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

for

## Water Column Monitoring: 2004-2005

**Massachusetts Water Resources Authority** 

Environmental Quality Department Report ENQUAD 2005-09 Version 1



#### Citation:

Libby PS, Gagnon C, Albro C, Mickelson M, Keller A, Borkman D, Turner J, Oviatt CA. 2005. **Combined work/quality assurance plan for water quality monitoring: 2004-2005**. Boston: Massachusetts Water Resources Authority. Report ENQUAD 2005-09 Version 1. 76 pp + apps.

## COMBINED WORK/QUALITY ASSURANCE PROJECT PLAN (CWQAPP)

for

WATER COLUMN MONITORING 2004 – 2005 Tasks 9, 10, 12, 13, 14, 15

#### **MWRA Harbor and Outfall Monitoring Project**

submitted to

# MASSACHUSETTS WATER RESOURCES AUTHORITY Environmental Quality Department 100 First Avenue Charlestown Navy Yard Boston, MA 02129 (617) 242-6000

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> > March 2005 ms-074 Version 1

## COMBINED WORK/QUALITY ASSURANCE PROJECT PLAN (CWQAPP)

for

#### WATER COLUMN MONITORING 2004 -2005

Tasks 9, 10, 12, 13, 14, and 15 MWRA Harbor and Outfall Monitoring Project

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#### 1.0 PROJECT NAME

MWRA Harbor and Outfall Monitoring Project Water Column Monitoring 2004-2005 Tasks 9, 10, 12, 13, 14, and 15

#### 2.0 PROJECT REQUESTED BY

Massachusetts Water Resources Authority Environmental Quality Department

#### 3.0 DATE OF REQUEST

November 7, 2001

#### 4.0 DATE OF PROJECT INITIATION

November 7, 2001

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#### 7.0 PROJECT DESCRIPTION

The Massachusetts Water Resources Authority (MWRA) is responsible for the operation and monitoring of the sewage effluent outfall (Figure 1) from the Deer Island Wastewater Treatment Plant, which began discharging into Massachusetts Bay on September 6, 2000. The outfall is regulated under a National Pollutant Discharge Elimination System (NPDES) permit issued by the U.S. Environmental Protection Agency (EPA) and the Massachusetts Department of Environmental Protection (EPA/MDEP 1998). The EPA Supplemental Environmental Impact Statement (SEIS) for the outfall (EPA 1988) determined that there would be no significant water quality or biological impacts associated with the outfall. Even so, the SEIS recommended a monitoring program for assessing compliance with the NPDES permit, assessing unacceptable impacts, and collecting data useful for outfall management considerations (MWRA 1990) be implemented. In response, the MWRA committed to implementing "long-term biological and chemical monitoring to describe existing conditions and evaluate the impacts of the treatment facility discharge." To develop the monitoring plan, public, scientific, and regulatory areas of concern were identified following guidance for coastal monitoring (i.e., NRC 1990). Areas of concern include water column, benthos, and fish and shellfish environments in addition to the effluent characteristics. On September 6, 2000 the program entered the outfall discharge monitoring phase designed to assess potential environmental impact of the effluent discharge into Massachusetts Bay, and evaluate compliance with the discharge permit.

A principal concern with the offshore outfall discharge is nutrients and their resultant eutrophication effects on the water column. Three specific effects are of paramount concern: (1) lowered dissolved oxygen concentrations (hypoxia/anoxia), (2) stimulation of nuisance/noxious algae populations, and (3) alteration of the offshore food web. Water quality monitoring centers on measurements keyed to these three principal ecological effects, including measurements of other physical and chemical properties. For example, temperature, salinity, and turbidity are used to distinguish water masses and are fundamental background data for interpreting biological fluctuations. Physical features such as thermal stratification strongly influence the expression of nutrient enrichment effects. Measured nutrient concentrations (particulate and dissolved forms) aid water mass analyses, assess biological variability in light of nutrient variability, and, ultimately, link cause (nutrient loading) and effect. Zooplankton monitoring, in tandem with physical and chemical measurements, may help explain any observed changes in the phytoplankton.

A comprehensive review of the data to date in June 2003 led to revisions, with concurrence from the Outfall Monitoring Advisory Panel and the EPA, to the Ambient Monitoring Plan that was first implemented in February 2004 (MWRA 2004). The changes to the water column monitoring program include reducing the number of nearfield surveys from 17 to 12 and reducing the number of nearfield stations from 21 to 7. These changes were supported by statistical analysis of baseline and post-discharge data collected from 1992-2002, which indicate that there will be little loss of information or in the ability of the monitoring program to detect changes (MWRA 2003). In 2003, the monitoring plan was revised to omit the urea sampling in the water column. These changes to the Ambient Monitoring Plan as well as other changes that have been implemented in field operations, analytical laboratories, and data management activities are captured in this revision to the Combined Work/Quality Assurance Project Plan (CW/QAPP) for Water Column Monitoring: 2002 – 2005 (Libby *et al.* 2002).

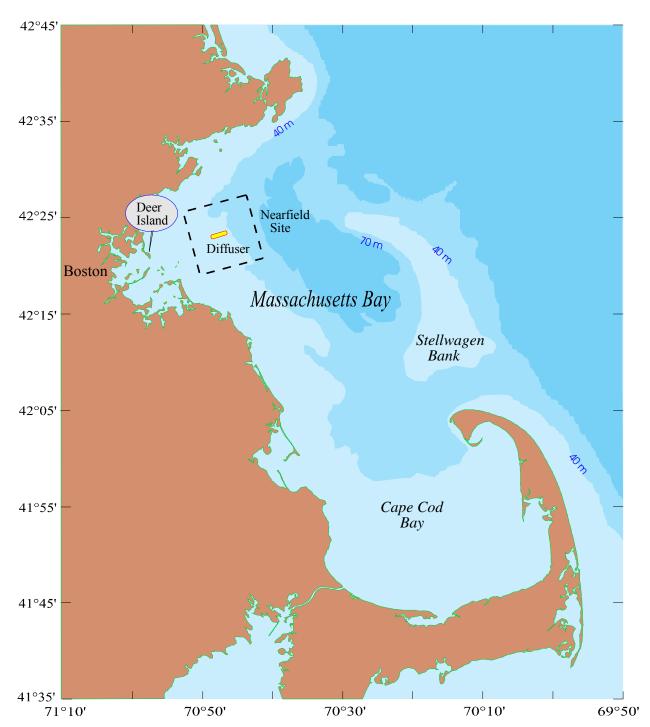


Figure 1. Location of MWRA Effluent Outfall in Massachusetts Bay

#### 7.1 Objectives and Scope

The primary objective of water column monitoring is to detect changes in the water column of Massachusetts and Cape Cod Bays that may be caused by relocating the effluent outfall. The main concern is that discharged nutrients will be detrimental. The rationale for the work is discussed in the Outfall Monitoring Plan (MWRA 1991, 1997). Changes in physical water properties, nutrient concentrations, dissolved oxygen, phytoplankton biomass, and phytoplankton and zooplankton community composition in Massachusetts Bay and Cape Cod Bay will be monitored.

This Combined Work/Quality Assurance Project Plan (CWQAPP) describes the sampling and analysis activities of MWRA's water column monitoring program to be conducted under MWRA Contract S366 from 2004 through 2005. This CWQAPP is based largely on water quality CWQAPPs of the MWRA monitoring program described in Libby *et al.* (2002). Water column surveys will be conducted to monitor water properties, nutrient concentrations, and other parameters that measure eutrophication, and to gain a better understanding of the physical processes that will affect the ecological response to the outfall in Massachusetts Bay.

The Harbor and Outfall Monitoring (HOM) Project water column surveys have been conducted since 1992 and are scheduled to continue through 2005. This CWQAPP describes activities specific to the six nearfield and six combined nearfield/farfield water column surveys of Massachusetts Bay and Cape Cod Bay scheduled to be conducted annually in 2004 and 2005. Physical and meteorological data collected by stationary moorings and satellites supplement data collected during the water column surveys. Under the water quality monitoring program, hydrographic and water quality parameters, nutrient concentrations, and metabolism will be measured. Phytoplankton and zooplankton communities will also be described. The study objectives are described below.

- Develop a three-dimensional picture of seasonal variability of water column properties in the nearfield. (Task 9: Nearfield Surveys)
- Determine conditions in the water column throughout Massachusetts and Cape Cod Bays; identify factors affecting the seasonal pattern of plankton communities and dissolved oxygen concentrations in Massachusetts Bay; describe the broad-scale interaction of water from Boston Harbor and the Gulf of Maine with Massachusetts Bay; and compare water quality of Massachusetts and Cape Cod Bays. (Task 10: Farfield Surveys)
- Use data from two U.S. Geological Survey (USGS) moorings (one near the outfall site and one offshore Scituate) to interpolate temperature, salinity, chlorophyll a, and beam transmittance data between surveys, and data from meteorological stations to support explanations of environmental patterns observed in other tasks. (Task 12: Moorings and Meteorology)
- Use satellite images to complement survey data for region response understanding and develop quantitative linkages between survey data and imagery data. (Task 13: Remote Sensing)
- Describe the water quality by measuring concentrations of dissolved inorganic nutrients (nitrate, nitrite, ammonium, phosphate, and silicate), total dissolved organic nitrogen and phosphorous, dissolved organic carbon, particulate carbon and nitrogen, particulate phosphorous, biogenic silica, chlorophyll *a* and phaeopigments, total suspended solids (TSS), dissolved oxygen (DO), respiration, and primary productivity. (Task 14: Water Chemistry and Metabolism)
- Characterize the phytoplankton and zooplankton communities and describe changes in community structure. (Task 15: Plankton Taxonomy)

The results of the sampling and analytical tasks will be reported in survey reports, data reports, synthesis reports (Task 33), and other interpretive reports (Task 29).

#### 7.2 Data Usage

Under the monitoring approach developed and adopted by MWRA and the Outfall Monitoring Task Force (OMTF)<sup>1</sup> in 1991, public, scientific, and regulatory areas of concern were identified following NRC (1990) guidance for coastal monitoring. Using this information, a draft Phase I Baseline Monitoring Plan (MWRA 1991) was developed, reviewed, and accepted by EOEA with revisions (Pederson 1992). This plan described and discussed the ecological and other potential responses that were of concern ("trigger parameters") and the field and laboratory studies that were necessary to acquire data to address these concerns. Details of the field and analytical program conducted under Phase I are described in a series of water quality Combined Work/Quality Assurance Project Plans (Albro *et al.* 1993; Bowen *et al.* 1998; Albro *et al.* 2002). Delay in the completion of the discharge into Massachusetts Bay has allowed the collection of almost nine years (1992 to September 2000) of baseline data rather than the originally required three years.

The Post-Discharge Monitoring Plan (MWRA 1997) was included in the MWRA NPDES permit and focuses on the environment in the vicinity of the outfall, with additional effort in Cape Cod and Massachusetts Bay. Improvements in Boston Harbor are also monitored. Based on the findings from over two years of post-discharge data, this monitoring plan was revised in 2004 and is hereafter referred to as the Ambient Monitoring Plan (MWRA 2004). The objectives of the Ambient Monitoring Plan are to (1) test for compliance with NPDES permit requirements; (2) verify that the impact of the discharge on the environment is within the bounds predicted by the EPA SEIS (with National Marine Fisheries Service concurrence), that is, no significant water quality or biological impacts are associated with the outfall; and (3) test whether change within the system exceeds the MWRA Contingency Plan (MWRA 2001) thresholds.

The Ambient Monitoring Plan is complemented by the Outfall Monitoring Overview (e.g. Werme and Hunt 2004), which describes the results of studies implemented under the Ambient Monitoring Plan (MWRA 2004), and the Contingency Plan (MWRA 2001) developed to protect the environment and public health. The Contingency Plan describes the Water Column Thresholds used to establish unacceptable responses in Massachusetts Bay.

The Contingency Plan thresholds are based on permit limits, observations from the baseline monitoring, national water quality criteria and state standards, and in some cases, best professional judgment. In the event that one of these thresholds is exceeded, the Contingency Plan sets into motion an environmental management process to (1) confirm the threshold exceedance; (2) determine the causes and significance of the exceedance; and, if the environmental changes are attributable to the effluent outfall, (3) identify the actions that will be taken to return the threshold parameter to an acceptable level. Examples of management actions include additional monitoring, development of response plans and performance of engineering feasibility studies.

#### 7.3 Technical Approach

The study consists of sampling surveys and analysis of samples collected during those surveys. The technical approach to completing those tasks is discussed below.

#### 7.3.1 Nearfield and Farfield Water Column Surveys (Tasks 9 and 10)

Water column sampling will be conducted 12 times per year in 2004 and 2005 (Figure 2). Figure 3 shows the location of the 7 nearfield stations (Table 1) and Figure 4 shows the 28 farfield stations (Table 2) that will be sampled each year.

<sup>&</sup>lt;sup>1</sup> The OMTF was established by the Massachusetts Executive Office of Environmental Affairs (EOEA) to oversee the monitoring program.

Figure 2. HOM4 Sampling Schedule, 2004-2005

				2004				_				2005			_
Week	Sun	Mon	Tue	Wed	Thu 1-Jan	Fri 2-Jan	Sat 3-Jan	Week	Sun	Mon	Tue	Wed	Thu	Fri	Sat 1-Jan
1					i odii	2 0011	o dan	1							1 oan
2	4-Jan	5-Jan	6-Jan	7-Jan	8-Jan	9-Jan	10-Jan	2	2-Jan	3-Jan	4-Jan	5-Jan	6-Jan	7-Jan	8-Jan
2	11-Jan	12-Jan	13-Jan	14-Jan	15-Jan	16-Jan	17-Jan		9-Jan	10-Jan	11-Jan	12-Jan	13-Jan	14-Jan	15-Jan
3	18-Jan	19-Jan	20-Jan	21-Jan	22-Jan	23-Jan	24-Jan	3	16-Jan	17-Jan	18-Jan	19-Jan	20-Jan	21-Jan	22-Jan
4	10 0411						210011	4			10 0411				
5	25-Jan	26-Jan	27-Jan	28-Jan	29-Jan	30-Jan	31-Jan	5	23-Jan	24-Jan	25-Jan	26-Jan	27-Jan	28-Jan	29-Jan
	1-Feb	2-Feb	3-Feb	4-Feb	5-Feb	6-Feb	7-Feb	J	30-Jan	31-Jan	1-Feb	2-Feb	3-Feb	4-Feb	5-Feb
6	8-Feb	9-Feb	10-Feb	11-Feb	12-Feb	13-Feb	14-Feb	6	6-Feb	7-Feb	8-Feb	9-Feb	10-Feb	11-Feb	12-Feb
7								7							
8	15-Feb	16-Feb	17-Feb	18-Feb	19-Feb	20-Feb	21-Feb	8	13-Feb	14-Feb	15-Feb	16-Feb	17-Feb	18-Feb	19-Feb
	22-Feb	23-Feb	24-Feb	25-Feb	26-Feb	27-Feb	28-Feb		20-Feb	21-Feb	22-Feb	23-Feb	24-Feb	25-Feb	26-Feb
9	29-Feb	1-Mar	2-Mar	3-Mar	4-Mar	5-Mar	6-Mar	9	27-Feb	28-Feb	1-Mar	2-Mar	3-Mar	4-Mar	5-Mar
10				40.14		40.14		10					40.14		40.14
11	7-Mar	8-Mar	9-Mar	10-Mar	11-Mar	12-Mar	13-Mar	11	6-Mar	7-Mar	8-Mar	9-Mar	10-Mar	11-Mar	12-Mar
	14-Mar	15-Mar	16-Mar	17-Mar	18-Mar	19-Mar	20-Mar		13-Mar	14-Mar	15-Mar	16-Mar	17-Mar	18-Mar	19-Mar
12	21-Mar	22-Mar	23-Mar	24-Mar	25-Mar	26-Mar	27-Mar	12	20-Mar	21-Mar	22-Mar	23-Mar	24-Mar	25-Mar	26-Mar
13	28-Mar	29-Mar	30-Mar	31-Mar	1-Apr	2-Apr	3-Apr	13	27-Mar	28-Mar	29-Mar	30-Mar	31-Mar	1-Apr	2-Apr
14	20 14101	20 14101	oo wa	OT WA	17101	2 / (pi	0 / (p)	14	27 10101	20 14101	20 Mai	oo wa	OT WILL	17101	2 / (p)
15	4-Apr	5-Apr	6-Apr	7-Apr	8-Apr	9-Apr	10-Apr	15	3-Apr	4-Apr	5-Apr	6-Apr	7-Apr	8-Apr	9-Apr
15	11-Apr	12-Apr	13-Apr	14-Apr	15-Apr	16-Apr	17-Apr	15	10-Apr	11-Apr	12-Apr	13-Apr	14-Apr	15-Apr	16-Apr
16	18-Apr	19-Apr	20-Apr	21-Apr	22-Apr	23-Apr	24-Apr	16	17-Apr	18-Apr	19-Apr	20-Apr	21-Apr	22-Apr	23-Apr
17								17							
18	25-Apr	26-Apr	27-Apr	28-Apr	29-Apr	30-Apr	1-May	18	24-Apr	25-Apr	26-Apr	27-Apr	28-Apr	29-Apr	30-Apr
	2-May	3-May	4-May	5-May	6-May	7-May	8-May		1-May	2-May	3-May	4-May	5-May	6-May	7-May
19	9-May	10-May	11-May	12-May	13-May	14-May	15-May	19	8-May	9-May	10-May	11-May	12-May	13-May	14-May
20						,		20							
21	16-May	17-May	18-May	19-May	20-May	21-May	22-May	21	15-May	16-May	17-May	18-May	19-May	20-May	21-May
	23-May	24-May	25-May	26-May	27-May	28-May	29-May		22-May	23-May	24-May	25-May	26-May	27-May	28-May
22	30-May	31-May	1-Jun	2-Jun	3-Jun	4-Jun	5-Jun	22	29-May	30-May	31-May	1-Jun	2-Jun	3-Jun	4-Jun
23	6-Jun	7-Jun	8-Jun	9-Jun	10-Jun	11-Jun	12-Jun	23	5-Jun	6-Jun	7-Jun	8-Jun	9-Jun	10-Jun	11-Jun
24	0-Juii	7-3uii	0-Juii	9-Juli	10-3011	i i-Juli	12-Juli	24	J-3uii	0-Juii	7-Juli	o-Juli	5-Juli	10-3411	i i-suii
25	13-Jun	14-Jun	15-Jun	16-Jun	17-Jun	18-Jun	19-Jun	25	12-Jun	13-Jun	14-Jun	15-Jun	16-Jun	17-Jun	18-Jun
	20-Jun	21-Jun	22-Jun	23-Jun	24-Jun	25-Jun	26-Jun		19-Jun	20-Jun	21-Jun	22-Jun	23-Jun	24-Jun	25-Jun
26	27-Jun	28-Jun	29-Jun	30-Jun	1-Jul	2-Jul	3-Jul	26	26-Jun	27-Jun	28-Jun	29-Jun	30-Jun	1-Jul	2-Jul
27								27							
28	4-Jul	5-Jul	6-Jul	7-Jul	8-Jul	9-Jul	10-Jul	28	3-Jul	4-Jul	5-Jul	6-Jul	7-Jul	8-Jul	9-Jul
	11-Jul	12-Jul	13-Jul	14-Jul	15-Jul	16-Jul	17-Jul		10-Jul	11-Jul	12-Jul	13-Jul	14-Jul	15-Jul	16-Jul
29	18-Jul	19-Jul	20-Jul	21-Jul	22-Jul	23-Jul	24-Jul	29	17-Jul	18-Jul	19-Jul	20-Jul	21-Jul	22-Jul	23-Jul
30	25-Jul	26-Jul	27-Jul	28-Jul	29-Jul	30-Jul	31-Jul	30	24-Jul	25-Jul	26-Jul	27-Jul	28-Jul	29-Jul	30-Jul
31		0.4						31						F.A.	
32	1-Aug	2-Aug	3-Aug	4-Aug	5-Aug	6-Aug	7-Aug	32	31-Jul	1-Aug	2-Aug	3-Aug	4-Aug	5-Aug	6-Aug
	8-Aug	9-Aug	10-Aug	11-Aug	12-Aug	13-Aug	14-Aug		7-Aug	8-Aug	9-Aug	10-Aug	11-Aug	12-Aug	13-Aug
33	15-Aug	16-Aug	17-Aug	18-Aug	19-Aug	20-Aug	21-Aug	33	14-Aug	15-Aug	16-Aug	17-Aug	18-Aug	19-Aug	20-Aug
34								34							

Figure 2. HOM4 Sampling Schedule, 2002-2005 (con't)

2004 2005 Mon 23-Aug Tue Wed Thu 24-Aug 25-Aug 26-Aug Fri 27-A Mon Tue 22-Aug 23-Aug Sun 21-Au Thu 25-Aug **26-**Aug Week Sun Sat Week Wed Sat 35 35 36 36 37 37 38 38 39 39 40 40 4-Oct 8-Oct 9-Oct 41 42 42 43 43 44 45 45 10-Nov 13-No 9-Nov 46 46 47 23-Nov 23-Nov 48 48 49 49 7-De 7-De 50 50 15-Dec 13-Dec 14-Dec 16-Dec 12-Dec 13-Dec 17-Dec 18-Dec 14-Dec 51 51 52 52 53 53

Key	Tasks	Survey Description
	9.2	Nearfield Water Column
	10.2	Farfield Water Column
	16.1	Nutrient Cycling
,,,,,,,,,,,	17.1	Harbor Traditional Benthic
,,,,,,,,,,	17.2	Harbor Reconnaissance
	18.1	Nearfield Benthic

Key	Tasks	Survey Description
	18.3	Nearfield Sediment Profile Image
mmmm	18.4	Nearfield Hardbottom
mmm	18.5	Farfield Benthic
	21.2	Flounder
as needed	26.4	Fecal Coliform Adverse Condition

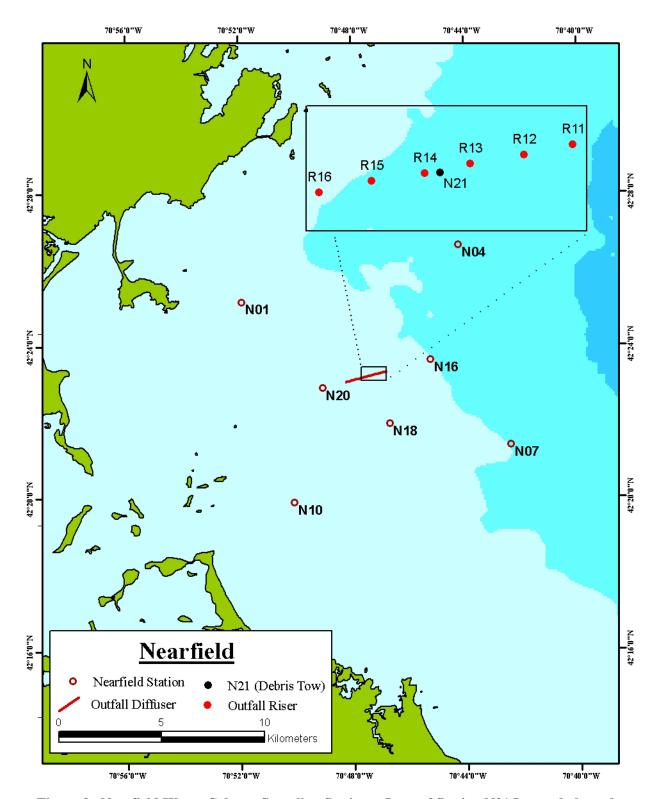


Figure 3. Nearfield Water Column Sampling Stations. Inset of Station N21 Located along the Outfall Diffuser near Riser 14 – Risers are 38 m apart.

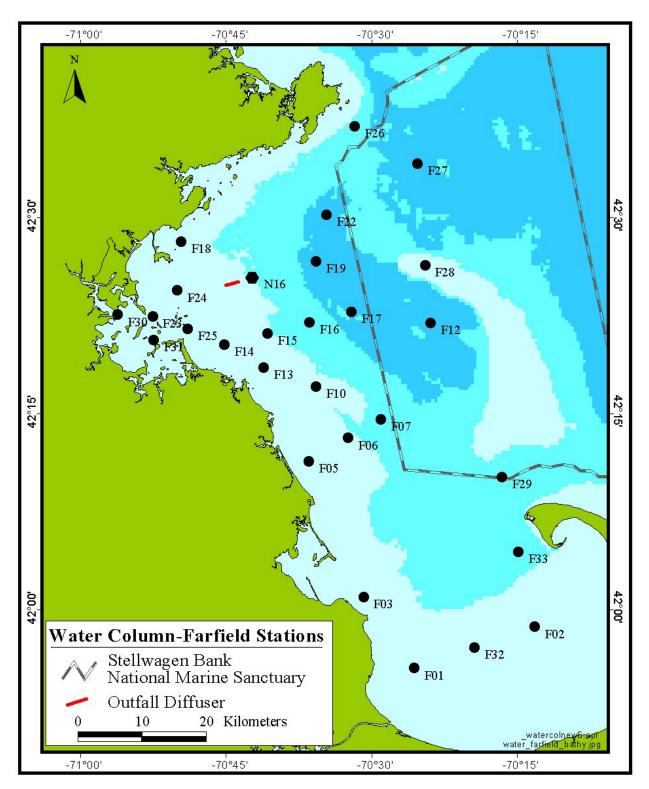


Figure 4. Farfield Water Column Sampling Stations

**Table 1. Nearfield Water Column Sampling Stations** 

Station	Latitude	Longitude	Depth	Station
	(N)	<b>(W)</b>	( <b>m</b> )	Type
N01	42.419	-70.865	31.2	A
N04 <sup>1</sup>	42.444	-70.737	49.8	P
N07	42.356	-70.706	50.2	A
N10	42.332	-70.834	24.8	A
N16	42.394	-70.753	42.2	A
N18 <sup>1</sup>	42.366	-70.778	26.6	P
N20	42.382	-70.817	31.3	A
N21 <sup>2</sup>	42.388	-70.785	34.8	

Stations NO4 and N18 will be sampled early enough in the day to initiate photosynthesis incubations. <sup>2</sup> Station N21 is no longer sampled, but is the location for one of the debris tows.

**Table 2. Farfield Water Column Stations** 

Station	Latitude	Longitude	Depth	Station
	( <b>N</b> )	<b>(W)</b>	( <b>m</b> )	Type
F01	41.851	-70.453	26.2	D
F02	41.908	-70.228	32.1	D
F03	41.950	-70.548	16.2	Е
F05	42.139	-70.650	19.1	Е
F06	42.171	-70.577	33.0	D
F07	42.197	-70.516	54.1	Е
F10	42.242	-70.637	32.9	Е
F12	42.330	-70.423	90.3	F
F13	42.268	-70.735	25.0	D
F14	42.300	-70.808	18.7	Е
F15	42.316	-70.728	38.3	Е
F16	42.331	-70.650	59.0	Е
F17	42.346	-70.571	76.4	Е
F18	42.442	-70.888	24.9	Е
F19	42.415	-70.637	80.0	A+R
F22	42.480	-70.618	79.5	D
F23 <sup>1</sup>	42.339	-70.942	24.7	P
F24	42.375	-70.896	21.2	D
F25	42.322	-70.876	15.0	D
F26	42.602	-70.565	52.8	D
F27	42.550	-70.447	105.1	D
F28	42.410	-70.433	30.5	Е
F29	42.117	-70.290	64.7	F
F30	42.341	-71.008	12.1	G
F31	42.306	-70.940	15.0	G
F32 <sup>2</sup>	41.880	-70.341	30.2	Z
F33 <sup>2</sup>	42.013	-70.259	44.1	Z
N16 <sup>3</sup>	42.394	-70.753	42.2	D

<sup>&</sup>lt;sup>1</sup>Station F23 will be sampled early enough in the day to initiate photosynthesis incubations.
<sup>2</sup> Stations F32 and F33 are sampled only during weeks 6, 9, and 15 each year.
<sup>3</sup> Station N16 will be visited on two separate days during combined nearfield and farfield surveys.

#### 7.3.1.1 Sampling Locations and Frequency

Nearfield stations are located within five kilometers of the outfall. Each nearfield sampling will be completed in one day. Two station types (A and P) are sampled in the nearfield. Table 3 shows subsampling by station type and sample depth. Stations N04 and N18 will be sampled early in the day to allow time for measurements of primary production (photosynthesis). Net tows for quantifying anthropogenic debris on the ocean surface will be conducted twice during each nearfield survey. Nearfield surveys are conducted 12 times per year (Figure 2).

Farfield stations are located beyond the nearfield to (1) cover regional-scale oceanographic processes in Massachusetts Bay and Cape Cod Bay; (2) broadly characterize reference areas; and (3) to verify that impacts by the outfall plume are not found beyond the nearfield. Each farfield sampling will be completed in three to four sequential days. The farfield areal productivity station (F23) will be sampled early in the day on the nearfield survey to confine all productivity processing to one day. During the first three-farfield surveys each year, two additional stations (F32 and F33) will be profiled for hydrographic data and sampled for zooplankton. The farfield surveys will capture the ecological conditions six times during the year: winter (early February), late winter (late February to early March), spring (early April), early summer (mid-June), late summer (mid-August), and fall (mid-October).

Table 3. Subsamples by Station Type Code and Sample Depth Class

Subsample Analysis		S	tatio	Sample					
		D	E	F	G	R	$\mathbf{P}^2$	Z	Depth Class <sup>3</sup>
Dissolved Inorganic Nutrients									A, B, C, D, E
									A, C, E
Dissolved Organic Carbon									
Total Dissolved Nitrogen									
Total Dissolved Phosphorous									
Particulate Organic Carbon									A, C, E
Particulate Organic Nitrogen									
Particulate Phosphorous									
Biogenic Silica									
Chlorophyll a and Phaeophytin a									A, B, C, D, E
									A, C, E
Total Suspended Solids									A, C, E
Dissolved Oxygen				$\checkmark$					A, B, C, D, E
									A, C, E
Zooplankton					<b>√</b>		<b>√</b>		Z
Phytoplankton (whole water)									A, C
Phytoplankton (screened water)									A, C
Respiration									A, C, E
Primary Productivity									A, B, C, D, E

<sup>&</sup>lt;sup>1</sup>Defined by Suite of Analyses.

<sup>&</sup>lt;sup>2</sup> P combines P+R+D from the contract

<sup>&</sup>lt;sup>3</sup>Sample Depth Classes.

A Surface (<3 meters)

B Mid-surface

C Mid-depth (chlorophyll *a* maximum)

D Mid-bottom

E Bottom (within 5 m of bottom)

Z Upper 30 m tow through water column

#### 7.3.1.2 Hydrocasts and Sensor Measurements

Hydrographic data will be collected at all nearfield and farfield stations. During the combined surveys, nearfield station N16 will be visited on both the nearfield and the farfield survey days. At each station, a hydrocast will be conducted with an underwater unit consisting of a conductivity–temperature–depth (CTD) system, various sensors (dissolved oxygen, chlorophyll fluorescence, optical beam transmittance, light irradiance (PAR), and altimeter), and a water-sampling system equipped with up to 12 9–L Rosette sampling bottles.

