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

for

BASELINE WATER QUALITY MONITORING: 1993-1994

Tasks 5, 6, 7, 8, and 9
MWRA Harbor and Outfall Monitoring Project

#### submitted to

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# 1. PROJECT NAME

MWRA Harbor and Outfall Monitoring Project — Baseline Water Quality Monitoring of Massachusetts Bay

#### 2. PROJECT REQUESTED BY

Massachusetts Water Resources Authority, Environmental Quality Department

#### 3. DATE OF REQUEST

December 3, 1992

#### 4. DATE OF PROJECT INITIATION

December 3, 1992

#### 5. PROJECT MANAGEMENT

- Dr. Michael Connor, MWRA Director of Environmental Quality Department
- Dr. Michael Mickelson, MWRA Harbor and Outfall Monitoring Project Manager, and MWRA Water Column Area Manager
- Dr. Carlton Hunt, Battelle Project Manager for Harbor and Outfall Monitoring
- Mr. Carl Albro, Battelle Water Column Project Area Leader
- Dr. Jack Kelly, Battelle Technical Director

# 6. QUALITY ASSURANCE (QA) MANAGEMENT

Ms. Rosanna Buhl, Battelle Project QA Officer

#### 7. PROJECT DESCRIPTION

# 7.1 Objective and Scope

The overall objective of the baseline water column monitoring program is to determine, through sample collection and direct measurements, the baseline conditions and variability of 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. With a sound baseline characterization of the water column in Massachusetts Bay, it should be possible to observe potential changes resulting from the outfall discharge.

To help define baseline water properties, nutrient concentrations, and other important parameters of eutrophication, 44 water quality surveys (22 each year) will be conducted in Massachusetts Bay during 1993 and 1994. This Combined Work/Quality Assurance Project Plan (CW/QAPP) describes the sampling and analysis activities associated with the water quality surveys that will be conducted under Tasks 5, 6, 7, 8, and 9 of MWRA contract S138. In addition, data quality requirements and assessments, project management (organization and responsibilities of Battelle 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 Nutrient/Hydrography Surveys (Task 5)

The objective of these surveys is to determine the baseline water column conditions throughout the year at 21 selected stations that may be influenced by changes in MWRA effluent discharge practices.

# 7.1.2 Farfield Nutrient/Hydrography Surveys (Task 6)

The surveys conducted under Task 6 will determine the baseline water column conditions throughout the year at 25 selected stations that may be influenced by changes in MWRA effluent discharge practices.

# 7.1.3 Biology/Productivity Surveys (Task 7)

The objective of the Task 7 surveys is to Characterize biological response parameters throughout the year at six nearfield stations and four farfield stations.

# 7.1.4 Nutrient Analyses and Respiration/Productivity Measurements (Task 8)

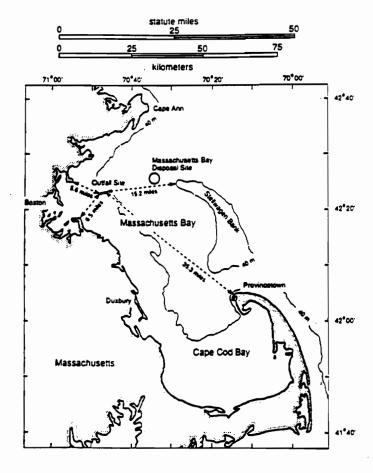
The objective of Task 8 is to analyze water samples (collected as part of Tasks 5, 6, and 7) for concentrations of DO, dissolved inorganic nutrients (nitrate, nitrite, ammonium, phosphate, and silicate), dissolved organic nitrogen and phosphorous, dissolved organic carbon, particulate carbon and nitrogen, chlorophyll a and phaeopigments, total suspended solids (TSS), respiration, phytoplankton abundance, and phytoplankton productivity.

## 7.1.5 Plankton Taxonomy (Task 9)

The objective of Task 9 is to analyze water samples (collected as part of Tasks 5, 6, and 7) to determine phytoplankton (whole water and screened dinoflagellate samples) or zooplankton community composition, and to separately estimate zooplankton abundance.

# 7.2 Data Usage

The Massachusetts Water Resources Authority (MWRA) is implementing Phase I of a longterm 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 endpoints are paramount: (1) lowered DO concentrations (hypoxia/anoxia), (2) stimulation of nuisance/noxious algal populations, and (3) alteration of the pelagic food web. Water column monitoring centers on measurements keyed to these three principal ecological endpoints. Measurements include phytoplankton biomass (chlorophyll, in situ fluorescence) and pelagic metabolism (respiration, production),



igure 1. Location of MWRA Effluent Outfall in Massachusetts Bay.

because both may be useful harbingers of DO concentration - the endpoint that is also measured directly. Phytoplankton species identification and enumeration is a second indicator measure that *is*, in fact, the endpoint. Monitoring 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 may influence phytoplankton as well as physical and chemical factors). The goal of Phase I monitoring is to provide

baseline data that may be used to assess potential environmental impact of effluent discharge into Massachusetts Bay and to evaluate compliance with the discharge permit.

The data obtained from the water column surveys and laboratory analyses will be used to define baseline properties of the water in both the nearfield and farfield monitoring regions of Massachusetts and Cape Cod Bays. The water column 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,

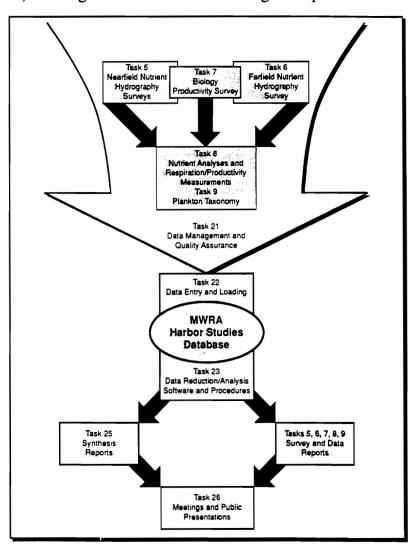


Figure 2. Three Types of Water Column Surveys Will Define Baseline Biological, Chemical, Physical Variability in Massachusetts Bay.

optical beam transmittance, and light irradiance) will be used to provide baseline seasonal characterization of the water column. Laboratory data for nutrient concentrations, plankton biomass and productivity, and phytoplankton composition and abundance will be used to establish baseline conditions from which any changes, potentially resulting from the proposed outfall, can be measured. Figure 2 illustrates how the data from these surveys flow into the MWRA Harbor Studies Database to providing information to the public.

# 7.3 Technical Approach

# 7.3.1 Field Program

To accomplish the objectives, hydrographic data will be collected at 46 selected stations (see Table 1). At each of the designated stations, a vertical downcast profile will be conducted with an underwater unit consisting of a SeaBird SBE-9 CTD, various sensors, and a General Oceanics Model 1015 rosette system with up to nine Niskin bottles. During the hydrocast, the following *in situ* measurements will be made using the underwater unit:

- Conductivity
- Temperature
- Depth of sensors/water sample
- DO
- Chlorophyll fluorescence
- Optical beam transmittance
- Light irradiance
- Altitude of the sensors above the sea floor
- Bathymetry

Salinity and sigma-t will be calculated from the conductivity, temperature, and depth data. The profile will be conducted from the near-surface to within approximately 5 m of the sea floor. Concurrently with the recording of profile measurements, measurements of total incident photosynthetically active radiation, bathymetry, navigational position, and time will also be recorded in the same data file.

At each station, 5- or 10-L GO-FLO or Niskin sampling bottles will be used to collect water from five depths during upcast. On deck, each Niskin bottle will be subsampled for dissolved inorganic nutrients and other chemical analyses as detailed below.

Table 1.	Water Column	Sampling .	Stations
Station	Latitude	Longitude	Depth (m)
F01P	41°51.05'N	70°27.20'W	27
F02P	41°54.49'N	70°13.70'W	33
F03	41°57.00'N	70°32.90'W	17
F04	42°04.78'N	70°16.88'W	63
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
F08	42°16.68'N	70°26.86'W	82
F09	42°13.29'N	70°41.20'W	19
F10	42°14.54'N	70°38.24'W	30
F11	42°16.23'N	70°35.08'W	53
F12	42°19.80'N	70°25.40'W	90
F13P	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
F20	42°29.65'N	70°46.45'W	36
F21	42°29.73'N	70°42.56'W	57
F22	42°28.79'N	70°37.06'W	80
F23P	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
N01P	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
N04P	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
N07P	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
N10P	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 <b>'W</b>	32
N14	42°24.58'N	70°47.57'W	34
N15	42°24.95'N	70°45.65'W	42
N16P	42°23.64'N	70°45.20'W	40
N17	42°22.32'N	70°44.74 <b>'W</b>	36
N18	42°21.95'N	70°46.66'W	30
N19	42°21.58'N	70°48.58'W	24
N20P	42°22.90'N	70°49.03'W	32
N21	42°23.27'N	70°47.12'W	34

To determine the variability of the various parameters, 32 two-day nearfield nutrient/hydrography surveys will be conducted during 1993-1994. Vertical profiles will be conducted on the first day of the surveys and tow-yo transects will be conducted on the second day of the surveys.

On the first day of the nearfield survey, 21 stations will be sampled as described above (see Figure 3 for station sampling order). In addition to the subsamples for dissolved inorganic nutrients (DIN), the surface and mid-depth Niskin bottles from three stations separated by 5 km or more will also be subsampled for chlorophyll, DO calibrations, and TSS. At six stations (N01P, N04P, N07P, N10P, N16P, and N20P), the surface Niskin bottle will be subsampled for phytoplankton. These samples will be preserved with Utermohl's solution instead of formalin because formalin will rupture the microflagellates, which comprise one of the major phytoplankton categories for quantification.

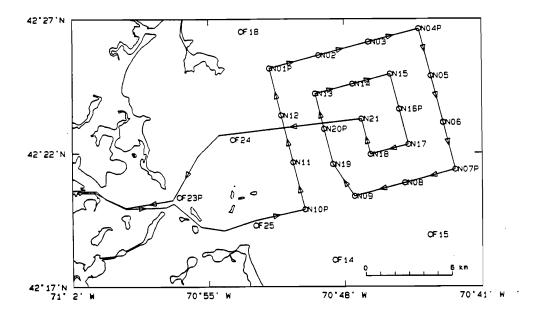


Figure 3. Tracklines for Day 1 of Nearfield Survey (Stations N10P, N11, N12, N01P through N09, N19, N20P, N13 through N18, and N21).

On the second day of each nearfield survey, high-resolution spatial hydrography will be performed to provide a three-dimensional description of water column properties in the nearfield region. The hydrographic data will be obtained with Battelle's Mini-BOSS underwater towing body containing an Ocean Sensor OS-100 CTD, and DO, chlorophyll fluorescence, and optical beam transmittance sensors. The body will be towed along the tracks that will touch each of 21 nearfield stations as shown in Figure 4. While being towed, the body will be continuously oscillated from near-surface to within 5 m of the bottom. The planned up and down oscillation distance will be approximately 500 m.

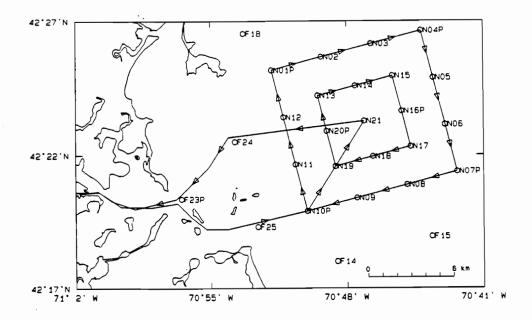


Figure 4. Tracklines for Day 2 of Nearfield Survey (Stations N10P to N01P, to N04P, to N07P, to N10P, N19 to N13, to N15, to N17, to N19, and N19 to N21).

During February, early March, early April, June, late August, and October, three-day farfield and biology/productivity surveys will be combined with the nearfield surveys. Figures 5, 6, and 7 illustrate the station sampling order. At station F25, the surface and mid-depth Niskin bottles will be subsampled for dissolved and particulate organic nutrients as well as DIN at all depths. The four farfield stations (F01P, F02P, F13P, and F23P) and six nearfield stations (N01P, N04P, N07P, N10P, N16P, and N20P) will include biology/productivity sampling in addition to sampling conducted for DIN. Niskin bottles will be subsampled for the following analyses:

- Dissolved inorganic nutrients (5 depths)
- Phytoplankton species enumeration (surface and mid-depth samples to be analyzed; samples from other depths to be archived)
- Dissolved and particulate organic nutrients (surface and mid-depth)
- Chlorophyll a and phaeopigments in extracts of filtered water (surface and mid-depth)
- TSS (surface and mid-depth)

- DO (surface, mid-depth, and mid-bottom)
- Respiration (surface, mid-depth, and mid-bottom)
- Photosynthesis parameters [P<sub>max</sub> by <sup>14</sup>C and P(I) by <sup>14</sup>C; surface and mid-depth]

After a hydrocast at a Biology/Productivity station, a zooplankton sample will be collected.

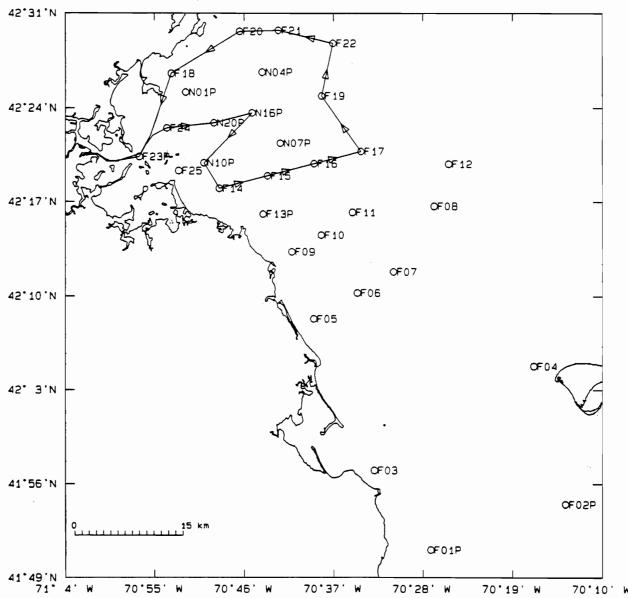


Figure 5. Tracklines for Day 1 of Farfield Survey (Stations F23P, F24, N20P, N16P, N10P, F14, F15, F16, F17, F19, F22, F21, F20, and F18).

