Appendix C - Technical Support for Nutrient Criteria Development: Southern California Estuarine Eutrophication Assessment Quality Assurance Project Plan

Technical Support for Nutrient Criteria Development: Southern California Estuarine Eutrophication Assessment

Quality Assurance Project Plan

FINAL

November 20, 2008

Prepared by

Southern California Coastal Water Research Project (SCCWRP)
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GROUP A ELEMENTS: PROJECT MANAGEMENT

1. TITLE AND APPROVAL SHEETS

Quality Assurance Project Plan

For

PROJECT NAME: Technical Support for Nutrient Criteria Development: Southern California Estuarine Eutrophication Assessment

Proposal Identification Number: 07-110-250

Date: 9/8/08

NAME OF RESPONSIBLE ORGANIZATION : Southern California Coastal Water Research Project (SCCWRP)

APPROVAL SIGNATURES

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QA Officer	Liesl Tiefenthaler		

STATE WATER RESOURCES CONTROL BOARD:

Title:	Name:	Signature:	Date*:
Grant Manager	Steve Camacho		
QA Officer	Bill Ray		

* This is a contractual document. The signature dates indicate the earliest date when the project can start.

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SWRCB Agreement no. 07-110-250 QAPP V1

3. DISTRIBUTION LIST

(If the QAPP is being prepared under the jurisdiction of the State Water Resources Control Board (SWRCB) rather than a Regional Board (RWQCB), substitute the SWRCB information for the RWQCB information.)

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4. PROJECT/TASK ORGANIZATION

4.1 Involved parties and roles.

This section describes names and roles for individuals expected to participate in carrying out the work for this project. If there are changes in staff during the course of this project, all new individuals not mentioned below will also be subject to the necessary training, as discussed in Section 8.

Table 1 lists names and contact information for individuals who will assume key roles to assure quality and timely delivery of project data. Collectively, they will be responsible for all major project tasks and deliverables. Descriptions of their duties, as well as the duties of some of the additional personnel, are provided below.

Table 1. (Element 4) Key Personnel responsibilities.

Name	Organizational Affiliation	Title	Contact Information (Telephone number, fax number, email address.)
Martha Sutula	SCCWRP	Project Manager	714-755-3222, 714-755-3299, marthas@sccwrp.org
Liesl Tiefenthaler	SCCWRP	QA Officer	714-755-3231, 714-755-3299, lieslt@sccwrp.org
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Jeff Crooks	TJNEER	Lead Scientist	619-575-3613 ext. 333, jcrooks@tijuanaestuary.org
Lisa Stratton	UCSB	Lead Scientist	805-893-4158, stratton@lifesci.ucsb.edu
Sean Bergquist	SMBRC	Lead Scientist	310-216-9899; sbergquist@santamonicabay.org
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Eric Zahn	CSU Long Beach	Lead Scientist	ezahn@csulb.edu
Gerald McGowan	City of Los Angeles	Lead Scientist	310-648-5611 Gerald.McGowen@lacity.org
Thomas Liddell	Ventura County Watershed Protection District	Lead Scientist	805-662-6758 Tommy.Liddell@ventura.org

Martha Sutula is a supervisory scientist at SCCWRP. As the Project Manager, she will be the project administrator and will oversee project coordination, purchases, budget analysis, monitoring, laboratory analysis, data management, education and outreach, and report writing. She will also participate in fieldwork, laboratory work, and data analysis.

Liesl Tiefenthaler will serve as the project QA Officer. His duties are described in Section 4.2, below.

Karen McLaughlin is a staff scientist at SCCWRP. She will organize training and coordinate fieldwork and data delivery among the Lead Scientists. She will supervise field and laboratory work for SCCWRP staff. She will also participate in fieldwork, laboratory work, and data analysis.

Jeff Crooks, Lisa Stratton, Sean Bergquist, Sean Anderson, Rosi Dagit, Tommy Liddell, Gerald McGowan, and **Eric Zahn** are Lead Scientists for this project. They will coordinate fieldwork, sample collection, and data delivery for their respective field teams. They will also participate in fieldwork and data analysis.

The **Bight '08 Coastal Wetlands Planning Committee** consists of the Co-chairs, **Martha Sutula** and **Lillian Busse,** the Field Coordinator, and the Lead Scientists.

The following chain-of-command is recommended to avoid confusion, identify responsible parties, and ensure that proper sampling protocols and information flow are followed by each organization:

1. The Project Manager (Martha Sutula) is the project administrator and will oversee project coordination, purchases, budget analysis, monitoring, laboratory analysis, data management, education and outreach, and report writing. She will also supervise the Field Coordinator.

2. The Field Coordinator (Karen McLaughlin) is responsible for coordinating all field teams and insuring that all participants receive proper training in protocols and QA/QC requirements. All technical matters, such as equipment problems, questions regarding station location, sampling schedules, etc. should be communicated to the Field Coordinator by the Lead Scientist as soon as possible.

3. Lead Scientists will be an organization's primary contact regarding all survey and field-related matters. Lead Scientists will be responsible for organizing and implementing monitoring efforts in their designated estuaries. They have the authority to delay sampling or alter sampling sites due to unsafe conditions according to the contingency plan guidelines presented in this document. Any changes in sampling should be documented and reported to the Field Coordinator.

4. Team leaders are designated by the Lead Scientists prior to each sampling day and will be responsible for supervising the field teams and sampling operations. They must insure that all sampling protocols are followed and that QA/OC standards are met. At the end of each sampling day, he/she will make sure that all field data and samples are delivered to the appropriate processing personnel within all designated holding times. Team leaders are not required to be the same person from field day to field day.

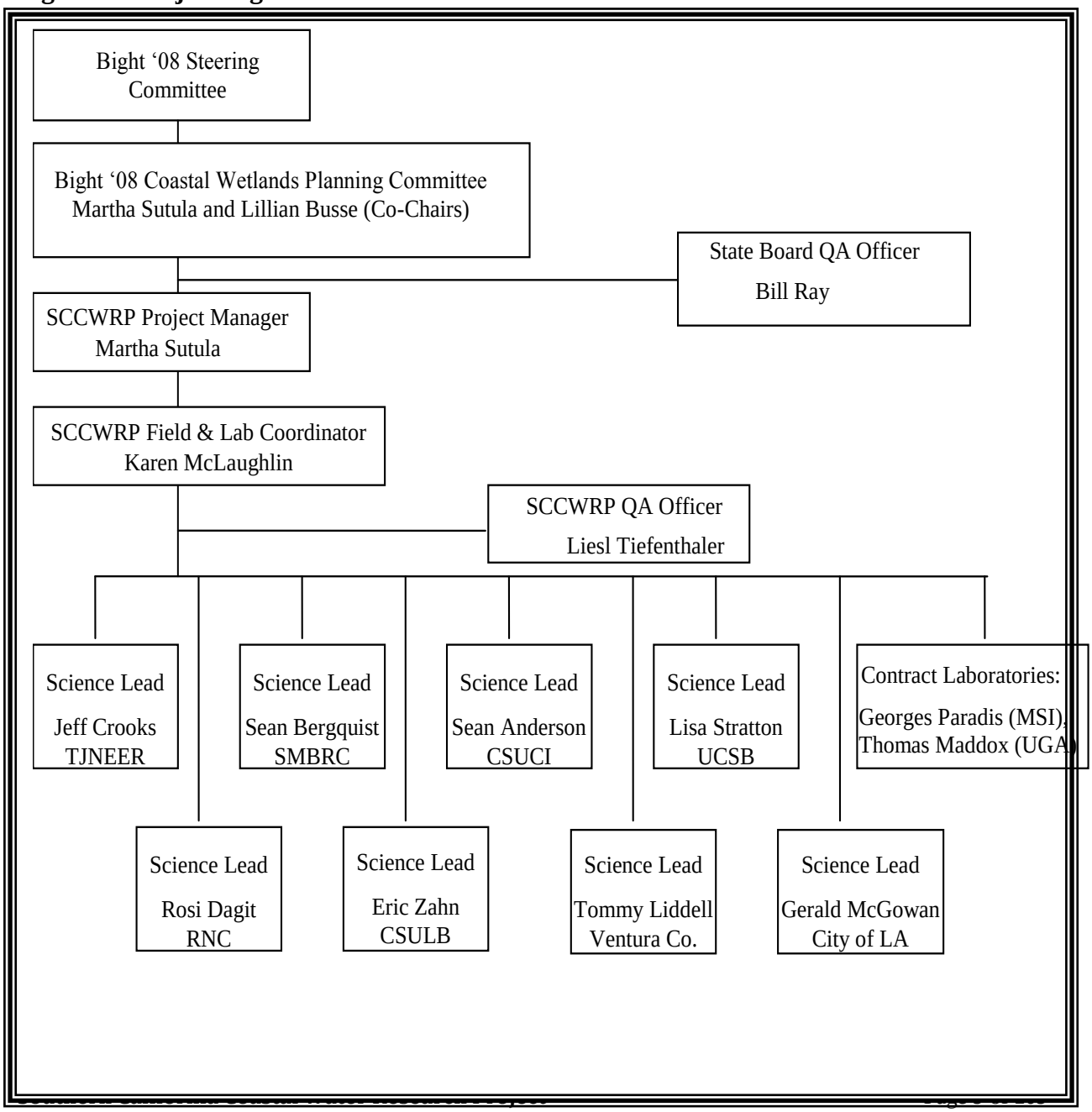
5. Field Teams may be subject to pre-survey field audit. Lead Scientists and Team leaders will be informed of any procedural deficiencies by the Q/A Auditor. The Lead Scientist will be expected to take appropriate action to correct the situation as soon as possible.

4.2 Quality Assurance Officer role

The Quality Assurance (QA) Officer will be responsible for maintaining the official, approved QAPP by tracking the QAPP versions, confirming that all parties listed in Element 3 are supplied with a current QAPP and have been trained in SOPs relating to their work, and conducting field audit(s) as necessary (detailed in Element 20 of this document). The QA Officer will also provide oversight as relates to observance and documentation of Quality Assurance activities. The QA Officer not involved in any aspect of data collection for this project.

4.3 Organizational chart and responsibilities

Figure 1. Project organization chart



5. PROBLEM DEFINITION/BACKGROUND

5.1 Problem statement.

Cultural eutrophication of estuaries and coastal waters is a global environmental issue, with demonstrated links between anthropogenic changes in watersheds, increased nutrient loading to coastal waters, harmful algal blooms, hypoxia, and impacts on aquatic food webs (Valiela et al. 1992, Kamer and Stein 2003). These ecological impacts of eutrophication of coastal areas can have far-reaching consequences, including fish-kills and lowered fishery production (Glasgow and Burkholder, 2000), loss or degradation of seagrass and kelp beds (Twilley 1985, Burkholder et al. 1992, McGlathery 2001), smothering of bivalves and other benthic organisms (Rabalais and Harper 1992), nuisance odors, and impacts on human and marine mammal health from increased frequency and extent of harmful algal blooms and poor water quality (Bates et al. 1989, Bates et al. 1991, Trainer et al. 2002). These modifications have significant economic and social costs, some of which can be readily identified and valued, while others are more difficult to assess (Turner et al. 1998). According to EPA, eutrophication is one of the top three leading causes of impairments of the nation's waters (US EPA 2001).

In California, the impacts of nutrient loading on estuaries and coastal waters have not been well monitored, with the notable exception of San Francisco Bay (Cloern 1982, Cloern et al. 1985, Cloern 1991, 1996, Cloern 1999). NOAA's National Estuarine Eutrophication Assessment Report illustrated a paucity of data on eutrophication for southern California estuaries. As the State Water Resources Control Board is initiating an effort to develop nutrient criteria for California estuaries, it is critical to improve understanding of the magnitude and extent of eutrophication in southern California, and provide regional data on the utility of candidate indicators.

2008 marks the first time that the assessment of eutrophication is incorporated into the Southern California Bight Regional Survey as the Coastal Wetlands component. This eutrophication assessment is one of six technical components in the Bight '08 Regional Survey (Coastal wetlands, Coastal ecology, Shoreline microbiology, Water quality, Hard bottom, Areas of special biological significance).

The focus of the Coastal Wetlands Component is three fold: (1) continuous monitoring of water quality parameters known to be sensitive to eutrophication, (2) assessment of primary producer biomass and percent cover and 3) measurement of freshwater nitrogen and phosphorus concentrations and water level (where pre-existing stream gauges are not available to provide flow. Two special studies are also being conducted in conjunction with the eutrophication assessment. The first seeks to assess the presence of harmful algal bloom toxins in estuarine sediment and surface water. The second will use stable isotopes of nitrogen to assess nitrogen sources and cycling within two of the estuaries being sampled.

5.2 Decisions or outcomes.

Eutrophication is the process by which increased nutrient loading and altered hydrology generally results in excessive primary production. The overall goal of this study is to assess the

condition of estuaries in southern California in terms of eutrophication and how different characteristics of the watershed and estuary affect the response to eutrophication. To accomplish this goal, Bight'08 will focus on the following objectives:

- Characterize the extent and magnitude of eutrophication in southern California Bight (SCB) estuaries.
- Determine whether differences in eutrophication exist between estuarine classes (protected embayments, perennially tidal lagoons, seasonally tidal lagoons, nontidal lagoons, river mouth estuaries)
- Determine how muting of the tidal forcing within an estuary impacts the biological response to nutrient loads.
- Determine the relationship between terrestrial nutrient loads and estuarine biological response

Very little is known about the condition of southern California estuaries with respect to eutrophication, and thus, the first objective aims to fill this gap in our understanding. The first objective should answer the questions: Which systems are impacted by eutrophication? At what time(s)? For what duration? Which of the symptoms of eutrophication are expressed (low dissolved oxygen, excessive macroalgae, excessive phytoplankton, excessive submerged aquatic vegetation, etc.)?

The remaining three objectives aim to further explore how specific characteristics of the watershed and estuary hydrogeology affect the condition of estuaries in terms of eutrophication. The second objective seeks to evaluate the differences between three estuarine classes: enclosed bays, perennially tidal lagoons, seasonally tidal lagoons, nontidal lagoons, and river mouth estuaries. Estuaries within southern California are highly variable in how they respond to nutrient loading due to differences in tidal forcing, freshwater residence time, salinity regime, stratification, denitrification, etc. This combination of factors results in differences in the dominant aquatic primary producer communities (i.e. phytoplankton, macroalgae, submerged aquatic vegetation, and other factors). This objective seeks to characterize differences in estuarine biological response to nutrient loads and residence time by three major classes: seasonally tidal lagoons, perennially tidal lagoons, and protected embayments. Additional sites will be sampled in a special study in the San Diego area to assess eutrophication in nontidal lagoons, and river mouths.

The second objective will determine the impact of muting of tidal forcing within an estuary on biological response to nutrient loads. Muting of tidal forcing occurs when a portion of the estuarine area is impounded by levees, tide gates or weirs. This muting results in an increased residence time of water within the impounded area and is hypothesized to result in stronger responses of indicators of eutrophication.

The third objective seeks to determine whether nutrient loads are predictive of biological response in estuaries. Total nitrogen and phosphorus loads into each estuary are being estimated as a component of the Bight '08 Offshore Water Quality study. The eutrophication assessment will use these data, with the intent to explore the development of regression models that establish the relationship between nutrient load (as the independent variable) and biological response (as

the dependent variable) over a gradient of disturbance. These regression models may in turn serve as one potential tool in the Total Maximum Daily Load (TMDL) toolbox.

5.3 Water quality or regulatory criteria

This project will provide information useful for the evaluation of draft nutrient numeric endpoints that have been proposed by the State Water Resources Control Board based on data generated through U.S. EPA. There are no applicable action limits for this study.

6. PROJECT/TASK DESCRIPTION

6.1 Work statement and produced products.

US EPA Region IX and the California State Water Board have previously developed a technical approach and framework for developing numeric nutrient endpoints (NNEs) for California estuaries (EPA 2007a). The stated goal of this effort is to develop a set of numeric endpoints and to support the Total Maximum Daily Load (TMDL) Program and to develop TMDL tools that can be used to address impacts from eutrophication through the water quality programs of the State Water Board, Regional Water Quality Control Boards (Region Water Boards) and the regulated community. EPA (2007a) presented a scientific framework to support the development of numeric endpoints for a suite of biological response indicators (e.g. algal biomass, dissolved oxygen, water clarity, etc.) that are directly linked with estuarine beneficial uses. The framework also highlighted data gaps and research recommendations critical for the development of numeric endpoints and TMDL tools (i.e. watershed loading and estuarine load-response models). These tools are critical because they provide the linkage between the numeric endpoints, which are based on biological response indicators, and watershed nutrient loads and other factors controlling eutrophication in estuaries. EPA (2007b) provided recommendations for an implementation plan to develop NNE and TMDL tools for California estuaries. According to the implementation plan, the general approach would involve establishing a statewide process to develop numeric endpoints, advised by a representative group of stakeholders and an independent panel of scientific experts. The purpose of this project is to initiate NNE development in California estuaries by implementing the first suite of work elements outlined in the implementation plan EPA (2007b).

The study design proposed below is divided into eight tasks. Project management and administration is the first task. Outreach with the California State Regional Technical Advisory Group (STRTAG) will be initiated in the second task. In the third task, technical, stakeholder, and scientific advisory board members will be identified. For the fourth task, technical documents will be prepared to support the initiation of NNE development. Statewide outreach on NNE development will be initiated in the fifth task with the review of the existing estuarine NNE documents and technical reports produced by the project by the stakeholders and science advisory board. The sixth task provides technical support to facilitate the process of numeric endpoint selection for dissolved oxygen. An ambient survey of eutrophication in southern California estuaries will be included in Task 7. Task eight includes the preparation of a summary report describing the results of the project and recommendations for the next steps.

This QAPP covers the ambient assessment of eutrophication in Southern California estuaries proposed under Task 7 (Table 4).

The basic approach to the eutrophication assessment is a probability-based survey in which sites are randomly selected from a comprehensive list of estuaries. Because eutrophication is likely to vary spatially within any given estuary, sampling will occur in a targeted index area, or segment, within each selected estuary; thus reporting on eutrophication will be on a "percent of estuarine segments" basis. This survey is not meant to be a comprehensive characterization of any

individual estuarine system, but rather to characterize the region overall. In each of these estuary segments, the magnitude of eutrophication of southern California estuaries will be assessed via a series of biological response indicators. Such biological response indicators are a more direct measure of estuarine beneficial use impairment. These biological response indicators include dissolved oxygen, macroalgal biomass and percent cover, surface water phytoplankton biomass (e.g. chlorophyll a), benthic algal biomass (sediment chlorophyll a), and nuisance submerged aquatic vegetation (SAV) density and percent cover. The use of multiple indicators in a "weight of evidence" approach provides a more robust means to assess ecological condition and determine impairment.

The eutrophication assessment sampling design for Bight 08 will be divided into three primary components: (1) continuous monitoring of water quality parameters (including dissolved oxygen, salinity, temperature, pH, and turbidity), and (2) transects of primary producer biomass and percent cover, 3) measurement of freshwater nitrogen and phosphorus concentrations and water level (where pre-existing stream gauges are not available to provide flow).

Continuous monitoring of water quality parameters is required from June through October 2009 for all perennially tidal estuaries, although where resources are available, sampling may be extended to include winter and spring seasons. The summer months were deemed most critical for continuous monitoring because these are the months during which dissolved oxygen demand is greatest and when hypoxia would be most likely to develop. In addition to the summer sampling, seasonally tidal estuaries will be monitored from December 2008 through October 2009. The additional sampling for seasonally tidal lagoons was due to the fact that some seasonally tidal lagoons are closed to ocean exchange during the summer, while others are closed during the winter. When the ocean inlets are closed, water residence time in these lagoons is greatly increased, which in turn increases the chance of low dissolved oxygen concentrations. Monitoring in these lagoons was extended beyond summer to capture this seasonal variation in dissolved oxygen levels.

Measurement of primary producer communities will occur every other month in all estuaries for a year beginning in October 2008 and ending in October 2009. This monitoring will provide information on when blooms occur in each class of estuary, how far they extend spatially, and how long they endure.

Measurement of freshwater nitrogen and phosphorus concentrations will be conducted every other month in the winter (coincident with primary producer monitoring) and every month in the summer (coincident with some maintenance events for continuous monitoring). Where no existing gauging of stream flow exists, water level will also be measured by continuous water level sensors in selected systems. Wetted channel width and velocity will be measured across the channel cross section in order to develop a rating curve for the channel. These data would be used to supplement the modeling of nutrient loads from the watershed shared by the Bight '08 Offshore Water Quality Component. Efforts in this area will be increased during dry periods (summer) due to the difficulties in modeling dry weather flows. Wet weather data will be used to ground-truth wet weather modeling already underway.

Monitoring for domoic acid will occur coincident with primary producer community monitoring in February, April, and June, the time period in which *Pseudo-nitzschia* is known to bloom. Monitoring for microcystin will occur once a month from June through September, the peak period for cyanobacteria production.

Table 2. Timeline of components of Eutrophication Assessment. ST = seasonally tidal; NT= Nontidal

Month	Continuous Monitoring	Primary Producer Communities	Freshwater Loading	HABs Toxins
Oct 08		X		
Nov 08				
Dec 08	X (ST and NT only)	X	X	
Jan 09	X (ST and NT only)			
Feb 09	X (ST and NT only)	X	X	X (domoic acid)
Mar 09	X (ST and NT only)			
Apr 09	X (ST and NT only)	X	X	X (domoic acid)
May 09	X (ST and NT only)			
Jun 09	X (All)	X	X	X (domoic acid + microcystin)
Jul 09	X (All)		X	X (microcystin)
Aug 09	X (All)	X	X	X (microcystin)
Sept 09	X (All)		X	X (microcystin)
Oct 09		X		

6.2. Constituents to be monitored and measurement techniques.

Continuous Monitoring.
Standard *in situ* methods for measurement of physiochemical parameters will be used. Water column temperature, pH, salinity, turbidity, chlorophyll fluorescence, and dissolved oxygen will be measured with a data sonde (YSI 6600v2 data sonde) deployed in each system. The list of constituents is provided in Table 3.

Primary Producer Communities.
Established methods will be used to monitor macroalgae, benthic microalgae via sediment chlorophyll a, phytoplankton (water column chlorophyll a) and submerged aquatic vegetation percent cover and biomass. Protocols have been adapted from Kennison et al. 2005 and Rodusky et al. 2005 and vetted by the Planning Committee. The list of constituents is provided in Table 3.

Ambient Nutrients.
The critical water chemical constituents to be laboratory analyzed for the project are: total nitrogen (TN), total dissolved nitrogen (TDN), nitrate (nitrate + nitrate), ammonium, total phosphorus (TP), total dissolved phosphorus (TDP), soluble reactive phosphorus (SRP), dissolved organic carbon (DOC), and chlorophyll a (CHLa). Analyses are described by the Standard Methods for the Examination of Water and Wastewater and the EPA standard methods. The list of water chemistry constituents and analytical methods is provided in Table 3. Field duplicate water chemistry samples will be collected and analyzed for at least 5 % of samples.