Sensor measurements will be collected during the downcast from near surface (approximately 1-2 meters) to within approximately 3-5 m of the sea floor at each station. Salinity and density (as sigma-t) will be calculated in real time from the conductivity, temperature and depth data. Total incident photosynthetically active radiation at the sea surface (SPAR), navigational position, and time will be recorded concurrently with the hydrocast measurements.

#### 7.3.1.3 Water Collection and Zooplankton Net Tows

During the upcast at each station (except stations F32 and F33), 9–L Rosette sampling bottles will be used to collect water from five depths: bottom, mid-bottom, middle (chlorophyll *a* maximum), mid-surface, and surface. Due to relatively shallow depths at Boston Harbor stations F30 and F31, only bottom, middle, and surface depths are sampled. On deck, water from the Rosette bottles will be subsampled for analysis of dissolved inorganic nutrients and other analytes as determined by the station type (Table 3). Vertical net tows to collect zooplankton will be conducted according to the scheme shown in Tables 1-3. Stations F32 and F33 are sampled only during the first three farfield surveys (weeks 6, 9, and 15). A detailed listing of samples collected at each station during nearfield and farfield surveys is provided in Appendix A.

#### 7.3.1.4 Whale Observations

During each nearfield survey and the first three farfield surveys of each year (weeks 6, 9, and 15), a trained whale observer will conduct sighting watches while on station and during transit between stations. The sighting operations will occur during daylight hours and when the vessel is in Massachusetts Bay or Cape Cod Bay. All sightings will be recorded on standardized marine mammal field sighting logs (see Section 12.1.8). The sampling vessels will operate according to protocols mandated by the Commonwealth of Massachusetts regarding right whales (Appendix B).

#### 7.3.1.5 Moorings and Meteorology (Task 12)

Physical oceanographic data collected by moored instruments operated by the U.S. Geological Survey (USGS) will be obtained under Task 12. Hydrographic data from stations near the mooring will be provided to the USGS on request. Meteorological data will be obtained from the National Weather Service weather stations at Logan Airport and Provincetown Airport, and from the MWRA weather station at Deer Island. This data may be supplemented with data from other regional weather stations as necessary. Solar radiation data will be obtained electronically from the MWRA Deer Island weather station. In addition, electronic copies of Boston Harbor tide data will be obtained from NOAA. These data provide useful supporting information for the data obtained from the water quality stations.

#### 7.3.1.6 Remote Sensing (Task 13)

The purpose of this task is to broaden the utility of the satellite data by providing numeric data that can be plotted on a time series graph and compared to field data. Sea surface temperature and chlorophyll satellite images that correspond to field survey days will be obtained directly from the Internet.

The satellite images will presumably correspond to days on which field surveys were undertaken, although alternate images can be designated by MWRA. The satellite data will be compared to MWRA *in situ* data at all stations where discrete chlorophyll a samples are collected. The chlorophyll (extracted)

and *in situ* temperature measurements from the surface water ("A" depth) at these stations will be compared to satellite derived data. The data derived from this task will be provided to authors of synthesis reports and the results will be reported to MWRA in a semiannual letter.

#### 7.3.1.7 Shipboard Processing of Discrete Water Samples

Sample aliquots are removed from the Rosette sampling bottles and are processed aboard ship in preparation for shipment to the analytical laboratories. The water-sample-filtration scheme is detailed and graphically shown in Section 12.

#### 7.3.1.8 Floating Debris

To address NMFS concerns about potential anthropogenic debris entering the marine environment, MWRA instituted surface net tows to sample for plastics and other such floatable objects in 1999. These tows are conducted in the vicinity of the outfall as part of each nearfield survey. Following each tow, the collected sample is placed in a white dissection basin and digitally photographed. Date and time are recorded on each print. The digital image and qualitative observations of debris will be included in each survey email summary. The observations will also be summarized in the survey report. All identifiable anthropogenic materials (*e.g.*, plastics) will be retained and archived.

#### 7.3.2 Laboratory Program (Tasks 14, 15)

Water samples collected during the surveys will be analyzed to determine concentrations of dissolved inorganic nutrients (DIN) (nitrate, nitrite, ammonium, phosphate, and silicate); dissolved and particulate organic nutrients (carbon, nitrogen, and phosphorus); biogenic silica; DO; TSS; chlorophyll *a* and phaeophytin; primary productivity, respiration rates, and phytoplankton and zooplankton community structure. The sample analyses are summarized in Table 4. Sampling and analytical methods are described in Section 12.

#### 7.3.3 Data Management (Tasks 9 through 15)

Figure 5 illustrates the water-column-monitoring data processing strategy for data entry into the MWRA Environmental Monitoring and Management System (EM&MS) and accessing the data for various reports. The data from the program will be compared by MWRA to the caution and warning threshold parameters included in the MWRA Contingency Plan (MWRA 2001).

#### 7.4 Monitoring Parameters and Collection Frequency

Table 4 lists analytical parameters and *in situ* hydrographic measurements and Table 5 presents the collection frequency of each. Sample collection plans for both nearfield and farfield surveys are presented in Appendix A (Tables A1 and A2, respectively).

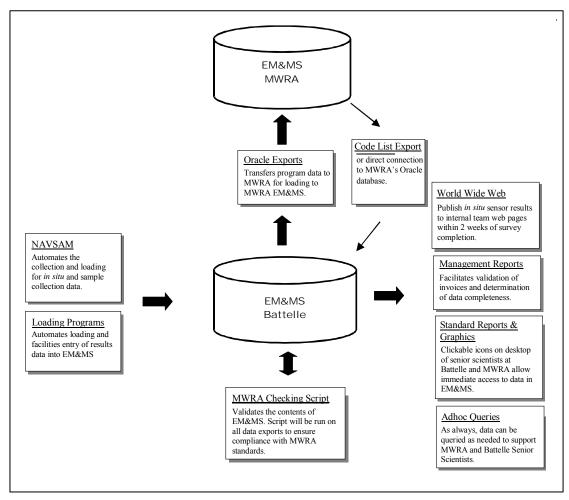


Figure 5. Overview of the Data Management Strategy for Water Column Monitoring

**Table 4. Water Column Sample Analyses** 

Parameter	Lab	Units	Instrument	Reference
Dissolved ammonium	DLS	μМ	Skalar Autoanalyzer	Oviatt and Hindle (1994); Solorzano (1969);
Dissolved inorganic nitrate/ nitrite and inorganic nitrite	DLS	μМ	Skalar Autoanalyzer	USEPA NERL 349.0; DLS SOP DCN1005.1  Bendschneider and Robinson (1952); Morris and Riley (1963); USEPA NERL 353.4; DLS SOP DCN 1007.0
Dissolved inorganic phosphate	DLS	μМ	Skalar Autoanalyzer	Murphy and Riley (1962); USEPA NERL 365.5; SOP 1006.1
Dissolved inorganic silicate	DLS	μМ	Skalar Autoanalyzer	Brewer and Riley (1966); Oviatt and Hindle (1994); USEPA NERL 366.0; DLS SOP 1017.1
Dissolved organic carbon	DLS	μМ	Tekmar-Dorhmann, Apollo 9000 Analyzer	Sugimura and Suzuki (1988); USEPA 415.1; DLS SOP 1126.0
Total dissolved nitrogen and Total dissolved phosphorus	DLS	μМ	Skalar Autoanalyzer	D'Elia et al. (1997); Valderrama (1981); DLS SOP 1072.1
Particulate carbon and Particulate nitrogen	DLS	μМ	Perkin Elmer CHN Elemental Analyzer II	Menzel and Vaccaro (1964); USEPA NERL 440.0; DLS SOP 1156.1
Particulate phosphorus	DLS	μM	Skalar Autoanalyzer	Solorzano and Sharp (1980); SOP 1102.0
Biogenic Silica	DLS	μM	Skalar Autoanalyzer	Paasche (1973); DLS SOP 1177.0
Chlorophyll a/phaeopigments	DLS	μg/L	Sequoia Turner Fluorometer Model 450-003	Arar and Collins (1992); USEPA NERL 445.0, V. 1.1, 1992; DLS SOP 1108.0
Total suspended solids	DLS	mg/L	Mettler 5-place balance	USEPA 160.2; DLS SOP 1104.0
Dissolved oxygen	Battelle	mg/L	Radiometer TitraLab	Battelle SOP 5-317 and Oudot et al. (1988)
Respiration	Battelle	μM/hr	Radiometer TitraLab	Battelle SOP 5-317 and Strickland and Parsons (1972)
Primary production by <sup>14</sup> C	URI	mgC/m³/h	Packard TriCarb scintillation counter Model 2900	Strickland and Parsons (1972); Lewis and Smith (1983); Libby <i>et al.</i> 2002
Whole-water phytoplankton	UMD	E6Cells/L	Olympus BH-2 compound microscope with phase-contrast optics	Borkman (1994), Borkman <i>et al.</i> (1993), Turner <i>et al.</i> (1995)
Screened phytoplankton	UMD	Cells/L	Olympus BH-2 compound microscope with phase-contrast optics	Turner et al. (1995)
Rapid phytoplankton	UMD	Cells/L (approx.)	Olympus BH-2 compound microscope with phase-contrast optics	Turner et al. (1995)
Zooplankton	UMD	Indiv./m <sup>3</sup>	Wild M-5 dissecting microscope	Libby et al. (2002), see Section 12.3.17 of this CWQAPP
In Situ Measurements				
Conductivity	Battelle	mS/cm	OS200 CTD	OS200 CTD Manual/ Battelle SOP 3-175
Temperature	Battelle	С	OS200 CTD	OS200 CTD Manual/ Battelle SOP 3-175
Pressure	Battelle	db	OS200 CTD	OS200 CTD Manual/ Battelle SOP 3-175
Dissolved oxygen	Battelle	mg/L	Seabird SBE 43 and 13	Weiss (1970)/Battelle SOPs 3-156 and 3-157
Chlorophyll fluorescence	Battelle	μg/L	WETStar	WET Labs WETStar Manual/Battelle SOP 3-163
Transmissometry	Battelle	m-1	WET Labs C-Star	WET Labs C-Star Manual/Battelle SOP 3-174
In situ irradiance	Battelle	μEm-2sec-1	Biospherical QSP-200L	Biospherical Manual/ Battelle SOP 3-127
Surface irradiance	Battelle	μEm-2sec-1	Biospherical QSR-240	Biospherical Manual/ Battelle SOP 3-127
Altimeter	Battelle	m	Data Sonic PSA-916	Data Sonic Manual
Bottom depth	Battelle	m	Furuno FCV-52	Furuno Manual/Battelle SOP 3-129
Navigational position	Battelle	degree	Northstar 941X	Northstar Manual/Battelle SOP 3-118
Secchi	Battelle	m	30-cm White Disk	Libby et al. (2002), see Section 12.1.7 of this CWQAPP
sigma-t	Battelle	unitless	OS200 CTD	OS200 CTD Manual/ Battelle SOP 3-175
Salinity	Battelle	PSU	OS200 CTD	OS200 CTD Manual/ Battelle SOP 3-175

Table 5. Water Column Sample Analysis Requirements by Station Type

Number stations each type per survey   S   O   Z   10   10   2   2   1   1   2		Station Type Code				Analyses						
Number stations each type per survey		N					Per Year					
Number of surveys per year   12   0   12   6   6   6   6   6   6   3		A	E	P	D	E	F	G	A+R	P	Z	
Dissolved Inorganic Nutrients	Number stations each type per survey	5	0	2	10	10	2	2	1	1	2	
Dissolved Inorganic Nutrients	Number of surveys per year	12	0	12	6	6	6	6	6	6	3	
Dissolved Organic Carbon	Subsample Analysis		N	umb	er of	Anal	lyse	s per	Station			
Total Dissolved Nitrogen	Dissolved Inorganic Nutrients				5	5	5				0	1176
Total Dissolved Phosphorous Particulate Organic Carbon Particulate Organic Nitrogen Particulate Phosphorous Biogenic Silica   Chlorophyll a/phaeophytin a   5   0   5   5   0   0   3   5   5   0   816	Dissolved Organic Carbon	3	0	3	3	0	0	3	3	3	0	504
Particulate Organic Carbon   Particulate Organic Nitrogen   Particulate Phosphorous   Biogenic Silica   Chlorophyll a/phaeophytin a   5   0   5   5   0   0   3   5   5   0   816												
Particulate Organic Nitrogen   Particulate Phosphorous   Biogenic Silica   Chlorophyll a/phaeophytin a   5   0   5   5   0   0   3   5   5   0   816												
Particulate Phosphorous   Biogenic Silica   Si												
Biogenic Silica												
Chlorophyll a/phaeophytin a         5         0         5         5         0         0         3         5         5         0         816           Total suspended solids         3         0         3         3         0         0         3         3         3         0         504           Dissolved oxygen         5         0         5         5         0         5         3         5         5         0         876           Phytoplankton – whole water         0         0         2         2         0         0         2         0         2         0         2         0         20         20         204           Phytoplankton – screened water         0         0         2         2         0         0         2         0         2         0         2         0         2         0         2         0         2         0         2         0         2         0         2         0         2         0         2         0         2         0         2         0         2         0         2         0         2         0         2         0         0         0         0												
Total suspended solids	<u> </u>	<u> </u>	_						_	_	_	
Dissolved oxygen					_							
Phytoplankton – whole water         0         0         2         2         0         0         2         0         0         2         0         0         0         1<												
Phytoplankton – screened water												
Zooplankton	· · ·		_				_		_		-	
Respiration	Phytoplankton – screened water	0	0	2	2	0	0	2	0	2	0	204
Photosynthesis	Zooplankton	0	0	1	1	0	0	1	0		1	108
Hydrographic profiles:  I I I I I I I I I I I I I I I I I I I	Respiration	0	0	3	0	0	0	0	3	3	0	108
Conductivity Temperature Pressure Dissolved oxygen Chlorophyll fluorescence Transmissometry In situ irradiance Surface irradiance	Photosynthesis	0	0	5	0	0	0	0	0	5	0	150
Temperature Pressure Dissolved oxygen Chlorophyll fluorescence Transmissometry In situ irradiance Surface irradiance	Hydrographic profiles:	1	1	1	1	1	1	1	1	1	1	246
Pressure Dissolved oxygen Chlorophyll fluorescence Transmissometry In situ irradiance Surface irradiance	Conductivity											
Dissolved oxygen Chlorophyll fluorescence Transmissometry In situ irradiance Surface irradiance	Temperature											
Chlorophyll fluorescence Transmissometry In situ irradiance Surface irradiance												
Transmissometry In situ irradiance Surface irradiance												
In situ irradiance Surface irradiance												
Surface irradiance												
sigma-t												
Salinity												
Altimeter  Pottom doub												
Bottom depth Navigational position	*											
Navigational position         0         0         1         1         1         1         1         1         162	<u> </u>	0	0	0	1	1	1	1	1	1	1	162

#### 8.0 PROJECT FISCAL INFORMATION

This project is being carried out under the Harbor and Outfall Monitoring contract (Contract No. S366) between MWRA and Battelle Duxbury Operations.

#### 9.0 SCHEDULE OF ACTIVITIES AND DELIVERABLES

Table 6 lists the delivery schedule for the various water-column monitoring reports. Table 7 provides the planned schedule for all farfield and nearfield surveys and associated deliverables.

Table 6. Schedule of Data Reports, Data Exports, and Synthesis Reports

Deliverable	Survey Period	Due Date		
Survey-Related Reports	Survey remains	2 40 2 400		
Survey Plans	Each survey	1 weeks prior to survey		
Survey Email Summaries	Each survey	7 days after survey		
Survey Reports – Draft	Each survey	14 days after survey		
Survey Reports – Final	Each survey	14 days after receipt of comments		
Data Reports and Exports				
Data Reports	February – April	July 15		
1) Nutrient	May and June	September 15		
2) Respiration/Productivity	July and August	November 15		
3) Plankton	September – December	March 15		
Data Exports	As above	As above		
1) Nutrient				
2) Respiration/Productivity				
3) Plankton				
Mooring and Meteorology Letters	January – June	July 14		
	July – December	January 14		
Remote Sensing Letter Reports	February – April	November 30		
	May and June			
	July and August	April 29		
X7	September – December	^		
Year's electronic word processing files	January – December	January 15		
for the survey plans and final survey				
reports, including all graphics and tables				
Synthesis or Interpretive Reports				
Annual Whale Observation – Draft	February – December	January 31		
Annual Whale Observation – Final	Teordary December	2 weeks after receipt of comments		
Semiannual Water Column – Draft	February – July	October 29		
Semiannual Water Column – Final	reordary – Jury	2 weeks after receipt of comments		
Semiannual Water Column – Prilar Semiannual Water Column – Draft	August – December	April 15		
Semiannual Water Column – Final	August – December	2 weeks after receipt of comments		
Annual Water Column – Outline	February – December	April 29		
Annual Water Column – Draft	redition – December	May 31		
Annual Water Column – Final		2 weeks after receipt of comments		
Outfall Monitoring Overview– Outline	February – December	May 31		
Outfall Monitoring Overview—Outfile  Outfall Monitoring Overview—Draft	1 Cordary – December	June 29		
Outfall Monitoring Overview—Outline		2 weeks after receipt of comments		
Outrain widintoring Overview— Outline		2 weeks after receipt of confinents		

	Additional Surveys		Planned Due Date <sup>a</sup>			
Survey ID	Combined	Plan	Date Start	Date End	Summary	Draft Report
WF041	WN041	01/26/04	02/02/04	02/05/04	02/12/04	02/19/04
WF042	WN042	02/16/04	02/23/04	02/26/04	03/04/04	03/11/04
WN043	None	03/10/04	03/17/04	03/17/04	03/24/04	03/31/04
WF044	WN044	03/29/04	04/05/04	04/08/04	04/15/04	04/22/04
WN046	None	05/05/04	05/12/04	05/12/04	05/17/04	05/24/04
WF047	WN047	06/07/04	06/14/04	06/17/04	06/24/04	07/01/04
WN049	None	07/14/04	07/21/04	07/21/04	07/28/04	08/04/04
WF04B	WN04B	08/09/04	08/16/04	08/19/04	08/26/04	09/02/04
WN04C	None	08/25/04	09/01/04	09/01/04	09/08/04	09/15/04
WN04D	None	09/22/04	09/29/04	09/29/04	10/06/04	10/13/04
WF04E	WN04E	10/11/04	10/18/04	10/21/04	10/28/04	11/04/04
WN04F	None	11/03/04	11/10/04	11/10/04	11/17/04	11/24/04
WF051	WN051	01/24/05	01/31/05	02/03/05	02/10/05	02/17/05
WF052	WN052	02/14/05	02/21/05	02/24/05	03/03/05	03/10/05
WN053	None	03/09/05	03/16/05	03/16/05	03/23/05	03/30/05
WF054	WN054	03/28/05	04/04/05	04/07/05	04/14/05	04/21/05
WN056	None	05/04/05	05/11/05	05/11/05	05/18/05	05/25/05
WF057	WN057	06/06/05	06/13/05	06/16/05	06/23/05	06/30/05
WN059	None	07/13/05	07/20/05	07/20/05	07/27/05	08/03/05
WF05B	WN05B	08/08/05	08/15/05	08/18/05	08/25/05	09/01/05
WN05C	None	08/24/05	08/31/05	08/31/05	09/07/05	09/14/05
WN05D	None	09/21/05	09/28/05	09/28/05	10/05/05	10/12/05
WF05E	WN05E	10/10/05	10/17/05	10/20/05	10/27/05	11/03/05
WN05F	None	11/02/05	11/09/05	11/09/05	11/16/05	11/23/05

Table 7. Schedule of Water Column Surveys and Related Survey Reports

WN: water column nearfield; WF: water column farfield

#### 10.0 PROJECT ORGANIZATION AND RESPONSIBILITIES

The Water Column Monitoring tasks will be accomplished through the coordinated efforts of several organizations. Figure 6 presents the Project Management structure and the major tasks necessary to complete the scope of work. Each element of the tasks has been assigned a separate subaccount with budget and milestones, and these accounts will be used to track costs against progress.

Dr. Andrea Rex is the Director of the MWRA Environmental Quality Department. Dr. Mike 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 CWQAPP. Mr. Ken Keay is the MWRA Deputy Project Manager and will serve as a backup to Dr. Mickelson. Ms. Wendy Leo is the MWRA EM&MS Database Manager.

Ms. Ellen Baptiste-Carpenter is the Battelle Project Manager. She is responsible for ensuring that products and services are delivered in a timely and cost-effective manner that meet MWRA's expectation, and for the overall performance of this project. Dr. Carlton Hunt is the Battelle Technical Director and is responsible for ensuring that data collection and interpretation are scientifically defensible, and for responding to technical challenges as they arise. Ms. Jeanine Boyle is the Deputy Project Manager. She will assist Ms. Baptiste-Carpenter in the day-to-day operation of the program. The Battelle Quality Assurance Officer for the project is Ms. Rosanna Buhl. For this task, Ms. Buhl is responsible for reviewing data reports and QA Statements submitted by members of the Water column monitoring team for completeness and adherence to the CWQAPP. She is also responsible for reviewing the data and synthesis reports for accuracy and completeness. Mr. Chris Gagnon is the Battelle Field Manager, he is

<sup>&</sup>lt;sup>a</sup> Tentative dates. Actual dates will be determined based on the previous survey completion date.

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responsible for the overall field program and for all day-to-day field activities conducted by Battelle for the project. Ms. Deirdre Dahlen Battelle's Laboratory Manager, is responsible for overseeing laboratory activities in the contract. Ms. Ellen Baptiste-Carpenter is also Battelle's Database Manager for this project. Mr. Scott Libby is the Battelle Senior Scientist responsible for the conduct of the water column monitoring tasks described in this CWQAPP. Dr. Ted Loder (UNH) will provide senior consulting on nutrient issues. Dr. Don Anderson (WHOI) will consult on nuisance phytoplankton issues. The key contacts at each of the supporting laboratories are shown in Figure 6. Addresses, telephone (and fax) numbers, and Internet addresses, as well as specific project roles and responsibilities, are presented in the HOM 4 Program Management Plan (Battelle 2002).

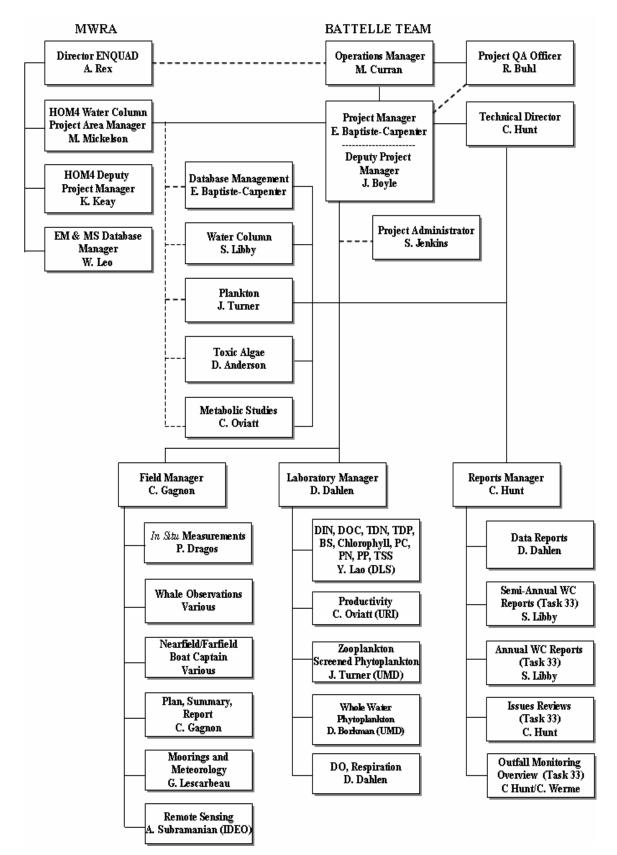


Figure 6. Water Column Study Area Organization

#### 11.0 DATA QUALITY REQUIREMENTS AND ASSESSMENTS

Data will be examined in terms of precision, accuracy, completeness, comparability, and representativeness to ensure that all data generated during the conduct of surveys, analyses, and reporting are of the highest quality. These terms are defined in the HOM 4 Quality Management Plan (Battelle 2002). The application of these data quality measures is described below.

#### 11.1 Navigational and Hydrographic Data

#### 11.1.1 Precision and Accuracy

Precision and accuracy objectives for navigation and hydrographic samplings are presented in Table 8. Section 12 provides details on sampling procedures established to ensure data quality. Section 14 contains instrument calibration methods and specifications. Navigational accuracy of 10m is required for this program.

Sensor	<b>Reporting Units</b>	Range	Accuracy	Precision
Pressure (depth)	M	0 to 200	1	< 0.1
Temperature	°C	0 to +30	0.01	0.01
Conductivity	mS cm <sup>-1</sup>	0.5 to 65	0.02	0.01
Transmissometer (20-cm)	m <sup>-1</sup>	0 to 40	0.20	0.01
Dissolved oxygen	mg L <sup>-1</sup>	0 to 20	0.10	0.05
<i>In-situ</i> irradiance (PAR)	μE m <sup>-2</sup> s <sup>-1</sup>	0 to 4000	10	1
On-deck irradiance (SPAR)	μE m <sup>-2</sup> s <sup>-1</sup>	0 to 4000	10	1
Fluorometer	μg L <sup>-1</sup>	0.03 to 75	50% of reading*	0.01
Echosounder (depth)	M	0 to 200	1	0.1
dGPS Navigation	Degree	coastal	1.8 x 10 <sup>-5</sup> degrees	1.8 x 10 <sup>-5</sup>
Altimeter	m	0 to 100	1	0.1
Secchi disk (30-cm, white)	m	0 to 40	0.5	0.5

Table 8. Accuracy and Precision of Instrument Sensors and Secchi Disc

#### 11.1.2 Completeness

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

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 Hz) and navigation systems (2-second intervals), sufficient data will be acquired to locate the depth of the pycnocline. Stations will not be occupied if CTD measurements and navigation coordinates (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. A 10% loss of hydrographic and navigation data over the entire program is not expected to compromise the objectives of the program.

<sup>\*</sup>When compared to wet chemistry results.

#### 11.1.3 Comparability

All sampling positions will be comparable to positions obtained by previous MWRA monitoring activities as well as by other researchers that have used or are using differential GPS at these stations. The station locations listed in Tables 1 and 2 are targets and sampling will be conducted within 300 m of the targets as visualized on the BOSS navigation display.

The electronic measurement instruments that will be used during the water quality monitoring surveys are similar to the instruments that have been used by MWRA contractors since 1992 (Albro *et al.* 1993; Bowen *et al.* 1998; Albro *et al.* 1998, 2002; Libby *et al.* 2002). Except for dissolved oxygen and chlorophyll fluorescence sensor values, the instrumentation data reduction methods are based on laboratory or vendor calibrations. To improve the representativeness of the electronic dissolved oxygen and chlorophyll fluorescence values to wet chemistry data collected during each survey, the electronic data is post-calibrated using the wet chemistry data. To maintain comparability with the 1995 through 2003 data, the same post-calibration methods will be used (Albro *et al.* 2002; *i.e.*, data will not be forced through zero). Thus, the data will be consistent with and comparable to previous studies. During preparation of the data reports and review and synthesis of the survey data, the results will be compared with the general ranges of water property data obtained from previous MWRA studies.

#### 11.1.4 Representativeness

The representativeness of the sampling program design is detailed in the Outfall Monitoring Plan (MWRA 1997) and defined by the results collected since 1992. Representativeness will also be ensured by proper handling, storage, and analysis of samples so that the materials analyzed reflect the collected material.

Deviations from the data collection procedures described in this CWQAPP will be documented in the survey logbook and described in the survey report.

#### 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 will follow standard methods that can achieve this objective. Each sample will be clearly labeled with a unique sampling identifier (survey ID and sample number) that will allow the sample to be traced from collection through analysis to reporting. All samples will be handled and stored according to the appropriate protocols.

#### 11.2.2 Completeness

The nearfield surveys will be considered complete if all seven stations are sampled. All farfield stations must be sampled for the farfield survey to be considered complete.

At each station (except zooplankton-only stations F32 and F33), discrete samples will be collected at 5 depths (only 3 depths collected at stations F30 and F31) 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) and will record such action in the survey notebook. 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 chlorophyll and DO measurements coincidentally with *in situ* electronically captured data will allow for calibration of the electronic sensor data. 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. This is also true for phaeophytin, phytoplankton and zooplankton. Reporting units for concentrations will follow standard convention for most oceanographic studies.

Comparability of the sampling procedures with previous studies will be achieved through adherence to procedures that are based on documented standard methods (*e.g.*, EPA or ASTM methods) or on methods previously described in the scientific literature or HOM program documents. Comparability throughout the project will be achieved through adherence to this CWQAPP.

#### 11.2.4 Representativeness

Water samples will be collected, handled, and transported using procedures that will ensure the resulting data represent the sample material collected.

Deviations from the sample collection procedures described in this CWQAPP will be documented in the survey logbook and described in the survey report.

#### 11.3 Laboratory Program

Table 9 summarizes the laboratory data quality objectives for water column monitoring. 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.

#### 11.3.1 Precision and Accuracy

Precision and accuracy of laboratory procedures are ensured by the analysis of quality control (QC) samples including procedural/filter blanks, prepared standards, SRMs, laboratory replicates and field replicates, as applicable. Appropriate QC samples analyzed in the laboratory for all water column parameters are presented in Table 9. In many cases, one or more QC samples of a selected type may not be applicable to all water column parameters. For example, procedural blanks are not applicable to dissolved oxygen, plankton or chlorophyll *a* analyses. Supplemental measures of precision and accuracy, not defined in Table 9, are discussed below.

#### 11.3.1.1 Particulate Nutrients

There is no SRM for particulate nutrients, but marine sediment SRM (BCSS sediment from Canada) is analyzed by the MWRA Department of Laboratory Services (DLS) on a quarterly basis. This sediment SRM is certified for total carbon and there is a reference value for total nitrogen. Analytical results are compared to those C and N values (certified and reference, respectively) and the data quality objective is 85%-115% recovery. Duplicate filter samples are collected for all particulate nutrients and 5% of the duplicate samples will be analyzed as a measure of precision. For particulate nutrients, analysis of duplicate filters is a measure of both laboratory and field precision as it is impossible to separate the effects of sample processing and instrumental analysis.

