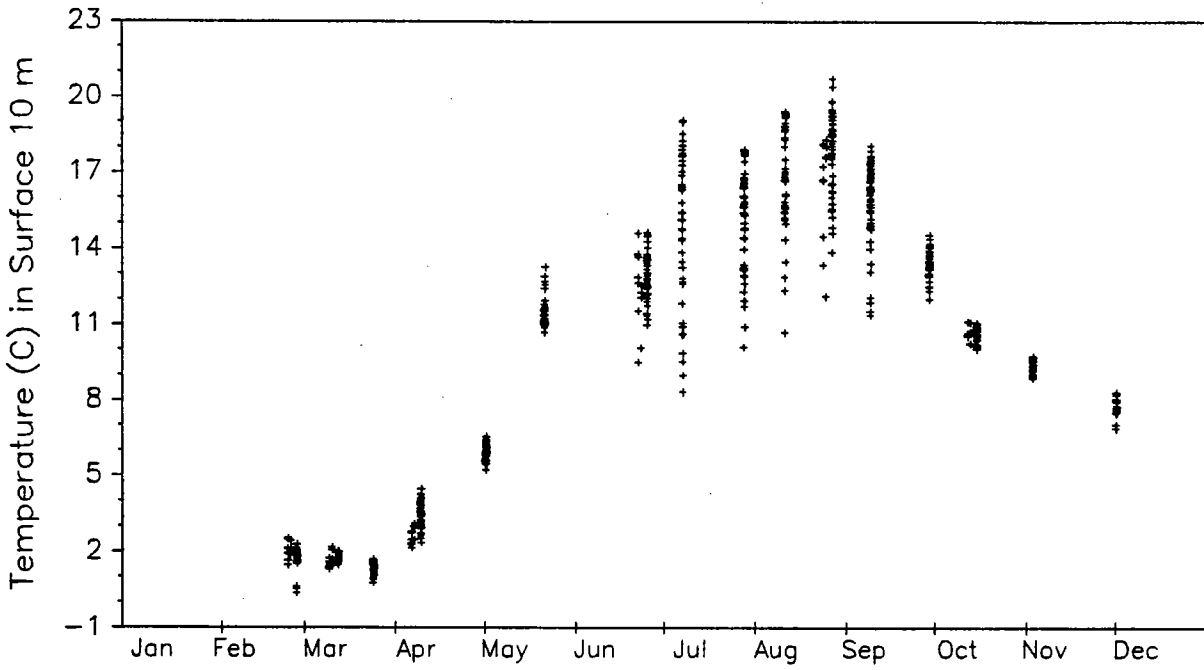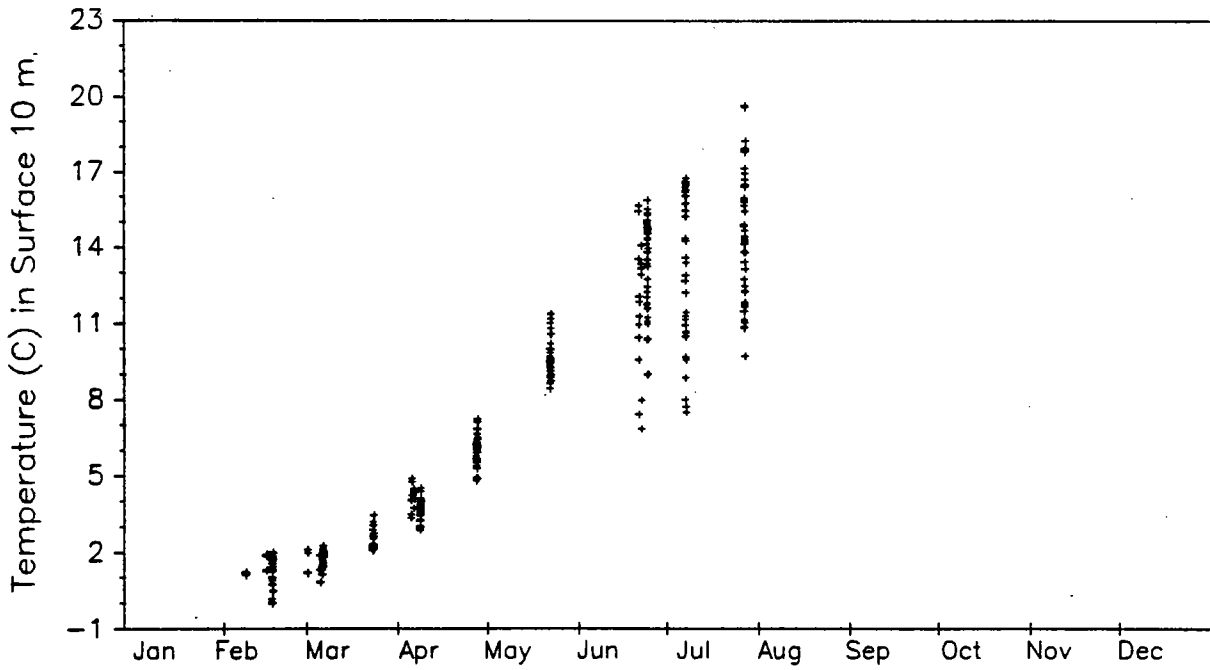