Sediment Properties.

The critical sediment physical and chemical constituents to be laboratory analyzed are: grain size (% sand), percent organic carbon (%OC), percent organic nitrogen (%ON), and percent total phosphorus (%TP). Analyses are described by EPA standard methods and from the literature. The list of sediment physical and chemical constituents and analytical methods is provided in Table 3. Field duplicates will be collected and analyzed for at least 5 % of samples.

Table 3. (Element 6) List of water and sediment chemical and physical constituents and analytical methods

Type	Analyte	Analytical Method	Target Reporting Limit
Data Sonde	Temperature	Data Sonde	0.1 °C
	Salinity	Data Sonde	0.1 ppt
	pH	Data Sonde	0.2
	Dissolved Oxygen (DO)	Data Sonde	1.00 mg/L
	Turbidity	Data Sonde	0.1 NTU
	Chlorophyll Fluorescence	Data Sonde	0.1 µg/L
Water Analysis	Total Nitrogen (TN)	USGS I-4650-03	0.5 mg/L
	Total Phosphorus (TP)	USGS I-4650-03	0.01 mg/L
	Total Dissolved Nitrogen (TDN)	USGS I-2650-03	0.5 mg/L
	Total Dissolved Phosphorus (TDP)	USGS I-2650-03	0.01 mg/L
	Nitrate-N	SM 4500-NO3 F	0.05 mg/L
	Nitrite-N	SM 4110 C	0.05 mg/L
	Ammonium-N	SM 4500-NH3 G	0.05 mg/L
	Soluble Reactive Phosphorus (SRP)	SM4500P C	0.05 mg/L
	Dissolved Organic Carbon (DOC)	SM 5310C	0.6 mg/L
	Chlorophyll a	EPA 445.0	2 µg/L
Sediment Analysis	% Sand	ASTM D-422 (1963) [1] EPA (1995) [2] Plumb (1981) [3]	1 %
	% Organic Carbon (%OC)	EPA 9060	0.01 %
	% Organic Nitrogen (%ON)	EPA 9060	0.01 %
	% Total Phosphorus (%TP)	Nelson (1987)[4]	0.01 %
	Sediment Chlorophyll a	SM 10200H	0.1 mg/m^3
Additional Primary Producers	Macroalgae Biomass % and Cover	Kennison et al. 2003[5]	5%
	SAV Biomass % Cover	Rodusky et al. 2005[6]	5%
	Wet/Dry weight	B-3520-85	0.5 %

1. ASTM D-2216, 1980. Laboratory Determination of Water (Moisture) Content of Soil, Rock, and Soil-Aggregate Mixtures. American Society for Testing and Materials.

2. U.S. EPA, 1995. Environmental Monitoring and Assessment Program (EMAP): Laboratory Methods Manual – Estuaries, Volume 1: Biological and Physical Analyses. United States Environmental Protection Agency, Office of Research and Development, Narragansett, RI. EPA/620/R-95/008.

3. Plumb, R. H., 1981. Procedure for Handling and Chemical Analysis of Sediment and Water Samples. Technical Report EPA/CE 81-1, prepared for Great Lakes Laboratory, State University College at Buffalo, NY, for the U.S. EPA/Corps of Engineers Technical Committee on Criteria for Dredged and Fill Material. U.S. Army Engineers Waterways Experiment Station, CE, Vicksburg, MS.
4. Nelson, N. S. 1987. An acid-persulfate digestion procedure for determination of phosphorus in sediments. Commun. In Soil Sci. Plant Anal. V.18 no.4 p.359-69.
5. Kennison, R., K. Kamer and P. Fong. 2003. Nutrient dynamics and macroalgal blooms: A comparison of five southern California estuaries. Southern California Coastal Water Research Project. Westminster, CA.
6. Rodusky, A.J., B. Sharfstein, T.L. East, R.P. Maki. 2005. A comparison of three methods to collect submerged aquatic vegetation in a shallow lake. Environmental Monitoring and Assessment. 110: 87-97.

6.3 Project schedule

Table 4 provides a timeline for major tasks and associated deliverables with the project. This QAPP concerns Tasks 7.1- 7.4.

Table 4. (Element 6) Project schedule timeline.

TASK #	SCHEDULE OF DELIVERABLE DUE DATES	ESTIMATED DUE DATE
1.2	Progress reports	October 20, 2008 and quarterly thereafter
2.1	Meeting STRTAG agenda, summary, and presentation materials	October 20, 2008
2.2	Revised conceptual approach and implementation plan for NNE and TMDL tool development	October 30, 2008
2.3	Target population of California estuaries for estuarine NNE work	October 20, 2008
3.1	Final list of TT, coastal SAG, SF Bay SAG and SAB	October 20, 2008
4.1	Study plan	October 20, 2008
4.2	Database of compiled data on estuaries	July 20, 2009
4.3	Technical memo summarizing data compilation and proposed classes/bioregions	July 20, 2009
4.4	Report on review of SF Bay science with respect to eutrophication	October 20, 2009
4.5	Report summarizing findings of expert review on DO impacts	January 20, 2010
5.1	Meeting agenda and summaries	60 days after each meeting
5.2	Revised implementation plan reflecting SAG and SAB feedback	October 20, 2010
5.3	List of prioritized study plans	January 20, 2010
6.1	Meeting agenda and summaries	90 days after each meeting
6.2	Technical memo summarizing DO numeric endpoint recommendations	October 20, 2010
7.1	QAPP	October 20, 2008

7.2	Graphical output from southern California regional survey	October 20, 2010
7.3	Survey database	December 20, 2010
7.4	Summary report on regional survey	December 20, 2010
8.1	Draft final project report	December 20, 2010
8.2	Final project report	February 20, 2011

6.4 Geographical setting

The estuaries of the Southern California Bight (SCB) serve as refuge, foraging areas, and breeding grounds for a number of threatened and endangered species as well as significant spawning and nursery habitats for commercial and non-commercial fish species. Urbanization of Southern California's coastal watersheds has increased the loads of nutrients and other contaminants to the estuaries, resulting in degradation of beneficial uses. This project is concerned with an assessment of the status of SCB estuaries with respect to nutrient loading/eutrophication.

Estuaries selected for the Eutrophication Assessment will be divided among Lead Scientists based on their interest and available resources. The estuaries and organizations leading the effort in each are listed in Table 5. A targeted "index area" will be sampled within each estuary. The aim is to choose a segment within each selected estuary that are most likely to exhibit symptoms of eutrophication (i.e., develop hypoxia, large primary producer community blooms, etc.). The segment designated as the "index area" will be selected based on existing data and best professional judgment. This segment should reflect the "worst case scenario" for each estuary because of longest residence time or other hydro-geomorphic characteristics. Continuous monitoring will occur at a single depth at this index site. Transects for primary producer communities will also be designated based on best-professional judgment.

<u>Development of Sample Frame:</u>

The sample frame was development by drawing up a comprehensive list of coastal drainages in southern California coastal watersheds and applying the SWRCB's definition of enclosed bay or estuary (see below). Estuarine class was attributed to each system, as defined below. Small creek mouths and open embayments were excluded from the frame.

For estuaries that are perennially tidal, the estuary was characterized as being either "muted" or "fully tidal." Estuaries that had both fully and muted tidal portions had two entries representing both types of regimes within that system.

Table 5. (Element 6): List of Estuaries in Sample Frame.

Estuary	Field Lead	Estuarine Class	Tidal Regime
Tijuana River estuary	Jeff Crooks, TJNERR	Perennially Tidal Lagoon	Full
San Diego Bay- fully tidal		Protected Embayment	Full
San Diego Bay- muted tidal		Protected Embayment	Muted
Famosa Slough*		Perennially Tidal Lagoon	Muted
San Diego River		River Mouth Estuary	Full
Mission Bay		Protected Embayment	Full
Los Penasquitos Lagoon		Seasonally Tidal Lagoon	N/A
San Elijo Lagoon	Doug Gibson, San Elijo Lagoon Conservancy	Seasonally Tidal Lagoon	N/A
Batiquitos Lagoon	Jeff Crooks, TJNERRS	Perennially Tidal Lagoon	N/A
Agua Hedionda		Perennially Tidal Lagoon	N/A
Buena Vista Lagoon*	Karen McLaughlin, SCCWRP	Nontidal Lagoon	N/A
Loma Alta Slough*		Seasonally Tidal Lagoon	N/A
Santa Margarita Estuary		Seasonally Tidal Lagoon	N/A
San Juan Creek		Seasonally Tidal Lagoon	N/A
San Mateo Creek		Nontidal Lagoon	N/A
Santa Ana River wetlands		Perennially Tidal Lagoon	Muted
Bolsa Chica – fully tidal		Perennially Tidal Lagoon	Full
Bolsa Chica – muted tidal		Perennially Tidal Lagoon	Muted
Seal Beach – fully tidal		Protected Embayment	Full
Seal Beach – muted tidal		Protected Embayment	Muted
Ballona Wetlands	Sean Bergquist, SMBRC and Gerald McGowan, City of Los Angeles (Ballona Lagoon only)	Perennially Tidal Lagoon	Muted
Ballona Lagoon		Perennially Tidal Lagoon	Muted
Topanga Lagoon	Rosi Dagit, RCD	Seasonally Tidal Lagoon	N/A
Trancas Lagoon	Sean Anderson, CSU Channel Islands	Seasonally Tidal Lagoon	N/A
Mugu Lagoon- fully tidal		Perennially Tidal Lagoon	Full
Mugu Lagoon – muted tidal		Perennially Tidal Lagoon	Muted
Santa Clara River Estuary	Sean Anderson, CSU Channel Islands and David Thomas, Ventura County Watershed Protection District	River Mouth Estuary	N/A
Devereaux Slough	Lisa Stratton, University of California, Santa Barbara	Seasonally Tidal Lagoon	N/A
Goleta Slough		Seasonally Tidal Lagoon	N/A
UCSB Campus Lagoon		Perennially Tidal Lagoon	Muted

*Asterisk indicates sites that have already been surveyed in 2007-2008 and whose data will be included in the study.

Figure 2. Map of Northern Region Estuaries.

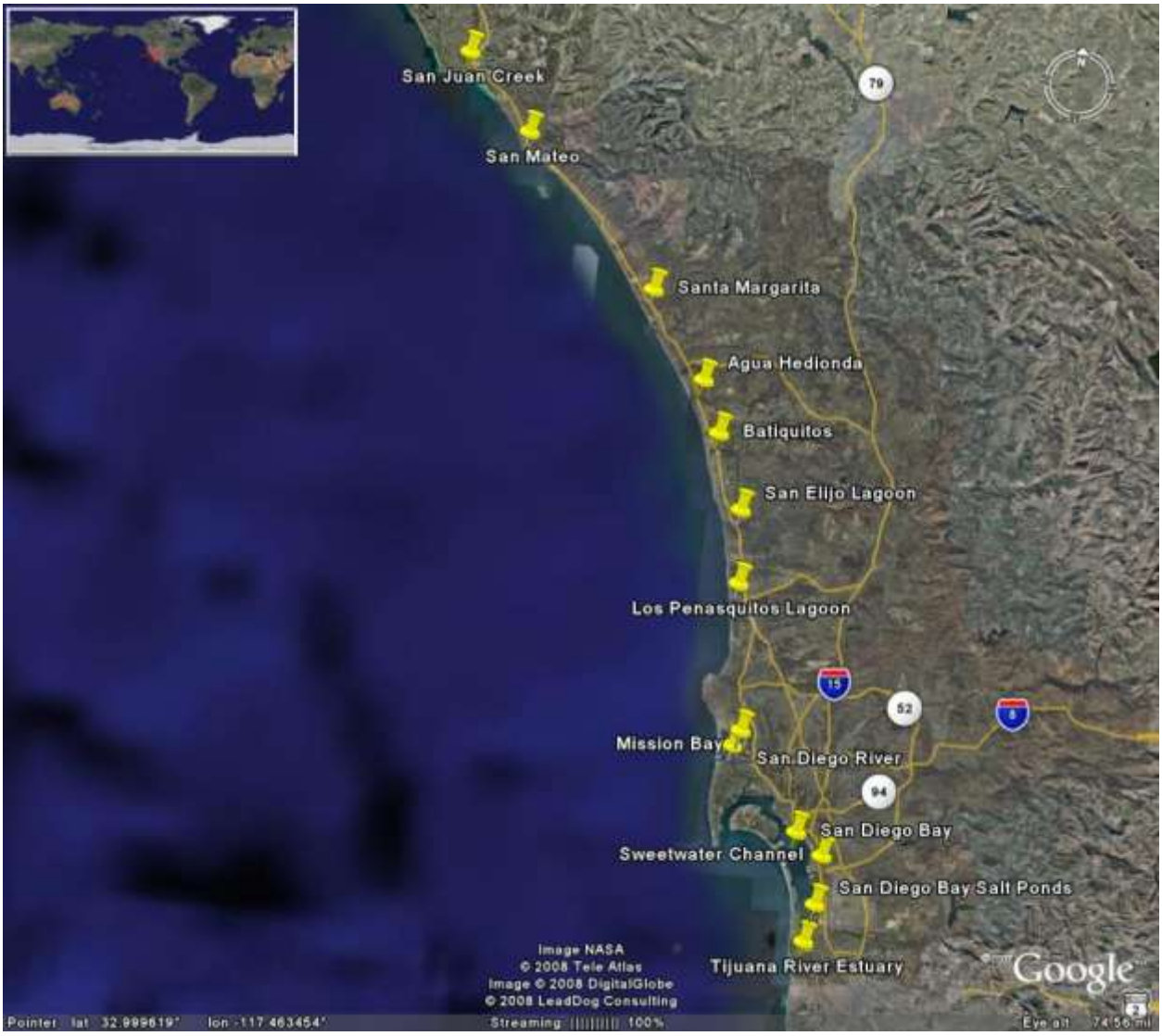


Figure 3. Map of San Diego Region Estuaries.

6.5 Constraints

Constraints on sampling are those outside of our control. For example, changes in estuaries bathymetry following storms, etc., could require a shifting of sampling from planned sites to new sites, or an inability to resample at previously sampled sites. If changes in plans with regard to which sites to sample occur, the Planning Committee will be notified.

Vandalism or other loss of sampling equipment could potentially constrain our ability to collect complete data sets for the continuous monitoring component of the study. Every effort will be made to secure equipment to prevent such losses but in the event of equipment loss, replacement equipment may not collect all required parameters and data sets will have gaps.

7. QUALITY OBJECTIVES AND CRITERIA FOR MEASUREMENT DATA

7.1 Measurement Quality Objectives

Measurement Quality Objectives (MQOs) are quantitative and qualitative statements that clarify study objectives, and specify the tolerable levels of potential errors in the data (U. S. EPA, 2000). As defined in this plan, MQOs specify the quantity and quality of data required to support the study objectives. MQOs are generally used to determine the level of error considered to be acceptable in the data produced by the sampling or monitoring program. They are used to specify acceptable ranges of field sampling and laboratory performance. Data quality objective categories associated with each type of measurement or analysis method in this study are described in the next section.

Measurement or Analyses Type	Applicable Data Quality Objective
Field Testing, dissolved oxygen, pH, salinity, temperature, turbidity, chlorophyll fluorescence	Accuracy, Precision, Completeness
Laboratory Testing, ambient nutrients	Accuracy, Precision, Recovery, Completeness
Laboratory Testing, chlorophyll a	Accuracy, Precision, Recovery, Completeness
Field Testing, primary producer biomass and percent cover	Completeness, Representitiveness
Laboratory Testing, sediment and algae	Accuracy, Precision, Completeness

7.2 Accuracy

Accuracy describes how close the measurement is to its true value. Determination of accuracy entails measurement of a sample of known concentration and comparison against the measured value. The accuracy of chemical measurements will be checked by performing tests on standards prior to and/or during sample analysis at the analytical laboratories. A standard is a known concentration of a certain solution. Standards can be purchased from chemical or scientific supply companies. Standards might also be prepared by a professional partner, *e.g.* a commercial or research laboratory. The concentration of the standards can be unknown to the analyst until after measurements are determined. The concentration of the standards should be within the mid-range of the equipment.

7.3 Precision

The **precision** objectives apply to duplicate and split samples taken during field sampling and laboratory analysis as part of periodic QC checks. Precision describes how well repeated measurements agree. The evaluation of precision described here relates to repeated measurements/samples taken in the field (i.e. field replicates) or the laboratory (laboratory replicates). Precision of laboratory measurements will also be controlled by comparison of the sample to a laboratory matrix spike/matrix spike duplicate (MS/MSD). Precision will be measured b the degree of agreement between the sample and MS/MSD results. Only samples with a ± 25% RPD will be accepted.

7.4 Recovery

Recovery is the accuracy of an analytical test measured against a known analyte addition to a sample, and is calculated as follows:

Recovery = [(Matrix plus spike result – Matrix result) X 100]/Expected matrix plus spike result

Recovery data for the fortified compounds ultimately provide a basis for determining the prevalence of matrix effects in the samples analyzed during the project. If the percent recovery for any analyte in the matrix spike (MS) or matrix spike duplicate (MSD) is less than the recommended warning limit, the analytical output and raw data quantization reports are reviewed. If an explanation for a low percent recovery value is not discovered, the instrument response may be checked using a calibration standard. Low matrix spike recoveries may be a result of matrix interferences and further instrument response checks may not be warranted, especially if the low recovery occurs in both the MS and MSD, and the other QC samples in the batch indicate that the analysis was "in control". An explanation for low percent recovery values will be discussed in reports. Corrective actions taken and verification of acceptable instrument response will be included, if applicable.

7.5 Completeness

Completeness is the fraction of planned data that must be collected in order to fulfill the statistical criteria of the project. There are no statistical criteria that require a certain percentage of data. However, it is expected that 90% of all measurements could be taken when anticipated. This accounts for adverse weather conditions, safety concerns, and equipment problems. We will determine completeness by comparing the number of measurements we planned to collect compared to the number of measurements we actually collected that were also deemed valid. An invalid measurement would be one that does not meet the sampling methods requirements and the data quality objectives. Completeness results will be checked quarterly. This will allow us to identify and correct problems.

7.6 Representativeness

Representativeness describes the degree to which the results of analyses represent the samples collected, and the samples in turn represent the environment from which they were taken. Achieving representativeness in conducting scientific studies or monitoring is important, because without adequate representativeness, it is not valid to extrapolate results of the study to generate conclusions about the system at large. A way to achieve representativeness is by sampling from several locations within the area of interest, and by choosing sampling locations at random, so as to remove the personal **bias** of the sample collector, which would skew the results.

7.7 Measurement Quality Objectives

Since no Water Quality Criteria will be applied as part of this project, target reporting limits or project-specific action levels are dealt with by the inclusion of the required SWAMP Target

Reporting Limits (or lower), where such values exist. There are no action limits for the parameters of interest and no previously collected data will be utilized for this study.

Field and Laboratory Measurement Quality Objectives for the project are provided in Tables 6 and 7.

Table 6. (Element 7) Measurement quality objectives for field measurements.

Group	Parameter	Accuracy	Precision	Recovery	Target Reporting Limit	Completeness
Field Testing	Dissolved Oxygen	± 0.5 mg/L	– will use field triplicates within ± 10%	NA	0.1 mg/L	80%
	Temperature	± 0.5 °C	– will use field triplicates within ± 5%	NA	-5 °C	
	Salinity	± 5%	– will use field triplicates within ± 5%	NA	0.1 ppt	
	pH by meter	± 0.5 units	– will use field triplicates within ± 0.5 or 5%	NA	0.1	
	Turbidity	± 5%	– will use field triplicates within ± 0.5 or 5%	NA	0.5 NTU	
	Chlorophyll Fluorescence	± 0.5 µg/L	– will use field triplicates within ± 0.5 or 5%	NA	0.1 µg/L	
	Macroalgae percent cover	NA	NA	NA	10%	
	SAV percent cover	NA	NA	NA	10%	

Table 7. (Element 7) Measurement quality objectives for laboratory measurements.

Group	Parameter	Accuracy	Precision	Recovery	Target Reporting Limits	Completeness
Conventional Constituents in Water Samples (Nutrients, Chlorophyll)	Nitrate + Nitrite	Standard Reference Materials (SRM, CRM, PT) within 95% CI stated by provider of material. If not available then with 80% to 120% of true value	Laboratory duplicate, Blind Field duplicate, and MS/MSD 25% RPD Laboratory duplicate minimum.	Matrix spike 80% - 120% of control limits at ± 3 standard deviations based on actual lab data.	0.1 mg/L	90 %
	Ammonium				0.1 mg/L	
	SRP				0.01 mg/L	
	Nitrite				0.01 mg/L	
	TN/TDN				0.5 mg/L	
	TP/TDP				0.05 mg/L	
	DOC				0.6 mg/L	
	Chlorophyll a				2.0 µg/L (500 mL filtration)	
Primary Producer Biomass	Wet/Dry Weight	Standard Reference Materials (SRM, CRM, PT) within 95% CI stated by provider of material.	25% RPD Laboratory duplicate minimum	NA	0.05 g	90 %
Sediment	Sediment Chlorophyll a	—±30% of standard reference material	—duplicate ±25% RPD	NA	2.0 µg/L (500 mL filtration)	90 %

	%OC/%ON	Standard Reference Materials (SRM, CRM, PT) within 95% CI stated by provider of material. If not available then with 80% to 120% of true value	Laboratory duplicate, Blind Field duplicate, and MS/MSD 25% RPD Laboratory duplicate minimum.	NA	0.01 %	
	%TP				0.05 %	

* NA, Not Applicable
SRM,standard reporting method
CRM, conventional reporting method
PT, Proficiency testing
CI, confidence interval
MS, matrix spike
MSD, matrix spike duplicate
RPD, relative percent difference

8. SPECIAL TRAINING NEEDS/CERTIFICATION

8.1 Specialized training or certifications.

Personnel assigned to perform field sampling will all participate in training exercises as described below. Personnel conducting laboratory analyses also have prior laboratory experience and training in chemistry, but do not require special certification for this project.

Contract laboratories' Quality Assurance (QA) Officers provide training to laboratory personnel. Information about the training is described in their respective Quality Assurance program documents (Appendices A through C).

Table 8. (Element 8) Required Training for Field Personnel.

Training	Objective

Primary Producer and Freshwater Loading Field Protocols	Train teams in field protocols including:
	• Macroalgae percent cover and biomass
	  ○ Mudflat transects
	  ○ Floating macroalgae
	• SAV percent cover and biomass
	• Simple ID of most common macroalgae and SAV species
	• Benthic diatom collection
	• Water column chlorophyll a, HABs toxin, and ambient nutrient sample collection and processing
	• Freshwater discharge measurements
	• Proper way to fill in data sheets, logs, and forms
	• Discuss chain of custody

Data Sonde Programming, Calibration, and Maintenance:	Train teams in proper use and maintenance of YSI 6600V2 data sondes: • Program all data sondes to record same parameters in same way • Proper calibration and drift check protocols • Deployment and recovery • Downloading data • Data delivery • Proper way to fill in field reports
Macroalgae and Submerged Aquatic Vegetation Identification Workshop	Train teams in identification of macroalgae and SAV species that could be encountered during the survey including. Instruction on how to key out algae species in the laboratory. Voucher specimens and photographs.
Endangered Species Training:	Train teams in recognizing sensitive habitat, protocols for working in sensitive habitat, and endangered species avoidance.
Data Management	Train teams in data management: • How to transfer data from field data sheets to excel templates • Data QA/QC • Data delivery to SCCWRP

8.2 Training and certification documentation.

Field staff training will be documented and filed at SCCWRP. Documentation will consist of a record of the training date, instructor, whether initial or refresher, and whether the training was completed satisfactorily.

