

**COMBINED WORK/QUALITY ASSURANCE PROJECT PLAN
(CW/QAPP)**

for

WATER QUALITY MONITORING: 1995-1997

**Task 9-11, 14 and 15
MWRA Harbor and Outfall Monitoring Project**

submitted to

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1.0 PROJECT NAME

MWRA Harbor and Outfall Monitoring Project
Tasks 9-11, 14 and 15
Baseline Water Quality Monitoring of Massachusetts Bay

2.0 PROJECT REQUESTED BY

Massachusetts Water Resources Authority, Environmental Quality Department

3.0 DATE OF REQUEST

November 2, 1994

4.0 DATE OF PROJECT INITIATION

November 9, 1994

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7.0 PROJECT DESCRIPTION

7.1 Objective and Scope

The overall objective of the water quality monitoring program is to detect, through sample collection and direct measurements, changes in the physical water properties, nutrient concentrations, dissolved oxygen (DO), phytoplankton biomass (chlorophyll, *in situ* fluorescence), and phytoplankton and zooplankton community composition in Massachusetts Bay and Cape Cod Bay.

Several types of surveys will be implemented in order to monitor water properties, nutrient concentrations and other important parameters of eutrophication, and to gain a better understanding of the physical processes which will affect the future outfall plume. Eleven nearfield, six combined nearfield/farfield water quality surveys of Massachusetts Bay, and three plume tracking surveys will be conducted during each year (1995, 1996 and 1997) of this project. Four additional plume tracking surveys will be performed near outfall commissioning.

This Combined Work/Quality Assurance Project Plan (CW/QAPP) describes the sampling and analysis activities associated with the water quality and plume tracking surveys that will be conducted under Tasks 9-11, 14, and 15 of MWRA contract S186. This document is based, in large part, on the CW/QAPP produced previously under an earlier contract between MWRA and Battelle Ocean Sciences (Albro, *et al.* 1993). Two other tasks that will be performed as part of MWRA contract S186 (Task 12 - Continuous Monitoring, Task 13 - Synoptic Overview) are considered to be part of the water quality project area. A description of scope of work, objectives, and procedures for these two tasks can be found in separate documents. Data quality requirements and assessments, project management (organization and responsibilities of ENSR staff and subcontractors), and a schedule of activities and deliverables associated with the water quality surveys are also described in this CW/QAPP. Specific objectives for each of the five tasks included in this CW/QAPP are described below.

7.1.1 Nearfield Surveys (Task 9)

The primary objective of these surveys is to provide a three-dimensional picture of seasonal variability of water column properties in the nearfield. Secondary objectives include the determination of the DO status in Stellwagen Basin before autumnal overturn, and the maximum winter concentration of dissolved inorganic nitrogen in Massachusetts Bay.

7.1.2 Farfield Surveys (Task 10)

There are three objectives of the Task 10 surveys:

- 1) to determine conditions in the water column throughout Massachusetts and Cape Cod Bays, including factors affecting the seasonal pattern of plankton abundance and species composition, and the seasonal decline of DO in Massachusetts Bay;
- 2) to determine the broad-scale interaction of water of Boston Harbor and the Gulf of Maine with Massachusetts Bay; and
- 3) to compare water quality of Massachusetts and Cape Cod Bays.

7.1.3 Plume Tracking Surveys (Task 11)

The three objectives of the Plume Tracking Surveys are:

- 1) to track the location, mixing, and nutrient transformations of the future outfall plume;
- 2) to map the pattern of water properties between Boston Harbor and Massachusetts Bay at a horizontal spatial scale (hundreds of meters) appropriate for understanding tidal dynamics and other interactions; and
- 3) to map fronts and gradients in other areas of the Bay where important nutrient-related processes and transformations occur on a scale of hundreds of meters.

Intensive vertical profiling in areas of particular interest, as determined by the results of modeling and the nearfield and farfield surveys, will produce detailed three-dimensional maps of the water column structure and nutrient distribution. Before the outfall is on line, these surveys will identify fronts and gradients associated with tidal, seasonal and meteorological phenomena. After the outfall is on line, these and additional surveys will determine the extent of the plume, identify fronts and gradients, and characterize the effects of these fronts on the plume.

7.1.4 Water Chemistry and Metabolism (Task 14)

The objective of Task 14 is to determine levels of nutrients, chlorophyll, suspended solids, DO, respiration, and phytoplankton productivity by collecting and analyzing water samples.

7.1.5 Plankton Taxonomy (Task 15)

The objective of Task 15 is to analyze water samples (collected as part of Tasks 9 and 10) to determine phytoplankton and zooplankton community composition. The phytoplankton and zooplankton communities form the basis of the marine food web. Subtle changes in community composition, potentially leading to alterations in higher trophic levels, can arise from both inhibitory effects due to toxicity and from stimulatory effects from nutrient enrichment. Monitoring for potential change in the structure of these communities is fundamental to the demonstration of anticipated improvements in Harbor water quality and the assessment of potential impacts from the relocated outfall.

7.2 Data Usage

The Massachusetts Water Resources Authority (MWRA) is implementing a long-term monitoring plan (MWRA, 1991) for the MWRA effluent outfall that will be located in Massachusetts Bay (see Figure 1). A principal concern with the offshore outfall discharge is nutrients and their resultant eutrophication effects on the water column. Three specific effects are of paramount concern: (1) lowered DO concentrations (hypoxia/anoxia), (2) stimulation of nuisance/noxious algal populations, and (3) alteration of the pelagic food web. Water quality monitoring centers on measurements keyed to these three principal ecological effects. Measurements include phytoplankton biomass (chlorophyll, *in situ* fluorescence) and pelagic metabolism (respiration, production), because these measures are useful predictors of DO concentration - the environmental effect that is also measured directly. Phytoplankton species identification and enumeration is a second indicator measure that is, like DO concentration, the effect of concern.

Monitoring also includes measurements of other physical and chemical properties; for example, temperature, salinity, and turbidity can help distinguish water masses and are fundamental background data for interpreting biological fluctuations. Physical features such as thermal stratification will strongly influence the expression of nutrient enrichment effects. Measured nutrient concentrations (particulate and dissolved forms) serve several purposes: to aid water mass analyses, to assess biological variability in light of nutrient variability, and ultimately, to link cause (nutrient loading) and effect. Finally, the zooplankton community will be measured to monitor the pelagic food web and to provide explanatory variables for phytoplankton changes (zooplankton as well as physical and chemical factors may influence

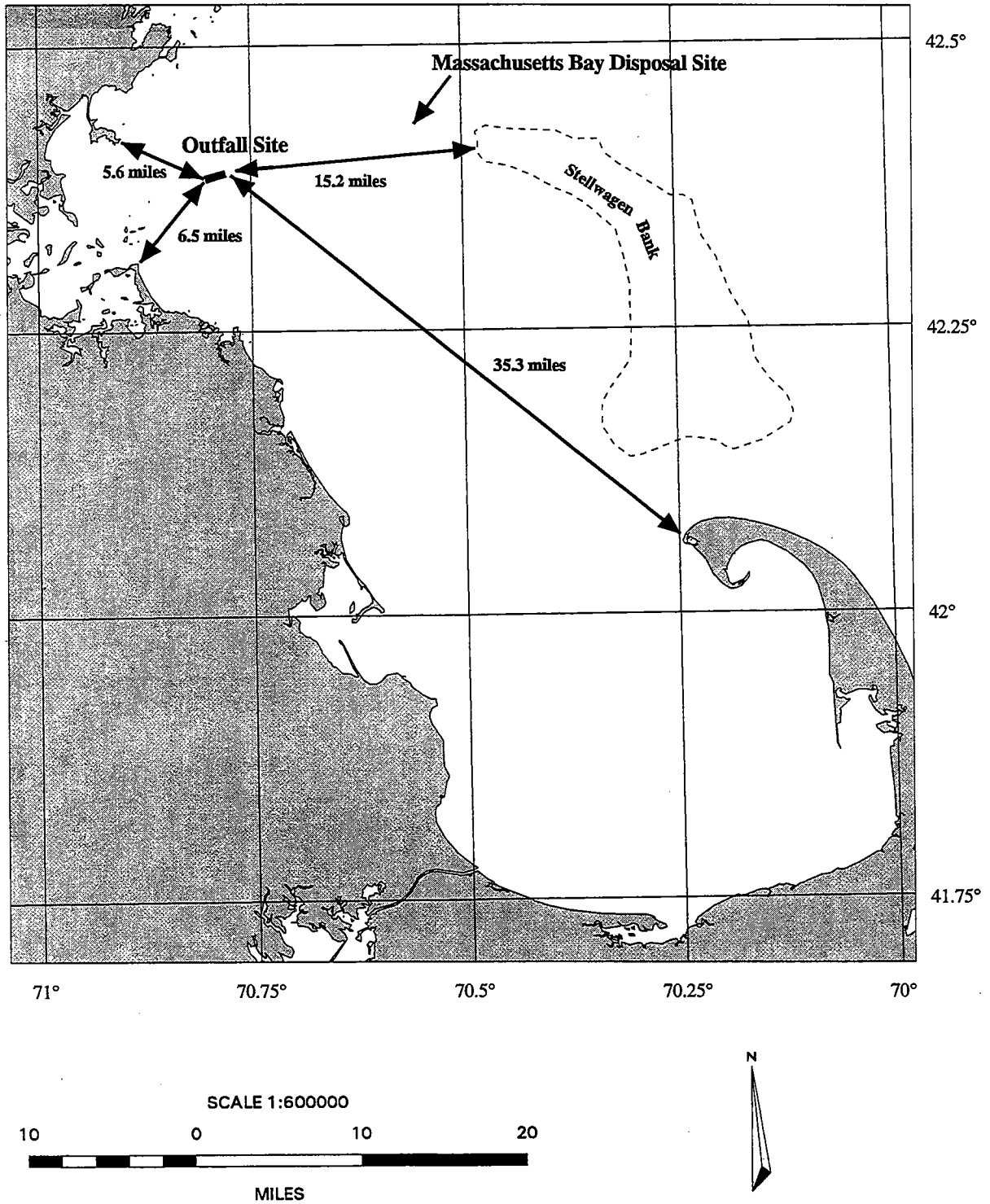


FIGURE 1
Location of MWRA Effluent Outfall in Massachusetts Bay

phytoplankton community dynamics). The goals of this monitoring program are to gather baseline data, assess potential environmental impact of effluent discharge into Massachusetts Bay, and evaluate compliance with the discharge permit.

The data obtained from the water quality surveys, laboratory analyses, continuous monitoring and synoptic imagery will be used to identify changes in water properties in both the nearfield and farfield monitoring regions of Massachusetts and Cape Cod Bays. The water quality surveys will generate both *in situ* hydrographic data and samples for various laboratory measurements. *In situ* hydrographic measurements (i.e., temperature, conductivity, depth, DO, chlorophyll fluorescence, optical beam transmittance, and light irradiance) will be used to provide seasonal characterization of changes in the water column. Laboratory data for nutrient concentrations, plankton biomass and productivity, and phytoplankton composition and abundance will be used to evaluate any changes potentially resulting from the proposed outfall. The moored sensor package will provide high temporal resolution measurements of water column properties in the near-field, while satellite images will provide high resolution synoptic coverage of water column properties over the far-field range. Figure 2 illustrates how the data from these surveys is processed to allow entry into the MWRA Environmental Monitoring and Management System (EM&MS) and to provide information to the public.

7.3 Technical Approach

7.3.1 Field Surveys Program

Sampling will be conducted 17 times per year in 1995, 1996 and 1997, with the most frequent sampling occurring between the middle of June and the middle of October. Six of the 17 one-day nearfield surveys will be combined with the three-day farfield surveys. During the combined surveys, farfield operations will be conducted prior to the nearfield operations to optimize mobilization of the respiration/productivity equipment, and ensure that farfield operations are conducted as soon as good weather permits.

Hydrographic data will be collected at 46 selected stations (21 nearfield, 26 farfield, one overlapping; Table 1). At each of the designated stations, a hydrocast will be conducted with an underwater unit consisting of a Seabird SBE-911 plus CTD system, various sensors, and a SBE 32 Carousel water sampling system with up to ten Niskin bottles.

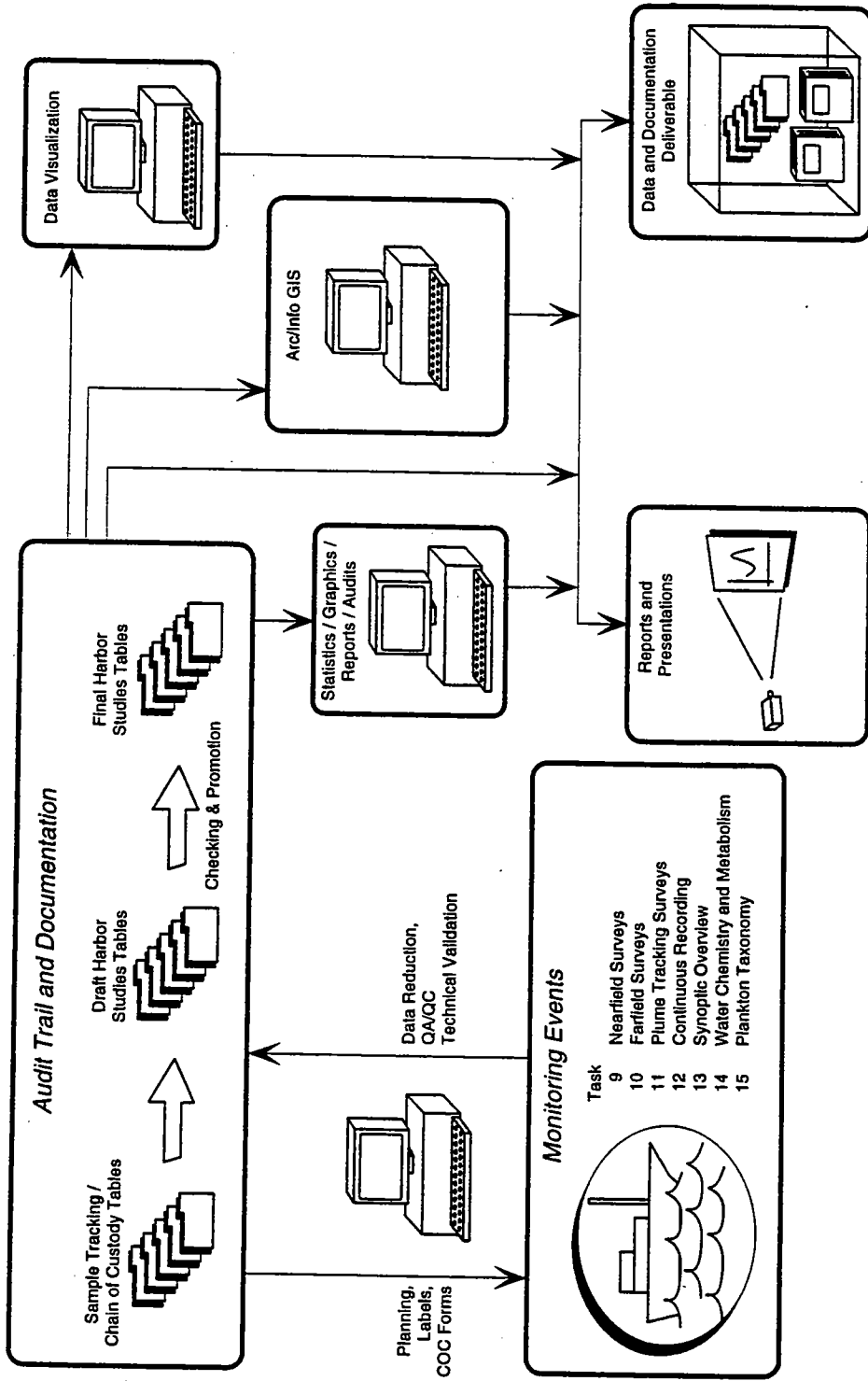


FIGURE 2
 Overview of Data Management Strategy for the Boston Harbor and Outfall Monitoring Project

TABLE 1

Water Column Sampling Stations

Station	Latitude	Longitude	Depth (m)
F01	41°51.05'N	70°27.20'W	27
F02	41°54.49'N	70°13.70'W	33
F03	41°57.00'N	70°32.90'W	17
F05	42°08.32'N	70°39.00'W	18
F06	42°10.24'N	70°34.60'W	35
F07	42°11.81'N	70°30.95'W	54
F10	42°14.54'N	70°38.24'W	30
F12	42°19.80'N	70°25.40'W	90
F13	42°16.10'N	70°44.10'W	25
F14	42°18.00'N	70°48.50'W	20
F15	42°18.93'N	70°43.66'W	39
F16	42°19.84'N	70°38.97'W	60
F17	42°20.75'N	70°34.23'W	78
F18	42°26.53'N	70°53.30'W	24
F19	42°24.90'N	70°38.20'W	81
F22	42°28.79'N	70°37.06'W	80
F23	42°20.35'N	70°56.52'W	25
F24	42°22.50'N	70°53.75'W	20
F25	42°19.30'N	70°52.58'W	15
F26	42°36.10'N	70°33.90'W	56
F27	42°33.00'N	70°26.84'W	108
F28	42°24.60'N	70°26.00'W	33
F29	42°07.00'N	70°17.40'W	66
F30	42°20.48'N	71°00.45'W	15
F31	42°18.38'N	70°56.40'W	15

TABLE 1 (Cont'd)

Water Column Sampling Stations

Station	Latitude	Longitude	Depth (m)
N01	42°25.16'N	70°51.87'W	30
N02	42°25.65'N	70°49.31'W	40
N03	42°26.14'N	70°46.75'W	44
N04	42°26.63'N	70°44.19'W	50
N05	42°24.88'N	70°43.58'W	55
N06	42°23.13'N	70°42.97'W	52
N07	42°21.38'N	70°42.37'W	52
N08	42°20.88'N	70°44.93'W	35
N09	42°20.39'N	70°47.48'W	32
N10	42°19.89'N	70°50.04'W	25
N11	42°21.65'N	70°50.65'W	32
N12	42°23.40'N	70°51.26'W	26
N13	42°24.21'N	70°49.49'W	32
N14	42°24.58'N	70°47.57'W	34
N15	42°24.95'N	70°45.65'W	42
N16	42°23.64'N	70°45.20'W	40
N17	42°22.32'N	70°44.74'W	36
N18	42°21.95'N	70°46.66'W	30
N19	42°21.58'N	70°48.58'W	24
N20	42°22.90'N	70°49.03'W	32
N21	42°23.27'N	70°47.12'W	34

During the downcast, the following measurements will be made using the underwater unit:

- Conductivity
- Temperature
- Depth of sensors/water sample
- Dissolved oxygen
- Chlorophyll fluorescence
- Optical beam transmittance
- Light irradiance (PAR)
- Altitude of the sensors above the sea floor

Salinity and sigma-t will be calculated from the conductivity, temperature and depth data. The downcasts will be conducted from the near-surface to within approximately 3-5 m of the sea floor. Total incident photosynthetically available radiation (SPAR), navigational position, and time will be recorded concurrently with the hydrocast measurements.

During the upcast at each station, 10-L Niskin bottles will be used to collect water from 5 depths: bottom, mid-bottom, middle (chlorophyll *a* maximum for a water quality cast), mid-surface, and surface. On deck the Niskin bottles will be subsampled for dissolved inorganic nutrients and other analyses as determined by the station type.

The nearfield sampling will be completed in one day by sampling 21 stations in the vicinity of the outfall (Figure 3). Three types of stations are sampled as part of a nearfield effort: A, D, and E. The station types differ in the list of analytes. Dissolved inorganic nutrients (DINuts) will be the only sample analysis performed at 15 of the 21 stations (Type E, Figure 4). Sampling for full chemical analysis (DINuts + dissolved organic carbon (DOC), total dissolved N & P, particulate C & N, particulate P, biogenic silica, chlorophyll *a* and phaeophytin, total suspended solids (TSS), and DO) is performed at the remaining 6 stations (Types A and D, Figures 5 and 6). Plankton taxonomy and enumeration, and urea analysis is conducted at the two Type D nearfield stations. Areal primary productivity and water column respiration (P+R) are measured at two of the six complete chemical analysis stations on all nearfield surveys. These two productivity and respiration stations differ between nearfield only and nearfield/farfield combined surveys (N04 and N07 for a nearfield combined with farfield survey, N04 and N16 for a "nearfield only" survey). Tables 2 and 3 provide more detailed analysis information for the nearfield stations.

