QUALITY ASSURANCE PROJECT PLAN

Elkhorn Slough National Estuarine Research Reserve
Volunteer Monthly Water Quality Program

Grant #20040581 and #20060387

Prepared for:
Central Coast Regional Water Quality Control Board
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San Luis Obispo, CA 939401

Prepared by:
Elkhorn Slough National Estuarine Research Reserve

May 15, 2009
Version 1 Draft 3

GROUP A ELEMENTS: PROJECT MANAGEMENT

1. Title and Approval Sheets

APPROVAL SIGNATURES

GRANT ORGANIZATION:

Title:	Name:	Signature:	Date:
Research Coordinator (Project Manager & QA Officer), Elkhorn Slough National Estuarine Research Reserve (ESNERR)	Kerstin Wasson		3/8/2006
Research Associate, Center for Agroecology and Sustainable Food Systems, University of California, Santa Cruz (UCSC)	Marc Los Huertos		4/8/06
Associate Professor, UCSC	Bruno Sansó		4/6/6
Water Monitoring Coordinator, ESNERR	John Haskins		3/15/2006
Water Quality Scientist, ESNERR	Kristy Meyer		3/8/2006
Executive Director, Elkhorn Slough Foundation (ESF)	Mark Silberstein		3/8/2006
Director, Moss Landing Marine Laboratories (MLML)	Kenneth Coale		3/8/2006
Laboratory Manager, Monterey County Consolidated Chemistry Laboratory (MCCCL)	Gerry Gulbert		4/19/2006

REGIONAL BOARD:

Title:	Name:	Signature:	Date:
Environmental Scientist, Central Coast Regional Water Quality Control Board (CCRWQCB) (Grant Manager)	Amanda Bern		5/9/06
Environmental Scientist, CCRWQCB (QA Officer)	Karen Worcester		4/26/06

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3. Distribution List

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Research Associate	Marc Los Huertos (UCSC)	(831) 459-4926	1
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Water Monitoring Coordinator	John Haskins (ESNERR)	(831) 728-2822	1
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Director	Kenneth Coale (MLML)	(831) 771-4400	1
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Environmental Scientist (CCRWQCB QA Officer)	Karen Worcester (CCRWQCB)	(831) 549-3333	1

4. Project/Task Organization

4.1. Involved parties and roles

The Elkhorn Slough Foundation (ESF) is a community-supported, non-profit organization dedicated to the conservation and restoration of the Elkhorn Slough and its watershed. ESF and the Elkhorn Slough National Estuarine Research Reserve (ESNERR) have worked in partnership for over 20 years to conserve, enhance, and restore the fragile estuarine ecosystems of the Elkhorn watershed using science-based management. ESNERR will serve as the lead agency for this project. ESNERR will organize sample collection, field and in-house analyses of samples, and the initiation and maintenance of contracts with the Monterey County Consolidated Chemistry Laboratory (MCCCL), Moss Landing Marine Laboratories (MLML), and the University of California, Santa Cruz (UCSC).

Kerstin Wasson is the Project Manager. She will oversee all aspects of this project including management of field staff, sample collection and analyses, and interactions with contracted agencies. She will also serve as the project's QA Officer. Mark Silberstein, ESF's Executive Director, will provide assistance with coordinating water monitoring and serve as a project advisor. Kristy Meyer is a water quality scientist hired with the funding provided by this grant. She will complete a Quality Assurance Project Plan approved by the Regional Board, coordinate and conduct sample collection with the Field Technician and volunteer staff, conduct supplemental nutrient analyses, serve as data manager, develop a GIS database, and supply a final technical report to the RWQCB that will be made public on the ESF website. John Haskins, ESNERR's Water Monitoring Coordinator, will provide mentoring to the water quality scientist. He will oversee data collection, nutrient analyses, and data management. He will also provide sampling and analyses training to field and laboratory staff. Sue Shaw, Field Technician, will collect water samples and will be assisted by volunteer staff.

ESNERR has sub-contracted with the University of California, Santa Cruz (UCSC). Marc Los Huertos (Research Association with the Center for Agroecology and Sustainable Food Systems) and Bruno Sansó (Associate Professor, Applied Math and Statistics) will use our database and also collect and evaluate additional water quality datasets to 1) determine statistically significant long-term trends in water quality and 2) design and test alternative sampling design. UCSC will perform additional nutrient analyses for QA/QC purposes and for specialized nutrient samples. USCS will analyze samples in accordance with their own protocols; however, these will meet or exceed all method and quality assurance requirements found in this QAPP. UCSC will submit publications resulting from analyses of this database to peer-reviewed journals for a scientific audience and present data at outreach education forums that include resource agencies and managers, landowners and users, growers, and other interested stakeholders.

ESNEER utilizes the Monterey County Consolidated Chemistry Laboratory (MCCCL) for nutrient analyses through an arrangement with the Monterey County Water Resources Agency. Gerry Guibert is the laboratory manager at MCCCL and oversees analyses completed at this facility. MCCCL will analyze samples in accordance with their own method and quality assurance requirements. These will meet or exceed the requirements outlined in this QAPP.

ESNERR utilizes Moss Landing Marine Laboratories (MLML) for QA/QC sample analysis. Kenneth Coale, Director, serves as liaison with ESNEER and oversees the Chemical Oceanography Laboratory at MLML where nutrient analyses are performed. A combination of ESNERR and MLML staff completes nutrient analyses at MLML. All nutrient analyses conducted at MLML will follow the method and quality assurance protocols attached to this QAPP; they will meet or exceed the requirements outlined in this QAPP.

Table 4.4.1.: (Element 4) Personnel Responsibilities

Name	Organizational Affiliation	Title	Contact Information (Telephone number, fax number, email address.)
Kerstin Wasson	ESNERR	Research Coordinator (Project Manager & QA Officer)	(831) 728-2822 research@elkhornslough.org
Mark Silberstein	ESF	Executive Director	(831) 728-5939 silbermud@elkhornslough.org
John Haskins	ESNERR	Water Monitoring Coordinator	(831) 728-2822 john@elkhornslough.org
Kristy Meyer	ESNERR	Water Quality Scientist	(831) 728-2822 kristy@elkhornslough.org
Marc Los Huertos	UCSC	Research Associate	(831) 459-4926 marcos@cats.UCSC.EDU
Bruno Sansó	UCSC	Associate Professor	(831) 459-1484 bsanso@ucsc.edu
Gerry Guibert	MCCCL	Laboratory Manager	(831) 755-4516 guibertg@co.monterey.ca.us
Kenneth Coale	MLML	Director	(831) 771-4400 coale@mlml.calstate.edu

4.2. Quality Assurance Officer role

Kerstin Wasson, ESNERR's QA Officer, will guarantee that data are collected and managed in accordance with this QAPP. She will review monthly QA reports from the Water Quality Scientist and initiate protocols to correct any quality assurance/control problems. The QA Officer will meet regularly (once per quarter), or sooner if concerns arise, with the Water Quality Scientist regarding quality assurance.

4.3. Persons responsible for QAPP update and maintenance

The Water Quality Scientist (Kristy Meyer) is responsible for maintaining and updating the official approved QAPP. Kerstin Wasson and Kristy Meyer may make changes to the QAPP as appropriate. Agencies listed above will notify ESNERR if their own quality assurance protocols are changed so that this QAPP may be amended accordingly.

4.4. Organizational chart and responsibilities

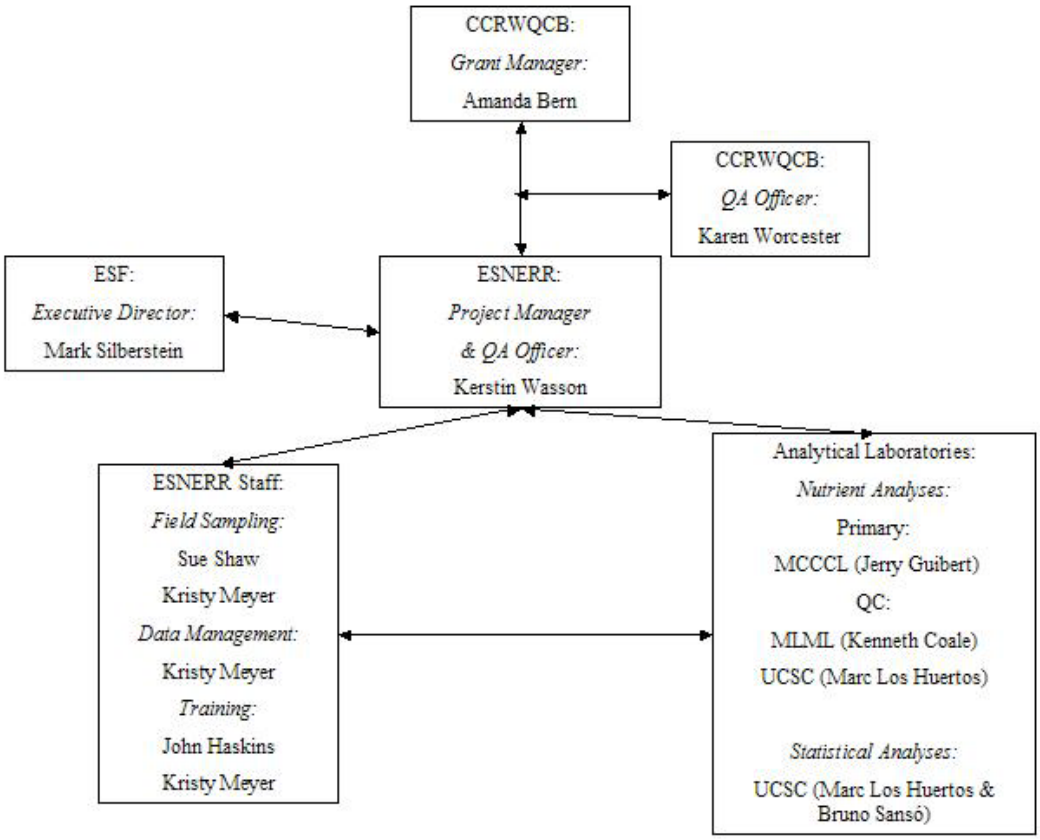

Figure 4.4.1. Organizational Chart

5. Problem Definition/Background

5.1. Problem statement

Elkhorn Slough is a small estuary in central California that opens into the Monterey Bay at Moss Landing. Elkhorn Slough provides critical plant, animal, and bird habitat and serves as an important regional fish nursery. Human activities and natural processes impact the slough's hydrography and biogeochemical cycling. Local land use includes residential development, recreation including a golf course, industry, and agriculture with both row crops and livestock operations in close proximity. The Elkhorn Slough Foundation (ESF) is a community-supported, non-profit organization. ESF and the Elkhorn Slough National Estuarine Research Reserve (ESNERR) have worked in partnership with local, state, and federal organizations to conserve and restore the Elkhorn Slough watershed's estuarine ecosystems.