The contract laboratories will maintain records of their training respectively. Those records can be obtained if needed from the contract laboratories through the Quality Assurance Officers.

8.3 Training personnel.

The Field Coordinator will coordinate field training of project personnel. The project's QA Officer will oversee training by reviewing documentation to confirm that training has taken place satisfactorily. Training will include proper field sampling techniques to ensure consistent, safe, and appropriate sampling, sampling handling and storage, and proper chain of custody procedures. All training units (described in Table 8) will be prior to the fall of 2008. Additional training will be provided onsite during sampling by either the project manager or field leads.

Day-to-day supervision of data collection activities is the responsibility of the Field Leads. Standard Operating Procedures (SOPs) for field tasks have been complied into a detailed field operations manual (Appendix C). SOPs for laboratory tasks have been developed and are discussed where appropriate in this document. The project SOPs will be updated on a regular basis in order to maintain procedural consistency. The maintenance of a consolidated SOP Manual (based on the project SOPs and currently being prepared) will provide project personnel with a single reference guide for training new personnel, as well as a standardized information source that can be accessed whenever needed.

Table 9. (Element 8) Specialized personnel training or certification.

Specialized Training Course Title or Description	Training Provider	Personnel Receiving Training/ Organizational Affiliation	Location of Records & Certificates *
Primary Producer and Freshwater Loading Field Protocols	Field Coordinator, Karen McLaughlin	All Field Staff	SCCWRP
Data Sonde Programming, Calibration, and Maintenance:	YSI, David Lee	Lead Scientists and Field Leads	SCCWRP
Macroalgae and Submerged Aquatic Vegetation Identification Workshop	Algal Expert, To Be Determined	All Field Staff	SCCWRP
Endangered Species Training	Experts, Richard Zembal Rosi Dagit	All Field Staff	SCCWRP
Data Management	Bight 08 Information Management, Shelly Moore	Lead Scientists	SCCWRP
Training of laboratory personnel in water chemistry analytical procedures	Contract Laboratories' QA Officers	Contract Laboratories' laboratory staff	MSI, UGA

9. DOCUMENTS AND RECORDS

9.1 Report format and data package

Data from this project will be summarized in the form of: 1) a draft and final report, and 2) a project database. All reports will be formatted as Microsoft Word documents. The project database will be in Microsoft Access. The reports and the project's master database will be relinquished to Bight 08 Regional Monitoring Program. Release of data will include comprehensive documentation. This documentation will include database table structures (including table relationships) and lookup tables used to populate specific fields in specific tables. Releases to the public will also include quality assurance classifications of the data (flags, as appropriate) and documentation of the methods by which the data were collected (metadata). Data will be released to the general public once a final report documenting the study has been prepared.

9.2 Field and laboratory records maintenance and storage

All field results will be recorded at the time of completion using standard field data sheets. Lead Scientists will keep all original copies of the field data sheets collected by their respective field teams and send a copy to SCCWRP. Data sheets will be reviewed for obvious outliers and omissions by the Field Leaders before leaving the sample site. Water and sediment sample collection will be cataloged before leaving each site. Chain of custody forms will accompany all samples sent to SCCWRP and contract laboratories. Laboratories will keep records for sample receipt and storage, analyses, and reporting. Data sheets and chains of custody will be stored by SCCWRP in hard copy form for three years from the time the study is completed.

9.3 Data maintenance and storage

Final data will be entered into an electronic database using a set of standardized data protocols for data entry and sharing which will be communicated to field teams during the Data Management Training Session. Interim data will be maintained by the parties generating the data (i.e., field collectors, contract laboratories.) The final forms of project data will be maintained by the Project Manager and kept at SCCWRP during the course of the project. Ultimately all data will be incorporated into the Bight '08 Database. Final database tables will include information on the location of each sampling site, continuous monitoring data, primary producer community biomass and percent cover, freshwater loading, and estuarine ambient nutrients. All files are backed up regularly: incremental backups to a removable disk are performed on all files that have changed on a daily basis. More details are described in section 19 Data Management.

9.4 QAPP maintenance and distribution

Copies of the most current version of the QAPP will be distributed to all parties (identified in A3) who are involved with the project prior to any data collection by the Project Manager (Dr. Sutula). These individuals include QA Officers, data collectors, and contractor laboratories. Copies of any obsolete versions will be destructively recycled, so as not to create confusion.

Table 10. (Element 9) Document and record retention, archival, and disposition information.

	Identify Type Needed	Retention	Disposition
Sample Collection Records	Chain of custody forms	SCCWRP; for 3 years following project completion	Recycled after 3 years
Field Records	Field data sheets	SCCWRP; for 3 years following project completion	Recycled after 3 years

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GROUP B: DATA GENERATION AND ACQUISITION

This section of the QAPP describes in greater detail all aspects of sample collection and analysis, including the sampling process, sample handling procedures, laboratory methods, analytical methods, quality control activities, equipment use and maintenance, and data management.

10. SAMPLING PROCESS DESIGN

10.1 Site selection

The eutrophication assessment aims to characterize the segment within each system that is most likely to develop symptoms of eutrophication. This segment will represent the "index area" for that estuary. The guidance criteria for selecting an "index area" includes: 1) proximity to major inputs of nutrients; 2) maximum residence time of the estuarine water column; 3) deep subtidal areas of the estuary, and 4) field crew safety and access; and 5) adequacy for field sampling.

Survey design takes into account the two gross hydrogeomorphic categories of interest to Bight '08 participants:

- Estuarine class
- Tidal regime (muted or fully tidal; perennially tidal estuaries only)

Resources for the survey provided sufficient funds for a comprehensive census of estuaries in the San Diego Regional Water Quality Control Board's jurisdiction. For this reason, the SCB estuaries were split into two regions: San Diego region estuaries (from San Juan Creek in Orange County south to Tijuana Estuary) and Other (north of San Juan Creek to Santa Barbara County).

For the Bight 08 eutrophication assessment, priority was assigned to protected embayments, seasonally tidal lagoons, and perennially tidal lagoons; river mouth estuaries and nontidal lagoons were given less priority but will be included in the survey as special studies in the San Diego region. Open embayments, creek mouth estuaries, marinas and ports have been excluded from the list of estuaries due to funding limitations. Initial site selection was not stratified by formal estuarine class but rather only used a gross tidal regime. However, post-hoc stratification of the data will be conducted in order to assess differences by estuarine class.

Estuaries were selected proportional to the total number in each class for protected embayments (excluding marinas and ports), seasonally tidal and perennially tidal lagoons in the "Other" region and all sites were selected in the San Diego Region to complete a census of estuaries.

<u>Criteria for site selection for continuous monitoring:</u>
Within the index area, one site will be selected as the continuous monitoring station. This site will be selected such that potential to capture hypoxia is maximized, while accounting for the need for the site to be accessible and minimizing potential vandalism. Water depth should be sufficient to keep the sonde wet during the spring low tides. Use of existing support structures (e.g. bridges abutments, rail road trestles, etc.) will also be explored. Data sondes will be deployed at the bottom of the water column. The location of the continuous monitoring station

should be recorded with a GPS unit. For seasonally tidal lagoons, every effort should be made to install the data sonde in the same locations for the winter and summer monitoring.
Site selection for deployment of data sondes follows the conceptual approach of an "index area" within the estuary that could be expected to exhibit the most severe symptoms of eutrophication. The following criteria should be used to select the site for deployment of data sondes:

- Logistics of sonde deployment, data sonde maintenance, safety and vandalism/theft.
- Existing site where historical continuous DO data exist.
- Area of maximum residence time, as identified by existing data and best professional judgment. Areas of an estuary with higher residence time could be expected to exhibit more severe symptoms of hypoxia
- Maximum depth. Areas that are deeper could be expected to exhibit extended periods of hypoxia. Every effort should be made to insure that the data sonde sensors remain under water at low tide.
- Proximal to the major site of wet weather fine-grained sediment deposition in the estuary

<u>Criteria for site selection for primary producer community assessment:</u>
General Guidance
In general, the location of the primary producer transects will be driven by the goal of capturing spatial variability in biomass and/or percent cover. In contrast to the continuous monitoring location, the primary producer transects might not all be located at the location in the estuary that displays the greatest symptoms of eutrophication. The three primary producer transects should be spaced throughout the system along spatial gradients. There are three major spatial gradients of interest within an estuary that should be considered:

- Salinity gradient/Hydrology
- Grain size
- Nutrient loading

In some estuaries, the observed gradients in these three variables co-occur. In other estuaries, it is possible to have them diametrically opposed. Site-specific considerations may cause a deviation from this general guidance and will be noted when this occurs. Transect locations should be agreed upon by the field coordinator and the lead scientist for each of the field teams.

Macroalgal Transects
Within each index area, three transects must be laid out in the intertidal area for macroalgae biomass and percent cover, parallel to the water's edge and along the same elevational contour. These transects should each be 30 meters long, unless the total length of the bank is less than 50 meters in which case each transects should be 10 meters long. Areas with extensive and accessible mudflats where algae is known to accumulate should be targeted. If wind conditions consistently blow algae to one particular section of the estuary, transect locations should be targeted this area. Areas with sensitive habitat (nesting grounds) and cut-banks should be avoided. Transects should be laid out during spring-low tides (when mudflat area is most exposed), approximately ¾ of the distance upslope from the water's edge at MLLW (approximately 1 to 2 feet above MLLW). To establish this transect as a permanent area, the distance to the start of the transect from the edge of the emergent vegetation (demarcated by a permanent stake of grey PVC pipe) should be measured and recorded. If water-levels in

seasonally tidal system exceed 30 cm at the transect location, sampling should be aborted or rescheduled. Transects should be located to capture the major areas of macroalgal accumulation. Macroalgal mats should recover between sampling events so transect sites can be the same for each sampling period. Sampling of this area has been demonstrated to be representative of macroalgae on intertidal channels and mudflats (Kennison et al. 2003).

Benthic Chlorophyll a
Sampling for the benthic chlorophyll *a* transects should be located just down-slope, when possible, of the macroalgal transects. To minimize trampling of the macroalgae transect, sampling for benthic chlorophyll *a* should occur at the start and end of the transects in water that is approximately 30 cm deep (down-slope of the macroalgae transect). Sediment sampling should always occur at this depth. For perennially tidal systems, this site can be established as a permanent location by measuring the distance from the edge of the emergent vegetation (staked with grey PVC pipe) to the benthic microalgal sampling locations as a means of relocating the appropriate area. However, in seasonally tidal systems, the mudflats may be flooded when the ocean inlet is closed. In which case the location of the sediment sampling may change along the elevation gradient (in rare cases, sediment may be collected from flooded emergent vegetation). In this case distance from the PVC pipe should be recorded for each sampling event.

Water Column Chlorophyll a *and HABs Toxin*
Samples for water column chlorophyll *a,* ambient nutrients, and for HABs toxins should only be collected at one transect in each estuary (transect nearest to data sonde location). These samples should be collected from the surface water co-incident with the downstream sediment sampling in water that is approximately 30 cm depth, co-located near the end of the macroalgae transects.

Floating Macroalgae
In systems where floating macroalgae is present (unattached to the sediment and floating on the water surface), percent cover and biomass will be estimated co-incident with the sediment and water column sampling in water that is 30 cm deep. Percent cover and biomass will be estimated from two quadrats floated on the surface at each of benthic and water column sampling locations (typically down-slope of the start and end of the macroalgae transect line).

Brackish Water Submerged Aquatic Vegetation
Three transects must be laid out in the shallow subtidal areas of seasonally tidal lagoons, these transects should be perpendicular to the channel contour. These transects should each extend from bank to bank (when channel width is $\leq$ 50 m) and may be variable in length. SAV transects can be located near one or more macroalgal transects, but do not necessarily have to be co-located. SAV transects are only required where brackish water SAV is known to occur, is accessible, and does not interfere with sensitive nesting habitat. Because SAV may not recover from the biomass removal in the interim between sampling events, the SAV transects may be relocated each month.

<u>Criteria for site selection for freshwater loading:</u>
Mass loading stations should be located in the stream, river or storm drain that represents the major freshwater source(s) to the site. The site should be located upstream of the range of tidal influence and should not possess any estuarine vegetation. Sites should be accessible by foot.

Where possible, the station should be co-located with existing U.S.G.S gauging station or County/City NPDES mass loading stations.

10.2 Sampling design strategy

The basic approach to the eutrophication assessment is a probability-based survey in which sites are randomly selected from a comprehensive list of estuaries. Because eutrophication is likely to vary spatially within any given estuary, sampling will occur in a targeted index area, or segment, within each selected estuary; thus reporting on eutrophication will be on a "percent of estuary segments" basis. This survey is not meant to be a comprehensive characterization of any individual estuarine system, but rather to characterize the region overall. In each of these estuary segments, the magnitude of eutrophication of southern California estuaries will be assessed via a series of biological response indicators. Such biological response indicators are a more direct measure of estuarine beneficial use impairment. These biological response indicators include dissolved oxygen, macroalgal biomass and percent cover, surface water phytoplankton biomass (e.g. chlorophyll a), benthic algal biomass (sediment chlorophyll a), and nuisance submerged aquatic vegetation (SAV) density and percent cover. The use of multiple indicators in a "weight of evidence" approach provides a more robust means to assess ecological condition and determine impairment.

The eutrophication assessment sampling design for Bight 08 will be divided into three primary components:

1. Continuous monitoring of water quality parameters (including dissolved oxygen, salinity, temperature, pH, and turbidity), and
2. Transects of primary producer biomass and percent cover,
3. Measurement of freshwater nitrogen and phosphorus concentrations and water level (where pre-existing stream gauges are not available to provide flow).

Details of the protocols used for each of these field surveys are contained in the Field Methods Manual which is attached to this QAPP in Appendix C.

The specific sampling work that will occur in each estuary is as follows:

- Continuous monitoring of water quality parameters
- Assessment of macroalgae biomass and percent cover
- Measurement of benthic diatom chlorophyll and sediment nutrient content
- Measurement of water column nutrient concentrations and suspended chlorophyll a
- Determination of suspended harmful algal bloom toxins domoic acid and microcystin
- Assessment of floating algae biomass and percent cover (where applicable)
- Assessment of brackish water submerged aquatic vegetation (where applicable)
- Estimates of freshwater nutrient concentrations and flow and thereby nutrient loading.

Timing for this work is indicated in Table 2.

Continuous Monitoring of Water Quality Parameters

The purpose of continuous monitoring is to obtain data on when hypoxia occurs in each estuary and the duration of hypoxic events. There is also interest in environmental conditions when

hypoxia occurs. Near-continuous measurements helps to assess if depressed DO occurs for short or long time periods, associated with hydrophysical events such as nocturnal low tides, or correlated with macroalgal biomass, chlorophyll *a*, or percent cover. Dissolved oxygen is being considered as a potential indicator for eutrophication and there is a need to assess appropriate thresholds at which dissolved oxygen levels become critical to the biological integrity of each estuary.

The following parameters will be continuously monitored at each site: temperature, salinity (conductivity), water depth (to interpret tidal exchange and water residence time), chlorophyll by fluorescence (to assess phytoplankton biomass), dissolved oxygen by optical probe, pH, and turbidity. These parameters will be measured using *in situ* sensors equipped with data loggers, YSI 6600 V2 data sondes. These data sondes should be programmed to measure parameters every 5 minutes and, with routine maintenance, will be deployed for approximately four months during the growing season (Jun-Oct) for perennially tidal systems, and from Dec 08- Oct 09 for seasonally tidal lagoons. The additional sampling months for seasonally tidal lagoons is designed to catch time periods when the lagoon is open to the ocean and when it is closed. Data sondes will need to be removed from the water to download the data and for maintenance (removal of biofouling, re-calibration, replace batteries, etc.) approximately once every two weeks (8 times during the four month deployment). Data sondes should be "down" for no more than 8 hours for maintenance. The sondes have internal batteries and memory cards. Deployment and recovery of data sondes typically requires 2 people. Most sites will be accessible by foot, though some sites may require use of a small boat or kayak. Training and intercalibration exercises will be conducted through SCCWRP to insure data comparability. YSI will provide training on proper maintenance and calibration of data sondes.

Assessment of Primary Producer Communities

Aquatic primary producer communities targeted for this survey include macroalgae, benthic microalgal mats, phytoplankton, and submerged aquatic vegetation. The purpose of this study element is to characterize seasonal variation in the standing biomass and cover of these primary producer communities.

Primary producer biomass will be measured in estuaries and lagoons every other month for one year. Macroalgae, benthic microalgae, water column phytoplankton, and nuisance SAV biomass and percent cover will be measured in three transects within the estuary. Optimally, these transects may be located in the same area of the estuary. Decision on the precise locations will depend on existing data on the presence and distribution of each primary producer type. Water column chlorophyll a and domoic acid samples will be measured in conjunction with the benthic microalgal transects. Monitoring primary producer biomass typically requires 2 people. Training will be provided by SCCWRP personnel to insure all parties are sampling in the same way.

Freshwater Nutrient Loading

One objective of the survey is to evaluate whether a dose-response relationship exists between nutrients loads and estuarine biological response. Terrestrial nutrient loads to each estuary will be estimated in the Bight '08 Water Quality Study through a combination of empirical wet and dry weather measurements at major mass emission stations and modeling studies. While these estimates may provide reasonable estimates of loads for most estuarine sites monitored in this

assessment, some sites may be decoupled from influence from watershed loads, because of fragmentation and impoundment from dikes, levees, etc.

The purpose of this task is to provide additional data that support modeling of nutrient loads to each site. Specifically, this includes: 1) measurement of total nitrogen and phosphorus concentrations at the major source of freshwater input to the site, and 2) where stream gauging does not exist, measurement of continuous water level and periodic measurements of channel cross section and velocity to develop a rating curve. This monitoring will occur at the site's designated "mass loading station," an area in a stream or river that is sufficiently upstream of tidal influence.

10.3. Field Data Sheets

Field data sheets for the primary producer biomass and percent cover estimates and field logs for continuous monitoring should be maintained by all field teams. Team leaders should review all data sheets and logs before leaving a site to insure that all data has been collected and all QA/QC guidelines have been met. Copies of the field data sheets should be sent as hard-copies to SCCWRP with the samples they accompany. Alternatively, hard-copies of field data sheets may be scanned and emailed to field coordinator as PDF files. Field logs can be sent to SCCWRP as hard-copies at the end of the monitoring period. Organizations will be expected to keep paper copies on file. Examples of data sheets and logs are in Appendix C.

10.4. Project activity schedules

Sampling to develop the dataset will occur during the water year November 2008 through October 2009. Continuous monitoring of water quality parameters is required from June through October 2009 for all perennially tidal estuaries, although where resources are available, sampling may be extended to include winter and spring seasons. The summer months were deemed most critical for continuous monitoring because these are the months during which dissolved oxygen demand is greatest and when hypoxia would be most likely to develop. In addition to the summer sampling, seasonally tidal estuaries will be monitored from December 2008 through October 2009. The additional sampling for seasonally tidal lagoons was due to the fact that some seasonally tidal lagoons are closed to ocean exchange during the summer, while others are closed during the winter. When the ocean inlets are closed, water residence time in these lagoons is greatly increased, which in turn increases the chance of low dissolved oxygen concentrations. Monitoring in these lagoons was extended beyond summer to capture this seasonal variation in dissolved oxygen levels.

Measurement of primary producer communities will occur every other month in all estuaries for a year beginning in November 2008 and ending in October 2009. This monitoring will provide information on when blooms occur in each class of estuary, how far they extend spatially, and how long they endure.

Measurement of freshwater nitrogen and phosphorus concentrations will be conducted every other month in the winter (coincident with primary producer monitoring) and every month in the summer (coincident with some maintenance events for continuous monitoring). Where no

existing gauging of stream flow exists, water level will also be measured by continuous water level sensors in selected systems. Wetted channel width and velocity will be measured across the channel cross section in order to develop a rating curve for the channel. These data would be used to supplement the modeling of nutrient loads from the watershed shared by the Bight '08 Offshore Water Quality Component. Efforts in this area will be increased during dry periods (summer) due to the difficulties in modeling dry weather flows. Wet weather data will be used to ground-truth wet weather modeling already underway.

Monitoring for domoic acid will occur coincident with primary producer community monitoring in March, May, and June, the time period in which *Pseudo-nitzschia* is known to bloom. Monitoring for microcystin will occur once a month from June through September, the peak period for cyanobacteria production.

Table 11. (Element 10) Timeline of components of Eutrophication Assessment

Month	Continuous Monitoring	Primary Producer Communities	Freshwater Loading	HABs Toxins
Oct 08				
Nov 08		X	X	
Dec 08	X (ST and NT only)			
Jan 09	X (ST and NT only)	X	X	
Feb 09	X (ST and NT only)			
Mar 09	X (ST and NT only)	X	X	X (domoic acid)
Apr 09	X (ST and NT only)			
May 09	X (ST and NT only)	X	X	X (domoic acid)
Jun 09	X (All)		X	X (domoic acid + microcystin)
Jul 09	X (All)	X	X	X (microcystin)
Aug 09	X (All)		X	X (microcystin)
Sept 09	X (All)	X	X	X (microcystin)
Oct 09				

note: ST = seasonally tidal lagoons, NT = nontidal

10.5. Action plan for changes to site accessibility

Over the course of the project, issues such as flooding or drought, channel migration, and changes in ownership of land or permission to access sites could result in an inability to resample at previously sampled sites. If this occurs, new sites fulfilling the criteria of the old sites will be identified, and changes will vetted by the Planning Committee.

10.6. Reconciliation of natural variation with project information

As with any study that takes place in the natural world, as opposed to a controlled laboratory environment, natural variation will play into this project in many ways. Such variation can be problematic, as it can result in "noise" in the dataset, which makes it more difficult to pick up the true signals under investigation, and establish relationships between stated predictor and response variables of interest. Potential sources of natural variation that can affect benthic nutrient flux, sediment deposition, and algal biomass, will be measured as either a part of this study or by the stakeholder sampling efforts (e.g. ambient water nutrient concentrations, nutrient

loading, surface sediment grain size and nutrient content, etc.), thus allowing the application of statistical means to normalize for parameters, as necessary, and minimize noise in the dataset.