**Table 9. Data Quality Objectives** 

<b>Quality Control Sample Type</b>	Frequency	Data Quality Indicator	Corrective Action	
Procedural Blanks				
Dissolved nutrients	1 per batch of 20	≤5 times MDL <sup>1</sup>	Results examined by laboratory	
Primary Productivity by <sup>14</sup> C	One with every	<mdl< td=""><td>manager, task leader, or project</td></mdl<>	manager, task leader, or project	
	station		manager. Corrective action	
Total suspended solids	1 per batch of 20	≤5 times MDL	(e.g., re-extraction, reanalysis,	
(DI water and seawater)			data qualifier) is documented.	
Filter Blanks <sup>2</sup>				
Particulate nutrients	1 per batch of 20	≤5 times MDL	As above	
Chlorophyll a/phaeophytin	1 per batch of 20	≤5 times MDL		
Total suspended solids	1 per batch of 20	≤5 times MDL		
<b>Prepared Standards and SRM</b>				
DIN	1 per batch of 20	≤15% PD <sup>3</sup>	As above	
DOC, TDN, and TDP	1 per batch of 20	≤15% PD	7	
Particulate nutrients <sup>4</sup>	1 per batch of 20	≤15% PD	7	
Primary Productivity by <sup>14</sup> C	One with every	- <2% PD	1	
	station			
Chlorophyll a	1 per batch of 20	<15% PD	7	
Total suspended solids <sup>5</sup>	1 per batch of 20	≤20% PD	7	
Laboratory Duplicates	_		•	
DIN	1 per batch of 20	≤2% RPD <sup>6</sup>	As above	
DOC, TDN, and TDP	1 per batch of 20	= ≤10% RPD	1	
Chlorophyll <i>a</i> /phaeophytin	1 per batch of 20	≤15% RPD	1	
Total suspended solids	1 per batch of 20	<20% RPD	1	
Laboratory Triplicates	1	<del>1-</del>	1	
Dissolved Inorganic Carbon	All samples	<2% RPD	As above	
Primary Productivity by <sup>14</sup> C	All samples	<10% RPD	1	
Field Duplicates				
DIN	mid-depth at 6 nearfield and 7 farfield stations	≤30% RPD	Data qualified with 'r' (precision does not meet DQO)	
DOC, TDN, and TDP	mid-depth at N16	≤30% RPD	1	
Particulate Nutrients	1 per batch of 20	≤30% RPD	1	
Chlorophyll <i>a</i> /phaeophytin	Each mid-depth	≤50% RPD	1	
Field Triplicates	<b>r</b>			
Dissolved oxygen	First and last station of each survey day	≤5% CV <sup>7</sup>	Data qualified with 'r' (precision does not meet DQO)	

<sup>&</sup>lt;sup>1</sup> MDL = method detection limit

<sup>&</sup>lt;sup>2</sup> Filter blanks used for QC purposes only (include method procedural and field filter blanks)

<sup>&</sup>lt;sup>3</sup> Percent Difference (PD) = [(true concentration – measured concentration)/true concentration]  $\[Harmonte 100\%$ .

<sup>4</sup> There is no SRM for particulate nutrients, but a marine sediment SRM (BCSS sediment from Canada) is analyzed quarterly.

<sup>&</sup>lt;sup>5</sup> The QC sample used to assess the accuracy of the TSS method is an SRM purchased from ERA, Arvada, Co.

<sup>&</sup>lt;sup>6</sup> Relative Percent Difference (RPD) = [(absolute value (replicate 1 - replicate 2) H 2/(replicate 1 + replicate 2)] H 100%.

<sup>&</sup>lt;sup>7</sup> Coefficient of Variation (CV) = (standard deviation of the sample concentration / mean sample concentration) H 100%.

#### 11.3.1.2 Whole-Water Phytoplankton

Based on a study conducted by Guillard (1973), counts of 400 phytoplankton cells will provide a precision of ±10% of the mean. For this program, a minimum of 400 entities (solitary single cells, chains, or colonies) will be tallied for each sample. Unicellular forms (*e.g.*, *Cryptomonas*, microflagellates), aggregate forms (*e.g.*, *Phaeocystis*), and chained forms (*e.g.*, *Skeletonema*) will each count as one entity towards the 400-entities-counted-per-sample minimum tally. To increase precision of the abundance estimates for the most abundant taxa, when practical at least 75 entities of each of the three most abundant taxa will be counted in each sample. The overall goal then is to enumerate a minimum of 400 entities total and the 3 most abundant taxa to at least 75 entities each.

#### 11.3.1.3 Screened Water Phytoplankton

As with whole water phytoplankton, counts of 400 phytoplankton cells will provide a precision of  $\pm 10\%$  of the mean. A minimum of 400 entities of the target dinoflagellate taxa will be counted, or an entire Sedgwick-Rafter cell, whichever comes first.

#### 11.3.1.4 Zooplankton

Zooplankton samples will be split with a Folsom plankton splitter, and an aliquot of at least 300 animals will be counted. If the total count in a split is less than 300 animals, the other half of the split is counted to make a combined split. If that still does not yield enough animals, then the penultimate split is counted. Total zooplankton counts under the HOM3 program were never below 300 and usually exceed that number by considerable amounts.

#### 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 <10% for the entire project will not compromise the objectives of the project.

#### 11.3.3 Comparability

Data will be directly comparable to results obtained previously at the same or similar sites in Massachusetts Bay and to those of similar studies conducted in Cape Cod Bay (Albro *et al.* 1993; Bowen *et al.* 1998; Albro *et al.* 2002; Libby *et al.* 2002), because field program design and analytical procedures are similar or identical. In addition, the use of written standardized procedures ensures that sample preparation and analyses will be comparable throughout the project and with other projects. Specific, potential comparability issues are addressed in Albro *et al.* 2002.

To verify that data generated by the Battelle team in 2002-2003 of HOM4 are comparable to data generated by DLS in 2004-2005, an intercomparison study was performed in 2003. The results of this study showed the data were comparable.

To verify that data generated for the HOM study are comparable to data generated for harbor monitoring studies, an inter-comparison study will be performed during 2004 and occasionally thereafter (at dates to be defined by MWRA). Samples from either HOM or Harbor (BHWQM) surveys or MWRA sampling activities will be split analyzed under both projects to establish comparability between projects.

Reporting units for concentrations will follow standard convention for most oceanographic studies.

#### 11.3.4 Representativeness

Representativeness is addressed primarily in sampling design. The laboratory measurements that will be made during the water quality monitoring task 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. Representativeness will also be ensured by proper handling, storage (including

appropriate preservation and holding times), and analysis of samples so that the material analyzed reflects the material collected as accurately as possible.

Deviations from the analytical scheme described in this CWQAPP will be noted in the laboratory records associated with analytical batches and in the QA statements and will be discussed in the quarterly QA/QC Corrective Action reports.

#### 11.3.5 Sensitivity

Sensitivity is the capability of methodology or instrumentation to discriminate among measurement responses for quantitative differences of a parameter of interest. The method detection limits (MDL) (Table 10) provide the sensitivity goals for the proposed procedures.

**Table 10. Method Detection Limits** 

Analysis	MDL
Dissolved ammonia	0.028 μΜ
Dissolved inorganic nitrate/nitrite	0.025 μΜ
Dissolved inorganic nitrite	0.013 μΜ
Dissolved inorganic phosphate	0.010 μΜ
Dissolved inorganic silicate	0.036 μΜ
Dissolved organic carbon	25 μΜ
Total dissolved nitrogen	1.61 µM
Total dissolved phosphorus	0.11 μΜ
Particulate carbon	0.78 μΜ
Particulate nitrogen	0.12 μΜ
Particulate phosphorus	0.006 μΜ
Biogenic silica	0.003 μΜ
Chlorophyll <i>a</i> and phaeophytin (IDL)	0.05 and 0.06 μg/L
Total suspended solids	0.24 mg/L

IDL: instrument detection limit

#### 12.0 SAMPLING AND ANALYTICAL PROCEDURES

Methods for collection and analysis of samples are described in the following sections. Analyses will be performed by Battelle, DLS, URI and UMD as defined below.

#### **12.1** Field Sampling and Measurements

#### 12.1.1 Navigation

Vessel positioning during sampling operations will be accomplished with Battelle's BOSS navigation system. This system consists of a Northstar dGPS interfaced to the BOSS computer. The GPS receiver has six dedicated channels and is capable of locking onto six different satellites at one time. To correct the GPS calculations, the Northstar dGPS will receive correction data from one of three USCG dGPS broadcast sites: Montauk Point, NY, Chatham, MA, or Portsmouth Harbor, NH (Figure 7). This capability ensures strong signal reception, and accurate and reliable positioning with 2-second updates.

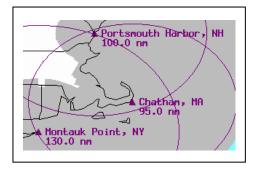


Figure 7. dGPS Master Stations Coverage

#### 12.1.2 Vessel Handling

Boston Harbor, Massachusetts Bay, and Cape Cod Bays are heavily trafficked by commercial, fishing, and recreational vessels. Endangered whales, as well as numerous other marine mammals seasonally frequent the Bays. The licensed boat captain will operate the vessel in a professional manner at all times during surveys to ensure the safety of passengers and crew and to minimize the possibility of collisions with other traffic (46 CFR 185¹) or with marine mammals (50CFR parts 217 and 222). Also required by National Marine Fisheries Service's rules, the vessel will maintain a minimum distance of 500 yards from right whales. If a right whale is within 500 yards of a sampling station, the vessel will wait at least 30 minutes for the right whale to move out of range or the station will be sampled as close to nominal as possible while maintaining the minimum required distance from the right whale(s).

At each sampling station, the vessel will be positioned upwind/upcurrent of the target station position with distance dependent upon wind/current strength and expected drift. The objective is to sample as close to the nominal station coordinates as possible, but at no more than 300m off the station. The vessel heading will be selected such that the underwater unit will be deployed on the side of the boat facing the sun and relative to the prevailing seas. The vessel will maintain this position during the cast. If a vessel positioning or safety issue causes shading of the CTD, the shading incident will be noted in the station log and shading will be eliminated from the light measurement data during post-processing.

<sup>&</sup>lt;sup>1</sup> 46 CFR 185, Subpart C – Miscellaneous Operating Requirements Sec. 185.304 Navigation underway:

<sup>(</sup>a) The movement of vessel shall be under the direction and control of the master or a licensed mate at all times. The master shall operate the vessel keeping the safety of the passengers and crew foremost in mind by directing the vessel in order to prevent a casualty. Special attention should be paid to:

<sup>(1)</sup> The current(s) velocity and direction of the transiting area;

<sup>(2)</sup> Tidal state;

<sup>(3)</sup> Prevailing visibility and weather conditions;

<sup>(4)</sup> Density of marine traffic;

<sup>(5)</sup> Potential damage caused by own wake;

<sup>(6)</sup> The danger of each closing visual or radar contact;

<sup>(7)</sup> Vessel's handling characteristics; and

<sup>(8)</sup> Magnetic variation and deviation errors of the compass

#### 12.1.3 Hydrographic Profiles

The hydrographic profile sampling equipment and data acquisition equipment consists of the following apparatus and instruments.

- Battelle-designed and fabricated winch with 150 m of 8-conductor double-armored stainless-steel cable and sheave
- 5- and 9-L Rosette sampling bottles (e.g., Go-Flo or Niskin)
- Sea-Bird 32 Carousel Water Sampling System or General Oceanics model 1015 Rosette system
- Ocean Sensors OS200 CTD system (three additional OS200-CTDs as backup) mounted on the Rosette and equipped with the following:
  - Sea-Bird SBE-43 DO sensor (intake at same depth as the pressure sensor) produces an
    oxygen-dependent electrical current and incorporates a thermistor for determining membrane
    temperature (one additional SBE-43 as backup). A Sea-Bird SBE-13Y, with a YSI type DO
    sensor, will serve as an additional backup if needed.
  - WET Labs C-Star 25 cm-pathlength transmissometer that provides in situ measurements of optical beam transmission (related to the concentration of suspended matter in the water at the point of measurement) mounted level with the pressure sensor
  - WET Labs WETStar chlorophyll fluorometer (intake at same depth as the pressure sensor)
  - Biospherical QSP-200L spherical quantum scalar irradiance sensor that measures underwater photosynthetically active radiation (PAR) – mounted 90 cm above the pressure sensor<sup>1</sup>
- Data Sonic PSA 900 or PSA 916 altimeter provides a measurement of underwater unit height from the bottom mounted level with the pressure sensor
- Biospherical QSR 240 reference hemispherical quantum scalar irradiance sensor that measures on-deck radiation conditions (*e.g.*, due to atmospheric conditions)
- Furuno FCV-582 video echosounder with color display and NMEA-0183 output to provide bathymetric measurements during vertical and horizontal profiling operations
- Computer with custom data-acquisition software (NavSam<sup>©</sup>)
- Color printer
- Navigation:
  - Northstar 952-XDW dGPS system aboard the R/V Aquamonitor
  - Northstar 941-XD dGPS system as backup

Battelle's software, NavSam<sup>©</sup> acquires data from all profile electronic-sampling-systems and navigation systems at the rate of four times per second. Once per second the software displays all of the information on a color monitor. The screen is split to show sensor data on the left and navigation data on the right (Figure 8). Once the data are acquired, they are automatically written to a data file and logged concurrently with position data and date and time from the navigation system. The navigation portion of the display will show the position of the vessel compared to the coastlines digitized from standard NOAA charts, navigation aids, preset sampling locations, and vessel track. During hydrocast operations, position fixes will be electronically recorded at 2-second intervals. Hard-copy printouts of position fixes will be made during discrete sampling events such as triggering of Rosette sampling bottles. During transit between stations, position fixes and deck irradiance will be electronically recorded at 5-minute intervals. Continuous irradiance measurements will be conducted from one-half hour before sunrise to one-half hour after sunset. Weather and waves permitting, the vessel will be oriented to avoid shading of the light sensors during measurements; otherwise the station log will annotate shading conditions. During post-

<sup>&</sup>lt;sup>1</sup> Location of light sensor relative to the pressure sensor (located at the bottom of the OS200 CTD) for depth offset of *in situ* irradiance (see Section 15.2.1).

processing of the hydrographic data, any ship shading incidents will be qualified as suspect ('s') and will be noted in the PROFILE.VAL\_QUAL field of the EM&MS database. Shading due to changes in cloud cover will not be qualifed in either the incident or profile light data. The readings of the two lights sensors will be formally compared on deck (in air) at the beginning of each survey day. The file containing the light sensor comparison data will be saved and the file name noted in the station log. Throughout the day, a check of the consistency of light sensor output will be conducted ondeck prior to each cast and any problems will be noted or corrected as appropriate.

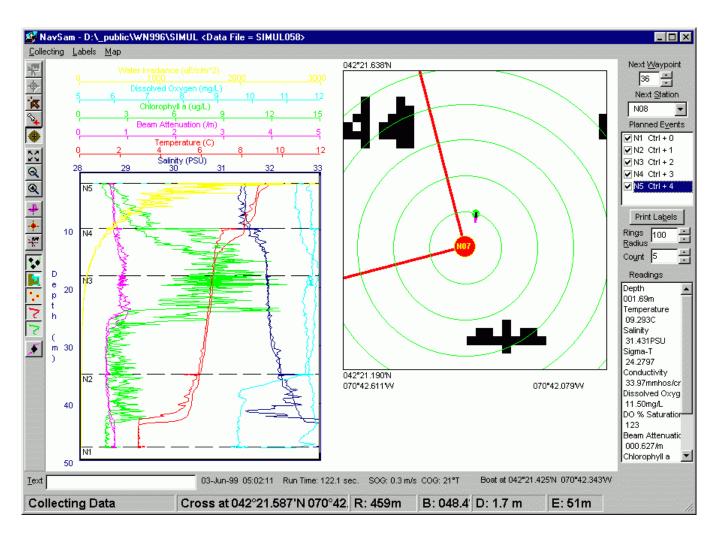


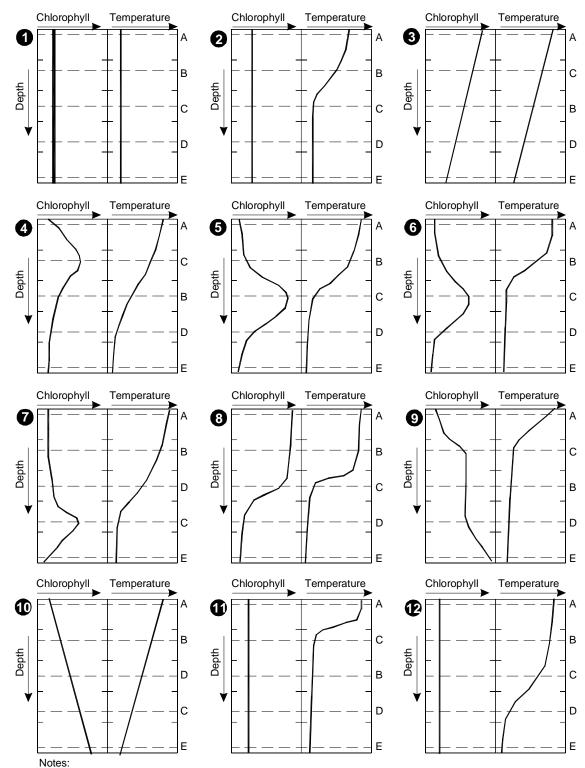
Figure 8. Sample NavSam<sup>©</sup> Data Acquisition Screen

## 12.1.4 Water Sampling

Water samples for dissolved inorganic nutrients, dissolved organic nutrients, particulate nutrients, chlorophyll *a*, TSS, DO, primary production and phytoplankton will be obtained with an underwater Rosette unit equipped with sampling bottles (GO-FLO, Niskin or comparable brand – referred to as Rosette sampling bottles in this document). The Rosette system is combined with the hydrographic profiling system. The following water sampling/hydrographic profiling procedures will be followed:

1. Before the start of each cast, each of the Rosette sampling bottles will be opened and attached to the Rosette triggering system.

- 2. After the vessel is positioned as described in section 12.1.2, NavSam<sup>©</sup> will be set to the hydrographic profiling mode and a data cast file will be opened. NavSam<sup>©</sup> will acquire data from the equipment while the underwater unit is on-deck prior to deployment. The operator will review the sensor data to verify that all sensors have reasonable in-air readings (*i.e.*, comparison of *in situ* vs. surface irradiance, beam attenuation less than 0.5/m). During the first deployment of the day, the pressure sensor will be used to adjust the depth offset based on atmospheric pressure.
- 3. After a successful on-deck check out, the underwater unit will be lowered into the water until completely submerged and held in this position.
- 4. Sensors will be held at this depth for at least two minutes to allow each sensor to equilibrate (*e.g.*, stable salinity, dissolved oxygen, and temperature readings), the unit will then be lowered at a descent rate of about 0.5 m/s to within 3-5 m of the sea floor.
- 5. During the lowering, NavSam<sup>©</sup> will record the hydrographic data and display these data on a computer screen. The Chief Scientist will monitor the downcast data to ensure data are within expected ranges and profiles are typical of the conditions expected during a survey. Once the profile is taken, the Chief Scientist will review the real-time display of data to determine the five water-sampling depths for the upcast. These are based on defined locations relative to a subsurface chlorophyll maximum detected by in situ fluorometer. The 5 sampling depths are designated surface (A), mid-surface (B), mid-depth (C), mid-bottom (D), bottom (E) as listed in Table 3, although actual sampling depths would not necessarily be evenly spaced. Depending on the depth of chlorophyll maximum, the mid-surface and mid-depth or mid-bottom and mid-depth levels can be exchanged. At all stations, the C-depth sample will be switched to a shallower (B depth) or deeper (D depth) to represent the subsurface chlorophyll maximum, as deemed appropriate by the Chief Scientist. For example, scenario 4 of Figure 9 shows an intense and shallow chlorophyll maximum. In this case, the sampling protocol for the mid-depth and midsurface would be exchanged so that the chlorophyll maximum would receive the full suite of analyses usually allocated to the water column mid-depth. If the chlorophyll maximum is at the surface, the C depth code is assigned to a subsurface maximum. Scenario 7 of Figure 9 shows an intense and deep chlorophyll maximum, thus the protocols for mid-depth and mid-bottom would be exchanged. In scenarios 9 and 11, the switch of C and B depths is driven by the importance of sampling at the pycnocline as fluorescence was consistent over these depths.
- 6. During the upcast, the unit will be maintained at each of the selected five depths until the sensor readings stabilize (*i.e.*, little fluctuation in the instrument readings), typically this is 30–60 seconds (may be longer in summer under strongly stratified conditions). Water will be collected by closing one or more Rosette sampling bottles, depending on the water volume needed for analysis. When the Rosette deck unit indicates that the bottles are closed, this event will be flagged electronically in the NavSam<sup>©</sup> data file. This marks the vessel position and the concurrent *in situ* water column parameters (salinity, temperature, turbidity, DO, chlorophyll *a*, irradiance, and depth) and links them to water collected in a particular set of Rosette sampling bottles. The NavSam<sup>©</sup> software will also generate unique bar-coded sample-bottle labels for attachment to sample bottles and survey logs. Onboard processing is described in Section 12.2.
- 7. After collecting the surface water sample, the operator will close the data cast file.
- 8. The underwater unit is then recovered. The Biospherical QSP-200L spherical quantum scalar irradiance sensor will be covered with a damp towel during transit between stations to prevent overheating of the sensor.
- 9. NavSam<sup>©</sup> will be put into navigation mode with a file created for transit to the next station.



- Mid-depth 'C' must be less than 30 meters and cannot be the bottom
- At station type 'P', try to position mid-bottom 'D' at 10% incident mid-depth 'C' at 25% incident light, and mid-surface 'B' at 50% incident

Figure 9. Twelve Scenarios for Selecting Sample Depths

### 12.1.5 Zooplankton Sampling

At "D", "G", "P", and "Z" type stations, a vertical–oblique zooplankton tow will be conducted with a 0.5-m diameter 102 µm-mesh net equipped with a flow meter. Tows will be in a vertical-oblique fashion, with just enough headway to keep the net stretched out. Tows will be made through approximately the upper 25 m (or less, at shallow stations) of the water column. Because nets are equipped with flow meters, net clogging is apparent when the flow meter is visibly not turning as the retrieved net nears the surface. In the event of net clogging due to large numbers of phytoplankton, the net will be emptied and rinsed with filtered seawater, and a second tow conducted over a shorter period of time (less depth). In addition, because it is not always easy to see the flow meter turning upon net retrieval, survey technicians will immediately review the flow meter readings for reasonableness. A reasonable reading for an average net tow is 500-1500 turns. If the reading does not fall within this range, the tow will be repeated, as above. When the net does not clog and a sample is collected successfully, the material retained by the net will be transferred to a jar as described in Section 12.2.16. The flow meter reading before and after the tow, the tow time, and the depth of the tow will be recorded on the zooplankton custody form.

## 12.1.6 Floating Debris

On all nearfield surveys, a Neuston net (1 x 2 meter with 500 micron mesh) will be towed twice to capture any floating man-made debris. The first tow (the control) will start 0.5 miles and 300° from station N01. The tow will be conducted at a heading of 060° for 10 minutes at 2 knots. The second tow will be conducted through the visible outfall plume in the vicinity of station N21, also for 10 minutes at 2 knots. If no visible plume exists, the tow will start at Station N21 and will be conducted at a heading of 45° for 10 minutes at 2 knots, crossing the diffuser line on the transect. The beginning and end coordinates of each tow will be recorded on the survey log.

#### 12.1.7 Secchi Disk

At each Farfield station, Secchi depth will be measured. A 30-cm (approximately 12 inches) diameter white disk will be lowered overboard on a line marked in 1-meter intervals (double marked every five meters). The disk will be slowly lowered over the side facing the sun. The depth at which the disk disappears, and the depth at which it reappears (after being lowered further and then raised) will be observed. The average of the two depths (disappearing and reappearing) will be recorded on the station log. Secchi readings will only be recorded between sunrise and sunset.

#### 12.1.8 Whale Observation

During each nearfield survey and the first three farfield surveys of each year, a trained whale observer will conduct sighting watches while on station and during transit between stations. The sighting operations will occur during daylight hours and when the vessel is in Massachusetts Bay or Cape Cod Bay. The observer will scan the ocean surface by eye for a minimum of 40 minutes every hour. The horizon will be swept 180° during transit between stations (± 90° of heading) and 360° while on station. All sightings will be recorded on standardized marine mammal field sighting logs (Figure 10). Header fields for sighting logs will include observer name and position on vessel; date; survey number; chief scientist, captain, and vessel name. Data fields on sighting logs will include: time, vessel position and heading (every 10 minutes), sighting event code (on or off watch, transiting or on station), relative bearing to sighting and distance from vessel, species name, group size, sea state, wind speed, swell, visibility, cloud cover, precipitation, and angle and severity of glare. A sighting while on station will be noted. Comments will be included, as needed.

Right whale sightings will be immediately reported to the National Marine Fisheries Service Northeast Right Whale Sighting Advisory System, Woods Hole MA (see Appendix B for contact information).

Task:	sk: Type: Date:					Page of				(	Observ	er:						
Date	Time	Positi Sigh	ion at nting	_	ssel iding	N	/lammal	Sighti	ng			Weath	er Cor	nditions			Gla	are
mmddyy	24-h clock	Latitude (°N)	Longitude (°W)	Direction	Speed	Species	Angle Rel. to Boat	Distance (m)	No. in Group	Sea State	Wind Speed	Swell	Visibility	Cloud Cover	Rain	Fog	Angle from Boat Head.	Glare Code
											<u>                                     </u>		1	1		1		
							С	ode Li	st									
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Figure 10. Example of Marine Mammal Sightings Log and Relevant Codes

## 12.2 Onboard Sample Processing

Depending on the subsampling requirements at each station, some or the entire following onboard sample processing procedures will be conducted. Appendix A Tables A1 and A2 lay out the required subsampling required for nearfield and farfield water column surveys, respectively.

Water from the Rosette sampling bottles is transferred to 1–L opaque polyethylene jars for onboard processing (filtration) of nutrients and chlorophyll. These transfer jars will be rinsed three times with Rosette sampling bottle water before filling with water up to the neck of the jar. The filtration apparatus will be rinsed with 10% HCL at the beginning of the survey day and with deionized water between sampling stations. The filtrate sample bottles will be rinsed three times with filtrate prior to filling. Figure 11 summarizes the onboard processing of the dissolved and particulate nutrient subsamples from the 1-L opaque polyethylene jars. The figure summarizes Battelle SOP No. 5-266, *Nutrient Sample Processing*. Sample volumes, containers, and storage conditions are listed in Table 11.

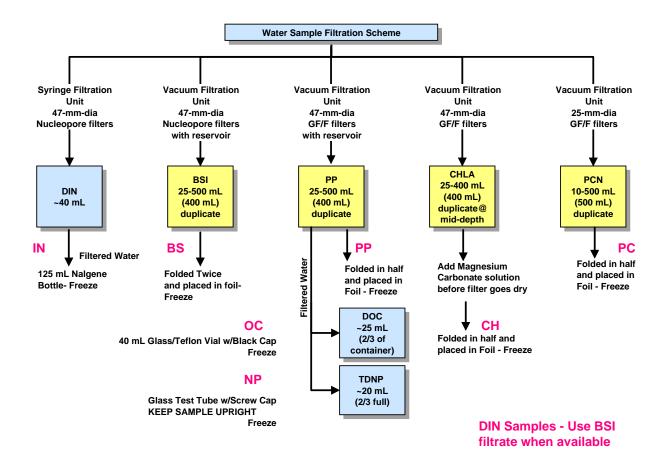


Figure 11. Onboard Processing Flow Chart

Table 11. Sample Volumes, Containers, and Processing for Field Samples

Parameter	Station Types	Sample Volume (Target) (mL) <sup>a</sup>	Sample Containers <sup>c</sup>	Shipboard Processing/ Preservation <sup>c</sup>	Maximum Holding Time to Analysis
Hydrographic Profiles <sup>b</sup>	All	NA	NA	Record data to floppy diskette.	NA
Secchi	Farfield	NA	NA	Record in field log.	NA
Subsamples from PVC Ro	sette Bottles				
Dissolved inorganic nutrients	All but Z	40	125-mL polyethylene bottle	Pass through a Nuclepore membrane filter. Freeze filtrate until analysis.	28 days
Dissolved organic carbon	A, D, G, P	25	40-mL borosilicate glass or Teflon vial	Pass sample through a GF/F. Freeze filtrate until analysis.	28 days
Total dissolved phosphorus and nitrogen	A, D, G, P	20	30 to 50-mL borosilicate glass test tube	Pass sample through a GF/F. Freeze filtrate until analysis.	28 days
Particulate organic carbon and nitrogen	A, D, G, P	10 – 500 (500)	Whatman GF/F in foil	Pass through a GF/F. Freeze filter until analysis.	28 days
Particulate phosphorus	A, D, G, P	25 – 500 (400)	Whatman GF/F in foil	Pass sample through a GF/F. Freeze filter until analysis.	28 days
Biogenic silica	A, D, G, P	25 – 500 (400)	Nuclepore filter in foil	Pass sample through Nuclepore filter. Freeze filter until analysis.	90 days
Chlorophyll <i>a</i> and phaeopigments	A, D, G, P	25 – 400 (400)	Whatman GF/F in foil	Pass through GF/F. Fix with a saturated MgCO <sub>3</sub> solution. Freeze filter until analysis.	4 weeks
Total suspended solids	A, D, G, P	100 - 500 (300)	1-L dark bottle	Store water in 1-L dark bottle at 4°C up to and during transport to DLS for filtration.	1 week
Dissolved oxygen	A, D, F, G, P, R	300	300 mL glass BOD bottle	Fix per Oudot <i>et al</i> (1988). Titrate 2-24h later.	24 hours
Respiration	R, P	300	300 mL glass BOD	Incubate in dark at in-situ temperature for 7±2 days. Fix initial samples on board and titrate within 24 h; fix and titrate as per initial samples.	24 hours
Primary Production by <sup>14</sup> C	P	5	1-L polyethelene bottle	Pass through 300-µm-mesh. Store water in 1-L dark bottle; keep cool up to and during transport to URI for incubation.	< 6 hours
Phytoplankton (whole water)	D, G, P	850	1000 mL HDPE bottle	Preserve with Utermöhl's solution.	6 months
Phytoplankton (screened water)	D, G, P	4000	1000 mL HDPE bottle	Strain through a 20-µm mesh netting; wash retained organisms into bottle. Preserve with Utermöhl's solution.	6 months
Rapid phytoplankton	Station N18 mid-depth	4000	1000-mL HDPE bottle	Strain through a 20-µm mesh netting; wash retained organisms into bottle. Preserve with Utermöhl's solution.	6 days
Sample from vertical net t					
Zooplankton	D, G, Z, P	800	1000-mL HDPE bottle	Wash with screened seawater into jar. Fix with formalin.	6 months

GF/F: pre-ashed glass fiber filter

<sup>&</sup>lt;sup>a</sup>Volume processed for analysis. Total volumes removed from Rosette sampling bottles are listed in Appendix A Tables A1-A2.

b Conductivity, temperature, pressure, dissolved oxygen, chlorophyll a fluorescence, transmissometry, *in situ* irradiance, surface irradiance, bottom depth, navigational position

Name brand items (e.g., Nuclepore, Whatman) may be substituted with comparable items from a different manufacturer.

### 12.2.1 Dissolved Inorganic Nutrients

A 60-mL syringe will be used to inject sample water from a transfer jar, through an in-line filter (Nuclepore 47-mm-diameter, 0.4-µm-membrane-fiber filter) and into a 125-mL white polyethylene (Nalgene) bottle. After rinsing the bottle three times, 40 mL of the remaining sample will be filtered into the bottle for analysis. Alternatively, according to Battelle SOP No. 5-266, *Nutrient Sample Processing*, the filtrate from the biogenic silica preparation may be used for these samples as pressure and vacuum filtration processes give similar results. The sample bottle will be labeled and the sample will be frozen. The samples will remain frozen until analyzed.