Sites monitored by this project include major water bodies of concern (i.e., TMDL listed) along the central coast: Salinas River (Lower) (Nutrients, Pesticides), Elkhorn Slough (Pesticides), Moss Landing Harbor (Pesticides), the Old Salinas River Estuary (Nutrients, Pesticides), Salinas River Lagoon (Nutrients, Pesticides), Moro Cojo Slough (Pesticides), and Tembladero Slough (Nutrients, Pesticides). There are a number of strategies used in the region to reduce pollutants in agricultural runoff. Effectiveness estimates have been used to justify installation. However, there have been no efforts along the central coast to develop a robust monitoring plan to empirically demonstrate and quantify the effectiveness of these strategies. Our program seeks to provide high quality data across a broad geographic area to assess long-term trends in water quality and evaluate land management practices.

5.2. Decisions or outcomes

Our overall goal is to continue, expand, and improve our 15 year broad-scale water quality monitoring program. Measurable results will include better coordination with the Central Coast Ambient Monitoring Program (CCAMP), improved statistical and GIS analysis of results in an agricultural management context, more accurate nutrient data, and dissemination of results through publications, presentations, and our website.

5.3. Water quality or regulatory criteria

ESNERR monitoring sites are diverse with respect to seawater exchange and freshwater inputs. Emphasis is placed on levels outside the historical normal range for individual sites rather than a set numeric criterion for all sites. Therefore, ESNERR utilizes CCAMP Attention Levels and other applicable water quality standards as screening levels rather than regulatory criteria (see Table 5.3.1.).

Table 5.3.1.: ESNERR Screening Levels for Conventional Water Quality Constituents (CCAMP, 2005)

Parameter	Criteria	Type	Qualifier
Temperature	> 22 °C	CCAMP Attention Level	
Conductivity	> 3000 μS	Basin Plan Severe Problems for Ag	Affected by water temperature and the concentration and charge of ions suspended in the water
Salinity	-	-	Variable by site
DO	< 85%	Basin Plan General	Mean
DO	< 7.0 mg/L	Basin Plan Cold Water Fish	
pH	< 6.5; >8.3	Basin Plan Cold Water Fish Habitat	
Turbidity	> 10 NTU	CCAMP Attention Level	During non-storm events
Nitrate (as NO_3)	> 45 mg/L	Basin Plan Drinking Water	
Ammonia (as N)	> 2.4 mg/L	California Ocean Plan Daily Maximum	
Unionized Ammonia	>0.025 mg/L	Basin Plan General Objective	Calculated from ammonia, pH, temperature
Orthophosphate (as P)	> 0.12 mg/L	CCAMP Attention Level	

6. Project/Task Description

6.1. Work statement and produced products

TASK 1: Coordination with CCAMP/RWQCB

- Evaluate current 24 site locations and plan up to 6 new sites with CCAMP/RWQCB staff to ensure broad and consistent coverage of area without duplication
- Develop and submit Quality Assurance Project Plan
- Work with CCAMP/RWQCB to ensure data format is appropriate

Deliverables: Approved Quality Assurance Project Plan

TASK 2: Field monitoring of watershed-scale water quality

- Monthly sampling at up to 30 stations in Elkhorn watershed (as carried out for past 15 years with modifications resulting from CCAMP/RWQCB coordination)
    - Includes *in situ* measurement of dissolved oxygen, temperature, turbidity, salinity, pH, and depth using a YSI 6600 sonde
    - Surface water samples are collected and iced for nutrient analysis
- We will also carry out additional targeted sampling at least once at a minimum of five sites, sampling hourly during day and night to better characterize the eutrophic conditions (detection of potential anoxia) and to better understand the context and limitations of the monthly daytime sampling
- We supplement monthly data with high-resolution water quality sampling to look at local temporal and spatial variation including dissolved oxygen, pH, electrical conductivity, and temperature

Deliverables: Consistent, scientifically robust water quality data and nutrient samples

TASK 3: Laboratory nutrient analysis

- Monthly analysis of samples from up to 30 stations in Elkhorn watershed and analysis of samples from targeted studies of eutrophic sites
    - Samples will be collected in field (see above), filtered, and analyzed at a contracted lab for ammonia, nitrate, and phosphate
    - At least twice per year, duplicate samples will be analyzed at additional laboratory
- Specialized nutrient samples collected to augment monthly samples and pollution abatement strategies (Task 5)
    - High spatial and temporal resolution samples collected, filtered, and analyzed by UC Santa Cruz for nitrate/nitrite, ammonium, phosphate, and total N and P (Task 5)

Deliverables: Consistent, high quality nutrient data

TASK 4: Data entry, processing, quality control, archiving, and dissemination

- The data and metadata will be entered with quality assurance/control procedures as per the approved Quality Assurance Project Plan
- The data will be backed up and archived by ESNERR
- The data will continue to be made available upon written request via the ESNERR website with links from the CCAMP and Monterey Bay National Marine Sanctuary's integrated monitoring web page
- All UC Santa Cruz data will be subject to an approved QAPP and provided to ESF/ESNERR
- Submittal of data via web-based templates to CCAMP for incorporation into master database

Deliverables: Water quality monitoring database for the Elkhorn watershed readily available to managers, students, and researchers

TASK 5: Statistical analysis of data – overall trends and correlations with management

- We will develop spatio-temporal models based on dynamic linear models to determine temporal trends and spatial correlations using long-term water quality data. These models allow for a time-varying description of the behavior of the process generating the observations including trends, spatial correlation, and the strength of the association with covariates such as land management or tide gate regime patterns
    - Collect existing water quality data that are either long-term or have been repeated over the years in the study area
    - Collect data on time varying processes drivers (including precipitation, land use, tide, and tide-gate regimes). This task will includes updating the existing GIS database to include water quality, soil characteristics, and relevant management practices (15+ years of data) for a minimum of two case study areas (e.g., Azevedo Ponds, Moro Cojo, and Tembladero Slough)
    - Identify and evaluate appropriate dynamic linear model(s) to determine water quality trends/changes and their relationship to land use
    - Develop and test alternative water quality sampling designs to the relative strengths of current monitoring programs to detect water quality changes
- We will evaluate water quality monitoring of constructed wetlands and sediment pond and determine the level of uncertainty of their purported effectiveness
    - Collate existing and appropriate water quality data on sediment ponds and constructed wetlands for the Central Coast of California
    - Initiate specialized sampling (e.g. temporal: diel, daily, weekly; spatial changes at varying depths and samples collected in a spatial grid) and analyze for nutrients (Task 3) to determine how variance is captured in alternative sampling regimes
    - Develop an end-user statistical model to determine the uncertainty with various sampling designs and costs. Resource agencies and researchers can use the model to design monitoring programs with explicit uncertainties can be evaluate appropriately

Deliverables: GIS maps and graphical and tabular results of statistical analyses of water quality trends and management correlates

TASK 6: Dissemination of results to scientific and management audiences

- We will summarize the resulting information on long-term water quality trends in the Elkhorn watershed, on geographic differences between sites and regions, and on correlates of the patterns with agricultural management practices in formats appropriate for audiences ranging from water quality scientists to laypeople to regional regulators and policy-makers.
- Develop and distribute a flow chart and calculation tool (e.g. spreadsheet model) to help resource agencies (RCD, NRCS, RWQCB) and researchers (USDA-ARS, universities, etc.) to develop monitoring programs that can adequately describe pollution abatement effectiveness and the relative uncertainties.
- We will develop and describe statistical models in published in a peer-reviewed scientific journal.
- Outreach and education forums to present water quality data for resource agencies (RCD, NRCS, UCCE) and growers, landowners, and other users and interested parties.

Deliverables: Technical Report written for lay audience and available on-line, peer-reviewed scientific publication, flow chart and calculation tool, and summary PowerPoint presentations tailored to the needs of local agencies

6.2. Constituents to be monitored and measurement techniques

Because our program is intended to be a long-term monitoring program, data that are not successfully collected for a specific sample event or site can typically be recollected at a later sampling event. For this reason, most of the data planned for collection cannot be considered absolutely critical. However, we have set some general guidelines for this program to maintain its effectiveness. Critical constituents include monthly monitoring of the parameters listed in Table 6.2.1. at the historically active sites. Diel, specialized high-resolution nutrient samples collected to augment monthly samples, and additional sampling at other sites and on other timeframes are considered secondary to the study.

Samples are collected per the standard operating procedure (SOP) outlined in Appendix I (ESNERR SOP #1). Data on dissolved oxygen, temperature, turbidity, salinity, and pH are obtained using a YSI 6000 and 6600 Multi-Parameter Water Quality Monitor (sonde).