10.7. Reduction of bias

Bias could affect the results of the work undertaken in this study. Use of the Master List to select estuaries included in the sample frame limited bias introduced during site selection. Another potential source of bias could be slight differences in execution of protocols by different participating organizations. To limit this bias, all field teams must participate in a series of rigorous training sessions (see Section 8) prior to the inception of field work. To the extent practicable, estuaries will be sampled synoptically to limit bias introduced by sampling under different environmental conditions.

11. SAMPLING METHODS

All field teams will receive "kits" of uniform equipment (sampling and monitoring equipment, prepared bottles and uniform, pre-printed labels, coolers, etc.) to insure that all sampling and monitoring is conducted uniformly among participating organizations. As necessary, sample bottles will be cleaned (via acid wash) and/or sterilized prior to use. For all analyses to be conducted in-house at SCCWRP and by MSI and UGA, sample containers will be prepared by SCCWRP staff. All SOPs for sampling protocol are attached in Appendix C- Bight 08 Estuarine Eutrophication Assessment Field Operations Manual VERSION 8.

11.1. Continuous Monitoring of Water Quality Parameters

Dissolved oxygen, chlorophyll fluorescence, turbidity, temperature, salinity, and pH will be continuously monitored using in situ (YSI 6600 V2 multiparameter water quality data sondes). A minimum of one sonde will be deployed in an index area of each estuary (area most likely to exhibit symptoms of eutrophication) for a minimum of four months (June 2009 through September 2009) to document periods of low dissolved oxygen. The data sondes will be programmed to log data in 15-minute intervals. The sondes have internal batteries and memory cards and will be cleaned, recalibrated, and data downloaded monthly, at minimum.

11.2. Macroalgae Percent Cover and Biomass

Macroalgae and percent cover will be monitored in each selected estuary every other month for one year. Within each index area, three transects will be laid out in the intertidal area for macroalgae biomass and percent cover, parallel to the water's edge and along the same elevational contour. These transects should each be 30 meters long, unless the total length of the bank is less than 50 meters in which case each transects should be 10 meters long. Transects should be laid out during spring-low tides (when mudflat area is most exposed), approximately ¾ of the distance upslope from the water's edge at MLLW (approximately 1 to 2 feet above MLLW). To establish this transect as a permanent area, the distance to the start of the transect from the edge of the emergent vegetation (demarcated by a permanent stake of grey PVC pipe) should be measured and recorded. If water-levels in seasonally tidal system exceed 30 cm at the transect location, sampling should be aborted or rescheduled. Transects should be located to capture the major areas of macroalgal accumulation. Macroalgal mats should recover between sampling events so transect sites can be the same for each sampling period. Sampling of this area has been demonstrated to be representative of macroalgae on intertidal channels and mudflats (Kennison et al. 2003).

Along each of the three transects we will estimate percent cover of macroalgae in 10 randomly chosen 0.5-m^2 quadrats using the point intercept method. Of those 10 quadrats, biomass will be harvested from a subset of 5 using a 4 in^2 PVC biomass sampler and stored in a labeled ziploc bag on ice in the dark until delivery to the lab. Not every site will be occupied by macroalgae during each sampling event, so the actual biomass samples will be dependent on seasonal patterns. Each of the biomass samples will be collected will be cleaned and weighed, dried in an oven at 60 ºC, and reweighed to determine wet and dry weights.

In addition, in systems where floating macroalgae is present (floating on the water surface, may or may not be attached to sediment), floating algae percent cover and biomass will be estimated co-incident with the sediment and water column sampling in water that is 30 cm deep. Percent cover and biomass will be estimated from two quadrats floated on the surface in water that is 30 cm deep just downslope to the start and end of the macroalgae transect line. Floating algae biomass will be cleaned, weighed, dried, and reweighed.

11.3. Assessment of Benthic Diatom Communities and Sediment Nutrient Content

Sampling for benthic chlorophyll *a* (i.e. benthic diatom communities) should be located just down-slope, when possible, of the macroalgal transects. To minimize trampling of the macroalgae transect, sampling for benthic chlorophyll *a* should occur at the start and end of each of the 3 macroalgae transects in water that is approximately 30 cm deep (typically down-slope of the macroalgae transect). Sediment sampling should always occur at this depth. At each of these locations, ten (10) small sediment samples should be collected from the top 1 cm of sediment using a syringe sediment sampler. The 10 samples should be collected and homogenized in a ziploc bag, labeled and stored on ice until delivery to the laboratory. Once in the laboratory, a split of each sample should be collected and frozen for benthic chlorophyll *a* analysis and the remaining sediment should be weighed wet, dried in an oven at 60 ºC, and reweighed dry. A subset of the dried sample will be ground for sediment total nitrogen, total phosphorus and total organic carbon. The remaining, un-ground sediment will be analyzed for percent sand using standard sieves.

11.4. Measurement of Estuarine Ambient Nutrients, Chlorophyll *a*, and HABs Toxins

At one of the three transect sites (the transect site closest to the continuous monitoring station), surface water grab samples (~10 cm below the surface in water that is 30 cm deep) will be collected and analyzed for TN and TP at minimum and may also be analysed for TDN, TDP, nitrate, nitrite, ammonia, SRP, DOC, chlorophyll a, and HABs toxins (domoic acid and microcystin when relevant) if funding allows. Dissolved constituents, if collected, will be field filtered through 0.45 μm filters into triple rinsed containers. This data will be collected to estimate the variability in nutrient concentrations within each estuary.

11.5. Submerged Aquatic Vegetation Percent Cover and Biomass

Three transects will be laid out in the shallow subtidal areas of estuarine systems that have brackish water habitat (seasonally tidal systems). These transects should be perpendicular to the channel contour. These transects should each extend from bank to bank and may be variable in length. SAV transects can be located near one or more macroalgal transects, but do not necessarily have to be co-located. SAV transects are only required where brackish water SAV is known to occur, is accessible, and does not interfere with sensitive nesting habitat. Because SAV may not recover from the biomass removal in the interim between sampling events, the SAV transects may be relocated each month.

For estuaries where the distance from bank to bank is greater than 50 m, five submerged aquatic vegetation sampling stations will be laid out (one in the thalweg, two sites located 1/3 of the

distance from the thaweg to each bank, and two sites located 2/3 of the distance from the thalweg to each bank). If the distance from bank to bank is less than 10 m, three submerged aquatic vegetation sampling stations will be laid out (one in the thalweg, and two additional sites located ½ the distance from the thalweg to each bank). Percent cover will be estimated using a viewing bucket at each of these sites and biomass will be collected using a rake sampler. Biomass samples will be stored in a labeled ziploc bag on ice in the dark until delivery to the lab. Not every site will be occupied by SAV during each sampling event, so the actual biomass samples will be dependent on seasonal patterns. Each of the biomass samples will be collected will be cleaned and weighed, dried in an oven at 60 ºC, and reweighed to determine wet and dry weights.

In addition, in systems where floating macroalgae is present (floating on the water surface, may or may not be attached to sediment), floating algae percent cover and biomass will be estimated co-incident SAV percent cover and biomass samples. Percent cover and biomass will be estimated from one quadrat floated on the surface above the SAV. Floating algae biomass will be cleaned, weighed, dried, and reweighed.

11.6. Freshwater Flow and Nutrient Concentrations

Loading of nutrients into each estuary will also be estimated by collecting flow data and nutrient concentrations at the major sources of freshwater input into each estuary. An AV flow meter (Marsh-McBirney, Inc. Flow-Mate 2000) will be used to measure stream flow in streams that do not currently have flow gauges (maintained by either the U.S. Geological Survey or other group). With this instrument, the velocity is measured with acoustic Doppler technology, and therefore capable of measure very slow flow velocities. Nutrient concentrations at each freshwater input will also be measured by collecting a water sample at approximately 10 cm depth from the thalweg of each stream. Water samples surface will be collected and analyzed for TN, and TP. Additional samples may be collected for TDN, TDP, nitrate, nitrite, ammonia, SRP, and DOC if additional funding can be obtained; however, these constituents are not critical to the study. Dissolved constituents, if collected, will be field filtered through 0.45 μm filters into triple rinsed containers and stored on ice in the dark until delivered to the lab where samples will be frozen until analysis.

11.6 Contingencies and corrective actions

Complete sample collection protocols can be found in the Eutrophication Assessment Field Methods Manual (Appendix C). Protocols mentioned above may not be modified without notifying the Field Coordinator. Permanent modifications to the protocols must be vetted fully by the Planning Committee.

The Lead Scientists have primary responsibility for responding to failures in the sampling or measurement systems. Deviations from defined protocols and the project QAPP are documented in the comment section of field notes. If any equipment fails, field personnel will report the problem in the comment section of their field notes and will not record data values for the variables in question. Actions will be taken to replace or repair broken equipment as soon as possible. Replacement equipment will be available to all field teams. No data will be entered

into the project database that are known to be collected with any faulty equipment. It is the combined responsibility of all members of the sampling crew to determine if the performance requirements of the specific sampling method have been met, and to collect an additional sample if required. Any deviations from field protocols defined in the project QAPP will be reported to the Project Manager immediately.

A close evaluation of data following the first sampling period will be conducted to identify any data gaps that should be filled or determine where loss of data occurred due to environmental factors. If any such problems are identified, sampling protocols will be modified accordingly (e.g., sampling sites may be moved to correct for environmental disturbances, etc.). Any corrective actions will be documented on the field data sheets and in the field SOPs by the Lead Scientist.

11.7. Support Facilities

MSI and UGA laboratories are the only support facilities used during this project.

11.8. Sampling locations and sampling methods

Table 12. (Element 11) Sampling locations and sampling methods.

Sampling Location	Matrix	Depth (units)	Analytical Parameter	# Samples (include field duplicates)	Sampling SOP #	Sample Volume	Containers #, size, type	Preservation (chemical, temperature, light protected)	Maximum Holding Time: Preparation/ analysis
All index areas	Water	Bottom water	dissolved oxygen, pH, temperature, salinity, turbidity, chlorophyll	Continuous for 4 month minimum (Jun-Sep 09) Every 15 mins	Field SOPs V6 Appx. C	N/A	N/A	N/A	N/A
Macroalgae transect site closest to data sonde	Water	0.1 m below surface	water column chlorophyll *a*	2 per site	Field SOPs V6 Appx. C	250 mL	2, Whatman GF/F glass fiber filter	Cool to 4°C, dark; freeze	30d
Macroalgae transect site closest to data sonde	Water	0.1 m below surface	Domoic acid	2 per site (Feb, Apr, Jun only)	Field SOPs V6 Appx. C	250 mL	2, Whatman GF/F glass fiber filter	Cool to 4°C, dark; freeze	30d
Macroalgae transect site closest to data sonde	Water	0.1 m below surface	microcystin	2 per site (Jun, Jul, Aug, Sept only)	Field SOPs V6 Appx. C	250 mL	2, Whatman GF/F glass fiber filter	Cool to 4°C, dark; freeze	30d
Macroalgae transect site closest to data sonde	Water	0.1 m below surface	nitrate + nitrite, nitrite, SRP, ammonium	1 of each per site (duplicate 5%)	Field SOPs V6 Appx. C	15 mL	1, 30 mL polyethylene bottle	Cool to 4°C, dark; filter 0.45 μm within 6h, Freeze	30d
Macroalgae transect site closest to data sonde	Water	0.1 m below surface	TDN and TDP	1 of each per site (duplicate 5%)	Field SOPs V6 Appx. C	15 mL	1, 30 mL polyethylene bottle	Cool to 4°C, dark; filter 0.45 μm within 6h, Freeze	30d
Macroalgae transect site closest to data sonde	Water	0.1 m below surface	TN and TP	1 of each per site (duplicate 5%)	Field SOPs V6 Appx. C	15 mL	1, 30 mL polyethylene bottle	4°C, dark, Freeze	30d

Sampling Location	Matrix	Depth (units)	Analytical Parameter	# Samples (include field duplicates)	Sampling SOP #	Sample Volume	Containers #, size, type	Preservation (chemical, temperature, light protected)	Maximum Holding Time: Preparation/ analysis
Macroalgae transect site closest to data sonde	Water	0.1 m below surface	DOC	1 of each per site (duplicate 5%)	Field SOPs V6 Appx. C	10 mL	1, 20 mL acid-washed glass bottle	Cool to 4°C, dark; filter 0.45 µm within 6h, Freeze	30d
Freshwater loading site	Water	0.1 m below surface	TN and TP	1 of each per site (duplicate 5%)	Field SOPs V6 Appx. C	15 mL	1, 30 mL polyethylene bottle	4°C, dark, Freeze	30d
Oceanward and landward ends of macroalgae transects	Sediment	Top 1 cm	Wet/dry weights	2 each, 10 subsamples composited into one	Field SOPs V6 Appx. C	30 mL	1, Ziploc bag	Cool to 4°C, dark; Oven dry 50°C for 48 h, room temp.	30d
Oceanward and landward ends of macroalgae transects	Sediment	Top 1 cm	% Sand	2 each, 10 subsamples composited into one	Field SOPs V6 Appx. C	30 mL	1, Ziploc bag	Cool to 4°C, dark; Oven dry 50°C for 48 h, room temp.	30d to dry; indefinitely once dried
Oceanward and landward ends of macroalgae transects	Sediment	Top 1 cm	%OC & %TN	2 each, 10 subsamples composited into one	Field SOPs V6 Appx. C	30 mL	1, Ziploc bag	Cool to 4°C, dark; Oven dry 50°C for 48 h, room temp.	30d to dry; indefinitely once dried
Oceanward and landward ends of macroalgae transects	Sediment	Top 1 cm	%TP	2 each, 10 subsamples composited into one	Field SOPs V6 Appx. C	30 mL	1, Ziploc bag	Cool to 4°C, dark; Oven dry 50°C for 48 h, room temp.	30d to dry; indefinitely once dried
Oceanward and landward ends of macroalgae transects	Sediment	Top 1 cm	Sediment chlorophyll *a*	2 each, 10 subsamples composited into one	Field SOPs V6 Appx. C	15 mL	2, 50 mL conical tube	Cool to 4°C, dark; freeze within 6 hours.	30d

Sampling Location	Matrix	Depth (units)	Analytical Parameter	# Samples (include field duplicates)	Sampling SOP #	Sample Volume	Containers #, size, type	Preservation (chemical, temperature, light protected)	Maximum Holding Time: Preparation/ analysis
All macroalgae transect sites	biomass	Sediment surface	Wet/dry weights	5 max per transect (when present)	Field SOPs V6 Appx. C	variable	1, Ziploc bag	Cool to 4°C, dark; clean, oven dry 60°C for 48 h, room temp.	30d
All floating algae samples for macroalgae transect sites	biomass	Water surface	Wet/dry weights	4 maximum (when present)	Field SOPs V6 Appx. C	variable	1, Ziploc bag	Cool to 4°C, dark; clean, oven dry 60°C for 48 h, room temp.	30d
All floating algae samples for SAV sites	biomass	Water surface	Wet/dry weights	3 max, transects < 50m; 5 max, transects > 50m (when present)	Field SOPs V6 Appx. C	variable	1, Ziploc bag	Cool to 4°C, dark; clean, oven dry 60°C for 48 h, room temp.	30d
All SAV transect sites	biomass	Sediment surface	Wet/dry weights	3 max, transects < 50m; 5 max, transects > 50m (when present)	Field SOPs V6 Appx. C	variable	1, Ziploc bag	Cool to 4°C, dark; clean, oven dry 60°C for 48 h, room temp.	30d
All macroalgae transect sites	biomass	Sediment surface	% cover	5 max per transect	Field SOPs V6 Appx. C	N/A	1, Ziploc bag	N/A	N/A
All floating algae samples for macroalgae sites	biomass	Water surface	% cover	4 maximum	Field SOPs V6 Appx. C	N/A	1, Ziploc bag	N/A	N/A
All floating algae samples for SAV sites	biomass	Water surface	% cover	3 max, trans < 50m; 5 max, trans > 50m	Field SOPs V6 Appx. C	N/A	1, Ziploc bag	N/A	N/A
All SAV transect sites	biomass	Sediment surface	% cover	3 max, trans < 50m; 5 max, trans > 50m	Field SOPs V6 Appx. C	N/A	1, Ziploc bag	N/A	N/A

12. SAMPLE HANDLING AND CUSTODY

Each sample will be identified and tracked by the estuary code, transect #, parameter, volume (if applicable), date and time sampled, and split number (if applicable). Sample log numbers will be handled by SCCWRP for the samples shipped.

All containers provided by SCCWRP will be pre-labeled and field teams will be responsible for filling in the required fields. Bottles should be labeled with Avery™ Weather Proof White Labels Labels 1" x 2⅝" (Avery # 5520). Dates will be reported as day/month/year. Following sampling external labels should be covered with clear postal tape to prevent them from falling off the container. Below follows a description of the fields for each sample type:

Water Column Chlorophyll a:

Bight 08 Eutrophication Assessment
Estuary_____
Date:_____ Time:_____
Water Chl *a* – Transect #:_____
Vol. filtered:_____ Rep.:_____

Benthic Chlorophyll a:

Bight 08 Eutrophication Assessment
Estuary_____ Transect #:_____
Date:_____ Time:_____
Benthic Chl – Upstream / Downstream
Plugs:_____

Water Column Harmful Algal Bloom Toxin:
Domoic Acid:

Bight 08 Eutrophication Assessment
Estuary_____ Transect #:_____
Date:_____ Time:_____
HABs (DA) – Upstream / Downstream
Vol. filtered:_____ Rep.:_____

Microcystin:

Bight 08 Eutrophication Assessment
Estuary_____ Transect #:_____
Date:_____ Time:_____
HABs (mcys) – Upstream/ Downstream
Vol. filtered:_____ Rep.:_____

Macroalgal Biomass:

Bight 08 Eutrophication Assessment
Estuary_____
Date:_____ Time:_____
Macroalgae Biomass
Quadrat #:_____ Transect #:_____

SAV Biomass:

Bight 08 Eutrophication Assessment
Estuary_____
Date:_____ Time:_____
SAV Biomass
Quadrat #:_____ Transect #_____

Ambient Nutrients:

Estuarine Ambient Nutrients:

Bight 08 Eutrophication Assessment
Estuary_____ Transect #:_____
Date:_____ Time:_____
Ambient Nuts. - Constituent:_____
Vol. filtered:_____ Rep.:_____

Freshwater Nutrients:

Bight 08 Eutrophication Assessment
Estuary_____ ME site #:_____
Date:_____ Time:_____
Freshwater Nuts. - Constituent:_____
Vol. filtered:_____ Rep.:_____

All observations recorded in the field as well as information recorded in processing all field samples in the laboratory will be entered into an Access database. Hard copies of the field and laboratory data sheets will be maintained in a project notebook by the Field Coorinator, and by laboratory personnel, respectively. Field data sheets and chain of custody forms (CoCs) will be filled out by field teams. CoCs will accompany the water, biomass, and sediment samples delivered to the laboratories. An example of CoC form is shown in Appendix C.

Water samples for ambient nutrients will be filtered in the field (where appropriate) through Fisher Brand MCE 0.45 μm filters (TDN/TDP, nitrate, nitrite, ammonium, phosphate) or Whatman puradisc 0.45 μm filters (dissolved organic carbon). All sample bottles/containers will

be triple rinsed and filled. Once sample containers are filled, they will be placed on ice, in a cooler, in the dark and transported to the laboratory for processing within specified holding times. As needed and appropriate, filtration and/or acidification will take place at the sampling sites or in the laboratory. Chlorophyll and HABs toxin samples will be filtered using Whatman GF/F glass fiber filters within 6 hours of collection. Filters will be kept in the dark (wrapped in aluminum foil) to minimize photodegradation and will be kept frozen until analysis, with a maximum holding time of 30 days. Filtrate will be discarded.

Biomass and sediment samples will be collected into Ziploc bags and stored on ice in the dark. Sediment chlorophyll samples will be subsampled from the homogenized sediment in the lab and stored frozen until analysis within 30 days. Remaining sediment will be stored refrigerated at 4 ^{o}C until it can be processed. Sediment will be weighed wet, dried at 50^{o}C for 48 hours, and reweighed dry within the 30 day holding time. A sub-sample of the dried portion will be hand ground in a morter and pestle to approximately 5 μm, placed in scintillation vials, capped, and shipped for analysis in size for total phosphorus, total nitrogen and total organic carbon. Biomass samples will be stored at 4 ^{o}C until they can be weighed wet, dried at 50^{o}C for 48 hours, and reweighed dry within 48 hours of collection.

Containers for organic carbon analyses will be in factory certified, pre-cleaned ICHEM vials. Unless otherwise stated, containers for conventional analysis, nutrient, and solid analysis will be in pre-combusted glass scintillation vials.

Table 13. (Element 12) Sample handling and custody.

Parameter	Container	Volume	Initial Preservation	Holding Time
TN/TP	HDPE bottle	30 mL	Cool to 4°C, dark, freeze	28 days at -20°C, dark
TDN/TDP	HDPE bottle	30 mL	Cool to 4°C, dark; filter within 24h, freeze	28 days at -20°C, dark
Nitrate + nitrite, Nitrite, SRP, Ammonium	HDPE bottle	30 mL	Cool to 4°C °C, dark; filter within 24h, freeze	28 days at -20°C, dark
DOC	Glass scintillation vial	20 mL	Cool to 4°C, dark; filter within 24h, freeze	28 days at 20°C, dark
Water column Chl *a*	Glass fiber filter	250 mL	Keep at 4°C, dark, but must filter within 24 hrs, freeze	30 days, -20°C, dark
Domoic Acid	Glass fiber filter	250 mL	Keep at 4°C, dark, but must filter within 24 hrs, freeze	30 days, -20°C, dark
Microcystin	Glass fiber filter	250 mL	Keep at 4°C, dark, but must filter within 24 hrs, freeze	30 days, -20°C, dark
Macroalgae biomass	Ziploc Bag	Quart	Cool to 4°C, dark	48 hours at 4°C, dark
SAV biomass	Ziploc Bag	Gallon	Cool to 4°C, dark	48 hours at 4°C, dark
Sediment Chl *a*	Centrifuge Tube	50 mL	Cool to 4°C, dark, freeze	30 days, -20°C, dark
Sediment %OC,%ON, TP	Glass scintillation vial	20 mL	Cool to 4°C, dark, oven dry	12 months, dried, desiccator
Sediment Grain Size	Ziploc Bag	quart	Cool to 4°C, dark, oven dry	12 months, dried, desiccator

All biomass and water samples will be collected by a SCCWRP representative at the end of the field day. Biomass, chlorophyll, HABs toxin, and grain size analysis will be conducted at SCCWRP. Water samples for nutrient analysis may be accumulated by SCCWRP before shipment to analytical labs. Water samples will be shipped to analytical labs within two weeks of collection to insure analysis before expiration of the holding times. Transport of the samples to the analytical laboratory will be coordinated by the Field Coordinator to insure that all samples are handled and analyzed within the proper holding time. CoCs will be reviewed by personnel at the receiving laboratories to ensure that no samples have been lost in transport, and the laboratories will also verify that each sample has been received within necessary holding times (Table 13.)