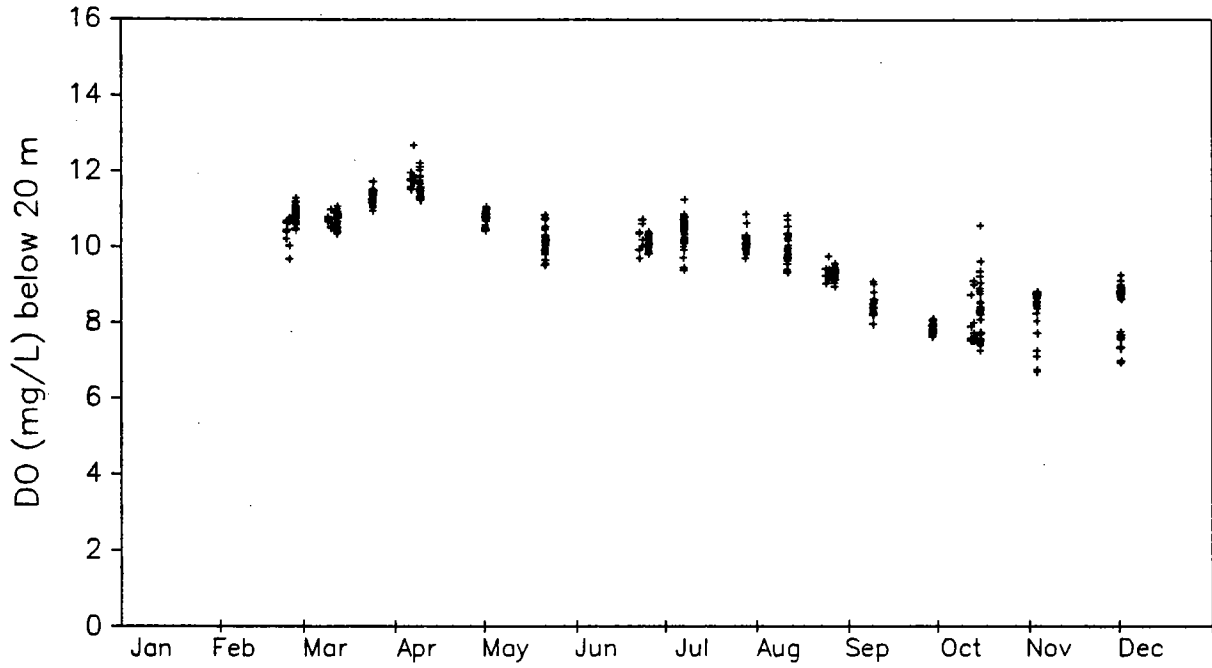