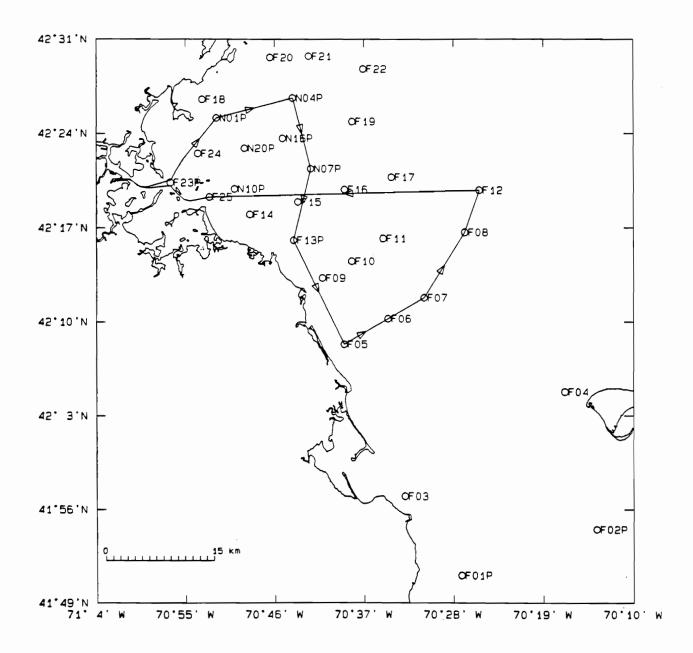


Figure 6. Tracklines for Day 2 of Farfield Survey (Stations N01P, N04P, N07P, F13P, F05, F06, F07, F08, F12, and F25).

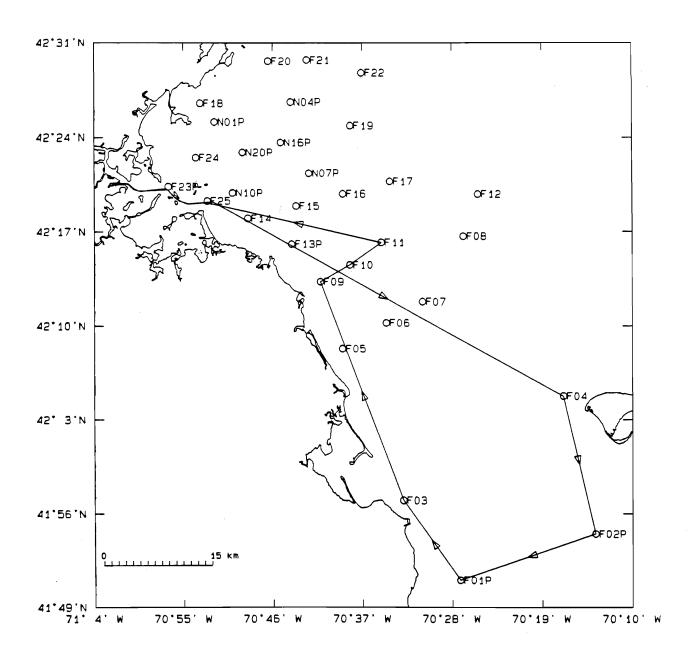


Figure 7. Tracklines for Day 3 of Farfield Survey (Stations F04, F02P, F01P, F03, F09, F10, F11).

#### 7.3.2 Laboratory Program

Water samples collected during the surveys will be analyzed to determine *in situ* concentrations of five dissolved inorganic nutrients (nitrate, nitrite, ammonium, phosphate, and silicate); three dissolved organic nutrients (carbon, nitrogen, and phosphorus); two particulate nutrients (carbon and nitrogen); DO; TSS; chlorophyll *a* and phaeopigments; and estimates of plankton respiration rates and productivity. Table 2 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 3 lists the *in situ* hydrographic measurements and the field samples to be collected. Table 4 presents the collection frequency of discrete water samples.

#### 7.5 Parameter Table

Table 2 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. PROJECT FISCAL INFORMATION

This project is being carried out under the Harbor and Outfall Monitoring contract (Contract No. S138) between MWRA and Battelle Ocean Sciences.

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

See Section 20 for literature references.

Table 3. Field Samples and Measurements								
Parameter	Stations	Sample Volume	Sample Containers	Shipboard Processing/ Preservation				
Following samples	are subsampled from water	collected with	Poly Vinyl Chloride Nis	skin GO-FLO Bottles				
Dissolved Inorganic Nutrients	All	60 mL	100 mL Polyethylene bottle	Pass through a filter. Fix with chloroform.				
Dissolved Oxygen	10 Biology/ Productivity and 3 Nearfield	300 mL	300 mL Glass BOD	Fix per Oudot <i>et. al.</i> (1988). Titrate within 24 hours.				
Dissolved Organic Carbon	10 Biology/ Productivity and F25	50 mL	100 mL amber glass bottle	Pass through a pre-ashed glass fiber filter. Fix with 0.5 mL of phosphoric acid.				
Dissolved Organic Nitrogen	10 Biology/ Productivity and F25	20 mL	50 mL glass digestion tube	Pass through a filter. Digest within 8 hours.				
Dissolved Organic Phosphorus	10 Biology/ Productivity and F25	20 mL	50 mL glass digestion tube	Pass through a filter. Digest within 8 hours.				
Particulate Organic Carbon	10 Biology/ Productivity and F25	50 mL	Whatman GF/F glass fiber filter	Pass through a pre-ashed glass fiber filter. Freeze (-5 °C).				
Particulate Organic Nitrogen	10 Biology/ Productivity and F25	50 mL	Whatman GF/F glass fiber filter	Pass through a pre-ashed glass fiber filter. Freeze (-5 ° C).				
Total Suspend Solids	10 Biology/ Productivity and 3 Nearfield	200 mL	Petri dish	Pass through a filter. Freeze (-5°C)				
Chlorophyll <i>al</i> Phaeopigments	10 Biology/ Productivity and 3 Nearfield	2 x 10 mL	Whatman GF/F glass fiber filter	Pass through filter. Fix with 1% MgCO <sub>3</sub> solution, wrap in foil, store over desiccant, and refrigerate.				
Phytoplankton (Whole Water)	10 Biology/ Productivity	800 mL	1000 mL glass bottle	Preserve with Utermohl's solution				
Phytoplankton (Screened Water)	10 Biology/ Productivity	2000 mL	100 mL Polyethylene bottle	Strain through a 20 $\mu$ m mesh; wash retained organism into a jar. Fix with Utermohl's solution.				
<sup>14</sup> C Production	10 Biology/ Productivity	300 mL	300 mL Glass BOD	Inoculate with 2.5 $\mu$ Ci of NA <sub>2</sub> <sup>14</sup> CO <sub>3</sub> and incubate.				
Following sample is	s collected with a vertically t	owed net						
Zooplankton	10 Biology/ Productivity	800 mL	1000 mL glass bottle	Wash into jar. Fix with a 5-10% Formalin solution.				
The following meas	surements are collected by t	he Battelle Oce	an Sampling System	Precision				
Conductivity	All		Floppy disk	0.01 mS/cm				
Temperature	All		Floppy disk	0.001 °C				
Pressure	All		Floppy disk	0.01 decibars				
Dìssolved Oxygen	All		Floppy disk	0.05 mg/L				
Chlorophyll <i>a</i> Fluorescence	All		Floppy disk	0.01 μg/L				
Transmissometry	All	•••	Floppy disk	0.01 m <sup>-1</sup>				
<i>In situ</i> Irradiance	All		Floppy disk	1 μE m <sup>-2</sup> s <sup>-1</sup>				
Surface Irradiance	All		Floppy disk	1 μE m <sup>-2</sup> s <sup>-1</sup>				
Bottom Depth	All		Floppy disk	1 m				
Navigational Position	All		Floppy disk	0.000017 deg				

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		Nearfield Nutrient/Hydrography			graphy	Biology/Productivity			Farfield Nutrient/						
			_		Sur	veys			Surv	eys	ŀ	lydr	ography	Surveys	
Refer to Notes Below for Stations IDs	Note 1	Note 2	Note 3	Note 4	Note 5	Totals per Survey	Totals for 32 Surveys	Note 6	Totals per Survey	Totals for 12 Surveys	Note 7	Note 8	Totals per Survey	Totals for 12 Surveys	Totals for all Surveys
Number of Hydrographic Stations	1	5	3	3	9	21	672	10	10	120	20	1	21	252	1044
Dissolved Inorganic Nutrients	5	5	5	5	5	105	3360	5	50	600	5	5	105	1260	5220
Chlorophyll a and Phaeopigments (2 reps)			2			6	192	2	20	240				0	432
Total Suspended Solids (2 reps)			2			6	192	2	20	240				0	432
Dissolved Organic Nitrogen and Phosphorus (2 reps)								2	20	240		2	2	24	264
Dissolved Organic Carbon								2	20	240		2	2	24	264
Particulate Carbon and Nitrogen (2 reps)								2	20	240		2	2	24	264
Phytoplankton (whole water) to analyze	1		_			1	32	2	20	240					272
Phytoplankton (whole water) to archive		1				5	160	3	30	360					520
Phytoplankton (screened) to analyze	1					1	32	2	20	240					272
Phytoplankton (screened) to archive		1				5	160	3	30	360					520
Initial Dissolved Oxygen (Note 9)				2		6	192	9	90	1080					1272
Respiration (Note 9)								9	90	1080					1080
Pmax by Carbon-14 (Note 10)								12	120	1440					1440
Pmax by Oxygen (Note 11)								6	60	720					720
P(I) by Carbon-14 (Note 12)								20	200	2400					2400
P(I) by Oxygen (Note 12)								20	200	2400					2400
Zooplankton								1	10	120					120

#### Notes:

- 1 Station N10P
- 2 Stations NO1P, NO4P, NO7P, N16P, and N20P
- 3 Any 3 nearfield stations
- 4 Any 3 nearfield stations (the same or different ones from Note 3)
- 5 Nine Stations not used for oxygen or chlorophyll a calibrations
- 6 Stations F01P, F02P, F13P, F23P, N01P, N04P, N07P, N10P, N16P, and N20P
- 7 All farfield stations except F25
- 8 Station F25
- 9 Collect 3 samples at 3 depths
- 10 Collect 6 samples at 2 depths
- 11 Collect 3 samples at 2 depths
- 12 Collect 10 samples at 2 depths

#### 9. SCHEDULE OF ACTIVITIES AND DELIVERABLES

The schedule of activities and deliverables for this project is tied to survey activities. Figures 8 and 9 provide a tentative schedule in 1993 and 1994 for all survey plans, surveys, and survey reports required for Tasks 5, 6, and 7. The deliverables for Tasks 5, 6, 7, 8, and 9 are (1) survey plans and survey reports for each of the 32 surveys, (2) 10 nutrient data and respiration/productivity data reports, and (3) 10 phytoplankton data reports and 10 zooplankton data reports. The due dates for the data reports are shown in Table 5.

Table 5.	Due Dates for Data Reports
Due Date	Surveys Included
May 31,1993	February and March 1993 surveys
June 30, 1993	April and May 1993 surveys
August 31, 1993	June and July 1993 surveys
October 29, 1993	August and September 1993 surveys
December 31, 1993	October, November, and December 1993 surveys
May 31, 1994	February and March 1994 surveys
June 30, 1994	April and May 1994 surveys
August 31, 1994	June and July 1994 surveys
October 31, 1994	August and September 1994 surveys
December 30, 1994	October, November, and December 1994 surveys

#### 10. PROJECT ORGANIZATION AND RESPONSIBILITIES

The project organization is shown in Figure 10. Dr. Michael Mickelson is the MWRA Project Manager and the MWRA Water Column Project Area Manager. He will be informed of all matters pertaining to work described in this CW/QAPP. Dr. Carlton Hunt is the Battelle Project Manager responsible for the overall performance of the project. Mr. Carl Albro is the Battelle Project Area Leader responsible for the overall performance of the water column monitoring tasks described in this CW/QAPP. Mr. Albro will be responsible for coordinating all survey operations and for ensuring successful completion of each survey. It is expected that Mr. Albro will be the Chief Scientist on three or four surveys each year; he will designate an alternate Chief Scientist (Paul Dragos or Debbie West) for the other surveys. During each survey, the Chief Scientist will be assisted by Jack Bechtold, Kevin King, or Bob Mandeville with BOSS

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M = Mob Day D = De-mob Day F = Farfield Day N = Nearfield Day P=Survey Plan R=Survey Report

Figure 8. Schedule of Water Column Surveys for 1993.

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M = Mob Day D = De-mob Day F = Farfield Day N = Nearfield Day P=Survey Plan R=Survey Report

Figure 9. Schedule of Water Column Surveys for 1994.

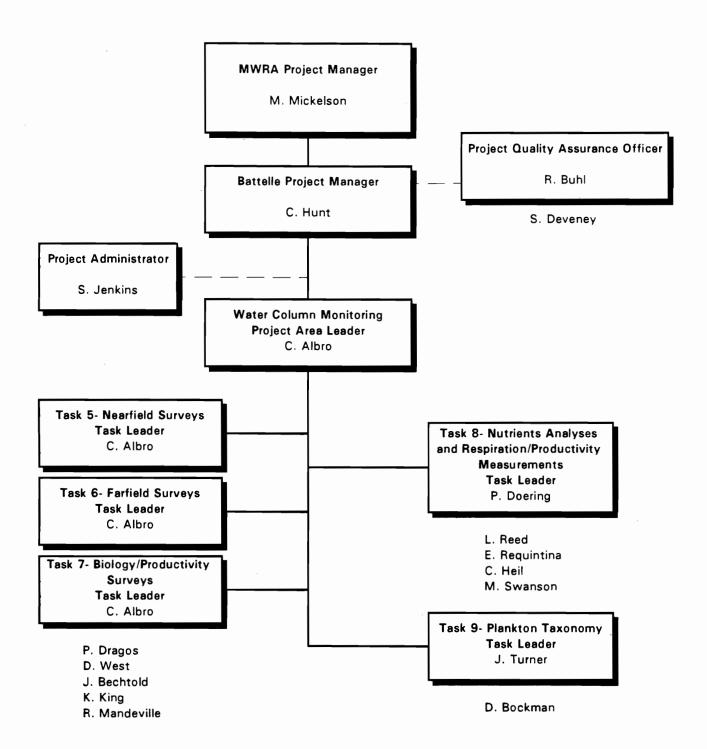


Figure 10. MWRA Water Column Monitoring Project Organization.

operations. The Chief Scientist for each survey will be responsible for preparing the survey plan and survey report, and will oversee/direct all survey activities. As Battelle's Technical Director, Dr. Kelly will assist Mr. Albro in overseeing subcontractors conducting the sampling and laboratory work related to plankton, nutrients, and respiration/productivity measurements.