The farfield sampling will be completed in three days by sampling at 26 stations located throughout Massachusetts and Cape Cod Bays (Figure 7). Four station types with associated sample collection

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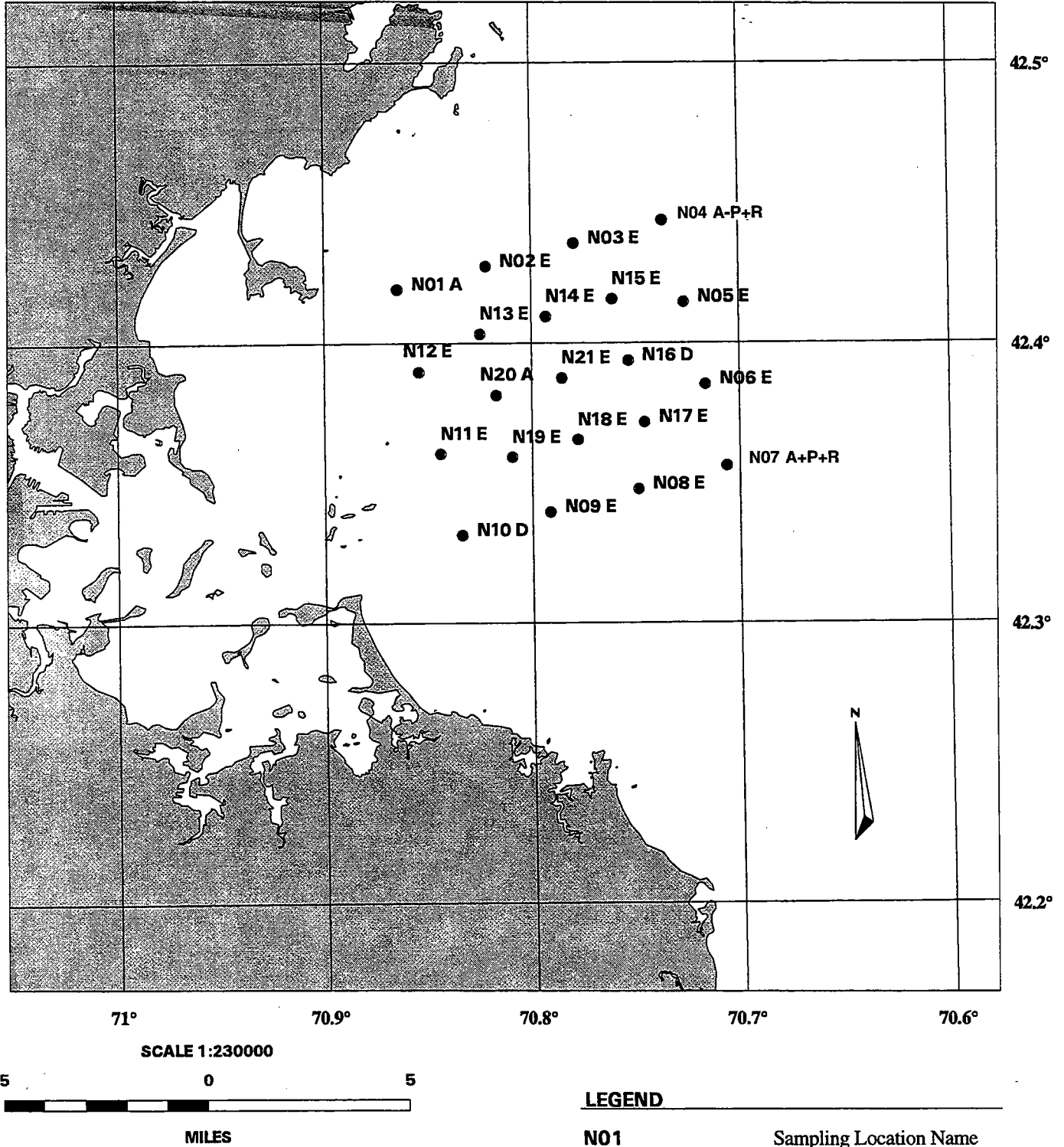


FIGURE 3
Nearfield Stations

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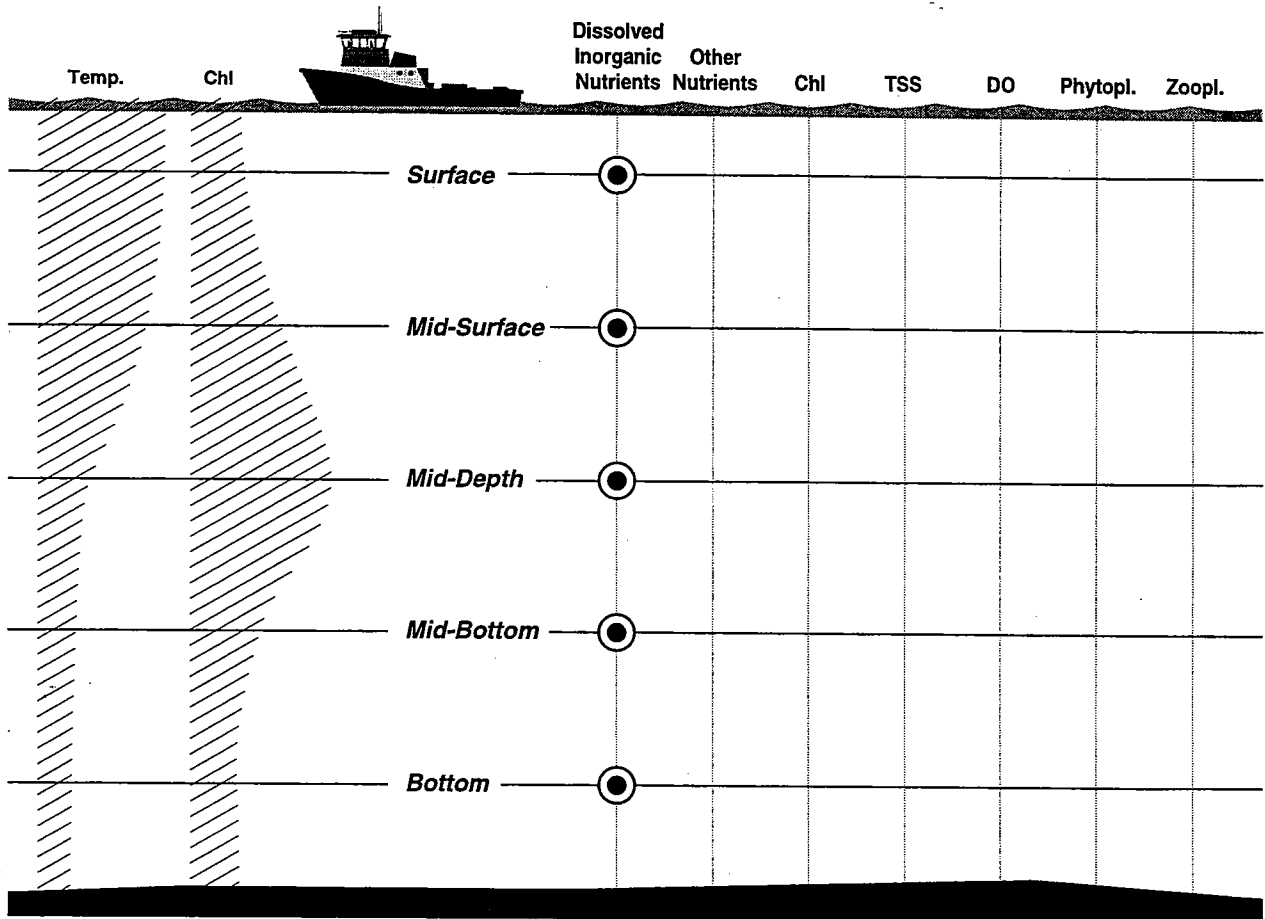


FIGURE 4
Station Type E

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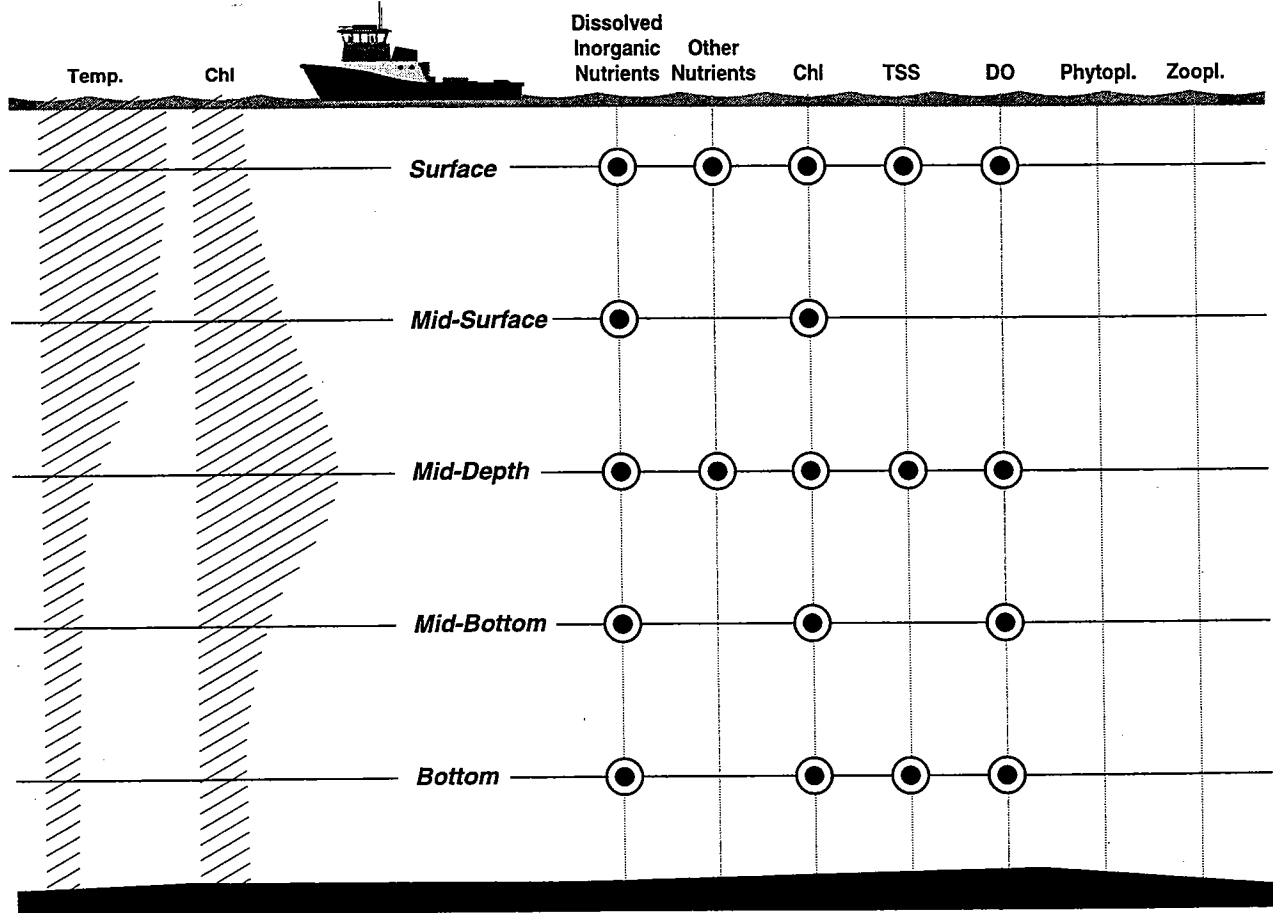


FIGURE 5
 Station Type A
 (areal productivity and respiration also measured at two of these stations)

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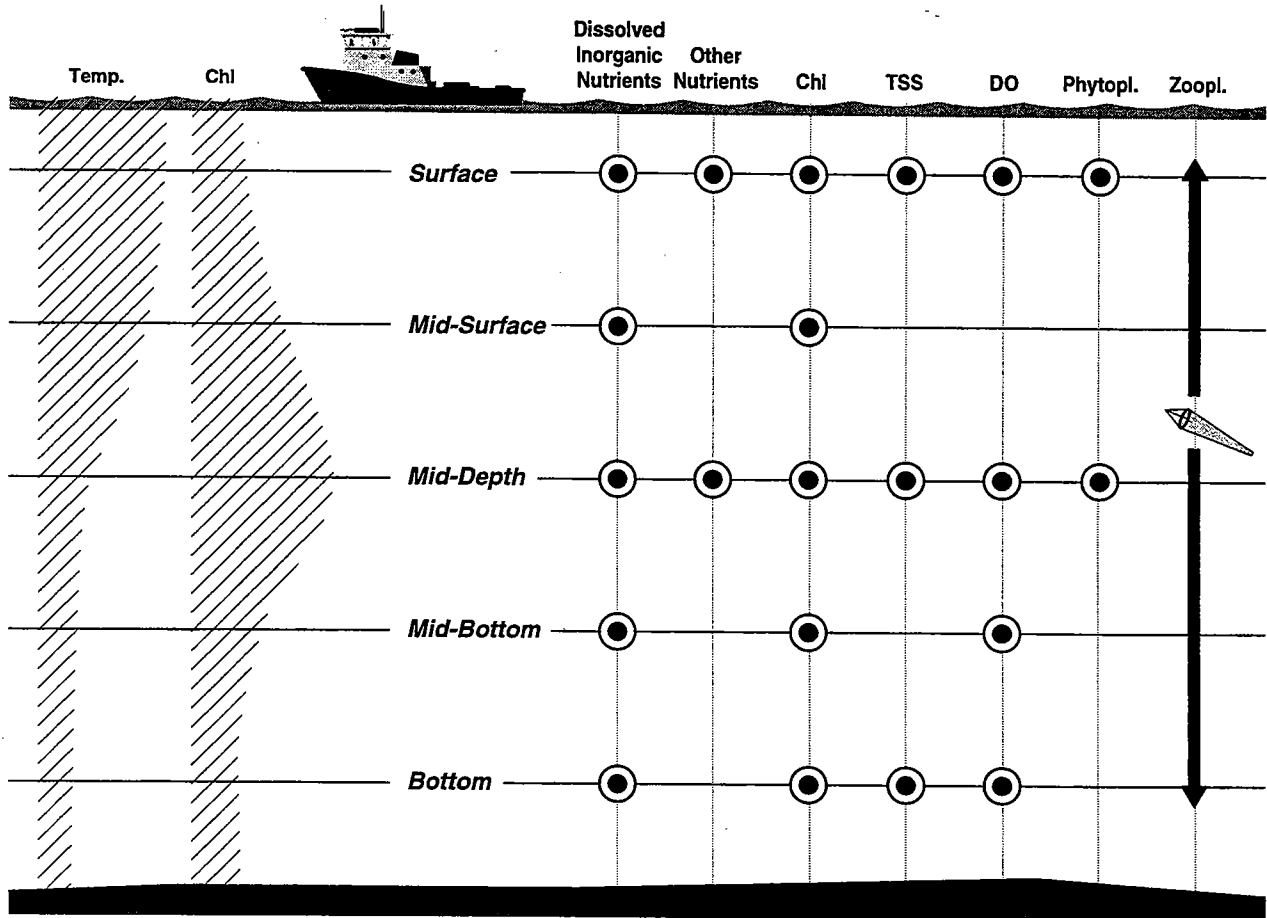


FIGURE 6
Station Type D
(areal productivity and respiration also measured at two of these stations)

TABLE 2

Analysis Group for Each Station and Depth, Nearfield Survey

Station Name	N01	N02	N03	N04	N05	N06	N07	N08	N09	N10	N11	N12	N13	N14	N15	N16	N17	N18	N19	N20	N21
Station Type	A	E	E	A+P+R	E	E	A+P+R	E	E	D	E	E	E	E	E	D	E	E	E	A	E
Nearfield Stations																					
Surface	G3	G8	G8	G3 + P + R	G8	G8	G3 + P + R	G8	G8	G1	G8	G8	G8	G8	G8	G1	G8	G8	G8	G3	G8
Mid-surface	G6	G8	G8	G6 + P	G8	G8	G6 + P	G8	G8	G6	G8	G8	G8	G8	G8	G6	G8	G8	G8	G6	G8
Middle	G3	G8	G8	G3 + P + R	G8	G8	G3 + P + R	G8	G8	G2	G8	G8	G8	G8	G8	G2	G8	G8	G8	G3	G8
Mid-bottom	G5	G8	G8	G5 + P	G8	G8	G5 + P	G8	G8	G5	G8	G8	G8	G8	G8	G5	G8	G8	G8	G5	G8
Bottom	G4	G8	G8	G4 + P + R	G8	G8	G4 + P + R	G8	G8	G4	G8	G8	G8	G8	G8	G4	G8	G8	G8	G4	G8

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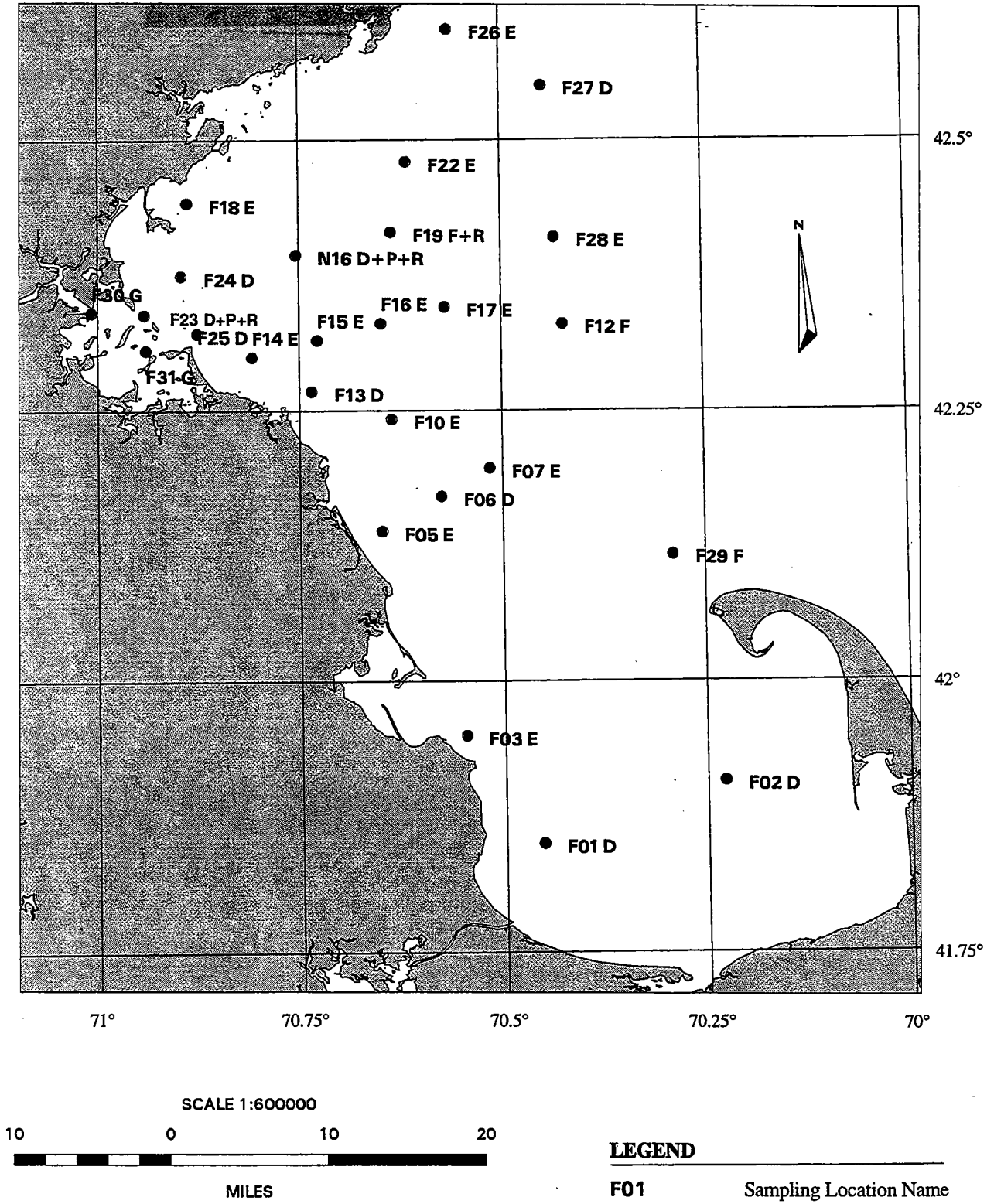
TABLE 3

Chemical and Biological Analysis Performed in Each Analysis Group

Analysis	Analysis Group											
	G0	G1	G2	G3	G4	G5	G6	G7	G8	G9	P	R
Dissolved Inorganic Nutrients		X	X	X	X	X	X	X	X			
Dissolved Organic Carbon		X	X	X								
Total Dissolved N & P		X	X	X								
Particulate C & N		X	X	X								
Particulate P		X	X	X								
Biogenic Silica		X	X	X								
Chlorophyll & Phaeopigments		X	X	X	X	X	X			X		
Total Suspended Solids		X	X	X	X					X		
Dissolved Oxygen		X	X	X	X	X		X		X		
Urea		X	X									
All Phytoplankton		X	X									
Screened Phytoplankton		X	X									
Zooplankton		X										
Areal Productivity											X	
Respiration												X

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**FIGURE 7
Farfield Stations**

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F01 Sampling Location Name
D, E, F, G Station Type
 Please refer to Table 1 for station type definition.

protocols are included in the farfield surveys: D, E, F, and G. Twelve of the 26 stations are Type E (Figure 4), and another 9 are Type D (Figure 6); both are described above. Station Type G has a set of analyses identical to Type D, but is performed at only three depths because of the relatively shallow water at these two stations (Figure 8). The remaining three stations are of Type F and include sampling for DINuts and DO (Figure 9). Areal primary productivity and water column respiration (P+R) are measured at two of the Type D farfield stations (F23 and N16). Samples for respiration analyses (R) are also collected at one Type F (F19). Tables 3 and 4 provide more detailed analysis information for the farfield stations.

The six farfield surveys conducted each year in 1995, 1996 and 1997 will capture the conditions at the following times of year :

- Winter (mid February)
- Late Winter, Early Spring (early March)
- Spring (early April)
- Early Summer (mid June)
- Late Summer (mid August)
- Early Fall (mid October)

All six farfield surveys will be combined with one-day nearfield surveys.

To meet the goals of the plume tracking task (Task 11), data profiles will be collected along transects and over grids to establish water quality parameter maps in areas of particular interest and to enhance understanding of basin dynamics. Three plume tracking surveys per year are scheduled for 1995, 1996 and 1997, with four additional surveys to be scheduled after the outfall goes on line.

During the three plume tracking surveys in 1995, 1996, and 1997, the equivalent of one day of a dedicated plume tracking survey will be obtained by additional vertical profiling at selected locations over the course of the four-day combined nearfield/farfield survey. The following day will be devoted to the plume tracking surveys and will provide spatially intensive vertical profiling in areas deemed particularly interesting after review of the first day of plume tracking data, near- and farfield data, and appropriate numerical modelling predictions. The four additional surveys performed soon after outfall commissioning will be aimed at gathering high resolution data during time-dependent events such as plume delineation immediately after the outfall is in operation, spring algal blooms, and dye studies. Each of these surveys will last two days.

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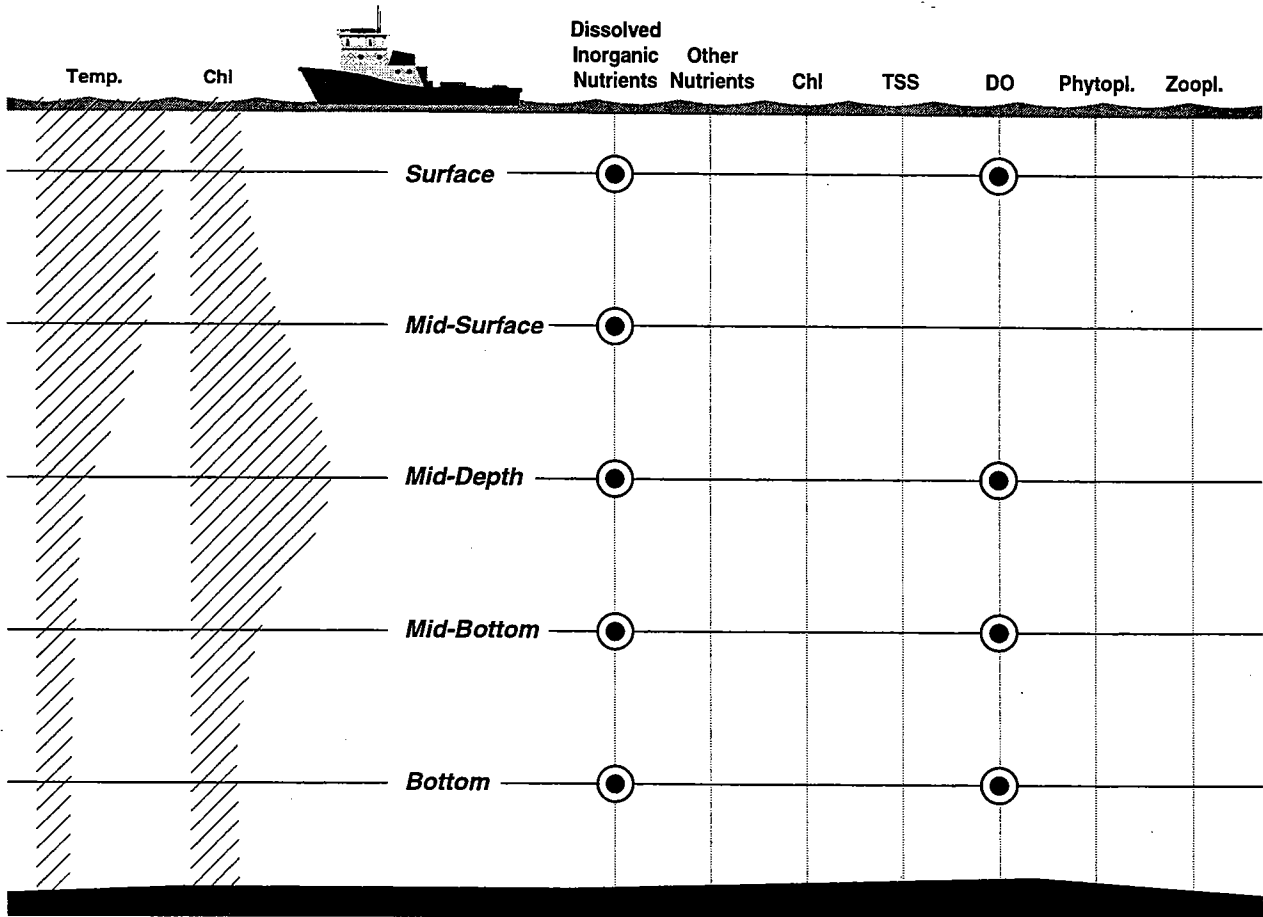