## 12.2.2 Dissolved Organic Carbon

Samples for dissolved organic carbon (DOC) will be processed according to Battelle SOP No. 5-266, *Nutrient Sample Processing*. A 25-mL aliquot will be obtained from the particulate phosphorous filtrate. The sample will be passed through a Whatman 47-mm-diameter GF/F and collected in a polysulfon filtration flask. A clean 40-mL borosilicate glass (or Teflon) vial will be rinsed three times with filtrate then filled with approximately 25 mL of filtrate. Samples will be frozen onboard and stored frozen until analysis.

## 12.2.3 Total Dissolved Nitrogen and Phosphorus

Samples for total dissolved nitrogen and phosphorus will be processed according to Battelle SOP No. 5-266, *Nutrient Sample Processing*. A 20-mL aliquot will be obtained from the particulate phosphorus filtrate. The sample will be passed through a Whatman 47-mm-diameter GF/F and collected in a polysulfon filtration flask. A clean 30-mL borosilicate glass vial will be rinsed three times with filtrate, shaken to remove excess sample and then filled with approximately 20 mL of filtrate. Samples will be stored upright and frozen until analysis.

## 12.2.4 Particulate Carbon and Nitrogen

Samples for particulate carbon and particulate nitrogen will be processed according to Battelle SOP No. 5-266, *Nutrient Sample Processing*. Between 10 and 500 mL of sample will be filtered<sup>1</sup>, depending on particulate density. The samples will be collected on 25-mm GF/F filters (nominal pore size 0.7 µm) using a vacuum-filter system. Each filter will be folded in half and placed in a labeled foil pouch and stored frozen until analysis. Samples will be processed in duplicate, but only one filter will be analyzed. The second filter is for duplicate analysis (1 per 20 samples) or as backup.

## 12.2.5 Particulate Phosphorus

Samples for particulate phosphorus will be processed according to Battelle SOP No. 5-266, *Nutrient Sample Processing*. Between 25 and 500 mL of sample<sup>1</sup> will be collected on 47-mm GF/F using a vacuum-filter system. Each filter will be folded in half and placed in a labeled foil pouch and stored frozen until analysis. Samples will be processed in duplicate, but only one filter will be analyzed. The second filter is for duplicate analysis (1 per 20 samples) or as backup.

#### 12.2.6 Biogenic Silica

Samples for biogenic silica will be processed according to Battelle SOP No. 5-266, *Nutrient Sample Processing*. Between 25 and 500 mL of sample<sup>1</sup> will be collected on 47-mm-diameter Nuclepore membrane filters (0.4-µm pore size) using a vacuum-filter system. Each filter will be folded in quarters and placed in a labeled foil pouch and stored frozen until analysis. Samples will be processed in

<sup>&</sup>lt;sup>1</sup> Exact volume filtered will be recorded on sample label and any deviations from standard volume (500 ml for PCN and 400 ml for PP and BSi) will be noted in station log.

duplicate, but only one filter will be analyzed. The second filter is for duplicate analysis (1 per 20 samples) or as backup.

## 12.2.7 Chlorophyll *a* and Phaeophytin

Samples for chlorophyll *a*/phaeophytin determination will be processed according to Battelle SOP No. 5-265, *Extraction and Analysis of Chlorophyll* a *and Phaeophytin* a *in Seawater using a Turner Designs Model 10AU Fluorometer*. Between 25 and 400 ml samples for chlorophyll *a* analysis will be collected on Whatman 47-mm-diameter GF/F using a vacuum-filter system. The final volume (if <400 ml) should result in a light green/brown residue on the filter and will be noted on the sample label. A saturated solution of MgCO<sub>3</sub> will be added to the sample during filtration to aid retention and buffer the sample against low pH (which converts chlorophyll to phaeophytin). Each filter will be folded in half and placed in a labeled foil pouch and stored frozen until analysis.

## 12.2.8 Total Suspended Solids

Whole water samples for TSS are collected in 1-L dark bottles and stored on ice (~4°C) and in the dark until they can be delivered to DLS for processing and analysis. A 7-day holding time from collection to analysis was established in a study conducted by the University of Rhode Island (Albro *et al.* 2002).

## 12.2.9 Dissolved Oxygen (DO)

Samples for dissolved oxygen determination will be processed and analyzed onboard the ship and calculated using the procedures described in Battelle SOP 5-317, *Determination of Dissolved Oxygen Concentration in Water by Modified Winkler Method using the Radiometer Titralab Type TIM860*. Samples for DO analysis will be collected in 300-mL BOD bottles. Using a hose (about 50-cm long) attached to the outlet on the Rosette sampling bottle, fill the BOD bottle from the bottom up with a minimum of bubbles and turbulence. The BOD bottle will be placed in an overflow container that has a volume 3-4 times greater than the BOD bottle. The BOD bottle will be filled and allowed to overflow until the overflow container is full. After filling the BOD bottles, the DO samples will be fixed with manganese sulfate and alkali-iodide-azide powder pillows as described in Oudot (1988) and Battelle SOP 5-317. The samples will be stored in the dark for a minimum of 2 h and shaken and titrated within 24 h. The fixed oxygen samples will be titrated in the BOD bottle using a programmed Radiometer Titralab Type TIM860 autotitrator with a precise potentiometric endpoint. These samples will be titrated either on board the vessel or onshore within 24 hours of being fixed. Bottles will be kept dark until the samples are analyzed.

#### 12.2.10 Floatable Debris

After the net tow is completed, the sample will be emptied into a white dissection basin for a visual, qualitative inspection. Types and relative amounts of anthropogenic and natural debris will be documented in the survey log. Each sample will be digitally photographed with the date, time, and survey ID, along with a ruler for visual scale. The basin filled with sample should take up the entire frame of the photograph. There should be no shadows over the basin and a flash will be used unless the day is cloudfree. Identifiable anthropogenic materials (*e.g.*, plastics) will be retained and archived. Digital images will be included in the survey email summary and described in the survey report.

## 12.2.11 Respiration

Water will be collected in six 300-mL BOD bottles at each of three depths (surface, mid-depth, and bottom). Three bottles will be fixed immediately according to Battelle SOP 5-317, *Determination of Dissolved Oxygen Concentration in Water by Modified Winkler Method using the Radiometer Titralab Type TIM860* and used to determine initial DO concentration. Three bottles will be incubated in the dark, in temperature-controlled incubators that are maintained to within 2°C of *in situ* temperature. The

incubation will last from five to nine days depending upon ambient water temperatures (longer in winter/shorter in summer). After the incubation period, the dark BOD bottles will be fixed for the determination of DO concentrations. These fixed samples will be analyzed within 24 h of being fixed.

# 12.2.12 Primary Productivity Analysis by <sup>14</sup>C

At each productivity station, samples from each of 5 depths from the Rosette sampling bottle are screened through a 300-µm-mesh screen (to remove large zooplankton) into opaque 1-L polyethylene bottles. The bottles will be rinsed three times with sample prior to filling. The samples will be placed in a cooler and transferred to the URI laboratory within a maximum of 8 hours of water sampling.

### 12.2.13 Whole-Water Phytoplankton

Water from the Rosette sampling bottle will be poured into a graduated cylinder that has been cut at the 850 mL mark. Before filling the cylinder, it is rinsed twice with water from the Rosette sampling bottle. The filled cylinder is then poured into a 1-L bottle containing 8 mL of Utermöhl's solution preservative. The preserved samples are stored at ambient temperature and in the dark until analysis. The Utermöhl's solution is prepared as described in Guillard (1973): 100 g potassium iodide, 50 g iodine, and 50 g sodium acetate each are dissolved incrementally in distilled water to a final volume of 1 L.

### 12.2.14 Screened and Rapid-Analysis Phytoplankton

For the screened and rapid analysis samples, a 4–L graduated cylinder is rinsed twice and filled (to 4-L) with sample water from the Rosette sampling bottle. The water from the filled cylinder is passed through a 20- $\mu$ m-mesh screen. Using a squeeze bottle containing seawater that has passed through the 20- $\mu$ m-mesh screen, the seawater is squirted back through the screen to wash the retained plankton into a 1-L sample bottle containing 8 mL of Utermöhls solution. The plankton samples will be stored at ambient temperatures in the dark until analyzed by UMD. The rapid analysis sample will be transferred to UMD for immediate analysis.

## 12.2.15 Zooplankton

After conducting the net tow, the net is suspended with the net opening 7-9 feet above the deck. The suspended net is washed down from the outside of the net with running seawater. Excess water is drained through the netting. The lower part of the net is again washed down from the outside of the net. This is repeated a couple of times until the net bottle is about ½ full and the netting is clear of material. The net bottle is removed from the end of the net and the retained water with material is transferred to a 1-L plastic jar. If ctenophores (*Beroe* sp.) are encountered, the sample will be passed through a coarse mesh screen to remove the ctenophores prior to preserving the sample. Using water from a squeeze bottle that was pre-screened with a 20-µm-mesh screen, any remaining material in the net bottle is washed into the plastic jar. Immediately, the sample will be preserved with enough formalin to produce a 10% formalin to seawater solution. All zooplankton samples will be stored at ambient temperature in the dark until they are analyzed.

## 12.3 Laboratory Sample Processing and Analysis

## 12.3.1 Dissolved Inorganic Nutrients

The analysis of dissolved inorganic nutrients is based on the cited EPA methods (Table 4). Dissolved inorganic nutrient concentrations are determined for samples that have been passed through a 0.4-µm pore size membrane filter in the field. The concentrations of ammonium, nitrate, nitrite, silicate, and phosphate are measured colorimetrically on a Skalar Autoanalyzer. This instrument automates standard manual techniques for the analysis of nutrients. The ammonium analysis is based on the technique of Solorzano (1969) whereby absorbance of an indophenol blue complex is measured at 660 nm. Nitrite is

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 is based on the molybdate blue procedure of Murphy and Riley (1962). The colorimetric analysis of silicate is based on that of Brewer and Riley (1966).

## 12.3.2 Dissolved Organic Carbon

A Tekmar-Dorhmann, Apollo 9000 Carbon Analyzer is used to perform this analysis, based on EPA method 415.1. This instrument uses an automated, high-temperature combustion technique where an exact volume of sample is injected into the instrument and oxidized into carbon dioxide. A platinum catalyst greatly enhances this reaction. Inorganic carbon is removed by acidification and sparging prior to analysis. The carbon dioxide content is measured via a non-dispersive infrared detector (Sugimura and Suzuki, 1988).

## 12.3.3 Total Dissolved Nitrogen and Phosphorus

DLS uses the Skalar Autoanalyzer to perform this analysis based on the D'Elia *et al.* (1997) and Valderrama (1981) methods. This method is a persulfate oxidation technique for nitrogen and phosphorus where, under alkaline conditions, nitrate is the sole nitrogen product and phosphate is the sole phosphorus product. Then the concentrations of nitrate and phosphate are measured on the Skalar Autoanalyzer. Dissolved organic P is the difference between total dissolved P and phosphate. Dissolved organic N is the difference between total dissolved N and dissolved inorganic nitrogen components.

## 12.3.4 Particulate Carbon and Nitrogen

The analysis, performed on a Perkin-Elmer CHN Elemental Analyzer II, is a high temperature combustion where the combustion products - water vapor, carbon dioxide and nitrogen gas are separated, quantitated with a thermal conductivity detector and compared to a known standard (EPA Method 440.0 [March 1997]). This analysis does not distinguish between particulate organic and particulate inorganic components of a sample. The results are corrected by subtracting the procedural filter blank result from the unadjusted sample result.

### 12.3.5 Particulate Phosphorus

Particulate Phosphorous analysis is based on the method of Solorzano and Sharp (1980). To convert the phosphorus to phosphates, filters are transferred to aluminum weighing dishes and placed in 550 degree oven for 1 hour. Cooled filters are placed in centrifuge tubes, 1ml of 10% HCL is added. The filters are digested overnight. The next day 19 ml of DI water is added, centrifuge tubes are shaken. The tubes are covered and precipitate is settled overnight. The unturbid portion of the sample is analyzed using a Skalar Autoanalyzer.

## 12.3.6 Biogenic Silica

Biogenic silica is analyzed according to the method outlined in Paasche (1973). This is an extraction/digestion technique using NaOH in a 100°C water bath followed by analysis of silicate in the extract by a Skalar Autoanalyzer. The results are corrected by subtracting the procedural filter blank result from the unadjusted sample result.

## 12.3.7 Chlorophyll a and Phaeophytin

Samples for chlorophyll a/phaeophytin are processed according to EPA method 445.0 using a Sequoia Turner Fluorometer, Model 450-003. All handling steps are performed in subdued light. The chlorophyll

a/phaeophytin is extracted from the cells retained on the GF/F filter by mechanical grinding followed by a 2-24 hour steep in 90% buffered acetone at 4°C. The sample is then centrifuged and the extract analyzed using a Sequoia Turner Fluorometer, Model 450-003. 150  $\mu$ L of 0.1 N HCl is added to the extract and the extract remeasured after 90 seconds to determine phaeophytin concentrations. The grinding apparatus and glassware are rinsed between samples with 90% buffered acetone.

#### 12.3.8 Total Suspended Solids

Samples for total suspended solids (TSS) determination are stored in an amber bottle at 4°C and processed in a particulate free area within 7 days of sampling. Using a vacuum-filter system, aliquots are vacuum filtered (<300 mmHg) through a tared 0.4-µm pore size polycarbonate (i.e. Nucleopore) 47-mm-diameter membrane filter. The volume filtered is determined by the analyst based on the rate of flow though the filter. When the entire aliquot has passed through the filter, the filtration apparatus is washed down with 20 mL of pH 8 deionized water three separate times, waiting for all the water to pass through the filter between rinses. Following filtration, the filters are folded in quarters, stored in a plastic petri dish, partially covered, labeled, and placed in a dessicator for at least 48 hours. Upon removal from the dessicator, the filter is weighed on a Microbalance. TSS is calculated as the net filter weight relative to the sample volume.

### 12.3.9 Dissolved Oxygen

After filling all required BOD bottles from the Rosette sampling bottles, the DO samples will be fixed with manganese hydroxide and alkali-iodide as described by Oudot *et al.* (1988) and documented in Battelle 5-317, *Determination of Dissolved Oxygen Concentration in Water by Modified Winkler Method using the Radiometer Titralab Type TIM860*. Fixed oxygen samples will be titrated in the bottle using a programmed Radiometer TIM860 autotitrator with a precise potentiometric endpoint. Within 24 hours 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:

$$DO = \frac{A F}{V}$$

where: A = Volume of titrant in (mL)

V = Volume of DO sample (mL; based on measured bottle capacity)

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

#### 12.3.10 Respiration

The rate of oxygen consumption will be calculated using the method described by Strickland and Parsons (1972) and Battelle 5-317, *Determination of Dissolved Oxygen Concentration in Water by Modified Winkler Method using the Radiometer Titralab Type TIM860*. As described in Section 12.2.11, two sets of triplicate DO samples will be collected for each respiration analysis. The first set will be fixed and analysed immediately providing a measurement of DO concentration for that sampling depth as well as the initial DO concentration for the respiration calculation. The second set will be fixed and analysed after the incubation period and provide a measure of the final or dark bottle DO concentration. The net respiration (NETR) in units of mg  $O_2$  L<sup>-1</sup> h<sup>-1</sup> will be determined using the equation below. The result is multiplied by 1000/32 to derive the rate of  $O_2$  decline in  $\mu$ M/h.

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

where:  $DO_{1B}$  = Initial DO concentration in mg  $O_2$  L<sup>-1</sup>  $DO_{DB}$  = Dark Bottle DO concentration in mg  $O_2$  L<sup>-1</sup> after incubation T = Incubation time in hours

# 12.3.11 Primary Production by <sup>14</sup>C

Under subdued green light, water from each depth sampled will be processed separately starting with the surface water sample. Primary production is measured using a small volume/short incubation time method (Lewis and Smith, 1983). Each sample is mixed thoroughly and then poured into a repipette set to deliver 5 mL. The repipette is rinsed twice with sample prior to use. The delivery tip of the repipette is flushed three times and 5 mL of sample is pipetted into 20 mL borosilicate vials. A total of 18 vials (16 light and 2 dark) are filled for each depth, and the two dark vials are immediately placed into opaque covers. These vials are incubated in a light and temperature controlled incubator (see Appendix C). Light bottles from each depth are incubated at 16 different light intensities (250 W Tungsten-halogen lamps attenuated with neutral density filters, range 0-2000  $\mu$ E m<sup>-2</sup> s<sup>-1</sup>) and all bottles are incubated within 2°C of the *in situ* temperature. It is not always possible, especially during summer-stratified conditions (large temperature gradient surface to bottom), to maintain the incubators at a temperature within 2°C of the *in situ* temperature throughout the incubation period. Therefore, a correction factor [C.F. = exp (0.0693 (*in situ* temperature – average incubation temperature))] is applied to hourly productivity values before fitting P-I curves.

The 5 mL samples are incubated with 100  $\mu$ L of 10  $\mu$ Ci/mL (1 $\mu$ Ci for 5 mL sample) Carbon-14 ( $^{14}$ C) stock solution. All vials are then placed in the incubator for one hour. Time and temperature is recorded at the start and end of the incubation period. The light intensity at each vial location within the incubator is measured before the incubation period. Light is measured with a LiCor 192SA cosine corrected irradiance sensor, which is calibrated every two years (calibration factors are stored in the LiCor data logger). Neutral-density screening is applied to selected vials to achieve a range of light intensities. Temperature is constantly monitored throughout the incubation period and the location of each vial in the incubator is recorded. Upon removal from the incubator, 100  $\mu$ L of 0.05N HCl is added to each vial. Vials remain loosely capped while shaken in the dark for 20 hours. After this time period, 17 mL of Universol Scintillation Cocktail is added to each vial and the vials are tightly capped, shaken vigorously, and are kept in the dark for at least 12 hours prior to being counted.

To calculate the specific activity added on each incubation date, 100 μL of 10 μCi/mL <sup>14</sup>C stock is added to each of three vials containing 17 mL of Universol and 3 mL of β-phenylethylamine. The three specific activity vials, along with one blank containing 17 mL of Universol, is counted with each set of samples. Prior to August, 2002, <sup>14</sup>C measurements were counted on a Beckman Liquid Scintillation Counter (Model LS 3801). Current measurements are counted on a Packard TriCarb Liquid Scintillation Counter (Model 2900). Each model is configured to measure single labeled <sup>14</sup>C samples as disintegrations per minute (DPM) for five minutes, and is set to repeat three times. The Model 2900 was calibrated on July 29, 2002, using Packard's <sup>14</sup>C and <sup>3</sup>H standards and background. The <sup>14</sup>C and <sup>3</sup>H efficiencies were 96.3% and 68.7% respectively.

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

$$P(i) = \underbrace{(1.05DPM(i))DIC}_{A_{sp}T}$$

$$P(d) = \underbrace{(1.05DPM(d))DIC}_{A_{en}T}$$

$$A_{sp} = DPM(sa)-DPM(back)$$

where: P(i) = primary production rate at light intensity i (µgC L<sup>-1</sup> h<sup>-1</sup> or mgC m<sup>-3</sup> h<sup>-1</sup>)

P(d) = dark production, (µgC L<sup>-1</sup> h<sup>-1</sup> or mgC m<sup>-3</sup> h<sup>-1</sup>)

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

DPM(d) = dpm of dark incubated sample

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

DPM(sa) = specific activity added to incubation samples (DPM)

T = incubation time (h)

DIC=concentration of dissolved inorganic carbon (µg mL<sup>-1</sup>)

Table 12 shows the frequency that primary productivity measurements and calculations are performed per vial, depth, station, and survey.

**Table 12. Measurement Frequency for Variables Involved in Calculation of Primary Production** 

Measurement/	Vial	Depth	Station	Survey
Calculation	(16/depth)	(5/stn)		
DPM(i)	$\checkmark$			
P(i)	√			
DIC		1		
P(d)		1		
DPM(d)		1		
$A_{sp}$			√	
T			<b>√</b>	
DPM(sa)			V	
DPM(back)				V

*P–I curves.* For each of the 5 depths at each photosynthesis station, a P–I curve is calculated from the data P(I) = P(i) - P(d) vs. the irradiance I, I which the incubating sample is exposed. The P–I curves are fit via one of two possible models, depending on whether significant photoinhibition occurs. In cases where photoinhibition is evident, the model of Platt *et al.* (1980) is fit (SAS, 1988) to obtain the theoretical maximum production and terms for light-dependent rise in production and degree of photoinhibition.

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

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

 $P_{sb}$  = theoretical maximum production without photoinhibition

 $a = \alpha I/P_{sb}$  where  $\alpha$  is the initial slope the light dependent rise in production

 $b = \beta I/P_{sb}$ , where  $\beta$  is a term relaying the degree of photoinhibition.

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

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

where: P(I) = primary production at irradiance I corrected for dark fixation (P(i)-P(d))  $P_{max}$  = light saturated maximum production

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

 $P_{\text{max}}$  and  $P_{\text{sb}}$  are not equivalent but they are mathematically related using the equation:

$$P_{\text{max}} = P_{sb} \left[ \alpha / (\alpha + \beta) \right] \left[ \beta / (\alpha + \beta) \right]^{\beta / \alpha}$$

*Light vs. Depth Profiles.* To obtain a numerical representation of the light field throughout the water column, downcast (see Section 15.3.2) CTD light profiles are fit (SAS, 1988) to an empirical sum of the exponential equation:

$$I_z = A_1 e^{-a1Z} + A_2 e^{-a2Z} + \dots$$

 $I_z = I_0 e^{-kZ}$ 

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

```
where: I_z=light irradiance at depth Z
I_o=incident irradiance (Z=0)
k=extinction coefficient
A_1, A_2,...=factors relating to incident (I_o=A_1+A_2+...)
a_1, a_2,...=coefficients relating to the extinction coefficient (k=a_1 + a_2+...)
```

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

Light profile data are reviewed during phase 1 post-survey processing (and again by Paul Dragos or Carl Albro prior to loading) during which data are qualified for:

- Ship shadow, manifested as reduced light values usually near the surface;
- Significant occurrences of a positive slope (light increasing with depth), not caused by corresponding increasing ambient light;
- Significant blips, beyond typical background noise, (approximately > 1/5th of a decade).

Any other anomalies in light profiles noted during this analysis that lead the investigator to exclude data from the fit will be communicated to the Battelle data management team.

**Daily Incident Light Field.** Incident light data are collected and recorded at 15-minute intervals by MWRA at Deer Island using a Biospherical Instruments QSR-240 reference scalar irradiance sensor. The same model instrument is used to routinely measure incident light on deck during surveys. The MWRA sensor is calibrated and maintained similarly to the Battelle sensor as described in Section 14.1.7.1 (calibration coefficients recorded in the MWRA database). The incident light data collected at Deer Island are used as the photoperiod incident light ( $I_0$ ) time series described below. The Deer Island data are collected using a scalar sensor and the light intensity measured in the incubator is collected with a cosine sensor. The cosine values are converted to scalar readings using an empirically determined equation<sup>1</sup>:

$$scalar = 19.2 + 1.098 (cos) - 0.00011 (cos)^2$$

<sup>1</sup> Equation was updated at URI on March 13, 2002 in comparison with Battelle's *in situ* irradiance sensor (Biospherical model Q-200L).

with both scalar and cosine light intensity in units of  $\mu E m^{-2} sec^{-1}$ . The  $r^2$  for the empirical equation is 0.997. The light data are converted prior to fitting the P-I curves.

Calculation of Daily Primary Production. Given the best fit parameters (P<sub>sb</sub> or P<sub>max</sub>, a, b) of the P–I curves obtained for each of the five sampling depths, the *in situ* light intensity (*i.e.* I<sub>z</sub>) at each depth determined from the sum of exponential fits on the *in situ* light field and the photoperiod incident light (I<sub>o</sub>) time series, it is possible to compute daily volumetric production for each depth. To do this at a given depth, instantaneous production, more commonly referred to as hourly production (P(I<sub>z</sub>); mgC m<sup>-3</sup> hr<sup>-1</sup>), is determined for the *in situ* light intensity (I<sub>z</sub>) computed for each 15 minute interval of the photoperiod (6 AM to 6 PM) using the appropriate equations and modeled P–I parameters (Platt *et al.*, 1980 or Webb *et al.*, 1974 see P–I Curves subsection). Daily production at each depth (P(z); mgC m<sup>-3</sup> d<sup>-1</sup>) is calculated as the sum of hourly production values from 6 AM to 6 PM divided by four 15-min intervals per hour.

*Calculation of Daily Areal Production.* Areal production (mgC m<sup>-2</sup> d<sup>-1</sup>) is obtained by trapezoidal integration of daily volumetric production vs. depth down to the depth of the bottom sample. The specific procedure is calculated from five depths  $z_1, z_2, ...z_5$  with values of daily productivity from the previous section  $P(z_1), P(z_2), ... P(z_5)$ . Daily areal production then equals:

$$\sum_{i=1}^{z=5} \frac{(P(z_i) + P(z_{i-1}))}{2} \times (z_i - z_{i-1})$$

where:  $z_0 = 0$  and  $P(z_0) = P(z_1)$ .

*Calculation of Chlorophyll-Specific Parameters.* Chlorophyll-specific measures of hourly production and related parameters of the fitted P(I) curve are calculated by dividing by chlorophyll concentration. Depth-averaged chlorophyll-specific production (denoted as P') is also of interest and is calculated as:

$$\frac{1}{z_5} \sum_{i=1}^{z=5} \frac{\left(P'(z_i) + P'(z_{i-1})\right)}{2} \times (z_i - z_{i-1})$$

where:  $z_0 = 0$  and  $P'(z_0) = P'(z_1)$ .

### 12.3.12 Dissolved Inorganic Carbon

Subsamples for DIC analysis are siphoned out of the productivity sample at URI with a small-bore tube into a 40ml vial so as not to introduce any bubbles. After replacing the volume 2 times, the tube is removed and two drops (0.1 mL) of Sodium Azide are added for preservation. The vial is capped with a Teflon/silica septa, making sure no bubbles are present, and stored at 4° C until analysis. Duplicate samples are collected, from which three replicates are measured. Samples are not filtered, but interference from particulate inorganic carbon is negligible.

Analysis is performed on a Total Organic Carbon Analyzer Model 700, which can analyze aqueous samples for DIC in the range from 1 ppb to 10,000 ppm C with no sample pre-treatment, prepurging, or dilution. Inorganic carbon is determined by the measurement of carbon dioxide released by acidification of a sample. As the pH of the sample is lowered, carbonate and bicarbonate ions are converted to dissolved carbon dioxide. This carbon dioxide is purged from solution, concentrated by trapping, then desorbed and carried into a non-dispersive infrared analyzer (NDIR) that has been calibrated to directly

display the mass of carbon dioxide detected. This mass is equivalent to the mass of DIC in the sample. Concentration of DIC is calculated by dividing this mass by the sample volume.

## 12.3.13 Whole-Water Phytoplankton

At the laboratory, Utermöhl's-preserved whole seawater samples will be prepared for analysis by concentrating the sample by gravitational settling as described by Borkman (1994), Borkman *et al.* (1993), and Turner *et al.* (1995). The method is similar to the methods of Hasle (1959), Iriarte and Fryxell (1995), and Sukhanova (1978). Samples will be settled in graduated cylinders with no more than a 5-to-1 height-to-width ratio.

Phytoplankton abundance is estimated by counting phytoplankton cells in a 1-mL capacity Sedgwick-Rafter chamber. Phytoplankton cells will be observed, counted, and identified in a two-stage counting protocol utilizing 250× and 500× magnifications. In this protocol, the Sedgwick-Rafter chamber is divided into equal, horizontal paths or strips and cells are enumerated as one moves across randomly selected strips. Small cells (*e.g.*, microflagellates, *Cryptomonas*) will be counted at 500×, with counting of small cells proceeding at 500× until the end of the path in which the 400-entities minimum tally is reached. The analysis will continue at 250× with paths of the Sedgwick-Rafter chamber being examined until, when practical, at least 75 entities (unicellular forms, colonies, or chains) of each of the three most abundant taxa are observed, and a minimum of 400 entities total.

The two-step counting protocol allows for improved precision in estimating abundances of small ( $<10\mu m$  greatest axial linear dimension) and larger phytoplankton forms. Counting large numbers of small forms at  $500\times$  increases the precision of the estimated abundances of these forms (see Section 11 for a discussion of precision). The counts at  $250\times$  allow for the examination of a larger volume of the sample, thereby increasing the likelihood of encountering larger, less abundant (or rare) forms. During the  $250\times$  analysis, the  $500\times$  objective can be used as needed to resolve key taxonomic characters.

Phytoplankton abundance is calculated by dividing the number of cells counted by the volume examined in Sedgwick-Rafter chamber. The theoretical maximum possible volume that would be examined would be an entire Sedgwick-Rafter cell (1 ml). Typical volumes are one path of the cell which at  $500 \times = 1/48$  of one ml of concentrate, and at  $250 \times = 1/24$  of one ml of concentrate. The volume of sample examined is dependent on number of cells encountered and how long it takes to reach cut-offs of 75 entities of the top 3 taxa and 400 cells total. Calculation of abundance also accounts for the concentration factor used in the settling process. Normally, the volume processed is 800 ml of whole-water sample, settled to 50 ml of concentrate, for a 16:1 ratio. Final abundance estimates will be reported as units of  $10^6$  cells per liter.

## 12.3.14 Screened Phytoplankton (Dinoflagellates)

A taxonomist will identify and count the following target dinoflagellates. Additional taxa may be noted at the discretion of the taxonomist.

Alexandrium tamarense Ceratium sp. Dinophysis sp. Gymnodinium sp. Gyrodinium sp. Prorocentrum sp. Protoperidinium sp.

The entire 4-liter screened sample is concentrated to 5-25 ml before counting; the final volume will depend upon the amounts of particulates present in the sample, which is a subjective judgment made by

the analyst prior to sample sedimentation. The final volume settled will be selected to minimize interference by detritus and to maximize the numbers of target organisms. A typical sample will be settled to final volumes of 5 to 10 mL. A Sedgwick-Rafter cell will be filled with 1 mL of concentrated sample and all target organisms (listed above) will be identified and counted until either 400 cells or all cells in the entire Sedgwick-Rafter cell are counted, whichever comes first. The taxonomist may choose to record selected zooplankton (e.g. tintinnids), and these numbers would appear in the database.

## 12.3.15 Rapid-Analysis Samples

The screened, rapid-analysis samples will be examined for qualitative impression of the dominant taxa and specific harmful or toxic alga (*i.e.*, *Alexandrium tamarense*, *Phaeocystis* sp., *Pseudo-nitzschia*). Within six days of sample receipt at the counting laboratory, an aliquot of this sample will be qualitatively analyzed using the Sedgwick-Rafter counting cell and viewed through an Olympus BH-2 compound microscope (phase-contract optics) to quickly verify the presence or absence of nuisance species. The analysis will also produce a qualitative impression of the types and abundance of dominant taxa.