Nutrient analyses for the program are completed by MCCCL. Nitrate is analyzed using ion chromatography (Dionex model 80). Phosphate is analyses using the ascorbic acid method and a spectrophotometer. Ammonia is analyzed using an ion selective electrode. Samples are filtered for chloride prior to analysis to reduce interference. They are also diluted on an as needed basis. The standard laboratory method utilized is listed in Table 6.2.1. The SOPs for nutrient analyses by MCCCL can be found in Appendix I. When additional laboratories are used for quality assurance/control purposes, nutrient analyses will be conducted per the individual laboratories' SOPs, which are included in Appendix I. Because ESNERR cooperates with MLML for laboratory equipment use with analyses facilitated by primarily ESNERR staff, the ESNERR's SOP for nutrient analyses (see Appendix I) is followed rather than the MLML Chemical Oceanography Laboratory's SOPs.

Table 6.2.1.: Conventional Constituents Monitored

Parameter	Monitoring Frequency	Method
Temperature (°C)	Monthly	Probe analysis
Conductivity (ms/cm)	Monthly	Probe analysis
Salinity (mg/L)	Monthly	Probe analysis
DO (%)	Monthly	Probe analysis
DO (mg/L)	Monthly	Probe analysis
pH	Monthly	Probe analysis
Turbidity (NTU)	Monthly	Probe analysis
Depth (m)	Monthly	Probe analysis
Nitrate (as NO_3)	Monthly	MCCCL: EPA 300.0[1] MLML: MBARI procedures[2] (modified SM4500-$NO3^-$)[3]
Ammonia (as N)	Monthly	MCCCL: EPA 350.3[1] MLML: SM 4500-$NH3^-$ DM[3]
Orthophosphate (as P)	Monthly	MCCCL: SM 4500 P E[3] MLML: MBARI procedures[2] (modified SM 4500 P G)[3]

[1]EPA 1993
[2]Sakamoto et al. 1990
[3]Clesceri et al. 1998

6.3. Project schedule

These dates include a 4-month, no additional cost extension.

Project Start Date: May 23, 2005
Reporting Schedule:
25% complete: meet with CCRWQCB staff 1/31/2006
50% complete: "Progress Report Form" 6/30/2006
75% complete: meet with CCRWQCB staff 1/31/2007
100% complete: "Final Report Form" 7/31/2007
Schedule for Deliverables:
See Table 6.3.1.
Sampling Schedule:
See Table 6.3.2. Grant-supported sampling will begin following approval of the QAPP. Based on December approval of the QAPP, monthly grant-supported water sampling will begin in January 2006 and end after the June 2007 sampling event.
Project End Date: August 31, 2007

Table 6.3.1.: (Element 6) Project Schedule Timeline – Schedule for Deliverables

Tasks	Description of Deliverables	Completion Dates
1.0	**Coordination with CCAMP/RWQCB**	
a)	Approved quality assurance project plan	11/30/05
2.0	**Field Monitoring of watershed-scale water quality**	
a)	Submission of 2005 data electronically in desired format to CCAMP*	3/31/06*
b)	Submission of 2006 data electronically in desired format to CCAMP	3/31/07
c)	Submission of 2007 data electronically in desired format to CCAMP	3/31/08 and annually thereafter in perpetuity
3.0	**Laboratory nutrient analysis**	
a)	Submission of 2005 data electronically in desired format to CCAMP*	3/31/06*
b)	Submission of 2006 data electronically in desired format to CCAMP	3/31/07
c)	Submission of 2007 data electronically in desired format to CCAMP	3/31/08 and annually thereafter in perpetuity
	[included with submission will be metadata including results of cross-lab calibration]	
4.0	**Data entry, processing, quality control, archiving, and dissemination**	
a)	All data 2005 - 2006 will be submitted to CCAMP in desired format and made electronically available to any requestor (the data are already made available to any user now, but the final completion date allows for additional formatting, QA/QC, etc. for data collection prior to approval of QAPP	3/31/07
5.0	**Statistical analysis of data**	
a)	GIS layers of land use, slope, soil, etc. used for spatial analyses of water quality trends	7/31/07
b)	Graphical and tabular results of statistical analyses of water quality trends and management correlates	7/31/07
6.0	**Dissemination of results to scientific and management audiences**	
a)	Summary report of temporal trends and management correlates available on ESNERR web page	7/31/07
b)	PowerPoint presentation prepared and delivered to relevant local agencies and user groups	7/31/07
c)	Statistical model made accessible to end-users with flow chart and calculation tool	7/31/07
d)	Publication submitted to peer-reviewed journal	7/31/07

*Providing QAPP approved and sampling begins prior to the end of 2005.

Table 6.3.2.: Field Sampling Schedule

Site Number	Site Name (ESNERR Site Code)	Frequency (number of samples during grant period[1])
Upper Slough Region:		
1	Carneros Creek (CC)	Monthly (18)
2	Hudson's Landing West (HLW)	Monthly (18)
3	Hudson's Landing East (HLE)	Monthly (18)
4	Azevedo Pond, North (APN)	Monthly (18)
5	Azevedo Pond, Central (APC)	Monthly (18)
6	Azevedo Pond, South (APS)	Monthly (18)
7	Kirby Park (KP)	Monthly (18)
Reserve Region:		
8	Strawberry Road (STB)	Monthly (18)
9	Reserve, South Marsh (RSM)	Monthly (18)
10	Reserve Bridge (RBR)	Monthly (18)
11	Cattail Swale (CAT)	Monthly (18)
12	Rookery Pond (ROK)	Monthly (18)
Lower Slough Region:		
13	Struve Pond (SP)	Monthly (18)
14	Bennett Slough, West (BSW)	Monthly (18)
15	Bennett Slough, East (BSE)	Monthly (18)
16	Jetty Road (JR)	Monthly (18)
17	Skipper's Landing (SKL)	Monthly (18)
18	Moss Landing Road, North (MLN)	Monthly (18)
19	Moss Landing Road, South (MLS)	Monthly (18)
20	Moro Cojo Slough (MCS)	Monthly (18)
21	Upper Moro Cojo Slough (MCS2)	Monthly (18)
Salinas River Region:		
22	Potrero Road, North (PRN)	Monthly (18)
23	Potrero Road, South (PRS)	Monthly (18)
24	Monterey Dunes Way (MDW)	Monthly (18)
25	Salinas River Bridge (SRB)	Monthly (18)
26	Tembladero Slough (TS)	Monthly (18)
27	Tembladero Slough 2 (TS2)	Monthly (18)
Variable Sites[2]:		
28	Rotating as indicated by need for additional data	Monthly or as needed (18)
29	Rotating as indicated by need for additional data	Monthly or as needed (18)
30	Rotating as indicated by need for additional data	Monthly or as needed (18)
Subtotal:		(540)
Additional Sampling:		
Diel Sampling	Five sites (selected based on nutrient-enrichment and other concerns)	5 times (120)
Specialized Sampling	To be determined by UCSC to better characterize areas of concern	To be determined
Field Duplicates	Purposeful selection of high and low nutrient sites	5% of samples collected in 12 months (≈33)
Field Blanks	During periodic field audits	≥1 per 12 months (2)
Expected Total Number of Field Samples[3]:		≈700

[1]Based on QAPP approved sampling beginning in December 2005. Actual number of samples will be adjusted accordingly based on QAPP approval date.
[2]Sites including but not limited to Moro Cojo, Castroville, Tembladero, and Elkhorn Sloughs as well as the Salinas River system.
[3]Does not include laboratory QC samples.

6.4. Geographical setting

Elkhorn Slough is located about 145 kilometers south of San Francisco and 32 kilometers north of Monterey (see Figure 6.4.1.). Elkhorn Slough opens into the Monterey Bay at Moss Landing. The slough's watershed area is 182 square kilometers. Monthly water quality monitoring stations are shown in Figure 6.4.2.

Figure 6.4.1.: Elkhorn Slough (Pease 2005)

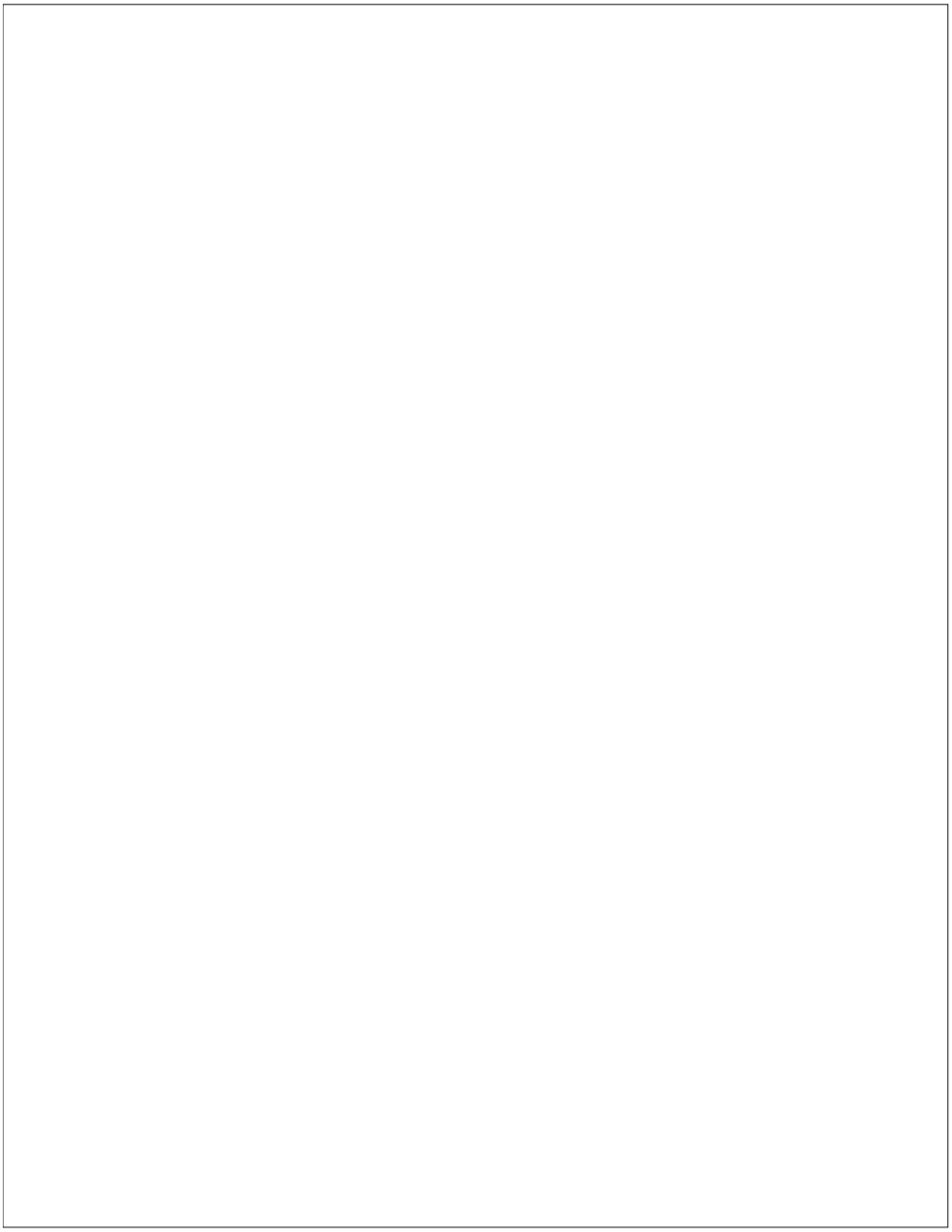

Figure 6.4.2.: Water Quality Monitoring Stations (as of October 2005)