FIGURE 8
Station Type F

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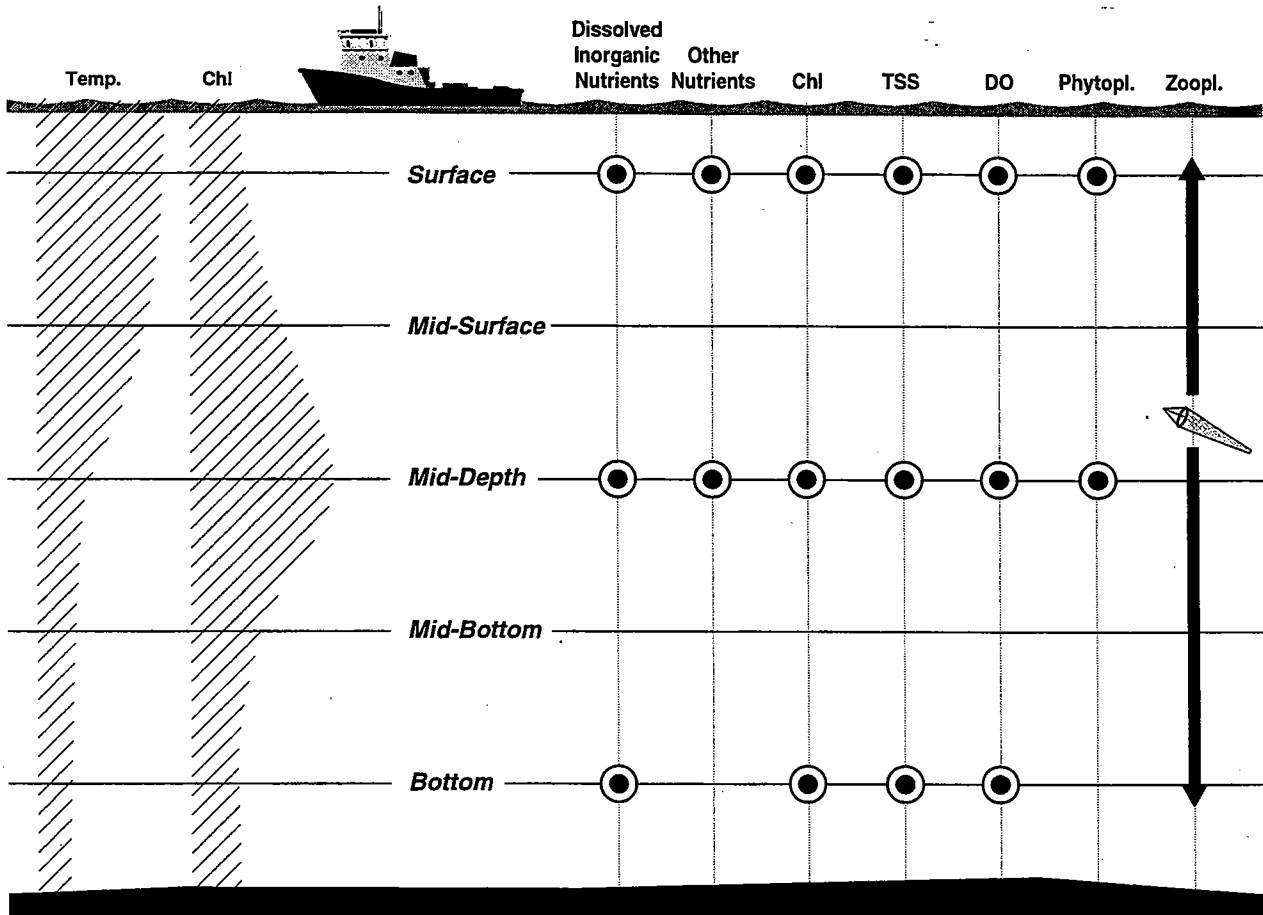


FIGURE 9
 Station Type G
 (mid-surface and mid-bottom samples are not
 taken due to the relatively shallow water at these stations)

TABLE 4

Analysis Group for Each Station and Depth, Fairfield Survey

Station Name ¹	F01	F02	F03	F05	F06	F07	F10	F12	F13	F14	F15	F16	F17	F18	F19	F22	F23	F24	F25	F26
Station Type	D	D	E	E	D	E	E	F	D	E	E	E	E	E	F+R	E	D+P	D	D	E
Farfield Stations																				
Surface	G1	G1	G8	G8	G1	G8	G8	G7	G1	G8	G8	G8	G8	G8	G7 + R	G8	G1 + P + R	G1	G1	G8
Mid-surface	G6	G6	G8	G8	G6	G8	G8	G8	G6	G8	G8	G8	G8	G8	G8	G8	G6 + P	G6	G6	G8
Mid-depth	G2	G2	G8	G8	G2	G8	G8	G7	G2	G8	G8	G8	G8	G8	G7 + R	G8	G2 + P + R	G2	G2	G8
Mid-bottom	G5	G5	G8	G8	G5	G8	G8	G7	G5	G8	G8	G8	G8	G8	G7	G8	G5 + P	G5	G5	G8
Bottom	G4	G4	G8	G8	G4	G8	G8	G7	G4	G8	G8	G8	G8	G8	G7 + R	G8	G4 + P + R	G4	G4	G8

Station Name	F27	F28	F29	F30	F31	N16
Station Type	D	E	F	G	G	D+P+R
Surface	G1	G8	G7	G1	G1	G1 + P + R
Mid-surface	G6	G8	G8	G0	G0	G6 + P
Mid-depth	G2	G8	G7	G2	G2	G2 + P + R
Mid-bottom	G5	G8	G7	G0	G0	G5 + P
Bottom	G4	G8	G7	G4	G4	G4 + P + R

¹Stations F04, F08, F09, F11, F20 and F21 have been replaced by or changed to stations F27, F28, F29, F30, F31 and N16.

7.3.2 Laboratory Program for Survey Tasks (Tasks 14, 15)

Water samples collected during the surveys will be analyzed to determine concentrations of five dissolved inorganic nutrients (nitrate, nitrite, ammonium, phosphate, and silicate); three dissolved organic nutrients (carbon, nitrogen, and phosphorus); three particulate nutrients (carbon, nitrogen, and phosphorus); biogenic silica; urea; DO; TSS; chlorophyll *a* and phaeophytin; and estimates of plankton productivity and respiration rates. Table 5 describes the parameters to be measured in the water samples. Sampling and analytical methods are described in Section 12.

7.4 Monitoring Parameters and Collection Frequency

Table 6 lists the *in situ* hydrographic measurements and the field samples to be collected. Table 7 presents the collection frequency of discrete water samples.

7.5 Parameter Table

Table 5 lists all parameters for which laboratory analyses will be conducted. For each parameter, pertinent information, such as reporting units, analytical method and reference, maximum holding time, and preservation is included in this table.

8.0 PROJECT FISCAL INFORMATION

This project is being carried out under the Harbor and Outfall Monitoring contract (Contract No. S186) between MWRA and ENSR Consulting and Engineering.

9.0 SCHEDULE OF ACTIVITIES AND DELIVERABLES

The schedule of activities and deliverables for this project is tied to survey activities. Figures 10, 11 and 12 provide tentative schedules for 1995, 1996 and 1997 for all survey plans, surveys, and survey reports required for Tasks 9 - 15. The deliverables for Tasks 9 - 15 are (1) survey plans and survey reports for each of the 51 surveys, (2) 15 nutrient data and respiration/productivity data reports, and (3) 15 phytoplankton data reports and 15 zooplankton data reports. The due dates for the data reports are shown in Table 8.

TABLE 5

Laboratory Analysis and Methods

Parameter	Units	Method	Reference ¹	Maximum Holding Time	Preservation	Lab
Dissolved Ammonia	µM	Lachat QuikChem 8000-FIA	Lachat (1994a)	3 mo.	Chloroform	UNH
Dissolved Nitrate	µM	Lachat QuikChem 8000-FIA	Morris and Riley (1963), Bendschneider and Robinson (1952), Lachat (1994b)	3 mo.	Chloroform	UNH
Dissolved Nitrite	µM	Lachat QuikChem 8000-FIA	Bendschneider and Robinson (1952), Lachat (1994b)	3 mo.	Chloroform	UNH
Dissolved Phosphate	µM	Lachat QuikChem 8000-FIA	Murphy and Riley (1962), Lachat (1994c)	3 mo.	Chloroform	UNH
Dissolved Silicate	µM	Lachat QuikChem 8000-FIA	Lachat (1993), Truesdale and Smith (1976)	3 mo.	Chloroform	UNH
DO	mg L ⁻¹	Manual titration	360.2 (EPA, 1983)	48 h	Dark/cool	E3I
DO (Respiration)	mg L ⁻¹	Radiometer Titralab Titrator	Oudot <i>et al.</i> (1988)	48 h	Dark/cool	WHOI
Dissolved Organic Carbon	µM	Dohrmann DC 80 Analyzer	415.1 (EPA, 1983)	3 mo.	Fix with 0.5 mL of sulfuric acid.	E3I
Dissolved Organic Nitrogen	µM	Lachat QuikChem 8000-FIA	Valderrama (1981), Lachat (1994b)	3 mo.	Add reagents immediately, heat to 100°C within 16 hours.	UNH
Dissolved Organic Phosphorus	µM	Lachat QuikChem 8000-FIA	Valderrama (1981), Lachat (1994c)	3 mo.	Add reagents immediately, heat to 100°C within 16 hours.	UNH
Particulate Organic Carbon	µM	Perkin Elmer Model 2400 Elemental Analyzer	Lambert and Oviatt (1986)	3 mo.	Pass through pre-ashed glass fiber filter. Freeze (-5°C).	WHOI
Particulate Organic Nitrogen	µM	Perkin Elmer Model 2400 Elemental Analyzer	Lambert and Oviatt (1986)	3 mo.	Pass through pre-ashed glass fiber filter. Freeze (-5°C).	WHOI

TABLE 5 (Cont'd)

Laboratory Analysis and Methods

Parameter	Units	Method	Reference ¹	Maximum Holding Time	Preservation	Lab
Urea	µM	Alpchem Autoanalyzer	Rahmatullah and Boyd (1980), Aninot and Kerouel (1982)	3 mo.	Freeze below -20°C.	WHOI
Particulate Phosphorus	µM	Lachat Quik Chem 8000-FIA	Lachat (1994c)	3 mo.	Store in digestion vial and freeze.	UNH
Biogenic Silica	µM	Lachat Quik Chem 8000-FIA	Krause <i>et al.</i> (1983), Lachat (1993)	3 mo.	Store in polyethylene digestion vial.	UNH
Total Suspended Solids	mg L ⁻¹	Analytical Balance	See Section 12.4.8	filter w/i 24 h analyze w/i 7 d	Pass through glass fiber filter. Dry over desiccant.	E3I
Chlorophyll <i>al</i> Phaeophytin	µg L ⁻¹	Perkin Elmer Fluorometer	SM 10200H (APHA, 1992), Lorenzen (1966)	2 wk	Store at <0°C in dark under air tight conditions.	E3I
Phytoplankton (Whole Water)	Cells L ⁻¹	Inverted phase-contrast microscopy	Hasle, 1978	3 y	Utermohil's solution. Store at room temperature.	ANS
Phytoplankton, (Screened)	Cells L ⁻¹	Inverted phase-contrast microscopy	Hasle, 1978	3 y	5-10% buffered formalin. Store at room temperature.	ANS
¹⁴ C (Production)	µg C L ⁻¹ hr ⁻¹	Liquid Scintillation Counter (Packard Tricarb 4000)	Strickland and Parsons (1972)	2 wk	Scintillation fluid	WHOI
Dissolved Inorganic Carbon (Production)	µg L ⁻¹	Beckman IR-315 Infrared Analyzer	Howes <i>et al.</i> (1985)	7 d	Store refrigerated until analysis.	WHOI
Chlorophyll <i>al</i> Phaeophytin (Production)	µg L ⁻¹	B&L Spectronic 2000	Parsons <i>et al.</i> (1989)	2 wk	Store in glass vial in dark container at -20°C until extraction.	WHOI
Zooplankton	Cells m ³	Dissecting Microscope	Turner <i>et al.</i> (1989)	3 y	5-10% buffered Formalin solution. Store at room temperature.	ANS

¹See Section 20 for literature references.

TABLE 6
 Field Samples and Measurements

Parameter	Stations	Sample Volume	Sample Containers	Shipping/Processing/Preservation
Following samples are subsampled from water collected with Poly Vinyl Chloride Niskin GO-FLO Bottles				
Dissolved Inorganic Nutrients	All, A, D, E, F, G	60 mL	60-mL polypropylene bottle	Pass through a filter. Fix with chloroform.
Dissolved Oxygen	A, D, F, G	300 mL	300-mL dark glass BOD	Fix with manganous sulfate and alkaline iodide-azide.
Dissolved Organic Carbon	A, D, G	50 mL (filtered)	40-mL glass vial	Pass through filter, preserve with H ₂ SO ₄ and store on ice.
Dissolved Organic Nitrogen	A, D, G	10 mL (filtered)	22-mL Teflon vial	Pass through a filter. Add persulfate oxidizing reagent. Digest within 16 hours. Store at room temperature.
Dissolved Organic Phosphorus	A, D, G	10 mL (filtered)	22-mL Teflon vial	Pass through a filter. Add persulfate oxidizing reagent. Digest within 16 hours. Store at room temperature.
Particulate Organic Carbon	A, D, G	300-500 mL (filtered)	25-mm Whatman glass fiber filter (grade GF/F)	Pass through a pre-ashed glass fiber filter. Store on ice.
Particulate Organic Nitrogen	A, D, G	300-500 mL (filtered)	25-mm Whatman glass fiber filter (grade GF/F)	Pass through a pre-ashed glass fiber filter. Store on ice.
Total Suspended Solids	A, D, G	1000 mL	1000-mL polyethylene	Store on ice.
Urea	D, G	50 mL (filtered)	50-mL polyethylene	Filter and store on ice.
Chlorophyll <i>a</i> /Phaeophytin	A, D, G	300-500 mL (filtered)	25-mm Whatman glass fiber filter (grade GF/F)	Pass through filter. Store filter on ice.
Particulate Phosphorus	A, D, G	200 mL (filtered)	25-mm Whatman glass fiber filter (grade GF/F)	Pass through pre-ashed glass fiber filter. Freeze (-5°C).
Biogenic Silica	A, D, G	200 mL (filtered)	25-mm Poretics polycarbonate filter	Pass through filter. Store at room temperature.
Phytoplankton (Whole Water)	D, G	1000 mL	1000-mL polyethylene bottle	Preserve with Utermohli's solution. Store at room temperature in dark.
Phytoplankton (Screened Water)	D, G	2000 mL (filtered)	250-mL polyethylene bottle	Strain through a 20 µm mesh; wash retained organism into a jar. Fix with 5-10% buffered formalin. Store at room temperature in dark.

TABLE 6 (Cont'd)

Field Samples and Measurements

Parameter	Stations	Sample Volume	Sample Containers	Shipboard Processing/ Preservation
¹⁴ C (Production)	+ P	75 mL	75-mL polycarbonate	Inoculate with 5-12 µCl of Na ₂ ¹⁴ CO ₃ and incubate.
Chlorophyll <i>a</i> / Phaeophytin (Production)	+ P	300-600 mL (filtered)	4.5-cm millipore filter (0.22 µm)	Pass through filter. Fix with 1% MgCO ₃ solution. Store on ice.
Dissolved Inorganic Carbon (Production)	+ P	300 mL	300-mL BOD dark glass	Acidify with 2N sulfuric acid.
Respiration	+ R	300 mL	300-mL dark glass BOD	Fix with manganous sulfate, alkaline iodide-azide, and sulfamic acid. In situ incubations.
Following sample is collected with a vertically towed net				
Zooplankton	D, G	Varies with tow	500-1000 mL polyethylene bottle	Wash into jar. Fix with a 5-10% buffered Formalin.
The following measurements are taken as vertical profiles using the sensor array				
PRECISION				
Conductivity	All	---	Floppy disk	0.004 mS/cm
Temperature	All	---	Floppy disk	0.0003 °C
Pressure	All	---	Floppy disk	0.1 psi
Dissolved Oxygen	All	---	Floppy disk	0.01 mL/L
Chlorophyll <i>a</i> Fluorescence	All	---	Floppy disk	0.015 µg/L
Transmissometry	All	---	Floppy disk	0.01 m ⁻¹
<i>In situ</i> 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	0.3 m
Navigational Position	All	---	Floppy disk	2 m

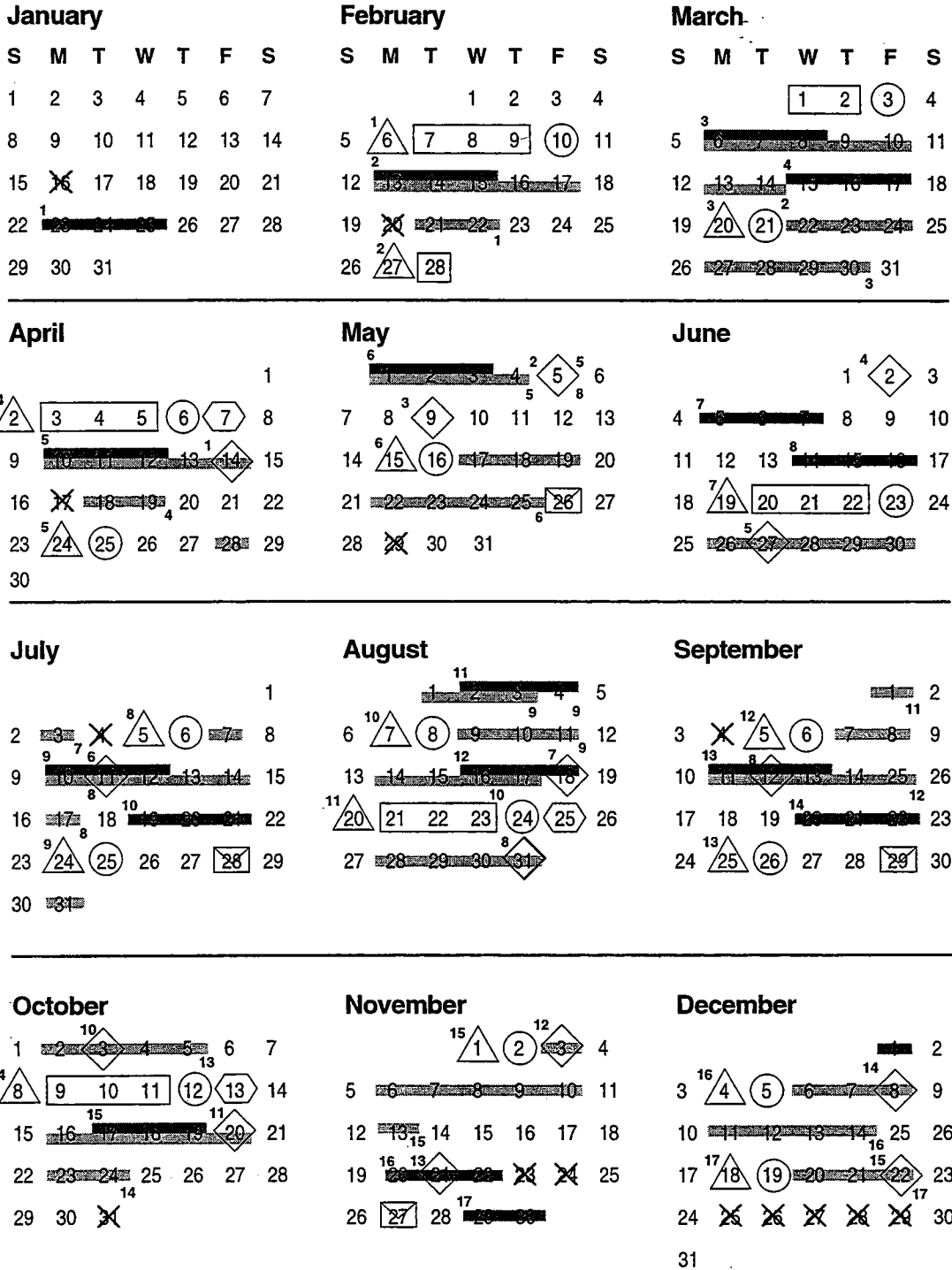
TABLE 7

Water Sampling Frequency

Station Type ¹	Task 9							Task 10							Task 11			Analyses Per Year
	A	B	C	+P	+R	D	E	F	G	+P	+R	H	I					
	Number of station-type/survey	4	15	2	2	2(0) ²	9	12	3	2	2	3(2) ²	30	6				
Number of surveys/year	17	17	17	17	17	6	6	6	6	6	6	3	3					
Analysis Type	Number of Analyses per Station																	
Dissolved inorganic nutrients (NH ₄ , NO ₃ , NO ₂ , PO ₄ , SiO ₄)	5	5	5	0	0	5	5	5	3	0	0	3	0	2811				
Other nutrients (DOC, TDN, TDP, POC, PON, PPO ₄ biogenic Si)	2	0	2	0	0	2	0	0	2	0	0	0	0	336				
Chlorophyll <i>a</i> , phaeophytin	5	0	5	0	0	5	0	0	3	0	0	0	3	870				
Total suspended solids	3	0	3	0	0	3	0	0	3	0	0	0	3	558				
Dissolved oxygen	4	0	4	0	0	4	0	4	3	0	0	0	3	786				
Phytoplankton, Urea	0	0	2	0	0	2	0	0	2	0	0	0	0	200				
Zooplankton	0	0	1	0	0	1	0	0	1	0	0	0	0	100				
Areal ¹⁴ C Productivity	0	0	0	1	0	0	0	0	0	1	0	0	0	46				
Water Column Respiration	0	0	0	0	3	0	0	0	0	0	3	0	0	156 (36) ²				
	A	B	C	+P	+R	D	E	F	G	+P	+R	H	I					
	Task 9							Task 10							Task 11			

¹Station type C is the same type of analyses as Type D as shown in Figures 6, and Type E is the same as Type E as shown in Figure 4. Contrastal number shown in parentheses.