### 12.3.16 Zooplankton

Upon return to shore, each sample for zooplankton is transferred to 70% ethanol solution to prevent inhalation of formalin fumes during counting. Samples are reduced to aliquots of at least 300 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. Counts of all copepodite stages of a given copepod genus will be combined. Copepod nauplii will not be identified to genus or species because nauplii species cannot be reliably identified to those levels by using a dissecting microscope. Meroplankters cannot be identified to genus or species in most cases, and such organisms will be identified to the lowest reliable taxon, such as barnacle nauplii, fish eggs, or gastropod veligers.

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.

#### 13.0 SAMPLE CUSTODY

Samples collected in the field will be identified by a unique eight character *Sample ID* which is a concatenation of a five character *Event ID* and a three-character hexadecimal number (*Sample\_Marker*). The *Sample ID* will identify the water collected in the Rosette sampling bottles from a certain depth during a particular station on the specified survey. The five character *Event ID* will be unique to each survey, such as WF041, with "WF" indicating that it is a farfield water column survey, "04" indicating the survey year, and "1" signifying the first survey of the year (for surveys higher than 9, letters are used where A and B are equal to 10 and 11, respectively). The *Sample\_Marker* is a non-repeating (within a survey) number generated by the NavSam® software during the closing of a set of Rosette sampling bottles at one depth or at completion of the vertical net tow.

Each portion of a sample separated for analytical purposes will be assigned a unique *Bottle ID*, composed of the eight–character *Sample ID* plus a 3–character suffix designating the nature and replicate number. For example, "IN2" indicates that the subsample is the second replicate for Dissolved Inorganic Nutrient analyses (see Table 13 for two-letter codes). Information relating to each sub-sample will then be recorded in the *Bottle* table in the EM&MS database.

The scientific crew member operating the data collection system will fill out the station log (Figure 12) at each station. These logs will be put into a survey notebook prior to the survey. The log includes fields for entering pertinent information about each station, such as time on station, bottom depth, weather

PP

RE

RP

SE

SW

TS

WW

ZO

observations, and general comments. During the hydrocast CTD data will be logged and stored electronically on the computer's hard disk. When Rosette sampling bottles are closed, the operator will enter the Group ID and mark an event into the CTD data file and the survey electronic log.

At the end of a profile, sample marker information is joined with the planned bottle table (Table 14) to generate station log label and bottle labels. The bottle label will include the Bottle ID in text and barcode (3 of 9 format), the station, date, time, latitude/longitude, depth for the sample, and analysis code. The data files saved by the software will also be used later as entry into the SAMPLE, STATION, PROFILE, BOTTLE, EVENT, STATION\_TYPE, SAMPLE\_DEPTH\_CLASS and ORDERED\_DEPTH\_CLASS tables of the EM&MS database (see Section 15 for more information).

After all of the samples for a survey are collected, custody forms (Figures 13 and 14) for each type of sample will be generated. Using the custody forms, the samples will be inventoried before the samples are transferred. When the custody of samples is transferred, the custody form will be signed by both the staff member that relinquishes custody and the staff member assuming custody for the samples. The relinquishing staff member will retain a photocopy of the signed chain. After the analysis is completed, the original (signed) chain will be given to the Battelle Laboratory Manager to be placed in the project files.

**Analysis Codes Description** Laboratory AP Primary productivity URI BS Biogenic silica DLS CH Chlorophyll DLS Dissolved oxygen DO Battelle IC Dissolved inorganic carbon URI IN Dissolved inorganic nutrients DLS Total dissolved nitrogen and phosphorous DLS NP OC Dissolved organic carbon DLS PC Particulate carbon and nitrogen DLS

DLS

Battelle

UMD

Battelle UMD

DLS

**UMD** 

UMD

Particulate phosphate

Total suspended solids

Rapid analysis phytoplankton

Screened water phytoplankton

Whole water phytoplankton

Respiration

Zooplankton

Secchi

Table 13. Analysis Codes used in *Bottle ID* 

Table 14. Planned Bottle Table Structure

Field Name	Description
Station ID	Station ID from Tables A1 and A2
Group ID	Group ID based on survey type and sampling depth ( <i>i.e.</i> , F3 is Farfield station sample taken at mid-depth)
Analysis ID	Two-letter analysis code list in Table 13
Rep Number	Replicate number (1 through 6)

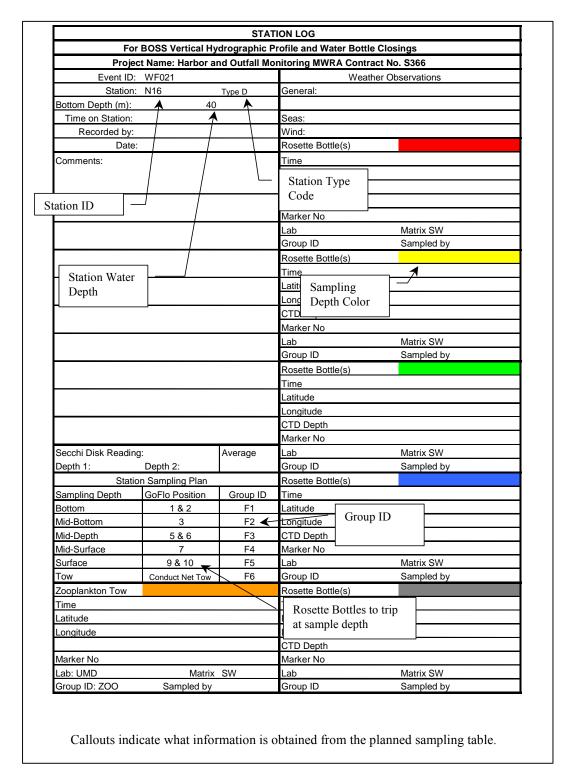


Figure 12. Sample Station Log

MEASUREM	MENT LOG	
For BOS	SS Sample Data C	Collection
Project Name: Harbor and Outfall M	onitoring MWRA	Contract No. S274
Survey ID: WF052	Protocol	
Station: F01		First Secchi Reading
		2. Second Secchi Reading
LABEL HERE		3. Tow Time (mm:ss.ss)
		4. Depth of tow (M)
		5. Formalin added (ml)
	Date:	Recorded by:
Station: F02		First Secchi Reading
		2. Second Secohi Reading
LABEL HERE		3. Tow Time (mm:ss.ss)
		4. Depth of tow (M)
		5. Formalin added (ml)
	Date:	Recorded by:
Station: F03		First Secchi Reading
		2. Second Secchi Reading
LABEL HERE		3. Tow Time (mm:ss,ss)
		4. Depth of tow (M)
		5. Formalin added (ml)
	Date:	Recorded by:
Station: F05		1. First Secchi Reading
		2. Second Secchi Reading
LABEL HERE		3. Tow Time (mm:ss.ss)
		4. Depth of tow (M)
		5. Formalin added (ml)
	Date:	Recorded by:
Station: F06		First Secchi Reading
		2. Second Secchi Reading
LABEL HERE		3. Tow Time (mm:ss.ss)
		4. Depth of tow (M)
		5. Formalin added (ml)
	Date:	Recorded by:

Printed by NavSam

Figure 13. Example of a Zooplankton Custody Form

Labor	190 Tafts Winthrop Mr. Yong 617-660-	o MA	A 02152	
: Sampling Date :	Winthrop Mr. Yong 617-660-	o M <i>A</i> JLao	A 02152	
: Sampling Date :	617-660-			
: Sampling Date :				
	Station ID:	Depth Code:	Ck 1	Ck
4CH1 2/23/2005 8:09:00 AM	BK1			
	F02	E		
ACCH1 2/23/2005 9:27:59 AM	F02	D		Е
	F02	С		E
ADCH2 2/23/2005 9:28:30 AM	F02	С		Ē
AECH1 2/23/2005 9:29:02 AM	F02	В		Ē
AFCH1 2/23/2005 9:29:38 AM	F02	A		
2/23/2005 12:36:45 PM	F01	E		
2/23/2005 12:37:29 PM	F01	D		Ε
2/23/2005 12:38:02 PM	F01	С		
2/23/2005 12:38:02 PM	F01	С		
2/23/2005 12:38:47 PM	F01	В		Ē
2/23/2005 12:39:30 PM	F01	A		
EDCH1 2/23/2005 12:47:08 PM	BK2			
2/26/2005 7:38:44 AM	BK1			Ε
Cold(ice):	F	rozen(dry ice	):	
Cold(ice):			:	
	ABCH1 2/23/2005 9:27:17 AM  AM  AM  AM  ADCH1 2/23/2005 9:27:59 AM  ADCH2 2/23/2005 9:28:30 AM  ADCH2 2/23/2005 9:28:30 AM  ABCH1 2/23/2005 9:29:02 AM  ABCH1 2/23/2005 9:29:02 AM  ABCH1 2/23/2005 9:29:38 AM  BECH1 2/23/2005 12:36:45 PM  BECH1 2/23/2005 12:38:02 PM  BECH1 2/23/2005 12:38:47 PM  BECH1 2/23/2005 12:39:30 PM  BECH1 2/23/2005 12:39:30 PM  BECH1 2/23/2005 12:39:30 PM  BECH1 2/23/2005 12:39:30 PM  BECH1 2/26/2005 7:38:44 AM  COId(ice):	AM  AM  AM  AM  AM  AM  AM  AM  AM  AM	AM  AM  AM  AM  AM  AM  AM  AM  AM  AM	BCH1   2/23/2005 9:27:17

Figure 14. Example of Water Chemistry Custody Form

## 13.1 Custody of Electronic Data

Field custody of electronic data will be the responsibility of the survey chief scientist. The field custody of the electronic data consists of creating floppy disk or compact disc backups of all electronic data generated each day. The label on the backup media will include a survey ID, date, name of person creating the backup files, and a disk number. The data will be transferred to Battelle's EM & ES database upon completion of the survey. The Field Manager or his designee maintains the disks until the annual archive cycle. HOM 4 disks are saved for six years from the time of collection.

Battelle, DLS, URI, and UMD will produce electronic data under this task. At Battelle, the electronic files for dissolved oxygen and respiration data will remain in the custody of the Task Leader (Ms. Jessica Fahey) until all analyses are completed and data have been audited. Two copies of each type of electronic file will be made. Set 1 will remain in custody of the Task Leader in the Task notebook. Set 2 will be transferred the HOM 4 Database Manager for entry into the MWRA database.

Electronic data will remain in the custody of laboratory managers and custodians [Dr. Yong Lao (DLS), Dr. Jefferson Turner (UMD), Dr. Candace Oviatt (URI)] until an independent QA audit has been completed. Once the data have passed the independent laboratory QA audit, three copies of each type of electronic file will be made. Set 1 will remain in the custody of each laboratory custodian and Sets 2 and 3 will be sent to the Battelle. Set 2 will be stored in the Task notebook and Set 3 will be given to the Battelle Database Manager for entry into the MWRA database.

## 13.2 Custody of Water Samples

During field collection, NavSam<sup>©</sup> will create chain forms from the sample table used to generate sample labels, thereby creating a link between the sample and data recorded on the chain form. The chain forms will have the same alphanumeric code as the corresponding label on the sample container, ensuring the tracking of sample location and the status.

The Chief Scientist will retain custody of samples during the survey. He is responsible for verifying each sample ID vs. the custody forms generated by NavSam<sup>©</sup> prior to delivering the samples to the Battelle laboratory. All samples will be delivered to the Battelle Field Sample Custodian who will distribute them to the appropriate laboratory personnel by hand or by Federal Express. All frozen samples will be shipped on dry ice with protective layers of foam or bubble wrap to ensure samples remain intact and frozen during shipment.

Upon receipt of the samples at Battelle or another laboratory, the Sample Custodian will examine the samples, verify that sample-specific information recorded on the chain is accurate and that the sample integrity is uncompromised, log the samples into the laboratory tracking system, complete the custody forms, and sign the chain form so that transfer of custody of the samples is complete. Any discrepancies between sample labels and transmittal forms, and unusual events or deviations from the project CWQAPP will be documented in detail on the chain and the Battelle Field Manager and the Battelle Laboratory Manager will be notified. The Sample Custodian at each laboratory will then sign and keep the original chain forms. Copies of the signed chain will be faxed to the Battelle Field Sample Custodian within 24 hours of receipt. The original chain forms will be submitted to the Battelle Laboratory Manager with the data submission and maintained in the MWRA project files. Sample numbers that include the complete field ID number will be used to track the samples through the laboratory. Alternately, unique laboratory IDs may be assigned by each laboratory for use during their sample analyses, but the data will be reported to the database by using the field-generated sample number.

Samples that have been analyzed and have passed their holding times will be discarded. No samples will be archived.

#### 14.0 CALIBRATION PROCEDURES AND PREVENTIVE MAINTENANCE

Logs of maintenance and repairs of instruments will be stored in the instrument files maintained by Battelle and by each laboratory. Maintenance of and repairs to instruments will be in accordance with manufacturers' manuals. Any deviations to this policy will be noted.

Most equipment used for hydrographic profiles is factory calibrated initially, and returned to the manufacturer for annual recalibration. Calibration records are maintained in the field equipment maintenance and calibration files. Prior to each survey, the NavSam<sup>©</sup> operator is responsible for ensuring that the most recent calibration records with factory offset forms are inserted into the survey log for all primary and back-up equipment. The Chief Scientist is responsible for verifying that the offsets and calibration factors for each piece of equipment have been entered into the data set-up files. The set-up and verification will be documented in the survey logbooks.

The Battelle Instrument History sheet and the factory calibration sheets along with records of periodic checks are maintained in the field equipment files.

## 14.1 Hydrographic Profiling Equipment

### 14.1.1 Pressure (Depth) Sensor

At the beginning of each day of each survey, the software offset of the Ocean Sensors OS200 CTD depth sensor is set to read zero meters 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. After the correction is made, the readings are checked again and should be with  $\pm$ 0.1 m. Although the readings are not recorded, the day-to-day drift is  $\pm$ 0.2 m for the normal range of atmospheric pressure.

## **14.1.2** Temperature and Conductivity

The software gain and offset of the temperature and conductivity sensors (OS200) are calibrated annually at the factory. The factory calibration settings are not changed by Battelle. 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 Ocean Sensors CTD, calibration drifts are approximately 0.018 °C for temperature, 0.042 mS/m for conductivity, 0.055 PSU for salinity, and 0.046 for sigma-*t* per year.

In the event that larger drifts in the salinity measurements are observed, the following additional calibration procedures will be employed. On each water column survey, 6-8 water samples will be collected for salinity measurements. An attempt will be made to collect a range of salinities from different stations and depths (stations and depths with sharp salinity gradients will be avoided). The samples will be transported to the NOAA Narragansett lab where they will be analyzed using a Guildline Autosal Salinometer. If the CTD is found to be more than 0.1 PSU out of calibration, a post-calibration correction will be applied.

### 14.1.3 Altimeter

The Data Sonic PSA-916 altimeter will be sent to the factory annually for a systems check. Records of factory maintenance are kept in an instrument history sheet in the field management files.

## 14.1.4 In Situ Dissolved Oxygen

The software gain and offset of the dissolved oxygen sensors (SeaBird Models 43 and 13) will be calibrated annually at SeaBird. The calibration settings may be changed thereafter using manufacturer software in conjunction with results from Winkler titrations.

The DO values determined by the sensor will be corrected for each survey based on a comparison with discrete water samples analyzed by titration. The DO data from the sensor (based on factory calibration settings) will be entered into a MS Excel spreadsheet along with the corresponding discrete sample titration data ("bottle samples"). Using the built-in linear regression analysis tool, the correction slope and intercept will be determined. The regression will be based on the following equation:

DO conc. (from sensor) = slope x DO conc. (bottle value) + intercept

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

Corrected sensor DO conc. = [DO conc. (from sensor) - intercept]/slope

The significance of F of the regression analysis must be <0.05. If not, the data will be reviewed by the senior scientist to identify non-representative values or outlier pairs that will be removed from the regression and identified in the database with the R qualifier. If the removal of aberrant points does not result in a significant regression, then the calibration is deemed suspect and the *in situ* data are not calibrated.

#### 14.1.5 Transmissometer

The WET Lab C-Star transmissometer is calibrated annually by the manufacturer. 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.

Before each survey the windows of the transmissometer will be rinsed with deionized water and methanol. To check that the transmissometer is working properly, each survey day the blocked and unobstructed readings in air will be observed. Typical blocked readings in air are greater than 40/m and typical unblocked readings in air are less than 0.5/m. Periodically throughout the survey day, the optics of the transmissometer will be rinsed with deionized water and checked for salt residues and cleaned as necessary.

## 14.1.6 In Situ Chlorophyll a Fluorometer

The WETStar fluorometer is sent to the manufacturer for maintenance and recalibration annually. A review of the calibration coefficients for this instrument indicates it is stable from year to year. The factory calibration is based on instrument response in distilled water and a 0.5 mg/L coproporphyrin standard solution (fluorescence signal equivalent to 50 µg/L chlorophyll in a *Thalassiosira weissflogii* phytoplankton culture). The fluorometer data, displayed with the NavSam® program, will approach 0.0 µg/L when the instrument is on deck. The ondeck reading will be checked prior to each survey day. Then, when the CTD is in the water, the reading will again be checked for a reasonable value. Errant readings will instigate corrective action. All errant readings and resultant corrective actions will be noted in the survey logbook. As daily maintenance, the fluorometer will be rinsed with deionized water. During farfield surveys, the instrument will be turned off between stations to prevent flash-lamp degradation. The *in situ* fluorescence readings will be calibrated in the same manner as described for the DO sensor above, using the chlorophyll *a* data measured in the laboratory from discrete bottle samples to develop a linear regression and correction slope and intercept.

The regression will be based on the following equation:

fluorescence (from sensor) = slope x Chl a conc. (bottle value) + intercept

To correct CTD value in the database, use the following equation:

Chl a from fluorometer = (fluorescence (from sensor) – intercept)/slope

The significance F of the regression analysis must be <0.05. If not, the data will be reviewed by a qualified senior scientist to identify non-representative values or outlier pairs that will be removed from the regression and identified in the database with the R qualifier.

## 14.1.7 Irradiance Profiling and On-deck Sensors

The proper conversion factors for the sensor voltages to engineering units are contained on the calibration certificate issued with the instrument, and are updated during factory recalibrations. These records are stored and maintained in the field equipment files.

## 14.1.7.1 QSR-240 (On-deck Irradiance Sensor)

The Biospherical Instruments Solar Reference Scalar Irradiance Sensor (QSR-240) is designed for monitoring total incident radiation in air. It is deployed at the surface as a surface irradiance reference sensor in conjunction with a profiling sensor in water column. When operated together, the QSR-240 sensor measures the sunlight in air to provide the reference ambient irradiance and the QSP-200L underwater sensor measures the sunlight penetrating the water column at depth.

The QSR-240 Sensor is calibrated annually by Biospherical Instruments Inc. In addition, this instrument should be checked every two to three months, depending on the amount of use, by verifying operation on a clear day. Solar irradiance at local noon, measured on a clear day, is typically between 2000 and 3000  $\mu E m^{-2} sec^{-1}$  depending upon the time of year. Any deviation of >40% is strong evidence of a problem. Whenever the instrument's calibration is in question for any reason, the instrument will be returned to Biospherical Instruments for recalibration and examination.

The Teflon collector sphere of the QSR-240 may become dirty during normal use. If any attempt is made to rotate, remove, tighten, push, or pull on the small white sensor ball, the calibration will be ruined and the unit must be sent the manufacturer for repair and recalibration. The sphere may be gently cleaned with soap and warm water, or a solvent such as alcohol, by using a soft tissue or towel. Acids, abrasive cleaners or brushes cannot be used as this will mar the surface of the sphere and void the instrument's calibration. If the sphere becomes damaged or heavily soiled, the instrument will be returned to the manufacturer for service and re-calibration. Maintenance records are maintained in the field equipment files.

The irradiance shield will be kept as clean as possible by periodically wiping with a damp cloth with care to avoid touching the Teflon sphere. A qualified technician will conduct maintenance. Battelle SOP for Biospherical Irradiance Sensors (No. 3-127) provides a complete description of the setup, use, calibration and maintenance of the QSR-240 On-deck Irradiance Sensor.

#### 14.1.7.2 OSP-200L (Underwater Irradiance Sensor)

The Biospherical Instruments Logarithmic Output Oceanographic Light Transducer (QSP-200L) is calibrated annually using a National Institute of Standards and Technology traceable 1000-watt type FEL Standard of Spectral Irradiance. Biospherical Instruments Inc. 5340 Riley Street San Diego, CA. 92110-2621, performs instrument calibration. The Battelle Calibration Results Check Sheet for Biospherical Irradiance Sensor QSP-200L is used to convert factory calibration coefficients to calibration coefficients in units used by the onboard computers. The factory calibration offset is applied to the data to achieve "zero" readings. The operation of the sensor is checked at the beginning of each survey day on deck capped (dark) and against the Biospherical QSR-240 surface irradiance sensor. The values from the QSP-200L sensor should be close to zero for the dark reading and approximately 40-50% higher than the surface irradiance sensor for the uncovered reading on deck. The difference in the readings between the two sensors is caused by field-of-view differences and a correction factor applied to the underwater

sensor to account for its lower collection efficiency when immersed. Calibration data are stored in the field equipment files (initial) or the survey log (daily survey check).

If it is clear that the instrument calibration has drifted over time and the factory calibration is no longer appropriate, deep profile readings could be used to determine a new calibration offset. These values could also be subtracted during data processing to remove any small zero offset remaining after applying the factory calibration coefficients for previous surveys. Following identification of this problem, the sensor will be returned to the manufacturer for maintenance and recalibration.

The Battelle Instrument History sheet and the factory calibration sheets along with records of periodic checks are maintained in the field equipment files.

The QSP-200 will be rinsed with fresh water after use. A qualified technician will conduct maintenance. The protective cap will be installed after the irradiance collector has dried. In addition, the o-rings should be replaced yearly when the instrument is returned to the manufacturer for calibration. Although its casing is robust, the sensor sphere of the underwater sensor is as delicate as that of the surface light sensor.

## **14.1.8** Navigation Equipment

Once the Northstar 952-XDW dGPS Navigation System has been switched on, there is typically no other setup interaction necessary between the NavSam<sup>©</sup> operator and the navigation system. The dGPS will also conduct an automatic self-test. The dGPS will display a latitude-longitude (L/L) position once the system has acquired an acceptable fix. The dGPS system guarantees position accuracy on the order of 2-5 meters 50% of the time, and to 10 meters 95% of the time.

Position calibration checks 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 NavSam<sup>©</sup> program is set to calibration-navigation mode.
- 3. Thirty fixes are obtained by the program, averaged, and then compared to the absolute position entered by the operator.
- 4. If a printer is connected to the system, a printout of the calibration is obtained. Otherwise, the data are manually entered into the first or last station log for that day.

#### **14.1.9** Rosette Sampling Bottles

The Rosette sampling bottles are maintained by conducting annual functional checkouts including replacing worn, damaged components. During the surveys, the bottles are closed between stations. Just before arriving at a station, the bottles are opened and their release cords attached to the Rosette mechanism. The bottles are "cleaned" during the downcast by the flushing of sample water through the bottles. The bottles are closed by the NavSam® operator at appropriate depths during the upcast.

### 14.1.10 Nets and Flowmeter

All nets used for zooplankton and marine debris tows and the flowmeter will be rinsed with fresh water and inspected for damage following each survey. If a flowmeter fails to produce expected results in the field, *i.e.*, readings appear lower than expected after a cast, then it will be replaced before the next survey.

## 14.2 Laboratory Instruments

Calibration procedures for laboratory instruments are summarized in Table 15. All laboratory calibration records will be reviewed by analysis task leaders and maintained in laboratory notebooks.

**Table 15. Calibration Procedures for Laboratory Instruments** 

Parameter Instrument Type			Initial Calibrati	on	Continuing (	Calibration	Corrective Action	
		No. Stds	Acceptance Criteria	Frequency	Acceptance Criteria	Frequency		
Dissolved inorganic nutrients	Skalar Autoanalyzer	4-5	r ≥.995	Prior to analytical run	PD¹ from initial ≤15%	Every 20 samples	Investigate, recalibrate	
Dissolved organic carbon	Tekmar-Dorhmann Apollo 9000 Analyzer	4-5	r ≥ .995	Monthly or if continueing calibration fails	PD from initial ≤15%	Every 20 samples	Investigate, recalibrate	
Total dissolved nitrogen and phosphorus	Skalar Autoanalyzer	4-5	r ≥ .995	Prior to analytical run	PD from true value ≤15%	Every 20 samples	Investigate, recalibrate	
Particulate carbon and nitrogen	Perkin Elmer CHN Elemental Analyzer II	1	NA	Prior to analytical run	PD from initial ≤15%	Every 20 samples	Investigate, recalibrate	
Particulate phosphorus	Skalar Autoanalyzer	4-5	r ≥0.995	Prior to analytical run	PD from initial ≤15%	Every 20 samples	Investigate, recalibrate	
Biogenic silica	Skalar Autoanalyzer	4-5	r ≥ 0.995	Prior to analytical run	PD from initial ≤15%	Every 20 samples	Investigate, recalibrate	
Chlorophyll a and phaeophytin	Sequoia Turner Fluorometer Model 450-003	5	r ≥ 0.995	Annually or if continuing calibration fails	PD from baseline ≤5%	Beginning and end of analysis	Investigate, recalibrate	
Total Suspended Solids (TSS)	Mettler 5- Place Balance	NA	Professionally Calibrated to Agree with NIST traceable Calibration Weights	Annually	PD less than 1% from reference weights	Daily	Professional Service requested for PD over 5%	
Dissolved oxygen and respiration	Radiometer Titralab TM	1	NA	Prior to Analysis for each survey	NA	NA	Investigate, recalibrate	
Dissolved Inorganic Carbon	Total Organic Carbon Analyzer Model 700	4	r ≥ 0.999	Prior to analytical run	PD from Initial ≤15%	Every 20 samples	Investigate, recalibrate	
Primary Production by <sup>14</sup> C	Packard TriCarb Liquid Scintillation Counter Model 2900	3	r ≥ 0.999	Prior to analytical run	PD from Initial ≤2%	Every 20 samples	Investigate, recalibrate	

<sup>&</sup>lt;sup>1</sup>Percent difference

## 15.0 DOCUMENTATION, DATA REDUCTION, AND REPORTING

## 15.1 Data Recording

All data will be initially recorded either (1) electronically onto computer storage media from BOSS or other laboratory systems or (2) manually into bound laboratory notebooks or onto established data forms. All notes will be written in black ink. Corrections to hand-entered data will be initialed, dated, and justified. Corrections to electronically captured data (*e.g.*, electronic "spikes") will be documented on a hard-copy plot of the data. Completed data forms or other types of hand-entered data will be signed and dated by the individual entering the data. Direct-entry and electronic data entries will indicate the person collecting or 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, station logs associated with field and laboratory custody and tracking will be kept in survey notebook for each survey. Contents of survey logbooks are defined in Battelle SOP 6-043. These notebooks will be stored at Battelle under the supervision of the Deputy Project Manager.

#### 15.2 Data Reduction

#### 15.2.1 Hydrographic and Navigation Data

The hydrographic data generated during the survey consists of rapidly sampled, high-resolution measurements of conductivity, temperature, depth, DO, transmissometry, underwater light levels, total incident radiation, and bathymetry. The BOSS data-acquisition software assigns a unique data filename to each vertical profile made during the survey. All data will be electronically logged with date, time, and concurrent vessel-position data. In the field, in real time, Battelle's NavSam® software converts the raw sensor analog signals into engineering units using instrument calibration coefficients. The station arrival time is marked as an event in NavSam® upon arrival at the station.

NavSam<sup>©</sup> records both the raw and calibrated data. During data reduction, NavSam<sup>©</sup>'s post-processing module will be used to 1) offset the *in situ* irradiance data by 0.9 m to account for distance sensor is located above pressure sensor, 2) generate final, calibrated data using laboratory calibration coefficients, and 3) visually review the profiles and mark any data as bad or suspect as appropriate. After the editing is complete, the profile upcast data recorded during discrete water sample collection will be processed. NavSam<sup>©</sup> post-processing will also combine the wet chemistry analytical results with profile data to develop calibrated dissolved oxygen and chlorophyll a profile data (see Sections 14.1.4 and 14.1.6). NavSam<sup>©</sup> post-processing will result in 2 tables. The first will contain the downcast data that excludes the ship's upward motions and is averaged to 0.5-m depth bins. The second table will average the upcast data corresponding to discrete samples (data within +/- 5 seconds of the moment of bottle closing). These files will serve as the export file to the EM&MS database. Project-specific SOP MWRA 001 *Processing and Calibrating CTD Data and Creating Profile Data Files* describes these procedures. Salinity and density are calculated from temperature and conductivity using the equations of Fofonoff and Millard (1980), and dissolved oxygen percent saturation is calculated from dissolved oxygen concentration, temperature, and salinity using the equations of Weiss (1970).

### 15.2.2 Laboratory Data

Data reduction procedures and formulae are defined in laboratory SOPs and in Section 12.0. All data generated by Battelle or another laboratory will be either electronically transferred from the instrument or manually read from the instrument display (or optical field of a microscope) and entered into a loading application or appropriate database formats (see DLS exception below), provided by the Battelle Data Management team. Data in laboratory notebooks will be manually entered into the loading application. All data reduction will be performed electronically either by the instrument software or in a spreadsheet and will be validated according to procedures described in Section 16. The format for final data submission is described below. All laboratory replicates will be reported as mean sample values and all field replicates will be reported as individual sample values.

## 15.3 Reporting Data to be Loaded into the Database

All field and laboratory data to be loaded into the EM&MS will be submitted to Battelle in electronic format. The field data collection will be available for data loading directly off the ship. The laboratories will be supplied a loading application based on collection data that will increase data quality and data flow efficiency. These applications eliminate the need for data reporting formats and deliver many of the

quality control checks upstream to the laboratories. The only exception will be data from DLS, which will be loaded into MWRA EM&MS work tables and submitted to Battelle as a dump file that meets applicable database constraints.

### 15.3.1 Navigation and Sample Collection Data

Navigation and sample collection data will be processed on-board the survey vessel and be ready for loading into EM&MS upon arrival at Battelle. A database application developed as part of the NavSam<sup>©</sup> system will query the on-board database tables for the fields necessary to populate the *Event, Station, Sample* and *Bottle* tables. The data will be loaded into the EM&MS database by clicking a button. All database constraints developed by MWRA will be applied to the tables so that the data are checked during the insert. The loading of sample collection data is detailed in SOP MWRA 001 *Processing and Calibrating CTD Data and Creating Profile Data Files*.

## 15.3.2 Hydrographic Data

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

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

A database application will be used to load the hydrographic data from the processing database directly into the EM&MS database. Table 16 shows the database codes for the hydrographic parameters. Database constraints will be in place to provide an initial check of the data integrity and validity.