All other samples will be properly and safely disposed of by the analytical laboratory once analyses are completed and all analytical quality assurance/quality control procedures have been reviewed and accepted.

13. ANALYTICAL METHODS

13.1. Field Analytical Methods

Field collection and preservation protocols are detailed in the Bight 08 Eutrophication Assessment Field Methods Manual Version V8 (Appendix C).

Data sondes are set up to log data in 15 minute intervals. The instrument has internal battery power and memory and will be maintained and data downloaded at minimum once per month (more regularly during summer when biofouling is more serious). Maintenance will include removing biofouling and ensuring correct operation as per manufacturer's specifications outlined in the YSI 6600V2 operations manual. Data is saved in the unit's internal memory and will be uploaded to YSI 650 hand held display units in the field during the regularly scheduled maintenance. Data will be transferred from YSI 650 units to laboratory computers and then to the Bight 08 database within two days of data upload. Continuously monitored parameters include temperature, water level, conductivity, salinity, turbidity, pH, dissolved oxygen, and chlorophyll fluorescence.

Field samples will be collected in appropriate pre-cleaned containers as specified in Section 12. Each sample will be affixed with sample labels, preserved where appropriate and stored according to requirements outlined in Section 12.

13.2. Laboratory Analytical Methods

Analytical methods conducted at SCCWRP are detailed in the Bight 08 Eutrophication Assessment Laboratory Methods Manual V1 (Appendix D). QA manuals for samples sent offsite for analysis are presented in Appendix A (MSI) and Appendix B (UGA).

13.2.1. Water chemistry

Nitrate + nitrite will be analyzed using the cadmium reduction method (SM 4500-NO3 F), nitrite will be analyzed using the colorimetric method (SM 4500-NO2 B), and ammonium will be analyzed using distillation and the automated phenate method (SM 4500-NH3 G) using a Lachat Instruments (division of Zelweger Analytics) Model QuikChem 8000 Flow Injection Analyzer.

For TN/TP (USGS I-4650-03) and TDN/TDP (USGS I-2650-03; Patton, C.J. and J.R. Kryskalla (2003)), persulfate will be used to digest unfiltered and filtered water samples to convert the nitrogen from all N compartments into nitrate and the phosphorus from all P compartments into orthophosphate for the simultaneous determination of TN and TP. The resulting digests will be analyzed by automated colorimetry for nitrate-N and orthophosphate using an Alpkem Colorimeter.

SRP will be analyzed using the automated ascorbic acid reduction method (SM 4500-P F), using a Lachat Instruments Model QuikChem 8000 Flow Injection Analyzer.

Dissolved organic carbon (DOC) will be determined for filtered sample water via the combustion infrared method (SM 5310-B) using a Shimadzu 5000 Total Organic Carbon Analyzer with an ASI-5000A Auto Sampler.

Rapid analysis of domoic acid and microcystin concentrations will be made using a new Enzyme Linked Immunosorbent Assay (ELISA) method (Garthwaite et al., 2001). The analysis (developed and now offered commercially by Mercury Science, Inc.) is based on a competitive binding assay and is highly specific for domoic acid. Sediment domoic acid will be analyzed by digestion, extraction and analysis by Liquid Chromatography Mass Spectrometery (LC-MS) (Sekula et al. 2007).

13.2.2. Sediment Analysis

Sediment grain size (% sand only) will be determined by wet sieving the sample through a 62 micron sieve to separate the course and fine fractions (EPA, 1995).

Sediment % organic carbon, % organic nitrogen will be determined on a CHN elemental analyzer (Exeter Analytical model CEC 440HA) by means of high temperature (1000ºC) combustion (Dumas method) in an oxygen- enriched helium atmosphere (EPA 9060).

Total sediment phosphorus will be determined by persulfate digestion, which will convert all organic P to orthophosphate. Digests will then be analyzed by automated colorimetry for nitrate-N and orthophosphate using an Alpkem Colorimeter (Nelson 1987).

13.2.3. Chlorophyll *a* Analysis

Chlorophyll from water-column samples will be concentrated by filtering at low vacuum through a Whatman glass fiber filter. Photosynthetic pigments will be extracted from filters and sediment in 90% acetone and allowed to steep overnight, but not to exceed 24 hrs, to ensure complete extraction of chlorophyll *a* (EPA 445). Using a self-calibrating Turner Designs Trilogy Laboratory fluorometer, the fluorescence of the sample will be measured before and after acidification with 0.1M HCl to determine the phaeophytin-corrected chlorophyll *a*.

13.2.4. Primary Producer Biomass Analysis

Algae wet/dry weight will be conducted by weighing the sample on an analytical balance before drying and after drying for 48 hours in an oven held at 60ºC (SM B-3520-85).

Details on field and analytical methods are provided in Tables 14 and 15.

Table 14. (Element 13) Field analytical methods.

Analyte	Laboratory / Organization	Project Quantization Limit (units)	Range	Resolution	Analytical Method	
					Analytical Method/ SOP	Modified for Method yes/no
Dissolved Oxygen	Field monitoring	0.1 mg/L	0-50 mg/L; 0-200% sat.	0.01mg/L; 0.1% sat.	SM 4500O-G	no
Temperature	"	-5°C	-5 - 45°C	0.1°C	SM 2550-B	no
Salinity	"	0.1 ppt	0- 70 ppt	0.01 ppt	SM 2520	no
Turbidity	"	0.1 NTU	0 to 1000 NTU	0.1 NTU	SM 2130 B	no
Chlorophyll	"	0.5 µg/L	0 to 400 µg/L chl*a*	0.1 µg/L chl *a*	YSI manual	no
pH by meter	"	N/A	0.00-14.00	0.01	SM 4500-H+B	no

(*) *Standard Methods for the Examination of Water and Wastewater*, 20th edition.

Table 15. (Element 13) Laboratory analytical methods.

Analyte	Laboratory / Organization	Matrix	Target Reporting Limit	Analytical Method	
				Analytical Method/ SOP	Modified for Method yes/no
TN	UGA	Water	0.5 mg/L	USGS I-4650-03	No
TP	UGA	Water	0.01 mg/L	USGS I-4650-03	"
TDN	UGA	Water	0.5 mg/L	USGS I-2650-03	"
TDP	UGA	Water	0.01 mg/L	USGS I-2650-03	"
Nitrate	MSI	Water	0.05 mg/L	SM 4500-NO3 F	"
Nitrite	MSI	Water	0.05 mg/L	SM 4110 C	"
Ammonium	MSI	Water	0.05 mg/L	SM 4500-NH3 G	"
SRP	MSI	Water	0.05 mg/L	SM4500P C	"
DOC	UGA	Water	0.6 mg/L	SM 5310C	"
CHL a	SCCWRP	Water	2 µg/L	EPA 445.0	"
Sediment Grain Size (% Sand)	SCCWRP	Sediment	1 %	ASTM D-422 (1963)	"
%OC	MSI	Sediment	0.01 %	EPA 9060	"
%ON	MSI	Sediment	0.01 %	EPA 9060	"
%TP	UGA	Sediment	0.01 %	Nelson (1987)	"
Sed CHL a	SCCWRP	Sediment	0.1 mg/m^3	SM 10200H	"
Wet/Dry weight	SCCWRP	Sediment	0.5 %	SM B-3520-85	"
Wet/Dry weight	SCCWRP	Algae/SAV	0.5 %	SM B-3520-85	"

*EPA, Method for Chemical Analysis of Water and Waste Water
** SM, Standard Methods for the Examination of Water and Waste Water
***USGS, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory
****ASTM D-2216, 1980. Laboratory Determination of Water (Moisture) Content of Soil, Rock, and Soil-Aggregate Mixtures. American Society for Testing and Materials.
*****Nelson, N. S. 1987. An acid-persulfate digestion procedure for determination of phosphorus in sediments. Commun. in Soil Sci. Plant Anal. v.18 no.4 p.359-69.

13.3. Addressing failures

Any failures (*e.g.*, instrument failures) that occur during data collection and laboratory analyses will be the responsibility of the field crew or laboratory conducting the work, respectively. In the

case of field instruments, problems will be addressed through instrument cleaning, repair, or replacement of parts or the entire instrument, as warranted. Crews will carry basic spare parts and consumables with them to the field, and will have access to spare parts to be stored at SCCWRP. Failures will be noted in the field data sheets in the comments section. Contract laboratories have procedures for dealing with failures (Appendix A and B). Records of all repairs or replacements of field instruments will be maintained at SCCWRP.

13.4. Sample disposal

Once analyses are completed and all analytical quality assurance/quality control procedures have been reviewed and accepted, all samples will be properly and safely disposed of by the analytical laboratory. Any hazardous material reagents used in sample preparation will be disposed of according to the appropriate Material Safety Data Sheet (MSDS) stipulations.

13.5. Laboratory turnaround times

All samples will be submitted to laboratories within the holding times required for specific analytes (see Table 13, Element 12 for holding times). Laboratories will be responsible for conducting analyses, or implementing appropriate preservation measures, within holding times as arranged ahead of time by the Project Manager. Laboratory turnaround times will be sufficiently timely to allow for QA checks of the data, entry into the database, analysis, and reporting by the project team in order to meet project planning and deliverable deadlines. Sample turnaround time for UGA and MSI is 90 days.

14. QUALITY CONTROL

14.1. Summary of Quality Control activities

Adherence to Standard Operating Procedures by all data collectors for this project will ensure that all samples are collected, handled, and processed with the highest level of quality control. Quality assurance and quality control activities for sampling processes include the collection of field replicates for chemical testing, and the preparation of field blanks, laboratory replicates, laboratory/equipment blanks, preparation of matrix spikes/matrix spike duplicates, and comparison to standard reference materials.

All field measurements for continuous monitoring of pH, temperature, salinity, conductivity, dissolved oxygen, turbidity, and chlorophyll fluorescence will be made using a YSI 6600V2 data sonde according to manufacturer's specifications. Calibration will be conducted and documented prior to use and during each of the routine maintenance events. Proper storage and maintenance procedures will be followed. Data sonde output will be compared to standard reference materials (SRMs) prior to deployment and during maintenance events and any drift will be recorded and applied during data correction.

Field replicates are used to assess variability attributable to collection, handling, shipment, storage, and/or laboratory handling and analysis. Procedures for collecting field replicates should be the same as that used for collecting the field samples. Replicates of grab samples will be collected by filling two grab samples containers at the same time or in rapid sequence at a minimum of 5 % of sites. Sample containers will be labeled separately, but will not be identified as "replicate" to the laboratory.

Field blanks are used to determine if field-sampling activities are a potential source for contamination. Field blanks will be periodically submitted to verify that sample contamination is not occurring through inadequately clean equipment. To collect field blanks for the assessment of grab sampling, the same equipment used for collection (*e.g.*, tubing and benthic chamber sample syringes) of the water samples should be used to pour blank water into the blank sample containers. Field blanks should be collected at least once per lot of sampling containers. The field teams will be responsible for conducting these internal checks and if necessary advise the Project Manager of quality control problems. If a problem occurs, all field collection will be halted until the source of the problem can be detected and rectified. Blanks will be prepared by pouring ultrapure water (ASTM Type I) known to be free of the substance of interest into a sample collection container.

Analytical quality assurance for this study includes the following:

- Employing analytical chemists trained in the procedures to be followed.
- Adherence to documented procedures, U.S. EPA methods, written Standard Operating Procedures (SOP), and other approved methods (e.g., Standard Methods).
- Adequate calibration of analytical instruments.
- Complete documentation of sample tracking and analysis.

Laboratory quality control checks will include the use of method blanks, matrix spikes (MS), matrix spike duplicates (MSD), laboratory duplicates, and laboratory control samples (LCSs). These QA/QC activities are discussed below.

Laboratory matrix spike and matrix spike duplicates A matrix spike (MS) or matrix spike duplicate (MSD) sample is an aliquot of a field sample into which the laboratory adds a known quantity of a compound. Reported percent recovery of the known compound in the sample indicates matrix effect on the analysis. Percent recovery will be assessed for 1 in 20 samples.

Replicates. A laboratory replicate (also called a laboratory split) sample is generated by the laboratory. Replicate analyses results are evaluated by calculating the relative percent difference (RPD) between the two sets of results. This serves as a measure of the reproducibility (precision) of the sample results. When a matrix spike is duplicated it is known as a matrix spike duplicate (MSD).

Blanks. To determine the level of contamination associated with laboratory reagents and equipment, the laboratory will run blanks, which consist of a sample of a known matrix that has been subjected to the same complete analytical procedure as the submitted samples to determine if contamination has been introduced into the samples during processing. Results of this analysis should be less than the reporting or minimum detection limits for each analyte.

Laboratory control samples. (LCSs) will be included in the program. The LCS involves spiking known amounts of the analyte(s) of interest into a known, clean matrix to assess the matrix effects on spike recoveries. High or low recoveries of the analytes in the matrix spikes may be caused by interferences in the sample. LCSs assess these possible matrix effects because the matrix is known to be free from interferences. LCSs are analyzed at a frequency of one per batch of 20 or fewer samples.

The Project Manager will review data generated by contract laboratories for completeness every index period. She will also review completed chain-of-custody forms as well as logged field observations.

14.2. Procedure for calculating Quality Control statistics

Contract laboratories will report the relative standard deviation (RSD) relative percent difference (RPD) for QA/QC analysis preformed. The RSD is a measure of the reproducibility of the analysis. This is determined by dividing the standard deviation by the mean for the same set and then multiplying by 100%.

The RPD is a measure of precision calculated by:

$RPD = [X_1 – X_2]/ X_{ave} * 100\%$

Where:

X_1 = concentration observed with the first detector or equipment

X_2= concentration observed with the second detector, equipment, or absolute value; and,

X_{ave}= average concentration of X= $[X_1 – X_2]/2$

The chemical analyses will operate using the quality assurance and quality control programs established by the contract laboratories (MSI, and UGA). Copies of the laboratories' QA plan documents are attached (Appendices A through C.) SCCWRP's Quality Assurance Officer has reviewed the Laboratory's quality assurance program. The Laboratories' QA plans were found in conformance with SWAMP requirements.

14.3. Quality Control limit exceedances and corrective actions

Corrective action is taken when an analysis is deemed suspect for some reason. These reasons include exceeding RPD ranges and/or problems with spike recoveries or blanks. The corrective action varies somewhat from analysis to analysis, but typically involves the following:

- A check of procedures.
- A review of documents and calculations to identify possible errors.
- Correction of errors.
- A re-analysis of the sample extract, if sufficient volume is available, to determine if results can be improved.
- Evaluation by principal investigator on validity of measured value.
- A complete reprocessing and re-analysis of additional sample material, if sufficient volume is available and if the holding time has not been exceeded.

Effectiveness of control actions will be assessed based on improved performance of analysis following these actions. Records on failures, corrective actions taken, and confirmation of correction will be kept by the contract laboratories, and made available to the project QA Officer upon request.

External reference standards Standard samples, disguised as samples, may be sent to the contract laboratories. Standard samples are water samples with known concentration. Such standards would be prepared with adding known amount of analytes and Ultrapure water in the same sampling containers. The analysis of the standard would be used to inspect the performance of the contract.

14.4. Sampling and analytical Quality Control Practices

Tables 16-19 summarize sampling and analytical quality control practices.

Table 16. (Element 14) Sampling (Field) QC for water samples.

Matrix: water
Sampling SOP: SWAMP QAMP Appx. D
Analytical Parameter(s): nutrients, DOC, chlorophyll *a*
Analytical Method/SOP Reference: USGS I-4650-03, USGS I-2650-03, SM 4500-NO3 F, SM 4110 C, SM 4500-NH3 G, SM4500P C, SM 5310C, EPA 445.0
Sample locations: 32

Field QC	Frequency/Number per sampling event	Acceptance Limits
Field Duplicate Pairs	At least 1 in every 20 samples	80 - 120%
Equipment Blanks	At least once per lot of filters	No detectable amount of analyte in blanks (<MDL)
Field Blanks	At least once per field team per sampling event	No detectable amount of analyte in blanks (<MDL)

Table 17. (Element 14) Analytical QC for water samples.

Matrix: water
Sampling SOP: SWAMP QAMP Appx. D
Analytical Parameter(s): nutrients, DOC, chlorophyll *a*
Analytical Method/SOP Reference: USGS I-4650-03, USGS I-2650-03, SM 4500-NO3 F, SM 4110 C, SM 4500-NH3 G, SM4500P C, SM 5310C, EPA 445.0
Sample locations: 32

Laboratory QC*	Frequency/Number	Acceptance Limits
Lab. Blank	1 in 20 samples or 1 per batch	No detectable amount of analyte in blanks (<MDL)
Lab. Duplicate	1 in 20 samples or 1 per batch	75 – 125%
Lab. Matrix Spike	1 in 20 samples or 1 per batch	80 – 120%
Lab. Control Sample	1 in 20 samples or 1 per batch	80 – 120%

Table 18. (Element 14) Sampling (Field) QC for solid samples.

Matrix: Sediment, Macroalgae, and SAV
Sampling SOP: SWAMP QAMP Appx. D
Analytical Parameter(s): grain size, wet/dry weight, nutrients
Analytical Method/SOP Reference: ASTM D-422 (1963), EPA 9060, Nelson (1987), SM 10200H, SM B-3520-85
Sample locations: 200

Field QC	Frequency/Number per sampling event	Acceptance Limits
Field Duplicate Pairs	At least 1 in every 20 samples	80 - 120%

Table 19. (Element 14) Analytical QC for solid samples.

Matrix: Sediment, Macroalgae, and SAV
Sampling SOP: SWAMP QAMP Appx. D
Analytical Parameter(s): grain size, wet/dry weight, nutrients
Analytical Method/SOP Reference: ASTM D-422 (1963), EPA 9060, Nelson (1987), SM 10200H, SM B-3520-85
Sample locations: 200

Laboratory QC*	Frequency/Number	Acceptance Limits
Lab. Blank	1 in 20 samples or 1 per batch	No detectable amount of analyte in blanks (<MDL)
Lab. Duplicate	1 in 20 samples or 1 per batch	75 – 125%
Lab. Control Sample	1 in 20 samples or 1 per batch	80 – 120%

15. INSTRUMENT/EQUIPMENT TESTING, INSPECTION, AND MAINTENANCE

15.1 Procedures for testing, inspecting, and maintaining instruments and equipment

SCCWRP staff has established standard operating procedures for each piece of field equipment in use. YSI data sondes and other laboratory equipment receive regular maintenance based on a combination of manufacturer requirements and the actual amount of equipment use in the field. This includes battery checks, routine replacement of membranes and other spare parts (to be stored at SCCWRP), and cleaning of probes. Replacement parts for instruments and duplicates of fragile equipment (e.g. glassware) will be brought to each field site so that equipment can be fixed or replaced onsite. All equipment will be inspected and maintained by the Project Manager for damage when first deployed and when returned from use. Solutions used for the calibration of the all meters are changed on an established schedule to ensure that contamination does not occur.

The project's contract laboratories maintain their equipment in accordance with their SOPs, which include those specified by the manufacturer and those specified by the methods listed in Table 15 and that are within the instrument specifications as determined by the manufacturer. Analyte SOPs within the National Environment Methods Index (NEMI) and are SWAMP approved (where SWAMP has set methods requirements). These SOPs have been reviewed by SCCWRP's QA Officer and found to be in compliance with SWAMP criteria. Contract Laboratories will record any corrective actions on laboratory data sheets and will provide a copy to SCCWRP as apart of data delivery.

Testing criteria depend on the type of instrument. In general terms, inability to equilibrate or lack of accuracy and repeatability of results when conducting repeat measurements on standards of known value provide criteria against which to test the functioning of instruments. Instruments will be run over the linear range as determined by the manufacturer's specifications or as required by specific SOPs.

Table 20. (Element 15) Testing, inspection, maintenance of field sampling equipment and analytical instruments.

Equipment / Instrument	Maintenance Activity, Testing Activity or Inspection Activity	Responsible Person	Frequency	SOP Reference
YSI 6600V2 Multi-Parameter Water Quality Logger	Clean and calibrate optical DO, turbidity, and chlorophyll probes, pH probe, conductivity, and temperature probes as per manufacturer's specifications	Field Team Leaders	When dirty, or when measurements equilibrate slowly	YSI 6600V2 User's manual Bight 08 Field Methods Manual
Percent Cover Quadrats	Remove biomass, clean, inspect for cracks and broken strings	Field Team Leaders	Each time used	Refer to Field Methods Manual
Viewing Buckets	Remove biomass, clean; Inspect for holes/leaks/cracks	Field Team Leaders	Each time used	Refer to Field Methods Manual
SAV Samplers	Remove biomass, clean, inspect for cracks and broken tines or chain-links	Field Team Leaders	Each time used	Refer to Field Methods Manual
Biomass delineators	Remove biomass, clean, inspect for cracks	Field Team Leaders	Each time used	Refer to Field Methods Manual

15.2 Resolution of deficiencies

Any deficiency found (*i.e.*, inability of instruments to pass testing criteria) will be resolved via cleaning, replacement of parts or consumables, or repair by a professional service technician, as deemed appropriate by the Project Manager. Documentation of any such actions will take place on an equipment/instrument log kept at SCCWRP.

16. INSTRUMENT/EQUIPMENT CALIBRATION AND FREQUENCY

16.1 Procedures for calibrating instruments/equipment

All SCCWRP instruments/equipment are calibrated based on manufacturer recommendations and accepted laboratory protocols and using certified standards of known values, often purchased directly from the dealers of those instruments. Balances are calibrated annually against National Institute of Standards and Technology (NIST) traceable weights by an external contractor. Pipettes are calibrated annually by delivering the exact amount and type of solvent corresponding to their planned use and weighing the amount of solvent delivered on a balance. Any pipette that cannot be adjusted to deliver a weight of a solvent within 5% of the required weight will be taken out of service for repair or replacement. All field water quality meters will be calibrated prior to each deployment (see Table 21). If any of the instruments or field meters fail to calibrate properly, they will be repaired or replaced, as necessary. Calibration results and any repairs made to the instruments will be recorded and maintained in a folder at SCCWRP.

Contract laboratories will perform calibration for their instruments according to their own SOP/QA plans, attached in Appendix A and B. These have has been reviewed by SCCWRP's QA Officer and found to be in compliance with SWAMP criteria. All instruments will be calibrated to manufacturer's specifications or as required by specific SOPs (listed in Table 15).

Table 21. (Element 16) Testing, inspection, maintenance of sampling equipment and analytical instruments.

Equipment / Instrument	SOP reference	Calibration Procedure	Frequency of Calibration	Responsible Person
YSI 6600v2 Sonde	YSI 6600v2 Sonde User's manual	Refer to manual	Prior to each deployment	Lead Scientist
OHAUS Balance	OHAUS Navigator Balance User's manual	Refer to manual	Annually	SY Nielson Services Inc.

16.2 Resolution of deficiencies

Any deficiency found (*i.e.*, inability of instruments to pass calibration criteria) will be resolved via cleaning, replacement of parts or consumables, or repair by a professional service technician, as deemed appropriate by the Project Manager. Documentation of any such actions will take place on an equipment/instrument log kept at SCCWRP.