**COMBINED WORK/QUALITY ASSURANCE PROJECT PLAN
 WATER QUALITY MONITORING, 1995-1997**



Legend

- | | | | |
|-----------|----------|------------------------------|---------------------|
| Mob | Farfield | Write Survey Plan | Plume Tracking |
| Nearfield | Holiday | Write and Mail Survey Report | Receive Lab Reports |
| | | | Mail Data Report |

FIGURE 10
 1995 Nearfield/Farfield Plume Tracking Survey Schedule

**COMBINED WORK/QUALITY ASSURANCE PROJECT PLAN
 WATER QUALITY MONITORING, 1995-1997**

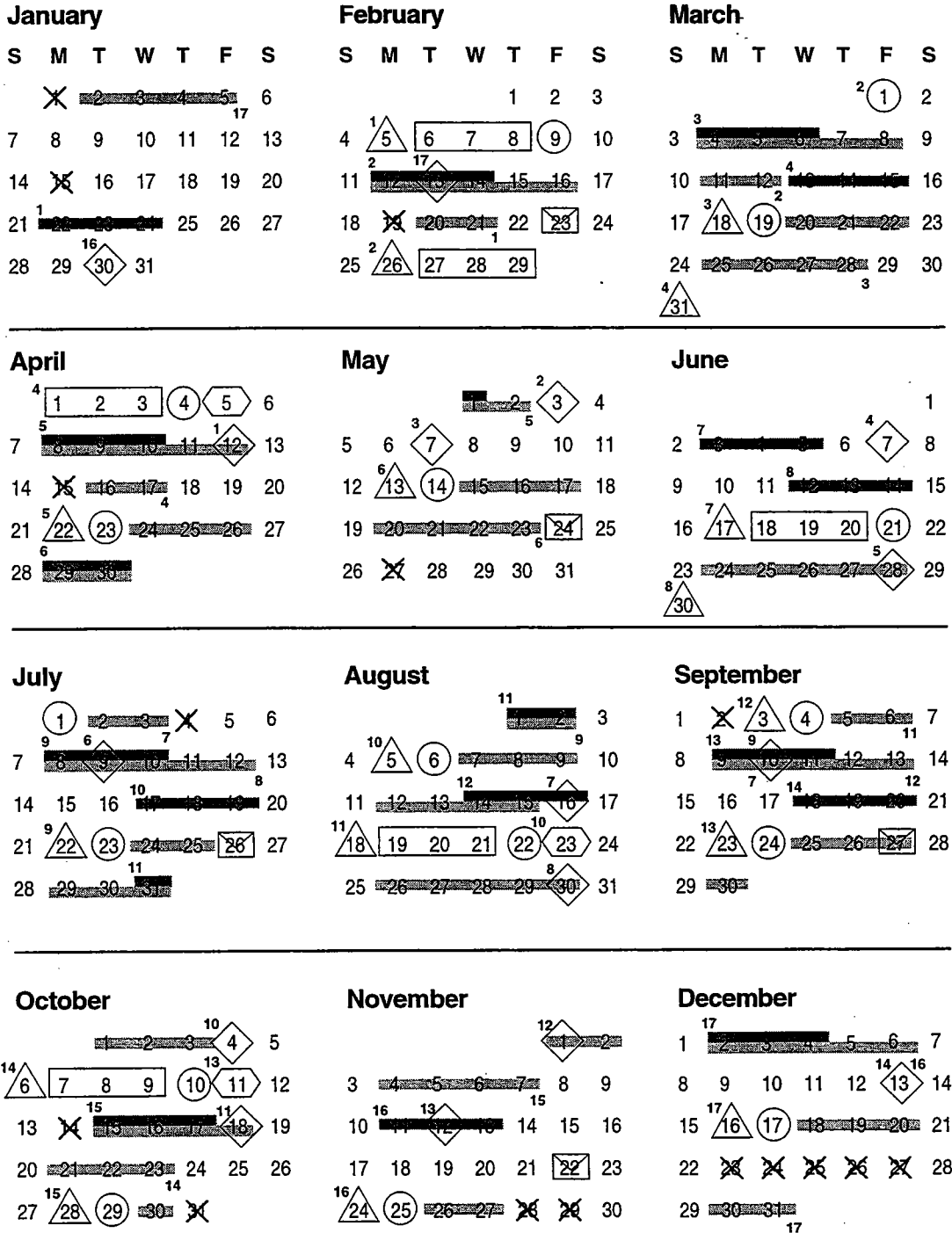
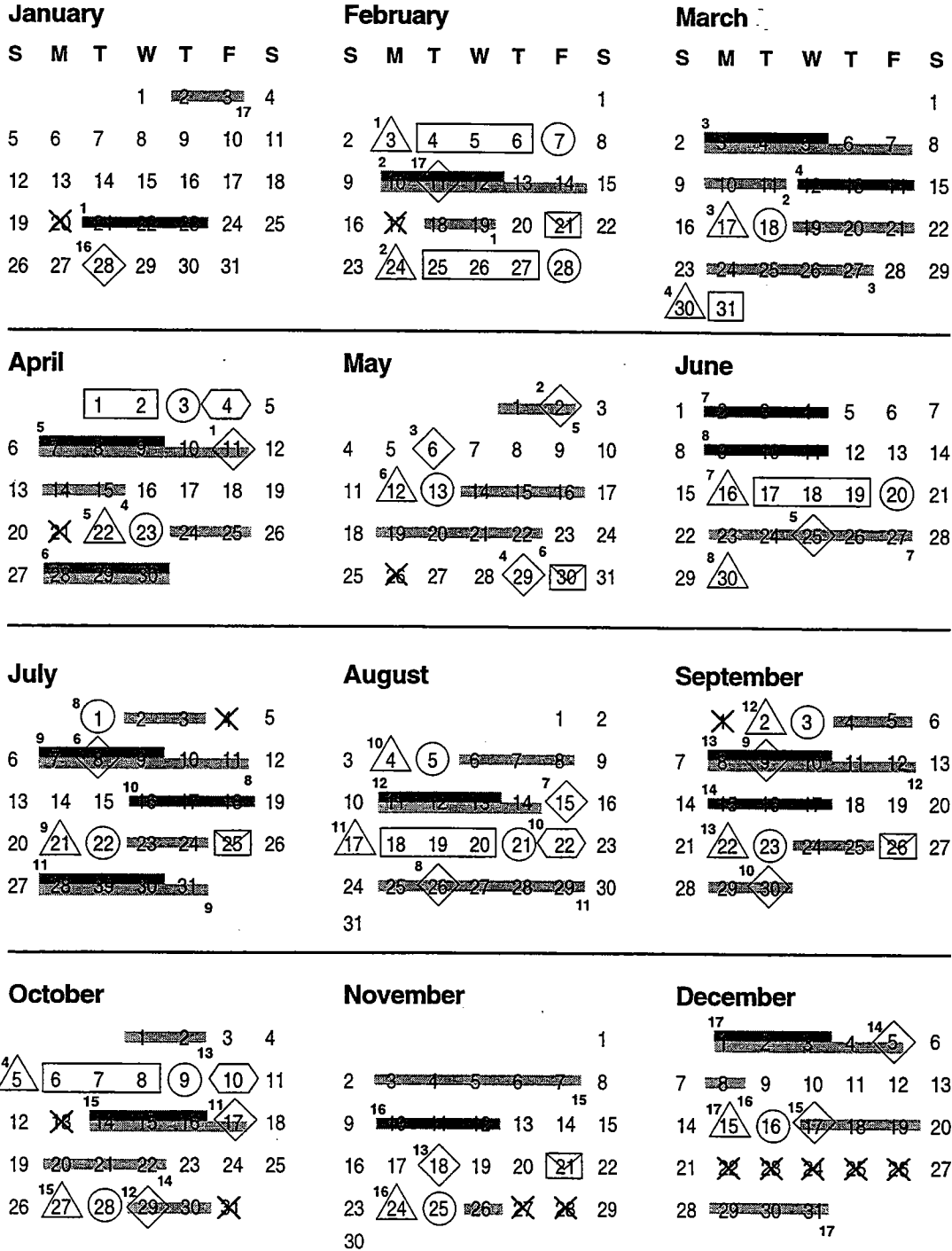


FIGURE 11
 1996 Nearfield/Farfield Plume Tracking Survey Schedule

**COMBINED WORK/QUALITY ASSURANCE PROJECT PLAN
 WATER QUALITY MONITORING, 1995-1997**



Legend

- Mob
- Farfield
- Write Survey Plan
- Plume Tracking
- Mail Data Report
- Nearfield
- Holiday
- Write and Mail Survey Report
- Receive Lab Reports

FIGURE 12
 1997 Nearfield/Farfield Plume Tracking Survey Schedule

TABLE 8

Due Dates for Data Reports

Mailing Date	Surveys Included
May, 1995	February, March and April 1995 surveys
July, 1995	May and June 1995 surveys
September, 1995	July and August 1995 surveys
November, 1995	September and October 1995 surveys
February, 1996	November and December 1995 surveys
May, 1996	February, March and April 1996 surveys
July, 1996	May and June 1996 surveys
September, 1996	July and August 1996 surveys
November, 1996	September and October 1996 surveys
February, 1997	November and December 1996 surveys
May, 1997	February, March and April 1997 surveys
July, 1997	May and June 1997 surveys
September, 1997	July and August 1997 surveys
November, 1997	September and October 1997 surveys
February, 1998	November and December 1997 surveys

10.0 PROJECT ORGANIZATION AND RESPONSIBILITIES

The water quality monitoring tasks will be accomplished through the coordinated efforts of several organizations (Figure 13). Dr. Michael Mickelson is the MWRA Project Manager and the MWRA Water Quality Project Area Manager. He will be informed of all matters pertaining to work described in this CW/QAPP. Mr. Kenneth Keay is the deputy MWRA program manager. Ms. Wendy Leo is MWRA's EM&MS database manager.

Dr. James Blake is the ENSR Project Manager responsible for the overall performance of the project. Ms. Debra McGrath will oversee the QA of all technical activities conducted by ENSR. Mr. Stephen Cibik is the ENSR Assistant Project Manager for Technical Studies, and Project Area Leader responsible for the overall performance of the water quality monitoring tasks described in this CW/QAPP. In this role, Mr. Cibik will also assist task managers with coordination of subcontractors within the water quality tasks and with other aspects of the Harbor and Outfall Monitoring Program.

Mr. Steven Wolf will act as the ENSR Assistant Project Manager for Operations. He will manage the nearfield, farfield, and plume tracking surveys (Tasks 9, 10, and 11), and will be the Chief Scientist on the majority of the cruises (Figure 13). In his role, Mr. Wolf will be responsible for coordinating survey operations and for ensuring successful completion of each survey. As Chief Scientist, Mr. Wolf will select sampling depths and locations, and will supervise and assist with sample collection. The equipment chief and *in-situ*/navigation data manager will be Mr. Kenneth A. Hickey. Mr. Hickey will operate the navigation equipment and assist Mr. Wolf with the collection of *in situ* measurements. Mr. Hickey and Mr. Wolf will serve as alternate chief scientists on the water quality cruises.

The remainder of the water quality survey tasks are managed by experienced ENSR scientists and engineers (Figure 13). The laboratory analysis tasks are managed by Dr. Eric Butler (Task 14 - Nutrients, Respiration/Productivity Measurements) and Mr. Stephen Cibik (Task 15 - Plankton Taxonomy). The appropriate task manager will oversee subcontractors conducting the sampling and laboratory work related to plankton, nutrients, and respiration/productivity measurements.

Subcontractors will contribute to all five tasks associated with the water quality surveys (Figure 13). The laboratory analysis conducted as part of Task 14 (Nutrients, Respiration/ Productivity Measurements) will be conducted by the University of New Hampshire (UNH), Woods Hole Oceanographic Institute (WHOI) and Energy and Environmental Engineering (E3I). Personnel from UNH and WHOI will also assist with sample collection on the cruises. Drs. Brian Howes and Craig Taylor (WHOI), and Dr. Ted Loder (UNH)

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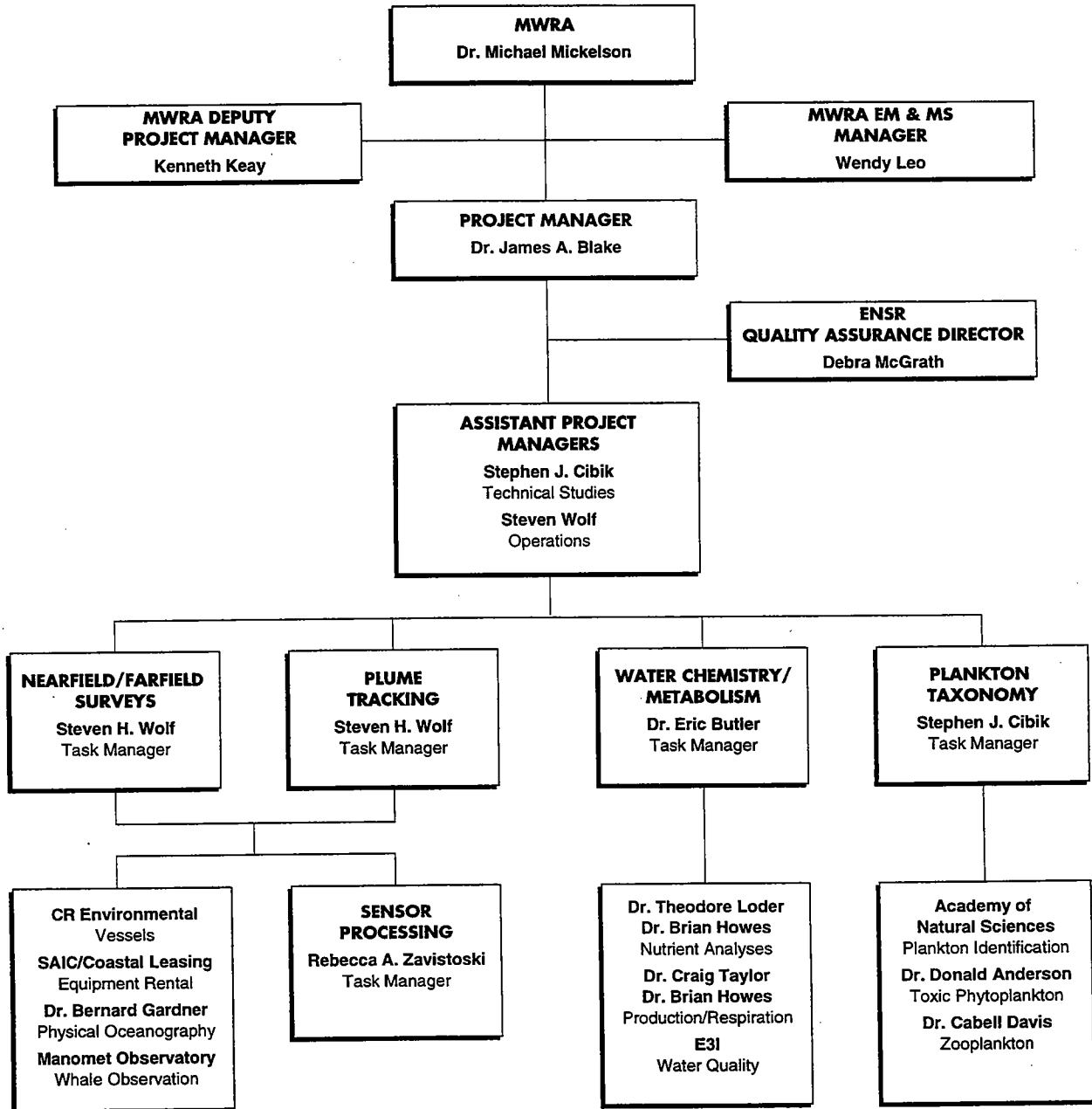


FIGURE 13
 Organization of Water Quality Surveys and Analyses

will supervise the laboratory analysis and consult with the project team on nutrient dynamics and analysis issues. Whale observation on the nearfield cruises will be performed by the Manomet Observatory. Plankton enumeration and taxonomy will be performed by the Academy of Natural Sciences, with phytoplankton and zooplankton oversight provided by Drs. Donald Anderson and Cabell Davis. Dr. Bernard Gardner of U. Mass/Boston will provide consulting on physical oceanography issues.

11.0 DATA QUALITY REQUIREMENTS AND ASSESSMENTS

To ensure that all data generated during the conduct of surveys, analyses, and reporting are of the highest quality, data will be examined in terms of the following characteristics:

- **Precision** — the extent of agreement among independent, similar, or related measurements
- **Accuracy** — the extent of agreement between the measured value and the true value
- **Completeness** — measure of the amount of data acquired relative to the amount of data required to fulfill the statistical criteria for the intended use of the data
- **Comparability** — the extent to which data from one study can be compared directly to similar studies
- **Representativeness** — the extent to which measurements represent true systems

11.1 Navigational and Hydrographic Data

11.1.1 Precision and Accuracy

Based on manufacturer specifications or ENSR's experience, precision and accuracy objectives for navigation and hydrographic samplings are presented in Table 9. Section 12 provides details on relevant sampling procedures to ensure data quality and Section 14 discusses instrument calibration methods.

11.1.2 Completeness

A Northstar 941xd differential GPS navigation system will be used to output navigation positions at 2-s intervals. The project's time interval requirement for obtaining positions during sampling is 5 min. Thus, even with a few bad data streams from the Northstar GPS to the computer, the software will provide enough fixes within each 5-min period for 100% data collection.

TABLE 9

Accuracy and Precision of Instrument Sensors

Sensor	Units	Range	Accuracy	Precision
Pressure	psi	0-10000	3	0.1
Temperature	°C	-5 to +35	0.001	0.0003
Conductivity	mS/cm	0-70	0.003	0.004
Transmissometer	m ⁻¹	0-40	0.20	0.01
Dissolved Oxygen	mL/L	0-15	0.1	0.01
Fluorometer	µg/L	0.1-100	5% of reading	0.015
<i>In situ</i> irradiance	µE m ⁻² s ⁻¹	0-4000	10	1
On-Deck irradiance	µE m ⁻² s ⁻¹	0-4000	10	1
Altimeter	m	0-150	1	0.1
Fathometer	m	0-100	2	0.3
Navigation	lat/long degrees° minutes'	Coastal	10 m (with differential signal)	2 m

Hydrographic data are acquired electronically and monitored in real time, to make loss of data highly unlikely. The sampling rates of the CTD (24 times per second) and navigation systems (2 sec intervals) assure that sufficient data will be acquired to map the water masses, and to locate the depth of the pycnocline and chlorophyll-*a* maximum in Massachusetts and Cape Cod Bays. Data loss could occur, however, during rare instances of equipment failure. Stations will not be occupied if CTD measurements (at a minimum) cannot be obtained. If instrument malfunctions occur and operations are modified or suspended during any survey day, a decision on modification of activities for that survey will be made with consultation and agreement of MWRA, whenever possible.

11.1.3 Comparability

Latitude/longitude positions will be recorded in Seasoft. These positions will be comparable to positions obtained by other tasks in the MWRA monitoring project as well as by other researchers that have used or are using differential GPS or corrected LORAN. The station locations are targets, and sampling will be conducted within 300 m of the targets, according to the Northstar navigation display. Sampling objectives will be achieved with respect to positioning by this level of station accuracy.

The instrumentation and methods of data reduction that will be used during the water quality monitoring surveys are similar to the instrumentation routinely used by EPA, the National Oceanic and Atmospheric Administration (NOAA), and other research institutions working in Massachusetts Bay. Thus, the data should be consistent with and comparable to previous studies. During review and synthesis of the survey data, the results will be compared with the general ranges of water property data obtained from previous studies, including recent surveys of Boston Harbor (Central Artery/Tunnel Project 1994), Massachusetts/Cape Cod Bays (Kelly *et al.*, 1992), and data from MWRA surveys conducted in 1992.

11.1.4 Representativeness

The corrected latitude/longitude positions are representative of the actual vessel coordinates and survey track because position data are collected and reviewed at a frequency that ensures that the measured latitudes/longitudes represent the actual vessel position.

The *in situ* instruments described above provide data to delineate water masses by monitoring changes in water properties at a high degree of resolution.

11.2 Water Sampling

11.2.1 Precision and Accuracy

Precision and accuracy of water sampling procedures are not directly quantified, but are ensured by the collection procedures. The sampling objective is to obtain uncontaminated samples representative of their location. Procedures (e.g. Lambert and Oviatt, 1986) will follow standard methods that can achieve this objective. Samples for dissolved and particulate nutrients, TSS, phytoplankton, and chlorophyll will be collected from labeled Niskin hydrocast bottles taken from depths recorded in the Seasoft profile data file. Samples for DO will be carefully siphoned into 300-mL BOD bottles with ground-glass stoppers. Each sample will be clearly labeled with a unique sampling identifier (survey ID and sample number) that will allow the sample to be traced from collection through analysis to reporting. All samples will be handled and stored according to the appropriate protocols (Lambert and Oviatt, 1986).

11.2.2 Completeness

At each station, discrete samples will be collected at five depths, based on positions relative to a subsurface chlorophyll maximum usually associated with the presence of a pycnocline separating surface and bottom water layers. In the event of sample loss or equipment malfunction, the Chief Scientist will determine the need for appropriate corrective action (e.g., resampling). The corrective action taken by the Chief Scientist will be recorded in the survey notebook. At the discretion of the Chief Scientist and, if no distinct vertical hydrographic structure is apparent from the real-time *in situ* sampling, the hydrocast will not be resampled. In all cases, the objectives of the project will not be compromised if representative surface and mid-depth ("chlorophyll maximum" if present) samples for nutrient and biological studies, and measurements of bottom-water DO are successfully collected.

11.2.3 Comparability

Collection of samples for both chlorophyll and DO coincidentally with *in situ* electronically captured data will allow field calibration of the electronic sensors. Nutrient concentrations (dissolved and particulate) will be comparable to data from other recent surveys of the study area, because standardized sampling procedures will be employed. Units for reporting concentrations will follow standard convention for most oceanographic studies: all nutrients (μM), chlorophyll ($\mu\text{g L}^{-1}$), TSS (mg L^{-1}), and DO (mg L^{-1} or % saturation).

Comparability of the sampling and laboratory (Section 11.3) procedures with previous studies will be achieved through adherence to the procedures established in this CW/QAPP. These procedures are based, in every case, on documented standard methods (e.g. EPA or ASTM methods) or on methods previously described in the scientific literature. Should it be decided at a later date to modify the procedures from those outlined here, and adopt procedures that do not meet the obligations outlined herein, then a special study will be conducted to assess the comparability of the new procedures. MWRA will be consulted in the design and implementation of this special study.

11.2.4 Representativeness

Water samples will be collected, handled, and transported using procedures (see Section 12 below) that will ensure that resulting data represent the sample material collected.

11.3 Laboratory Program

11.3.1 Precision and Accuracy

For the water quality monitoring study, UNH, WHOI, and E3I will generate data on dissolved inorganic nutrients, chlorophyll *a* and phaeophytin (used for calibrating the *in situ* sensor and calculating productivity), TSS, particulate and dissolved organic carbon, nitrogen, and phosphorus, biogenic silica, DO (used for calibration of *in situ* sensor and calculating respiration), and ¹⁴C (used for calculations of primary production). Precision of these analyses for replicate samples, along with other aspects of the laboratory QC program, is shown in Table 10. Section 12.3 provides additional details on the analytical procedures, including QC procedures (e.g., prepared standards, QC analyses) that will ensure data quality. Section 14 describes instrument calibration methods. ANS will generate data for phytoplankton (whole water), phytoplankton (screened), and zooplankton. Based on a study conducted by Guillard (1973), counts of phytoplankton aliquots containing at least 400 cells will provide 10% precision.

11.3.2 Completeness

It is expected that 100% of the samples collected and intended for analysis will be analyzed; however, a sample loss of less than 10% would not compromise the objectives of the project. Sufficient sample volumes will be collected to conduct more than one analysis, thus providing a safeguard against any instrument malfunction during a given analysis.