1994, Nearfield Stations

Figure 6-1. Comparison of the nearfield region in 1994 to the annual cycle of 1993: temperature (°C).

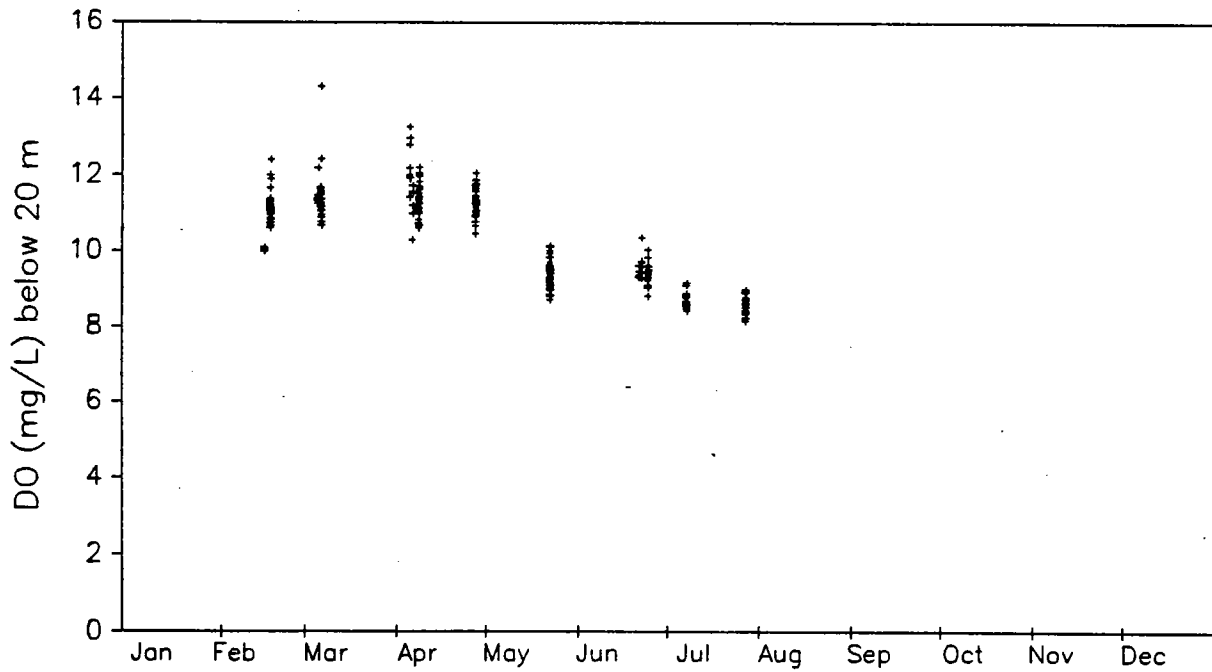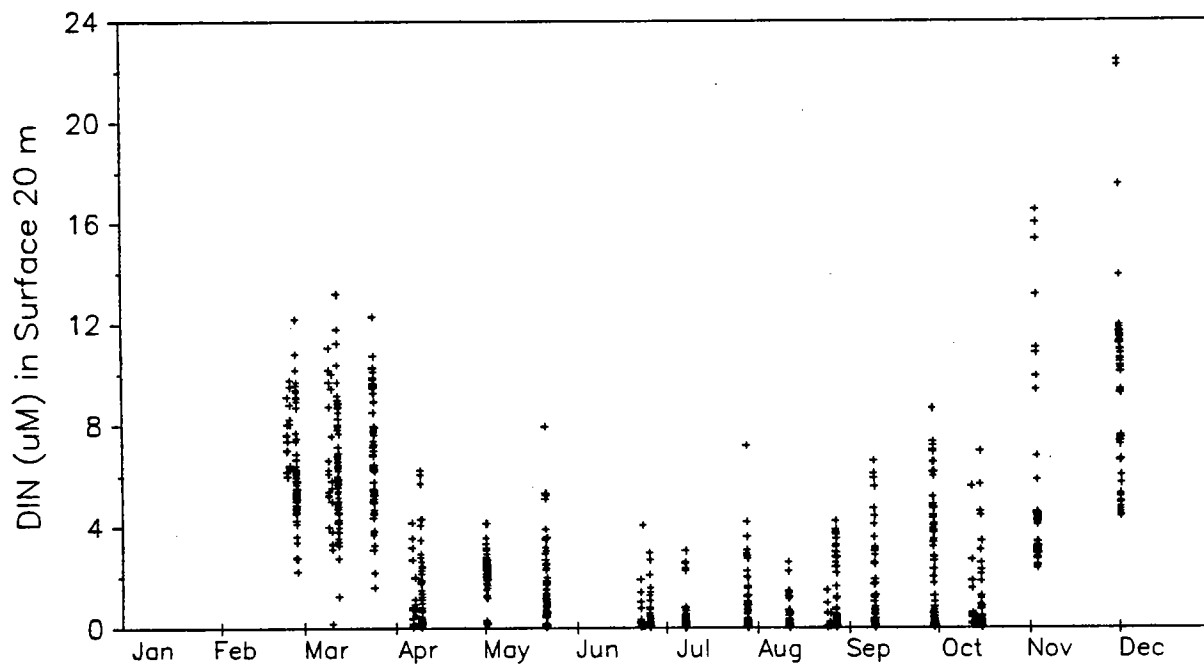## 1993, Nearfield Stations

1994, Nearfield Stations

Figure 6-2. Comparison of the nearfield region in 1994 to the annual cycle of 1993: dissolved oxygen (mg L^{-1}).