Dr. Jefferson Turner will be the Subconsultant Project Manager for UMD and will either perform or oversee the Task-9 taxonomic analyses. Mr. David Borkman of UMD will perform phytoplankton taxonomy and will assist with sample collection.

Battelle's subcontractor, the University of Rhode Island (URI), will perform work under Tasks 5, 6, 7, and 8. As Subconsultant Project Manager for URI, Dr. Peter Doering will oversee all analyses of nutrients and respiration/production. Dr. Candace Oviatt will assist Dr. Doering in technical oversight of all work conducted by URI. Ms. Laura Reed and Mr. Edwin Requintina will assist with sample collection and analysis. Mr. Eric Klos will serve as a URI alternate to assist with field sampling.

Ms. Rosanna Buhl will oversee the QA of all technical activities conducted by Battelle.

#### 11. DATA QUALITY REQUIREMENTS AND ASSESSMENTS

To ensure that all data generated during the conduct of Tasks 5, 6, 7, 8, and 9 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 Battelle's experience, precision and accuracy objectives for navigation and hydrographic samplings are presented in Table 6. Section 12 provides details on relevant sampling procedures to ensure data quality and Section 14 discusses instrument calibration methods.

Table 6. A	lccuracy and	Precision of	f Instrument S	Sensors
Sensor	Units	Range	Accuracy	Precision
Pressure	decibars	0-1000	0.60	0.1
Temperature	°C	-2 to +30	0.015	0.01
Conductivity	mS/cm	0.5-65	0.02	0.01
Transmissometer	m <sup>-1</sup>	0-40	0.20	0.01
Dissolved Oxygen	mg/L	0-15	0.50	0.05
Fluorometer	$\mu { m g}/{ m L}$	0.1-100	50% of reading	0.01
In situ irradiance	$\mu E m^{-2} s^{-1}$	0-4000	10	1
On-Deck irradiance	$\mu E m^{-2} s^{-1}$	0-4000	10	1
Altimeter	m	0-150	1	0.1
Echosounder	m	0-200	2	0.1
Navigation	degree	World	100 m	30 m

#### 11.1.2 Completeness

The BOSS navigation system outputs navigation positions at an interval of 2 s. The BOSS software system will display all position fixes and save these fixes in an electronic file during hydrocasts and sampling or towing operations. The project's time interval requirement for obtaining positions during sampling is 1 min. Thus, even with a few bad data streams from the Northstar to the computer, the software will provide enough fixes within each 1-min period for 100% data collection. During transit between stations, the BOSS software system will save vessel coordinates in an electronic file every 5 min.

Because hydrographic data are acquired electronically and monitored in real time, no loss of data is expected. With the sampling rates of the CTD (4 times per second) and navigation systems (2 s intervals), 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. The 6- to 7-kn survey speeds during towing operations at the outfall site will also allow a large area to be covered in the one-day tow operation. Stations will not be occupied if CTD measures (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. 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 undifferentiated GPS or corrected LORAN. The station locations are targets and sampling will be attempted within 300 m of the targets, according to the BOSS navigation display; objectives will not be compromised if conditions force sampling within 600 m from the targets.

The instrumentation and methods of data reduction that will be used during the water column 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 (McDowell et al., 1991), Massachusetts/Cape Cod Bays (Townsend et al., 1991 and Kelly et al., 1992), and data from MWRA surveys conducted in 1992.

#### 11.1.4 Representativeness

The LORAN TDs and 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 latitude/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. The vertical profiles and horizontal tows conducted under this project will provide more data than have previously been acquired in the region of the future outfall. These data will be used, in part, to determine what is representative and required to meet the monitoring objectives.

# 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 (Lambert and Oviatt, 1986) will follow standard methods that can achieve this objective. Samples for dissolved inorganic nutrients, organic nutrients, TSS, phytoplankton, and chlorophyll will be collected from labeled GO-FLO or Niskin hydrocast bottles taken from depths recorded in the BOSS software event log. 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 BOSS marker) that will allow the sample to be traced from collection through analysis to reporting. All samples will be handled and stored according to the procedures in 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 coincidently 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 ( $\mu$ M), chlorophyll ( $\mu$ g L<sup>-1</sup>), TSS (mg L<sup>-1</sup>), and DO (mg L<sup>-1</sup> or % saturation).

#### 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 baseline water quality monitoring study, URI will generate data on dissolved inorganic nutrients, chlorophyll a, TSS, particulate and dissolved organic carbon and nitrogen, DO (used for calibration of *in situ* sensor and calculating respiration and primary production), and <sup>14</sup>C (used for calculations of primary production). Precision of these analyses for replicate samples is shown in Table 7. Section 12 provides additional details on the analytical procedures (e.g., prepared standards) that will ensure data quality and Section 14 describes instrument calibration methods.

UMD 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.

#### 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 Buzzard Bay, because analytical procedures are similar or identical.

# 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.

	Table 7.	Objectives for Laboratory Measurem	nent
Parameter	Units	Method by which Analytical Accuracy is Assessed	Precision <sup>1</sup> (Better than)
Dissolved Ammonia	$\mu$ M	Ammonium Chloride Primary Standard	± 0.3%
Dissolved Nitrate	$\mu$ M	Sodium Nitrate Primary Standard	± 0.2%
Dissolved Nitrite	$\mu$ M	Sodium Nitrite Primary Standard	± 0.2%
Dissolved Phosphate	$\mu$ M	Potassium phosphate Primary Standard	± 0.6%
Dissolved Silicate	$\mu$ M	SiO <sub>2</sub> with Sodium Carbonate Primary Standard	± 0.4%
Dissolved Oxygen	mg L <sup>-1</sup>	Potassium Iodate Primary Standard	± 0.5%
Dissolved Organic Carbon	$\mu$ M	Potassium Biphthalate Primary Standard	± 5.0%
Dissolved Organic Nitrogen	$\muM$	% recovery of N from glycine	± 1.0%
Dissolved Organic Phosphorus	$\mu$ M	% recovery of P from Fructose	± 4.0%
Particulate Organic Carbon	$\mu$ M	Acetanilide Primary Standard	± 10%
Particulate Organic Nitrogen	μM	Acetanilide Primary Standard	± 8.0%
Total Suspend Solids	mg L <sup>-1</sup>	Manufacturer's Weight Standard	± 5.0%
Chlorophyll <i>al</i> Phaeopigments	$\mu$ g L $^{-1}$	Chlorophyll a Standard from Sigma Chemical	± 5.0%
<sup>14</sup> C Production	<sup>14</sup> C hr <sup>-1</sup>	Quench using external channels ratio method	± 12%

<sup>&</sup>lt;sup>1</sup>Based on replicate sample analyses.

#### 12. 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 BOSS navigation system. This system consists a Northstar model-800 integrated global positioning system (GPS)/LORAN interfaced to the BOSS computer. 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 GPS/LORAN system will automatically choose between GPS and LORAN, based on best accuracy.

The hydrographic profile sampling equipment consists of the following:

- Mini-BOSS winch with 150-m 9-conductor double-armored stainless steel cable and sheave
- General Oceanics model 1015 rosette system
- 5- and 10-L GO-FLO (or Niskin) bottles
- SeaBird CTD interface deck unit
- SeaBird SBE-9 CTD system with
  - SeaBird SBE-13 DO sensor which is a "Beckman" polarographic type that produces an oxygen-dependent electrical current and incorporates a thermistor for determination of membrane temperature;
  - SeaTech 25-cm-pathlength transmissometer 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;
  - Chelsea Aquatracka III in situ fluorometer;
  - Biospherical QSP-200L spherical quantum scalar irradiance sensor will be used to measure underwater photosynthetically active radiation (PAR); and
  - Datasonics altimeter provides a measurement of underwater unit height off the bottom
- Biospherical QSR 240 reference hemispherical quantum scalar irradiance sensor will also be used on deck to monitor changing radiation conditions above the surface of the water (e.g., due to atmospheric conditions)

- JRC JFV-120 dual-frequency color video echosounder to provide bathymetric measurements during vertical and horizontal profiling operations
- BOSS computer with data acquisition software
- Barcode printer
- Hewlett-Packard PaintJet color printer

The BOSS software acquires data from all onboard electronic sampling systems and navigation systems. The software queries each system four times per second. The software displays all of the information once per second on a color monitor. The screen is split to show sensor data on the left and navigation data on the right (see Figure 11). Once the data are acquired, they are automatically written to a data file and logged concurrently with position data from the navigation system. The navigation portion of the display will show the coastlines digitized from standard NOAA charts, navigation aids, sampling stations, and vessel track. A second monitor will be furnished to the helmsman as a steering display. During hydrocast operations, position fixes will be electronically recorded at 2-s intervals. Hard-copy printouts of position fixes will be made during discrete sampling events such as triggering of Niskin bottles. During transit operations between stations, position fixes will be electronically recorded at 5-min intervals.

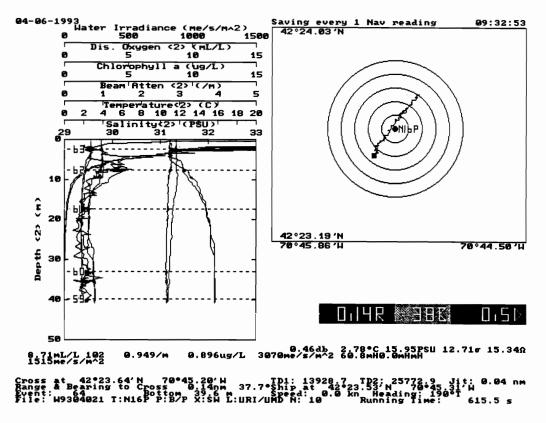


Figure 11. Sample BOSS Data Acquisition Screen

Water samples for phytoplankton, dissolved inorganic nutrients, particulate and dissolved organic nutrients, chlorophyll, TSS, DO, and respiration/production will be obtained with a General Oceanics model 1015 rosette system equipped with 5- and 10-L Niskin or GO-FLO 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 stern of the boat toward the sun during the downcast, the BOSS software program will be set to the hydrographic profiling mode and a data cast file will be opened.
- 3. The BOSS 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 (i.e., 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 1-2 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 BOSS 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 12 for examples of selection criteria). The twelve plots show chlorophyll and temperature profiles and positions of each type of protocol sampling.

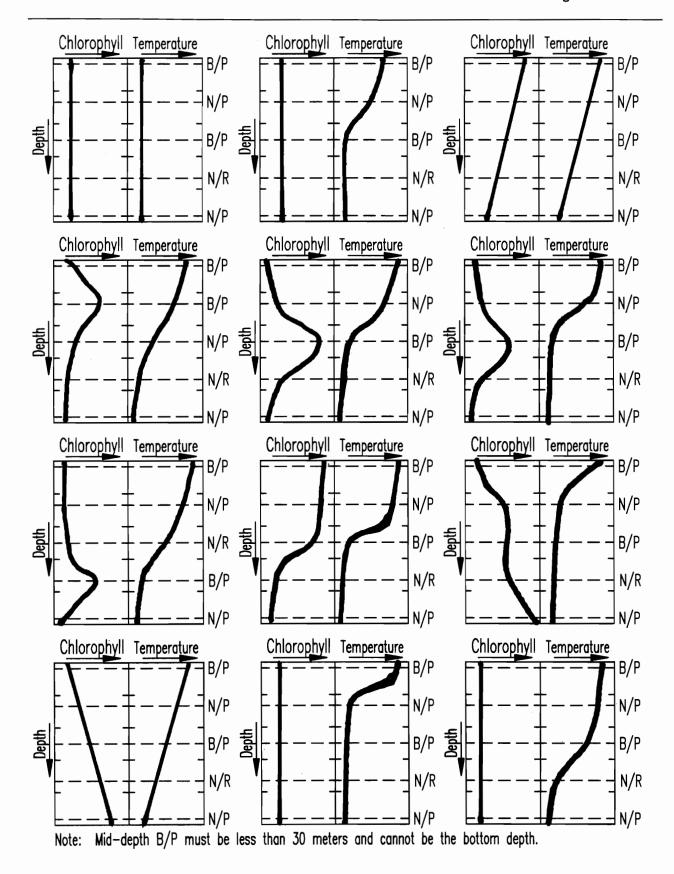


Figure 12. Criteria for Selecting Sample Depths.

- 7. During the upcast, the rosette will be momentarily maintained at each of the selected five depths. Water will be collected by closing one or more Niskin bottles, depending on the amount of water needed. Using the rosette deck unit, the Niskin bottles will be electronically closed. When the rosette deck unit indicates that the Niskin bottles are closed, this event will be electronically flagged in the BOSS data file using an unique "event mark" 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. The BOSS program will also generate bar-coded sample bottle labels for attaching to sample bottles. These labels are uniquely identified by survey ID and BOSS marker number.
- 8. After collecting the near-surface water sample, the operator will close the cast file.
- 9. The CTD system will be recovered.
- 10. The BOSS software program will be put into navigation mode with a file created for transit to the next station.
  - Note: Steps 11 through 16 depend upon the requirements for the station that is being sampled.
- 11. At each of three depths (surface, mid, and mid-bottom), three 300-mL BOD bottles will be filled for initial DO determination and three dark BOD bottles will be filled for respiration incubations. The bottles will be filled to overflowing conditions (three times) before capping (Lambert and Oviatt, 1986).
- 12. From surface and mid-depth Niskin bottles, three BOD bottles will be filled for analysis of the photosynthetic parameter  $P_{\text{max}}$  via oxygen techniques.
- 13. From surface and mid-depth Niskin bottles, 10 BOD bottles will be filled for analysis of the photosynthetic parameter P(I) via oxygen techniques.
- 14. From the surface and mid-depth Niskin bottles, 16 BOD bottles will be filled for analysis of the photosynthetic parameters  $P_{max}(6)$  and P(I)(10) via  $^{14}C$  techniques.