TABLE 10

Data Quality Objectives for Laboratory Measurement

Parameter	Quality Control (QC) Sample Types	Frequency of QC Sample	Data Quality Objective	Reporting Limit	Corrective Action
Dissolved Ammonia	Field Duplicate Matrix Blank Lab Control Sample Lab Duplicate	1/20 Samples 3 per Batch 2/10 Samples 1/15 Samples	RPD ¹ < 10% RPD < 0.02 µM RPD < 5% RPD < 5%	0.03 µM	Investigate Reanalyze Reanalyze Reanalyze
Dissolved Nitrate	Field Duplicate Matrix Blank Lab Control Sample Lab Duplicate	1/20 Samples 3 per Batch 2/10 Samples 1/15 Samples	RPD < 10% RPD < 0.01 µM RPD < 5% RPD < 2%	0.01 µM	Investigate Reanalyze Reanalyze Reanalyze
Dissolved Nitrite	Field Duplicate Matrix Blank Lab Control Sample Lab Duplicate	1/20 Samples 3 per Batch 2/10 Samples 1/15 Samples	RPD < 10% RPD < 0.01 µM RPD < 5% RPD < 2%	0.01 µM	Investigate Reanalyze Reanalyze Reanalyze
Dissolved Phosphate	Field Duplicate Matrix Blank Lab Control Sample Lab Duplicate	1/20 Samples 3 per Batch 2/10 Samples 1/15 Samples	RPD < 10% RPD < 0.01 µM RPD < 5% RPD < 2%	0.02 µM	Investigate Reanalyze Reanalyze Reanalyze
Dissolved Silicate	Field Duplicate Matrix Blank Lab Control Sample Lab Duplicate	1/20 Samples 3 per Batch 2/10 Samples 1/15 Samples	RPD < 10% RPD < 0.01 µM RPD < 5% RPD < 2%	0.03 µM	Investigate Reanalyze Reanalyze Reanalyze
Dissolved Oxygen	Baseline - Thiosulphate Standardization Lab Duplicate	1 per Batch 1/20 Samples	< 1000 µg/L RPD < 10%	50 ug/L	Reanalyze Reanalyze
Dissolved Organic Carbon	Method Blank Lab Duplicate	1 per Batch 1/20 Samples	< 100 µg/L RPD < 15%	100 ug/L	Reanalyze Reanalyze
Total Dissolved Nitrogen (DIN + DON)	Field Duplicate Matrix Blank Lab Control Sample Lab Duplicate	1/20 Samples 3 per Batch 2/10 Samples 1/15 Samples	RPD < 25% RPD < 0.02 µM RPD < 5% RPD < 2%	0.01 µM	Investigate Reanalyze Reanalyze Reanalyze
Total Dissolved Phosphorus (DIP + DOP)	Field Duplicate Matrix Blank Lab Control Sample Lab Duplicate	1/20 Samples 3 per Batch 2/10 Samples 1/15 Samples	RPD < 25% RPD < 0.02 µM RPD < 5% RPD < 2%	0.02 µM	Investigate Reanalyze Reanalyze Reanalyze

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TABLE 10 (Cont'd)

Data Quality Objectives for Laboratory Measurement

Parameter	Quality Control (QC) Sample Types	Frequency of QC Sample	Data Quality Objective	Reporting Limit	Corrective Action
Particulate Organic Carbon	Acitanilide Standard	1 per Batch	RPD < 1%	10 µg/L	Repeat
Particulate Organic Nitrogen	Acitanilide Standard	1 per Batch	RPD < 1%	10 µg/L	Repeat
Particulate Phosphorus	Field Duplicate Matrix Blank Lab Control Sample Lab Duplicate	1/20 Samples 3 per Batch 2/10 Samples 1/15 Samples	RPD < 10% RPD < 0.02 µM RPD < 2% RPD < 2%	0.002 µM	Investigate Reanalyze Reanalyze Reanalyze
Biogenic Silica	Field Duplicate Matrix Blank Lab Control Sample Lab Duplicate	1/20 Samples 3 per Batch 2/10 Samples 1/15 Samples	RPD < 10% RPD < 0.02 µM RPD < 2% RPD < 2%	0.005 µM	Investigate Reanalyze Reanalyze Reanalyze
Total Suspended Solids	Method Blank Lab Control Sample Lab Duplicate	1 per Batch 1 per Batch 1/20 Samples	< 1000 µg/L 95% ² ci RPD < 10%	1000 µg/L	Reanalyze Reanalyze Reanalyze
Chlorophyll <i>a</i> / Phaeopigments	Method Blank Lab Duplicate	1 per Batch 1/20 Samples	< 0.05 µg/L RPD < 10%	0.05 µg/L	Reanalyze Reanalyze
¹⁴ C Production	Isotope Blank	1 per Cruise	< 200 ³ DPM	N/A	Repeat
Respiration	Baseline - Thiosulphate Standardization Lab Duplicate	1 per Cruise 1/20 Samples	RPD < 2% RPD < 15%	N/A	Repeat Repeat
Urea	Method Blank Lab Control Sample Lab Duplicate	1/10 Samples 1 per Batch 1/20 Samples	RPD < 1% RPD < 10% RPD < 15%	.3 µM	Repeat Repeat Repeat
Dissolved Inorganic Carbon (Production)	Lab Control Sample Lab Duplicate	1/10 Samples Every Sample	RPD < 10% RPD < 25%	20 µg/L	Reanalyze Reanalyze

¹RPD = relative percent difference

²ci = confidence interval

³DPM = disintegrations per minute

11.3.3 Comparability

Data will be directly comparable to results obtained previously at the same or similar sites in Massachusetts Bay and Cape Cod Bay, and to those of similar studies conducted in Buzzards Bay, because analytical procedures are similar or identical. Additional discussion on this issue is included in Section 11.2.3.

11.3.4 Representativeness

Evaluation of previous studies has helped ensure that the sampling sites selected for the Harbor and Outfall Monitoring Project will be representative of the Massachusetts Bay system around the outfall. The laboratory measurements that will be made during the conduct of the Baseline Water Quality Monitoring Study have already been used in many systems to characterize eutrophication effects on the water column and are, therefore, considered to yield data representative of the study area.

12.0 SAMPLING AND ANALYTICAL PROCEDURES

Methods for collection and analysis of samples are described in the following sections.

12.1 Navigation, Hydrographic Profile, and Water Sampling

Vessel positioning during sampling operations will be accomplished with the Northstar navigation system. The GPS receiver has six dedicated channels and is capable of locking onto six different satellites at one time. This capability ensures strong signal reception, and accurate and reliable positioning with 2-s updates.

The hydrographic profile sampling equipment consists of the following:

- SeaBird 32 Carousel water sampling system
- as many as 12 10-L Niskin bottles
- SeaBird SBE-11plus CTD interface deck unit
- SeaBird SBE-9plus CTD system with
 - SeaBird SBE-13Y DO sensor which is a polarographic type that produces an oxygen-dependent electrical current and incorporates a thermistor for determination of membrane temperature

- SeaTech 25-cm-pathlength transmissometer ($\lambda = 660$ nm) that provides accurate *in situ* measurements of optical beam transmission, which is related to the concentration of suspended matter in the water at the point of measurement
- SeaTech *in situ* fluorometer: $\lambda_{ex} = 425$ nm (peak), $\lambda_{em} = 685$ nm (peak)
- Biospherical QSP-200L spherical quantum scalar irradiance sensor used to measure underwater photosynthetically available radiation (PAR)
- Tritech ST200-LP altimeter provides a measurement of underwater unit height off the bottom
- Biospherical QSR 240 hemispherical reference sensor that is used on deck to monitor changing radiation conditions above the surface of the water (*e.g.*, due to atmospheric conditions)
- CoStar LabelWriter XLplus barcode printer and scanner
- Hewlett-Packard DeskJet 560C 4-color printer
- Dell Latitude 486 dx4-100 computer

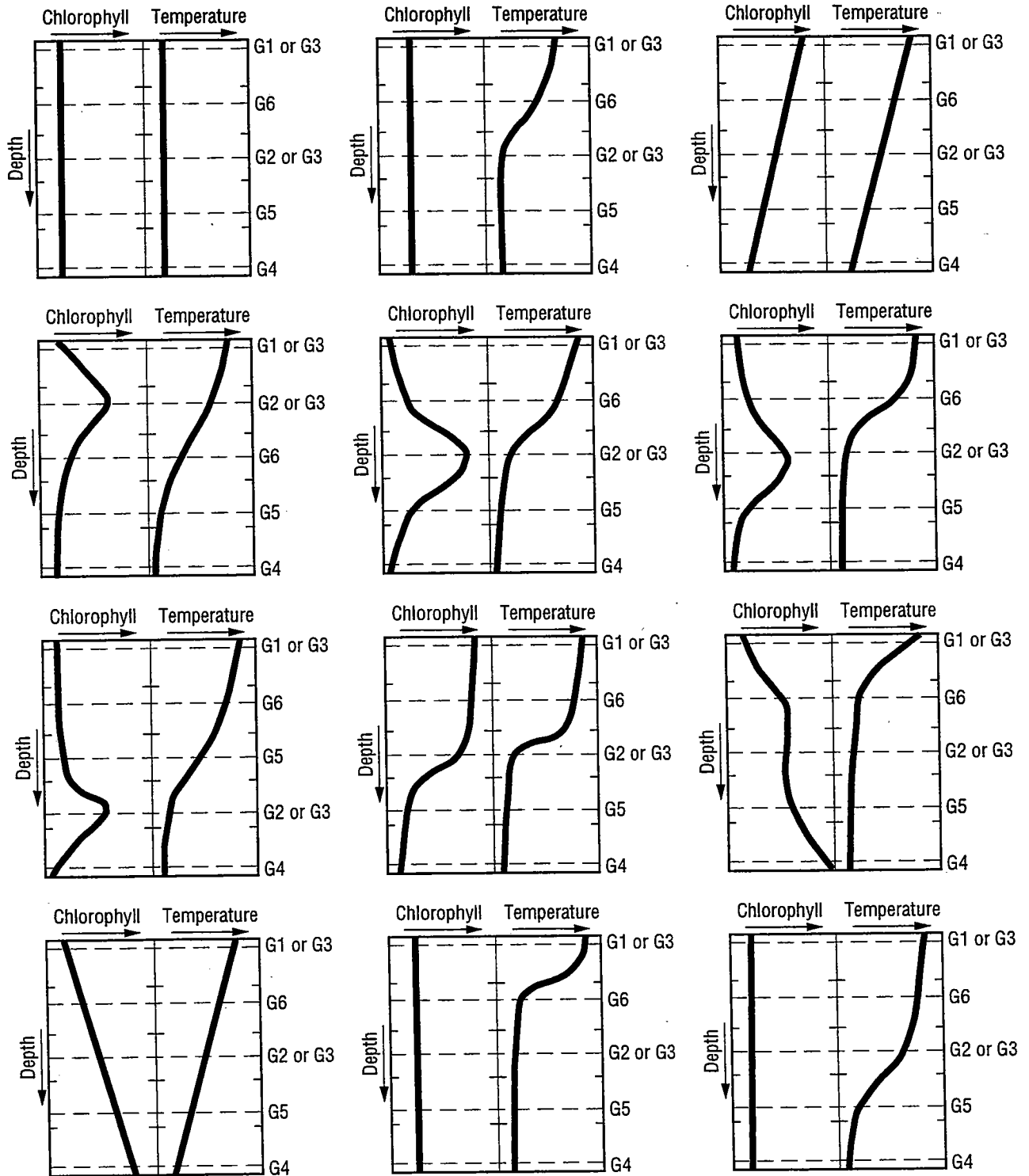
Seabird software acquires data from all onboard electronic sampling systems and navigation systems. The software queries the sampling system 24 times per second and the navigation system once every 2 seconds. The Seabird Seasoft data acquisition program will then average the 24-Hz data. Typically the software will be set to average the data to 4-Hz. The software displays four selected parameters on an x-y plot once per second on a color monitor. Navigation data is also displayed on the Northstar screen. Once the sensor data are acquired, they are automatically written to a data file and logged concurrently with position data from the navigation system. The Northstar unit also displays navigation aids, sampling stations, and vessel track. The Northstar screen will be available to the helmsman as a steering display. During hydrocast operations, position fixes will be electronically recorded at 2-s intervals.

Water samples for chemical analysis, plankton enumeration and taxonomy, and respiration/production analyses will be obtained with a SeaBird 32 Carousel water sampling system equipped with 10-L Niskin bottles. The rosette system is combined with the hydrographic profiling system. The following water sampling/hydrographic profiling procedures will be used:

1. Before the start of each cast, each of the Niskin bottles will be opened and attached to the rosette triggering system.
2. With the vessel positioned about 300 m upwind of the station position and the deployment side of the boat toward the sun during the downcast and the vessel situated parallel to the oncoming waves, the Seasoft software program will be set to the hydrographic profiling

mode and a data cast file will be opened. Safety issues are of overriding concern in vessel positioning, thus it may not always be possible to prevent shading of the CTD near the surface.

3. The Seasoft software acquires data from the equipment while the underwater unit is on-deck prior to deployment. The operator reviews the sensor data to verify that all sensors have reasonable readings (e.g., both irradiance sensors are uncovered and beam attenuation less than 0.5/m). These on-deck readings will be used to adjust the depth offset and match the irradiance sensors).
4. After a successful on-deck checkout, the CTD system will be lowered into the water until completely submerged.
5. After the CTD system has been submerged for 2-4 min to allow all of the sensors to equilibrate, the system will be lowered at a descent rate of about 0.5 m/s to within 3-5 m of the bottom.
6. During the lowering, the Seasoft software will record the hydrographic data and display these data on a computer screen. The Chief Scientist will then review the real-time display of data to determine the five water-collection depths that are based on positions relative to a subsurface chlorophyll maximum determined with the *in situ* fluorometer (see Figure 14 for examples of selection criteria). The twelve plots show chlorophyll and temperature profiles and positions of each type of protocol sampling.
7. During the upcast, the rosette will be maintained at each of the selected five depths until the sensor readings stabilize. Typically this is 30-60 seconds. Water will be collected by closing one or more Niskin bottles, depending on the amount of water needed. Using the Seabird software system, the Niskin bottles will be electronically closed. When the software indicates that the Niskin bottles are closed, this event will be electronically flagged in the Seasoft data file so that a precise vessel position and the concurrent *in situ* water column parameters (salinity, temperature, turbidity, DO, chlorophyll *a*, irradiance, and depth) will be linked to a particular water sample. Labeling software will generate bar-coded sample bottle labels for attaching to sample bottles. These labels are uniquely identified by a bottle ID.



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FIGURE 14
Criteria for Selecting Sample Depths, Station Types A, C, D

8. After collecting the near-surface water sample, the operator will close the cast file. In the event that a Niskin did not close properly, the Chief Scientist will determine whether a re-cast is necessary.
9. The CTD system will be recovered.
10. The Maptech software program will be put into navigation mode with a file created for transit to the next station.

12.2 Zooplankton Sampling

After water sample collection, a vertical oblique zooplankton tow will be conducted with a 0.5-m diameter, 102- μ m mesh net equipped with a General Oceanics flow meter. Tows will be in a vertical-oblique fashion, with just enough headway to keep the net stretched out. Tows will be made over about the upper 30 m (or less, at shallow stations). Net clogging is indicated when the flow meter stops turning under water. In the event that the meter is observed to have stopped spinning as the net nears the water surface, the net will be emptied, washed and re-towed. The net will be pulled faster to make the tow more vertical. If that fails, the tow will be restricted in depth. The depth of each tow will be recorded along with the flow meter counter value.

Contents of sample nets will be washed into a jar to collect all material. The sample will be preserved immediately with a 5-10% buffered formalin:seawater solution. All zooplankton samples will be stored at ambient temperature in the dark.

12.3 Onboard Sample Processing

12.3.1 Dissolved Inorganic Nutrients

A 60-mL aliquot will be obtained from a 1-L sample bottle using a 60-ml acid-washed, sample-rinsed plastic syringe. An inline filter with a 25-mm 0.45 μ m Poretics Mixed cellulose ester (MCE) or Millipore Type HA membrane filter will then be placed on the syringe and 5 mL passed through the filter into the nutrient sample vial to rinse the filter and vial. Alternatively, a peristaltic pump will be used to pump the sample from the sample bottle, through the inline filter and into the nutrient sample vial. After rinsing the sample vial twice, the remaining sample will be filtered into the vial. Five drops of chloroform will be added to preserve the sample which will then be capped and gently shaken. The vial will be labeled

and stored on ice for later return to the lab. These samples will later be analyzed for all the inorganic nutrients using a Lachat QuikChem 8000 Ion analyzer.

12.3.2 Dissolved Organic Carbon

About 50 mL of sample will be passed manually with a syringe through a pre-ashed (425°C) Whatman GF/F glass fiber filter. The filtrate will be retained in 40-mL vials preloaded with H₂SO₄.

12.3.3 Total Dissolved Nitrogen and Phosphorus

A 20-mL aliquot will be obtained from a 1-L sample bottle using a 20-mL acid-washed sample-rinsed plastic syringe. An inline filter holder with a 25-mm 0.45µm Poretics Polycarbonate track-etch (PCTE) screen membrane filter will then be placed on the syringe. 5 mL will be passed through the filter into the 22-mL Teflon® digestion vial to rinse the filter and vial. After rinsing the digestion vial twice, exactly 10 mL will then be filtered into the digestion vial. Alternatively, a peristaltic pump will be used to pump the sample from the sample bottle, through the inline filter and into the digestion vial. Using a digital macropipet exactly 10 mL will be measured from the digestion vial, the excess will be removed, and then only the 10 mL will be returned to the digestion vial. Persulfate oxidizing reagent (2 mL) will then be added to the vial and the vial will be tightly capped. Within 16 hours (at the end of each day's sampling), the sample will be digested by heating the tubes in a pressure cooker at 110-115°C for at least one hour. Samples may be stored at room temperature until later analysis of the resulting nitrate and phosphate.

12.3.4 Particulate Carbon and Nitrogen

Two 300-500 mL aliquots (measured with a graduated cylinder) will be filtered through pre-combusted (at 500°C) 25-mm Whatman GF/F glass fiber filters held in a plastic filter funnel using a vacuum of no more than 10-12 inches of Hg. It may be necessary to vary the actual amount filtered depending on the water turbidity. After the sample passes through the filter, the funnel and filter will be rinsed with less than 10 mL of filtered seawater. Using stainless steel forceps, the filter will be then placed into a labeled clean plastic petri dish, which will be taped shut, placed in a labeled plastic bag and kept on ice until it can be frozen. The actual volume filtered will be recorded in a laboratory notebook and on the sample label.

12.3.5 Particulate Phosphorus

A 200-mL aliquot (measured with a graduated cylinder) will be filtered through a 25-mm Whatman GF/F glass fiber filter held in a plastic filter funnel (Gelman #4203) using a vacuum of no more than 10-12

inches of Hg. It may be necessary to vary the actual amount filtered depending on the water turbidity. After the sample passes through the filter, the funnel and filter will be rinsed with less than 10 mL of filtered seawater. Using stainless steel forceps, the filter will then be placed into a labeled clean plastic petri dish, which will be taped shut, placed in a labeled plastic bag and kept on ice until it can be frozen. The actual volume filtered will be recorded in a laboratory notebook and on the sample label.

12.3.6 Biogenic Silica

A 200-mL aliquot (measured with a graduated cylinder) will be filtered through a 25-mm Poretics 0.4-0.45 μm pore size polycarbonate filter held in a plastic filter funnel (Gelman #4203) using a vacuum of no more than 10-12 inches of Hg. It may be necessary to vary the actual amount filtered depending on the water turbidity. After the sample passes through the filter, the funnel and filter will be rinsed with less than 10 mL of filtered seawater. Using stainless steel forceps, the filter will then be placed into a labeled pre-oxidized high density polyethylene digestion vial and stored at room temperature in a labeled plastic bag. The actual volume filtered will be recorded in a laboratory notebook and on the sample label.

12.3.7 Chlorophyll *a*

Approximately 300-500 mL of seawater will be filtered through 25-mm Whatman GF/F glass fiber filters held in a plastic filter funnel using a vacuum of no more than 10-12 inches of Hg. It may be necessary to vary the actual amount filtered depending on the water turbidity. After the sample passes through the filter, the funnel and filter will be rinsed with less than 10 mL of filtered seawater. Using stainless steel forceps, the filter will then be folded and placed into aluminum foil which will be folded, taped shut, placed in a labeled plastic bag and kept on ice until it can be frozen. The actual volume filtered will be recorded in a laboratory notebook and on the sample label.

12.3.8 Total Suspended Solids

Approximately 1000 mL of seawater will be withdrawn from each Niskin bottle and placed in a 1000-mL polyethylene sample bottle. The bottles will be stored on ice for filtration and analysis at the laboratory.

12.3.9 Dissolved Oxygen (DO)

Samples for DO analysis will be collected in 300-mL BOD bottles at a maximum of four depths (surface, middle, mid-bottom, bottom). Tubing (about 50 cm) will be attached to the nipple on the Niskin bottle and inserted to the bottom of the BOD bottle. The bottle will be placed in an overflow container which

has a volume 3-4 times greater than the BOD bottle. The BOD bottle will be filled and allowed to overflow until the overflow container is full. Samples will be fixed with manganous sulfate and alkaline iodide azide as described in EPA method 360.2. Samples will then be shaken gently and a squeeze bottle will be used to add water along the joint of the bottle/stopper prior to storage.

12.3.10 Urea

A 50-mL aliquot will be filtered through a polycarbonate filter into a cleaned and acid-washed 50-mL polyethylene container. The samples will be stored on ice during the cruise and frozen to -20°C upon return to the laboratory until analysis.

12.3.11 Respiration

Water will be collected in six 300-mL BOD bottles at each of three depths (surface, middle, bottom) directly from the Niskin bottles as described earlier for DO. The bottles will be incubated in the dark, in temperature controlled incubators that are maintained to within 2°C of *in situ* temperature. Triplicate bottles from each depth will be fixed with the Winkler reagents manganous sulfate, alkaline iodide-azide, and sulfamic acid to obtain the zero time oxygen concentration and to begin timing of the incubation. The fixed bottles will be stored in the dark on ice until analysis at the WHOI laboratory. After approximately 3-7 days incubation, the remaining three unfixed samples will be fixed with the above reagents and stored as above until analysis. The exact incubation time will depend upon incubation temperature (lower temperature, longer incubation) and will be recorded.

12.3.12 Production Analyses by ^{14}C

From each of the five productivity depths at each productivity station, samples will be obtained from the Niskin bottles into opaque 1-gallon polyethylene bottles. Under green light, sub-samples will be transferred by siphon through 300-um Nitex screen (to remove zooplankton) into individual 75-mL acid cleaned polycarbonate bottles. Each bottle will be flushed with approximately 250 mL of sample. A total of 16 bottles (14 light bottles, 2 dark bottles) will be filled for each depth, 5-12 μCi ^{14}C -bicarbonate added (higher activity during winter and spring season) and the bottles incubated in a controlled light and temperature incubator. Light bottles from each depth will be incubated at 14 light intensities (using neutral density filters). Irradiance within the incubator will be measured with a light sensor. All bottles will be incubated within 2°C of the *in situ* temperature at each depth for 4-6 hr (actual time will be recorded). Single bottles of sample collected from each depth will be assayed for background (time-zero) activity.

Biological activity in the 75-mL incubated samples will be terminated by filtration of the entire contents of the bottles through 2.5-cm diameter Whatman GF/F glass fiber filters and immediate contact of the filters with 0.2 mL of a 20% aqueous solution of acetic acid contained in pre-prepared 20-mL glass scintillation vials (vials immediately recapped). For specific activity determination, 0.1-mL aliquots of sample will be placed in pre-prepared 20-mL scintillation vials containing 0.2 mL of benzethonium hydroxide (approximately 1.0 M solution in methanol; Sigma Chemical Company) to covalently sequester the ^{14}C inorganic carbon (vials immediately recapped).

During summer months the ^{14}C incubations may be incubated on shore in the MWRA laboratory at Deer Island. Samples will be collected in opaque bottles and maintained at *in situ* temperature until transport to the lab. The ^{14}C incubations will be begun approximately 2-3 hr from sample collection and should compare favorably with samples that are incubated aboard the ship.

Chlorophyll a determinations. Niskin samples from each depth (300-600 mL) will be filtered through 4.5-cm, 0.22- μm Millipore filters for chlorophyll *a* analysis. When approximately 20 mL of sample remains to be filtered, 3-4 drops of saturated aqueous magnesium carbonate will be added. Each filter will be briefly rinsed with 1-2 mL filtered seawater and placed into 7-mL screw topped vial and stored on ice for transport the WHOI laboratory where it will be then frozen at -20°C until analyzed.