1993, Nearfield Stations
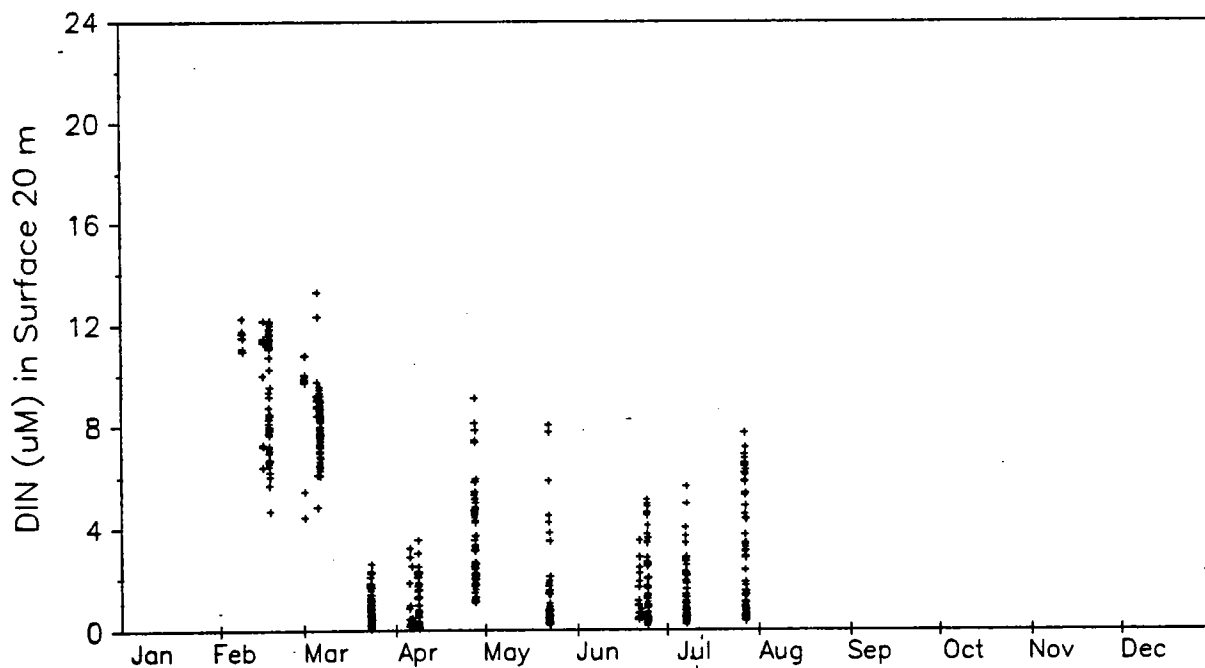
1994, Nearfield Stations

Figure 6-3. Comparison of the nearfield region in 1994 to the annual cycle of 1993: dissolved inorganic nitrogen (μM).
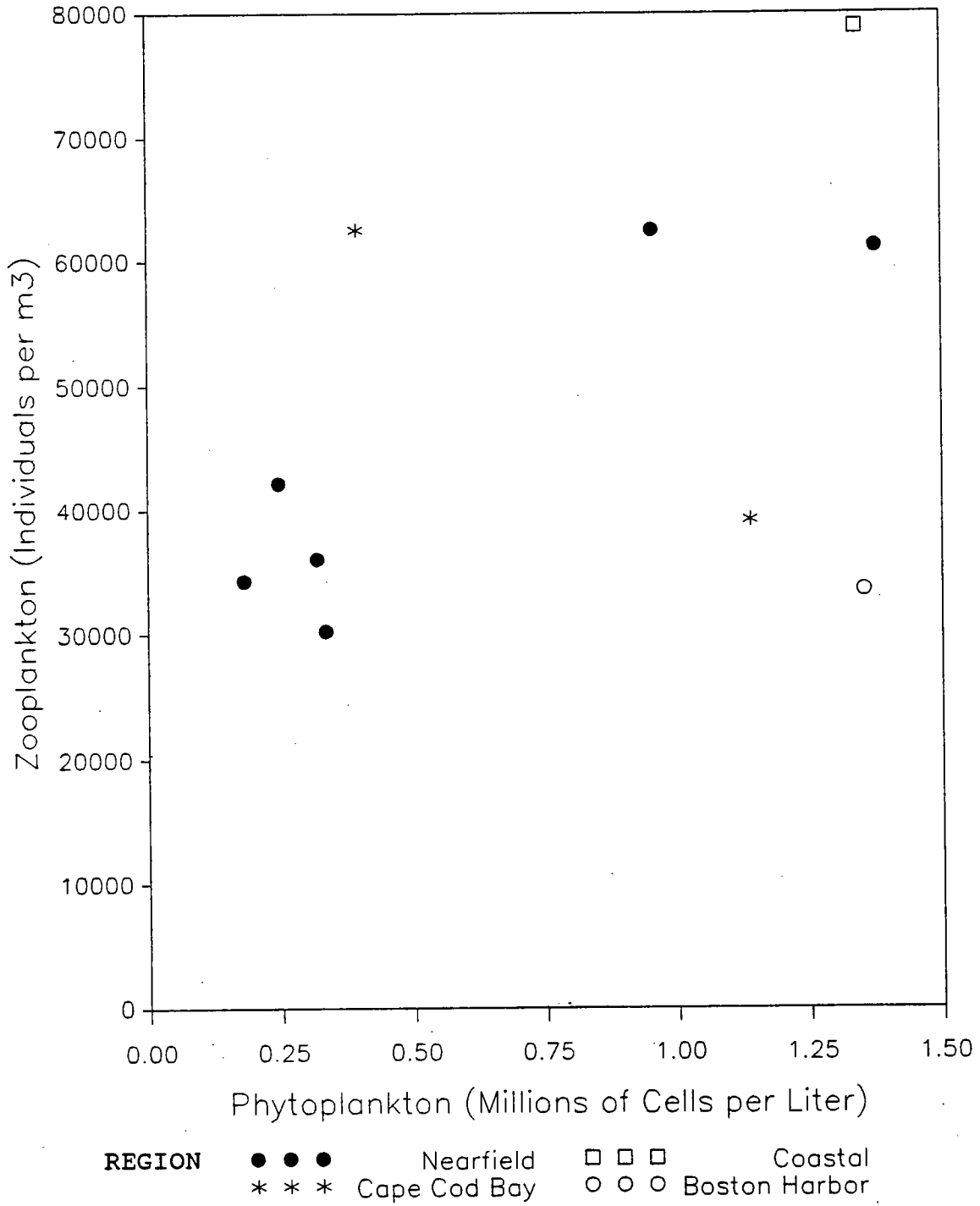
June (W9407)