- 15. For the whole-water phytoplankton analyses, 1-L will be withdrawn from Niskin bottles and preserved immediately with Utermohl's solution. All phytoplankton samples will be stored at ambient temperature in the dark.
- 16. 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 in Utermohl's solution. These samples will be stored at ambient temperature in the dark.
- 17. An amber 2-L bottle will be rinsed with sample water and filled from the Niskin bottle. Aliquots from this amber bottle will be processed as described below for dissolved inorganic nutrients, dissolved and particulate organic nutrients, chlorophyll *a* and phaeopigments, and TSS.
- 18. After water sample collection at each biology/productivity station, a vertical zooplankton tow will be conducted with a 0.5-m diameter 102-μm-mesh net equipped with a flow meter. Tows will be 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). Because nets are equipped with flow meters, net clogging becomes apparent when a net is retrieved and the flow meter is no longer turning. In the event of net clogging due to large amounts of phytoplankton, 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 sample will be taken from a non-clogged net and preserved with 5-10% formalin: seawater.

# 12.2 Tow-yo Hydrographic Profiling

On the second day of each nearfield survey, a high-resolution spatial tow-yo hydrographic profiling will be performed. To conduct this profiling operation, the following sampling equipment will be used:

- Mini-BOSS winch with 150-m 9-conductor double-armored stainless steel cable and sheave
- Towed body
- Ocean Sensor OS-100 CTD interface deck unit
- Ocean Sensor OS-100 CTD system with

SeaBird SBE-13 DO sensor;

SeaTech 25-cm-pathlength transmissometer;

Chelsea Aquatracka III in situ fluorometer;

- JRC JFV-120 dual-frequency color video echosounder
- BOSS computer with data acquisition software
- Barcode printer
- Hewlett-Packard PaintJet color printer

This system will be checked out in a similar manner as described in Section 12.1

The towed body with sensor instrumentation will be towed at about 6-7 kn along tracks that will touch each of 21 nearfield stations as shown in Figure 4. While being towed, the body will be continuously oscillated from near-surface to within 5 m of the bottom. The planned up and down oscillation distance will be approximately 500 m.

If, at any time during tow-yo operations, the DO % saturation goes below 70%, the towed body will be maintained at that depth for at least 2 min before continuing with tow-yo operations. The DO % saturation will be displayed on the BOSS computer screen.

# 12.3 Onboard Sample Processing

## 12.3.1 Dissolved Inorganic Nutrients

A 60-mL aliquot will be obtained by manually filling a 60-mL plastic syringe. The sample will then be passed through a 47-mm-dia 0.4- $\mu$ m Nuclepore membrane filter into a 100-mL plastic bottle. The syringe, filter, and bottle will be rinsed with 5-10 mL of sample prior to obtaining the final sample. Samples will be preserved in chloroform until analysis.

# 12.3.2 Chlorophyll a

Two 10-mL aliquots will be withdrawn with a calibrated Oxford pipette and will be separately filtered, under vacuum (<125 mm mercury), through 25-mm-dia Gelman GF/F glass-fiber filters (nominal pore size = 0.7  $\mu$ m). To preserve the filters, a 1% (w/v) MgCO<sub>3</sub> solution is added above the filter and a vacuum is briefly applied. The filter is removed from the filtering system, wrapped in foil, stored over desiccant, and refrigerated before analysis.

### 12.3.3 Total Suspended Solids

Using a vacuum-filter system, approximately 200 mL of seawater will be passed through a preweighed 0.4- $\mu$ m Nuclepore membrane filter. The actual amount of sample filtered will be recorded in a laboratory notebook. Filters will be placed in labeled petri dishes and dried over desiccant. The material retained on the filter will be weighed in the laboratory to determine TSS in units of mg/L according to the following equation:

TSS = (weight of loaded, dried filter in mg - weight of unused filter in mg)

(volume of seawater filtered in L)

### 12.3.4 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 a pre-ashed (425°C) 100-mL amber-glass bottle. Exactly 0.5 mL of concentrated phosphoric acid will be added to preserve the sample.

### 12.3.5 Total Dissolved Nitrogen and Phosphorous

Two 20-mL aliquots will be passed with syringe through 47-mm-dia 0.4- $\mu$ m pore-size Nuclepore membrane filters into 50 mL screw-cap digestion tubes. Persulfate oxidizing reagent (2.5 mL) is added and the digestion tubes are tightly capped. Within 8 h, the sample is digested by placing the tightly capped digestion tube in a bath of boiling water for 15 min.

# 12.3.6 Particulate Carbon and Nitrogen

Two 50-mL aliquots will be passed with a syringe through pre-ashed (425°C) 13-mm-dia Whatman GF/F glass-fiber filters. Each filter will be placed in labelled filter holders and dried over desiccant.

# 12.3.7 Dissolved Oxygen (DO)

After filling all of the BOD bottles from the Niskin bottles, the nine initial DO samples from the surface, mid, and mid-bottom depths will be fixed with manganese hydroxide and iodide as described by Oudot *et al.* (1988). The remaining DO samples will be fixed after incubation is completed. Fixed oxygen samples will be titrated in the bottle using a programmed Radiometer ABU91-21/TIM90-1 autotitrator with a precise potentiometric endpoint. Within 24 h of being fixed, these samples will be titrated either on board the vessel or onshore. The concentration of DO in units of (mg O<sub>2</sub> L<sup>-1</sup>) will be determined using the following equation:

$$DO = \frac{160 \times A \times F}{V - 2}$$

A = Volume of titrant in mL

V = Volume of BOD in mL

F = Factor based on standardization of thiosulfate titrant against a potassium iodate standard of known molarity.

## 12.3.8 Respiration

From each biology/productivity station, nine (3 from 3 depths) dark BOD bottles will be incubated in the dark for 6 h before being fixed for DO titration. Also, nine BOD bottles will be fixed immediately to serve as initial DO samples. 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 O<sub>2</sub> L<sup>-1</sup> h<sup>-1</sup> will be determined using the following equation:

$$NETR = \frac{(DO_{IB} - DO_{DB})}{T}$$

 $DO_{IB} = DO_{DB} =$ where

Initial DO concentration in mg  $O_2$   $L^{-1}$  Dark Bottle DO concentration in mg  $O_2$   $L^{-1}$  after

incubation

Т Incubation time in hours

#### 12.3.9 Production Analyses by Oxygen

Phytoplankton production and respiration will be measured by the light-dark bottle oxygen technique (Strickland and Parsons, 1972). Light and dark bottles are incubated in a photosynthetron with tungsten halogen lights using a modification of the methods of Lewis and Smith (1983). Nineteen 300-mL BOD bottles will be filled with water from given depths (surface and mid-depth) at each of the biology/productivity stations. Thirteen bottles will be incubated to simulate an irradiance gradient with light levels ranging from about 20 to 2000  $\mu E \text{ m}^{-2} \text{ sec}^{-1}$ . Three of the BOD bottles will be in the 400-600  $\mu$ E m<sup>-2</sup> sec<sup>-1</sup> range to be used for determining P<sub>max</sub>. Light levels within the incubator will be created by covering individual bottles with appropriate neutraldensity screening. Three dark BOD bottles will be placed in the photosynthetron to simulate zero irradiance. The ambient temperature of the incubator will be maintained by flowing surface seawater through the surface sample set. For the mid-depth (chlorophyll maximum) sample set, a separate compartment of the

concentrations, as well as initial values for the incubations. After approximately 6 h (actual time will be recorded), the remaining 16 BOD bottles from a given sampling location will be fixed for DO titration. All titrations will be performed on board as seas permit.

A sequence of two models will be used to fit data derived from metabolism incubations, as follows.

The first model will fit four parameters, including both a respiration and photoinhibition term, and will follow Platt *et al.* (1980). The model to predict net production is

$$P_B = P_{SB} (1 - e^{-a}) e^{-b} - R_B$$

P<sub>B</sub> = net production (chlorophyll-normalized) and

 $P_{SB}$  = theoretical maximum *gross* production (chlorophyllnormalized) without photoinhibition

where

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

$$b = BI/P_{SB}$$

 $\alpha$  = initial slope of the rise in net production with light increasing from zero irradiance [units of  $(\mu g O_2/\mu g Chl/h)/(\mu E/m^2/s)$ ], calculated from I (light irradiance level,  $\mu E/m^2/s$ ) and  $P_{SB}$ .

 $R_B$  = chlorophyll-normalized respiration (units of  $\mu g O_2/\mu g$  Chl/hr), fit by the model.

The maximum achievable gross (g) production may be calculated from this as

$$Pg_{max} = P_{SB} (\alpha/(\alpha + B)) (B/\alpha + B)^{B/\alpha}$$

and the achievable maximum net (n) production is

$$Pn_{max} = Pg_{max} - R_{R}$$

For the second model, a hyperbolic tangent function (Platt and Jassby, 1976), three parameters will be fit to predict net production; no photoinhibition term is included.

Here,  $P_B = P_{max} \times Tanh (\alpha I/P_{max}) - R_B$ 

and Pg is defined as  $P_{max} \times Tanh \ (\alpha \ I/P_{max})$ .

In this model, when R is included, the  $P_{max}$  estimated is gross production.

The parameters in each model will be fit simultaneously for each incubation series that measured paired  $P_B$  - I points, by least squares using the NLIN procedure in SAS (1985). Fitting will be accomplished by the secant method where parameters are estimated if, within 50 iterations, the model converges on a suitable simultaneous fit (SAS, 1985). If the four-parameter model does not fit, the hyperbolic model will be attempted; if neither fit, the data will so indicate. The bottle measurements of dark respiration will not be not used in this fitting procedure; rather,  $R_B$  will be derived from fitting from the P-I data. In general, however, it is expected that respiration will be low and difficult to measure directly or to fit by the model. Note, importantly, that in both model cases, the  $P_{\rm max}$  of interest is net production, so from the model parameters,  $Pn_{\rm max}$  can be calculated as  $Pg_{\rm max}$  - R, or roughly read directly from the chlorophyll-normalized P-I curves.

# 12.3.10 Production Analyses by <sup>14</sup>C

Primary productivity by  $^{14}$ C will be measured using the same incubation scheme described above for oxygen. Prior to incubation, 16 300-mL BOD bottles will be inoculated with 2.5  $\mu$ Ci of  $^{14}$ C-sodium carbonate. The inoculated bottles, together with three dark bottles, will be incubated in a photosynthetron for 4-6 h (actual time will be recorded). At the end of the incubation period, labeled particulate matter from each bottle will be collected on a 47-mm-dia glass-fiber filter. The filter will be rinsed with seawater and then placed in a 20-mL vial with scintillation fluid. The models described in Section 12.3.10, less a respiration term after dark bottle correction, will be used to fit the data.

## 12.3.11 Zooplankton

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

# 12.4 Laboratory Sample Processing and Analysis

# 12.4.1 Dissolved Inorganic Nutrients

The methods for analysis of dissolved inorganic nutrients are described by Lambert and Oviatt (1986). Briefly, dissolved inorganic nutrient concentrations will be determined on samples that have been passed through a 0.4- $\mu m$  Nuclepore membrane filter. The concentrations of ammonia, nitrate, nitrite,

silicate, and phosphate will be measured colorimetrically on a Technicon II Autoanalyzer. This instrument simply automates standard manual techniques for the analysis of nutrients. The analysis of ammonia will be based on the technique of Solorzano (1969) whereby absorbance of an indophenol blue complex is measured at 630 nm. Nitrite will be measured by the method of Bendschneider and Robinson (1952). The total of nitrate and nitrite is determined by reducing all nitrate in the sample to nitrite and analyzing for nitrite as above. The concentration of nitrate is obtained by difference. The reduction is accomplished using a cadmium column (Morris and Riley, 1963). The analysis of phosphate will be based on the molybdate blue procedure of Murphy and Riley (1962). The colorimetric analysis of silicate will be based on that of Brewer and Riley (1966).

#### 12.4.2 Chlorophyll a

The concentrations of chlorophyll a and phaeopigments will be determined fluorometrically using a Turner fluorometer by the method of Yentsch and Menzel (1963) as modified by Lorenzen (1966). Chlorophyll and phaeophytin concentrations are calculated using the equations of Lorenzen (1966):

$$\mu$$
g/L Chl  $a = \frac{F_o/F_{a \text{ max}}}{(F_o/F_{a \text{ max}}) - 1} (K_X)(F_o - F_a) \left(\frac{V_E}{V_F}\right)$ 

$$\mu g/L \ phaeophytin = \left(\frac{F_o/F_{a \ max}}{(F_o/F_{a \ max}) - 1}\right) (K_x) [(F_o/F_{a \ max})(F_a) - F_o] \left(\frac{V_E}{V_F}\right)$$

where:

 $F_0$  = fluorescence before acidification

F<sub>a</sub> = fluorescence after acidification

 $F_o/F_{a \text{ max}}$  = maximum acid factor expected from pure Chl a

 $K_x$  = calibration constant for a particular sensitivity scale

 $V_F$  = volume filtered in liters

 $V_E$  = volume of extracted chlorophyll a

### 12.4.3 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 Carlo Erba Model-1106 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.

### 12.4.4 Dissolved Organic Nitrogen and Phosphorus

The concentration of dissolved organic nitrogen or phosphorus currently must be determined by difference between total dissolved inorganic plus organic and total dissolved inorganic. The procedures by which the concentrations of dissolved inorganic nitrogen and phosphorus are obtained have already been described. The method of Valderrama (1981) will be used to determine the concentrations of total dissolved nitrogen and phosphorus. This wet-chemical technique utilizes persulphate to oxidize organic nitrogen and phosphorus to nitrate and phosphate. The concentrations of the latter are then determined colormetrically on a Technicon Autoanalyzer, as described above.