DIC analyses. Samples for DIC analysis will be collected from the Niskin bottles into 300-mL BOD bottles, following collection procedures used for oxygen analyses. Within 6 hr of BOD sample collection, duplicate 10-mL samples will be injected into 20-mL crimp-sealed serum bottles containing 0.5 mL of a 2N aqueous solution of sulfuric acid for subsequent I.R. analysis (Beckman IR-315 infrared analyzer) of the gaseous phase (5-150- μL subsamples analyzed) at the WHOI laboratory.

12.3.13 Phytoplankton and Screened Phytoplankton

For the whole-water phytoplankton analyses, 1 L will be withdrawn from Niskin bottles and preserved immediately with Utermohl's solution. Utermohl's solution contains 100 g of potassium iodide, 50 g of iodine, and 50 g of sodium acetate, each dissolved incrementally in equal fractions of distilled water to make a final volume of 1 L. All phytoplankton samples will be stored at ambient temperature in the dark.

For screened phytoplankton analyses, 2-L water samples taken from the Niskin bottles will be strained through a 20- μm -mesh screen. The retained organisms will be washed into a jar with a small volume of pre-screened seawater and then preserved with 5-10% buffered formalin. These samples will be stored at ambient temperature in the dark.

12.4 Laboratory Sample Processing and Analysis

12.4.1 Dissolved Inorganic Nutrients

The concentrations of ammonium, nitrate, nitrite, phosphate, and silicate will be determined on the filtered and preserved samples using a Lachat QuikChem 8000 Ion Analyzer. This analyzer uses flow injection analyses (FIA) to automate standard manual or AutoAnalyzer nutrient analyses techniques. After the samples are warmed, they will be shaken gently prior to the analyses. The analysis of ammonium (Lachat, 1994a) will be based on the Berthelot reaction whereby absorbance of an indophenol blue complex is measured at 630 nm. Nitrite will be measured by the method of Bendschneider and Robinson (1952) automated for FIA (Lachat, 1994b). The total of nitrate and nitrite will be determined by reducing all nitrate in the sample to nitrite and analyzing for nitrite as above. The concentration of nitrate will be obtained by difference. The reduction will be accomplished using a cadmium column (Morris and Riley, 1963) and automated for FIA by Lachat (1994b). The analysis of phosphate will be based on the molybdate-blue procedure of Murphy and Riley (1962) automated for FIA by Lachat (1994c). Finally, the analysis of silicate (Lachat, 1993) will be based on formation of a silicomolybdate complex which is reduced with stannous chloride (Truesdale and Smith, 1976). All samples will be compared to 3 in 4 calibration standards made up in low nutrient seawater diluted to match the sample salinities.

12.4.2 Dissolved Organic Carbon

Dissolved organic carbon will be determined by persulfate digestion (Method 415.1; EPA, 1983) using a Dohrmann DC 80 analyzer.

12.4.3 Dissolved Organic Nitrogen and Phosphorus

The method of Valderrama (1981) will be used to determine the concentrations of total dissolved nitrogen and phosphorus. This wet-chemical technique utilizes persulfate to oxidize organic nitrogen and phosphorus to nitrate and phosphate. The concentrations of the latter are then determined using standard nutrient analyses for nitrate and phosphate as described above. The concentration of dissolved organic nitrogen or phosphorus is then determined by difference between total dissolved inorganic plus organic and total dissolved inorganic nitrogen and phosphorus.

12.4.4 Particulate Carbon and Nitrogen

Methods for the analysis of particulate carbon and nitrogen are described by Lambert and Oviatt (1986). Particulate matter collected on a glass-fiber filter will be ignited at high temperature (1050°C) in a Perkin Elmer Model 2400 CHN elemental analyzer. The combustion releases total carbon and nitrogen in gaseous form. These products will be quantified by the analyzer using gas chromatography with a thermal conductivity detector.

12.4.5 Particulate Phosphorus

The particulate phosphorus filter will be placed into a labeled glass petri dish and ignited in a muffle furnace at 520°C for 1-2 hr. Then the filter will be transferred to a 50-mL centrifuge tube and 1 mL of 10% HCl is added to hydrolyze the phosphorus for 24 hr. The sample will be then diluted with 19 mL of deionized water, mixed, and the glass fibers allowed to settle for several hours. The supernatant will be then transferred to a acid-washed sample vial for the standard nutrient phosphate analysis using a Lachat QuikChem 8000 Ion Analyzer (Lachat, 1994c) and the particulate phosphorus concentration calculated based on the volume filtered.

12.4.6 Biogenic Silica

Biogenic silica will be analyzed using the method of Krausse *et al.* (1983). Biogenic silica on the filter will first be dissolved by adding 4 mL of 0.2M NaOH to the high density polyethylene digestion vial and heating the vial in boiling water for 10-15 minutes. The vial will be then removed from the water and 1 mL of 0.5M H₂SO₄ will be added to neutralize the sample and stop the dissolution of non-biogenic silicate. The sample will be then diluted with deionized water and analyzed for reactive silicate with the standard nutrient silicate analysis utilizing a Lachat QuikChem 8000 Ion Analyzer (Lachat, 1993) and the biogenic silica concentration calculated based on the volume filtered.

12.4.7 Chlorophyll *a*

At E3I, the concentrations of chlorophyll *a* and phaeophytin will be determined fluorometrically using a Perkin-Elmer fluorometer using Standard Method 10200H (APHA, 1992). Chlorophyll and phaeophytin concentrations will be calculated using the equations of Lorenzen (1966):

$$\text{Chla } (\mu\text{g/L}) = \frac{\frac{F_0}{F_{a \text{ max}}} (K_x)(F_0 - F_A) \frac{V_E}{V_F}}{\frac{F_0}{F_{a \text{ max}}} - 1}$$

$$\text{Phaeophytin } (\mu\text{g/L}) = \frac{\frac{F_0}{F_{a \text{ max}}} (K_x) \left(\frac{F_0 F_A}{F_{a \text{ max}}} - F_0 \right) \frac{V_E}{V_F}}{\frac{F_0}{F_{a \text{ max}}} - 1}$$

where:

- F_0 = fluorescence before acidification
- F_a = fluorescence after acidification
- $F_0/F_{a \text{ max}}$ = maximum acid factor expected from pure chlorophyll *a*
- K_x = calibration constant for a particular sensitivity scale
- V_F = volume filtered in liters
- V_E = volume of extracted chlorophyll *a*

At the WHOI laboratory, the filters for chlorophyll *a* and phaeophytin analysis will be cold-extracted using 10 mL of ice cold 90% acetone. The absorbance of the solution will be measured with a B&L Spectronic 2000 at several wavelengths before and after acidification, and will be applied to the trichromatic equations in Parsons *et al.*, 1989 (equivalent to the equations above) for computing chlorophyll *a* and phaeophytin concentration.

12.4.8 Total Suspended Solids

To determine TSS, the weight of material suspended in seawater is obtained by filtering an appropriate volume (up to 1 L) through a pre-weighed 25-mm Whatman GF/F glass fiber filter. The filter will be rinsed with deionized water to remove salt, dried to constant weight at 140°C, and reweighed. All weighings will be performed on an analytical balance.

12.4.9 Dissolved Oxygen

DO concentrations will be measured using the Winkler titration method (Method 360.2; EPA, 1983) using manual titration.

12.4.10 Urea

Samples will be analyzed for urea using an Alchem autoanalyzer according to the methods of Rahmatullah and Boyd (1980) and Aninot and Kerouel (1982).

12.4.11 Respiration

At the WHOI laboratory, 100 ml aliquots of each of the Winkler reagent-fixed samples will be analyzed according to Outdot *et al.* (1985) using an automated Radiometer TitraLab titrator.

The rate of oxygen consumption will be calculated using the method described by Strickland and Parsons (1972). The corresponding initial DO samples will be used in the calculation. The net respiration (NETR) in units of mg O₂ L⁻¹h⁻¹ will be determined using the following equation:

$$\text{NETR} = \frac{(\text{DO}_{\text{IB}} - \text{DO}_{\text{DB}})}{\text{T}}$$

where DO_{IB} = Initial DO concentration in mg O₂ L⁻¹
DO_{DB} = Dark Bottle DO concentration in mg O₂ L⁻¹ after incubation
T = Incubation time in hours

12.4.12 Production Analyses by ¹⁴C

Sample processing. Upon arrival to the WHOI laboratory, scintillation cocktail (10 ml Scintiverse II) will be added to the scintillation vials containing the specific activity samples and analyzed using a Packard Tricarb 4000 liquid scintillation counter which possesses automated routines for quench correction. Vials containing acidified filters will be opened and placed in a ventilator in the hood for 24-48 hr to allow the filters to dry and excess ¹⁴C carbon dioxide to dissipate. The vials containing the filters will be analyzed by scintillation spectroscopy as described above.

Calculation of Primary production. Volume specific primary production will be calculated using equations similar to that of Strickland and Parsons (1972) as follows:

$$P(i) = \frac{1.05(DPM(i) - DPM(blk))}{V_s A_{sp} T}$$

$$P(d) = \frac{1.05(DPM(d) - DPM(blk))}{V_s A_{sp} T}$$

$$A_{sp} = \frac{DPM(sa) - DPM(back)}{V_{sa} DIC}$$

where:

P(i) = primary production rate at light intensity i, (ugC L⁻¹h⁻¹ or mgC m⁻³h⁻¹)

P(d) = dark production, (ugC L⁻¹h⁻¹ or mgC m⁻³h⁻¹)

A_{sp} = specific activity (DPM/ugC)

DPM(i) = dpm in sample incubated at light intensity i

DPM(blk) = dpm in zero time blank (sample filtered immediately after addition of tracer)

DPM(d) = dpm in dark incubated sample

DPM(back) = background dpm in vial containing only scintillation cocktail

DPM(sa) = dpm in specific activity samples

V_s = volume of incubated sample (L)

T = incubation time (h)

V_{sa} = volume counted of specific activity sample (mL)

DIC = concentration of dissolved inorganic carbon (ug/mL)

P-I curves. For each of the 5 depths for each photosynthesis station a P-I curve will be obtained from the data P(I) = P(i)-P(d) vs. the irradiance (I, uE m⁻²s⁻¹) that the incubating sample is exposed. The P-I curves will be fit via one of two possible models, depending upon whether or not significant photoinhibition occurs. In cases where photoinhibition is evident the model of Platt *et al.* (1980) will be

fit (SAAM II, 1994) to obtain the theoretical maximum production, and terms for light-dependent rise in production and degree of photoinhibition:

$$P(I) = P_{sb}(1 - e^{-a})e^{-b}$$

where:

$P(I)$ = primary production at irradiance I , corrected for dark fixation ($P(i) - P(d)$)

P_{sb} = theoretical maximum production without photoinhibition

$a = \alpha / P_{sb}$, and α is the initial slope the light-dependent rise in production

$b = \beta / P_{sb}$, and β is a term relating the degree of photoinhibition

If it is not possible to converge upon a solution, the model of Webb *et al.* (1974) will be similarly fit to obtain the maximum production and the term for light-dependent rise in production:

$$P(I) = P_{max}(1 - e^{-a'})$$

where:

$P(I)$ = primary production at irradiance I corrected for dark fixation ($P(i) - P(d)$)

P_{max} = light saturated maximum production

$a' = \alpha / P_{max}$, and α is the initial slope the light-dependent rise in production

Light vs. depth profiles. To obtain a numerical representation of the light field throughout the water column bin averaged CTD light profiles (0.5 m intervals) will be fit (SAAM II, 1994) to an empirical sum of exponentials equation of the form:

$$I_z = A_1 e^{-a_1 z} + A_2 e^{-a_2 z} + \dots$$

which is an expansion of the standard irradiance vs. depth equation:

$$I_z = I_0 e^{-kz}$$

where:

I_z = light irradiance at depth Z

I_0 = incident irradiance ($Z=0$)

k = extinction coefficient

$A_1, A_2 \dots$ = factors relating to incident irradiance ($I_0 = A_1 + A_2 + \dots$)

$a_1, a_2 \dots$ = coefficients relating to the extinction coefficient ($k = a_1 + a_2 + \dots$)

The expanded equation will be used in most instances as pigment absorption and other factors result in deviation from the idealized standard irradiance vs. depth equation. The simplest form of the expanded equation will be implemented to adequately model the light field, which in the large majority of cases will be the sum of two exponentials.

Daily incident light field. During normal CTD hydrocasts the incident light field is routinely measured via a deck light sensor at high temporal resolution. The average incident light intensity will be determined for each of the CTD casts to provide, over the course of the photoperiod (12-hr period centered upon solar noon), a quite well resolved irradiance time series consisting of 12-17 data points. A 48-point time series (every 15 min) of incident will be obtained from these data by linear interpolation.

Calculation of daily primary production. Given the best fit parameters (P_{sb} or P_{max} , a , b) of the P-I curves obtained for each of the five sampling depths, the *in situ* light intensity (i.e., I_z) at each depth determined from the sum of exponential fits of the *in situ* light field, and the photoperiod incident light (I_0) time series, it will be possible to compute daily volumetric production for each depth. To do this at a given depth, hourly production is determined for the *in situ* light intensity computed for each 15 min interval of the photoperiod, using the appropriate P-I parameters and *in situ* irradiance. Daily production ($\mu\text{gC L}^{-1}\text{d}^{-1}$) is obtained by integration of the determined activity throughout the 12-hr photoperiod. An advantage of this approach is that seasonal changes in photoperiod length are automatically incorporated into the integral computation. For example, during winter months computed early morning and late afternoon production contributes minimally to whole day production, whereas during summer months the relative contribution during these hours is more significant. The investigator does not have to decide which factor to employ when converting hourly production to daily production. The primary assumption for the approach is that the P-I relationship obtained at the time of sample procurement (towards the middle of the photoperiod) is representative of the majority of production occurring during the photoperiod, which should be the case.

Calculation of daily areal production. Areal production ($\text{mgC m}^2\text{d}^{-1}$) will be obtained by trapezoidal integration of daily volumetric production vs. depth down to the 1% light level.

Calculation of chlorophyll-specific parameters. Chlorophyll-specific measures of the various parameters (including the P-I parameters) will be determined by dividing by the appropriate chlorophyll term obtained from independent measurements.

12.4.13 Whole-Water Phytoplankton

Phytoplankton taxonomic identification and enumeration will be carried out using inverted microscopy and a modified Utermohl sedimentation technique (Hasle, 1978). For whole-water samples (Task 15.1.1), the sample will first be homogenized by repeated inverting of the sample bottle. An aliquot of sample (typically 50-100 mL) will be transferred into a settling chamber which consists of a volumetric acrylic cylinder and a counting chamber equipped with an ultra-thin glass baseplate. After 48-72 hr of gravitational settling, the cylinder will be displaced by a cover glass and the concentrated phytoplankton sample in the base plate examined using a Leitz Diavert inverted microscope equipped with phase-contrast illumination. The phase-contrast microscopy will be employed to enhance cell morphology and ultrastructure to facilitate taxonomic definition. Each annulus in the phase condenser will be aligned for its corresponding objective through the use of a phase telescope eyepiece.

Samples will be counted at two magnifications, typically 500x and 312x. The higher magnification will enable identification of smaller taxa while examination of a relatively larger area with the lower magnification will permit quantification of relatively large, rarer forms which might not be retained by the 20- μ m mesh used for the screened-water samples.

A minimum of 20 random fields and 400 individual cells per sample will be counted at the higher magnification. If 400 cells are not found in the initial 20 fields, additional fields will be counted until the 400 cell minimum is achieved. For the lower magnification, a total of 20 random fields will be counted without the 400 cell minimum requirement. While individual cells will be counted at both magnifications, notations will be made regarding the relative occurrence of chain-forming and other colonial forms. These observations will facilitate interpretation of the data.

All phytoplankton cells will be identified to the lowest practical taxonomic level, typically to the species level. Taxonomic identifications and raw counts will be directly entered into a computer using NODC codes and software which will subsequently convert the data to cell density per liter. Phytoplankton densities will be calculated as follows:

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$$\frac{\# \text{ cells}}{\text{liter}} = \frac{\# \text{ cells counted}}{\# \text{ fields} \times \text{vol/field (mL)}} \times \frac{1000 \text{ mL}}{1 \text{ L}}$$

The volume per field is a function of field area (determined by magnification and the individual optical setup of each microscope) and the volume of whole water sample concentrated. For example, for microscope "A" at a magnification of 312x, the area of the chamber bottom is equivalent to the area of 1380 fields. For a typical concentrated volume of 50 mL, therefore, the volume per field is equal to 0.04 mL. The field area for each microscope in the laboratory has been calibrated for each magnification using a stage micrometer. Data entry software has been developed for each microscope which accurately converts raw cell counts to densities per liter of original sample.

The cell densities calculated in the counting program will also be converted to biomass estimates (carbon/liter) through the application of ANS's program which estimates carbon content for individual taxa based on biovolume. Periodic size measurements of dominant taxa shall be taken to calibrate biovolume estimates to Massachusetts Bay taxa. The eyepiece micrometer used to take these measurements will be calibrated using a stage micrometer.

Quality control procedures will include weekly examination of blanks (dilution water, if used, and cleaned counting chambers) to ensure against artifacts, and examination of settling chamber supernatant to ensure that all cells were adequately settled. Intra-laboratory QA counts will be performed on 5 percent of the total number of samples to ensure accuracy for taxonomic identification and cell densities. Upon completion of analysis, all phytoplankton samples will be concentrated by gravitational settling, transferred into 30-mL screw-capped test tubes, and archived for the contract period. Utermohl's solution will be added to the archived samples as needed (based on visual examination of samples) to replace loss due to volatilization.

12.4.14 Screened Phytoplankton (Dinoflagellates)

Analysis of screened-water samples for dinoflagellate species (Task 15.1.2) will also be performed using inverted microscopy. For these concentrated samples, a smaller volume of sample is settled in a 10-mL or 25-mL settling chamber and examined with the Leitz Diavert (or equivalent) at 312x until 20 random fields and a minimum of 200 individual cells have been enumerated. Higher magnifications will be used (as necessary) to determine cell structures which are required for taxonomic identification. A low-power sweep of the entire chamber will be performed to quantify large rare taxa.

Particular attention will be paid to bloom forming dinoflagellates (*Alexandrium tamarense*, *Ceratium*, *Dinophysis*, *Gymnodinium*, *Gyrodinium*, *Heterocapsa triquetra*, *Prorocentrum*, *Protoperidinium*, *Heterosigma akashiwo* (formerly *Olisthodiscus luteus*), and *Phaeocystis pouchetti*) and other taxa not enumerated in the whole water samples. Calculations are similar to those for the whole seawater sample and are based on the number of organisms counted corrected for the concentration factor.

12.4.15 Zooplankton

Screened zooplankton samples will be processed to facilitate counting of at least 250 animals. Subsampling will be performed using Hensen-Stempel pipette or a Folsom plankton splitter, depending on organism densities. Samples will then be counted in a zooplankton counting wheel using a Wild dissecting microscope. Identification will be to species level where possible using the NODC species list. Adult copepods will be identified to species, and copepodite and naupliar stages will be grouped. Intra-laboratory QA counts will be performed on 5 percent of the total number of samples to ensure accuracy for taxonomic identification and cell densities. Species and total densities (number/m³) for each sample will be calculated based on the number of individuals counted in the subsample, the subsample volume, and the concentration factor derived from the net tow.

12.5 Whale Observations

As part of every nearfield survey, observers from the Manomet Observatory will conduct sighting watches while on station and during transit between stations. The observer will scan the ocean surface by eye for 40 minutes every hour. All sightings will be recorded on standardized marine mammal field sighting logs. Header fields for sighting logs will include: observer name, time, date, weather, wind speed, sea state, vessel name, heading and speed. Data fields on sighting logs will include: vessel position every 5 minutes, time, observer position on vessel, sighting event code (on or off watch, transiting or on station), compass bearing to mammal, species name, number of animals, behavior, and sighting cue code.

13.0 SAMPLE CUSTODY

Samples collected in the field will be identified by a unique nine character *Sample_ID* which is a concatenation of *Event_ID_4*, a four character version of *Event_ID*, and a five character *Marker_No*. The *Sample_ID* will identify the water collected in the Niskin bottles from a certain depth during a particular cast at a given station on the specified survey. The five character *Event_ID* will be unique to each survey, such as W9508, with the "W" indicating that it is a water survey, "95" indicating the survey year, and "08"

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indicating that it is the eighth survey of the year. The four character *Event_ID_4* will be also unique for a survey, and will be formed by shortening the survey number to one character by using the letter designations A-I for surveys 10 through 17 (e.g. W9508 becomes W958 and W9514 becomes W95E, see Table 11 for an example). The *Marker_No* will be a five character code indicating the cast number at a particular station during this survey, the *Station_ID* (e.g., N16, F23), and depth of the sample (A, B, C, D, and E for surface, mid-surface, middle, mid-bottom, and bottom). Thus a *Marker_No* = 2N16A represents the water collected at the surface during the second cast at station N16.

Each portion of a sample separated for analytical purposes will be assigned a unique *Bottle_ID*, composed of the nine-character *Sample_ID* plus a 2 to 6-character suffix designating the nature and purpose of the subsample. For example, "T7" indicates that the subsample is a triplicate for chlorophyll and phaeopigment analysis. Information relating to each sub-sample will then be recorded in the *Bottle* table in the EM&MS database (see Section 15 for table format).

Before the field surveys are initiated, a checklist of all samples to be collected will be prepared. At each station, water from five depths will be sampled for various analyses. To identify the group of analyses at a particular station and depth, a protocol coding system has been developed specifically for this project. Each analysis group is a unique combination of the laboratory analyses (Table 3). Different sets of analysis groups, depending on the station type, are combined to sample the five depths at a particular station (Tables 2 and 4). Based on this information, one set of station logs (described below) and four sets of chain-of-custody (COC) forms (one for each lab) will be generated for each survey. Manual entries will be recorded in indelible ink. Each completed form will be signed and dated by the staff member entering the information.

The scientific crew member operating the data collection system will fill out the station log (see Figure 15) at each station. These logs will be put into a survey notebook prior to the survey. The log includes fields for entering pertinent information about each station, such as time on station, bottom depths, weather observations, sample identification numbers, and general comments. During the hydrocast CTD data will be logged and stored electronically on the computer's hard disk. When a Niskin bottle is closed, a flag will be entered into the CTD data file.

At the end of a profile, computer software written by ENSR (ML) will be run to query the CTD data file and to record information written onto the station log (e.g. *Station_ID*, arrival time, water depth). The software will then save the following information in a number of data files:

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**TABLE 11
Bottle_ID Formation**

Survey Designation		Marker_No			Resample Suffix							
Event_ID	Event_ID_1	Cast	Station_Id	Set	Depth	Code	Field Duplication	Analysis	Code	Subsample	Code	
W9501	W951	1	N16	1	Surface	A	Sample	S	DIN	1	1st Subsample	1
W9502	W952	2	.	1	Mid-surface	B	Duplicate	D	DOC	2	.	
W9503	W953	3	.	1	Middle	C	Triplicate	T	TDN/TDP	3	.	
W9504	W954	4	.	1	Mid-bottom	D	Quadruplicate	Q	PC/PN	4	.	
W9505	W955			1	Bottom	E	5th Replicate	5	Particulate P	5	9th Subsample	9
W9506	W956			2	Surface	F	.	.	Biogenic Silica	6	10th Subsample	10
W9507	W957			2	Mid-Surface	G	.	.	Chl & Phae	7	.	
W9508	W958			2	Middle	H	.	.	TSS	8	.	
W9509	W959			2	Mid-bottom	I			DO	9	.	
W9510	W95A			2	Bottom	J			Urea	A	35th Subsample	Z
W9511	W95B								WW Phyto	B		
W9512	W95C								Screened Phyto	C		
W9513	W95D								Zooplankton	D		
W9514	W95E								Photosynthesis	E		
W9515	W95F								Respiration	F		

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**TABLE 11 (Cont'd)
Bottle_ID Formation**

Survey Designation		Marker_No			Resample Suffix						
Event_ID	Event_ID_A	Cast	Station_ID	Set	Depth	Code	Field Duplication	Analysis	Code	Subsample	Code
W9516	W95G										
W9517	W95H										

Examples
 Sample ID: W9582N16A Designation for water collected at the surface depth at station N16 during the second cast on the eighth water quality survey of 1995.
 Resample Suffix: T7 Triplicate chlorophyll & phaeopigment resample
 Bottle ID: W9582N16AT7 Label ID for the bottle containing the triplicate chl & phase resample from the surface depth at N16 during the second cast of W9508.
 Bottle ID: W9582N16JSF Bottle ID for the water collected for water column respiration analysis from the sample W9582N16J (the 2nd cast @ N16 during W9508, the bottom sample of the 2 set of samples collected on that east).
 Bottle ID: W9582N16ASE1 Water taken from sample W9582N16A for primary productivity; the first subsample from this bottle.