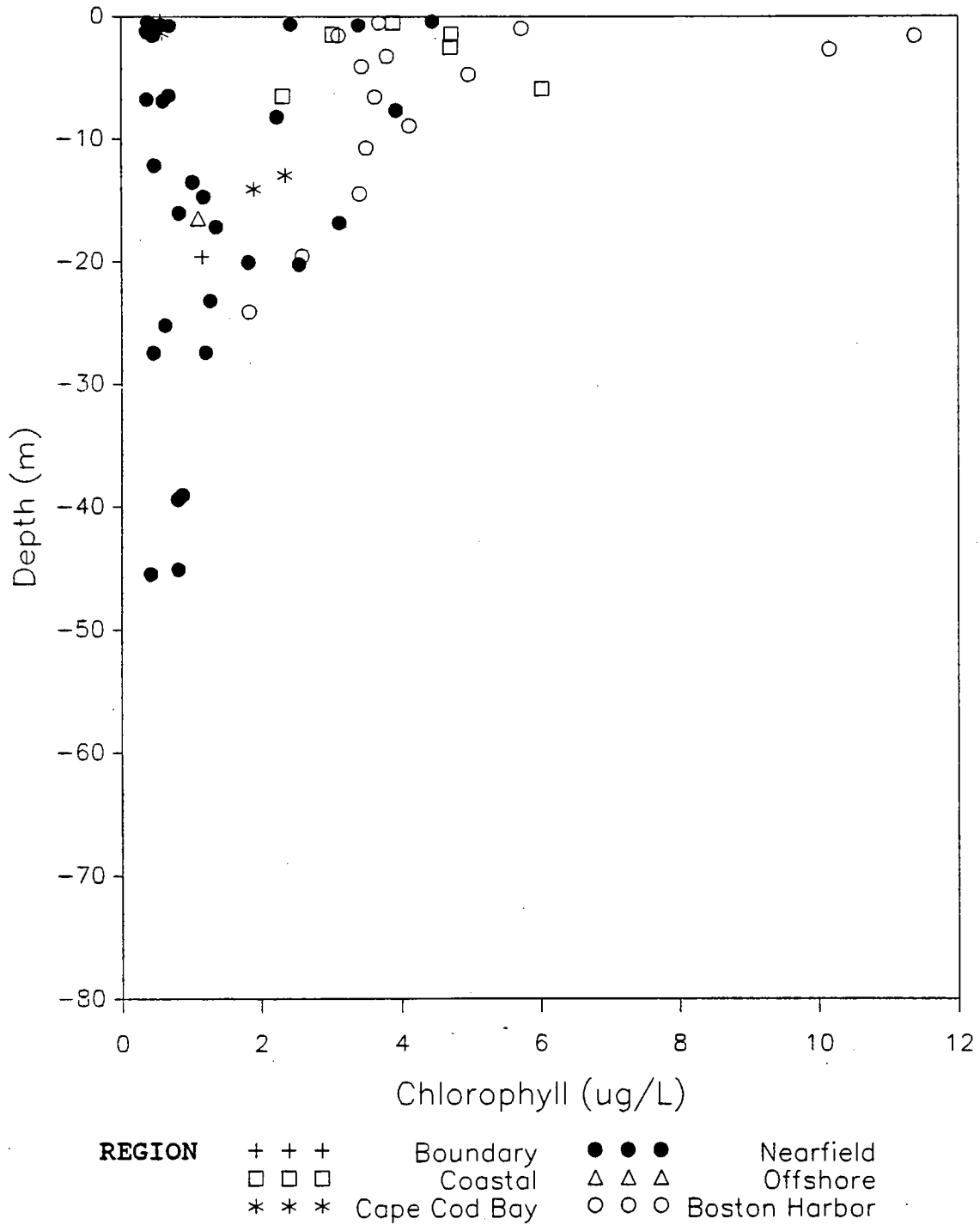**Figure 6-4.**   **Zooplankton abundance vs. phytoplankton abundance for June 1994.**