6.5. Constraints

Flooding during extreme weather events may preclude access to a site. Other sites may dry up during warm weather. In addition, access to some sites requires private landholder permission, and sampling at these sites is contingent upon the landowners' permission.

7. Quality Objectives and Criteria for Measurement Data

7.1. Data quality objectives

Data quality objectives for this project include:

Sample Collection

Representativeness:

Representativeness is the degree to which the environmental data generated by the monitoring program accurately and precisely represent actual environmental conditions (EPA 2002a). This objective is addressed through the overall design of the monitoring program. Sampling schedules will be designed with respect to frequency, locations and methodology in order to maximize representativeness, where possible and applicable. Monitoring sites were chosen to characterize the slough's hydrographical heterogeneity. Diel sampling and specialized sampling events will supplement monthly monitoring to better characterize eutrophic conditions and to better understand the context and limitations of the monthly data sampling.

Completeness:

The completeness of data is a relationship of how much of the data are available for use compared to the total potential data before any conclusion is reached (EPA 2002a). Ideally, 100% of the data should be available. However, the possibility of data becoming unavailable due to laboratory error, insufficient sample volume, or samples broken in shipping must be expected. Also, unexpected situations may arise where field conditions do not allow for 100% data completeness. Because our program is intended to be a long-term monitoring program, data that are not successfully collected for a specific sample event or site can typically be recollected at a later sampling event. For this reason, most of the data planned for collection cannot be considered absolutely critical, and it is difficult to set a meaningful objective for data completeness. However, some reasonable objectives for data are desirable as a measure of the effectiveness of the sampling program. Our program goals for data completeness are listed in Table 7.2.1. below.

Bias/Comparability:

Comparability of the data can be defined as the similarity of data generated by different monitoring programs (EPA 2002a). Bias is systematic or persistent distortion of a measurement process that causes error (EPA 2002a). Reduction of bias subsequently increases data comparability. Standard sampling techniques will used to minimize sampler bias, and technicians are trained prior to fieldwork to ensure that these standardized techniques are followed.

Field Analyses

Field analyses include dissolved oxygen, temperature, turbidity, salinity, and pH.

Precision:

The precision and accuracy of data are determined by particular actions of the analytical laboratory and field staff. The precision of data is a measure of the reproducibility of the measurement when an analysis is repeated. It is reported in Relative Percent Difference (RPD) or Relative Standard Deviation (RSD) (Puckett 2002). This objective will be achieved through documentation of compliance with the requirements listed in Table 7.2.1.

Accuracy:

The accuracy of an analysis is a measure of how much of the constituent actually present is determined. It is measured, where applicable, by adding a known amount of the constituent to a portion of the sample and determining how much of this spike is then measured. It is reported as Percent Recovery. The acceptable percent deviations and the acceptable percent recoveries are dependent on many factors including: analytical method used, laboratory used, media of sample, and constituent being measured (Puckett 2002). This objective will be achieved through documentation of compliance with the requirements listed in Table 7.2.1.

Completeness:

Our program goals for data completeness are listed in Table 7.2.1. below.

Bias:

Instrument bias will be reduced through calibration of equipment using purchased standards within 24 hours of entering the field and a calibration check following completion. Equipment calibration is discussed further in Section 16 of this document. The Water Monitoring Coordinator and Water Quality Scientist will reduce technician bias through training prior to fieldwork.

Laboratory Analyses:

Laboratory analyses of water samples include nitrate, phosphate, and ammonia.

Accuracy:

This objective will be achieved through documentation of compliance with the requirements listed in Table 7.2.2.

Precision:

This objective will be achieved through documentation of compliance with the requirements listed in Table 7.2.2.

Recovery:

This objective will be achieved through documentation of compliance with the requirements listed in Table 7.2.2.

Completeness:

This objective will be achieved through documentation of compliance with the requirements listed in Table 7.2.2.

Bias:

The analytical laboratory will reduce bias through compliance with their training and calibration protocols.

Sensitivity:

Sensitivity is the capability of a method or instrument to discriminate between measurement responses representing different levels of the variable of interest (EPA 2002a). Sensitivity can be regarded as detection limit. This objective will be achieved through documentation of compliance with the requirements listed in Table 7.2.2.

These objectives as related to quality control are discussed further in Section 14 of this document.

7.2. Field and laboratory measurements data quality objectives tables

Table 7.2.1.: (Element 7) Data Quality Objectives for Field Measurements

Parameter	Accuracy	Precision	Completeness
Temperature (°C)	± 0.5 °C	No SWAMP requirement – will use ± 25%	No SWAMP requirement – will use 80%
Conductivity (ms/cm)	± 5%	No SWAMP requirement – will use ± 25%	No SWAMP requirement – will use 80%
Salinity (mg/L)	± 10%	No SWAMP requirement – will use ± 10%	No SWAMP requirement – will use 80%
DO (%)	± 10%	No SWAMP requirement – will use ± 25%	No SWAMP requirement – will use 80%
DO	± 0.5 mg/L	No SWAMP requirement – will use 25%	No SWAMP requirement – will use 80%
pH	± 0.5 units	No SWAMP requirement – will use 25%	No SWAMP requirement – will use 80%
Turbidity (NTU)	No SWAMP requirement – will use ± 10%	No SWAMP requirement – will use ± 25%	No SWAMP requirement – will use 80%

Table 7.2.2.: (Element 7) Data Quality Objectives for Laboratory Measurements

Parameter	**Accuracy**	**Precision**	**Recovery**	**Sensitivity (Target Reporting Limits)**	**Completeness**
Nitrate (as NO_3)	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, or MS/MSD <25% RPD. Laboratory duplicate minimum	Matrix spike 80% - 120% or control limits at $\pm$ 3 standard deviations based on actual lab data	0.07 mg/L (0.015 mg/L as N)	No SWAMP requirement – will use 80%
Ammonia (as N)	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, or MS/MSD <25% RPD. Laboratory duplicate minimum	Matrix spike 80% - 120% or control limits at $\pm$ 3 standard deviations based on actual lab data	0.05mg/L	No SWAMP requirement – will use 80%
Orthophosphate (as P)	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, or MS/MSD <25% RPD. Laboratory duplicate minimum	Matrix spike 80% - 120% or control limits at $\pm$ 3 standard deviations based on actual lab data	0.03 mg/L	No SWAMP requirement – will use 80%

8. Special Training Needs/Certification

8.1. Specialized training or certifications

No specialized training or certifications are required for this project. All new ESNERR field and laboratory personnel receive training and demonstrate knowledge of the guidelines and SOPs included in this QAPP. Annual refresher training will occur on an informal basis during period field audits. California Department of Fish and Game driving certification is required prior to driving Reserve vehicles and to driving on Reserve property.

Analytical laboratories provide training to personnel in accordance with their respective protocols. Analytical laboratories are not required to be certified but should be able to demonstrate experience with the requested analyses.

8.2. Training and certification documentation

ESNERR training records prior to September 2005 do not exist. Training records from September 2005 are kept on file in ESNERR's research office with the Water Quality Scientist. Documentation consists of a record of the training date, instructor, whether initial or refresher, and whether the course was completed satisfactorily. A sample training record is attached in Appendix II. California Department of Fish and Game driving certification documentation is kept with Fish and Game personnel housed on the Reserve. It includes the trainee, date, instructor, and whether the course was completed satisfactorily.

Analytical laboratories are responsible for maintaining their own training records, which will be made available upon request.

8.3. Training personnel

Training sessions are overseen by the QA Officer (Kerstin Wasson) and conducted by the Water Monitoring Coordinator (John Haskins) and the Water Quality Scientist (Kristy Meyer).

Analytical laboratories are responsible for providing training to their own personnel.

9. Documents And Records

9.1. Information included in the data reports

For each sample collected, field personnel will keep a log of the following at minimum:

- Unique sample ID
- Monitoring location (station number or station name)
- Sample type
- Quality control (QC) sample (if appropriate)
- Date and time of collection

Field data will be recorded electronically as well as in hard form on the Field Data Collection Form (see ESNERR SOP #1 in Appendix I). Field observations will be noted on the Field Data Collection Form as well. Field data sheets will be provided to the Water Quality Scientist following each sampling event.

For each sample analyzed in the laboratory, the laboratory will provide the following records, at minimum, to the Water Quality Scientist:

- Unique sample ID
- Date of sample receipt
- Date of analysis
- Analytical methods (including dilution, if appropriate)
- Method detection limit (if appropriate)
- Reporting limit (if appropriate)
- Measured value

The laboratory will also provide the Water Quality Scientist with results from laboratory QC procedures including blanks, duplicates, spikes, standard reference material, etc. The laboratory will identify the sample IDs corresponding to analytical batches.