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ENSR		STATION LOG			
MWRA Harbor and Outfall Monitoring Program					
Event ID:		Date:		Recorded By:	
Station ID: F01 D		Time on Station:		Time Off:	
Station Location:		On Station Position:			
Latitude: 41 51 .050		Latitude:			
Longitude: 70 27.200		Longitude:			
Depth: 27 m		Depth:			
Weather Observations:		Off Station Position:			
Skies:		Seas:		Latitude:	
Temp:		Wind:		Longitude:	
		Reference Time:		EST	EDT
Sampling Information					
Depth ID	Depth Sampled	Analysis Group ID	Time	Bottles	
Surface					
Mid-Surface					
Middle					
Mid-Bottom					
Bottom					
Zooplankton Tow (Y/N):					
Time:					
Latitude:					
Longitude:					
Depth:					
Count:					

FIGURE 15
Sample Station Log

- Sample_ID's
- Bottle_ID's
- Water Depth and Arrival Time for each "station-cast"
- Beginning and ending Latitude for each station-cast
- Beginning and ending Longitude for each station-cast
- Date and Time of each sample
- Rosette bottle numbers making up each sample
- Latitude and Longitude of each sample
- CTD sensor values for each sample
- Analysis to be performed on each sample
- Container for each analysis
- Laboratory performing each analysis
- Preservation method for each analysis

The information recorded in the data files will be used to create the chain-of-custody record and to create labels that are placed on each bottle and in the station logs. The bottle label will include the Bottle_ID in text and barcode (barcode format 128A), the date, time, and depth of the sample, the analysis, the lab performing the analysis, and the preservative method. The data files saved by the software will also be used later as entry into the *Sample*, *Station*, and *Profile* tables of the EM&MS database (see Section 15 for more information).

The chain of custody forms (Figure 16) will travel with the samples to each particular lab. If the custody of samples is transferred, the custody form will be signed by both the staff member that relinquishes custody and the staff member assuming custody of the samples. Duplicate copies will be generated on board so that signed originals can be given to both parties. After a survey, the chain-of-custody originals will be given to the Database Manager to be placed in the Data Sources Notebook.

13.1 Custody of Electronic Data

Field custody of electronic data will be the responsibility of the chief scientist for a specific survey. This person will be identified in each survey plan. The field custody of the electronic data consists of creating floppy-disk back-ups of all electronic data generated each day. Each floppy disk label will include the Event_ID, date, name of person creating the backup files, and a disk number. When the equipment is returned to ENSR's office, a second complete backup, labeled as "Set 2", will be generated on floppy disks. "Set 2" will be in the custody of the Water Quality Project Area Leader. "Set 1" will be maintained by the *in-situ*/navigation data manager.

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ENSR		CHAIN OF CUSTODY RECORD							
MWRA Harbor and Outfall Monitoring					Event ID: W9515				
Chief Scientist: Jim Bowen					Field Logbook No:				
Signature:					Chain of Custody Tape No:				
Send	Jennifer Chiapella				Analytical	c/o Richard LaCouture			
Results	ENSR				Laboratory	The Academy of Natural Sciences			
To	35 Nagog Pk. Acton, MA 01720				(Destination)	Benedict Estuarine Research Center 10545 Mackall Road, St. Leonard, MD 20685			
Relinquished by:	Date:				Received by:	Date:			
(print name)					(print name)				
Signature	Time:				Signature	Time:			
Relinquished by:	Date:				Received by:	Date:			
(print name)					(print name)				
Signature	Time:				Signature	Time:			
Relinquished by:	Date:				Received by:	Date:			
(print name)					(print name)				
Signature	Time:				Signature	Time:			
#	Cooler	Bottle ID	Date	Time	Analysis	Contain.	Media	Preserv.	Filtered?
1		W95F1N16CSB	Nov 03 1995	10:44:27	AllPhytop	1000 ml PE	water	Utermi	N
2		W95F1N16ASB	Nov 03 1995	10:47:02	AllPhytop	1000 ml PE	water	Utermi	N
3		W95F1N10CSB	Nov 03 1995	17:05:59	AllPhytop	1000 ml PE	water	Utermi	N
4		W95F1N10ASB	Nov 03 1995	17:09:23	AllPhytop	1000 ml PE	water	Utermi	N
1		W95F1N16CSC	Nov 03 1995	10:44:27	ScrndPhyt	250 ml PE	water	formln	Y
2		W95F1N16ASC	Nov 03 1995	10:47:02	ScrndPhyt	250 ml PE	water	formln	Y
3		W95F1N10CSC	Nov 03 1995	17:05:59	ScrndPhyt	250 ml PE	water	formln	Y
4		W95F1N10ASC	Nov 03 1995	17:09:23	ScrndPhyt	250 ml PE	water	formln	Y
1		W95F1N16ASD	Nov 03 1995	10:47:02	Zooplankt	500 ml PE	water	formln	Y
2		W95F1N10ASD	Nov 03 1995	17:09:23	Zooplankt	500 ml PE	water	formln	Y

FIGURE 16
Sample Chain-of Custody Record

13.2 Custody of Water Samples

Subcontractors will assume custody of samples immediately upon sample collection or if necessary (e.g., ANS, E3I), after shipment to the lab. Field documentation will consist of laboratory notebooks, field log sheets, and custody forms containing the project name, station code, sample type designation, and other pertinent information on the sample. During field collection, custody forms will be completed and labels will be affixed to the sample containers, thereby creating a link between the sample and data recorded on the custody form. The custody forms will contain the *Bottle_ID* numbers with the same alphanumeric code as the corresponding label on the sample container, ensuring the tracking of every sample. A duplicate original of the custody form will be kept by the subcontractor along with the samples during transport and storage. The other duplicate original custody form will be submitted to the Database Manager and maintained in the Data Sources Notebook.

Laboratory custody of all samples will be the responsibility of ENSR's subcontractors. Upon receipt of samples at the subcontractor's laboratory, the subcontractor will examine the samples received, verify that the information recorded on the custody forms is accurate, log the samples into the laboratory by signing the custody form on the *Received By* line, and by entering the date and time of sample receipt. Any inconsistencies between samples listed as having been released and samples that were actually received, or any damage to containers, labels, etc. will be noted in the laboratory sample log book and immediately communicated to the Project Area Leader. The *Bottle_ID* described earlier will be used to track the samples through the laboratory. All archived samples will remain in the custody of the subcontracting laboratory for a period of one year after sample collection, at which time the MWRA will be contacted about their disposition.

14.0 CALIBRATION PROCEDURES AND PREVENTIVE MAINTENANCE

Logs of maintenance, calibrations, and any repairs made to instruments will be stored in the instrument files maintained by ENSR and by the subcontractors. Maintenance of and repairs to instruments will be in accordance with manufacturers' manuals. Any deviations to this policy will be noted.

14.1 Hydrographic Profiling Equipment

14.1.1 Depth Sensor

At the beginning of each survey, the software offset of the depth sensor will be checked and adjusted if necessary so that the depth sensor reads zero when the sensor is on deck. The offset will be entered into the equipment setup file.

14.1.2 Temperature and Conductivity

The software gain and offset of the temperature and conductivity sensors will be calibrated semi-annually at SeaBird and the calibration settings will be not changed.

14.1.3 *In Situ* Dissolved Oxygen

The software gain and offset of the dissolved sensors will be calibrated semi-annually at SeaBird and the calibration settings will not be changed. The DO values determined by the sensor will be corrected for each survey based on a comparison with discrete water samples in which DO concentration is determined by titration. The DO data from the sensor (based on factory calibration settings) will be entered into a Microsoft Excel 5.0 spreadsheet with the corresponding bottle samples data. Then, using the built-in linear regression analysis tool, the correction slope and intercept will be determined. The regression will be based on the following equation:

$$\text{DO conc. (from sensor)} = \text{slope} \times \text{DO conc. (bottle value)} + \text{intercept}$$

To correct the CTD values in the database, the following equation will be used:

$$\text{Corrected sensor DO conc.} = \text{DO conc. (from sensor)} - \text{intercept/slope}$$

14.1.4 Transmissometer

The transmissometer will be calibrated semi-annually at SeaBird. This calibration will consist of obtaining voltage readings under the following three conditions:

V_o = voltage when the light path is blocked

V_a = voltage in air

V_w = voltage in distilled water.

Beam attenuation for the 25-cm pathlength will be calculated using the following equation:

$$c = A - 4 \ln (V_m - V_o)$$

where

c = beam attenuation

A = offset coefficient

V_m = measured *in situ* voltage.

Knowing that the beam attenuation of particle free distilled water at the transmitted wavelength of 660 nm is 0.364/m, the value of A is calculated as follows:

$$A = 0.364 + 4 \ln (V_w - V_o).$$

To check that the transmissometer is working properly, it will be checked during mobilization by reading blocked and unobstructed output readings in air. The blocked transmittance voltage should be 0.0. After cleaning the windows using kimwipes and a solution of dishwashing liquid and water, the unobstructed output transmittance will be checked against a calibration value provided by the factory, and software settings adjusted as necessary. After each survey day, the optics of the transmissometer will be rinsed with deionized water. During the farfield survey, the transmissometer will be turned off between stations to preserve the LED source. It is expected that the light source may decrease by 1% in 1000 hours of operation. This change can be compensated for through air calibrations and the following correction:

$$V = (A/B) * (X-Z)$$

$$\% \text{ Transmission} = 20 * V$$

V = Corrected output voltage.

A = Air calibration value as specified by manufacturer (4.667 VDC).

B = Air calibration (present value).

X = Data value (output voltage measured in water).

Z = Zero offset with light path blocked.

14.1.5 *In Situ* Chlorophyll *a* Fluorometer

Based on manufacturer's recommendations, the software gain and offset of the Sea Tech fluorometer are set annually. The Sea Tech fluorometer data, displayed with the Seasoft program, will approach 0.0 µg/L when the instrument is on deck. The voltage output is generally within 20mV of zero. Placing a finger in the sample volume should increase the voltage output towards the full scale value of 5 VDC. As daily maintenance, a light cleaning of the windows with a mild dish soap detergent and a lint-free damp cloth will be performed. During farfield surveys the instrument will be turned off between stations to prevent flash lamp degradation. The calculated readings will be corrected in the same manner as described for the DO sensor above, using the measured chlorophyll *a* and phaeophytin data from discrete bottle samples to develop a linear regression and correction slope and intercept. In this case the "bottle value" will be taken as the chlorophyll concentration plus the phaeophytin concentration reduced by a factor (1.7) to account for its lower fluorescence efficiency.

14.1.6 Irradiance Profiling and On-deck Sensors

The QSP200L Biospherical irradiance sensor is interfaced to the Seasoft system via the CTD and is used to measure photosynthetically available radiation underwater. The QSR240 hemispherical reference sensor is used to measure surface solar irradiance, and is interfaced to the Seasoft system via the systems analog-to-digital converter. Both sensors will be calibrated at the factory every year, in accordance with the manufacturer's recommendations. On a clear day at local noon, the surface solar irradiance as measured by the QSR240 should be 2000-3000 µEs⁻¹cm⁻². The same measurement on deck using the underwater sensor (QSP200L) should be 3500-4000 µEs⁻¹cm⁻². The difference in the readings is caused by field of view differences and a correction factor applied to the underwater sensor to account for its lower collection efficiency when immersed. Both instruments should read zero when their protective caps are installed.

Before each cast, the Seasoft software acquires readings from the sensors while the underwater unit is on deck. This information will be saved in a raw data file. The on-deck readings will be compared to see that both instruments are operating correctly. The sensors will be cleaned daily with a non-abrasive cloth and a solution of dish soap and water.

14.2 Navigation Equipment

Once the Northstar 941xd navigation system has been switched on, there is typically no other setup interaction necessary between the Seasoft operator and the navigation system. The GPS will conduct an automatic self-test, and then begin acquiring satellites and a beacon. This process normally takes 2-5

minutes. An error message will be displayed if the system has trouble acquiring satellites or a beacon. The DGPS system provides guaranteed position accuracy of 10 meters 95% of the time. During mobilization at the staging location, the Northstar position will be recorded and checked against previously recorded values.

14.3 Laboratory Instruments

Preventive maintenance of all subcontractor laboratory equipment will follow manufacturers' recommendations. The calibration procedures for various laboratory analyses that will be followed are briefly summarized below.

- Dissolved Inorganic Nutrients, Dissolved Organic Nitrogen and Phosphorus, Particulate Phosphorus, and Biogenic Silica - After filtration, various oxidation, or digestion processes, these parameters are analyzed on a LaChat QuikChem 8000 Ion Analyzer. Concentrations are calculated from a standard curve made by 4 dilutions of a primary standard covering the normal range of sample concentrations. Primary standards are used for 6 months to 1 year. When they are replaced, new standards are verified against the old standards. There are no standard reference materials (SRMs) for nutrients in seawater. Intercalibrations with other laboratories serve to ensure reliability of primary standards.
- Chlorophyll *a* — This is analyzed by extracted fluorescence on a Perkin-Elmer fluorometer. Values are calculated from calibration equations derived using purified chlorophyll *a* purchased from Sigma Chemical. The instrument is calibrated once per year.
- Particulate Carbon and Nitrogen — These are determined on a Perkin Elmer Model 2400 elemental analyzer using standard curves generated with acetanilide. There are no SRMs for this analysis.
- Dissolved Organic Carbon — This is determined on an Dohrmann DC 80 TOC analyzer by persulfate oxidation. Values are calculated from standard curves using a potassium biphthalate standard.
- Dissolved Oxygen — This is measured by the Winkler titration method using manual titration. The thiosulfate titrant is standardized against a potassium iodate standard of known molarity. The degree to which the molarity is known depends on the accuracy of

the balance used to weigh out the material. The balances are standardized and adjusted by factory certified technicians.

- TSS — This is measured with an analytical balance, which is standardized and adjusted by factory certified technicians.
- ^{14}C — This is measured with a scintillation counter that is calibrated for quench using the external channels ratio method.
- Dissolved Inorganic Carbon - Total DIC concentration is measured on a Beckman IR-315 infrared analyzer calibrated by injection of certified CO_2 gas standards to create a standard curve which encompasses the range of field values.
- Chlorophyll *a* (Production) - The B&L Spectronic 2000 is calibrated using a multi-point initial calibration. Calibration is verified using check standards of known concentrations obtained from Sigma Chemical.
- Respiration - DO is measured using a Radiometer Titralab Titrator. The accuracy of the titrant is checked against a commercially purchased titrant of known value. The value of a bubbled seawater control is compared to the theoretical O_2 saturation level of the control.

15.0 DOCUMENTATION, DATA REDUCTION AND REPORTING

15.1 Data Recording

All data will be initially recorded either (1) electronically onto computer storage media from the Seasoft software or other laboratory system or (2) manually into bound laboratory notebooks or onto established data forms. All notes will be written in ink. Corrections to hand-entered data will be initialed, dated, and justified. Completed forms, laboratory notebooks, or other forms of hand-entered data will be signed and dated by the individual entering the data. It will be the responsibility of the laboratory managers to ensure that all data entries and hand calculations are verified in accordance with procedures described in Section 16 (below). In addition to these documentation procedures, sample logs associated with field and laboratory custody and tracking will be kept in a survey notebook for each survey. These notebooks will be stored under the supervision of Mr. Wolf.

The hydrographic data generated during the survey will consist of rapidly sampled, high-resolution measurements of conductivity, temperature, depth, DO, turbidity, chlorophyll *a*, underwater light levels, total incident radiation, and altitude above bottom. A unique data filename will be assigned to each vertical profile made during the survey. All data will be electronically logged with date, local time, and concurrent GPS vessel-position data. The data-acquisition system stores the data on hard disk to facilitate efficient data archiving, and post-survey data processing and editing, as well as to prevent manual transcription errors. A copy on a 3.5" diskette will be produced at the end of the profile. On each survey, the screen dumps will be printed on the HP Deskjet and stored in the survey notebook.

15.2 Data Reduction

15.2.1 Hydrographic and Navigation Data

Data reduction procedures differ between the upcast and downcast data. For the downcast data, all raw *in situ* instrument measurement data will be transformed into engineering units following the survey. This transformation will involve several operations using the Seasoft software including removal of outliers, temporal alignment of downcast data based on instrument response characteristics, and depth averaging of downcast data. The direct conversion of raw data to engineering data involves use of calibration coefficients determined as described in Section 14. To convert oxygen current and membrane temperature to DO, the method developed by Owens and Millard (1985) will be used. To calculate salinity and density from conductivity, temperature, and pressure, the algorithms developed by Fofonoff and Millard (1983) will be used. To determine the percent saturation of oxygen, the calculated DO will be divided by the solubility of oxygen based on the algorithm developed by Weiss (1970).

Much of the processing and reduction of sensor data associated with Niskin bottle closings (the upcast data) will be conducted onboard. After every cast, the upcast data will be extracted from the raw data file and converted to engineering units using SeaBird software as described above for the downcast. The sensor data will be then time-averaged over a six second window surrounding each Niskin bottle closing. These data will then be averaged using the onboard software if more than one Niskin bottle is used for a particular sample and combined with the navigation data and the sampling times recorded in the raw data file. The onboard software will then save the resulting upcast data as a comma delimited ASCII text file.

When checking for representativeness onboard, each sensor parameter will be checked before profile operations. Four parameters (salinity, temperature, fluorescence, and DO) are displayed during the cast and then plotted in high-resolution, *xy* graphic form for visual inspection of data quality by an oceanographer. These plots will be stored under the supervision of the *in-situ*/navigation data manager,

to allow inspection by QA staff or MWRA staff. During data reduction of the downcast data, vertical profiles of all sensor parameters will be plotted and checked by an oceanographer.

After conducting the first-pass edited engineering data, the DO and chlorophyll *a* values for both the up and downcast are adjusted based on a calibration with discrete water samples (Figure 17, and Sections 14.1.3 and 14.1.5). The procedure uses the analytical data as the independent variable in a linear regression of the sensor values measured *in situ*. Data for these regressions will be compiled by first entering the uncorrected sensor and the analytical data into draft tables of the EM&MS database (see later sections for reporting and loading procedures). A query will be run that matches sensor values with corresponding analytical data for chlorophyll *a* and phaeophytin. These data will be read into EXCEL and the calibration procedure described in Sections 14.1.3 and 14.1.5 will be performed. The sensor values will then be transformed according to the calculated regression parameters using update queries applied to the draft tables. The applied regression coefficient will be noted in every record that has been updated.

15.2.2 Subcontractor Laboratory Data

All data generated by ENSR's subcontractors will be either electronically transferred from the instrument to a PC-based spreadsheet or manually read from the instrument display (or optical field of a microscope) and entered into laboratory notebooks. Data in laboratory notebooks will be manually entered into a PC-based spreadsheet. All data reduction methods, described in the methods referenced in Section 12, will be performed electronically either by the instrument software or in a spreadsheet and will be validated according to procedures described in Section 16. The format for final data submission is described below.

15.3 Reporting Data to be Loaded into the Database

The Water Quality Project Area Manager will designate data that is ready for entry into the draft tables of ENSR's version of the EM&MS database. The ENSR QA Officer and the Database Manager will designate data from the draft tables as final. These data will then be considered suitable for the production tables within ENSR's copy of the EM&MS Database. All data submitted for inclusion in the Harbor Studies Database will adhere to the formats described below.

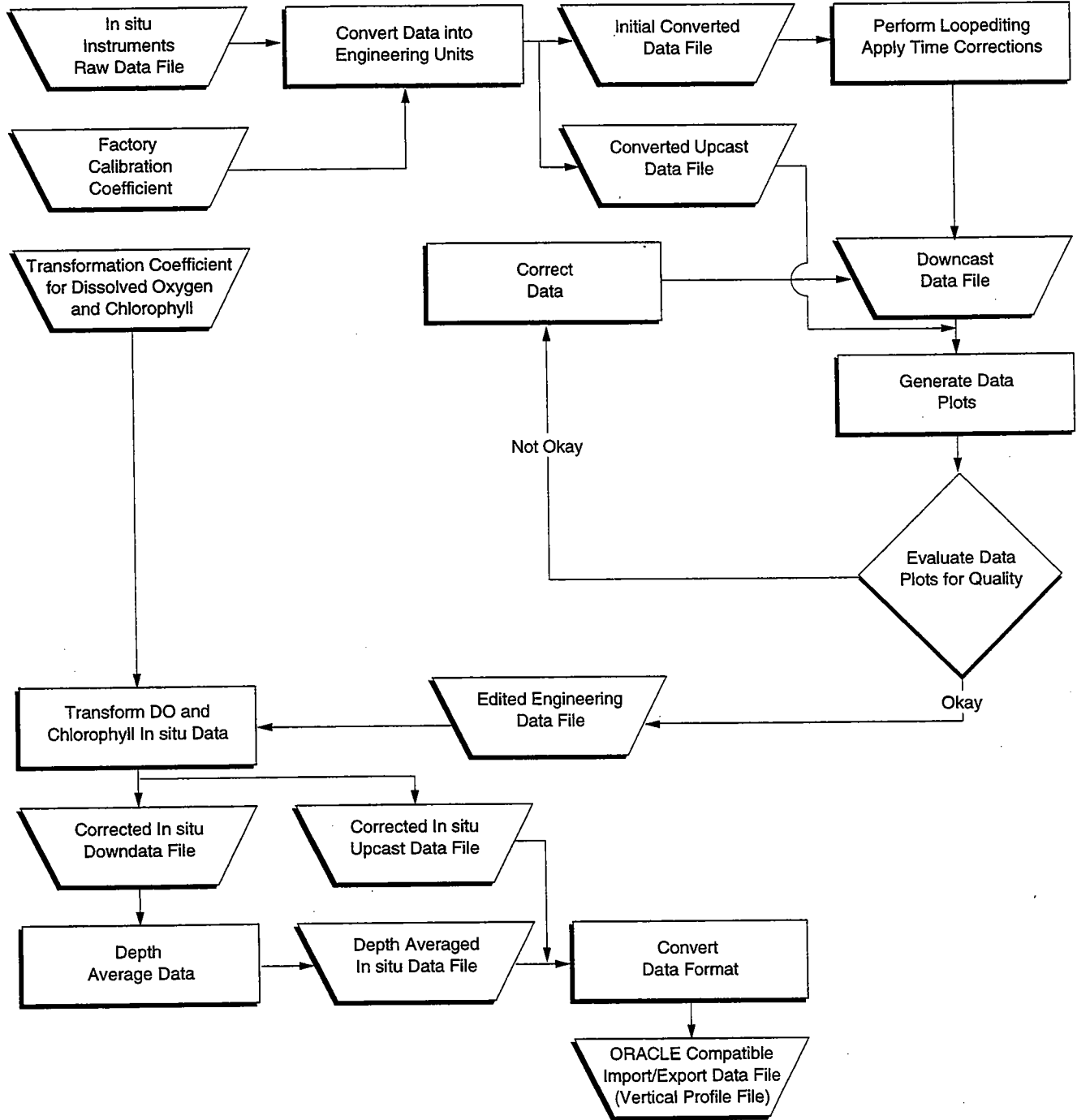


FIGURE 17
Process for Generating Vertical Profile Data Files
for Import to ORACLE Database

15.3.1 Navigation and Sample Collection Data

Navigation and sample collection data will be saved onboard, using software developed by ENSR, as comma delimited ASCII files with appropriate headers. These text files will conform to the *Station* (Table 12) and *Sample* (Table 13) formats of the EM&MS database. Subsampling information will be documented in the *Bottle* table of the EM&MS database (Table 14). The *Bottle* records will be extracted electronically from chain-of-custody records or entered by hand as appropriate for each type of sub-sample.