Figure 6-5.   Chlorophyll (extracted) vs. depth for the study area in June 1994.

June (W9407)

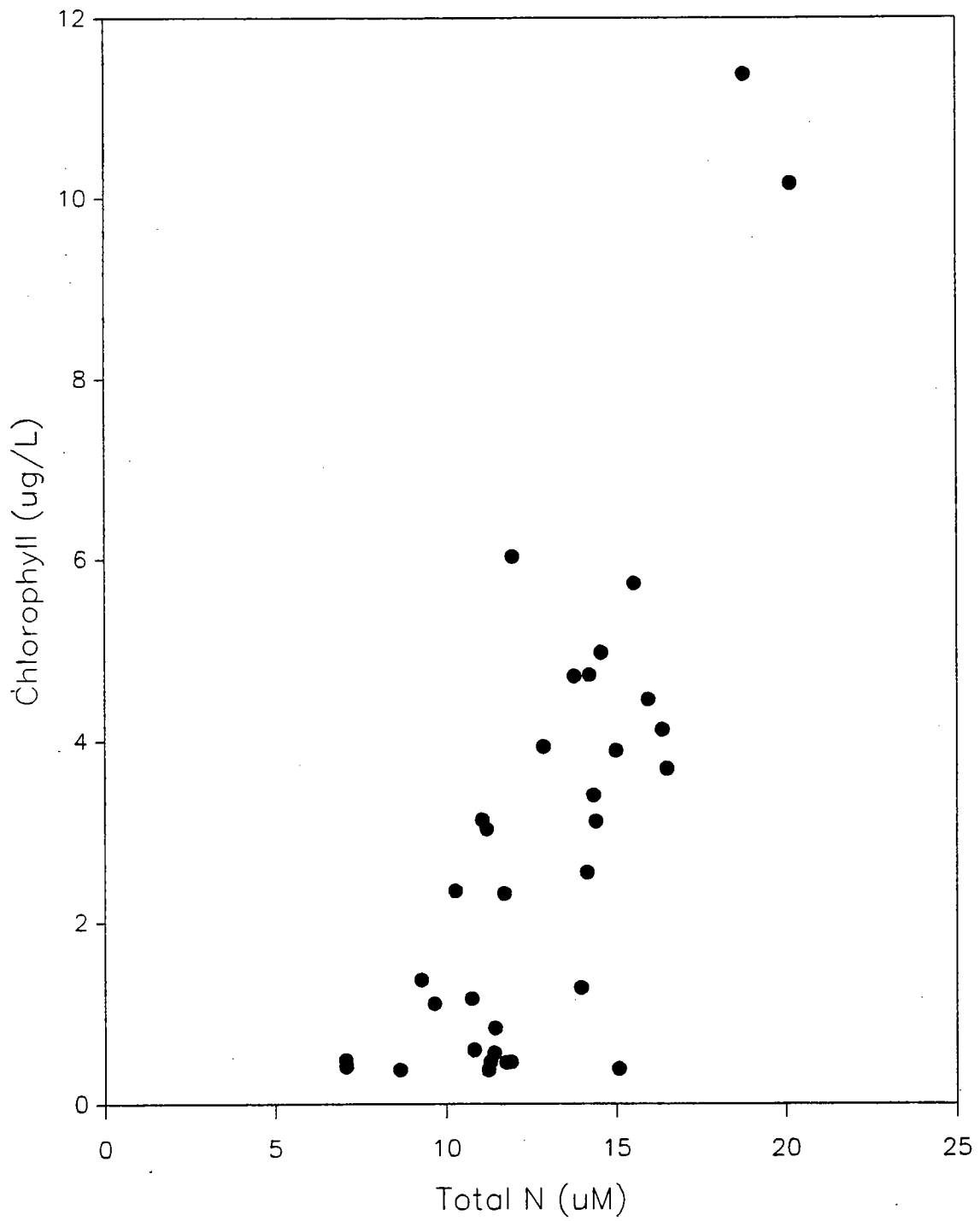**Figure 6-6 