### 12.4.5 Dissolved Organic Carbon

Dissolved organic carbon will be determined by persulphate digestion (Lambert and Oviatt, 1986) using an O.I. Model-700 TOC Analyzer. Some doubt concerning the accuracy of this method exists, and recent work suggests that the higher concentrations obtained by high-temperature combustion more nearly reflect true levels of DOC in nature (Sugimura and Suzuki, 1988). The analysis to be used has been intercalibrated with an Ionics high-temperature combustion instrument. Results for both fresh- and salt-water samples agreed to within 6%. In addition, a recent comparison of methods revealed no difference between concentrations obtained by wet oxidation with persulphate and those obtained by high-temperature combustion (J.I. Hedges, personal communication), and claims of greater accuracy by high-temperature combustion have not been substantiated.

The methods chosen for the determination of dissolved organic nitrogen, phosphorus, and carbon rely on the oxidation of organic matter by the persulphate ion and are, therefore, comparable. The methods are well established and are widely used by oceanographic researchers.

# 12.4.6 Production Analyses by <sup>14</sup>C

The radioactive <sup>14</sup>C retained on the filter will be determined with a Beckman LS-3801 liquid scintillation counter. Cpm is converted to dpm using the quench correction method. Primary production is calculated using the equations of Strickland and Parsons (1972) and expressed as mg C m<sup>-3</sup> h<sup>-1</sup>.

mg Cm<sup>-3</sup> h<sup>-1</sup> = 
$$\frac{(R_s - R_b) W \times 1.05}{R \times T}$$

where:  $R_s = light bottle dpm$ 

 $R_b = dark bottle dpm$ 

W = weight of carbonate carbon or mg C m<sup>-3</sup>

R = dpm added to sample

T = incubation time in hours

### 12.4.7 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 0.4- $\mu$ m Nuclepore membrane filter. The filter is rinsed with deionized water to remove salt, dried to constant weight at 60°C, and reweighed. All weighings are performed on a Cahn electrobalance with removal of static charges on filters and sample prior to weighing.

# 12.4.8 Whole-Water Phytoplankton

At the laboratory, Utermohl's-preserved whole seawater samples will be prepared for analysis by concentrating the sample via gravitational settling. Samples will be placed in 40-cm tall glass settling chambers (graduated cylinders) that are scrubbed clean before each sample is processed. The initial volume of each sample will be recorded to the nearest 0.5 mL and the sample allowed to stand undisturbed in the covered settling chamber for a period of one week. After the one-week settling period, the settling chamber is uncovered and the upper 700-750 mL of seawater siphoned out of the settling chamber with a pipette attached to a 0.5-cm-dia hose. The supernatant fluid that is siphoned off will be occasionally examined to ensure that no cells are inadvertently removed from the settling chamber. The fluid remaining in the settling chamber (containing the settled-out phytoplankton) is then gently mixed and transferred to a 250-mL jar. This concentrated (by a factor of approximately 10:1) plankton is examined microscopically.

Phytoplankton cells are counted in a 1-mL subsample placed in a 1-mL Sedgwick-Rafter cell. Phytoplankton cells will be observed, counted, and

identified to lowest possible taxa at 200X magnification. However, 400X will be used when needed to identify small cells or to discern important taxonomic features. A Whipple-grid disk, placed in one ocular lens of the microscope, allows partitioning of the Sedgwick-Rafter chamber into areas of known volume (0.000195 mL per Whipple grid). A minimum of 200 cells and usually >400 cells will be counted for each sample. When 200 cells are counted in less than 200 Whipple grids, counting will be continued until 200 Whipple grids are examined. Examining a relatively large subsample (200 Whipple grids) increases the probability of observing relatively rare cells, while counting between 200 and 400 cells per sample allows estimates of total phytoplankton abundance that have a precision of  $\pm 10\%$  (for 400 cells counted) to  $\pm 20\%$  (for 200 cells counted) of the mean (Anonymous, 1978).

The following example demonstrates the method that will be used to determine total phytoplankton abundance:

$$\frac{\text{\# cells}}{\text{liter}} = \frac{\text{\# cells counted}}{\text{\# grids} \times \text{vol/grid}} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{V_s}{V_o}$$

where:

$$V_s$$
 = Volume of settled sample (typically 50-100 mL)   
 $V_o$  = Volume original sample minus volume of preservative (usually 800 mL)   
 $V_o$  = 0.000195 mL per Whipple grid (@200X)

Therefore, if 410 cells are counted in 200 Whipple grids (@ 200X) and the initial seawater sample is 800 mL settled to a volume of 80 mL, the density of phytoplankton in the water sample would be determined as follows:

$$\frac{\text{\# cells}}{\text{liter}} = \frac{410 \text{ cells}}{200 \text{ grids} \times 0.000195 \text{ mL/grid}} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{80 \text{ mL}}{800 \text{ mL}}$$

$$\frac{\text{\# cells}}{\text{liter}} = 1.051 \times 10^6 \text{ cells per liter}$$

### 12.4.9 Screened Phytoplankton (Dinoflagellates)

Methods for the analysis of dinoflagellates are similar to the method described in Section 12.4.8. Cells will be concentrated by gravimetric sedimentation and the concentrated aliquots will be examined in a Sedgwick-Rafter cell. Enough aliquots will be examined to provide a volume representative of 677 mL of collected seawater. A taxonomist will identify and count Alexandrium tamarense, Ceratium sp., Dinophysis sp., Gymnodinium sp., Gyrodinium sp., Heterocapsa triquetra, Prorocentrum sp., Protoperidinium sp. and other toxic algae such as Heterosigma akashiwo (formerly Olisthodiscus luteus) and Phaeocystis pouchetti. Only the samples from station N10P from the nearfield surveys, and the surface and mid-depth samples from the 10 biology/productivity stations will be enumerated. Other collected samples will be archived.

Because these samples are screened to obtain the large dinoflagellates, diatoms will not be counted. Calculations are similar to those for the whole seawater sample and are based on the number of organisms counted in a concentrated 1-mL subsample multiplied by the concentration factor.

#### 12.4.10 Zooplankton

Upon return to shore, samples for zooplankton are transferred to 70% ethanol solutions to prevent inhalation of formalin fumes during counting. Samples are reduced to aliquots of at least 500 animals with a Folsom plankton splitter, and animals are counted under a dissecting microscope and identified to the lowest possible taxon. In most cases, this will be to species; adult copepods will be additionally characterized by sex. All copepodite stages of a given copepod genus will be lumped because copepod nauplii of small species cannot be reliably separated to genus under a dissecting microscope. Concentrations of total zooplankton and all identified taxa are calculated based on the number of animals counted, divided by the volume of water filtered by the net, multiplied by the aliquot concentration factor.

### 13. SAMPLE CUSTODY

Samples collected in the field are identified by a unique sample ID which is a concatenation of event id (five-character ID unique to each survey (e.g., see Table 8 for list of event ids) and marker no (which is a non-repeating number generated by the BOSS software for each survey). Before the field surveys are initiated, a checklist of all samples to be collected is prepared. At each station, water from five depths will be sampled for various analyses. To identify the suite of samples, a protocol coding system has been developed specifically for this project. Table 9 shows the protocol codes and samples to be collected with each protocol code. Based on the project sampling requirements, station sampling plans have been developed for Task 5 (see Table 10), and for Tasks 6 and 7 (see Table 11). Based on the information included in Tables 9, 10, and 11, one set of station logs and four sets of chainof-custody (COC) forms will be generated for each survey. Manual entries will be recorded in indelible ink. Each completed form will be signed and dated by

Table 8. Ev	ent_IDs for Each S	Survey
Survey Date	Туре	Event ID
23-27 Feb 1993		_
10-14 Mar 1993		W9302
24-25 Mar 1993	Nearfield	W9303
6-10 Apr 1993	Farfield/Nearfield	W9304
28-29 Apr 1993	Nearfield	W9305
19-20 May 1993	Nearfield	W9306
22-26 Jun 1993	Farfield/Nearfield	W9307
7-8 Jul 1993	Nearfield	W9308
28-29 Jul 1993	Nearfield	W9309
11-12 Aug 1993	Nearfield	W9310
24-28 Aug 1993	Farfield/Nearfield	W9311
8-9 Sep 1993	Nearfield	W9312
29-30 Sep 1993	Nearfield	W9313
12-16 Oct 1993		W9314
3-4 Nov 1993	Nearfield	W9315
1-2 Dec 1993	Nearfield	W9316
22-28 Feb 1994	Farfield/Nearfield	W9401
	Farfield/Nearfield	
23-24 Mar 1994	Nearfield	W9403
5-9 Apr 1994	Farfield/Nearfield	W9404
27-28 Apr 1994	Nearfield	W9405
18-19 May 1994	Nearfield	W9406
21-25 Jun 1994	Farfield/Nearfield	W9407
6-7 Jul 1994	Nearfield	W9408
27-28 Jul 1994	Nearfield	W9409
10-11 Aug 1994	Nearfield	W9410
23-27 Aug 1994	Farfield/Nearfield	W9411
7-8 Sep 1994	Nearfield	W9412
28-29 Sep 1994	Nearfield	W9413
11-15 Oct 1994	Farfield/Nearfield	W9414
2-3 Nov 1994	Nearfield	W9415
30 Nov-1 Dec 1994	Nearfield	W9416

the staff member entering the information.

The BOSS computer operator will fill out a station log (see Figure 13) at each station. These logs will be put into a BOSS 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, *marker\_no* data, and general comments. When a Niskin bottle is closed or a zooplankton tow is completed, this action will be electronically flagged in the BOSS data file using

	Tal	ble 9. Codes for Protocols and Related Samples
Protocol	Lab	Description
B/P	URI/UMD	Biology/Productivity Niskins (3) (Surface and Mid-Depth)  - Dissolved Inorganic Nutrients  - Phytoplankton (Whole Water and Screened)  - Dissolved and Particulate Organic Nutrients  - Chlorophyll a and Phaeopigments  - Total Suspended Solids  - Initial Dissolved Oxygen (3)  - Respiration (3)  - Pmax by Oxygen (10)  - P(I) by Oxygen (3)  - Pmax by Carbon-14 (6)  - P(I) by Carbon-14 (10)
N/R	URI/UMD	DO/Phytoplankton/DIN Niskin (Bottom Depth) - Dissolved Inorganic Nutrients - Initial Dissolved Oxygen (3) - Respiration (3) - Phytoplankton (Whole Water and Screened)
Z00	UMD	Zooplankton Tow Sample
DIN	URI	Dissolved Inorganic Nutrients Niskin (All Depths)
ANU	URI	All Nutrients Niskin (Surface and Mid-Depth) - Dissolved Inorganic Nutrients - Dissolved and Particulate Organic Nutrients
NOC	URI	Nutrients and Chlorophyll Niskin (Nearfield = Surface and Mid-Depth)  - Dissolved Inorganic Nutrients  - Dissolved Oxygen (2)  - Chlorophyll a and Phaeopigments  - Total Suspended Solids
N/P	URI/UMD	Nutrients/Phytoplankton Niskin (Nearfield = Surface, B/P = Mid-Surface and Mid Bottom) - Dissolved Inorganic Nutrients - Phytoplankton (Whole Water and Screened)
N/C	URI/UMD	Nutrients/Phytoplankton/DO/Chlorophyll Niskin - Dissolved Inorganic Nutrients - Chlorophyll <i>a</i> and Phaeopigments - Total Suspended Solids
N/O	URI	Nutrients and Dissolved Oxygen Niskin (Nearfield = All Depths) - Dissolved Inorganic Nutrients - Dissolved Oxygen (2)
TOW	BOS	Initial descent of each tow-yo cycle

Table 10. Station	Sampli	ing Plan fo	or Task 5		
Stations	Bottom	Mid-Bottom	Mid-Depth	Mid-Surface	Surface
N01P, N04P, N07P, N10P, N16P, and N20P	DIN	DIN	DIN	DIN	N/P
N02, N05, and N19	DIN	DIN	N/O	DIN	N/O
N03, N08, N09, N11, N13, N14, N15, N17, and N18	DIN	DIN	DIN	DIN	DIN
N06, N12, and N21	DIN	DIN	N/C	DIN	N/C

Table 11. Sta	tion Sa	mpling Pla	n for Tas	ks 6 and 7	•	
Stations	Bottom	Mid-Bottom	Mid-Depth	Mid-Surface	Surface	TOW
F01P, F02P, F13P, F23P, N01P, N04P, N07P, N10P, N16P, and N20P	N/P	N/R	B/P	N/P	B/P	ZOO
F03 through F12, F14 through F22, and F24	DIN	DIN	DIN	DIN	DIN	
F25	DIN	DIN	ANU	DIN	ANU	

		STATIO					
		•	ile and Water Bottle				
-		utfall Monit	oring MWRA Contrac				
Station:	F25			r Observations			
Bottom Depth (m):			General:				
Time on Station:							
Recorded by:			Seas:				
Date:	_		Wind:				
Comments:			Niskin Bottle(s)	,			
			Time				
			Latitude				
			Longitude				
			CTD Depth				
			Event				
			Lab	Matrix SW			
			Protocol	Sampled by			
			Niskin Bottle(s)				
			Time				
			Latitude				
			Longitude				
			CTD Depth				
			Event				
			Lab Matrix SW				
			Protocol Sampled by				
			Niskin Bottle(s)				
			Time				
			Latitude				
			Longitude				
			CTD Depth				
			Event				
			Lab	Matrix SW			
			Protocol	Sampled by			
Station	Sampling Plan		Niskin Bottle(s)				
Sampling Depth	Niskins	Protocol	Time				
Bottom	2	DIN	Latitude				
Mid-Bottom	4	DIN	Longitude				
Mid-Depth		ANU	CTD Depth				
Mid-Surface		DIN	Event				
Surface	10	ANU	Lab	Matrix SW			
Tow	none		Protocol Sampled by				
Zooplankton Tow		Niskin Bottle(s)					
Time			Time				
Latitude			Latitude				
Longitude			Longitude				
			CTD Depth				
Event			Event				
Lab: UMD	Matrix	SW	Lab	Matrix SW			
Protocol: ZOO	Sampled by		Protocol	Sampled by			

Figure 13. Sample of BOSS Station Log.

an unique *marker\_no* so that pertinent information can be recorded. When this *marker\_no* is created by BOSS, the software electronically saves the following information in a log file:

- Station ID
- Marker no
- Date and time of event
- Position of vessel at time of event
- Depth of Niskin bottle
- ID of Niskin bottles triggered for event
- Protocol code
- Lab code

This same information will also be printed on barcoded labels. The barcode contains the sample ID. One label will be attached to the BOSS station log form, one label will be attached to each sample, and another label will be attached to its accompanying COC form.