15.3.2 Hydrographic Data

ENSR will also load into the database the following two types of data collected with the sensor package:

- Date, time, location, and corrected sensor data associated with each each sample (upcast data), and
- Date, time, location and corrected vertical profile sensor data that has been bin-averaged into 0.5-m bins (downcast data)

Both of these data sets will be reformatted into the *Profile* format (Table 15) of the EM&MS database using EXCEL macros. After running the macro, EXCEL spreadsheets will be saved and later imported into the draft tables of the EM&MS database.

15.3.3 Analytical and Experimental Data

Researchers from ANS will provide data spreadsheets containing species enumeration data for each type of data: whole-water phytoplankton, screened phytoplankton (dinoflagellates), and zooplankton. These spreadsheets will be formatted by ANS according to the *Abundance* format of the EM&MS database (Table 16). The Harbor Studies Database maintained by ENSR will distinguish the cells counted by the two phytoplankton methods using by designating unique *Bottle_ID*'s for each analysis.

Researchers from UNH, WHOI, and E3I will submit data for nutrients, organic constituents, chlorophyll *a*, TSS, DO, respiration, and productivity by ¹⁴C in spreadsheets that can be read into EXCEL. The format for these data (Table 17) will be compatible with the *Analytical_Results* format of the EM&MS database. Analyses will be identified in this format using specific parameter codes (Table 18). Reported values may be qualified using a specific set of qualifier codes (Table 19). Results of respiration and ¹⁴C analyses

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TABLE 12

Format for Reporting Station Data (Station Format)

Column	Type	Field Size	Fract. Digits	Must Report	Description
Study_ID	Char	10		Y	indicates type of study
Event_ID	Char	10		Y	indicates sampling event (e.g. W9516)
Stat_ID	Char	9		Y	identifies station sampled (e.g. N10)
Stat_Arriv	Date			Y	indicates date and time sampling began
Stat_End	Date			N	indicates date and time sampling ended
Beg_Latitude	Num	9	7	N	indicates latitude component of location when sampling began
End_Latitude	Num	9	7	N	indicates latitude component of location when sampling ended
Beg_Longitude	Num	9	7	N	indicates longitude component of location when sampling began
End_Longitude	Num	9	7	N	indicates longitude component of location when sampling ended
Water_Depth	Num	5	2	N	indicates depth at which water sample was obtained
Depth_Unit	Char	2		N	indicates units of water depth measurement
Navigation	Char	20	5	N	indicates type of equipment used to collect navigation data
Nav_Qual	Char	10	5	N	provides information regarding navigation data
Filename	Char	12		N	name of processing spreadsheet from which data is loaded
Login_ID	Char	8		N	
Day_N	Number	7	0	N	
<p>Notes</p> <ol style="list-style-type: none"> 1) Data resulting from laboratory QC samples should be submitted along with the data package. For laboratory QC samples, no entry should be reported for Sample_ID, but a Labid must be reported. 2) Codes are provided in the code list for the following fields: meth_code, inst_code, unit_code, and val_type. Codes for val_qual are provided in the qualifier list. If you require a code that is not in the code list, please contact the ENSR task manager. 					

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TABLE 13

Format for Reporting Sample Data (Sample Format)

Column	Type	Field Size	Fract. Digits	Must Report	Description
Study_ID	Char	10		Y	indicates type of study
Event_ID	Char	10		N	indicates sampling event
Stat_ID	Char	9		N	identifies station sampled
Stat_Arriv	Date			N	indicates time and date sampling began
Sample_ID	Char	15		Y	uniquely indentifies each sample
Matrix	Char	4		N	indicates matrix (e.g. water) from which sample was collected
Gear_Type	Char	6		N	specifies type of equipment used to collect sample
Samp_Dep_Bot	Num	5	2	N	indicates depth at which bottom sample was collected
Samp_Dep_Top	Num	5	2	N	indicates depth at which top sample was collected
Depth_Unit	Char	3		N	indicates units of depth measurement
Sieve	Num	6	3	N	
Sieve Unit	Char	3	5	N	indicates units of sieve measurement
Wet_Wt	Num	6	3	N	contains value for sample wet weight
Wet_Wt_Unit	Char	3		N	indicates units of wet weight measurement
Dry_Wt	Num	6	3	N	contains value for sample dry weight
Dry_Wt_Unit	Char	3		N	indicates units of dry weight measurement
Samp_Vol	Num	7	3	N	indicates volume of sample collected
Samp_Vol_Unit	Char	3		N	indicates units of sample volume measurement
Marker_No	Char	10		N	
Rosette_Bottle	Char	2		N	
Time	Date			N	
Filename	Char	12		N	specifies processing spreadsheet from which data was loaded
Login_ID	Char	8		N	indicates origination of data submittal
Day_N	Number	7		N	
Time_Qual	Char	3		N	
Notes:					
1) Data resulting from laboratory QC samples should be submitted along with the data package. For laboratory QC samples, no entry should be reported for Sample_ID, but a Labid must be reported.					
2) Codes are provided in the code list for the following fields: meth_code, inst_code, unit_code, and val_type. Codes for val_qual are provided in the qualifier list. If you require a code that is not in the code list, please contact the ENSR task manager.					

TABLE 14
Format for Reporting Bottles Collected During Survey

Column	Type	Field Size	Fract. Digits	Must Report	Description
Study_ID	Char	10		Y	indicates type of study
Sample_ID	Char	15		Y	unique sample identifier
Bottle_ID	Char	15		Y	unique bottle identifier
Event_ID	Char	10		Y	sampling event
Anal_Lab_ID	Char	4		Y	lab doing analysis
Coc_ID	Num	3	0	Y	
Sub_Type	Char	2		N	
Parent_ID	Char	15		N	
Cooler_Num	Num	3	0	N	
Coll_Time	Date			N	
Analysis_Code	Char			N	
Container_Code	Char			N	
Media_Code	Char			N	
Preservative_Code	Char			N	
Comment	Char			N	

TABLE 15

Format for Reporting Hydrographic Data (Profile Format)

Column	Type	Field Size	Fract. Digits	Must Report	Description
Study_ID	Char	10		y	indicates type of study
Event_ID	Char	10		Y	indicates sampling event
Stat_ID	Char	10		Y	specifies station sampled
Stat_Arriv	Date	8		Y	indicates date and time sampling began
Depth	Num	7	2	Y	indicates depth at which sample was collected
Depth Unit	Char	2	0	N	provides units of water depth measurement
Prof_Date_Time	Date			N	
Prof_Time				N	
Day_N	Num	7	0	N	
Latitude	Num	9	7	N	indicates latitude component of location at the time sample collected
Longitude	Num	9	7	N	indicates longitude component of location at the time sample collected
Marker No	Char	10	3	N	
Upcast	Char	1	3	Y	
Param_Code	Char	20	3	Y	indicates parameter for which analysis was performed
Value	Num	10	5	N	contains the parameter value
Val_Qual	Char	3		N	indicates data value qualifier
Unit Code	Char	5		N	indicates units in which the parameter is measured
Meth_Code	Char	5		N	indicates method used to perform analysis
Instr_Code	Char	5		N	specifies equipment used to make measurement
Filename	Char	12		N	specifies processing spreadsheet from which data was loaded
Login_ID	Char	8		N	specifies source of data submittal

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TABLE 16

Format for Reporting Plankton Data (Abundance Format)

Column	Type	Field Size	Fract. Digits	Must Report	Description
Sample_ID	Char	9		Y	uniquely identifies each sample
Study_ID	Char	10		Y	identifies type of study
Bottle_ID	Char	15		Y	uniquely identifies each bottle
Spec_Code	Char	12		Y	contains identity of plankton species
Spec_Qual	Char	3		Y	provides descriptive information regarding plankton species
Value	Num	12	3	N	contains parameter value
Val_Qual	Char	3		N	contains data qualifier associated with the parameter value
Anal_Rep	Num	3	0	N	analytical replicate
Unit_Code	Char	12		N	units for value
Lab_Sample_ID	Char	35		N	lab sample ID
Anal_Lab_ID	Char	4		N	lab identifier
Meth_Code	Char	8		N	method code
Filename	Char	12		N	spradsheet from which data was loaded
Login_ID	Char	6		N	source of data submittal
Carbon	Num	12	3	N	organic carbon conc. (ug/l)
Tow_Vol	Num	12	3	N	tow volume (M3)
Notes:					
1)	A column to report value qualifier (val_qual) will be added if appropriate				
2)	Enumerated to species, but when no species name available then use SP.A, SP.B etc.; use these designations consistently across all samples for this program				
3)	When identification to species is impossible use genus (or higher taxon) name + "SPP."				

TABLE 17

Qualifier List

Qualifier Type	Qualifier	Description
Val_qual	a e	not detected not reported
Val_qual	k l	calculated value dark bottle
Val_qual	j m	estimated value initial
Val_qual	n p	light bottle lab sample bottles mislabelled caution data use
Val_qual	s x	suspect value matrix interference
Val_qual	f b	below method detection limit below limit of quantitation
Val_qual	p <	present, but uncountable less than
Spec_qual	C	Copepodites
Spec_qual	Y	Cyprids
Spec_qual	K	Colonial species, not counted individually
Spec_qual	X	Complex Complex (dense assemblage not sorted to species)
Spec_qual	F	Female
Spec_qual	G	Fragment
Spec_qual	J	Juvenile (unspecified stage)
Spec_qual	L	Larvae
Spec_qual	M	Male
Spec_qual	N	Nauplii

TABLE 18

Codes for Analytical Parameters

Data Type	Param Code	Unit Code	Instr Code	Instr Code Description	Meth Code	Meth Code Description
Chlorophyll <i>a</i>	CHLA	µg/L	FLU4	SeaTech Fluorometer	10200H	EPA (1983)
Phaeophytin	MWRA79	µg/L	FLU4	SeaTech Fluorometer	10200H	EPA (1983)
Ammonia	NH4	µM	LATFI	Lachat QuikChem 8000 FIA	BW1241	Bowen <i>et al.</i> (1996)
Nitrite	NO2	µM	LATFI	Lachat QuikChem 8000 FIA	BW1241	Bowen <i>et al.</i> (1996)
Nitrate plus nitrite	N03+ N02	µM	LATFI	Lachat QuikChem 8000 FIA	BW1241	Bowen <i>et al.</i> (1996)
Phosphate	TDP	µM	LATFI	Lachat QuikChem 8000 FIA	VALD81	Valderrma (1981)
Silicate	SI04	µM	LATFI	Lachat QuikChem 8000 FIA	BW1241	Bowen <i>et al.</i> (1996)
Dissolved organic carbon	DOC	mg/L	DOHR	Dohrmann DC80 Analyzer	415.1	EPA (1983)
Total dissolved nitrogen	TDN	µM	LATFI	Lachat QuikChem 8000 FIA	VALD81	Valderrama (1981)
Total dissolved phosphorus	TDP	µM	LATFI	Lachat QuikChem 8000 FIA	VALD81	Valderrama (1981)
Particulate organic carbon	POC	µM	PE24CHN	Perkin Elmer Model 2400 CHN Elemental Analyzer	QP1234	Bowen <i>et al.</i> (1996)
Particulate organic nitrogen	PON	µM	PE24CHN	Perkin Elmer Model 2400 CHN Elemental Analyzer	QP1234	Bowen <i>et al.</i> (1996)
Total suspended solids	TSS	mg/L	CAHN	Cahn electrobalance	160.2	EPA (1983)
Dissolved oxygen	DISS_OXYGEN	mg/L	WTTR	Winkler titration	360.2	EPA (1983)
Respiration	Respiration	µmol/h	RTL	Radiometer Titralab Titrator	QP12311	Bowen <i>et al.</i> (1996)
Urea	57-13-6	µM	ALPAA	Alchem Autoanalyzer	QP12310	Bowen <i>et al.</i> (1996)
Biogenic silica	BIOSI	µM	LATFI	Lachat QuikChem 8000 FIA	KRAU83	Krausse <i>et al.</i> (1983)
Dissolved oxygen	DISS_OXYGEN	mg/L	RTL	Radiometer Titralab Titrator	QP1239	Bowen <i>et al.</i> (1996)
Particulate phosphorus	PARTP	µM	LATFI	Lachat QuikChem 8000 FIA	BW1245	Bowen <i>et al.</i> (1996)

TABLE 18 (Cont'd)
 Codes for Analytical Parameters

Data Type	Param Code	Unit Code	Instr Code	Instr Code Description	Meth Code	Meth Code Description
Areal production	AREAL_PROD	mgCm-2d-1	PT4000	Packard Tricarb 4000 Liquid Scintillation Counter	BW12412	Bowen <i>et al.</i> (1996)
Daily production	DAILY_PROD	mgCm-3d-1	PT4000	Packard Tricarb 4000 Liquid Scintillation Counter	BW12412	Bowen <i>et al.</i> (1996)
Hourly production	HOURLY_PROD	mgCm-3h-1	PT4000	Packard Tricarb 4000 Liquid Scintillation Counter	BW12412	Bowen <i>et al.</i> (1996)

Notes: 1) Dissolved organic nitrogen (DON) will be calculated as: $DON = TDN - Ammonia - Nitrate - Nitrite$
 2) Dissolved organic phosphorus (DOP) will be calculated as: $DOP = TDP - Phosphate$

TABLE 19

Codes for Analytical Value Qualifiers

Qualifier Type	Qualifier	Description
Val_Qual	a e	not detected not reported
Val_Qual	k l	calculated value dark bottle
Val_Qual	j m	estimated value initial
Val_Qual	n p	light bottle lab sample bottles mislabelled caution data use
Val_Qual	s x	suspect value matrix interference
Val_Qual	f b	below method detection limit below limit of quantitation
Val_Qual	p <	present, but uncountable less than
Spec_Qual	C	Copepodites
Spec_Qual	Y	Cyprids
Spec_Qual	K	Colonial species, not counted individually
Spec_Qual	X	Complex Complex (dense assemblage not sorted to species)
Spec_Qual	F	Female
Spec_Qual	G	Fragment
Spec_Qual	J	Juvenile (unspecified stage)
Spec_Qual	L	Larvae
Spec_Qual	M	Male
Spec_Qual	N	Nauplii
Spec_Qual	O	Ova
Spec_Qual	P	Post Larvae
Spec_Qual	S	Spores
Spec_Qual	T	Trochophore
Spec_Qual	V	Veliger
Spec_Qual	Z	Zoea

include additional information on these experiments. Relevant procedural parameters such as irradiance or length of incubation are recorded in the *Experiment* table by laboratory or field personnel. The fields in this table are shown in Table 20.

15.4 Loading Analytical and Experimental Data into the Harbor Studies Database

Data provided by the project team will be loaded into the EM&MS Database by ENSR's data management staff. Upon receipt from the subcontractor, each diskette will be logged in and assigned a unique login identifier. The data will first be read into EXCEL and checked for proper format. Any necessary reformatting will be performed in EXCEL. The tables will then be imported into the draft tables of the ENSR's version of the EM&MS database. Any changes or additions to the draft tables will be made using well-documented SQL scripts that indicate the original values. A set of constraints will then be imposed upon the draft tables to ensure data uniqueness and consistency between related data, and the tables will be edited as necessary to conform to the constraints. The original diskette, SQL scripts, and data-loading and editing documentation will be filed according to login identifier at ENSR. The Data Sources file will contain copies of this CW/QAPP, the custody forms, the Survey Plans and Reports, data entry information, and SQL scripts.

15.5 Reporting Data to MWRA

Data and the accompanying documentation prepared for each data report will be delivered to MWRA as described in Task 7 of Contract S186. Copies of all data reduction and analysis software will be delivered to MWRA upon request.

16.0 DATA EVALUATION

All data reported for this project will be reviewed to check for errors in transcription, calculation, or computer input by the technical staff of the appropriate laboratory. ENSR will perform these reviews for all sample, navigation, and sensor data. The subcontracted laboratories will perform these reviews prior to submission of the data to ENSR. The validation procedures that will be performed are:

- 100% of data that are hand-entered into a database or spreadsheet will be verified for accuracy either by (1) printing the spreadsheet and proofreading against the original hand entry or by (2) duplicate entry into the database and comparison of the entries to detect

TABLE 20

Format for Reporting Experimental Conditions

Column	Type	Field Size	Fract. Digits	Must Report	Description
Study_ID	Char	10		Y	type of study
Bottle_ID	Char	15		Y	uniquely identifies each bottle
Param_Code	Char	20		Y	parameter code
Value	Num	12	5	Y	value of parameter
Unit_Code	Char	4		Y	units code for value
Comments	Char	150		N	comments

any differences. These tasks will be carried out by two people and documented for each data set.

- All manual calculations will be checked for accuracy by a second staff member.
- Calculations performed by software will be checked by the technical staff member during the preparation of each data report to ensure the accuracy of the calculations. All data-reduction algorithms will be verified prior to final data submission.
- Subsets of the analytical data will be reviewed by in-house or subcontractor data validators. The data will be reviewed for adherence to analytical protocols and to pre-established criteria (e.g., for holding times, surrogate recoveries, initial and continuing calibration, matrix spikes, laboratory duplicates, blank contamination, SRM recoveries).
- Database staff will check the received data and associated documentation for completeness, freedom from errors, and technical reasonableness.
- All new software developed for this task will be validated before entry of data.

The ENSR Project Area Manager will be responsible for validation of all data generated by ENSR to ensure that the data are accurate, complete, and scientifically reasonable. Subcontractors will be responsible for conducting similar data validations. As an additional data validation step, the ENSR Project Area Manager will review all subcontractor data for technical reasonableness.

17.0 PERFORMANCE AND SYSTEM AUDITS

This project will be monitored by the ENSR Project QA Director. All tabular and graphic data reported in deliverables and associated raw data generated by ENSR will be reviewed by the Project QA Director or his/her designee. Raw data will be reviewed for traceability, accuracy, completeness, and proper documentation.

All deliverables generated during the course of this project will be submitted to an internal review prior to delivery of drafts to MWRA.

Audits of the subcontractor laboratory data-collection programs will be the responsibility of the subcontractor. During the time work is in progress, an inspection will be conducted by the subcontractor QA officer or their designee to evaluate the laboratory data-production process. All data must be reviewed by the Subcontractor QA Officer prior to submission to the ENSR Project Area Manager and must be accompanied by a signed QA statement that describes the types of audits and reviews conducted and any outstanding issues that could affect data quality.

Performance audits, procedures used to determine quantitatively the accuracy of the total measurement system or its components, will be the responsibility of subcontractor laboratories and may include internal performance evaluation samples and participation in external certification programs.

18.0 CORRECTIVE ACTION

Identification of problems regarding technical performance is the responsibility of all staff members working on this project. Responsibility for overall conduct of the project, including schedule, costs, and technical performance lies with the ENSR Project Manager. The Project Manager is responsible for identifying and resolving problems that (1) have not been addressed promptly or successfully at a lower level, (2) influence other components of the project, (3) require changes in this CW/QAPP, or (4) require consultation with ENSR management or with MWRA.

Technical problems relating to sample collection (schedule changes, modifications to the sampling plan, etc.) will be resolved through discussion with the MWRA Task Manager and ENSR Project Area Manager. Problems relating to the overall successful completion of the project will be reported to the MWRA Task Manager in a timely manner for discussion and resolution between the ENSR and MWRA managers.

Identification of problems and corrective action at the laboratory level will be resolved by the laboratory staff. Issues that affect schedule, cost, technical performance, or data quality will be reported to the ENSR Project Area Manager or the ENSR Project Manager. They will be responsible for evaluating the overall impact to the project and for discussing corrective actions with the MWRA Task Manager.

A QA/QC Corrective Action Log will be maintained by the ENSR Project QA Director and submitted to MWRA at quarterly intervals. The log will include documentation of QA/QC activities as they occur, descriptions of the methods and procedures recommended to prevent the problem from reoccurring, and verification that these actions have corrected the problem.

19.0 REPORTS

Reports that will be generated under Tasks 9, 10, 11, 12, 13, 14 and 15 include water quality survey plans and report, data reports, and monthly data letters. Each of these reports are described below.

The following reports will be generated as part of the nearfield (Task 9), farfield (Task 10), and plume tracking (Task 11) surveys:

- 55 Survey Plans, one for each of the 55 water quality surveys (33 nearfield surveys, 4 plume track surveys near outfall commissioning, 9 combined nearfield/farfield surveys, 9 combined nearfield/farfield/plume tracking surveys)
- 55 Survey Reports (one for each of the 55 water quality surveys)
- 15 Nutrient Data and Respiration/Productivity Data Reports
- 15 Phytoplankton Data and Zooplankton Data Reports
- Approximately 36 Sensor Data Processing Letters

Each survey plan will follow the guidelines established by U.S. Environmental Protection Agency for use of the OSV *Anderson* and will include the following information:

- Documentation of any deviations from this CW/QAPP
- Schedule of operations
- Specific location and coordinates of each station
- Survey/sampling methods
- Navigation and positioning control
- Vessel, equipment, and supplies
- Scientific party
- Tide and tidal current data for each survey day (determined 0.2 nm south of Boston Light using Micronautics, Inc. Tide.1 and Tide.2 software)

Two unbound copies of the final survey plan will be submitted to MWRA at least one week prior to the start of the survey. No draft survey plans will be prepared.

Survey reports will describe the survey conducted, station coverage, samples collected, measurements made, problems experienced, and general observations. A survey report is expected to be about 4-5 pages of text, with accompanying station maps and sample table. A tabular summary of stations occupied, station locations, and samples collected will be included in the survey reports. Any deviations from this

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CW/QAPP, not known at the time of survey plan preparation, will also be incorporated into the survey reports. Two unbound, single-sided copies of the draft survey report will be submitted to MWRA no later than two weeks after the completion of each survey. MWRA's comments will be due two weeks after receipt of the draft report. The final survey report, addressing MWRA's comments, will be due two weeks after receipt of the comments. If MWRA does not submit comments within the two-week period, the draft survey report will be considered final.

Five times each year, nutrient and respiration/productivity data reports will be prepared and submitted to MWRA. These reports will contain tabular summaries of concentrations of nutrients, chlorophyll *a* and phaeophytin, DO, and TSS for each bottle sampled and analyzed. In addition, a tabular summary of the results of respiration, and areal productivity analyses will be provided for each bottle sampled and analyzed.

Five times each year, separate phytoplankton and zooplankton data report will be prepared and submitted to MWRA. These reports will contain tabular summaries of phytoplankton and zooplankton counts and identifications.

These data will also be used in reports to be prepared under Task 33: semi-annual water quality reports, annual water quality reports, and nutrient issues reviews. The semi-annual and annual water quality reports will use the following outline:

- Executive Summary (2-5 pages)
- Introduction (8 pages)
- Survey Methods (12 pages)
- Results (for each survey in the reporting period; 50 pages)
- Discussion (30 pages)

20.0 REFERENCES

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