Parameter	Param_Code	Unit_Code	Instr_Code	Meth_Code
Conductivity	CONDTVY	mS/cm	CTD1	BOSS
Dissolved Oxygen	DISS_OXYGEN	mg/L	DO1	BOSS
Fluorescence	FLUORESCENCE	μg/L	WETSTAR	BOSS
in situ Irradiance level	LIGHT	μEm-2sec-1	LIG4	BOSS
Water Pressure	PRESSURE	db	CTD1	BOSS
Salinity	SAL	PSU	CTD1	BOSS
Density as measured by sigma-t	SIGMA_T		CTD1	BOSS
Surface irradiance level	SURFACE_IRRAD	μEm-2sec-1	LIG2	BOSS
Temperature	TEMP	С	CTD1	BOSS
Transmissivity	TRANS	m-1	T1R25	BOSS
Percent Saturation, Dissolved Oxygen	PCT_SAT	PCT	DO1	BOSS

**Table 16. Database Codes for Hydrographic Parameters** 

## 15.3.3 Analytical and Experimental Data

The data reporting for analytical and experimental data begins with the Battelle Data Management Team who will populate a loading application that is then sent to each laboratory for their data entry. As defined above, the collection data from field activities are delivered to the data manager as an Access database. Sample Ids and analysis protocols are extracted from this database and used to populate a database within the laboratory loading application. A separate loading application is prepared for each

data deliverable. Data contributors open the database and are presented with a form that already contains the Sample Ids and analyte list for their data submittal (Figure 15). The laboratory enters the results and other supporting information such as qualifiers. All entries are constrained by the rules of EM&MS. Errors are caught on entry and fixed by the data contributor. Primary keys are in place so duplication cannot occur. Entry applications are developed on an individual laboratory basis. Laboratory staff receive one day of training on the application prior to their first set of samples. When data entry is complete, the database is sent back to Battelle. Laboratories with existing data processing capability will be supplied a loading application that can import their final spreadsheet and then run the quality control checks. The laboratory will have to meet their own internal laboratory format for the data to load successfully.

Due to the unique association between Battelle and MWRA DLS and MWRA's familiarity with the format of the database, all DLS data will be submitted electronically as Oracle export files that meet applicable database constraints. Please see Leo *et al.* (2004) for details.

The loading application provides the laboratory many available functions (Figure 16), including hardcopy report, quality control checks, exception report, and analysis summary. The hardcopy report function allows the laboratory to create a hardcopy report to check for entry errors and to submit a final report to Battelle with the data deliverable. The quality control checks are comprised of the applicable sections of EM&MS check and constraints scripts and also checks for outliers. This report gives the data contributor a chance to confirm the reasonableness of their data prior to submission to Battelle. The exception report checks the data that were expected against the results loaded. The data contributor must account for any entries in the exception report. The analysis report produces a report of the number of analyses by analyte. A copy of this report is included with the data deliverable and with the invoice for the analyses.

Within the loading application, the data entered by the laboratory is translated into the correct codes and inserted into database tables with the same structure as the matching EM&MS table. Table 17 shows the qualifiers to be used by the laboratory. Database codes for plankton taxonomy and species qualifiers are presented in Tables 18 and 19, respectively. Table 20 shows the analytical parameters, codes, and units of measure for the analytes collected under this task. Additional database codes are described in Table 21. The laboratory will have the ability to add additional codes to describe their results but the new qualifiers will be highlighted in the exception report. Battelle will notify MWRA concerning the new qualifier and will adjust the code table in the application to agree with any changes to the EM&MS code list table. MWRA has the responsibility for maintaining the code list for the EM&MS. A laboratory submission is not accepted as complete unless it includes the QA statement, QA/QC corrective action log, electronic data, hardcopy data report, exceptions report, and analysis summary. Processing of laboratory data is further described in MWRA SOP 004, *Loading and Reporting Water Column Data*.

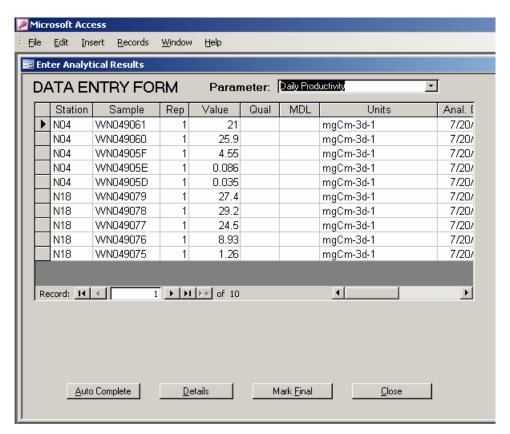


Figure 15. Example of Loading Application Data Entry Form

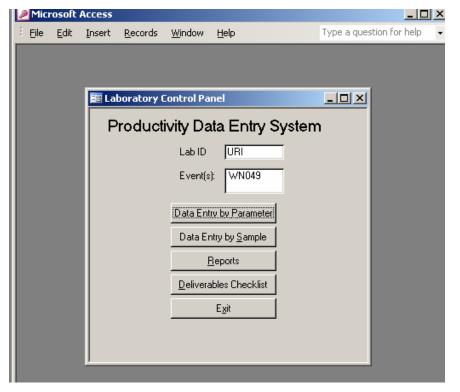


Figure 16. Loading Application Main Menu

**Table 17. Laboratory Qualifiers** 

Qualifier	Description	Value Reported?
	Value is not qualified	yes
A	Value above maximum detection limit, e.g. too numerous to count or beyond range of instrument	yes
a	Not detected - value reported as negative or null	No, may be a negative
b	Not blank corrected, blank ≥5x MDL	yes
c	Ambient	yes
d	Accuracy does not meet data quality objectives	yes
Е	Calibration level exceeded	yes
e	Results not reported, value given is NULL, see comments field	no
f	Value reported <mdl< td=""><td>yes</td></mdl<>	yes
g	Recovery outside DQO	yes
h	Reported value is extrapolated beyond the standard curve	yes
j	Estimated value	yes
L	Analytical concentration reported from dilution	yes
1	Dark bottle	yes
m	Initial	yes
n	Light bottle	yes
0	Value out of normal range judged fit for use by principal investigator	yes
P	Present but uncountable, value given is NULL	yes
p	Lab sample bottles mislabeled - caution data use	yes
q	Possibly suspect/invalid and not fit for use. Investigation pending.	Yes
R	Outlier data point not used in calibration regression	Yes
r	Precision does not meet data quality objectives	Yes
S	Suspect/Invalid. Not fit for use	Yes
Т	Holding time exceeded	Yes
V	Arithmetic mean	Yes
W	This datum should be used with caution, see comment field	Yes

Table 18. Database Codes for Plankton Taxonomy

Plankton Analysis	Unit_Code	Meth_Code	Biomass_Unit_ Code	Anal_Lab_ID
Whole-Water Phytoplankton	E6CELLS/L	COU_WW	ug/L	UMD
Screened Phytoplankton	CELLS/L	SCR20U	ug/L	UMD
Zooplankton	ind/m3	COU_ZO	ug/L	UMD

Table 19. Database Codes for Species Qualifiers

Qualifier	Description
В	Cyst
С	Copepodites
F	Female
L	Larvae
M	Male
N	Nauplii
О	Ova
S	Spores
T	Trochophore
V	Veliger
Y	Cyprids
Z	Zoea
null	No value, used as a place holder for a key field

Table 20. Database Codes for Chemistry Analytical and Experimental Parameters

Parameter	Param_Code	Unit_Code	Anal_Lab_ID	Instr_Code	Meth_Code
Chlorophyll a	CHLA	ug/L	DIL	FLU6	CHLASWFLU
Dissolved Oxygen	DISS_OXYGEN	mg/L	BOS	RTL	OUD88
Net Respiration	Respiration	uM/hr	BOS	RTL	SP1972
Total Suspended Solids (TSS)	TSS	mg/L	DIL	METLR	TSS-SWGRV
Phaeophytin	PHAE	ug/L	DIL	FLU6	PHAESWFLU
Biogenic Silica	BIOSI	uM	DIL	SKALAR	BSI-SWAAN
Dissolved Organic Carbon	DOC	uM	DIL	TDA9000	DOC-SWCIR
Particulate Organic Carbon	POC	uM	DIL	PECHNII	PC-SWCHN
Particulate Organic Nitrogen	PON	uM	DIL	PECHNII	PN-SWCHN
Total Dissolved Nitrogen	TDN	uM	DIL	SKALAR	TDN-SWAAN
Total Dissolved Phosphorus	TDP	uM	DIL	SKALAR	TDP-SWAAN
Ammonium	NH4	uM	DIL	SKALAR	NH3-SWAAN
Nitrite	NO2	uM	DIL	SKALAR	NO2-SWAAN
Nitrate	NO3	uM	DIL	SKALAR	NO3-SWAAN
Particulate Phosphorus	PARTP	uM	DIL	SKALAR	PP-SWOXA
Phosphate	PO4	uM	DIL	SKALAR	PO4-SWAAN
Silicate	SIO4	uM	DIL	SKALAR	SI04SWAAN
Areal Production	AREAL_PROD	mgCm-2d-1	URI	PTLSC2900	LIBBY02
Daily Production	DAILY_PROD	mgCm-3d-1	URI	PTLSC2900	LIBBY02
Maximum for P/I Curve	Pmax	mgCm-3h-1	URI	PTLSC2900	LIBBY02
Alpha parameter for productivity curve	Alpha	ALPHA	URI	PTLSC2900	LIBBY02
Beta parameter for productivity curve	Beta	ALPHA	URI	PTLSC2900	LIBBY02
Hourly Production	HOURLY PROD	mgCm-3h-1	URI	PTLSC2900	LIBBY02
Incubation Time	MWRA63	hours	URI	NA	NA
Temperature	TEMP	С	URI	NA	NA
Light Exposure	MWRA53	uEm-2sec-1	URI	NA	NA
Depth-average chlorophyll- specific primary production	PROD_CHLA_Z	mgC(mg Chla)-1d-1	URI	PTLSC2900	LIBBY02
Potential Areal Productivity	AREAL PROD POT	mgCm-2d-1	URI	PTLSC2900	LIBBY02
Depth-averaged chlorophyll-specific	PROD_POT_CHLA_Z	mgC(mg Chla)-1d-1	URI	PTLSC2900	LIBBY02
potential primary production	DAHA BROD BOT	0 211	LIDI	DTI 002000	I IDDX/02
Potential Daily Productivity	DAILY_PROD_POT	mgCm-3d-1	URI	PTLSC2900	
R-Squared parameter for	PROD_R2	NA	URI	PTLSC2900	LIBBY02
non-linear curve fit of productivity vs. irradiance					
Incubation point for a two-	INCUB POINT	NA	URI	NA	NA
point incubation (initial or final)	INCOD_IOINI	INA	OKI	INA	INA

NA: Not applicable

**Table 21. Description of Database Codes** 

Field_Name	Code	Description
ANAL LAB ID	BOS	Battelle Ocean Sciences, Duxbury, MA
	DIL	MWRA Dept of Lab Services Central Lab
ANAL LAB ID	UMD	University of Massachusetts, Dartmouth, MA
ANAL_LAB_ID	URI	University of Rhode Island, Narragansett, RI
INSTR_CODE	CTD1	OS-200 CTD
INSTR_CODE	DO1	Seabird DO Probe (Beckman/YSI)
INSTR_CODE	FLU6	Turner Designs Model 450-003 Fluorometer
INSTR_CODE	LIG2	Biospherical model QSR-240 hemispherical scalar irradiance sensor
INSTR_CODE	LIG4	Biospherical Instruments QSP-200L: quantum scalar irradiance profiling sensor
INSTR_CODE	METLR	Mettler Model H-6 pan balance (0.1 mg)
INSTR_CODE	PECHNII	Perkin Elmer CHN Elemental Analyzer II
INSTR_CODE	PTLSC2900	Packard TriCarb Liquid Scintillation Counter Model 2900
INSTR_CODE	RTL	Radiometer TitraLab Titrator
INSTR_CODE	SKALAR	Skalar autotitrator
INSTR_CODE	TDA9000	Tekmar-Dorhmann Apollo 9000 Carbon Analyzer
INSTR_CODE	T1R25	WET Labs C-Star 25cm transmissometer 660 nm fixed wavelength
INSTR_CODE	WETSTAR	WET Labs WETStar chlorophyll a fluorometer
METH_CODE	1168	Organic carbon by combustion with infrared detection, DLS SOP 1168
METH_CODE	BSI-SWAAN	Biogenic silica-seawater-Autoanalyzer
METH_CODE	BOSS	Battelle Ocean Sampling System
METH_CODE METH_CODE	CHLASWFLU COU WW	Chlorophyll a-sea water-fluorometric
	_	Enumeration method for whole-water phytoplankton (Libby et al. 2002)
METH_CODE	COU_ZO	Enumeration method for zooplankton (Libby et al. 2002)
METH_CODE	DOC-SWCIR	Dissolved Organic Carbon-seawater-Combustion Infrared  Productivity solvulated as in Libburg at al. 2002 CWOARD for water quality manifestings 2002 2005.
METH_CODE METH_CODE	LIBBY02	Productivity calculated as in Libby <i>et al.</i> 2002 CWQAPP for water quality monitoring: 2002-2005  Seawater Autoanalyzer method for ammonium
METH_CODE	NH3-SWAAN NO2-SWAAN	EPA 354.1 nitrite-seawater Autoanalyzer
METH_CODE	NO3-SWAAN	Nitrate in seawater by autoanalyzer
METH_CODE	OUD88	Oudot et al. (1988)
METH_CODE	PCSWCHN	Particulate carbon-seawater-CHN analyzer
METH_CODE	PHAESWFLU	Phaeophytin-sea water-fluorometric
METH_CODE	PNSWCHN	Particulate nitrogen-seawater-CHN analyzer
METH_CODE	PO4-SWAAN	Seawater Autoanalyzer method for phosphate
METH CODE	PPSWOXA	Auto Analyzer method with oxidation step
METH CODE	SCR20U	Large dinoflag. screening technique 20 microns
METH CODE	SIO4SWAAN	Silicate in seawater by autoanalyzer
METH CODE	SP1972	Strickland and Parsons (1972)
METH CODE	TDN-SWAAN	Total dissolved nitrogen-seawater-Autoanalyzer
METH_CODE	TDP-SWAAN	Total dissolved phosphorus-seawater-Autoanalyzer
METH_CODE	TSS-SWGRV	Seawater gravimetric analysis for TSS
UNIT_CODE	ALPHA	mgCm-3h-1uE-1m2s
UNIT_CODE	С	Degrees Celsius
UNIT_CODE	CELLS/L	Cells per liter
UNIT_CODE	db	Decibars
UNIT_CODE	E6CELLS/L	Millions of cells per liter
UNIT_CODE	Hours	Hours
UNIT_CODE	ind/m3	Individuals per cubic meter
UNIT_CODE	m-1	Inverse meters
UNIT_CODE	mg/L	Milligrams per liter
UNIT_CODE	mgCm-2d-1	Milligrams of carbon per square meter per day
UNIT_CODE	mgCm-3d-1	Milligrams of carbon per cubic meter per day
UNIT_CODE	mgCm-3h-1	Milligrams of carbon per cubic meter per hour
UNIT_CODE	mmhos/cm	Millimhos per centimeter
UNIT_CODE	PSU	Practical salinity units
UNIT_CODE	uEm-2sec-1	Micro-Einsteins per square meter per second
UNIT_CODE	ug/L	Micrograms per liter
UNIT_CODE	uM	Micromoles per liter
UNIT_CODE	uM/hr	Micromoles per liter per hour
UNIT_CODE	m C(ma Chla) 1d 1	Meters Millioners of earlier par millioners of chlorophyll a par day
UNIT_CODE	mgC(mg Chla)-1d-1	Milligrams of carbon per milligram of chlorophyll a per day
UNIT_CODE	mS/cm	Millisiemens per centimeter
UNIT_CODE	PCT	Percent

# 15.4 Loading Analytical and Experimental Data into the Harbor Studies Database

Data submissions from the laboratories are the final loading applications or the export for DLS data. The submissions are logged in upon receipt and a copy is maintained on file under the login id. Data are loaded into a temporary table space by a button on the application. A transfer script will copy the data into the proper table in Battelle's copy of the EM&MS. Data from the laboratories receive a quality assurance review after the data has been synthesized into a data report. Any issues are corrected in the database and the well-documented script that is available to MWRA upon request. The MWRA check script will be run on the database prior to export of a dataset to ensure that all data conform to quality control checks and database constraints. Project-specific SOP MWRA 004 *Loading and Reporting Water Column Data* describes these procedures.

# 15.5 Reporting Data to MWRA

The data contained in each hard copy data report are submitted to MWRA as a database export. The supporting documentation files are included with the data submission. Data deliverables will be combined only with permission from MWRA.

# 15.6 Threshold Testing

One of the requirements of the discharge permit is to test the current environmental conditions against baseline conditions to detect any noticeable changes. These thresholds are identified in the Contingency Plan (MWRA 2001). Under Task 30 of the HOM4 contract, Battelle will review all the survey summaries, survey reports, and data reports for comparison the monitoring thresholds. SQL scripts provided by MWRA will be run on data to determine if the relevant monitoring thresholds (*e.g.*, seasonal chlorophyll) may have been exceeded. Since the data will not yet have been delivered to, checked and accepted by MWRA, results of tests that exceed a threshold value will be referred to as potential exceedances. If the test indicates potential for caution threshold exceedance, Battelle will notify MWRA's Project Manager via phone or email regarding the results of the review. If the test indicates potential for exceedance of a warning level, Battelle will notify relevant Consultant team members and accelerate confirmation of the validity of the results.

A letter report detailing activities under Task 30 will be prepared quarterly. Battelle's requirement under HOM4 in regard to threshold testing is to:

- Maintain threshold, threshold\_baseline and threshold\_test tables in the local copy of EM&MS
- Import new threshold and threshold baseline tables if MWRA makes changes
- Maintain current version of threshold test scripts as provided by MWRA
- Run current version of threshold test script on newly loaded data as appropriate
- Maintain a record of all threshold runs in local copy of threshold test table
- Report running of threshold tests in a quarterly letter report
- Report results of threshold tests in data reports
- Advise MWRA of potential exceedance of threshold values

The documentation for each threshold test is maintained by MWRA in a series of SOPs. The SOP(s) pertinent to this CWQAPP are found in Appendix D.

#### 16.0 DATA VALIDATION

The data validation procedures for this project are defined in the HOM 4 Quality Management Plan. As a part of data validation, each Task Leader ensures that:

- Any data that are hand-entered (*i.e.*, typed) are validated by qualified personnel prior to use in calculations or entry into the database.
- All manual calculations are performed by a second staff member to verify that calculations are accurate and appropriate. For data submitted from DLS, only 20% of manual calculations are verified by a second staff member.
- Calculations performed by software are verified at a frequency sufficient to ensure that the
  formulas are correct, appropriate, and consistent, and that calculations are accurately reported.
  All modifications to data reduction algorithms are verified prior to submission of data to MWRA.
- Electronic data loading and transfer are swift and routine; data fields and formats are defined in the CWQAPPs. Electronic submissions are loaded to temporary files prior to incorporation into the database, and are analyzed selectively using methods such as scatter plots, univariate and multivariate analyses, and range checks to identify suspect values. Routine system back-ups are performed daily.
- Once data have been generated and compiled in the laboratory, senior project scientists review data to identify and make professional judgments about any suspicious values. All suspect data are reported with a qualifier and appropriate comment. These data may not be used in calculations or data summaries without the review and approval of a knowledgeable Senior Scientist. No data measurements are eliminated from the reported data or database and data gaps are never filled based on other existing data. If samples are lost during shipment or analysis, it is documented in the data reports to MWRA and noted in the database.
- Final data reports are reviewed by the water column senior scientist, Mr. Scott Libby, prior to submission to MWRA.

#### 17.0 PERFORMANCE AND SYSTEM AUDITS

The Battelle QA Officer for the Harbor and Outfall Monitoring Project is Ms. Rosanna Buhl. She will direct the conduct of at least one systems audit to ensure that Tasks 9-15 are carried out in accordance with this CWQAPP. A systems audit will verify the implementation of the Quality Management Plan and this CWQAPP for the work conducted in the Water Quality monitoring.

Tabular 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. Errors noted in data audits will be communicated to analysts and corrected data will be verified.

Audits of the data collection procedures at each of the laboratories will be the responsibility of the laboratories. Each laboratory is fully responsible for the QA of the data it submits. Data must be submitted in CWQAPP-prescribed formats; no other will be acceptable. During the time that work is in progress, an inspection will be conducted by each laboratory QA Officer or their designee to evaluate the laboratory data-production process. All data must be reviewed by each laboratory QA Officer prior to submission to the Battelle Database Manager and must be accompanied by a signed QA statement that describes the types of audits and reviews conducted and any outstanding issues that could affect data quality and a QC narrative of activities.

The Battelle QA Officer will conduct an initiation audit and, as needed, a laboratory inspection to access compliance with the Quality Management Plan and this CWQAPP. Performance audits, procedures used to determine quantitatively the accuracy of the total measurement system or its components, will be the responsibility of each laboratory and may include internal performance evaluation samples and participation in external certification programs.

#### 18.0 CORRECTIVE ACTION

All technical personnel share responsibility for identifying and resolving problems encountered in the routine performance of their duties. Ms. Ellen Baptiste-Carpenter, 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. She 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 CWQAPP, or (4) require consultation with Battelle management or with MWRA. Dr. Carlton Hunt is the Battelle Technical Director and is responsible for ensuring that data collection and interpretation are scientifically defensible, and for responding to technical challenges as they arise.

Identification of problems and corrective action at the laboratory level (such as meeting data quality requirements) will be resolved by laboratory staff or by laboratory managers (see Figure 5). Issues that affect schedule, cost, or performance of the water-column monitoring tasks will be reported to the Task Leader or to the Battelle Project Manager. Battelle's Technical Director will be notified of any issues affecting data quality. The Technical Director and Task Leaders will be responsible for addressing these issues and, with the Project Manager, will be responsible for evaluating the overall impact of the problem on the project and for discussing corrective actions with the MWRA Project Management. Problems identified by the QA Officer will be reported and corrected as described in Section 17.0.

#### 19.0 REPORTS

Water column surveys (Tasks 9 and 10), *in situ* data processing (Task 6), data loading and quality assurance (Tasks 5 and 7), results from moorings and meteorology and remote sensing (Tasks 12 and 13), and sample analysis (Tasks 14 and 15) are reported to MWRA in formats defined in the HOM 4 contract. Tasks 9 and 10 will be reported in survey reports while task 14 and 15 will be reported in data reports as described in Sections 19.1.3 and 19.2 below, respectively. Data synthesis reports (Task 33) are described in Section 19.3.

Survey-related deliverables that will be generated under this CWQAPP include:

- 24 Survey Plans (one for each of the Nearfield water column surveys; farfield surveys plans will be combined with the Nearfield Plans)
- 24 Survey Reports (one for each of the Nearfield water column surveys; farfield surveys reports will be combined with the Nearfield Reports)
- 24 Rapid Phytoplankton Email Reports
- 24 Email Survey Summaries
- 8 Nutrient Data and Respiration/Productivity Data Reports
- 8 Phytoplankton Data and Zooplankton Data Reports
- 4 Moorings and Meteorology (Task 12) and 4 Remote Sensing (Task 13) Letter Reports

All survey plans and reports will be submitted annually on CD after final acceptance by MWRA. Hard copy data reports will be submitted with an accompanying PDF file. Final synthesis reports will be submitted as electronic word processing documents and PDF files (containing all appendices).

#### 19.1 Survey-Related Reports

For each nearfield survey, one survey plan, one survey email, and one survey report will be prepared. For combined nearfield and farfield surveys, these documents will also be combined. A total of 24 nearfield and combined nearfield/farfield surveys will be reported as described below.

#### 19.1.1 Survey Plans

Survey plans will be prepared for each survey conducted. In the case of combined surveys, a single plan covering all aspects the combined surveys will be submitted to MWRA. Each survey plan will follow Battelle SOP 6-043 *Preparation, Distribution, and Implementations of Field Survey Plans* that is based on the guidelines established by U.S. Environmental Protection Agency for use of the OSV *Anderson*. Each survey plan will be submitted as a final unbound, double side copy on 3-hole paper at least one week prior to the start of the survey and will include the following information:

- Purpose, background, and data use for survey
- Schedule of operations
- Specific location and coordinates of each station
- Survey/sampling methods
- Sample Handling and Custody
- Sequence of Tasks and Events
- Navigation and positioning control
- Vessel, equipment, and supplies
- QA/QC Procedures
- Documentation procedures
- Scientific party
- Reporting requirements
- Safety Procedures
- Documentation of any deviations from this CWQAPP

# 19.1.2 Survey Email Summary

A survey summary will be delivered to MWRA via Email within 1 week of completion of each survey. This Email will include a summary of the survey operational dates, weather conditions, stations not sampled and reason, summary of preliminary water quality observations, deviations from survey scope, results of the rapid phytoplankton analysis, observations from marine mammal sightings, and identify technical problems encountered and resolutions. These summaries will also include photo documentation of the two marine debris tows, and if available, satellite images of chlorophyll distribution from the day of the survey to make a comparison to the *in situ* observations. This summary will also highlight any potential exceedance of monitoring thresholds, or conditions, which, if continued, might lead to exceedances.

#### 19.1.3 Survey Reports

Survey reports will describe the survey conducted, stations occupied, measurements made, samples collected, problems experienced, and general observations from *in situ* sensor data, and summarize observations made by the certified whale observer. Unusual observations of environmental conditions, especially those with implications for the later testing of Contingency Plan thresholds, will be emphasized. Survey reports are expected to be 4-5 pages of text with accompanying station maps and a complete sample collection table generated directly from the Battelle HOM4 database. The sample collection table will be a tabular summary of stations occupied, station locations, and samples collected. Any deviations from this CWQAPP, not known at the time of survey plan preparation, will also be incorporated into the survey reports. One unbound, double-sided, 3-hole punched copy of the draft survey report will be submitted to MWRA no later than two weeks after the completion of each survey. MWRA's comments on the report will be due to Battelle two weeks after receipt of the draft report. The final survey report, addressing MWRA's comments, will be due to MWRA 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.

# 19.2 Data Reports

Four Nutrient, four Respiration/Productivity, and four Plankton data reports will be submitted to MWRA per year. Each report is final. The data reports are formatted to provide a user-friendly view of the data. The data reports are created directly from the Battelle version of the EM&MS. One unbound, double sided, 3-hole punched copy of the data report will be submitted according to the report schedule defined in Table 6. The format and the content of the data report are reviewed with the MWRA technical task leader prior to the submission of the first set. All subsequent reports are submitted in this format.

Data reporting and loading procedures for the water column data are documented in SOP MWRA 004. Water Column data reports will be submitted to MWRA in both hard-copy and electronic forms (PDF file and database export). Included will be all sample collection information summarized from the Survey Reports from each sampling event. Data will be presented in tables containing the results of all individual sample analyses. QC checks of the data will also be included in the data reports in graphical format. The QC checks for the water column analysis data reports are described in Table 22.

#### 19.2.1 Nutrient Data Reports

Each Nutrient Data Report will contain tabular summaries of concentrations of all nutrient species measured, chlorophyll *a*, DO, and TSS for each bottle sampled and analyzed. The report will also include hydrographic data (salinity, temperature, DO, chlorophyll fluorescence, optical beam transmittance, light irradiance, and sensor altitude above the seafloor), Secchi disk depth, surface irradiance data from Deer Island, and results of QC checks.

#### 19.2.2 Respiration/Productivity Data Reports

Each Respiration/Production Data Report will include a tabular summaries of water-column respiration rates, primary production calculations including the  $P_{max}$  and P(I) analyses will be provided for each sample depth or profile measured, and results of QC checks.

#### 19.2.3 Plankton Data Reports

Each Plankton Data Report will contain tabular summaries of phytoplankton and zooplankton counts and identifications and results of QC checks.

## 19.2.4 Sensor Data Processing (Task 6) Letter

A summary of the sensor data processing accomplished each month will be included with the monthly progress report. The summary will document sensor processing completed each month including any problems encountered and a list of sensor data provided to the database administrator.

Table 22. Data Report Quality Control Checks - Water Quality Area

#### General:

A tabular summary of the following will be included with each data report:

Planned analyses against actual number of analyses

List of missing samples

Individual station depth against expected depth at station MDW depth based on Geo station table

Count of samples with non-detectable results by variable

Number of null values by variable

	Type of Quality Control Check											
Parameter	Plot <sup>1</sup>	Range check <sup>2</sup>										
<i>In situ</i> profile data	1) Comparison of down and upcast (discrete depth) values at depth of upcast sampling events to see if they are within 10%. If not flag for scientists review.	Each variable										
Dissolved Nutrients	<ol> <li>Parameter vs. depth plots (NH<sub>4</sub>, NO<sub>2</sub>+NO<sub>3</sub>, PO<sub>4</sub>, SiO<sub>4</sub>, TDN, TDP and DOC) – plot per parameter per survey including all stations. All plots for one parameter per page.</li> <li>NO<sub>2</sub>+NO<sub>3</sub> vs. SiO<sub>4</sub> including previously accepted data from the data report interval</li> <li>NH<sub>4</sub> vs. PO<sub>4</sub> including previously accepted data from the data report interval</li> <li>TDN vs. TDP including previously accepted data from the data report interval</li> </ol>	Each variable										
Particulate nutrients	Parameter vs. depth plots (POC, PON, and PartP) – plot per parameter per survey including all stations. All plots for one parameter per page     PON vs. POC against Redfield ratio and previously accepted data from the data report interval     PartP vs. PON against Redfield ratio and previously accepted data from the data report interval	Each variable										
Total suspended solids	1) TSS vs. depth plot – one plot per survey including all stations. All plots on one page T	ΓSS										
Chlorophyll Phaeophytin Florescence	<ol> <li>Parameter vs. depth plots (calibrated <i>in situ</i> fluorescence<sup>3</sup>, Chla extracted, and Phaeo) plot per parameter per survey including all stations. All plots for one parameter per page</li> <li><i>In situ</i> fluorescence versus Chla scatter plot against previously accepted data</li> <li>POC versus Chla scatter plot against previously accepted data</li> </ol>	Each variable										
Dissolved Oxygen and %Sat	1) Paramter vs. depth plot (calibrated <i>in situ</i> DO concentration and %saturation) <sup>3</sup> – one plot per survey including all stations. All plots for one parameter per page	Each variable										
Biogenic Si	1) BSI vs. depth plot – one plot per survey including all stations. All plots on one page	BSI										
Respiration	None	Respiration Rate										
Primary Productivity		Each calculated variable										
Phytoplankton	to	Fotal count and otal by major group										
Zooplankton	to	Fotal count and otal by major group										

<sup>&</sup>lt;sup>1</sup> For each data period being reported

<sup>&</sup>lt;sup>2</sup> Range check against highest and lowest value by sample from baseline period or all previously accepted data. Flag samples outside of this range for more detailed review by senior scientist

<sup>&</sup>lt;sup>3</sup> In situ data from discrete sampling depths only

## 19.2.5 Moorings and Meteorology (Task 12) and Remote Sensing (Task13) Reporting

The results of the mooring, meteorology are reported in letter format, twice annually, in April for the January –June surveys and in November for the July- December surveys.

# 19.3 Synthesis Reports

The data delivered above will be used in synthesis reports prepared under Task 33.2 (Periodic Water Column Reports), Task 33.3 (Annual Water Column Reports), and Task 33.10 (Nutrient Issues Reviews). A detailed outline of each of the above synthesis reports will be prepared for MWRA approval. Following approval, a draft report will be prepared and submitted to MWRA. MWRA comments on each report will be provided to Battelle within 4 weeks of report receipt. Final reports, addressing MWRA comments, will be due to MWRA within two weeks of comment receipt.