Figures 14 through 17 show additional COC forms to be used during the water column monitoring surveys. These forms will accompany samples to their final destination. If the custody of samples is transferred, the COC form will be signed by both the staff member that relinquishes custody and the staff member assuming custody of the samples. Copies of all COC forms will be returned to Battelle's water column Project Area Leader and 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 primary BOSS software operator 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 a survey ID, date, name of person creating the backup files, and a disk number. When the equipment is returned to Battelle's laboratory, a second complete backup, labeled as "Set 2", will be generated on floppy disks. "Set 2" will be in the custody of Mr. Albro. "Set 1" is maintained by the survey chief scientist.

CHAIN-OF-CUSTODY RECORD					
For Nutrients, Chlorophyll a, TSS, and Productivity Samples					
	all Monitoring MWRA Contract No. S138				
Station:	University of Rhode Island				
Recorded by:	MERL - GSO				
Date:	Narragansett, RI 02882-1197				
Niskin Bottle(s)	Comments:				
Time					
Latitude					
Longitude					
CTD Depth					
Event	·				
Lab Matrix SW					
Protocol Sampled by					
Niskin Bottle(s)	Comments:				
Time					
Latitude					
Longitude					
CTD Depth					
Event					
Lab Matrix SW					
Protocol Sampled by					
Niskin Bottle(s)	Comments:				
Time					
Latitude					
Longitude					
CTD Depth					
Event					
Lab Matrix SW					
Protocol Sampled by					
Niskin Bottle(s)	Comments:				
Time					
Latitude					
Longitude					
CTD Depth					
Event					
Lab Matrix SW					
Protocol Sampled by	2				
Niskin Bottle(s)	Comments:				
Time	<del></del>				
Latitude					
Longitude CTD Donth					
CTD Depth Event	<del></del>				
Lab Matrix SW					
Protocol Sampled by					
Relinquished By/Date/Time/Company   Transport/Air	rbill # Received By/Date/Time/Company				
	Theoested by/Date/Tittle/Company				
	<del></del>				
PLEASE RETURN THE ORIGINAL OF THIS COMPLETE	ED CHAIN-OF-CUSTODY FORM TO CARL ALBRO -BATTELLE				

Figure 14. Sample Chain-of-Custody Form for Nutrients, Chlorophyll a, TSS, and Productivity Samples.

CHAIN-OF-CUSTODY RECORD					
	n (Whole Water and Screened) Samples				
Project Name: Harbor and Outfall I	Monitoring MWRA Contract No. S138				
Station:	UMass Dartmouth				
Record by:	Biology Dept. and CMST				
Date:	North Dartmouth, MA 02747-2300				
Niskin Bottle(s)	Comments:				
Time					
Latitude					
Longitude					
CTD Depth					
Event	· · · · · · · · · · · · · · · · · · ·				
Lab Matrix SW					
Protocol Sampled by					
Niskin Bottle(s)	Comments:				
Time					
Latitude					
Longitude					
CTD Depth					
Event	-				
Lab Matrix SW					
Protocol Sampled by	<del></del>				
Niskin Bottle(s)	Comments:				
Time	Comments				
Latitude					
Longitude					
CTD Depth					
Event	-				
Lab Matrix SW	· · · · · · · · · · · · · · · · · · ·				
Protocol Sampled by					
Niskin Bottle(s)	Comments:				
Time					
Latitude					
Longitude					
CTD Depth					
Event					
Lab Matrix SW					
Protocol Sampled by					
Niskin Bottle(s)	Comments:				
Time					
Latitude					
Longitude					
CTD Depth					
Event					
Lab Matrix SW					
Protocol Sampled by					
Relinquished By/Date/Time/Company   Transporter/Airt	sill # Received By/Date/Time/Company				
DI EASE BETLIEN THE ORIGINAL OF THIS COMPLETED O	CHAIN OF CUSTODY FORM TO CARL ALREO BATTELLE				

Figure 15. Sample Chain-of-Custody Form for Biology/Productivity Phytoplankton (Whole Water and Screened) Samples.

	CHAIN-OF	-CUSTODY RECORD
For Nea	rfield Phytoplankton	(Whole Water and Screened) Samples
		all Monitoring MWRA Contract No. S138
		UMass Dartmouth
		Biology Dept. and CMST
		North Dartmouth, MA 02747-2300
Station:		Comments:
Time	Date:	
Latitude		
Longitude		
CTD Depth: Surfa	nce	
Event		
Lab: UMD	Matrix SW	
Protocol: N/P	Sampled by	
Station:		Comments:
Time	Date:	Commonto.
Latitude	Date.	
Longitude		
CTD Depth: Surfa		
Event	<u> </u>	
Lab: UMD	Matrix SW	
Protocol: N/P	Sampled by	
	Sampled by	0
Station:	Dete	Comments:
Time	Date:	·
Latitude		
Longitude		
CTD Depth: Surfa	ice	
Event Lab: UMD	Matrix SW	
Protocol: N/P	Sampled by	
Station:	Sampled by	Comments:
Time	Date:	Comments.
Latitude	Date	
Longitude		
CTD Depth: Surfa		
Event		
Lab: UMD	Matrix SW	
Protocol: N/P	Sampled by	
Station:		Comments:
Time	Date:	- Carrier No.
Latitude		
Longitude		
CTD Depth: Surfa	nce	
Event		
Lab: UMD	Matrix SW	
Protocol: N/P	Sampled by	
	Time/Company   Transporter/	Airbill # Received By/Date/Time/Company
PLEASE RETURN TH	E ORIGINAL OF THIS COMPLET	ED CHAIN-OF-CUSTODY FORM TO CARL ALBRO -BATTELLE

Figure 16. Sample Chain-of-Custody Form for Nearfield Phytoplankton (Whole Water and Screened) Samples.

Project Nam  Gear Type: 102 um  Station: Time Latitude Longitude  Event Lab: UMD Protocol: ZOO Station: Time Latitude	e: Harbor and Outfa	UMass Dartmou Biology Dept. a	uth	(end)
Gear Type: 102 um Station: Time Latitude Longitude  Event Lab: UMD Protocol: ZOO Station: Time	NET  Date:  Matrix SW Sampled by	UMass Dartmot Biology Dept. at North Dartmout Flowmeter: Tow Time:	uth nd CMST h, MA 02747-2300 (start)/	
Station: Time Latitude Longitude  Event Lab: UMD Protocol: ZOO Station: Time	Date:  Matrix SW Sampled by	Biology Dept. an North Dartmouth Flowmeter: Tow Time:	nd CMST h, MA 02747-2300 (start)/	(end)
Station: Time Latitude Longitude  Event Lab: UMD Protocol: ZOO Station: Time	Date:  Matrix SW Sampled by	North Dartmout Flowmeter: Tow Time:	h, MA 02747-2300 (start)/	(end)
Station: Time Latitude Longitude  Event Lab: UMD Protocol: ZOO Station: Time	Date:  Matrix SW Sampled by	Flowmeter: Tow Time:	(start)/	(end)
Time Latitude Longitude  Event Lab: UMD Protocol: ZOO Station: Time	Matrix SW Sampled by	Tow Time:		(end)
Latitude Longitude  Event Lab: UMD Protocol: ZOO Station: Time	Matrix SW Sampled by		Tow Depth:	
Event Lab: UMD Protocol: ZOO Station: Time	Sampled by	Comments:		
Event Lab: UMD Protocol: ZOO Station: Time	Sampled by			
Lab: UMD Protocol: ZOO Station: Time	Sampled by			
Lab: UMD Protocol: ZOO Station: Time	Sampled by			
Protocol: ZOO Station: Time	Sampled by			
Station: Time				
Time				
		Flowmeter:	(start)/	(end)
Latitude	Date:	Tow Time:	Tow Depth:	
Longitude				
Event				
Lab: UMD	Matrix SW			
Protocol: ZOO	Sampled by			
Station:		Flowmeter:	(start)/	(end)
Time	Date:	Tow Time:	Tow Depth:	
Latitude				
Longitude				
Event				
Lab: UMD	Matrix SW			
Protocol: ZOO	Sampled by			
Station:		Flowmeter:	(start)/	(end)
Time	Date:	Tow Time:	Tow Depth:	
Latitude				
Longitude				
T				
Event Lab: UMD	Matrix SW			
Protocol: ZOO	Sampled by			
Station:	Oampied by	Flowmeter:	(start)/	(end)
Time	Date:	Tow Time:	Tow Depth:	(end)
Latitude		10 111110.	. C. Doptii.	
Longitude		<u> </u>		
Event				
Lab: UMD	Matrix SW			
Protocol: ZOO	Sampled by			
Relinquished By/Date/Tim	ne/Company   Transporter/A	Airbill #	eceived By/Date/Time/Con	npany

Figure 17. Sample Chain-of-Custody Form for Zooplankton Samples.

# 13.2 Custody of Water Samples

Subcontractors will assume custody of samples immediately upon sample collection. Field documentation will consist of laboratory notebooks, field log sheets, and COC forms containing the project name, station code, sample type designation, alphanumeric sample codes, and other pertinent information on the sample (see Figures 14 through 17). During field collection, COC 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 COC form. The COC forms will have a duplicate label that also contains the same alphanumeric code as the corresponding label on the sample container, ensuring the tracking of sample location and the status. A copy of the COC form will be kept by the subcontractor along with the samples during transport and storage. The original COC 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 Battelle'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 COC forms is accurate, log the samples into the laboratory by signing the COC 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. Sample numbers that include the complete field ID number 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. CALIBRATION PROCEDURES AND PREVENTIVE MAINTENANCE

Logs of maintenance, calibrations, and any repairs made to instruments will be stored in the instrument files maintained by Battelle 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 Sensor Depth

At the beginning of each survey, the software offset of the depth sensor is set to read zero when the sensor is on deck. The offset is entered into the equipment setup file. The offset of the pressure reading is affected by the atmospheric pressure which has resulted in adjustment of the offset by up to 0.4 db. Based on two yearly manufacturer's calibrations of the Ocean Sensor pressure sensor, the change in gain was 0.07% which will result in an 0.04 db change in depth at 90 db. Thus the effect of offset is an order of magnitude greater than gain.

### 14.1.2 Temperature and Conductivity

The software gain and offset of the temperature and conductivity sensors are calibrated annually at the factory and the factory calibration settings are not changed. A review of the calibration coefficients for the CTDs shows that they are quite stable from year to year. Based on the annual calibrations of the Sea-Bird, the drifts are 0.002°C for temperature, 0.0396 mS/m for conductivity, 0.036 PSU for salinity, and 0.028 for Sigma-t. Based on the annual calibrations of the Ocean Sensors, the drifts are 0.018°C for temperature, 0.042 mS/m for conductivity, 0.055 PSU for salinity, and 0.046 for Sigma-t.

## 14.1.3 In situ Dissolved Oxygen

The software gain and offset of the dissolved sensors are calibrated annually at the factory and the factory calibration settings are not changed. The calculated DO values are adjusted for each survey based on a comparison with discrete water samples in which DO concentration is determined by titration. The calculated DO data (based on factory calibration settings) is entered into a Microsoft Excel 4.0 spreadsheet with the corresponding bottle samples data. Then, using the built-in linear regression analysis tool, the correction divider is determined after forcing the regression through the origin. The regression is based on the following equation:

Calculated CTD value = slope  $\times$  bottle value

For comparative purposes, a second regression is conducted based on the following equation:

Calculated CTD value = slope  $\times$  bottle value + intercept

To correct the CTD values in the database, the following equation is used: Corrected CTD value = Calculated CTD value / slope

Figure 18 shows the spreadsheet used for the October 1992 water column survey conducted for MWRA.