The Water Quality Scientist will include copies of these data in her monthly report to the QA Officer.

9.2. Reporting format

Data from laboratories will be reported in each laboratory's standard format. Data that does not meet the objectives outlined in the approved QAPP will be flagged as qualified but acceptable or unacceptable. Laboratories may choose to submit their data in hard only or electronic and hard copy. The Water Quality Scientist will transfer laboratory data submitted in hard copy only to electronic format.

The Water Quality Scientist will report data to the CCRWQCB/CCAMP electronically in the approved CCAMP format.

9.3. Data archiving/retention

The Water Quality Scientist is responsible for maintaining and archiving records. Because this is a long-term monitoring project, electronic data will be retained permanently. Hard copies of field and laboratory data will be kept on file at the ESNERR office for a minimum of five years. Individual laboratories will retain data in accordance with their QAPP requirements. Electronic records will be archived by ESNERR at minimum once per month on an external data storage device (flash memory, CD, etc.) and retained at the ESNERR office. Backups may be written over after two months. At least once per quarter, a duplicate archive will be made and stored off-site.

The Water Quality Scientist is also responsible for retaining a hard and electronic copy of the approved QAPP along with any subsequent revisions.

9.4. Distribution of the QAPP

The Water Quality Scientist is responsible for distributing signed copies of the approved QAPP and any subsequent revisions to the individuals listed in Section 3 of this document. This may be accomplished through traditional or electronic mail.

GROUP B: DATA GENERATION AND ACQUISITION

10. Sampling Process Design

10.1. Design strategy

Most sites in the ESNERR monitoring network are historical; our program has provided large scale watershed monitoring for over 15 years. The Elkhorn Slough watershed covers approximately 182 square kilometers (Caffrey et al. 2002). In the past sites were chosen to include key waterways that drain into the central portion of the Monterey Bay, study critical habitat, and measure the effectiveness of management practices (construction of sediment ponds, installation of tide gates, etc.). We have continued monitoring at the historical sites to preserve continuity of our long-term dataset. New sites were purposefully selected to better characterize areas of concern and expand the scope of our monitoring network. Specific areas of concern include the Old Salinas River channel and Tembladero Slough. These areas demonstrate high nitrate values, averages above 40 mg/L, at our historical monitoring locations.

10.2. Sampling design

Our program will monitor water quality at sites within the Elkhorn Slough watershed each month. ESNERR staff and volunteers collect monthly grab samples and field data at each location. Samples are analyzed for the conventional constituents listed in Table 6.2.1. above; expected number of samples is shown in Table 6.3.2. above. Site locations were shown above in Figure 6.4.2. as well. Table 10.2.1. lists the monitoring sites with their global positioning system (GPS) coordinates.

The Water Quality Scientist will collect diel samples at least five times during the contract period. Sites for diel sampling will include the most nutrient enriched sites but may include other sites as indicated. The purpose of these sampling events is to better characterize eutrophic conditions and to better understand the context and limitations of the monthly data sampling at areas of concern.

Monthly sampling will be supplemented with high-resolution water quality sampling at least once during the contract period. The purpose of the supplemental sampling is to quantify local temporal and spatial variation in water quality. UCSC will design the sampling scheme based on field observations, historical data, and relevant literature; supplemental sampling will be a collaborative effort between UCSC and ESNERR staff. Sampling strategy and design for the supplemental collections will occur per UCSC's protocols.

Field staff will locate the water monitoring stations using maps, site descriptions, and/or a GPS as necessary to ensure sampling occurs at the specified location. If a site becomes consistently inaccessible or permanently dry, the site will be removed from the monitoring network. The Water Quality Scientist will choose a replacement site, ideally one that characterizes the same area from an alternate location.

All information collected during monthly and diel sampling events will be recorded on the Field Data Collection Form and provided to the Water Quality Scientist. All UCSC data will be subject to their QAPP and will be provided to ESNERR.

Critical constituents were discussed above in Section 6.2.

Table 10.2.1.: ESNERR Monitoring Sites

Station Code	Station Description	LAT (DD)*	LONG (DD)*	Initiation Date	Tidal Exchange
306MSLSKL	Moss Landing Harbor at Skipper's Landing	36.8106	-121.7864	9/20/1988	Full
306MOREH1	Moro Cojo Slough East of Highway 1	36.7963	-121.7832	9/21/1988	Minimal
305BENSTP	Bennett Slough at Struve Pond	36.8247	-121.7774	9/21/1988	Minimal
306BENWH1	Bennett Slough West of Highway 1	36.8209	-121.7909	9/21/1988	Minimal
306BENEH1	Bennett Slough East of Highway 1	36.8215	-121.7834	9/21/1988	Minimal
306BENJTR	Bennett Slough at Jetty Road	36.8171	-121.7871	9/21/1988	Muted
309SLRBRG	Salinas River at the Highway 1/Railroad Bridge	36.7321	-121.7807	9/22/1989	Minimal in dry season; full in rainy season
309SLRLAG	Salinas River Lagoon (inactive)	36.7480	-121.7835	9/22/1989	Minimal in dry season; full in rainy season
306ELKRNM	Elkhorn Slough at Reserve, North Marsh (inactive)	36.8364	-121.7323	9/23/1989	Muted
309OSRPRN	Old Salinas River at Potrero Road, North	36.7908	-121.7904	9/23/1989	Full
309OSRPRS	Old Salinas River at Potrero Road, South	36.7904	-121.7907	9/23/1989	Minimal
306ELKRSM	Elkhorn Slough at Reserve, South Marsh (Whistle Stop Lagoon)	36.8240	-121.7400	9/23/1989	Muted
306ELKHLW	Elkhorn Slough at Hudson's Landing West	36.8565	-121.7550	9/23/1989	Full
306CARBLR	Carneros Creek at Blohm Road	36.8601	-121.7401	9/23/1989	Minimal
306ELKKPD	Elkhorn Slough at Kirby Park Dock	36.8398	-121.7437	9/23/1989	Full
306ELKRBR	Elkhorn Slough at Reserve Bridge	36.8199	-121.7371	9/23/1989	Full
306ELKHLE	Elkhorn Slough at Hudson's Landing East	36.8563	-121.7549	10/1/1989	Minimal
306MORMLS	Moro Cojo Slough at Moss Landing Road, South	36.7997	-121.7847	3/5/1991	Minimal
306MORMLN	Moro Cojo Slough at Moss Landing Road, North	36.8000	-121.7844	3/5/1991	Full
309OSRMDW	Old Salinas River at Monterey Dunes Way	36.7719	-121.7897	12/14/1991	Minimal
306ELKAPN	Elkhorn Slough at Azevedo Pond, North	36.8471	-121.7545	3/27/1992	Muted
306ELKAPS	Elkhorn Slough at Azevedo Pond, South	36.8423	-121.7469	3/28/1992	Minimal
306ELKAPC	Elkhorn Slough at Azevedo Pond, Central	36.8439	-121.7513	3/28/1992	Minimal

Station Code	Station Description	LAT (DD)*	LONG (DD)*	Initiation Date	Tidal Exchange
309TEMPRS	Tembladero Slough at Preston Street	36.7651	-121.7596	6/13/1994	Minimal
306ELKSTB	Elkhorn Slough at Strawberry Rd	36.8296	-121.7340	4/28/1998	Muted
306ELKROK	Elkhorn Slough at Rookery Pond			11/1/2005	Non-tidal (freshwater pond)
306ELKCAT	Elkhorn Slough at Cattail Swale			11/1/2005	Non-tidal (freshwater pond)
306MORCAS	Moro Cojo Slough at Castroville Road (inactive)			2/7/2006	Minimal (seasonal only)
309TEMMDW	Tembladero Slough at Monterey Dunes Way			2/7/2006	Minimal

***Collected in UTM WGS 84**

10.3. Natural variability

Time and location of sample collection may affect the outcome of sample analyses. In order to reduce bias and misrepresentation of the site, samples will be collected as consistently as possible:

- Samples should be collected at sites following the established route/sequence.
- Samples should be collected as closely in time as in the previous sampling event.
- Sampling events should occur at consistent intervals.

Whenever this consistency is not possible, field staff will record notes on the Field Data Collection Form.

11. Sampling Methods

Samples will be collected from water only. Sampling staff will have read all applicable sections of the QAPP and appropriate SOPs prior to entering the field and will bring these documents with them as needed during sampling events. It is the responsibility of all members of the sampling staff to determine if the performance requirements of the specific sampling method have been met and to collect an additional sample if required. Water samples are collected according to ESNERR's SOP for field collection of water samples for analysis of conventional constituents (see Appendix I). This SOP is based on the SWAMP SOP for field collection of water samples (Puckett 2002).

11.1. Sample collection

Mid-depth grab samples will be collected at each site either directly into pre-cleaned 250 mL polyethylene sample containers or into a polyethylene bucket then transferred to a sample container. Care will be taken to avoid potential sources of contamination. Samples will be capped, placed on ice and out of direct light, secured, and transported to the laboratory. The analytical laboratory will aliquot samples as appropriate and measure nitrate (NO_3), orthophosphate (P), and ammonia (N).

11.2. Sample identification

Samples will be identified using a standard code. Sample containers are pre-labeled with the station name and/or site code, date, time, sample number (if greater than 1), and sampler's name prior to sample collection. Codes for each site are listed above in Table 10.2.1.

11.3. Field measurements

Field staff will measure dissolved oxygen, temperature, turbidity, salinity, and pH in the field as described in Section 13 in this document. Field notes will be recorded on the Field Data Collection Form (see ESNERR SOP#1 in Appendix I); field measurements will be recorded electronically and on the Field Data Collection Form.

11.4. QC sample collection

Additional samples are collected for quality assurance/control to meet requirements outlined in Section 14 of this document.

11.5. Field instrument calibration

Field instruments will be calibrated per the requirements outlined in Section 14 of this QAPP. Field instruments will be inspected prior to and after sampling events for damage. Maintenance will occur as outlined in Section 15 of this QAPP.