#### 19.3.1 Periodic Water Column Reports

These twice-annual periodic water column reports chronicle the basic results from Task 6, and Tasks 9 through 15. The report will present meteorological, oceanographic, chemical, and biological conditions over a 6-month period. The semi-annual water quality reports provide summaries of patterns in the water column data, highlight unusual events of the period, and relate the information to the caution and warning thresholds of the Contingency Plan as appropriate. Any potential exceedances of these thresholds will be summarized in this report.

The Periodic Water Column Reports will subscribe to the outline shown below. Standardized graphic presentations supporting the discussions will be included:

- Executive Summary (including summary of any thresholds exceeded)
- Introduction (program overview, report purpose, report organization)
- Methods (References the water column CWQAPP, describes methodological changes, and scope deviations).
- Data Summary (Chronological table of summary data for each water column survey performed during the reporting period. Data from Tasks 12, 13, 26 and 28 will be summarized in this section.)
- Water Column Results. (Includes a brief discussion of the water column results and characteristics to introduce the section)
- Physical characteristics (standardized graphics of nutrient, chlorophyll a, and DO by survey)
- Nutrients
- Chlorophyll *a*
- Dissolved oxygen.
- Results Summary (brief discussion of primary productivity, respiration, and plankton data).
- Primary Production (Description of the spatial and temporal characteristics of areal, chlorophyll specific and potential primary production)
- Respiration (description of water column respiration)
- Phytoplankton (Seasonal trends in abundance, nearfield community structure, regional assemblages, nuisance algae)
- Zooplankton (Seasonal trends in abundance, nearfield community structure, regional assemblages)
- Major events (Summary of any major spatial-, temporal-, or regional-scale events, major deviations from the baseline conditions, and summary of data with respect to thresholds).

- References (list of all references cited)
- Appendices (Additional graphics from the various surveys, including individual station profile plots, photosynthesis-irradiance curves, and other routine figures and graphs that convey the basic results of the measurements made on the water column surveys. Format after content of Libby *et al.* (2003)

#### 19.3.2 Annual Water Column Report

The annual water quality report will synthesize results from water column monitoring activities for each calendar year. It will describe the status of the ecosystem, including annual and seasonal patterns. The annual report will provide statistical descriptions of critical parameters and evaluate critical interactions among biological, physical, and chemical factors. The report also will include summaries of annual minimums and maximums (identified according to time and location), frequency distributions, seasonal, and annual averages as appropriate to the monitoring caution and threshold values. The annual report will focus on assessing the status of the ecosystem in comparison to baseline monitoring results and the caution and warning thresholds. Should any exceedances of the relevant monitoring thresholds be observed, Battelle will summarize any assessment of the likely cause conducted by MWRA (supported by Battelle as requested) and whether the cause can be attributed to the outfall.

Each annual water column report will address the following areas:

- Executive Summary (including summary of any thresholds exceeded and possible factors responsible)
- Introduction (program overview, report purpose and organization, summary of baseline results)
- Data Sources and Overview of each Years' Program
- Environmental Setting: Physical Oceanography and Meteorology (Temperature cycle, Salinity, Water Column Stratification, Water Mass Source and Movement, Rainfall, Light cycle)
- Nutrients (Annual cycle in the Nearfield and in Massachusetts Bay and Cape Cod Bay)
- Chlorophyll (Nearfield. Regional and Inter-annual Comparisons)
- Dissolved Oxygen (Annual cycle in the Nearfield and in Massachusetts Bay and Cape Cod Bay, seasonal decline in bottom waters of the Nearfield and Stellwagen Basin)
- Productivity and Respiration (Seasonal and Annual Production, chlorophyll specific measures of production, Water column respiration)
- Plankton (Abundance and seasonal succession, regional comparisons, Inter-annual comparisons, and algal nuisance species
- Overview of Annual Results (Integration and Synthesis)
- References

#### 19.3.3 Nutrient Issues Review

This report draws from a variety of reports and data to evaluate the potential for response related to relocation of the MWRA outfall and associated nutrients in Massachusetts and Cape Cod Bays. Topics may vary as information and data gaps are identified.

#### 19.3.4 Outfall Monitoring Overview

This report will summarize key findings of the ambient monitoring program including any special studies and threshold violations. The report will be written toward the general public, regulators, and interested scientists.

#### 20.0 REFERENCES

- Albro CS, Kelly J, Hennessy J, Doering P, Turner J. 1993. Combined Work/Quality Assurance Project Plan (CWQAPP) for Baseline Water Quality Monitoring: 1993-1994. MWRA Environmental Quality Technical Report No. ms-14. Massachusetts Water Resources Authority, Boston, MA. 73 pp.
- Albro CS, Trulli HK, Boyle JD, Sauchuk S, Oviatt CA, Keller A, Zimmerman C, Turner J, Borkman D, Tucker J. 1998. Combined Work/Quality Assurance Plan for Baseline Water Quality Monitoring: 1998-2000. MWRA ENQUAD Technical Report ms-48, Massachusetts Water Resources Authority, Boston MA. 123 pp.
- Albro CS, Trulli HK, Boyle JD, Sauchuk S, Oviatt CA, Keller A, Zimmerman C, Turner J, Borkman D, Tucker J. 2002 (in prep). Combined work/quality assurance plan for baseline water quality monitoring: 1998-2001 Revision 1. Boston: Massachusetts Water Resources Authority. Report ENQUAD ms-48. 123 pp.
- Arar, E.J., and G.B. Collins. 1992. *In Vitro* Determination of Chlorophyll *a* and Phaeophytin *a* in Marine and Freshwater Phytoplankton by Fluorescence. Method 445.0 Version 1.1 (November 1992). U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Office of Research and Development, Cincinnati, OH.
- Battelle. 2002. Project Management Plan for Professional Services on Harbor and Outfall Monitoring Project (Contract 366). Massachusetts Water Resources Authority Environmental Quality Department, Boston, MA 29 pp + apps.
- Bendschneider, K., and R.J. Robinson. 1952. A New Spectrophotometric Determination of Nitrite in Seawater. *J. Mar. Res.* 11:87-96.
- Borkman, D. 1994. Phytoplankton and Nutrients in Buzzards Bay, Massachusetts 1987-1988. M.S. Thesis. University of Massachusetts Dartmouth, Dartmouth, MA. 203 pp.
- Borkman, D., R.W. Pierce, and J.T. Turner. 1993. Dinoflagellate blooms in Buzzards Bay, Massachusetts. Pp. 211-216 in Smayda, T.J., and Y. Shimizu (Eds.), *Proceedings of the Fifth International Conference on Toxic Marine Phytoplankton*, Elsevier.
- Bowen JD, Zavistoski RA, Cibik SJ, Loder T. 1998. Combined Work/Quality Assurance Project Plan (CWQAPP) for Water Quality Monitoring: 1995-1997. MWRA Enviro. Quality Dept. Misc. Rpt No. ms-45. Massachusetts Water Resources Authority, Boston, MA.
- Brewer, P.G., and J.P. Riley. 1966. The Automatic Determination of Silicate Silicon in Natural Waters with Special Reference to Seawater. *Anal. Chim. Acta.* 35:514-519.
- D'Elia, C.F., E.E. Connor, N.L. Kaumeyer, C.W. Keefe, K.V. Wood, and C.F. Zimmermann. 1997. Nutrient Analytical Services Laboratory: Standard Operating Procedures. Technical Report Series No. 158-97. May 1997. Chesapeake Biological Laboratory Center for Environmental Science, Solomons, MD. 77 pp.
- EPA 600/R-97-072 Methods for the Determination of Chemical Substances in Marine and Estuarine Environmental Matrices. 2nd edition. September 1997. (NSCEP or NTIS /PB97-127326 or <a href="http://www.epa.gov/nerlcwww/ordmeth.htm">http://www.epa.gov/nerlcwww/ordmeth.htm</a>)

- Fofonoff, N.P., and R.C. Millard, Jr. 1983. Algorithms for Computation of Fundamental Properties of Seawater. *UNESCO Technical Papers in Mar. Sci.* 44.
- Guillard, R.R.L. 1973. Division rates. Pages 289-311 In: J.R. Stein, (Ed.) *Phycological Methods*. Cambridge Univ. Press.
- Hasle, G.R. 1959. A Qualitative Study of Phytoplankton from the Equatorial Pacific. *Deep Sea Res.* 6:38-59
- Iriarte and G. Fryxell. 1995. Micro-Phytoplankton at the Equatorial Pacific (140° W) during the JGOFS EqPac Time Series studies: March to April and October 1992. *Deep Sea Res.* II 42 (2-3): 559-583.
- Lewis, M.R. and J.C. Smith. 1983. A small volume, short-incubation-time method for measurement of photosynthesis as a function of incident irradiance. *Mar. Ecol. Progr. Ser.* 13:99-102.
- Libby PS, Keller AA, Turner JT, Borkman D, Oviatt CA, Mongin CJ. 2003. Semiannual Water Column Monitoring Report: February June. Boston: Massachusetts Water Resources Authority. Report ENQUAD 2003-14. p. 392.
- Libby PS, Gagnon C, Albro C, Mickelson M, Keller A, Borkman D, Turner J, Oviatt CA. 2002. Combined work/quality assurance plan for baseline water quality monitoring: 2002-2005. Boston: Massachusetts Water Resources Authority. Report ENQUAD ms-074. 79 p.
- Menzel, D.W., and R.F. Vaccaro. 1964. The Measurement of Dissolved Organic and Particulate Carbon in Seawater. *Limnol. Oceanogr.* 9:138-142.
- Morris, A.W., and J.P. Riley. 1963. The Determination of Nitrate in Seawater. *Anal. Chim. Acta.* 29:272-279.
- Murphy, J., and J.P. Riley. 1962. A Modified Single Solution Method for the Determination of Phosphate in Natural Waters. *Anal. Chim. Acta*. 27:31-36.
- MWRA. 1990. G.L.C. 30 Section 61. Revised Final Findings by the Massachusetts Water Resources Authority on the Secondary Treatment Facilities Plan/EIR for Boston Harbor, Massachusetts Executive Office of Environmental Affairs File Number 6136. Boston, MA.
- MWRA. 1991. Massachusetts Water Resources Authority Effluent Outfall Monitoring Plan Phase I: Baseline Studies. MWRA Environmental Quality Department, November 1991. Massachusetts Water Resources Authority, Boston, MA. 95 pp.
- MWRA. 1997. Massachusetts Water Resources Authority Effluent Outfall Monitoring Plan: Phase 2 post-discharge outfall monitoring. December 1997. MWRA Enviro. Quality Dept. Misc. Rpt. ms-44. Massachusetts Water Resources Authority, Boston, MA.
- MWRA. 2001. Massachusetts Water Resources Authority Contingency Plan Revision 1. Boston: Massachusetts Water Resources Authority. Report ENQUAD ms-071. 47 p.
- MWRA. 2003. Briefing for OMSAP workshop on ambient monitoring revisions: June 18-19, 2003. Boston: Massachusetts Water Resources Authority. Report ENQUAD ms-085. 250 p.

- MWRA. 2004. Massachusetts Water Resources Authority effluent outfall ambient monitoring plan Revision 1 March, 2004. Boston: Massachusetts Water Resources Authority. Report ENQUAD ms-092. 65 p.
- NRC. 1990. *Managing Troubled Waters: The Role of Marine Monitoring*. National Research Council. National Academy Press, Washington, DC. 125 pp.
- Oudot, C., R. Gerard, and P. Morin. 1988. Precise Shipboard Determination of Dissolved Oxygen (Winkler Procedure) for Productivity Studies with a Commercial System. *Limnol. Oceanogr.* 33:146-150.
- Oviatt, C. A. and K. M. Hindle, 1994. Manual of Biological and Geochemical Techniques in Coastal Areas. MERL Series, Report No. 1. Third Edition. The University of Rhode Island, Kingston, Rhode Island. Marine Technical Report No. 85. 281 pp.
- Paasche, E. 1973. Silicon and the Ecology of Marine Plankton Diatoms *Thalassiosira pseudonana* (*Cyclotella nana*) Grown in Chemostat with Silicate as the Limiting Nutrient. *Mar. Biol.* 19:117-126.
- Pederson, J. 1992. Letters to Susan F. Tierney and Julie Belaga Recommending Approval of Monitoring Plan, Dated March 9, 1992. Also, Letter from Susan Tierney to Douglas MacDonald Urging Support of Monitoring Plan. dated March 19, 1992.
- Platt, T., C.L. Gallegos, and W.G. Harrison. 1980. Photoinhibition of Photosynthesis and Light for Natural Assemblages of Coastal Marine Phytoplankton. *J. Mar. Res.* 38:687-701.
- Price, N.M., and P.J. Harrison. 1987. Comparison of Methods for the Analysis of Dissolved Urea in Seawater. *Marine Biology* 94:307-317.
- Rahmatullah, M. and T.R.C. Boyde, 1980. An improvement in determination of urea using diacetyl-monoxime method with and without deproteinization. Clinica Chemica Acta. 107:3-9.
- SAS. 1988. SAS Procedures Guide, release 6.03 ed. SAS Institute, Inc., Cary, NC.
- Solorzano, L. 1969. Determination of Ammonia in Natural Waters by the Phenol Hypochlorite Method. *Limnol. Oceanogr.* 14:799-801.
- Solorzano, L., and J.H. Sharp. 1980. Determination of Total Dissolved Phosphorus and Particulate Phosphorus in Natural Waters. *Limnol. Oceanogr.* 25:758-760.
- Strickland, J.D.H., and T.R. Parsons. 1972. A Practical Handbook of Seawater Analysis. *Fish. Res. Board Can. Bull.* 167:310.
- Sugimura, Y. and Y. Suzuki. 1988. A High Temperature Catalytic Oxidation Method for the Determination of Non-Volatile Dissolved Organic Carbon in Seawater by Direct Injection of a Liquid Sample. Mar. Chem. 24:105-131.
- Sukhanova, I.N. 1978. *Phytoplankton Manual*. Monographs on Oceanographic Methodology, 6th Edition. A. Sournia (Ed.). UNESCO, Paris. (especially sections 2.1, 5.1, 5.2, 7.1.1, 7.1.2, and 7.2.2).
- Turner, J.T., D.G. Borkman, and R.W. Pierce. 1995. Should Red Tide Dinoflagellates be Sampled Using Techniques for Microzooplankton Rather than Phytoplankton? Pp. 737-742 in P. Lassus *et al.* (Eds.), Harmful Marine Algal Blooms, Lavoisier, Paris, France.

- Valderrama, J.C. 1981. The Simultaneous Analysis of Total Nitrogen and Total Phosphorus in Natural Waters. *Mar. Chem.* 10:109-122.
- Webb, W.L., M. Newron, and D. Starr. 1974. Carbon Dioxide Exchange of *Alnus rubra*: a Mathematical Model. *Oecologica* 17:281-291.
- Weiss, R.F. 1970. The Solubility of Nitrogen, Oxygen, and Argon in Water and Seawater. *Deep-Sea Res.* 17:721-735.
- Werme C, Hunt C. 2004. 2003 Outfall monitoring overview. Boston: Massachusetts Water Resources Authority. Report ENQUAD 2004-13. 97 p.

# **Appendix A**

Nearfield and Farfield Sample Collection Requirements

Table A-1. Nearfield Water Column Sampling Plan. Dissolved Oxygen Quality Assurance Samples will be Collected at the First and Last DO Calibration Station of Each Day.

Note				N	bar	fio	ΙЧ М	/at	or C	ىلى	ımı	2	an	nnl	inc	ı DI	an					
				IN	cai	116	iu V	val	CI C	UIL	41111	1 3	all		1116	J [7]	all	1	I	I		
	StationID	Depth (m)	Station Type	Depths	Total Volume at Depth (L)	Number of 9-L GoFlos	Dissolved Inorganic Nutrients	Dissolved Organic	Total Dissolved Nitrogen and Phosphorous	Particulate Organic Carbon and Nitrogen	Particulate Phosphorous	Biogenic silica	Chlorophyll a	Total Suspended Solids	Dissolved Oxygen	Rapid Analysis Phytoplankton	Whole Water Phytoplankton	Screened Water Phytoplankton	Zooplankton	Respiration	Photosynthesis by carbon-14	Dissolved Inorganic Carbon
				Pro	tocol (	Code	IN	ОС	NP	PC	PP	BS	СН	TS	DO	RP	WW	SW	ZO	RE	AP	IC
Not   State   Montage							1											4			1	1
Not   30   A   3   3   3   3   4   4   Mid-Surface   2   2   1   1   2   2   2   2   1   1				1_Bottom	8.5	2	1	1	1	2	2	2	1	1	3							
				2_Mid-Bottom	2.5	1	1						1		1							
Solution	N01	30			10	2	2	1	1	2	2	2	2	2	1							
Note   1						1	1						1		1							
Not   So				5_Surface	8.5	2	1	1	1	2	2	2	1	1	3							
Note   N				1_Bottom	15.5	2	1	1	1	2	2	2	1	1						6	1	1
Record   R													1		1						1	
NOT   P   S. Surface   20.6   2   1   1   1   2   2   2   1   1   1	N04	50				2	2	1	1	2	2	2	2	1			1	1		6	1	1
													1		1						1	
NOT   STATE					20.6	2	1	1	1	2	2	2	1	1			1	1_		6	1	1
NOT 52 A 3 Mid-Depth 10 2 2 2 1 1 1 2 2 2 2 1 1 1 1 3																			1			
NOT								1	1	2	2	2		1								
A_Mid-Surface																						
	N07	52						1	1	2	2	2		1								
N10																						
N10 25 A 3_Mid-Depth																						
N10								1	1	2	2	2		1								
Marting	N14.0	0.5																				
S   Surface	N10	25						1	1	2	2	2		2								
N16   40   A   3   Mid-Depth   10.2   2   2   2   2   2   2   2   2   1   1								1	1	2	2	2		1								
N16   40   A   3   Mid-Depth   10.2   2   2   2   2   2   2   2   2   2					_				_				_									
N16 40 A 3 Mid-Depth 10.2 2 2 2 2 2 2 2 1 1 1				_				1	-						_							
	N16	40	Δ	_				2	2	2	2	2		1								
Solution	1410	70																				
1							1_	1	1	2	2	2		1								
D+ 2_Mid-Bottom							1					_								6	1	1
N18   30   R+   2   3   Mid-Depth   26.1   3   1   1   1   2   2   2   2   1   1   1			D+			-	-						$\overline{}$		1							
P 4_Mid-Surface	N18	30			_			1	1	2	2	2		1		1	1	1		6		
5_Surface 20.6 2 1 1 1 1 2 2 2 1 1 1 1 1 1 6 1 1 1 6 1 1 1 6 1 1 1 6 6 1 1 1 6 6 1 1 1 6 6 6 1 1 1 6 6 6 1 1 1 6 6 6 1															1							
Totals								1	1	2	2	2		1			1	1		6		
N20   32   A   3   Mid-Depth   10   2   2   1   1   1   2   2   2   1   1																			1			
N20   32   A   3   Mid-Depth   10   2   2   1   1   1   2   2   2   1   1				1_Bottom	8.5	2	1	1	1	2	2	2	1	1	1							
N20 32 A 3_Mid-Depth 10 2 2 1 1 2 2 2 1 1 1							1						1		1							
4_Mid-Surface     2.5     1 <td>N20</td> <td>32</td> <td></td> <td></td> <td></td> <td></td> <td></td> <td>1</td> <td>1</td> <td>2</td> <td>2</td> <td>2</td> <td>2</td> <td>1</td> <td>1</td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td>	N20	32						1	1	2	2	2	2	1	1							
Totals 41 22 22 42 42 42 23 37 1 4 4 2 36 10 10					2.5	1	1						1		1							
				5_Surface	8.5	2	1	1	1	2	2	2	1	1	1							
Blanks A 1 1 1 1 1 1 1					Totals	3	41	22	22	42	42	42	42	23	37	1	4	4	2	36	10	10
	Blank	s A								1	1	1	1	1								

Table A-2. Farfield Water Column Sampling Plan (3 Pages). Dissolved Oxygen Quality Assurance Samples will be Collected at the First and Last DO Calibration Station of Each Day.

	Farfield Water Column Sampling Plan																				
StationID	Depth (m)	Station Type	Depths	Fotal Volume at Depth (L)	Number of 9-L GoFlos	d rients		ved	_		<i>-</i>	Chlorophyll a	Total Suspended Solids	Dissolved Oxygen	Secchi Disk Readina	er	Screened Water Phytoplankton	Zooplankton	Respiration	Photosynthesis by carbon-14	Dissolved Inorganic Carbon
		Ö	D	tocol																	
			Pro	Volum		IN 1	OC 0.1	NP 0.1	PC 1	PP 0.3	BS 0.3	0.5	TS 1	DO 1	SE 0	WW 1	SW 4	ZO 1	RE 1	AP 1	IC 1
			1_Bottom	7.9	2	1	1	1	2	2	2	1	1	3					-		
			2_Mid-Bottom	2.5	1	1						1		1							
F01	27	D	3_Mid-Depth	14	2	1	1	1	2	2	2	2	1	1		1	1				
			4_Mid-Surface	2.5	1	1						1		1							
			5_Surface	13	2	1	1	1	2	2	2	1	1	3	1	1	1	4			
-			6_Net Tow	7.0	2	4	4	4	2	2	2	4	4	4				1			
			1_Bottom 2_Mid-Bottom	<b>7.9</b> 2.5	2	1	1	1	2	2	2	1	1	1							
F02	33	D	3_Mid-Depth	15	2	2	1	1	2	2	2	2	2	1		1	1				
			4_Mid-Surface	2.5	1	1						1		1							
			5_Surface	13	2	1	1	1	2	2	2	1	1	1	1	1	1				
			6_Net Tow															1			
			1_Bottom	1	1	1															
F00	47	_	2_Mid-Bottom	1	1	1															
F03	17		3_Mid-Depth 4_Mid-Surface	1	1	1															
			5_Surface	1	1	1									1						
-			1 Bottom	1	1	1															
			2_Mid-Bottom	1	1	1															
F05	18	Е	3_Mid-Depth	1	1	1															
			4_Mid-Surface	1	1	1															
			5_Surface	1	1	1									1						
			1_Bottom	7.9	2	1	1	1	2	2	2	1	1	3							
<b>500</b>	0.5	_	2_Mid-Bottom	2.5	1	1						1		1							
F06	35	D	3_Mid-Depth 4_Mid-Surface	15 2.5	2	1	1	1	2	2	2	1	1	1		1	1				
			5_Surface	13	2	1	1	1	2	2	2	1	1	3	1	1	1				
			6_Net Tow	10	_							Ė			Ė			1			
			1_Bottom	1	1	1															
			2_Mid-Bottom	1	1	1															
F07	54	Е	3_Mid-Depth	1	1	1															
			4_Mid-Surface	1	1	1															
<u> </u>			5_Surface	1	1	1									1						
1			1_Bottom 2_Mid-Bottom	1	1	1															
F10	30	Е	3_Mid-Bottom	1	1	1															
10	30		4_Mid-Surface	1	1	1															
1			5_Surface	1	1	1									1						
			1_Bottom	4	1	1								1							
			2_Mid-Bottom	2	1	1								1							
F12	90		3_Mid-Depth	2	1	1								1							
			4_Mid-Surface	2	1	1								1							
<u> </u>			5_Surface	4	1	1								1	1						
-			1_Bottom 2_Mid-Bottom	7.9	2	1	1	1	2	2	2	1	1	1							
F13	25	D	2_Mid-Bottom 3_Mid-Depth	2.5 15	2	2	1	1	2	2	2	2	1	1		1	1				
1 13	20		4_Mid-Surface	2.5	1	1						1		1							
ı	1	L	IIIIa - Galilage											<u> </u>							

	Farfield Water Column Sampling Plan																				
StationID	Depth (m)	Station Type	Depths	Total Volume at Depth (L)	Number of 9-L GoFlos	Dissolved Increase Nutrients	Dissolved Organic	Total Dissolved	Particulate Organic Carbon	Particulate Phosphorous	Biogenic silica	Chlorophyll a	Total Suspended Solids	Dissolved Oxygen	Secchi Disk Reading	Whole Water Phytoplankton	Screened Water Phytoplankton	Zooplankton	Respiration	Photosynthesis by	Dissolved Inorganic Carbon
				otocol		IN	ОС	NP	РС	PP	BS	СН	TS	DO	SE	WW	SW	ZO	RE	AP	IC
			5_Surface 6_Net Tow	13	2	1	1	1	2	2	2	1	1	1	1	1	1	1			
			1_Bottom	1	1	1															
			2_Mid-Bottom	1	1	1															
F14	20	Е	3_Mid-Depth	1	1	1															
			4_Mid-Surface	1	1	1															
			5_Surface	1	1	1									1						
			1_Bottom 2_Mid-Bottom	1	1	1															
F15	39	Е	3_Mid-Depth	1	1	1															
			4_Mid-Surface	1	1	1															
			5_Surface	1	1	1									1						
			1_Bottom	1	1	1															
F16	60	Е	2_Mid-Bottom 3_Mid-Depth	1	1	1															
1 10	00	_	4_Mid-Surface	1	1	1															
			5_Surface	1	1	1									1						
			1_Bottom	1	1	1															
			2_Mid-Bottom	1	1	1															
F17	78	E	3_Mid-Depth	1	1	1															
			4_Mid-Surface 5_Surface	1	1	1									1						
			1 Bottom	1	1	1									_						
			2_Mid-Bottom	1	1	1															
F18	24	Е	3_Mid-Depth	1	1	1															
			4_Mid-Surface	1	1	1															
			5_Surface	1	1	1									1						
			1_Bottom 2 Mid-Bottom	<b>7</b>	2	1	1	1	2	2	2	1	1	1					6		
F19	81	Α	3_Mid-Depth	7	2	1	1	1	2	2	2	2	2	<u> </u>					6		
0		+R	4_Mid-Surface	2	1	1						1		1							
			5_Surface	7	2	1	1	1	2	2	2	1	1		1				6		
			1_Bottom	7.9	2	1	1	1	2	2	2	1	1	3							
F00	00		2_Mid-Bottom	2.5	1	1						1		1							
F22	80	D	3_Mid-Depth 4_Mid-Surface	14 2.5	1	1	1	1	2	2	2	1	1	1		1	1				
			5_Surface	13	2	1	1	1	2	2	2	1	1	3	1	1	1				
			6_Net Tow															1			
			1_Bottom	18	3	1	1	1	2	2	2	1	1						6	1	1
F6.5			2_Mid-Bottom	8.5	1	1						1		1						1	2
F23	25		3_Mid-Depth 4_Mid-Surface	24	3	1	1	1	2	2	2	2	1	1		1	1		6	1	1
		+12	5_Surface	<b>7.5</b> 23	3	1	1	1	2	2	2	1	1		1	1	1		6	1	1
			6_Net Tow															1			
			1_Bottom	7.9	2	1	1	1	2	2	2	1	1	3							
1			2_Mid-Bottom	2.5	1	1						1		1							
F24	20	D	3_Mid-Depth	14	2	1	1	1	2	2	2	2	1	1		1	1				
			4_Mid-Surface 5_Surface	2.5	1 2	1	4	1	2	2	2	1	1	3	1	1	1				
			5_Surrace 6_Net Tow	13	2	1	1		2		2			3	1	1		1			
			1_Bottom	9.9	2	1	1	1	2	2	2	1	1	1							
			2_Mid-Bottom	2.5	1	1						1		1							

			Fa	rfie	ld \	<b>N</b> a	ter	Со	lur	nn	Sa	mp	lin	g F	lar	)					
StationID	Depth (m)	Station Type	Depths	Total Volume at Depth (L)	Number of 9-L GoFlos	d rients		ved	_		_	Chlorophyll a	Total Suspended Solids		Secchi Disk Reading	re C	Screened Water Phytoplankton	Zooplankton	Respiration	Photosynthesis by carbon-14	Dissolved Inorganic Carbon
			Pro	otocol	Code	IN	OC	NP	PC	PP	BS	СН	TS	DO	SE	WW	SW	ZO	RE	AP	IC
F25	15	D	3_Mid-Depth	15	2	2	1	1	2	2	2	2	1	1		1	1				
			4_Mid-Surface	2.5	1	1						1		1							
			5_Surface 6_Net Tow	15	2	1	1	1	2	2	2	1	1	3	1	1	1	1			
			1_Bottom	7.9	2	1	1	1	2	2	2	1	1	1				'			
			2_Mid-Bottom	2.5	1	1	•	·		_	_	1		1							
F26	56	D	3_Mid-Depth	15	2	1	1	1	2	2	2	2	1	1		1	1				
			4_Mid-Surface	2.5	1	1						1		1							
			5_Surface 6_Net Tow	13	2	1	1	1	2	2	2	1	1	1	1	1	1	1			
			1_Bottom	7.9	2	1	1	1	2	2	2	1	1	1							
			2_Mid-Bottom	2.5	1	1	·					1		1							
F27	108	D	3_Mid-Depth	15	2	2	1	1	2	2	2	2	1	1		1	1				
			4_Mid-Surface	2.5	1	1						1		1							
			5_Surface 6_Net Tow	13	2	1	1	1	2	2	2	1	1	1	1	1	1	1			
			1_Bottom	1	1	1															
			2_Mid-Bottom	1	1	1															
F28	33	Е	3_Mid-Depth	1	1	1															
			4_Mid-Surface	1	1	1															
			5_Surface	1	1	1									1						
			1_Bottom 2_Mid-Bottom	2	1	1								1							
F29	66	F	3_Mid-Depth	2	1	1								1							
			4_Mid-Surface	2	1	1								1							
			5_Surface	2	1	1								1	1						
			1_Bottom 3_Mid-Depth	9.9	2	1	1	1	2	2	2	1	1	3		4	4				
F30	15	G	5_Surface	14 15	2	1	1	1	2	2	2	1	1	3	1	1	1				
. 00			6_Net Tow														Ė	1			
			1_Bottom	9.9	2	1	1	1	2	2	2	1	1	3							
			3_Mid-Depth	14	2	1	1	1	2	2	2	2	1	1		1	1				
F31	15	G	5_Surface 6_Net Tow	15	2	1	1	1	2	2	2	1	1	3	1	1	1	1			
F32	30	Z	5_Surface												1			ı ı			
. 02		_	6_Net Tow															1			
F33	30	Z	5_Surface												1						
			6_Net Tow															1			
			1_Bottom	8.1	2	1	1	1	2	2	2	1	1	1							
N16	40	D	2_Mid-Bottom 3_Mid-Depth	2.5 15	1	1	2	2	2	2	2	1	1	1		1	1				
410	+0	, U	4_Mid-Surface	2.5	1	1			_		_	1		1							
			5_Surface	13	2	1	1	1	2	2	2	1	1	1	1	1	1				
			6_Net Tow															1			
			D		otals	133	43	43	84		84	80	44	96	28	26	26	15	36	5	6
			Blanks B						1			1	1								
			Blanks C						1		1	1	1								
			Blanks D						1	1	1	1	1								

# **Appendix B**

Right Whale Guidance Protocol for Vessels Operated/Contracted by the Commonwealth of Massachusetts (21 November 1997)

# Guidance Protocol on the Interaction with Whales Specifically Northern Right Whales for Vessels Operated/Contracted by the Commonwealth of Massachusetts

#### Introduction

The northern right whale is the most endangered large whale in the world. In the western north Atlantic the population is estimated to be about 300 animals. Massachusetts coastal waters are part of the range of the northern right whale and Cape Cod Bay has been designated a critical habitat for the whale under the federal Endangered Species Act because of its high use by the species in the late winter and early spring for feeding. The Great South Channel, east of Cape Cod, has also been designated critical habitat because of its importance to the right whale as a feeding area. It has been determined that the most significant human induced causes of mortality are ship strike and entanglements in fishing gear.