					Survey MFF06 Diss	olved Oxyger	Calibration				
Marke	Statio	Bottle DO	CTD D	Predicted DO	Regression Statis						
	F01P	7.634	5.48685	7.230	Tregression states			_			
	F01P	8.667	6.34471	8.361	Multiple R	0.9705328				_	
	F01P	8.601	6.45067	8.500	R Square	0.941934					
	F02P	8.413	6.07658	8.007	Adjusted R Squ			_			
	F02P	8.648	6.47609	8.534	Standard Error	0.1286618					
	F02P	8.985	6.77921	8.933	Observations	33					
	F13P	7.910	5.88937	7.761	Observations	- 33		-			
	F13P	9.127	6.92133	9.121	Analysis of Varia	nce				_	
	F13P	9.348	7.06424	9.309	Analysis of varia	df	um of Squares	ean Square		ignificance F	
	N07P	7.330	5.64684	7.441	Regression	1		8.59305271	519.09693	6.36603E-21	
	N07P	9.222	6.91692	9.115	Residual	32		0.01655385	319.09093	0.30003E-21	
	NO7P	9.188	6.97072	9.113	Total	33		0.01033363			
	N16P	7.518	5.8308		1 Otal	33	9.12277392				
	N16P			7.684		Conff of our	111-F	. Continuin	Donator	7 050	71 O.C.
		9.029	6.87432	9.059		Coefficients	tandard Error	t Statistic	P-value	Lower 95%	Upper 95%
	N16P	9.072	6.92311	9.123	I		#D1/4	#N1/4	#N1/A	40.774	40.174
	N10P	7.005	5.49944	7.247	Intercept	0.750060		#N/A	#N/A	#N/A	#N/A
	N10P	8.269	6.29736	8.298	x1	0.758869	0.002709052	280.123437	2.688E-57	0.753350876	0.7643872
	N10P	8.300	6.30258	8.305							
	F23P	7.216		7.537	_						_
	F23P	7.323	5.5579	7.324							
	F23P	7.323	5.51725	7.270	Regression Statis	tics					
-	N10P	7.410	5.72198	7.540							
	N10P	8.223	6.27116		Multiple R	0.9733048	<del></del>				
457	N10P	8.134	6.14199	8.094	R Square	0.9473223					
	N04P	7.671	5.99627	7.902	Adjusted R Squ	are 0.945623		_			
476	N04P	9.172	6.99238	9.214	Standard Error	0.1245077					
478	N04P	9.193	7.0065	9.233	Observations	33					
488	N20P	7.355	5.77194	7.606							
494	N20P	8.398	6.30794	8.312	Analysis of Vario	ince					
496	N20P	8.459	6.45082	8.501		df	um of Squares	ean Square	F	ignificance F	
544	N21	8.667	6.75433	8.901	Regression	1	8.642208975	8.64220897	557.4842	2.23355E-21	
553	N18	7.374	5.52803	7.285	Residual	31	0.480566945	0.01550216			
623	N13	7.595	5.86565	7.729	Total	32	9.12277592				
		0	0	0							
						Coefficients	tandard Error	t Statistic	P-value	Lower 95%	Upper 95%
											-
				se Dissolve	Intercept	0.4401077	0.247152846	1.78071049	0.0844561	-0.06396417	0.9441795
		Ох	ygen (	Calibration	x1	0.7058408		23.6111033	8.17E-22	0.644870619	
							0.027077710		01172	0.011070017	0.7000107
1 🕝	10.000	-									
(mg/L)	9.000	i t		•	_						
٤	8.000			_							
E	7.000	:		7							
39	6.000	:	,	/-	-						
ő	5.000		, ,								
þ	4.000	2			1						
UR! Dissolved Oxyg	3.000		/								
SS	2.000	. /									
٥	1.000										
2	0.000										
	0.000			_	10						
		0		5	10						
!	ı	Factory C		n CTD Dissolv	ed						_
			Oxygen	Reading	·						

Figure 18. Sample Calibration Spreadsheet for Dissolved Oxygen.

#### 14.1.4 Transmissometer

The transmissometer is calibrated annually in the laboratory at Battelle. This calibration consists of obtaining voltage readings under the three following 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 is 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 clear distilled water is 0.364/m, the value of A is calculated as follows

$$A = 0.364 + 4 \ln (V_w - V_0).$$

A review of the calibration coefficients for the transmissometer shows that it is quite stable from year to year. The drift of the transmissometer is dependent on the amount of time it is operated. Assuming 288 h of operation in 1992, the transmissometer drift was approximately 0.01/m.

To check that the transmissometer is working properly, it will be checked each survey day by checking blocked (more than 40/m) and unobstructed (less than .5/m) readings in air using the BOSS program display. After each cast, the optics of the transmissometer will be rinsed with deionized water.

# 14.1.5 In situ Chlorophyll a Fluorometer

Based on past experience, the software gain and offset of the Chelsea fluorometer are set annually. The Chelsea fluorometer data, displayed with the BOSS program, will approach  $0.0~\mu g/l$  when the instrument is on deck. Placing your hand at a 45 degree angle to both the light source and the detector should increase the data displayed to greater than  $50~\mu g/l$ . After each cast, the optics of the Chelsea fluorometer will be rinsed with deionized water. The calculated readings are corrected in the same manner as described for the DO sensor above, using the measured chlorophyll a data from discrete bottle samples to develop a linear regression and correction factor.

### 14.1.6 Irradiance Profiling and On-deck Sensors

The QSP200L Biospherical irradiance sensor is interfaced to the BOSS system via the CTD and is used to measure photosynthetically radiation active underwater, the QSR240 is used to measure surface solar irradiance, and is interfaced to the BOSS system via the systems analog-to-digital converter. Both sensors are annually calibrated at the factory. On a clear day at local noon, the surface solar irradiance as measured by the QSR240 should be 2000-3000  $\mu \text{Em}^{-2} \text{s}^{-1}$ . The same measurement on deck using the underwater sensor (QSP200L) should be 3500-4000  $\mu \text{Em}^{-2} \text{s}^{-1}$ . The difference in the readings is caused by the "immersion effect" calibration factor used for the wet sensor and by the different geometry of the two sensor housings. Both instruments should read zero when their protective caps are installed.

Before each cast, the BOSS software acquires readings from the sensors while the underwater unit is on deck. This information will be saved in a raw data file. This file will be post-processed by the BOSS software. The readings will be reviewed to determine if an adjustment to the irradiance ratio is necessary.

## 14.2 Navigation Equipment

Once the 12Vdc power supply for the Northstar LORAN 800/GPS 8000 navigation system has been switched on, there is typically no other setup interaction necessary between the BOSS operator and the navigation system. The LORAN C will go through its automatic hardware test routine, which can be observed on the front panel display. The GPS will also conduct an automatic self-test. Once the GPS has acquired at least one satellite, the green LED on the front panel will start flashing. When the GPS has acquired at least three satellites to give a correct position, the green LED will remain lighted constantly. The LORAN C will display a latitude-longitude (L/L) position once either of the two systems has acquired an acceptable fix. If the position displayed is from the GPS, a "G" will be displayed before the latitude. GPS selection can be toggled between "only", "never", and "auto" by using the command 61 entry. Typical operation is in "auto". LORAN C time delays can be displayed by pushing the "position" key on the display panel. Signal-to-noise ratios can be checked by using the command 99 entry. L/L position, TDs, SNRs, and "jitter" are all automatically recorded with the BOSS software. Position calibration will be performed twice per day as follows:

- 1. An absolute position is obtained from published charts with a position accuracy approaching 2 sec (approx. 40 m).
- 2. The BOSS program is set to calibration-navigation mode.

- 3. Thirty fixes are obtained by the BOSS program, averaged, and then compared to the absolute position entered by the BOSS operator.
- 4. If a printer is connected to the BOSS system, a printout of the calibration is obtained. Otherwise, the data are manually entered into the first or last station log for that day.
- 5. If the position offset is determined to be greater than 100 m, a correction offset can be entered by the BOSS operator. This offset will be applied to all navigation fixes that day.

## 14.3 Laboratory Instruments

Preventive maintenance of all subcontractor laboratory equipment will follow manufacturers' recommendations. Calibration procedures for all laboratory analyses performed by URI are described in references cited in Section 12.7 Oviatt *et al.* (1986). A brief summary of URI's wet chemical procedures are described below.

- Dissolved Inorganic Nutrients These are analyzed on a Technicon II autoanalyzer. Concentrations are calculated from a standard curve made from dilutions of a primary standard. Primary standards are used for 1 to 2 years. When they are replaced new standards are verified against the old standards. There are no standard reference materials (SRMs) for dissolved inorganic nutrients in seawater. Intercalibrations with other laboratories serve to ensure reliability of primary standards.
- Chlorophyll a This is analyzed by extracted fluorescence on a Turner Designs 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 Carlo Erba elemental analyzer using standard curves generated with acetanilide. There are no SRMs for this analysis.
- Dissolved Organic Carbon This is determined on an OI Corporation Model 700 TOC analyzer by persulphate digestion.
   Values are calculated from standard curves using a potassium biphthalate standard. There are no SRMs. Intercalibration with other

laboratories is the only method of verifying the accuracy of the analysis.

- Dissolved Oxygen This is measured using the Winkler titration method with an autotitrator. 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 weight out the material. The balances are standardized and adjusted by factory certified technicians.
- TSS This is measured with a Cahn electrobalance. It is standardized and adjusted by factory certified technicians.
- 14C This is measured with a scintillation counter that is calibrated for quench using the external channels ratio method.

#### 15. DOCUMENTATION, DATA REDUCTION, AND REPORTING

# 15.1 Data Recording

All data will be initially recorded either (1) electronically onto computer storage media from BOSS 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 the BOSS survey notebook for each survey. These notebooks will be stored on the BOSS field logs bookcase in the physical oceanography laboratory under the supervision of Carl Albro.

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, altitude above bottom, and bathymetry. The BOSS data-acquisition software assigns an unique data filename to each horizontal transect or vertical profile made during the survey. All data will be electronically logged with date, time, and concurrent GPS/LORAN vessel-position data. The PC-based BOSS 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 hard-copy printout is simultaneously created. The printouts will be punched and inserted in the BOSS survey notebook. At the end of each profile or transect, the graphic screen of navigation and hydrographic data will be saved to a file on the computer hard disk. On each survey, the screen dumps will be printed in color on the HP PaintJet and stored in the BOSS survey notebook.

#### 15.2 Data Reduction

## 15.2.1 Hydrographic and Navigation Data

Following the survey, all raw in situ instrument measurement data will be transformed into engineering units data. This transformation will involve several operations using the BOSS software (see Figure 19 for creating half-meter bin averaged data file). 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) is used. To calculate salinity and density from conductivity, temperature, and pressure, the algorithms developed by Fofonoff and Millard (1983) are used. To determine the percent saturation of oxygen, the calculated DO is divided by the solubility of oxygen based on algorithm developed by Weiss (1970). When checking for representativeness, each parameter will be plotted in high-resolution, xy graphic form for visual inspection of data quality by an oceanographer. The vessel position will be plotted on map form. These plots will be stored in physical oceanography group files, under the supervision of Carl Albro, to allow inspection by QA staff or MWRA staff.

After conducting the first-pass edited engineering data, the DO and chlorophyll a values are adjusted based on a calibration with discrete water samples as described in Section 14 (See Figure 20 for details of Battelle's process for post-calibrating *in situ* instrument data with water samples collected during a survey.

# 15.2.2 Subcontractor Laboratory Data

All data generated by Battelle'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

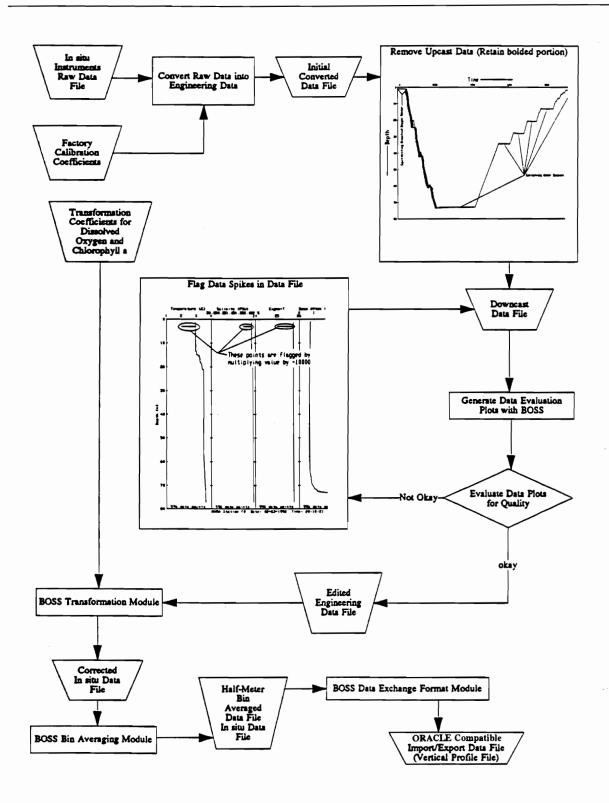


Figure 19. Process for Generating Vertical Profile Data Files on In Situ Instruments for Import to ORACLE Database. Shown are Actual Profiles from Farfield Station F08 on February 23, 1992.

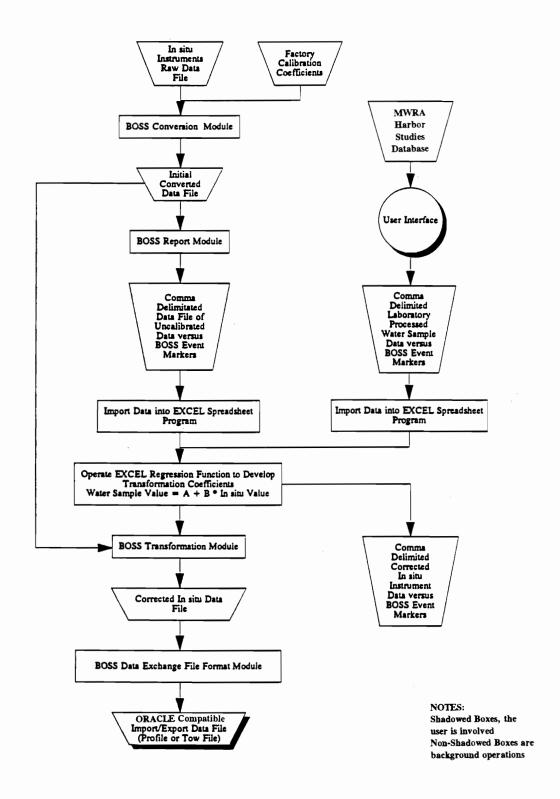


Figure 20. Process for Post-Calibrating In Situ Instrument Data with Water Sample Data Collected during a Survey.

procedures described in Section 16. The format for final data submission is described below.

## 15.3 Reporting Data to be Loaded into the Database

Only data that the Task Leader has designated as final will be loaded into Battelle's copy of the Harbor Studies Database. All data submitted for inclusion in the Harbor Studies Database will adhere to the formats described below.

### 15.3.1 Navigation and Sample Collection Data

Navigation and sample collection data contained in the BOSS electronic log file will be provided as Lotus spreadsheet files after completion of the survey report. The columns will include sample\_id, stat\_id, water\_depth, ddate, ttime, latitude, longitude, sample\_depth, and protocol code as listed in Table 9.

### 15.3.2 Hydrographic Data

Battelle will also load into the database the following three types of data collected with the BOSS sensor package:

- Niskin bottle closings that will include 20-s averaged BOSS sensor data at the time of each Niskin sampling event
- Vertical profile data that will be bin-averaged at 0.5-m intervals
- Tow-yo data that will be time-averaged at 2-s intervals

The BOSS software will generate comma-delimited ASCII data using the format presented in Table 12.

# 15.3.3 Analytical and Experimental Data

Researchers from UMD will provide separate Lotus spreadsheets containing species enumeration data of each type of data — zooplankton, whole-water phytoplankton, and screened phytoplankton (dinoflagellates). The format for transmittal of zooplankton data to Battelle is defined in Table 13. The format for transmittal of phytoplankton data, both whole-water and screened, is defined in Table 14. The Harbor Studies Database maintained by Battelle will distinguish the cells counted by the two phytoplankton methods.