11.6. Cleaning of sample containers

The analytical laboratory (MCCCL) provides clean containers for sample collection. When QC samples are collected for alternate laboratories, containers will be washed thoroughly per the individual laboratories' SOPs then triple rinsed with de-ionized water prior to use. Field personnel will triple rinse all sample containers with sample water prior to collection.

12. Sample Handling and Custody

Proper sample handling procedures for water samples are provided below and in the SOP for Field Collection of Water Samples for Analysis of Conventional Constituents (see Appendix I). Field personnel are responsible for completing necessary field data collection and chain-of-custody (COC) forms as well as for adhering to sample handling and custody requirements outlined in this document. The Water Quality Scientist is responsible for archiving COC forms with the corresponding laboratory reports. The QA Officer receives monthly reports from the Water Quality Scientist and is responsible for ensuring that samples are collected and handled according to procedures documented in this QAPP.

12.1. Field log

The field crews will have custody of samples during field sampling. Field crews will keep a written record for each sampling event. The following items should be recorded in the Field Data Collection Form for each sampling event:

- time and date of sample collection;
- sample ID numbers and unique IDs for any replicate or blank samples;
- the results of any field measurements and the time that measurements were made;
- qualitative descriptions of relevant water conditions or weather at the time of sample collection;
- a description of any unusual occurrences associated with the sampling event, particularly those that may affect sample or data quality.

12.2. Sample storage and preservation

In the field, all samples will be packed in wet ice or frozen ice packs during shipment so that they will be kept at approximately 4˚C. Samples will be kept out of direct sunlight as much as possible. Samples will be shipped in insulated containers. All caps and lids will be checked for tightness prior to shipping. All samples will be handled, prepared, transported and stored in a manner so as to minimize bulk loss, analyte loss, contamination, or biological degradation. Sample containers will be clearly labeled with an indelible marker.

12.3. Sample transportation

Ice chests will be sealed with tape before shipping if the ice chest does not have a secure latch. Samples shipped via commercial delivery service will be taped prior to shipping regardless of latching capabilities. Samples will be placed in the ice chest with enough ice to completely fill the ice chest. COC forms will be placed in an envelope and taped to the top of the ice chest or placed in a plastic bag and taped to the inside of the ice chest lid. It is assumed that samples in tape-sealed/latched ice chests are secure whether being transported by staff vehicle, by common carrier, or by commercial package delivery. All water quality samples will be transported to the analytical laboratory directly by the field crew unless a commercial carrier is used.

12.4. Chain-of-custody form

Chain-of-custody procedures require that possession of samples be traceable from the time the samples are collected until completion and submittal of analytical results. A complete chain-of-custody form will accompany the transfer of samples to the analyzing laboratory. The analytical laboratory receives the original COC form; a copy is given to the staff member relinquishing the samples. The copy of the COC is stored with the field data sheets. The COC form provided by MCCCL is included in ESNERR SOP#1 (see Appendix I). It contains the project name, billing information, name of sampler, type of samples,

date and time samples were collected, sample identification names, type of analyses to be performed, relinquishing signature, and the receiving signature.

12.5. Sample holding times

All samples should reach the laboratory within 24 hours of the time of the first sample collection. Maximum holding times prior to specific analyses are shown in Table 12.4.1. Samples will be preserved in the laboratory as appropriate according to the analytical laboratory's protocol for each requested analyses.

Table 12.4.1.: (Element 12) Sample Handling and Custody

Parameter	Sample Container	Sample Volume (Per Laboratory)*	Immediate Processing & Storage	Maximum Holding Time
Temperature (°C)	Probe analysis	N/A	Store on electronic data recorder & field data log	N/A
Conductivity (ms/cm)	Probe analysis	N/A	Store on electronic data recorder & field data log	N/A
Salinity (ppt)	Probe analysis	N/A	Store on electronic data recorder & field data log	N/A
DO%	Probe analysis	N/A	Store on electronic data recorder & field data log	N/A
DO (mg/L)	Probe analysis	N/A	Store on electronic data recorder & field data log	N/A
pH	Probe analysis	N/A	Store on electronic data recorder & field data log	N/A
Turbidity (NTU)	Probe analysis	N/A	Store on electronic data recorder & field data log	N/A
Nitrate	Polyethylene	50 mL	MCCCL: Store at 4°C; MLML: Store at 4°C up to 48 hours or freeze up to 1 month	MCCCL: 48 hours MLML: 1 month
Ammonia	Polyethylene	50 mL	MCCCL: Store at 4°C (acidified by laboratory upon transfer); MLML: Store at 4°C	MCCCL: 48 hours (28 days after acidification) MLML: 48 hours (additional 24 hours after reagents are added)
Phosphate	Polyethylene	50 mL	MCCCL: Store at 4°C; MLML: Store at 4°C up to 48 hours or freeze up to 1 month	MCCCL: 48 hours MLML: 1 month

*Samples are usually collected in a single 250 mL bottle then split at the laboratory. Collection volume allows for laboratory QA procedures. If additional laboratories are being used for QC purposes, 250 mL of sample water are collected for each laboratory.

12.6. Laboratory custody

The receiving analytical laboratories will follow sample custody procedures outlined in their respective QA plans. Laboratories will maintain custody logs sufficient to track each sample submitted and to analyze or preserve each sample within specified holding times. Laboratory QA manuals are on file with the respective laboratory.

12.7. Sample disposal

All samples remaining after successful completion of analyses will be disposed of properly. It is the responsibility of the personnel of each analytical laboratory to ensure that all applicable regulations are followed in the disposal of samples or related chemicals.

13. Analytical Methods

The following analytical methods for water samples are used in this project:

Table 13.1.: (Element 13) Field Analytical Methods.

Analyte	Laboratory / Organization	Range	Reporting Limit (RL)	Analytical Method	
				Analytical Method/ SOP	Modified for Method yes/no
Temperature	Field monitoring by ESNERR staff	-5 – 45 ºC	0 ºC	ESNERR SOP #1	None
Conductivity	Field monitoring by ESNERR staff	0 – 100 mS/cm	0.1 mS/cm	ESNERR SOP #1	None
Salinity	Field monitoring by ESNERR staff	0 – 70 ppt	0.1 ppt	ESNERR SOP #1	None
DO	Field monitoring by ESNERR staff	0 – 500% air saturation	2%	ESNERR SOP #1	None
DO	Field monitoring by ESNERR staff	0 – 50 mg/L	0.2 mg/L	ESNERR SOP #1	None
pH	Field monitoring by ESNERR staff	2 – 14 standard units	3 standard units	ESNERR SOP #1	None
Turbidity	Field monitoring by ESNERR staff	0 – 1000 NTU	0.5 NTU	ESNERR SOP #1	None

Table 13.2: (Element 13) Laboratory Analytical Methods

Analyte	Laboratory / Organization	Method Detection Limit (MDL)[1]	Reporting Limit (RL)[1]	Analytical Method	
				Analytical Method	Modified for Method yes/no
Nitrate (NO_3)	MCCCL	0.07 mg/L	0.07 mg/L	EPA 300.0[2]	None
Ammonia (N)	MCCCL	0.05 mg/L	0.1mg/L	EPA 350.3[2]	None
Orthophosphate (P)	MCCCL	0.03 mg/L	0.03 mg/L	SM 4500 P E[3]	None
Nitrate (NO_3)	MLML	Calculated each sampling event	Calculated each sampling event	SM 4500-$NO3^{-3}$	MBARI[4]
Ammonia (N)	MLML			SM 4500-NH3- DM[3]	Strickland & Parsons[5]
Orthophosphate (P)	MLML			SM 4500 P G[3]	MBARI[4]

[1]For undiluted samples
[2]EPA 1993
[3]Clesceri et al. 1998
[4]Sakamoto et al. 1990
[5]Strickland and Parsons, 1972

14. Quality Control

14.1. Sampling

Quality assurance and quality control activities for sampling processes include the collection of field replicates and the preparation of field blanks. The number of replicates has been established earlier as 5% of the total number of field samples per analytical procedure per year, rounded up to the nearest whole number. Field blanks will be used during random performance evaluations during field audits at the rate of at least once per 12 months. If the field blank is within the recommended control limit, no field blanks will be required until the next field audit. If the field blank is not within the recommended control limit, field blanks must be utilized at a rate of 5% until the next field audit.

Blanks will be prepared by pouring water known to be free of the substance of interest (de-ionized) into a sample collection container then aliquotting into the appropriate number of replicate sample containers.

In order to monitor the sampling process, ESNERR's Water Monitoring Coordinator will randomly observe sampling processes and compare the actual actions against the sampling SOP during field audits.

Relative percent difference (RPD) will be calculated as follows:

RPD = [(largest value – smallest value) / average] * 100

Table 14.1.1.: (Element 14) Water Sampling (Field) QC

Field QC	Objective	Frequency of Analysis	Control Limits	Corrective Action
Field Replicates	Assess method precision routinely. Assess total variability (i.e., population variability, field or sampling variability, & analytical method variability).	5% annual rate (5% of total number of field samples per analytical procedure per year, rounded up to the nearest whole number).	RPD[1] < 25% for duplicates	Determine cause and take appropriate corrective action. Recalibrate and reanalyze all suspect samples or flag all suspect data.
Field Blanks	Assess contamination from equipment, from air, from surrounding environment, etc.	Random performance evaluation during field audits (≥1 per 12 months). If acceptable performance, no field blanks required until next field audit. If non-acceptable, 5% field blanks must be conducted until the next field audit.	<MDL[2] for target analyte	Determine cause of problem (e.g., equipment contamination, improper cleaning, exposure to airborne contaminants, etc.), remove sources of contamination, & reanalyze all suspect samples or flag all suspect data.

[1]Relative Percent Difference
[2]Method Detection Limit

14.2. Field measurements

All field measurements will be made in triplicate. Each result will be recorded along with the average of the three results, the difference between the largest and smallest result, and the relative percent difference between the largest and smallest result.