17. INSPECTION/ACCEPTANCE OF SUPPLIES AND CONSUMABLES

Glassware, sample bottles, and collection equipment will be purchased from biological and chemical suppliers, such as Fisher and VWR. They will all be inspected prior to their use. Supplies will be examined for damage as they are received. Bottles and caps will be inspected for damage prior to sampling, and only sound bottles with intact threads will be used. Caps will be tested for tightness prior to transport of samples.

The Project Manager will make sure sufficient field supplies are on hand prior to the start of sampling for each index period. An inventory of supplies will be maintained to assure that stores are not exhausted prior to the end of each sampling event, thus potentially holding up fieldwork. Each filed team will receive a "kit" including all necessary sampling equipment and sample bottles, plus one additional replacement set of equipment. Field supplies and additional replacement equipment will be stored at SCCWRP. Laboratory supplies will be stored at the laboratories conducting the work.

Table 22. (Element 17) Inspection/acceptance testing requirements for consumables and supplies.

Project-Related Supplies / Consumables	Inspection / Testing Specifications	Acceptance Criteria	Frequency	Responsible Individual
Water Sample Bottles	Inspected for cracks and stripped threads.	Acid-washed or pre-combusted, non-damaged bottles and lids with intact threads	Prior to each sampling event.	Field team leaders
Sediment Sample bags	Inspected for tears or damage and functional closure.	Clean, undamaged bags with intact closures	Prior to each sampling event.	Field team leaders
Algae Sample Bags	Inspected for tears or damage and functional closure.	Clean, undamaged bags with intact closures	Prior to each sampling event	Field team leaders

18. NON-DIRECT MEASUREMENTS (EXISTING DATA)

18.1 Identification and selection of existing data to aid project

This study does not represent a census of systems which limits our ability to fully characterize southern California estuaries with respect to eutrophication. However, similar data has been collected in several systems which provide either data on additional systems, or historical data at the same site. These data will be used to help interpret results of the present study. Furthermore, flow data collected by USGS gauging stations will be used to calculate freshwater loading into relevant estuaries. This data is available real-time on the web. Table 23 indicates existing data which can be utilized for this study.

Table 23. (Element 18) Existing data.

Organization	Date	Title of Report/ Name of Data Set	Principle Author(s)
SCCWRP & San Diego Stakeholders	2008; report in prep	San Diego Regional Water Quality Control Board (SDRWQCB) Investigation Order No. R9-2006-0076 to conduct monitoring in support of the nutrient TMDLs	Martha Sutula (project manager)
SCCWRP	2006	Relationship between dissolved oxygen and macroalgal distribution in Upper Newport Bay	Nezlin, N., K. Kamer, E.D. Stein, A. Carr and J. Hyde
SCCWRP	2003	Nutrient dynamics and macroalgal blooms: A comparison of five southern California estuaries.	Kennison, R., K. Kamer and P. Fong
U.S. Geological Survey	2003-present	Continuous monitoring data for Camp Pendleton Lagoons: - Cockleburr Creek Lagoon, Aliso Creek Lagoon, Hidden Creek Lagoon, Las Flores Creek at Mouth, San Onofre Creek Lagoon, San Matau Creek Lagoon	Tom Haltom, Bruce Hill
Tijuana National Estuarine Research Reserve	2000-present	Continuous monitoring data for sites within the Tijuana River Estuary	Jeff Crooks http://www.nerrs.noaa.gov/Monitoring/Data.html
U.S. Geological Survey: National Water Information System (NWIS)	2008-2009	Stream Gauging Stations	http://waterdata.usgs.gov/

18.2 Limits to data usability

Existing data will be subject to the QA/QC standards outlined in this report. Data that fail to meet these QA/QC standards will not be utilized.

19. DATA MANAGEMENT

19.1 Data Management Scheme

Data documentation will be maintained as established in Element 9. All original data sheets will be maintained by the Lead Scientists and copies will be accumulated into project-specific files that are maintained at SCCWRP. Data-files, data bases, report text, and tables will be stored digitally onto both off-site and on-site severs.

The management scheme for all project data will be initiated with the use of field and laboratory data sheets. The data sheets will contain entries for identification of the sample as well as reports of field conditions at the time of sampling (See examples of field sheets in Appendix C). SCCWRP will be responsible for maintaining paper copies of all the accumulated field and laboratory data sheets for participating organizations.

Continuous data measurements will be collected during this project and downloaded from the moored data sondes monthly (at minimum). Original data sonde files will be stored as .dat files and manipulated sonde data files will be stored as .csv or Microsoft Excel files.

Analysis results from contract laboratories will be sent electronically in a format that matches SWAMP requirements following the Surface Water Ambient Monitoring Program Information Management Plan (MPSL, 2005). These electronic data delivery files will be sent to the to the Project Manager following the completion of quality control checks by each of the laboratories. Data will be screened for the following major items:

- A 100 percent check between electronic data provided by the laboratory and the hard copy reports
- Conformity check between the Chain-of-Custody Forms and laboratory reports
- A check for laboratory data report completeness
- A check for typographical errors on the laboratory reports
- A check for suspect values (i.e., are TP values within an acceptable range based on historical analytic results)

Following the initial screening, a more complete QA/QC review process will be performed by the Project Manager with the assistance of the QA Officer. This will include an evaluation of holding times, blank contamination, and analytical accuracy and precision. Accuracy will be evaluated by reviewing MS and LCS recoveries; precision will be evaluated by reviewing laboratory sample duplicate RPDs.

All data for this project will be entered into the Bight 08 database (which is SWAMP compatible). The Bight 08 database is a Microsoft © Access database.

19.2 Recordkeeping and tracking

SCCWRP support staff will be responsible for making hard copies of these data and making back up disks of field data. Data will be backed up daily onto external hard-drives and an off-site server.

Field data sheets will be checked against electronic data by the Project Manager. The field data will be validated by the lead field scientist and then entered into electronic form by SCCWRP support staff. The field data sheets will be signed and archived at SCCWRP for at least 3 years following project completion.

The Project Manager will review all the field and laboratory information to verify that the sampling and analysis procedures were conducted in accordance with the QAPP. After performing data checks, and ensuring that data quality objectives have been met, data analyses will be performed.

All field and laboratory data sheets, logs, and checklists and how they are used can be located in Appendices C & D.

19.3 Document control

Document control measures will ensure that documents relating to this project can be reviewed and revised periodically, while allowing for obsolete versions to be electronically archived in such a way that prevents their alteration, which could result in confusion between versions. Examples of documents that fall into this category include SOPs, manuals, and QAPPs. A naming convention will be used to provide unique identifiers for documents and versions. Outdated versions of documents will be archived as read-only or PDF files, such that they can be reviewed electronically if needed, but not altered. SCCWRP Information Management staff will be responsible for maintaining the document control system.

19.4 Data Handling and Formatting, and Database Compatibility with SWAMP

The required form of electronic submittal will be provided to contract labs by the Project Manager to make sure the files can be imported into the project database with minimum of editing. This will be an electronic, relational database that includes field data, lab data, QA flags, results of data analyses, and other pertinent information. The database will be designed by SCCWRP Information Management staff, and made to be amenable to SWAMP standards. As such, any or all of these data could be added to the SWAMP database. All software and hardware configurations will meet industry standards (*i.e.*, be Windows compatible.)

GROUP C: ASSESSMENT AND OVERSIGHT

20. ASSESSMENTS & RESPONSE ACTIONS

The Project Manager will be responsible for the day-to-day oversight of the project. The QA Officer and Project Manager will communicate on a quarterly basis with regard to Quality Assurance aspects of the project. Every index period, the Project Manager will meet with field personnel to discuss the collection process, data management, and the overall status of the project. Any deviations from, or changes to, the SOPs or the QAPP will be reported to the Project Manager and QA Officer within 30 days, and appropriately revised documents will be distributed to all team members, under direction of the project QA Officer. Three types of assessments will be performed as part of this project to ensure that the sampling and analysis activities are in accordance with the approved QAPP. They are as follows:

1) *Surveillance of Sample Collection Activities*. The Lead Scientists will be responsible for oversight of sampling activities and will review field logs to verify that the samples were collected in accordance with QAPP requirements. The Field Coordinator will facilitate sample collection amongst all Lead Scientists to insure that data is being collected uniformly. A SCCWRP QA-representative will accompany all field teams at least once, toward the beginning of the data collection phase of the project (the estimated date for this activity is October 2008), and again at some later point, if deemed necessary, to observe activities. If the QA representative finds any of the field activities to be in violation of QAPP requirements, he/she has the authority to stop these activities until corrective actions are successfully implemented. These include additional training to improve field team performance and QAPP compliance, and appropriate re-sampling of sites, as needed. The QA representative will report all such actions to the Project Manager and Field Coordinator.

2) *Data Quality Assessment*. Contract laboratories will be responsible for providing a summary of QA/QC data to the Field Coordinator, who will consult with the Project Manager/QA Officer to verify that the performance criteria of the QAPP were met. This will occur following receipt of each report from the contract laboratories. If it is determined that the precision and accuracy objectives were not met, the contract laboratory QA Officer will review laboratory techniques to minimize errors, and samples will be re-analyzed, if possible.

3) *Assessment of Data Entry*. Field data is entered into computers within one week of collection by the field team leader. This data is then double checked by the Lead Scientist and uploaded to the Bight 08 database. Once the performance criteria for field and laboratory data are met, data analysis can be conducted. The Field Coordinator will review data files to ensure that errors are detected and corrected. Data entry will be reviewed by creating histograms to identify outliers, and sorting the data to identify missing values.

Any corrective actions taken will be verified based on satisfactory collection of data in accordance with the QAPP, following these actions. The QAPP violation(s), corrective action(s), and verification of correction will be reported by the QA Officer / Project Manager and kept on record.

21. REPORTS TO MANAGEMENT

The status of data collection during this project will be reported to the Planning Committee on a quarterly basis beginning with the approval of the Workplan and continuing until the completion of the field activities (November 2009). Quarterly reporting will occur starting October 20, 2008 and run through the completion of the project. A final project report will be filed as a part of the Bight 08 regional monitoring program no later than 1/10/2011.

Table 24. (Element 21) QA management reports.

Type of Report	Frequency (daily, weekly, monthly, quarterly, annually, etc.)	Projected Delivery Dates(s)	Person(s) Responsible for Report Preparation	Report Recipients
Quarterly Progress Reports	quarterly	On 20th of month after end of quarter	Project Manager (Martha Sutula)	Bight 08 Coastal Wetlands Planning Committee
Complete data set and summary	once	10/10/2010		
Draft final report for review	once	12/10/10		
Final Report	once	1/10/2011		

GROUP D: DATA VALIDATION AND USABILITY

22. DATA REVIEW, VERIFICATION, AND VALIDATION REQUIREMENTS

This section of the QAPP addresses the quality assurance activities that occur following completion of sampling activities, including data review, verification and validation. Data generated by project activities will be reviewed against the data quality objectives cited in Element 7 and the quality assurance/quality control practices cited in Elements 14, 15, 16, and 17. Data will be separated into three categories:

1. data meeting all data quality objectives,
2. data failing precision or recovery criteria, and
3. data failing to meet accuracy criteria.

Data meeting all data quality objectives, but with failures of quality assurance/quality control practices will be set aside until the impact of the failure on data quality is determined. Once determined, the data will be moved into either the first category or the last category.

Field and Lab Personnel will be responsible for verifying that the sample collection, handling, and analysis procedures were in accordance with the approved Field Methods Manual and QAPP. The Field Coordinator will be primarily responsible for initially reviewing the data and will report to the Project Manager. Data falling in the first category are considered usable by the project. Data falling in the last category are considered not usable. Data falling in the second category will have all aspects assessed. If sufficient evidence is found supporting data quality for use in this project, the data will be moved to the first category, but will be flagged with a "J" as per EPA specifications (USEPA 2002).

23. VERIFICATION AND VALIDATION METHODS

23.1 Data Verification and Validation Overview

Data verification is the process of evaluating the completeness, correctness, and conformance of the dataset against the method, procedural, or contractual requirements. The goal of data validation is to evaluate whether the data quality goals established during the planning phase have been achieved (USEPA 2002). Data quality indicators will be continuously monitored by the analyst producing the data (*i.e.*, field and lab personnel), as well as the Field Coordinator, with direction from the Project Manager /QA Officer, throughout the project to ensure that corrective actions are taken in a timely manner. Data validation is an analyte- and sample-specific process that extends verification to determine the analytical quality of the dataset (USEPA 2002). Laboratory and field personnel responsible for conducting QA analysis will be responsible for documenting on field and laboratory datasheets when data do not meet measurement quality objectives as determined by data quality indicators. These notes will be transferred as QA flags into the Bight 08 database.

23.2 Process for Data Verification and Validation

Data verification and validation for sample collection and handling activities will consist of the following tasks:

- Verification that the sampling activities, sample locations, number of samples collected, and type of analysis performed is in accordance with Field Methods Manual and QAPP requirements;
- Documentation of any field changes or discrepancies;
- Verification that the field activities (including sample location, sample type, sample date and time, name of field personnel. etc) were properly documented.
- Verification of proper completion of sample labels and Chain of Custody forms, and secure storage of samples.
- Verification that all samples recorded on Chain of Custody forms were received by the laboratory/organization.

Data verification and validation for the sample analysis activities will include of the following tasks:

- Appropriate methodology has been followed;
- Instrument calibrations have been adequately conducted;
- QC samples meet performance criteria;
- Analytical results are complete;
- Documentation is complete.

Verification and validation of data entry includes:

- Sorting data to identify missing or mistyped (too large or too small) values;
- Double-checking all typed values.
- Correct data types correspond to database fields and lookup tables (i.e., text for text, integers for integers, number for numbers, dates for dates, times for times, etc.)

23.3 Parties Responsible for Data Verification and Validation

Data collected in the field will be validated and verified by the Lead Scientists and Field Coordinator. Laboratory validation and verification of the data generated is the responsibility of each laboratory. Each laboratory supervisor maintains analytical reports in a database format as well as all QA/QC documentation for the laboratory. The laboratories also maintain all chain of custody and sample manifests. The Field Coordinator and Lead Scientists are responsible for oversight of data collection and the initial analysis of the raw data obtained from the field and/or the contracted laboratories. The Field Coordinator reports on all field and laboratory activities and QA/QC to the Project Manager. The Project Manager's responsibilities also include the generation of project quarterly and draft and final reports.

23.4 Issue Resolution Process

Whenever possible, individual samples not meeting data quality objectives will be re-run or re-collected, unless evidence suggests that DQOs were not met due to natural variation outside the control of field or laboratory personnel (USEPA 2002). Instances where DQOs are not met will be documented and appropriate corrective actions taken. At the completion of data collection for each sampling event, the Field Coordinator will gather the data, DQO records, and other appropriate records, to evaluate whether criteria described in the QAPP were met, overall, and report to the Project Manager. If any of the criteria are not met, whenever possible, corrective actions will be taken by the Project Manager after consultation with the Bight 08 Coastal Wetlands Planning Committee. Software for data verification will aid database entry and submittal.

The final outputs of the data verification process will be verified data and data verification records that narrate any non-compliance issues or shortcomings of the data produced in field and laboratory activities and a certification statement that the data have been verified by the Field Coordinator and the Program Manager. This certification should be made available to Bight 08 Program and data users to inform them that the data have been verified.

Records in the database for which data do not meet data quality objectives will be flagged with a coded or narrative note. These flags will be carried through to the final data to ensure that data users are aware of any validation issues. Following data verification at the completion of data collection, data will also be validated (USEPA 2002) by the Field Coordinator, with guidance from the Program Manager/QA Officer. Field activities will be validated by 1) evaluating the field records for consistency, 2) reviewing QC information, 3) summarizing deviations and determining the impact on data quality, and 4) assign data validation qualifiers as necessary. Laboratory data will be validated by 1) assembling planning documents and data; 2) reviewing verified, reported sample results collectively for the dataset as a whole, including laboratory qualifiers; 3) summarizing data and QC deficiencies and evaluating the impact on overall data quality; and 4) assigning data validation qualifiers as necessary. Data verification and data validation issues will be summarized in the final report if deficiencies in the data exist.

23.5 Conveying Results to Data Users

Data from this project will be made publicly available through the Bight 08 Regional Monitoring Program. Release of data will include comprehensive documentation, such as database table structures (including table relationships) and lookup tables used to populate specific fields in specific tables. Releases to the public will also include quality assurance classifications of the data (flags, as appropriate) and documentation of the methods by which the data were collected (metadata). Data will be released to the general public once a final report documenting the study has been prepared.

24. RECONCILIATION WITH USER REQUIREMENTS

The goal of the present study is to assess the condition of estuaries in southern California in terms of eutrophication and how different characteristics of the watershed and estuary affect the response to eutrophication. The end result is to 1) characterize the extent and magnitude of eutrophication in southern California Bight (SCB) estuaries, 2) determine whether differences in eutrophication exist between estuarine classes (protected embayments, perennially tidal lagoons, seasonally tidal lagoons, nontidal lagoons, river mouth estuaries), 3) determine how muting of the tidal forcing within an estuary impacts the biological response to nutrient loads, and 3) to determine the relationship between terrestrial nutrient loads and estuarine biological response.

These data will contribute to the development of nutrient numeric endpoints for California coastal estuaries. The reports produced by this project will describe some of the limitations of the data. The samples collected will only describe observed conditions on a limited timescale. The report describing the data will detail those limitations and assumptions to allow the user to determine their usefulness in other applications. Data generated by project activities will be reviewed against the data quality objectives cited in Element 7 and the quality assurance/quality control practices cited in Elements 14, 15, 16, and 17 and acceptance criteria set in Element 22. Data developed for this project will be entered into the Bight 08 Regional Monitoring Program database and submitted to the SWAMP database.

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Appendix A – MSI QA/QC Plan

University of California, Santa Barbara

Marine Science Institute - Analytical Laboratory

QUALITY ASSURANCE MANUAL

Revision Date: 5/10/2007

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SECTION 1. INTRODUCTION

1.1 Background

The Marine Science Institute (MSI), a Regents-approved organized research unit of the University of California at Santa Barbara (UCSB), was established in 1969. The Marine Science Institute Analytical Laboratory (MSIAL) was created in 1977 to provide analytical chemistry support, services, and consultation to the UCSB marine science community. The MSIAL is both a service lab and an instrumentation facility. Researchers may either submit samples to be analyzed by MSIAL staff on a fee-for-service basis, or perform their own analyses using instrumentation owned and maintained by the Analytical Laboratory. Staff is available to assist in equipment operation and to offer training and guidance with analytical protocols.

As a service lab, the MSIAL analyzes thousands of samples per year, submitted by investigators not only from UCSB, but also from other American and International research institutions. In many cases, sample material has been gathered at great expense and is unique and irreplaceable. Researchers rely on the data produced to accurately represent the nature of the material submitted. The procedures outlined in this quality assurance document provide a means of assuring the output of reliable and valid analytical data.

1.2 Organization of MSIAL

The Director of MSI is Steven D. Gaines, Professor of Ecology, Evolution, and Marine Biology at UCSB. Georges L. Paradis, B.A. in Aquatic Biology, is manager of the MSI Analytical Lab and has over 19 years professional experience in analytical chemistry. Mr. Paradis has ultimate responsibility for all aspects of laboratory operation, including instrument scheduling, use, performance, and maintenance, as well as receipt and analysis of submitted samples and verification and reporting of generated data. Staff Research Associates include William J. Clinton, B.A. in Biochemistry/Molecular Biology; Kate Steger, Ph. D. in Marine Ecology; and Jen Massey, B.S. Marine Biology. They are responsible for the operation and maintenance of the analytical instrumentation of the Analytical Lab including the organic elemental analysis (CHN) instruments and the automated nutrient analysis system (FIA). Robert L. Petty, Ph. D. in Chemistry, is the MSIAL expert consultant.

In addition to the staff listed above, the Laboratory also employs UCSB students. As a teaching and research institution, the University of California strongly encourages the utilization of students in laboratory settings. The MSIAL shares this commitment and has trained many undergraduates in general laboratory procedures, safe laboratory practices, and specialized analytical techniques. This combination of experience, education, and enthusiasm has helped to create a laboratory setting in which consistently high quality work is performed.

1.3 Scope of QA Document

Due to the nature of the MSI Analytical Lab as an academic, research-oriented facility, many of the analytical procedures performed are not routine; they often involve extensive development work and close interaction with the involved researchers. Although quality of generated data is obviously important in these investigations, they generally do not lend themselves to specific, detailed QC procedures. This document covers only those analyses performed by the MSIAL that are well-established, routine analytical procedures. These include twelve specific analyses which fall into three general groups: organic elemental analysis (carbon, hydrogen, nitrogen analysis or CHN); seawater micronutrient analysis (often referred to simply as nutrients or Flow

Injection Analysis or FIA); and metals analysis by Inductively Coupled Plasma Mass Spectrometry (ICPMS). The analyses are the following.

CHN -
- Particulate Organic Carbon (POC)
- Particulate Organic Nitrogen (PON)
- Organic Carbon
- Organic Hydrogen
- Organic Nitrogen

FIA -
- Nitrate + Nitrite
- Nitrite
- Ammonium/Ammonia
- Phosphate (ortho)
- Silicate (dissolved)

ICPMS -
- Elemental ratios in carbonates
- Metal composition of natural waters

SECTION 2. QUALITY ASSURANCE OBJECTIVES

The quality assurance objectives for the MSI Analytical Laboratory are the following.

1. To set forth guidelines to standardize laboratory practices through the development and implementation of standard operating procedures (SOPs)

2. To provide for the detection and correction of problems in the analytical procedures through the use of data quality monitoring

3. To produce data of known quality and validity which can be utilized with confidence

SOPs insure that all sampling and analyses are performed in a manner consistent from analyst to analyst. This minimizes measurement variability and, in turn, error in data produced. SOPs are included in this document in Section 8, Detailed Analytical Procedures. Copies of these procedures are included as part of the operating manuals of the pertinent instruments, and are available as separate reprints for bench-top use.

Problems in analytical procedures are detected through the use of data quality indicators. These include: representative calibration data; field, method, and reagent blanks; replicate analyses; and percent recovery analyses of spiked and control samples. The QA guidelines for each method (Sections 5 and 6) define acceptable levels for these parameters and provide a means of monitoring data quality. This allows timely detection of problems and application of corrective action.

In addition to these internal QC checks, samples obtained from the National Institute of Standards and Technology (NIST, formerly the National Bureau of Standards), and other producers of certified reference materials, are analyzed periodically to audit performance. Details are provided in Section 6, Assessment of Precision and Accuracy.

Data produced in accordance with SOPs is of known, acceptable precision and accuracy and can be utilized with a high level of confidence. It is important to document the utilization of QA guidelines when data is reported. This insures that any future question regarding the reliability of the results can be answered adequately. Consequently, all reported data is accompanied by QC information. Sample result data and QA parameter reporting guidelines are presented in Section 7, Data Reduction, Validation and Reporting.