#### **Purpose**

The purpose of this protocol is to give guidance to the vessels owned by the Commonwealth and those operating under contract to the Commonwealth as to proper operational procedures if the vessels should encounter whales - *i.e.*, sighting and reporting procedures, and entanglement and carcass reporting protocol.

#### **Applicability**

This protocol will apply to all vessels owned by the Commonwealth of Massachusetts and/or contracted out by the Commonwealth of Massachusetts.

# **Geographic Scope/Operational Scope**

This protocol applies to all applicable vessels operating in or adjacent to Commonwealth waters. When vessels are operating in the designated critical habitat areas (Cape Cod Bay or the Great South Channel) heightened operation is applicable, especially during the late winter and spring when the right whales are expected to be located in these areas.

#### **Sightings of Right Whales**

The Executive Office of Environmental Affairs and the National Marine Fisheries Service is interested in receiving reports from individuals who observe right whales during vessel operations. Reports should be made to the National Marine Fisheries Service Clearinghouse. Patricia Gerrior, NMFS Right Whale Early Warning System Coordinator, who manages the Clearinghouse and her numbers are 508-495-2264 (work), 508-495-2393 (fax) and pager 508-585-8473. Please report your name, agency and phone numbers at which you can be contacted. The vessel's name, the date, time and location of the sighting, the numbers of whales sighted and any other comments that may be of importance. If a camera or video camera is available please take some photographs. These photographs should be provided to Pat Gerrior or Dan McKiernan, Massachusetts Division of Marine Fisheries. They will in turn send copies to the New England Aquarium for comparison to the Right Whale Photo Identification Catalog. Please remember that Massachusetts has Right Whale Conservation Regulations (322 CMR 12:00) which establishes a 500 yard buffer zone surrounding a right whale. Vessels shall depart immediately from any buffer zone created by the surfacing of a right whale.

#### Physical Contact with a Whale

If a vessel owned by the Commonwealth of Massachusetts or under contract with the Commonwealth of Massachusetts comes into physical contact with any whale it should be noted in the vessel's logbook. The vessel's logbook should include the time and location of the incident; weather and sea conditions; vessel speed; the species of whale struck if known; the nature of any injures to crew, and/or the whale, and/or damage to the vessel. Also record the name of any other vessels in the area that may have witnessed the incident or can provide information about circumstances. A copy of the vessel's log for the entire trip should be submitted to the Director of the Division of Marine Fisheries, the Director of the Division of Law Enforcement, the Secretary of Environmental Affairs and the National Marine Fisheries Service, Northeast Region in Gloucester.

If after hitting the whale, the animal is incapacitated or appears to have life threatening injuries and the vessel is safe and secure, immediately call the Center for Coastal Studies, entanglement hotline at 800-900-3622 or via their pager at 508-803-0204 and the Massachusetts Environmental Police Communications Center at 800-632-8075 or 617-727-6398. Stay with the whale until the Coast Guard or Center for Coastal Studies arrives on scene.

#### **Entanglements**

If the vessel come upon or entangles a right whale immediately notify the Center for Coastal Studies' entanglement hotline at 800-900-3622 or via their pager at 508-803-0204 and the Massachusetts Environmental Police Communications Center at 800-632-8075 or 617-727-6398. Do not attempt to remove any debris from the whale, stay on station with the whale or follow at a safe distance. As relocating an entangled whale can be extremely difficult, staying on station or following the animal is very important. However, if following the whale is not possible contact, the Coast Guard and/or the Center for Coastal Studies and note the last direction the animal was heading and any other pertinent information that would assist in relocating the whale.

#### **Stranded Whales**

For a stranded right whale please notify the Stranding Network immediately call Connie Merigo or Howard Krum, New England Aquarium, Central Wharf, Boston, MA 02110. The standing Network's hotline is 617-973-5247 (pager) or as a second resort call 617-973-5246/6551.

## **QUICK REFERENCE**

# **Sightings & Photographs**

Patricia Gerrior, NMFS Right Whale Early Warning System Coordinator, manages the Clearinghouse and her numbers are 508-495-2264 (work), 508-495-2393 (fax) and pager 508-585-8473

# **Photographs**

Dan McKiernan, Massachusetts Division of Marine Fisheries, 19th Floor, 100 Cambridge Street, Boston, MA 02202. 617-727-3193 ext. 369.

#### **Entanglements or Injured whales**

Center for Coastal Studies, entanglement hotline at 800-900-3622 or pager at 508-803-0204

Massachusetts Environmental Police Communications Center at 800-632-8075 or 617-727-6398.

#### **Stranded Animals**

The standing Network's hotline is 617-973-5247 (pager) or as a second resort call 617-973-5246/6551.

# Appendix C Productivity Incubation Apparatus

# Photosynthetrons – <sup>14</sup>C Productivity Incubators

The small volume/short time incubations for primary production are conducted by URI in a photosynthetron, which is a 51 x 57 x 18 cm chamber constructed out of PVC sheets, and divided in half into two trays Figure C-1. Each PVC tray (24 x 49 cm) has sixty 2-cm diameter holes, which can hold 20-ml borosilicate scintillation vials. The bottom of the chamber is composed of Lexan plastic, which in addition to being transparent is also scratch resistant and can withstand the high temperatures produced by the lights. The light source is provided by two 250 Watt Hubbell brand lamps (120 volts/2.6 amps) equipped with 250 W metal halide light bulbs (Philips), which is located 8 cm below the incubation chambers. The light intensity in each hole was measured and then basic house screening and neutral density screening with various degrees of transparency are used to adjust light intensity for each vial hole. An example of the light field for one incubation station and depth (16 light levels) is as follows (values in  $\mu E m^{-2} s^{-1}$ ):

1960	569	224	54
1485	356	152	40
855	297	96	17
677	250	77	5

There is a flow-through water system connected to each half of the photosynthetron to maintain desired water temperatures (Figure C-2). Each half receives water from one of two temperature control systems (bath and circulator Model 2067 obtained from Fisher) that regulate the temperatures. The setup enables simultaneous incubations to take place when temperatures in the water column are stratified. Additional tubing and valves can be used to switch between the warm and cold water bathes. The objective is to incubate the samples at  $\pm 2^{\circ}$ C of *in situ* temperature, but as mentioned in Section 12.3.12, the system may not be able to reproduce the range of *in situ* temperatures that occur and a temperature correction will be applied.

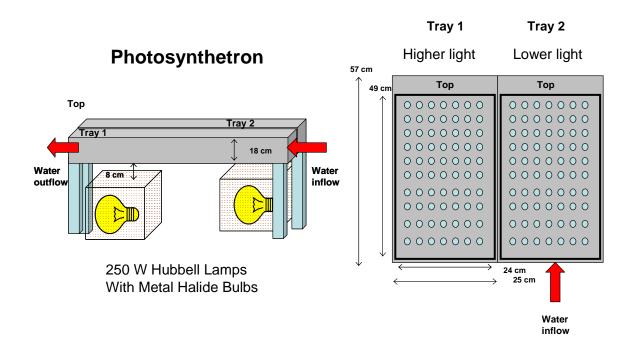


Figure C-1. Layout of Photosynthetron trays and light source.

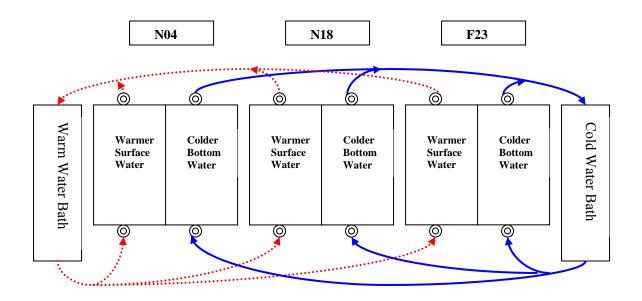


Figure C-2. Schematic depicting one option for cooling/warming baths for Photosynthetron.

# Appendix D MWRA Threshold Testing SOPs

To: Wendy Leo, Mike Mickelson, Andrea Rex

From: Joe LoBuglio, Suh Yuen Liang

Date: December 21, 2001

Subject: Calculation methods for threshold values for *Alexandrium*.

This memo summarizes the methods used to calculate the *Alexandrium* threshold (WNSAL). For each post-discharge event, the *Alexandrium* concentration for each sample is compared against the caution threshold of 100 cells/liter. If any sample exceeds the threshold, there is an exceedance for that event.

#### Data Source (Data from EM&MS database):

- Species concentrations from screened water samples are obtained from the ABUNDANCE and SAMPLE tables via the view PSC\_AVG\_VALUE\_PER\_SAMPLE. This view performs the two steps of the data aggregation discussed below.
- "Nearfield" and "Farfield" days are specified in the BWQM DAY table.
- Depth classification is obtained from the ORDERED\_DEPTH\_CLASS table.

# Data To Be Used In The Analysis:

- Data collected on nearfield or farfield days are included.
- Data from nearfield stations (station identifier beginning with "N") are used in the threshold calculation. Data from farfield stations (those with identifiers beginning with "F") are used in calculations that provide auxiliary information.
- Two *Alexandrium* taxa are included in the threshold: *Alexandrium tamarense* and *Alexandrium spp.* (SPECIES\_CODE = '12041008TAMA' or '12041008SPP')
- Samples from all depths are used.
- Data qualified as suspect/invalid (VAL\_QUAL contains 's') are not used.
- Screened samples are identified in the ABUNDANCE database table by METH\_CODE = 'SCR20U'.

# Data Aggregation:

- The following two steps describe the data aggregation in the view PSC\_AVG\_VALUE\_PER\_SAMPLE.
- For each species code, bottle (or subsample) averages are generated by averaging analytical replicates. Since only species which are seen are recorded in the abundance table, the averaging requires summing individual species concentrations over all replicates for a bottle and dividing by the number of replicates for that bottle. For example, there are species A, B, and C with abundance 4, 2, and 7 in replicate 1 and species B and C with abundance 4 and 3 in replicate 2. The bottle averages for the species is the sum of replicate 1 and 2 divided by 2 (two replicates). The bottle averages for species A, B, and C are therefore 2, 3, and 5.
- Sample averages are generated by averaging the bottle averages. As with the bottle averages, this requires summing the bottle average concentrations for each species for a sample and dividing by the number of bottles for that sample.

# Baseline Calculation:

• There is no baseline calculation for this threshold. The threshold was recommended by EPA based on the observed maximum of 163 cells/l in baseline samples.

# Threshold Testing:

• For each post-discharge event, the *Alexandrium* concentration for each nearfield sample is compared against the caution threshold of 100 cells/liter. If any sample exceeds the threshold, there is an exceedance for that event.

Written by:		
	Joseph LoBuglio	Date
Data Group Manager:		
	Wendy Leo	Date
MWRA Scientist		
Responsible for Nuisance		
Algae Data:	Mike Mickelson	Date

To: Wendy Leo, Mike Mickelson, Ken Keay, Andrea Rex

From: Joe LoBuglio, Suh Yuen Liang

Date: July 18, 2001 Revised: October 24, 2001

Subject: Calculation methods for annual and seasonal threshold values and baselines for

chlorophyll.

There are three seasonal and one annual threshold tests for average nearfield areal chlorophyll levels (expressed in mg/m^2). All four tests are compared to baseline values derived from baseline monitoring data. This memo summarizes the methods used to calculate the baseline and post-discharge test values.

# **Revision History:**

Revision 1: Threshold values corrected due to (1) recalibration of 1998-2000 fluorescence data to corrected bottle chlorophyll values and (2) correction of error in baseline data from survey WF984 due to misapplied calibration.

#### Periods Tested:

Period	Baseline years	Threshold level	Baseline Value (mg/m2)
Winter/Spring (Jan 1 - Apr 30)	1992-2000	Caution	182
Summer (May 1 - Aug 31)	1992-2000	Caution	80
Autumn (Sep 1 - Dec 31)	1992-1999	Caution	161
Annual (Sep 6 - Sep 5 for baseline calculation	9/6/1992 -	Caution	107
Jan 1 - Dec 31 for post discharge tests)	9/5/2000	Warning	143

#### Data Source (Data from the EM&MS database):

- Downcast fluorescence data (from the PROFILE\_DOWNCAST\_BWQM table, PARAM\_CODE = 'FLUORESCENCE', UNIT\_CODE = 'ug/L') will be used. These data are reported at 0.5-meter depth intervals.
- Where entire surveys have invalid or missing downcast fluorescence data (surveys WF981 and WN99H), the upcast laboratory bottle chlorophyll (from the ANALYTICAL\_RESULTS table, PARAM\_CODE = 'CHLA', UNIT\_CODE = 'ug/L') will be used. These data are taken at five depths per station.
- Nominal station depths are the average station depths during HOM3 station visits. These are stored in the GEO STATION table.

#### Data to be used in the analysis:

- Only data taken on nearfield survey days will be included. (Nearfield days are specified in the BWQM DAY table.)
- All nearfield stations are included. (Nearfield stations have a leading 'N' in their identifier.)
- No surveys will be excluded based on the number of stations sampled per survey. This currently ranges from 3 to 21 stations per survey.
- Data qualified as invalid/suspect (those having qualifiers including 's') are excluded. No other exclusions are made. Data qualified as "uncalibrated but deemed fit for use by the principal investigator" or "use with caution" will be used if they exist. All chlorophyll data taken between 1998 and 2000 are qualified as "use with caution". The existence of data that are qualified as "possibly suspect/invalid, investigation pending" (those having qualifiers including 'q') will prevent a calculation from occurring.
- Data qualified as below detection limit ('a' qualifier) are treated as zero values even if the values in the database are negative.
- No exclusions are made based on the fraction of the water column covered by the cast although casts covering less than 50% of the water column depth exist.

# Data Aggregation:

- Data for each individual station and depth for a given nearfield day are averaged to account for multiple casts.
- The average chlorophyll concentration for each station is calculated for each survey.
- Each average station value is multiplied by the nominal station depth to come up with a measure of station areal chlorophyll.
- Each station is assumed to influence an equal area of the nearfield during a particular nearfield day. Therefore, the survey average nearfield chlorophyll areal concentration is calculated simply as the average of the station areal chlorophyll concentrations.
- A period average is obtained by averaging all the survey averages during the period of interest. No accounting is made for differences in the number of surveys per period for the different years or for unequal spacing of surveys during a particular period.

# Baseline Calculation (WCHL BASE.SQL):

- The baseline values for each seasonal period are determined by calculating the period average for each year and using the resulting eight or nine values to estimate the upper 95% limit for the period average chlorophyll values. All data for nearfield areal chlorophyll means are normally distributed for each season as shown by a Kolmogorov-Smirnov test. The baseline, that is the 95th percentile of each fitted distribution, is thus equal to the mean + 1.645\*standard deviations.
- The baseline values for the annual threshold are calculated as 1.5 times (caution) or 2 times (warning) the average of the eight annual averages. The baseline years begin on September 6th.
- Values are rounded to the nearest whole number.

# Threshold Testing (WCHL.SQL):

• For threshold testing, the period average for the current period is compared against the baseline values. An exceedance is recorded if the current period exceeds the baseline value. Although the annual baseline is calculated based on years that begin in September, the annual post-discharge threshold testing value will be based on a calendar year.

# Approvals:

1 1		
Written by:		
	Suh Yuen Liang	Date
	Joseph LoBuglio	Date
Data Group Manager:		
	Wendy Leo	Date
MWRA Manager		
Responsible for Water		
Column Data:	Mike Mickelson	Date

To: Wendy Leo, Ken Keay, Mike Mickelson

From: Suh Yuen Liang, Joe LoBuglio

Date: May 29, 2001

Subject: Calculation method for baseline and test values for water column bottom

dissolved oxygen and percent saturation at the nearfield and Stellwagen Basin.

Contingency plan threshold comparisons for both the nearfield and Stellwagen Basin for bottom-water dissolved oxygen (mg/L) and percent oxygen saturation (%) are performed for each event occurring from June through October. The mean event values are compared to the threshold and background values to determine if there is an exceedance (event means below the threshold values can trigger an exceedance). The comparisons for these parameters are unusual in that there is no threshold exceedance unless the event mean is below both the threshold value (caution or warning) and the background value. The background values are calculated from data gathered during the baseline period (summers of 1992 through 1999). The table below shows the caution, warning, and background values for each parameter and location.

Parameter	Location	Caution	Warning	Background
Dissolved Oxygen	Nearfield	6.5	6.0	5.75
(mg/L)	Stellwagen Basin	6.5	6.0	6.2
Percent Oxygen	Nearfield	80	75	64.3
Saturation (%)	Stellwagen Basin	80	75	66.3

This memo describes how event means are calculated, how background values are calculated, and how the threshold comparison is performed.

Data Source (Data from EM&MS database):

- Data for bottom-water dissolved oxygen and percent saturation are from the water column upcast data (calibrated sensor reading from the PROFILE table).
- "Nearfield" and "Farfield" days are specified in the BWQM DAY table.
- Bottom depth classification is obtained from the ORDERED DEPTH CLASS table.

# Data To Be Used In The Analysis:

- Dissolved oxygen data (PARAM\_CODE = 'DISS\_OXYGEN', UNIT\_CODE = 'mg/L') or percent saturation data (PARAM\_CODE = 'PCT\_SAT', UNIT\_CODE = 'PCT').
- Data qualified as suspect/invalid ('s'), under investigation ('q'), and missing ('e') are not used.
- Non-detects will be treated as zeros if they occur. (There are currently no non-detects ('a' qualified values) in the database.)
- Only data from June 1st to October 31st is included in calculations.
- Stations and event days:

Nearfield: All nearfield stations (station identifiers beginning with 'N')

on "Nearfield" days.

Stellwagen Basin: Stations F12, F17, F19, and F22 on all event days.

• Only bottom depth (ORDERED\_DEPTH\_CODE='E') are included. Obtaining the bottom depths necessitates joining the PROFILE table with a view of the SAMPLE and

ORDERED\_DEPTH\_CLASS tables; this is done in such a way as to insure no duplication of profile data when multiple samples are taken. However, profile data without a corresponding sample are not included. There were no such exclusions in the background calculation. There is currently one nearfield station where the bottom measurement would be excluded (N21 on 06-July-2000) but it occurs after the last complete background summer and before the first post-discharge survey on October of 2000.

# Data Aggregation:

- Calculate the mean bottom dissolved oxygen and percent saturation for each station on each day to remove double casts.
- Calculate the station mean for each event to combine measurements taken over more than one day.
- Calculate the event mean by averaging station means of the event. The stations for the nearfield and Stellwagen basin are as specified in "Data to be used in the analysis" above.

# Background Calculation:

- Find the lowest event mean for each of the eight years (1992 through 1999) for all months.
- Fit a normal distribution to the eight annual minimum event means. All data for bottom dissolved oxygen and percent saturation at the nearfield and Stellwagen Basin are normally distributed as shown by a Kolmogorov-Smirnov test and a Shapiro-Wilk test.
- Take the 5<sup>th</sup> percentile of this fitted distribution.

  Baseline of bottom dissolved oxygen or percent saturation = mean 1.645\*Standard deviations.

#### Threshold Testing:

- Compare the event mean to the threshold value (caution or warning) and to the background value. If it is below the background value and the threshold value then there is an exceedance. If the mean is not below both values then there is no exceedance.
- The results of the comparisons are recorded in the database table THRESHOLD\_TEST.

Written by:		
	Suh Yuen Liang	Date
	Joseph LoBuglio	Date
Data Group Manager:		
	Wendy Leo	Date
MWRA Scientist Responsible for Water		
Column Data:	Mike Mickelson	Date

To: Wendy Leo, Mike Mickelson, Andrea Rex

From: Joe LoBuglio, Suh Yuen Liang

Date: December 3, 2001

Subject: Calculation methods for seasonal threshold values for *Phaeocystis pouchetii* and

Pseudonitzschia multiseries.

There are three seasonal caution-level threshold tests for each of two nuisance algae: *Phaeocystis pouchetii* and *Pseudonitzschia multiseries*. This memo summarizes the methods used to calculate these seasonal averages and the baseline values against which they are compared.

**Table 1: Nuisance Algae Thresholds.** 

Algae	Threshold ID	Season	Caution Level (million cells/liter)	Baseline Years	Baseline Method
Phaeocystis pouchetii	WNSPHSP R	Winter/Spring	2.02	1992-2000 (detected only in 1992, 1994, 1996, 1997 and 2000)	95th percentile of annual means using Solow method for nondetect correction.
	WNSPHSU M	Summer	0.000334	1992-2000 (detected only in 1994 and 1997)	95th percentile of annual means using Solow method for nondetect correction.
	WNSPHAU T	Autumn	0.00237	1992-1999 (detected only in 1993)	Use the only nonzero value measured.
Pseudonitzschia multiseries (Pseudonitzschia	WNSPSSP R	Winter/Spring	0.0210	1992-2000	95th percentile of log- transformed annual means.
pungens, Pseudonitzschia cf. pungens, and Pseudonitzschia spp.)	WNSPSSU M	Summer	0.0379	1992-2000	95th percentile of annual means.
, shh•)	WNSPSAU T	Autumn	0.0246	1992-1999	95th percentile of annual means.

# Data Source (Data from EM&MS database):

- Whole water cell counts and sample information are obtained from the ABUNDANCE and SAMPLE tables via the view PWW\_AVG\_VALUE\_PER\_STAT\_DAY. This view performs the first three data aggregation steps listed below.
- "Nearfield" and "Farfield" days are specified in the BWQM DAY table.
- Depth classification is obtained from the ORDERED DEPTH CLASS table.

# Data To Be Used In The Analysis:

- Only data collected on "Nearfield" and "Farfield" days are included in the averages.
- Baseline calculations are performed on nearfield and farfield stations (station IDs beginning with 'N' or 'F'.)
- Post-discharge seasonal averages for threshold testing only include data from nearfield stations (stations having identifiers beginning with 'N').
- Seasonal averages are calculated for the following periods, except that for autumn 2000, the date begins on September 6 (the day after the Outfall went on line) and ends on December 31.

Season	Dates to include for a given year	
Winter/Spring	Jan 1 – Apr 30	
Summer	May 1 – Aug 31	
Autumn	Sep 1 – Dec 31	

- Data qualified as suspect/invalid (VAL QUAL contains 's') are not used.
- Whole water samples are identified in the ABUNDANCE database table by METH CODE = 'COU WW'.

#### Data Aggregation:

- The following three steps describe the data aggregation in the view PWW AVG VALUE PER STAT DAY.
- For each species code, bottle (or subsample) averages are generated by averaging analytical replicates. Since only species which are seen are recorded in the abundance table, the averaging requires summing individual species concentrations over all replicates for a bottle and dividing by the number of replicates for that bottle. For example, there are species A, B, and C with abundance 4, 2, and 7 in replicate 1 and species B and C with abundance 4 and 3 in replicate 2. The bottle averages for the species is the sum of replicate 1 and 2 divided by 2 (two replicates). The bottle averages for species A, B, and C are therefore 2, 3, and 5.
- Sample averages are generated by averaging the bottle averages. As with the bottle averages, this requires summing the bottle average concentrations for each species for a sample and dividing by the number of bottles for that sample.
- Daily station averages are calculated for each depth by averaging the sample averages for each station, day and depth. As with the bottle averages, this requires summing the

- sample average concentrations for each species for a station, day, and depth and dividing by the number of samples taken at a particular station, day and depth.
- Fill in zero for each station at each depth on each station day where the whole-water samples were taken but *Phaeocystis pouchetii* or any of the three congeners of *Pseudonitzshia* were absent. The species codes that identify these species are listed below. These records are joined with the view PWW\_AVG\_VALUE\_PER\_STAT\_DAY for further calculations.

Species	Species Code	Taxa Description
Phaeocystis pouchetii	0603020101	Phaeocystis pouchetii
Pseudonitzschia	0703100113	Pseudonitzschia pungens
multiseries	0703100113CF	Pseudonitzschia cf. pungens
	07031001PSEUSPP	Pseudonitzschia spp.

- The sum of the three congeners of *Pseudonitzschia* is taken as the computed value for *Pseudonitzschia multiseries* for each station day at each depth.
- For each station and date, the average value over all depths is computed for *Phaeocystis pouchetii* and *Pseudonitzschia multiseries*.
- For each season, the average value over all daily station averages is computed for *Phaeocystis pouchetii* and *Pseudonitzschia multiseries*.

# Baseline Calculation:

#### Pseudonitzschia

• There were detections of *Pseudonitzschia* each year and for every season, so the eight or nine seasonal values were used to calculate the 95th percentile. The summer and autumn thresholds were determined to be normal using Kolmogorov-Smirnov (Lilliefors Significance Correction) and Shapiro-Wilk tests for normality so the 95th percentiles for these thresholds were calculated using: Threshold = baseline mean + 1.64\*(baseline standard deviation). The winter-spring threshold was log-normal according to the same tests, so the 95th percentile was calculated using: Threshold =  $10^{[baseline log mean + 1.64*(baseline log std. dev.)]}$ 

#### Phaeocystis

• As shown in Table 1, there were several years when *Phaeocystis* was not detected. For the winter-spring and summer thresholds an alternative method outlined by Andrew Solow (Solow, personal communication 2000) was used for nondetect correction, as described below.

N = Total number of baseline years (years with observations)

 $N_a$ = Number of years with zero mean

y = Mean of all non-zero years

sd =Standard deviation of all non-zero years

The fraction of zero years is

$$f = N_a/N$$

and the probability at the 95<sup>th</sup> percentile is

$$p = (0.95-f)/(1-f)$$
.

If NORMSINV(p) is a function that returns the inverse of the standard normal cumulative distribution then the 95th percentile is calculated as:

$$Threshold = y + NORMSINV(p)*sd$$

• There was only one year with a nonzero Autumn average concentration. Since there were not enough data on which to base a distribution, the nonzero value was used as the threshold. Since this value was observed only once in eight years, it should represent a number closer to the 88th percentile, resulting in a more stringent threshold.

# Threshold Testing:

• For each post-discharge season, the average concentration is compared against the caution threshold in table 1. If the seasonal average exceeds the threshold, there is an exceedance for that season.

Written by:		
	Joseph LoBuglio	Date
	Suh Yuen Liang	Date
Data Group Manager:		
	Wendy Leo	Date
MWRA Scientist Responsible for Nuisance		
Algae Data:	Mike Mickelson	Date

To: Wendy Leo, Ken Keay, Mike Mickelson

From: Suh Yuen Liang
Date: December 20, 2001

Subject: Calculation method for baseline and test values for water column bottom

dissolved oxygen depletion rate at the nearfield.

The contingency plan threshold comparison for the nearfield bottom-water dissolved oxygen (DO) depletion rate (mg/L/day) is performed each year during the stratification period from June through October. The yearly bottom-water DO depletion rate is compared to the threshold to determine if there is an exceedance (rapid DO decline threshold value can trigger an exceedance). The table below shows the caution and warning values for bottom-water DO depletion rate.

Threshold ID	Testing area	Caution Level (mg/L/day)	Warning Level (mg/L/day)	Baseline Years	Baseline Method
WORATE	Nearfield	0.037	0.049	1992-1999	Arithmetic mean

**Table 1: Bottom-water DO Depletion Rate Thresholds** 

Data Source (Data from EM&MS database):

- Dissolved oxygen data (PARAM\_CODE = 'DISS\_OXYGEN', UNIT\_CODE = 'mg/L') are obtained from the water column upcast data (calibrated sensor reading from the PROFILE table).
- Bottom depth classification is obtained from the ORDERED\_DEPTH\_CLASS table.
- Nearfield stations are specified as station IDs beginning with 'N' on "Nearfield" days.
- "Nearfield" days are specified in the BWQM\_DAY table.

# Data To Be Used In The Analysis:

- Baseline calculations and threshold testing are performed on all nearfield stations on nearfield days.
- Only data from June 1st to October 31st are included in calculations and there were six to nine surveys per year in the baseline period.
- Data qualified as suspect/invalid (VAL\_QUAL contains 's'), investigation pending (VAL\_QUAL contains 'q'), and missing data (VAL\_QUAL contains 'e') are not used. There is one 's' qualified sample at N01 on 13-July-1998 and one missing sample at N10 on 08-Oct-1999 in the baseline years.
- Non-detects ('a' qualified values) are treated as zeros if they occur. (There are currently no non-detects in the data set.)
- Only bottom depths (ORDERED\_DEPTH\_CODE='E') are included. Obtaining the bottom depths necessitates joining the PROFILE table with a view of the SAMPLE and

ORDERED\_DEPTH\_CLASS tables; this is done in such a way as to ensure no duplication of profile data when multiple samples are taken. For example, there are two samples at station N04 on 04-December-1997 that have the same profile primary keys. Ten duplications of profile data would have created in the data set if profile data with multiple samples were not first fixed. In addition, profile data without a corresponding sample are not included. There were no profile data without a corresponding sample in the baseline calculation

# Data Aggregation:

- Calculate the mean bottom dissolved oxygen for each station on each day to average replicate casts if any.
- Calculate the linear regression of station-day bottom-water DO averages versus time for each year, including y-intercept, slope, R<sup>2</sup>, and P value. The independent variable for the regression is the Julian day for the station-day minus the Julian day for May 31 of the year. This is to ensure that the y-intercepts approximate to the DO at setup of stratification (*i.e.*, June 1). The absolute value of the slope is the yearly bottom-water DO depletion rate.

#### **Baseline Calculation:**

• The average of the eight yearly bottom-water oxygen depletion rates (the absolute value of the slope, see table below) is the baseline mean (0.0244 mg/L/day).

Year	N	Y_intercept(day)	Slope	$R^2$	P
			(mg/L/day)		
1992	125	11.7	-0.030	0.87	< 0.001
1993	168	11.1	-0.024	0.80	< 0.001
1994	162	9.9	-0.028	0.80	< 0.001
1995	142	9.8	-0.023	0.76	< 0.001
1996	135	9.9	-0.017	0.70	< 0.001
1997	153	9.9	-0.018	0.61	< 0.001
1998	146	11.5	-0.032	0.81	< 0.001
1999	176	9.3	-0.024	0.74	< 0.001

Table 2. Statistical summary of linear regression on bottom-water dissolved oxygen

- Caution threshold is 1.5\* baseline mean.
- Warning threshold is 2\*baseline mean.

# Threshold Testing:

• For each post-discharge year, the nearfield bottom-water oxygen depletion rate from June to October is compared against the caution and warning thresholds in table 1. If the DO decline is faster than the threshold, there is an exceedance for that year.

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