Relative percent difference (RPD) will be calculated as follows:

RPD = [(largest value – smallest value) / average] * 100

The RPD will be compared against the criteria established for field measurements in Section 7 Table 7.2.1.

14.3. Laboratory analyses

The MCCCL will analyze the field blanks submitted.

The analysis of nitrate, ammonia, and phosphate will operate using the standard procedures established by MCCCL. A copy is attached in Appendix II. MCCCL's quality assurance program will meet or exceed the data quality objectives outlined in Section 7 Table 7.2.2. and Table 14.3.1. below.

Inter-laboratory comparison exercises will be conducted at a rate of at least once per 12 months with UCSC and once per quarter (every 3 months) with MLML. The purpose of these exercises will be to demonstrate laboratory capability. The duplicate analyses of nitrate, ammonia, and phosphate will operate using the quality assurance and quality control programs established by UCSC and ESNERR for nutrient analyses at MLML. Duplicate analyses will meet or exceed quality assurance and quality control protocols established in this QAPP.

Relative percent difference (RPD) will be calculated as follows:

RPD = [(largest value – smallest value) / average] * 100

Percent recovery (PR) will be calculated as follows:

PR = [(matrix plus spike result – matrix result) / expected matrix plus spike result] * 100

Table 14.3.1.: (Element 14) Analytical QC of Water Samples

Field QC	Objective	Frequency of Analysis	Control Limits	Corrective Action
Laboratory Blanks	Assess contamination from equipment, reagents, etc.	One method blank per 20 samples or one per batch, whichever is more frequent. At least one bottle blank per batch. One reagent blank prior to use of a new batch of reagent and whenever method blank exceeds control limit.	Blanks < MDL[1] for target analyte.	Determine cause of problem, remove sources of contamination, and reanalyze all suspect samples or flag all suspect data.

Standard Reference Materials (SRMs)	Assess method performance (initial method validation and routine accuracy assessment).	As many as required to assess accuracy and precision of method before routine analysis of samples. Routine accuracy assessment: 1 per 20 samples or one batch, whichever is more frequent.	Measured value <95% confidence intervals, if certified. Otherwise, % Recovery = 80% - 120%.	Determine cause and take appropriate corrective action. Recalibrate and reanalyze all suspect samples or flag all suspect data.
Laboratory Duplicate	Assess method precision.	1 per 20 samples or one per batch, whichever is more frequent.	RPD[2] < 25% for duplicates.	Determine cause and take appropriate corrective action. Recalibrate and reanalyze all suspect samples or flag all suspect data.
Field Replicates	Assess method precision routinely. Assess total variability (i.e., population variability, field or sampling variability, & analytical method variability).	5% annual rate (5% of total number of field samples per analytical procedure per year, rounded up to the nearest whole number).	RPD[2] < 25% for duplicates	Determine cause and take appropriate corrective action. Recalibrate and reanalyze all suspect samples or flag all suspect data.
Matrix Spikes	Assess matrix effects and accuracy (%R) routinely.	One per 20 samples or one per batch, whichever is more frequent.	% Recovery = 80 – 120% or Control Limits based on 3x the standard deviation of laboratory's actual method recoveries.	Determine cause and take appropriate corrective action. Recalibrate and reanalyze all suspect samples or flag all suspect data. Zero percent recovery requires rejection of all suspect data.
Matrix Spike Replicates	Assess method precision routinely.	One duplicate per 20 samples or one per batch, whichever is more frequent.	RPD[2] < 25% for duplicates.	Determine cause, take appropriate corrective action. Recalibrate & reanalyze all suspect samples or flag all suspect data.
Inter-laboratory Exercises	Ongoing demonstration of laboratory capability	One exercise per 12 months with UCSC. Once exercise per 3 months with MLML.	Determined by study manager.	Determine cause of problem and reanalyze samples. Further corrective action to be determined by the Water Quality Scientist and QA Officer.

[1]Method Detection Limit
[2]Relative Percent Difference

15. Instrument/Equipment Testing, Inspection, and Maintenance

To minimize downtime of measurement systems, all field sampling and laboratory equipment must be maintained in working condition. Also, backup equipment or common spare parts will be available so that if any piece of equipment fails during use, repairs or replacement can be made as quickly as possible and the measurement tasks resumed.

Field measurement equipment will be checked for operation in accordance with the manufacturer's specifications. This includes battery checks, routine replacement of membranes, and cleaning of conductivity electrodes. All equipment will be inspected when first handed out and when returned from use for damage. A log will be maintained for each type of equipment. All preventive or corrective maintenance will be recorded.

MCCCL maintains its equipment in accordance with its SOPs, which include those specified by the manufacturer and those specified by the method. These procedures are included in the MCCCL quality assurance/control manual provided in Appendix III and within the standard operating procedures for each analysis (see Appendix I). Any deficiencies in equipment performance should be managed in accordance with MCCCL's QA plan. Any equipment performance issues that affect the quality of the data generated for samples collected under this QAPP must be reported to the Water Quality Scientist.

Table 15.1. : (Element 15) Testing, Inspection, Maintenance of Sampling Equipment and Analytical Instruments

Equipment / Instrument	Maintenance Activity, Testing Activity or Inspection Activity	Responsible Person	Frequency	SOP Reference
YSI 6000, 6600, and 600XL Multi-Parameter Water Quality Monitor (sonde meter and probes)	Inspect for damage	Water Quality Scientist	Pre- and post- each sampling event	ESNERR SOP #2
YSI 6000, 6600, and 600XL Multi-Parameter Water Quality Monitor (sonde meter and probes)	Calibrate; check that parameters are within acceptable range	Water Quality Scientist	Pre- and post- each sampling event	ESNERR SOP #2
YSI 6000, 6600, and 600XL Multi-Parameter Water Quality Monitor (sonde meter and probes)	Replace/repair parts	Water Quality Scientist or the Water Monitoring Coordinator	As needed	ESNERR SOP #2
Digital Camera	Inspect for damage and check batteries	Water Quality Scientist	Pre- and post- each sampling event	ESNERR SOP #1
Laboratory Equipment	All testing, inspection, and maintenance activities	MCCCL	Per MCCCL's protocols	MCCCL SOP #1-3; MCCCL QA/QC Manual

16. Instrument/Equipment Calibration and Frequency

16.1. Field instruments

Required calibration of field equipment is completed within 24 hours before use and within 24 hours after measurement activities in the field are performed (post-sampling calibration check). The Water Quality Scientist performs this task. Equipment to be calibrated includes but is not limited to the multiparameter field meter (dissolved oxygen, pH, turbidity, and conductivity probes). Calibration of the YSI Multi-Parameter Water Quality Monitors used for field instruments is completed in accordance with the manufacturer's guidelines (see ESNERR SOP#2 in Appendix I). One calibration log is to be used per multiprobe instrument. This log is kept in the ESNERR office and only taken to the field when instruments are to be used over a period of days requiring post-calibration or calibration in the field.

If the calibration results in errors that do not meet the instruments' specifications, the Water Quality Scientist must recalibrate the instrument. If errors still occur, a calibration should be performed with new calibration solutions and/or maintenance should be performed (e.g., replace DO membrane, etc.). If the errors cannot be rectified, the Water Quality Scientist must report the problem to the QA Officer and record the appropriate information in the field log calibration sheets. The meter should be returned to the manufacturer for maintenance.

If, after post-calibration checks, it is determined that the acceptable amount of drift has been exceeded for a multiprobe instrument, data collected by the probe out of compliance for that sampling event should not, in most cases, be submitted to the SWAMP Program for inclusion into the database unless appropriately flagged and tracked as such. The Water Quality Scientist or Water Monitoring Coordinator will resolve the problem with the instrument, either by conducting routine maintenance or by sending the instrument to the manufacturer for repair.

Table 16.1.1.: (Element 16) Calibration of Field Sampling Equipment

Equipment / Instrument	SOP reference	Calibration Description and Criteria	Frequency of Calibration	Responsible Person
Conductivity probe	ESNERR SOP #2	Standard solution. Cell constant must be between 4.6 – 5.45.	Pre- and post- each sampling event (no SWAMP requirement)	Water Quality Scientist
Dissolved oxygen probe	ESNERR SOP #2	Oxygen-saturated water sample. Must pass DO membrane test, DO warm-up test. DO gain must be between 0.8 – 1.7.	Pre- and post- each sampling event (no SWAMP requirement)	Water Quality Scientist
Temperature probe	ESNERR SOP #2	Factory-set and requires no subsequent calibration	(no SWAMP requirement)	Water Quality Scientist
pH probe	ESNERR SOP #2	Two-point with standard buffer solution. pH 7: pH mV 0 ± 50. pH 10: pH mV -180 ± 50.	Pre- and post- each sampling event (no SWAMP requirement)	Water Quality Scientist
Turbidity probe	ESNERR SOP #2	Two-point with standard solution. Must be ± 10 of standard.	Pre- and post- each sampling event (no SWAMP requirement)	Water Quality Scientist

16.2. Laboratory analytical equipment

Frequency and procedures for calibration of analytical equipment used by each laboratory is documented in each laboratory's standard operating procedures and quality assurance manual. Laboratory QA manuals are available for review at the analyzing laboratory (see Appendix I for MCCCL's standard protocols and Appendix III for MCCCL's QA manual). Any deficiencies in equipment calibration performance will be managed in accordance with the individual laboratory's QA plan. Laboratories should comply with the SWAMP requirements for calibration of instruments used for conventional constituents in water listed below. Any equipment calibration issues that affect the quality of the data generated for samples collected under this QAPP must be reported to the Water Quality Scientist.