Chlorophyll (extracted) vs. total nitrogen concentrations for the study area in June 1994.**
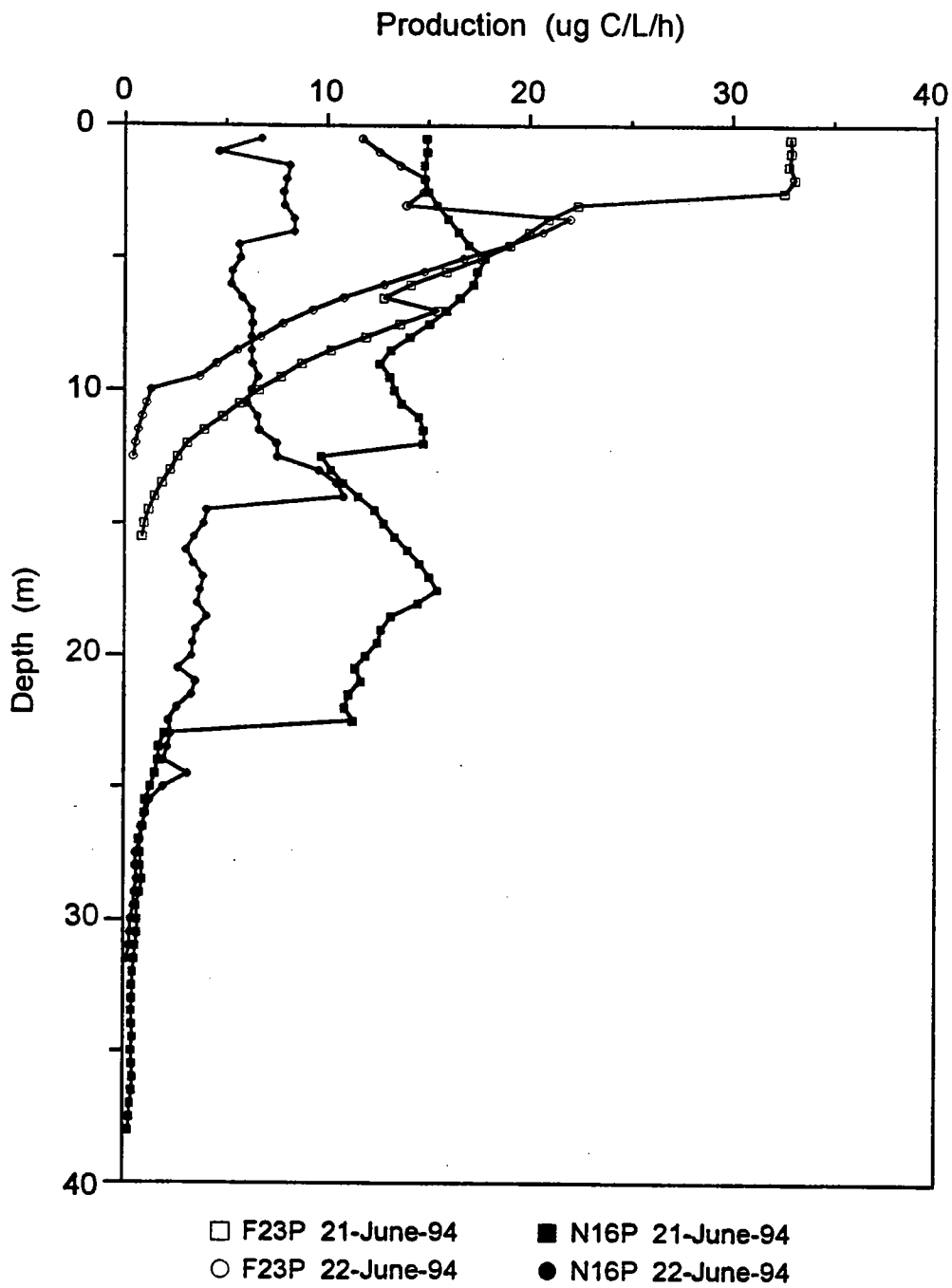
Production (ug C/L/h)