SECTION 3. SAMPLE CUSTODY

Proper sample handling is essential to the production of high-quality data. No amount of care taken in an analytical procedure can produce worthwhile data from a degraded or suspect sample. From the moment a sample arrives at the MSIAL, it is the responsibility of laboratory staff to ensure that appropriate handling procedures are followed. These procedures are:

1. Inspect shipping container for damage (in the event that samples are ruined in shipping, the researcher may have recourse with the shipper).
2. Inspect the sample containers for leaks or breakage.
3. Insure that sealed containers of the appropriate type have been used for the analyte(s) in question and any preservation regimes have been maintained (e.g. cold, dry, etc.).
4. Inspect any paperwork included to ascertain if all samples thought to be submitted have arrived and whether any special handling has been requested.
5. Log samples on the Sample Receipt Master Log and the log sheet for the specific analysis. Make sure the following information is included for each sample batch: MSIAL sample batch number, date received, analysis requested, name and institution of the Principle Investigator submitting the samples, number of samples, storage location, billing information, and initials of MSIAL staff receiving samples. Note any special handling requirements.
6. Inform the Laboratory Manager of all new sample arrivals.

It is imperative that adequate records be maintained for each sample. All future references to any given sample will begin with the information recorded at the time of receipt. Following the steps outlined above will help to insure the integrity of a sample and the data it provides.

SECTION 4. INSTRUMENT MAINTENANCE

The Laboratory Manager oversees the maintenance, calibration, and operation of all laboratory instrumentation. This includes insuring that all potential users are familiar with the operation of a given instrument. Maintenance and repair guidelines for each instrument are kept on file in the laboratory, and regular maintenance and calibration is performed on each instrument as recommended by the manufacturer. A logbook is kept with each instrument to document use and maintenance. Periodic meetings are held to refresh users on the operation of the instrumentation, particularly if problems have occurred or procedural changes have been made. At these

meetings, techniques are reviewed, questions are answered, and specific problems with any particular instrument are discussed. Analysts are encouraged to maintain their expertise in the understanding and operation of an instrument through continuing education.

SECTION 5. CALIBRATION PROCEDURES

Instrument calibration is performed at the beginning of every batch of samples. Specific criteria are evaluated during calibration which determine whether calibration will be repeated, or whether the sample run can be started. It is important with all samples, and imperative with irreplaceable samples, that the operator be confident the instrument is producing verifiable data before continuing with samples. In addition, calibration check standards are run periodically throughout an automated batch run, and the results of these analyses are monitored and evaluated. The specific procedures for elemental analysis (CHN) and seawater nutrients (FIA) differ, and will be discussed separately.

5.1 CHN Calibration

The linear detector response of the CHN instruments used by the MSIAL allows the use of a simple two-point calibration curve, consisting of a blank and a single calibration standard. The calibration procedure involves running a series of samples consisting of conditioners, blanks, standards and controls, and evaluating the values generated from these samples on both an absolute and relative basis.

5.1.1 Conditioner

Under normal operating conditions, the sample conduits of the CHN instrument are coated with a small residual of combustion gases (carbon dioxide, nitrogen and especially water vapor), resulting in a slight memory effect from sample to sample. A "conditioner" (typically a non-critically weighed portion of the material used as calibration standard) is run as the first or second sample in a batch to coat the internal surfaces, resulting in more representative values from the blank run which follows.

5.1.2 Blanks

Analysis of the conditioner is followed by analysis of an empty sample capsule to provide an indication of the background levels of each of the elements. The resulting "blank" values are then subtracted from the sample signals in all subsequent analyses (except a new "blank" run). To meet manufacturer specifications for precision and accuracy, blank values must be within certain limits (see also Section 6). The acceptable range of absolute values, and differences allowed between values from consecutive determinations, are given in the table below. If any value falls outside these ranges, an additional blank is immediately analyzed. If the value is still outside the acceptable limits, the run is stopped and the cause of the problem is investigated. If the values are within the allowable ranges, a calibration standard is analyzed.

5.1.3 Standards

The material typically used for standardization of the CHN analyzer is high-purity acetanilide, a synthetic organic compound of known elemental composition (C_8H_9NO). The sample is carefully weighed before analysis; the exact amount of each element in the sample is therefore known. The detector signal (in microvolts, minus the blank value) resulting from combustion of the sample is then divided by the weight of the element to give the calibration factor, or "K" value for the element (in microvolts per microgram). The K values must also be within certain limits to meet manufacturer specifications; these limits are given in the table below. A second

calibration standard is analyzed immediately after the first, and the K values are compared with those of the first standard to determine whether the instrument precision is acceptable. If the replicate K values are not within limits, an additional calibration standard is run. If these values are still outside the acceptable limits, when compared with either of the first two standards, the run is terminated and the cause of the problem is investigated.

	Blanks (μV)		**K Values (μV/μg)**	
Element	**Absolute Value**	**Max. Range**	**Absolute Value**	**Max. Range**
C	< 100	80	18 – 25	0.16
H	< 1000	278	55 – 76	2.80
N	< 100	22	7 - 10	0.28

5.1.4 Control Sample

If the K values are acceptable, a "control" sample is run. The control sample is a known substance of independent origin from the calibration standard material, and is run as a check on instrument accuracy (see Section 6). The MSIAL commonly uses one of three different materials. The materials used, and the ranges of acceptable values for them, are shown in the table below.

	Acceptable	**Weight Percent**	**Values**
Material	**C**	**H**	**N**
Acetanilide	71.03 – 71.35	6.55 – 6.87	10.19 – 10.53
NIST Citrus Leaves	43.0 – 45.0	5.95 – 6.55	2.55 – 3.15
NIST Oyster Tissue	45.6 – 47.6	6.74 – 7.34	6.53 – 6.83

5.1.5 Calibration Sequence

The sequence of conditioners, blanks and standards is dependent on the type of samples to be run. For samples expected to have low organic carbon content (<200 μg), the sequence is conditioner, blank, blank, conditioner, standard, standard, and control. In addition, an empty slot, or spacer, is left after the control and before the first sample. This gives a more representative low-sample blank value, and minimizes carry-over from the control to the first sample. For samples containing "normal" levels of organic carbon (>200 μg) the sequence is blank, conditioner, blank, conditioner, standard, standard, control.

The weight of calibration standard used is also dependent on the characteristics of the sample material. In the case of samples anticipated to contain relatively high levels of organic carbon, standards in the range of 2500 to 3500 micrograms are used. For low-carbon samples, 1000 to 1500 micrograms of standard is analyzed.

5.1.6 Re-calibration

Additional blanks and standards are analyzed periodically during the run to check performance and adjust for drift. The interval at which these are run depends on the stage of use of the reduction tube in the instrument. (When the reduction tube becomes exhausted, nitrogen background readings increase dramatically. It is therefore important to monitor nitrogen blanks more frequently as the tube approaches the end of its lifetime.) For a new reduction tube (< 150 runs since replacement) there are 17 runs between each blank/standard set. When a reduction tube has been in place for more than 150 runs, this interval is shortened to eight runs.

5.2 FIA Calibration

The automated nutrient analyzer is subjected to a multiple-standard calibration run prior to running a sample batch. For the determination of dissolved nutrients in coastal and open-ocean sea water samples, a series of six standards containing all of the nutrient species of interest (up to five species) in a 30, 20, 10, 3, 2, 1 μM concentration sequence is prepared in deionized (DI) water, along with a DI water blank and sea water blank (low-nutrient natural sea water, aged to allow nutrient values to drop to near-zero levels). An independently-prepared "control" solution containing an intermediate concentration of each of the nutrients is also prepared.

5.2.1 Refractive Index Correction

The chemistries used in determining the various nutrient species on this instrument have been developed by the manufacturer to have little or no salt effect, so the analytical response is the same for fresh/DI water samples/standards as for salt water samples/standards. Salt water samples, however, exhibit a refractive index-related response in the flow-through detectors, so the sea water blank is used to adjust the measurement timing parameters to compensate for the refractive index effect.

5.2.2 Calibration Curve Precision

Each calibration standard is analyzed in duplicate, and the resulting data is used to establish calibration curves for each nutrient species. Curves may be either first-order (linear) or second-order fits to the data. If the mean of the two replicates of any standard differs from the known concentration of that standard by more than 10%, or more than one-half the concentration of the lowest standard, whichever is greater, the calibration for that species is considered invalid and the calibration run is repeated. In addition, if the value for the control sample differs from the known concentration by more than 10%, that calibration run must be repeated, after determining and correcting the source of the discrepancy. (See Section 6 for more information on precision and accuracy evaluation.)

5.2.3 Calibration Checks

Instrument calibration is checked at the beginning of a sample-batch run, at the end of the run, and periodically during the run. At the beginning of the run, an intermediate-concentration standard (check standard) and the control sample are analyzed. The value from each of these samples must be within 10% of the known concentration for each of the nutrient species, or the run is aborted. Only the check standard is used for monitoring performance later in the run. The check standard is re-analyzed after every twenty sample analyses. If the value is not within 10% of the value for the last-run check standard for each of the nutrient species, the cause of the discrepancy is investigated; if the cause is not immediately apparent and correctable, the run is aborted. After the last sample is analyzed, the check standard is analyzed a final time. The value from this analysis is used in the post-run data reduction to adjust for instrument drift, if necessary, or to trigger a re-run of the last group of samples if a serious anomaly is discerned.

SECTION 6. ASSESSMENT OF PRECISION AND ACCURACY

Analytical precision and accuracy are monitored by means of periodic analysis of known substances (controls) or of unknown samples spiked with known amounts of analytes (spikes), and by replicate sample analyses.

Analytical precision is the variability of the results of repeated analysis of the same sample. (This also includes a measure of sample homogeneity, in the case of heterogeneous samples.) If

many repeated determinations are made, the relative standard deviation of the determinations is the most common indication of precision. For duplicate determinations, the range of the results, expressed as relative percent difference (RPD), may be used. RPD is calculated as follows.

$$RPD = \frac{|X_1 - X_2|}{M} \times 100$$

where

$|X_1 - X_2|$ = absolute value of the difference in the two determinations,

M = mean of the two determinations

Accuracy is the degree to which an analytical measurement matches the true value of the measured substance. It is assessed by determining the percent recovery (PR) from controls and spikes. PR is calculated as follows.

$$PR = \frac{X - B}{T} \times 100$$

where

X = measured value after spiking

B = background amount in sample (= 0 for controls)

T = amount of spike added to sample

6.1 CHN Accuracy and Precision

CHN analysis accuracy is assessed during initial instrument calibration by analysis of a control sample. The MSIAL uses one of three possible materials as a control: acetanilide, NIST Oyster Tissue, or NIST Citrus Leaves (see Section 5.1.4). Precision is also assessed during the initial calibration sequence by comparison of two standard samples. The allowable variance for these parameters is given in Section 5.1.3. Continued accuracy and precision is determined during a sample run by subsequent analyses of blanks and standards at regular intervals (Section 5.1.6).

6.2 FIA Accuracy and Precision

Accuracy is assessed in the nutrient determinations by analysis of controls and spikes. The first sample following the initial calibration standard series is an independently prepared standard solution with intermediate concentrations of analytes. The PR for this sample must be within the range of 90 - 110%.

A duplicate of one sample in every 20 is spiked with analytes from an independently prepared and/or certified stock standard solution. The concentration of the standard is such that the volume of solution added to the sample is no more than 1% of the total volume, and the concentrations of spike analytes in the sample are at intermediate levels. The spike is run immediately after the unspiked sample, which itself follows a check-standard solution. Spike PRs must be within the range of 80 - 120%.

If any control or spike is not within the acceptable range, and the problem is not immediately obvious and correctable, the run is aborted and the cause of the discrepancy is investigated.

Precision is determined by means of replicate sample analyses. One sample in every 15 is run in duplicate, with one replicate immediately following the other. The RPD for these samples must be within 10%, or within the absolute limits shown in the following table.

Analyte	Maximum Difference (μM)	Concentrations Less Than (μM)
PO_4	0.1	1.0
NO_2	0.1	1.0
NH_4	0.15	1.5
NO_3	0.2	2.0
SiO_2	0.5	5.0

SECTION 7. DATA ACQUISITION, REDUCTION, VALIDATION, AND REPORTING

7.1 Data Acquisition

The raw analytical data and quality control results are reviewed during each sample-batch run. It is the responsibility of the analyst to monitor for any anomalies in both unknowns and quality control samples and to stop a run if there is any question as to the quality of the data being produced. Special care should be taken to note results that are outside the calibration range. Depending on the analysis, an appropriate dilution could be performed and the sample re-analyzed during or immediately after the run. A sample whose results might otherwise be invalid could be saved in this manner. Other things that should attract an analyst's attention include a sample result outside the range of the expected values or a sample that unexpectedly appears to be a blank. Appropriate care and observation at the bench level can save time, materials, and samples.

7.2 Data Reduction

As soon as possible after the completion of a sample run, the raw data should be exported from the instrument controller and a hard copy is printed out. Under no circumstances should raw data be left only on an instrument controller's hard drive before securing the system for the day; data files must be backed-up to another network computer or floppy disc. It is desirable to review the data while the particulars of the sample run are fresh to the analyst; data workup must therefore be completed within one week of sample analysis. The results obtained are to be reviewed for calculation and transcription errors, proper use of formulas, and appropriate significant figures and units of measurement. In addition, each type of analysis has its own particular data reduction steps.

7.2.1 CHN Data

Raw CHN data is recorded on the hard drive of the instrument controller during a sample run. At the completion of a run, the data file is transferred to one of the networked laboratory computers. A custom Basic program is then used to read the raw data file and print the summarized and formatted data to a spreadsheet file, as well as to the printer for a hard copy. The Basic program allows the selection of printout precision (number of decimal places), and the option to use an average of the K factor values, rather than the most recent values, in subsequent calculations.

7.2.2 FIA Data

The operating software of the FIA instrument stores the raw data in a proprietary format, but includes modules for printing 'custom reports', as well as for exporting the data in spreadsheet-compatible format. The first step in working up the data from a sample batch is to prepare a custom report, in which all instrument parameters and analysis results, including tabular data and

analog output (traces of detector output versus time), are printed out for reference purposes. The data is then exported as a tab-delimited text file, and the results are copied into an Excel template file. This allows the easy application of dilution factors, and incorporation of any minor corrections that may be required due to instrument drift between calibration check standards.

7.3 Data Validation

The data validation process evaluates sample preservation and holding time, precision and accuracy data, calibration and standardization data, data from blanks and control samples, the analytical method employed, and the level of detection achieved. The data produced is considered valid when all applicable quality control guidelines are met. If QC parameters are not met, corrective action must be taken and, if necessary, the sample must be re-run. Note that a single faulty QC value does not necessarily invalidate a sample run. However, the cause of the failure must be determined and shown not to effect sample results. The Laboratory Manager makes the final decision regarding the validation of sample data.

7.4 Data Reporting

Upon validation of the data for the sample batch, a final, formatted report is generated. This report includes sample identifier, constituent(s) determined, units of measurement, and analytical methods used. Quality control data for blanks, spike samples, duplicates and control samples are highlighted within the summary report. After final review by the Laboratory Manager, the report, along with a descriptive cover sheet, is transmitted to the researcher (electronically and/or by mail, as requested). A hard copy of the summary is filed with the raw data and archived, and an electronic copy is saved as well. Archived data is kept for a minimum of five years before being discarded.

SECTION 8. DETAILED ANALYTICAL PROCEDURES

8.1 CHN Analysis

Elemental analysis for carbon, hydrogen, and nitrogen is performed using either of two Control Equipment Corporation (now Exeter Analytical) Model 440XA Elemental Analyzers.

8.1.1 Instrument Description

With these instruments, precisely weighed sample material is subjected to high temperature and an excess of oxygen, and the resulting combustion gases are detected and quantified to yield the weight-percent of each of the three elements in the original sample. Samples are weighed into tin or aluminum capsules, which are then sealed and placed in an autosampler carousel ('sample wheel'). This is placed in the instrument's sample compartment, and the compartment is then sealed under a helium atmosphere. Samples are mechanically inserted into the combustion chamber (tube) via a quartz ladle, and oxygen is injected. A regulated flow of helium carries the combustion products through reagents in the combustion tube which ensure complete oxidation and remove undesirable by-products such as sulfur, phosphorous, and halogen gases. The resultant mixture of nitrogen oxides, carbon dioxide, water, and excess oxygen passes through a reduction tube containing elemental copper. Residual oxygen is removed, and the oxides of nitrogen are reduced to elemental nitrogen. The mixture of gases is thoroughly homogenized at a precise volume, temperature, and pressure in the mixing volume area of the instrument, and then passes into the thermal conductivity detector. Between the first of three pairs of thermal

conductivity cells, an absorption trap removes water from the sample gas. The differential signal (in microvolts) read before and after the trap reflects the water concentration and, therefore, the amount of hydrogen in the sample. A similar measurement is made of the signal output from a second pair of thermal conductivity cells, between which a trap removes carbon dioxide, thus determining the carbon content. The remaining gas now consists only of helium and nitrogen, which passes through a final thermal conductivity cell. The output signal is compared to a reference cell through which pure helium flows, giving the nitrogen concentration.

8.1.2 Sample Considerations

Sample types typically analyzed for CHN content include biological materials, geological materials, and glass fiber filters. In the case of biological and geological materials, it is important that the sample be thoroughly dried and finely ground. Sample homogeneity is critical, as this is generally the limiting factor for analytical precision. It is usually the responsibility of the investigator submitting material for analysis to ensure appropriate sample preparation. Care must be taken to note instances in which samples do not appear properly prepared. This information could be very useful should any questions arise regarding the resultant data.

Geological materials such as sediments pose another challenge in that the organic carbon content is often very low. While sample weights of about two milligrams are common for biological materials, weights in excess of 20 mg are often required to produce adequate response from geological samples. In cases where the expected organic carbon content is less than one percent, up to 40 mg may be analyzed using the 'double-drop' capability of the instrument – the autosampler is programmed to drop two capsules simultaneously onto the sampling ladle. It is important to note that the instrument does not differentiate between organic carbon and inorganic carbonates. Geological samples to be analyzed for organic carbon content only must be pre-treated to remove the inorganic carbon compounds.

When the particulate organic carbon and nitrogen content (POC/PON) of natural waters is desired, the water sample is filtered through a glass fiber filter, and the filter is combusted in the CHN instrument. In this method, a pre-combusted glass fiber filter is used to filter a known volume of water. The filter is then placed in a small nickel cylinder ('sleeve'), loaded into the instrument and analyzed. Filters up to 25 mm in diameter can fit into one sleeve, and larger filters up to 47 mm may be cut in half and run as double-drop samples. The samples are assigned a nominal weight of 100 ug, and the results are reported directly in micrograms of the element on the filter. As in the case with geological materials, filter samples that may contain carbonates must be treated before analysis to ensure that only organic carbon is detected.

8.1.3 Sample Weighing Procedure

All standards, controls and unknown samples (except filters) must be precisely weighed before analysis in the CHN instrument. A Cahn Model C-33 microbalance is used for this purpose. A tin or aluminum capsule is placed on the balance and tared. An appropriate amount of sample is placed in the capsule, and the weight is determined to a precision of 1 ug. The weight is recorded on a Sample Data Sheet (SDS), along with sample ID, sample type, and position in the sample wheel. The sample capsule is then crimped shut and placed in a nickel sleeve (as a protective carrier), and the sleeve is placed in the sample wheel. This process is repeated for all samples and standards in the sample batch, or until the sample wheel is filled (there are 64

positions available in a sample wheel). (See Section 5.1, CHN Calibration, for a description of the order and frequency of analysis for QC and unknown samples.)

8.1.4 Batch-Run Procedure

A CHN batch run is initiated by entering the sample ID and weight information from the Sample Data Sheet into the computer. The sample compartment is then opened, the old (empty) sample wheel is removed, and the spent sample capsules and sleeves from the previous run are cleaned from the waste bin. The new sample wheel is then placed in the instrument, the compartment is closed and sealed, and the run is started. Although a sample wheel holds a maximum of 64 unknown and QC samples, the instrument also has a discrete sampling port, through which individual samples can be inserted after the run has been started. (This is useful for verifying calibrations or running 'rush' samples). Up to a total of 70 samples may be run in a batch. During a run, results are stored on the controlling computer's hard drive and also printed to a dedicated printer. See Section 5.1, CHN Calibration, for details on monitoring calibration and performance during the run. When the run is finished, the data is worked up as described in Section 7.2.1, CHN Data.

8.2 Nutrient Analyses

Nutrient analyses are carried out with a Lachat Instruments (division of Zelweger Analytics) Model QuikChem 8000 Flow Injection Analyzer. This system is equipped for the simultaneous analysis of up to five nutrient species in aqueous samples. The autosampler holds racks which accommodate up to 120 sample tubes plus additional locations for blanks, standard solutions, and control samples.

8.2.1 Instrument Description

Flow injection analysis is a continuous-flow technique for automated wet-chemical analysis, similar in overall operation to AutoAnalyzer instruments. In this system, solutions are continuously pumped, in appropriate proportions, into a reaction manifold, where they combine at the proper points and react to form detectable derivatives with the sample analyte. FIA differs from the more conventional bubble-segmented technique used by AutoAnalyzers in that (a) no bubble segmentation is used, (b) the fluid conduits are laminar flow channels, and (c) the sample is injected as a discrete plug into the carrier stream in order to effect the production of the detectable species. The output from the FIA detectors, which are simple colorimeters, is a peak-shaped signal corresponding to passage of the injected solution (now mixed with other solutions and having generated the detectable species) through the detector flow-cell. The height and area of the peak are proportional to the analyte concentration. Peaks are measured against baseline output for every injection.

A sample is aspirated from its sample tube in the autosampler racks and pumped through the sample loops in the injection valves - each analytical channel is equipped with a separate injection valve. Timing parameters are set to allow complete filling of the valves of all channels being utilized. Once the loop is filled, the sample is injected – injections for different channels may be staggered according to the time required to fill each loop. A complete analysis cycle takes 40 to 80 seconds, depending on which channels are being used.

8.2.2 Batch-Run Procedure

Several tasks must be performed in preparation for nutrients analysis. For highest efficiency, they should be performed in the sequence given. Once the preliminary tasks are completed, the sample run is initiated.

8.2.2.1 Instrument Startup

Prepare fresh reagents as needed for all active channels according to manufacturer instructions. Switch on the power strip that controls the instrument modules and then start the operating program on the computer. Make sure all reagent containers are full and any required auxiliary components such as the Ascarite trap are in place. Switch the pump speed to Standby, and start the pump. Set the temperatures on the heating coils for the phosphate and silicate channels, if active. Check system timing parameters if necessary by running the dye solution. Switch the heating bath (for thawing samples) on and set to 50^{o}C.

8.2.2.2 Calibration Standards Preparation

Prepare calibration standard solutions from the stock standard solution, using calibrated pipettes and 200 ml volumetric flasks. Prepare control solution from control stock solution using a 100 ml volumetric flask.