Researchers from URI will submit data for nutrients, organic constituents, chlorophyll a, TSS, respiration, productivity by oxygen, and productivity by <sup>14</sup>C in Quattro spreadsheets. The format for these data is presented in Table 15. The codes and specific parameters that will be reported are presented in Table 16.

	Table	12. Form	at for	Reporti	ing Hydrographic Data
		Size or		Must	
Column	Type	Precision	Scale	Report	Description
Cruise	Char	5		Y	Code identifying cruise
Stat_ID	Char	6		Y	Station identifier
Latitude	Number	7	5	Y	Latitude as decimal degrees
Longitude	Number	7	5	Y	Longitude as decimal degrees
Pro_dat	Number	8	0	Y	Date of reading as Julian date (Days since Jan 1, 4713 BC at noon Greenwich time)
Time	Number	8	0	Y	Time of reading, milliseconds since midnight
Event	Number	4	0	Y	BOSS Event number
Conductivity	Number	8	3		Conductivity (mmhos/cm)
Diss_oxygen	Number	6	3		Dissolved oxygen (mg/L)
Fluorescence	Number	8	4		Fluorescence (as $\mu g/L$ Chlorophyll)
Pressure	Number	5	2		Pressure (dB)
Salinity	Number	6	3		Salinity (PSU)
Sigma_t	Number	6	3		Sigma-t
Temp	Number	6	3		Temperature (C)
Light	Number	6	2		Corrected irradiance at depth (µEsec <sup>-1</sup> m <sup>-2</sup> )
Light_surf	Number	6	2		Corresponding irradiance at surface $(\mu \text{Esec}^{-1}\text{m}^{-2})$
Trans	Number	10	5		Beam attenuation (1/m)

7.	able 13.	Spread	sheet	Forma	t for Reporting Zooplankton Data.
	_	Size or		Must	
Column	Type	Precision	Scale	Report	Description
Sample_ID	Char	9		Y	Unique sample ID assigned during field collection (i.e., number on bar-coded label).
Category	Char	40		Y	Scientific name of organism quantified and reported in value column
Sex/Stage	Char	1			Sex or life stage of organism(s):  C = COPEPODITES, F = FEMALE,  M = MALE, N = NAUPLII
Value	Number	8	0	Y	Number of organisms per category reported as organisms per $m^3$

- 1) A column to report value qualifier (val\_qual) will be added if appropriate.
- 2) Enumerated to species, but when no species name available use SP.A, SP.B, etc.; will be consistent across all samples for this program

Table 14. Spreadsheet Format for Reporting Phytoplankton (Whole Water and Screened) Data									
		Size or		Must					
Column	Type	Precision	Scale	Report	Description				
Sample_ID	Char	9		Y	Unique sample ID assigned during field collection (i.e., number on bar-coded label).				
Category	Char	40		Y	Scientific name of organism quantified and reported in value column				
Value	Number	8	0	Y	Number of organisms in sample per category				
Units	Char	10	0	Y	Units associated with value column				

- 1) A column to report value qualifier (val\_qual) will be added if appropriate.
- 2) Enumerated to species, but when no species name available use SP.A, SP.B, etc.; will be consistent across all samples for this program

Table 15. Spreadsheet Format for Reporting Chemical Analytical Results									
	_	Size or		Must					
Column	Type	Precision	Scale	Report	Description				
Sample_ID	Char	10		Y	Unique sample ID assigned during field collection (i.e., number on bar-coded label).				
Labid	Char	8		Y	Identifier assigned to sample by analytical laboratory (bottle number for respiration experiment)				
Val_type	Char	20		Y	Code that describes the type of value reported (i.e., CHLA, TSS, etc.)				
Anal_date	Char	8		Y	Date of sample analysis reported as MM/DD/YY				
Value	Number	12	5	Y	Resultant data value determined by analytical procedure				
Unit_code	Char	10		Y	Code for value units				
Inst_code	Char	20			Code for analytical instrument used to analyze sample				
Val_qual	Char	1			Code that qualifies data value (I = Initial, D = Dark, e = value not reported)				
Meth_code	Char	8		Y	Code for method used to analyze sample				
QC_code	Char	4		Y	Code indicating type of sample (QC = QC sample, SAMP = Regular Sample)				
Anal_rep	Number	3	0		Sequential number, beginning with 1, assigned to replicate analyses of a single sample				
Batch_ID	Char	10			Identifier assigned to batch of samples by the analytical laboratory (no spaces or punctuation marks)				
Detect_limit	Number	9	5	Y	Detection limit				
Comments	Char	30			Comments				

- Data resulting from laboratory QC samples should be submitted along with your 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, val\_qual, and val\_type. If you require a code that is not in the code list, please contact us.
- 3. Precision is the maximum size of a number excluding the decimal point. Scale is the number of places after the decimal place. For example, 10.234 is stored with precision = 5 and scale = 3.

		Table	16. Co	ode List for U	RI Anal	yses	
				Inst_code		Meth_code	Val_qual
Data Type	$Val\_type$	$Unit\_code$	Inst_code	Description	$Meth\_code$	Description	Description
Chlorophyll a	CHLA	$\mu \mathrm{g}/\mathrm{L}$	FLUM2	Turner Fluorometer	LO186	Lambert and Oviatt (1986)	
Phaeopigments	PHA	$\mu g/L$	FLUM2	Turner Fluorometer	LO186	Lambert and Oviatt (1986)	
Ammonia	NH4	$\mu$ M	T2A	Technicon II autoanalyzer	LO186	Lambert and Oviatt (1986)	
Nitrite	NO2	$\mu M$	T2A	Technicon II autoanalyzer	LO186	Lambert and Oviatt (1986)	
Nitrate	NO3	$\mu M$	T2A	Technicon II autoanalyzer	LO186	Lambert and Oviatt (1986)	
Phosphate	PO4	$\mu M$	T2A	Technicon II autoanalyzer	LO186	Lambert and Oviatt (1986)	
Silicate	SIO4	$\mu M$	T2A	Technicon II autoanalyzer	LO186	Lambert and Oviatt (1986)	
Dissolved organic carbon	DOC	$\mu M$	TOCA	OI Model 700 TOC analyzer	MV164	Menzel and Vaccaro (1964)	
Total dissolved nitrogen	TDN	$\mu M$	T2A	Technicon II autoanalyzer	LO186	Lambert and Oviatt (1986)	
Total dissolved phosphorus	TDP	$\mu M$	T2A	Technicon II autoanalyzer	LO186	Lambert and Oviatt (1986)	
Particulate organic carbon	POC	μΜ	EA	Carlo Erba Model 1106 CHN elemental analyzer	LO186	Lambert and Oviatt (1986)	
Particulate organic nitrogen	PON	μΜ	EA	Carlo Erba Model 1106 CHN elemental analyzer	LO186	Lambert and Oviatt (1986)	
Total suspended solids	TSS	mg/L	EB1	Cahn electrobalance	LO186	Lambert and Oviatt (1986)	
Dissolved oxygen	DO	mg/L	WTTR	Winkler titration	LO186	Lambert and Oviatt (1986)	
Incubation light exposure	LIG	μEm <sup>-2</sup> sec <sup>-1</sup>	PHO	Photosynthetron	LO186	Lambert and Oviatt (1986)	
Incubation time	TIME	HOURS	WATC	Watch	LO186	Lambert and Oviatt (1986)	
Incubation temperature	TEMP	С	THER	Thermometer	LO!86	Lambert and Oviatt (1986)	
Net production rate	NPR	mgO <sub>2</sub> /L/hr	NA	Not applicable	LO186	Lambert and Oviatt (1986)	Calculated
Net Respiration	NETR	mgO <sub>2</sub> /L/hr	NA	Not applicable	LO186	Lambert and Oviatt (1986)	Calculated

Dissolved organic nitrogen (DON) will be calculated as: DON = TDN - Ammonia - Nitrate - Nitrite
 Dissolved organic phosphorus (DOP) will be calculated as: DOP = TDP - phosphate

# 15.4 Loading Data into the Harbor Studies Database

Data provide by UMD, URI, and Battelle will be loaded into the Harbor Studies Database by Battelle data management staff. Upon receipt, each diskette will be logged in and assigned a unique login identifier. Any changes or additions to data, necessary for loading into the Harbor Studies Database, will be made using well-documented SQL scripts that indicate the original values. The original diskette, SQL scripts, and data-loading documentation will be filed according to login identifier at Battelle. The data sources notebook will contain copies of the COC forms, the MWRA data documentation form, and data entry information.

## 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 22 of Contract S138. Copies of all data reduction and analysis software will be delivered to MWRA as described in Task 23 of the contract.

#### 16. DATA VALIDATION

A primary component of data validation is compliance with the quality control (QC) criteria specified in (1) the QA Project Plan developed specifically for the Harbor and Outfall Monitoring Project and (2) Section 11 (Data Quality Requirements and Assessments) of this CW/QAPP.

All data collected and analyzed as part of Tasks 5, 6, 7, 8, and 9 will be subject to checks for errors in transcription, calculation, or spreadsheet input. Validation procedures for data generated at Battelle or by the subcontractors will include the following:

- 100% of the data hand-entered into a database or spreadsheet will be verified for accuracy by (1) printing the spreadsheet and proofreading against the original hand entry or by (2) duplicate entry into the database and comparison of the dual entries to reveal any differences.
- Manual calculations (e.g., of concentrations or productivity rates) will be checked for accuracy by a second staff member.

- Electronic calculations will be checked by the technical staff member at a frequency sufficient to ensure the accuracy of the calculations. All data reduction algorithms will be verified by the subcontractor prior to final data submission.
- Electronically generated data will be reviewed in graphical form to ensure that the data are complete, accurate, and technically reasonable. The removal of all outliers, either manually or by computer algorithm, will be reviewed by the subconsultant Project Managers or Battelle Task Leader.
- Analytical results and supporting data will be reviewed by the technical supervisor to ensure that the data are complete, accurate, and technically sound.
- Battelle database staff will check the submitted data and associated documentation for completeness, freedom from errors, and technical reasonableness. Database staff will also check their data entry process for errors.
- Battelle database staff will ensure that all new software developed for this task is validated prior to the entry of data.

The Battelle Task Leader will be responsible for validation of all data generated by Battelle. Subcontractor Project Managers will be responsible for conducting similar data validation procedures to ensure that the data provided to Battelle are accurate, complete, and scientifically reasonable. Missing or suspect data will be explained by data qualifiers given in the data submission. As an additional validation step, the Battelle Task Leader will review all subcontractor data for completeness, internal consistency, and technical reasonableness.

#### 17. PERFORMANCE AND SYSTEMS AUDITS

The Battelle QA Officer for the Harbor and Outfall Monitoring Project is Ms. Rosanna Buhl. She will direct the conduct at least one systems audit to ensure that Tasks 5, 6, 7, 8, and 9 are carried out in accordance with this CW/QAPP and will oversee the implementation of this CW/QAPP for the work conducted under Tasks 5, 6, 7, 8, and 9. Tabular and graphical data reported in deliverables, and associated raw data generated by Battelle will be audited under the direction of the Project QA Officer. Raw data will be reviewed for completeness and proper documentation. For electronically acquired data (e.g.,

navigational data), Ms. Buhl will verify that computer software used to process the data has been validated.

Audits of the data collection procedures at subcontractor laboratories will be the responsibility of the Subcontractor Project Managers, Dr. Jefferson Turner and Dr. Peter Doering. All data and deliverables will be audited by an individual who is not directly associated with the technical conduct of the work. Each deliverable 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. The implementation of performance audits is the responsibility of the Task Leader; performance audits to verify data accuracy will be conducted at the discretion of Mr. Albro or Dr. Jack Kelly. Performance reviews may include assessment of QC samples such as blanks, spikes, SRMs, reference materials, and replicates.

#### 18. CORRECTIVE ACTION

All technical personnel share responsibility for identifying and resolving problems encountered in the routine performance of their duties. Dr. Carlton Hunt, Battelle's Project Manager, will be accountable to MWRA and to Battelle management for overall conduct of the Harbor and Outfall Monitoring Project, including the schedule, costs, and technical performance. He is responsible for identifying and resolving problems that (1) have not been addressed timely or successfully at a lower level, (2) influence multiple components of the project, (3) necessitate changes in this CW/QAPP, or (4) require consultation with Battelle management or with MWRA.

Identification of problems and corrective action at the laboratory level (such as meeting data quality requirements) will be resolved by laboratory staff or by Subcontractor Project Managers. Issues that affect schedule, cost, or performance of Tasks 5, 6, 7, 8, and 9 will be reported to the Task Leader or to the Battelle Project Manager. They will be responsible for evaluating the overall impact of the problem on the project and for discussing corrective actions with the MWRA Project Manager.

Problems identified by the QA Officer will be reported and corrected as described in the QA Program Plan for the Harbor and Outfall Monitoring Project.

#### 19. REPORTS

Reports that will be generated under Tasks 5, 6, 7, 8, and 9 include the following:

- 32 Survey Plans (one for each of the 32 water column surveys)
- 32 Survey Reports (one for each of the 32 water column surveys)
- 10 Nutrient Data and Respiration/Productivity Data Reports
- 10 Phytoplankton Data and Zooplankton Data Reports

Each survey plan will follow the new 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 unbounded 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 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 phaeopigments, DO, and TSS for each bottle sampled and analyzed. In addition, a tabular summary of the results of respiration,  $P_{max}$ , and P(I) analyses will be provided for each bottle sampled and analyzed.

Five times each year, separate phytoplankton and zooplankton data reports 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 25: periodic water column reports, annual water column reports, and nutrient issues reviews. The periodic water column reports will use the following outline:

- Executive Summary (2 pages)
- Introduction (8 pages)
- Survey Methods (12 pages)
- Results (for each survey in the reporting period; 50 pages per survey)
- Discussion (30 pages)
- Summary of season dynamics (3 pages)
- Appendices containing graphical and tabloid presentations of all data collected during the reporting period (75 pages per survey)

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