□ F23P 21-June-94   ■ N16P 21-June-94
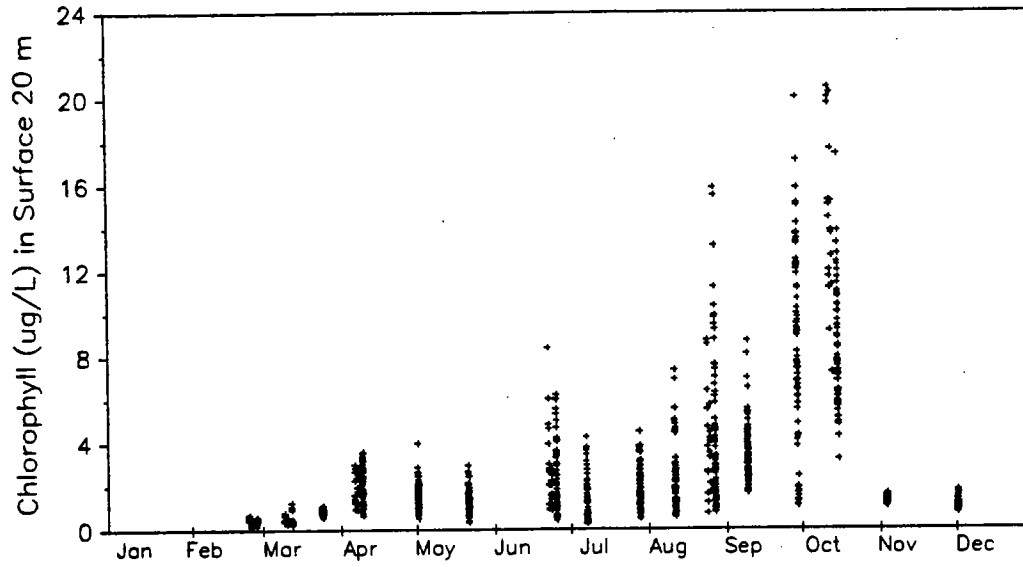O F23P 22-June-94   ● N16P 22-June-94

Figure 6-7. ^{14}C production vs. depth at BioProductivity stations F23P and N16P in June 1994.

1993, Nearfield Stations

1994, Nearfield Stations

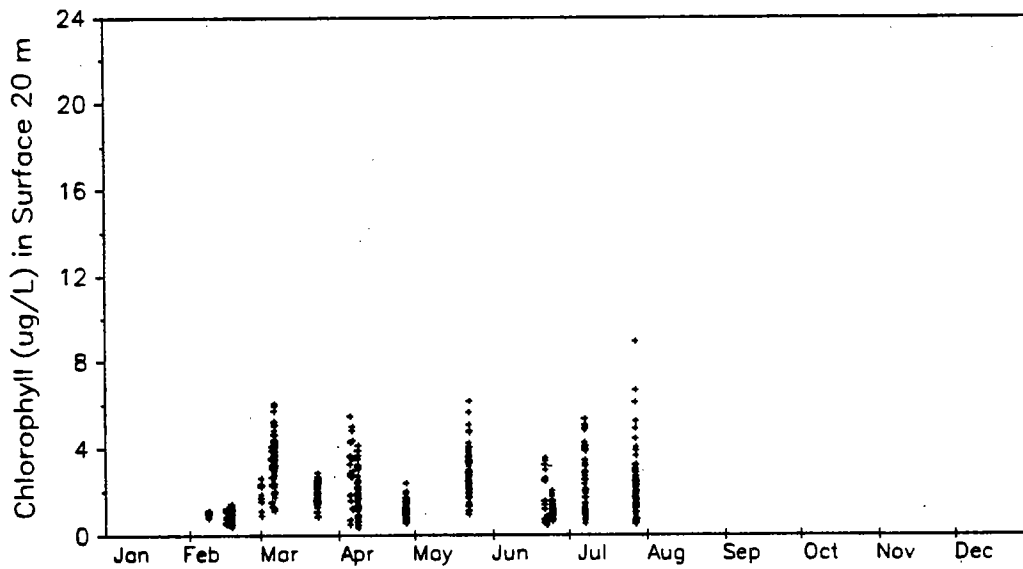**Figure 6-8.** Comparison of the nearfield region in 1993 to the annual cycle of 1994: chlorophyll (μg L^{-1}) as estimated from *in situ* fluorescence.

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