8.2.2.3 First Calibration Run

Fill the calibration standard tubes and blank solution tubes and place them in the sampler rack. Select an appropriate tray table from the operating program, assign a name to the data file, and start the calibration run. Calibration data files are named according to the number of active channels, the date, and the number of calibration runs performed that day, e.g., "4_0312b" for the second 4-channel calibration performed on March 12.

8.2.2.4 Sample Preparation

While the calibration standards are being run, prepare the samples for analysis. Remove samples from freezer and place in heating bath. Set timer to 40 minutes. Fill out the Sample Data Sheet with sample IDs in the order the samples will be run. When the calibration run is finished, open a new tray table and enter the sample ID information, including QC samples. Open the Data Quality Management (DQM) file and assure that control sample, check standard, and spike sample concentrations are correct. At the end of the 40 minutes, remove the samples from the heating bath, rinse the containers briefly with DI water and place them in the dark to cool. Place the next group of samples in the heating bath, if appropriate. Set the timer for 40 minutes for both cooling samples and heating samples.

8.2.2.5 Second Calibration Run

If there were any problems with the first calibration run, or if it has been more than one hour since the run, perform another calibration run. Make sure there is sufficient standard solution in each of the sample tubes, select the appropriate tray table, and start the run.

8.2.2.6 Calibration Curve Check

When the calibration run is finished, examine the generated calibration curves. Make adjustments to peak-integration timing and other parameters as necessary to optimize the analysis conditions and the calibration curves. Print out the final calibration curves.

8.2.2.7 Analyze Samples

After the thawed samples have cooled, mix each sample thoroughly by inverting all containers at least five times, transfer them into sample tubes and place them in the autosampler racks. When all analysis conditions have been optimized, calibrations are acceptable, and sample data has been entered in the tray table, the batch run may be started. Check that the Auto DQM Schedule is correct, then choose Run Tray from the menu and assign the data file name. Sample-batch data file names also include the number of active channels, but use the first four letters of the investigator's name at the beginning and a 3-digit number corresponding to the sequential sample batch number run on the instrument at the end. Thus, a run analyzing only nitrate and phosphate for Clinton, for example, might have the file name Clin2150, where 150 represents the 150^{th} sample batch run on the FIA system (since installation). Start the run. Monitor the initial check standard and control sample results displayed on the computer screen as described in Section 5.2.3, Calibration Checks; be ready to abort the run if any problems appear. Continue to monitor the run, with special attention to the periodic QC samples, until the run is completed. Work up the data as described in Section 7.2.2, FIA Data.

SECTION 9. CORRECTIVE ACTIONS

In the event that QA/QC requirements are not met, the cause of the failure must be determined, and the sample batch run may have to be aborted. Certain types of failure are relatively

common, and can be diagnosed quickly and easily. Others may require extensive evaluation and referral to instrument trouble-shooting charts. After a determination of the problem has been made, corrective action must take place to bring the system back into control. It must also be determined whether the sample results prior or subsequent to the failure were compromised. After corrective action has been performed, it must be documented both to verify that it has occurred and to provide a reference for future trouble-shooting. If sample results were compromised, the affected samples, if additional material exists, must be re-analyzed. All major incidences of corrective action must also be brought to the attention of the Laboratory Manager.

A source of potential problems common to many of the Analytical Lab's instruments is the fact that the sample containers required by an autosampler are impossible or impractical to label. Great efforts are therefore made to keep samples well organized and to keep track of their final locations in the autosamplers. Corrective actions are possible if the misplaced items are standards, blanks, or certain QC samples, since the results from these materials are predictable and carefully monitored. However, reversed or otherwise mixed up samples could be impossible to detect, and the results could be inadvertently judged to be valid. The importance of careful sample handling cannot be overemphasized to operators. All sample transfers and ID transcriptions must be checked and double-checked.

Other problems are unique to the specific analysis.

9.1 CHN Analysis

A possible source of failure for controls and check standards in CHN analysis is weighing errors. The symptom in this case is that while the weight percents or K values for carbon and nitrogen are out of acceptable range, the C/N ratio is consistent with the material analyzed. Corrective action in this case is to carefully weigh a new standard or control sample and analyze it via the single-sample insertion port. This evaluation and action should be clearly noted on the printout for that day's sample run.

Another source of possible problems is underestimating routine maintenance needs, such as replacement of spent reduction or combustion tubes and/or spent traps. The symptoms can vary, and it is suggested the analyst refer to the trouble-shooting section of the instrument manual for evaluation. If detected early, these problems usually do not result in lost data. The corrective action for each of these problems is to perform the required maintenance. All maintenance procedures are recorded in the sample log book; if done as a corrective action, it is noted as such.

Mechanical malfunctions can occur with these instruments. The sample wheel may fail to advance properly, in which case a "sample" appears to have very low (blank) levels, and a subsequent blank may appear quite high. This condition is verified by stopping the run, opening the sample wheel compartment, and visually determining the position of the sample wheel. The data obtained after this particular failure can be salvaged by simply shifting the raw data back one sample, and re-calculating the results using the correct sample weights.

Another malfunction causing a sample to appear to have very low levels is when the sample fails to drop properly from the sample wheel onto the ladle. In this case, however, subsequent results, including the blank, appear normal. As long as this does not result in complete jamming of the sample wheel, it is not necessary to halt a run. However, care must be taken to salvage the un-dropped sample when the run is completed. It can then be re-analyzed with a subsequent group of samples. (These results are indistinguishable from having a normally dropped sample that is

truly low in combustible material. Care should be taken in removing the sample wheel whenever an unexpectedly low sample result is observed.)

9.1 FIA Analysis

With the multitude of operator tasks required to run this system, the possibility of operator error is significant. Mis-dilution of a standard solution, for example, is occasionally encountered. This problem is easily detected by the outlying location of the data points on the calibration curves (all analytes exhibit the same behavior); the corrective action is to re-make the standard and re-run the calibration. Incorrectly prepared reagent solutions can cause a range of symptoms, from minor changes in sensitivity to total lack of response; a properly prepared solution, placed in the wrong container, can have dire consequences. These types of errors can be difficult to troubleshoot, but once the problem is diagnosed the corrective action is clear.

Potential mechanical problems with this system also abound. Some, such as pump-tube deterioration, can be anticipated and remedied with routine maintenance. Some appear gradually, such as sluggish injection valves, and can be recognized and corrected before they cause significant problems. Others happen suddenly and/or intermittently, such as a jammed autosampler probe, and can cause interruption or abortion of a run along with possible loss of data. A perennial problem is the occurrence of air bubbles in the manifold lines. The symptom is intermittent spikes in the detector signal, which may or may not interfere with peak integration. The source of the bubbles is usually a leak in a fitting on the intake side of the pump, but the cause of this leak is often a restriction in the inlet tubing rather than a faulty fitting. The origin of a bubble problem can be difficult to trace, and can meanwhile result in compromised or lost data, requiring the re-analysis of samples.

Constant vigilance is required with this instrument.

Section 10. ICPMS ANALYSIS

The Finnigan Element 2 Inductively Coupled Plasma Mass Spectrometer (ICPMS) is used for metals determination in carbonates (foraminifera, fish Otoliths) and natural waters (marine and fresh).

Section 10.1 Instrument Description

The Element 2 ICPMS is a high resolution double focusing magnetic sector mass spectrometer with an argon inductively coupled plasma ion source. It is utilized for determination of elemental composition, usually limited to metals with ionization potentials much lower than argon. Solid carbonate samples are dissolved in 1% nitric acid and aspirated into the ICPMS. Alternatively, solid samples can be analyzed directly using the New Wave UP213 laser ablation system. The ablated material constitutes a dry aerosol that is swept into the ICPMS with helium carrier gas. Natural water samples are digested using EPA Method 200.8 and then aspirated into the ICPMS.

Section 10.2 Calibration Procedures

The ICPMS is calibrated for carbonate analysis using matrix matched standards (spiked gravimetric standard, SGS). The SGS contains known amounts of each analyte of interest and the appropriate amount of the spike mixture. The spike mixture contains known amounts of internal standard elements as well as enriched isotopes for those elements that are quantified using the method of isotope dilution. Isotope ratios are collected for each analyte. The ratio of enriched isotope to natural isotope is collected when using the method of isotope dilution. The ratio of an internal standard isotope to analyte isotope is collected when using internal standardization. The SGS is run before sample analysis to obtain a mass bias correction for the isotope ratios collected using the mass spectrometer. The mass bias correction is applied to each sample isotope ratio to obtain the actual isotope ratio of the unkown.

The ICPMS is calibrated in a similar manner when ablating solids using the laser ablation system. Solution standards are used to calibrate the instrument. The solutions are prepared in 1% nitric acid. When ablating a sample, the dry aerosol is directed to the spray chamber where blank 1% nitric acid is being aspirated. This mixture of ablated material and 1% nitric acid is then directed to the plasma. This maintains similar plasma conditions both when running solution standards and ablating solids. The actual mass of ablated analyte can't be determined by this method, so absolute concentrations are not possible. However, elemental ratios can be determined by this method. All analytes are quantified as ratios to calcium, which is the most abundant element in the matrix.

Natural waters are calibrated using the method of standard additions, method of isotope dilution, or external calibration curve. Internal standards are added when using both the method of standard additions and external calibration curve systems. Trace elements in seawater samples are calibrated using the method of standard additions to overcome the severe matrix effects in high dissolved solid solutions. Minor elements in seawater are analyzed by isotope dilution (magnesium and strontium) or external calibration curve (calcium). Fresh water samples are calibrated using multiple point external calibration curves.

Section 10.3 Assessment of Accuracy and Precision

Precision is calculated as % relative standard deviation (% rsd) as follows:

standard deviation / mean, expressed as a percentage

Accuracy is calculated as percent deviation as follows:

expected value / measured value -1, expressed as a percentage

Accuracy and precision estimates are determined using consistency standards with every analytical batch of carbonate samples. The consistency standards are mock foraminifer solutions containing ratios of elements that are within the range of natural variability. The consistency standards are prepared with calcium concentrations such that when 100ul is diluted with 500ul of spike mixture, the resulting calcium concentration is approximately 2.5mM, which reflects the calcium concentration of 125ug of solid calcium carbonate dissolved in 500ul of spike mixture. Replicate analyses of the consistency standards within each run allows for estimates of external

precision. The consistency standards are of known analyte concentration, so accuracy estimates are determined as well. The control criteria for carbonate analyses are 2% rsd and 3% percent deviation for elemental ratios to calcium.

When ablating solid carbonate samples, solution consistency standards are utilized in a similar fashion, but a solid standard, NIST612, is also run in replicate to provide estimates of precision and accuracy for laser ablated materials. The control criteria for carbonate analyses by laser ablation are 20% rsd and 20% percent deviation.

Precision and accuracy for natural water samples are determined by replicate check standards, spiked samples, and spiked blanks. The precision control criteria for natural water analyses are 10% rsd. The accuracy control criteria for check standards is 10% percent deviation. The accuracy control criteria for spiked samples is 70-130% percent recovery. The accuracy control criteria for spiked laboratory blanks is 85-115% percent recovery.

If the control criteria for accuracy and/or precision are not met for any method, the analysis is aborted and corrective action is taken to resolve the analytical problem.

10.4 Instrument and Procedural Blanks

Instrument blanks are determined for all isotopes for all methods. The instrument blank intensities are subtracted from raw isotope intensities for all samples and standards. Absolute instrument blank values are monitored daily to check for any unusual rise that may warrant aborting an analysis run and taking corrective action.

Procedural blanks are prepared for all water samples that undergo dilution and/or digestion. These blanks utilize the same reagents and similarly prepared lab-ware as all samples and spiked laboratory blanks. If procedural blanks exceed the target reporting limit, the analysis for that analyte is out of control and should be re-prepared.

10.5 Target Report Limits and Method Detection Limits

Target Reporting Limits and Method Detection Limits

Method	Constituent	Target Reporting Limit	Method Detection Limit
SM 4500-NH3 G	Ammonium (as N)	0.1 mg/L	0.03 mg/L
SM 4500-NO2 B	Nitrite (as N)	0.01 mg/L	0.003 mg/L
SM 4500-NO3 F	Nitrate+nitrite (as N)	0.1 mg/L	0.03 mg/L
SM 4500-P F	Orthophosphate (as P)	0.01 mg/L	0.003 mg/L
SM 4500-Si F	Silicate (as Si)	0.1 mg/L	0.03 mg/L
EPA 200.8	Calcium	0.05 mg/L	0.01 mg/L

EPA 200.8	Copper	0.5 μg/L	0.1 μg/L
EPA 200.8	Iron	0.02 mg/L	0.007 mg/L
EPA 200.8	Magnesium	0.02 mg/L	0.007 mg/L
EPA 200.8	Manganese	0.1 μg/L	0.03 μg/L
EPA 200.8	Zinc	0.5 μg/L	0.2 μg/L

Appendix B – UGA QA Summary

QUALITY ASSURANCE PROCEDURES SUMMARY

University of Georgia Institute of Ecology

STABLE ISOTOPE/SOIL BIOLOGY LABORATORY
Analytical Chemistry Lab, Rm154
Institute of Ecology, Green Street
University of Georgia
Athens, Georgia 30602

February 28, 2007

Quality Assurance Measures

With respect to precision, accuracy, recovery, and blanks, UGA Laboratory adheres to the following procedures:

1) Precision:
To confirm precision UGA Laboratory runs multiple (20 +) injections of the exactly the same analyte. The variation in peak height is assessed, and cannot exceed the detection limit for a given manifold/concentration range setup. This roughly translates into 1/100th of the concentration of the measured standard (*e.g.*, 1mg/L (or 1000ug/L) standard should not vary more than +/- 10ug/L for a set of 20 measured standards.

2) Accuracy:
UGA Laboratory uses two different standards to determine accuracy. One standard is a QC standard available from Spex Certiprep that comes in a sealed glass ampoule, and comes with certified values for nitrate, phosphate and ammonium. The other standard is prepared from dry chemicals in the laboratory. The known concentrations of these two standards are compared the two measured values to determine acceptability of the run. For sample runs, one standard-containing samples is run for every 20 unknowns.

3) Recovery:
To determine % recovery, a known concentration of standard is analyzed and compared to the output concentration value. If, for example a 1mg/L concentration of analyte is used for the spike, and the output reads 0.9mg/L, it is interpreted as 90% recovery. Runs will not be accepted unless they match known concentration spikes within +/-2% or better. % Recovery is used when digesting nonlabile QC standards as a reference check for running with total persulfate N or P.

4) Blanks:
UGA incorporates blanks into the run setup of samples. Every 20 samples, a series of 6 blanks are run. The format is as follows: samples (n=20) followed by blank, the working standard, another blank, working standard again, two more consecutive blanks, then back to samples (n=20), and so on. The second working standard is tagged by the software to serve as a drift correction. The last blank is tagged by the software to serve as a baseline correction/reading.

General Quality Assurance measures carried out by UGA Laboratories are as follows:

- 1000 ppm standard stocks are made from appropriate dry reagents (KNO3, NaNO2, (NH4)2SO4, and KH2PO4) and are checked by analyzing Environmental Protection Agency certified Nutrient-1 quality control (QC) solutions of known analyte values. If the determined value of the QC solution differs from the known value by > 1%, the stock is discarded.
- Working standards are made daily from standard stocks
- Calibration of each run is accomplished by linear regression on a descending sequence of three working standards and a blank at the start of the run. Within-run drift correction is achieved by one recalibrant standard and baseline blank every twenty samples. Recovery check standards are included once for every twenty samples.

- Digests for total nitrogen and total phosphorus are also checked by digesting and analyzing E.P.A. Nutrient-2 QC solutions formulated to challenge digestion techniques alongside every batch of unknowns, one EPA-QC2 standard per twenty unknowns.
- Clients are referred to the colorimetric analysis instructions for methods of sample treatment that will ensure the best possible precision and accuracy.
    - Liquid samples must be free of turbidity and particulate matter. Any such substances must be removed before analysis by filtering or centrifugation.
    - Strongly colored samples may contribute confounding absorbance at the analytical wavelength.
    - Water samples which cannot be analyzed immediately after collection must be preserved for shipment. The E.P.A. publication Methods for Chemical Analysis of Water and Wastes lists acceptable preservation methods and holding times for many analytes

Standard Operating Procedures for Simultaneous Determination of Total Nitrogen and Total Phosphorus (USGS Methods I-4650-03 & I-2650-03)

Equipment

1) Chemical autoclave
2) 13x100 mm glass screw-cap culture tubes with teflon-lined caps. (Tubes are acid-washed in 20% HCl and muffled at 500 degrees C for two hours. Caps are acid-washed in 50% HCl)
3) autoclave-safe test tube racks
4) 100 ml, 200 ml or 500 ml acid-washed volumetric flask for oxidizing reagent (depending on how much reagent is needed)
5) 500 ml acid-washed volumetric flask for 3.75M NaOH stock
6) 1000 ul and 5000 ul automatic pipetters
7) weigh boats and clean chemical spatula

Reagents

1) fresh deionized H2O
2) low-N potassium peroxydisulfate (e.g. Fisher P282-100)
3) boric acid (e.g. Baker 0084-01)
4) low-N NaOH if stock is needed
5) EPA-certified Nutrient 2 quality control digest standard

NaOH stock:

Place ~350 ml diH2O in 500 ml volumetric on stir plate. Add 75.0 g NaOH. Stir to dissolve; remove stir bar and bring to volume. Cap with parafilm and invert to mix. Allow to stand ~30 minutes and recheck volume.

Oxidizing reagent:

Place clean volumetric of appropriate size on stir plate; into it rinse in the appropriate amounts of reagent from the table below with diH2O. Bring to about 80% of flask volume with diH2O and stir to dissolve; takes ~15 minutes on stir plate (gentle warming may help.) When dissolved, remove stir bar and bring to final volume with diH2O. Cap with parafilm and invert to mix. Allow to stand ~30 minutes and recheck volume.

	100 ml	200 ml	250 ml	500 ml
persulfate	5.2 g	10.4 g	13 g	26 g
boric acid	3.12 g	6.24 g	7.8 g	15.6 g
NaOH stock	10 ml	20 ml	25 ml	50 ml

(This reagent may be stored 7 days at room temperature. Crystalizes when refrigerated.)

EPA Nutrient-2:

10 ml concentrate from ampoule in 1000 ml diH2O (or 5 ml concentrate in 500 ml.) yields 5.00 mg/liter total nitrogen and 1.50 mg/liter total phosphorus.

Procedure

1) bring samples to room temperature if chilled or frozen
2) make up fresh digest reagent, and NaOH stock if needed
3) obtain acid-washed, muffled digest tubes; label them.
4) for unknowns and EPA2 samples:

- on first pass through the sample set, pipette 5 ml sample into each labeled digest tube. Cap loosely to exclude dust.
- on second pass, pipette 1 ml oxidizing reagent into each digest tube. Cap tightly and mix well (invert several times.)

5) For reagent blanks, pipette only 1 ml oxidizing reagent into tube and cap tightly. (N.B., take care! Qualls (5) p.136: "For low level samples the variability in the reagent blanks determines the limit of detection, not the error associated with the NO3 and PO4 analyses themselves.")
6) Place capped tubes in autoclave, 30 minutes on liquid cycle. (= 30 minutes on "sterilize" in addition to all other cycle segments. If using pressure-cooker field method, time 30 minutes after coming to canning temperature in addition to warmup and cooldown times.)
7) After tubes are cool, add 5 ml diH2O to all reagent blank tubes so that the total volume of liquid in these tubes is the same as in the others. (N.B. Qualls (5) p.136: "Since distilled or deionized water contains significant N, the dilution water [for the blanks] is added after the digestion.")
8) Analyze digest-tube contents on Alpkem using the nitrate-nitrite and orthophosphate manifolds.

Post-analysis calculations

1) Take the mean of the reagent blank determined values. Throw out any that are >2 std. deviations above the mean (for nitrogen in particular this indicates that the tube cap has cracked during the autoclave step and admitted atmospheric N to the tube.)
2) To compensate for color absorption by the digest reagents, subtract the mean reagent blank N and P values from the Alpkem determined values for each unknown or EPA2 sample.
3) The effect of diluting the samples by the addition of digest reagents must be reversed:

$$df = \frac{\text{sample volume} + \text{reagent volume}}{\text{initial sample volume}}$$

In the case of the above procedure, where initial sample volume is 5 ml and reagent volume is 1 ml,

$$df = \frac{5 \text{ ml sample} + 1 \text{ ml reagent}}{5 \text{ ml sample}} = 1.2$$

Find the actual value of the undiluted sample by multiplying the determined value (after reagent blank subtraction) by the df.

True analyte concentration

=

(Alpkem raw determined value - rblank value)*(df)

Comments

1) Successful digests have pH in the range 5 to 8; incomplete digests are ~2. This can be checked with wide-range pH paper. We have observed no reliable correlation between final digest pH and the yellow color developed in some digests, so the color cannot be used to spot incomplete digests.
2) Instead of using reagent blanks, it is possible to digest the calibration standards (including water blanks, i.e. calibration standards of content zero), the D3 (recalibrant) and ref3 (reference check) and the W (baseline drift correction) cups. Thus with digest reagent in both samples and calibants, the reagent's contribution to total absorbance will be compensated for automatically. (This strategy is of course useable only if all samples in the run are using the same reagent/diluent ratio.)
It may be necessary to have different dilutions of the EPA2 QC standards for nitrate and phosphate to get both into the optimum manifold range (e.g. if the PO4 manifold range is 0.2-1 ppm while the expected TP content of EPA2 is 1.5 ppm PO4, the QC digests will be offscale for phosphate unless diluted.) Perform these dilutions before digestion and then use the same reagent/diluent ratio for everything.

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Appendix C – Bight 08 Coastal Wetlands: Eutrophication Assessment Field Methods Manual

Appendix D – Bight 08 Coastal Wetlands: Eutrophication Assessment Laboratory Methods Manual

Appendix E- List of Acronyms

ASTM	American Society for Testing and Materials
chl *a*	Chlorophyll *a*
CI	Confidence Interval
CRM	Conventional Reporting Method
DO	Dissolved Oxygen
DOC	Dissolved Organic Carbon
DQO	Data Quality Objective
MS	Matrix Spike
MSD	Matrix Spike Duplicate
NA	Not Applicable
NAWQA	National Water Quality Assessment
NPDES	National Pollutant Discharge Elimination System
%OC	Percent Organic Carbon (sediment)
%ON	Percent Organic Nitrogen (sediment)
PT	Proficiency testing
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QC	Quality Control
RPD	Relative Percent Difference
SCCWRP	Southern California Coastal Water Research Project
SDRWQCB	San Diego Regional Water Quality Control Board
SM	Standard Methods for the Examination of Water and Wastewater
SOP	Standard Operating Procedure
SRM	Standard Reporting Method
SRP	Soluble Reactive Phosphorus
TAC	Technical Advisory Committee
TDN	Total Dissolved Nitrogen
TDP	Total Dissolved Phosphorus
TMDL	Total Maximum Daily Load
TP	Total Phosphorus

Appendix F – QAPP Checklist