Table 16.2.1.: (Element 16) Calibration of Laboratory Analytical Equipment

Equipment / Instrument	SOP reference	Calibration Description and Criteria	Frequency of Calibration	Responsible Person
Laboratory Equipment	MCCCL SOP#1-3; MCCCL QA/QC Manual	External calibration with ≥ 3 standards covering the range of sample concentrations prior to sample analysis (at the low end, the lowest standard at or near the MDL). Linear regression $r^2 \leq 0.995$.	Calibration verification every 20 samples after initial calibration. Standard source different than that used for initial calibration. Recovery 80% - 120%.	MCCCL

17. Inspection/Acceptance of Supplies and Consumables

The procurement of supplies, equipment, and services must be controlled to ensure that specifications are met for the high quality and reliability required for each field and laboratory function. The Water Monitoring Coordinator or the Water Quality Scientist will order supplies used by ESNERR staff. It is the responsibility of each staff person doing the ordering to inspect the equipment and materials for quality as well as reject/return the maternal if any obvious signs of error or contamination are observed. Calibration supplies in particular must be ordered on a timely basis to ensure that they are available when needed and have not exceeded the manufacturer's expiration date. Upon receipt of materials or equipment, a designated employee receives and signs for the materials. The items are reviewed to ensure the shipment is complete, and they are then delivered to the proper storage location. All chemicals are dated upon receipt. All supplies are stored appropriately and are discarded upon expiration date.

All supplies used by MCCCL's are procured and controlled per their own procedures and policies, which are available upon request at the laboratory.

18. Non-Direct Measurements (Existing Data)

ESNERR manages a historical database of water quality information and a photographic archive from the majority of the sites included in this project. These data were collected prior to development of a QAPP. CCAMP has stringent quality assurance/quality control requirements for data entered into the official database. Data collected prior to implementation of an approved QAPP may not meet CCAMP acceptance criteria. However, they are the only historical data available at this time and are vital to analyzing long-term trends in water quality within the watershed.

Our historical water quality monitoring data will not be entered into the official CCAMP database at this time. Data collected prior to approval of the QAPP will be used for statistical analyses of water quality trends and management correlates only. Future programmatic funding and staffing provisions may allow for the inclusion of these non-direct measurement data in the CCAMP database once additional formatting, QA/QC, etc., has been completed. Historical data will be made available electronically to any requestor, including CCAMP, in the meantime.

Scientific literature may be consulted during the course of the project for project planning and decision making purposes. Literature will be from peer-reviewed sources.

19. Data Management

Data will be maintained as established in Section 9 above. Upon receipt of field and laboratory data, the Water Quality Scientist will complete any required data entry, inspect data for errors, and correct errors as appropriate. Following this review, a final QA check for errors will be completed. Averages, etc., will be calculated using database management or statistical software (Access, Excel, SAS, Minitab, and ArcGIS). Data will then be added to the ESNERR database.

ESNERR will maintain an inventory of data and its forms and will periodically check the inventory against the records in their possession. MCCCL will maintain a record of transferred records and will periodically assess their record of transferred records against those actually held by ESNERR.

ESNERR also maintains a log showing who accessed the database, when, and what was done during the session (see Appendix II). All changes to the database are stored in a transaction database with the possibility of rollback, if necessary.

19.1. Computerized information systems

The various data and information generated for CCAMP will be stored and maintained in the ESNERR office. Computerized information systems will be updated periodically so that they are kept current as software changes occur. Versions of Microsoft Office and ESRI ArcGIS will be maintained at industry standards. The computer systems will be scanned for viruses weekly.

19.2. Metadata

Metadata will be created for all data generated during this project. Metadata will follow guidelines from the Federal Geographic Data Committee (FGDC 1998). For tabular data, metadata are contained in a Microsoft Word document. For ArcGIS coverages, metadata are in an .xml file embedded in the coverage. This file stays with the coverage.

19.3. Data access

All measurement and supporting data gathered this project (including metadata) will be made available to all participating organizations and to the general public, though the schedule of availability and point of contact will vary by user. The different schedules reflect the differing levels of quality assurance and data documentation that will have been completed at various stages in the project.

The data generated from the monitoring program must be transmitted to CCAMP by the deadlines listed in Table 6.3.1. above.

GROUP C: ASSESSMENT AND OVERSIGHT

20. Assessments & Response Actions

Section 14 above outlined routine quality control procedures, control limits, and corrective actions. ESNERR will conduct performance and system audits to ensure compliance with quality control procedures. ESNERR's QA Officer has the power to halt all sampling and analytical work by both ESNERR and the analytical laboratories if any deviation(s) noted are considered detrimental to data quality.

20.1. Field sampling

Field technicians will conduct performance assessments of the sampling procedures during each sampling event. Technicians will implements corrective measures, record their actions, and report them to the Water Quality Scientist. ESNERR's QA Officer will review monthly QA reports from the Water Quality Scientist.

As described in Section 8 above, periodic field audits will be conducted by ESNERR's Water Monitoring Coordinator and overseen by ESNERR's QA Officer. Reviews will be observed practices against those found in ESNERR's sampling SOP. If a discrepancy/error is discovered, ESNERR's QA Officer will discuss the observed discrepancy with the appropriate person responsible for the activity. The discussion will begin with whether the information collected is accurate, what were the cause(s) leading to the deviation, how the deviation might impact data quality, and what corrective actions might be considered.

20.2. Laboratory analyses

Respective laboratory managers are responsible for the assessing of laboratory QC results, implementing corrective actions, and reporting these corrective actions to ESNERR's Water Quality Scientist. ESNERR's Water Quality Scientist will maintain frequent contact with the analytical laboratories and will maintain a log of all communications with the laboratories with regard to QA issues.

ESNERR's Water Quality Scientist will review the laboratory hard copy and electronic reports within 30 days of receipt, notify the QA Officer of any observed problems, and develop corrective actions if appropriate.

Inter-laboratory exercises will be conducted as outlined in Section 14 above to assess laboratory capabilities. Results will be discussed between the Water Quality Scientist and the respective laboratory managers and reported to the QA Officer. Discussions will include whether the information collected is accurate, what were the cause(s) leading to the deviation, how the deviation might impact data quality, and what corrective actions might be considered.

21. Reports to Management

The Water Quality Scientist will receive either a written or oral progress report from MCCCL once per quarter (every three months). This report will include project status, any significant field or laboratory issues, timeliness of scheduled field and analytical activities, any significant QA problems, or other issues and will provide recommended solutions, if applicable.

The Water Quality Scientist will prepare a monthly QA/QC report to be submitted to the QA Officer for review. This report will highlight any deviations from standard protocols and results that did not meet the project QA/QC objectives.

The Water Quality Scientist will prepare a detailed quality assurance report, which will be approved by the QA Officer, every 12 months of the project. This report will be included in the annual data report submitted to the CCRWQCB and CCAMP. It will include a summary of:

- QA/QC assessments and evaluations including accuracy, precision, representativeness, completeness, bias, recovery, and sensitivity,
- interlaboratory exercise findings,
- 5% field duplicate analyses, and
- any lab and/or field performance audits that were conducted.

The annual report will be distributed to individuals listed in Section 3 above as well as to other interested parties per the timetable presented Section 6.3. and Table 6.3.1. above.

GROUP D: DATA VALIDATION AND USABILITY

22. Data Review, Verification, and Validation Requirements

Data verification and validation will generally follow the guidelines suggested in "Guidance in Environmental Data Verification and Data Validation" (EPA 2002b). Data generated by project activities will be reviewed against the data quality objectives listed in Section 7 and the quality assurance/quality control practices listed in Sections 14, 15, 16, and 17 above. Data will be separated into three categories:

- data meeting all data quality objectives
- data failing to meet precision or recovery criteria, and
- 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. Data that does not meet the objectives outlined in the approved QAPP will be flagged as qualified but acceptable or unacceptable.

Data meeting each of the applicable SWAMP Data Acceptability Criteria for Conventional Constituents in Water (Puckett 2002) will be submitted electronically to the CCAMP database in a SWAMP compatible format. Data that do not meet these requirements will not be submitted for inclusion in the CCAMP database. However, all data will be recorded in the ESNERR database with its appropriate qualifier.

23. Verification and Validation Methods

23.1. Verification

Self-verification will be performed at each level of data generation. ESNERR's Water Quality Scientist will be responsible for internal verification of field and laboratory data. Data will be checked for completeness, correctness, and conformance/compliance. Results will be recorded on the Data Verification Checklist, which is signed and dated by the Water Quality Scientist (see Appendix II). All data will be assessed for errors in transcription, calculation, and computer input. Field data will be entered electronically and compared against the field data logs. Field and laboratory data will be reviewed and qualified based on QA guidelines in this QAPP and in the SWAMP QAPP.

All laboratory data forms must be accurate and complete. Any changes to the data forms will be noted, initialed, and dated on the form. Any actions taken as a result of the data review will also be noted on the data sheet.

For laboratory data, when the data are reported to the Water Quality Scientist, if an outlier or other question arises with the data the Water Quality Scientist refers the data in question to the appropriate laboratory personnel who verifies the data. Usually, the individual who reported the data is contacted directly to resolve any discrepancies. When the Water Quality Scientist is satisfied with the accuracy of the laboratory data in question, she notes the issue on the Data Verification Checklist and uploads the data into the ESNERR database.

23.2. Validation

The Water Quality Scientist will perform validation of field and laboratory data as well. Data validation criteria are based on the measurement quality objectives outlined in this QAPP. Field data validation will consist of:

- Evaluation of the field records for consistency,
- Review of QC information,
- Summarization of deviations and a determination of the impact on data quality,
- Summarization of samples collected, and
- Preparation of a field data validation report.

Laboratory data validation will consist of:

- Assemblage of planning documents and data to be validated with a review summary of data verification to determine method, procedural, and contractual required QC compliance/non-compliance,
- Review of verified, reported sample results collectively for the dataset as a whole, including laboratory qualifiers,
- Summarization of data and QC deficiencies and evaluation of the impact on overall data quality,
- Assignment of data qualification codes as necessary, and
- Preparation of an analytical data validation report.

24. Reconciliation with User Requirements

The overall goal of this project is to continue, expand, and improve our long-term broad-scale water quality monitoring program. Measurable results will include better coordination with CCAMP, improved statistical and GIS analysis of results in an agricultural management context, more accurate nutrient data, and dissemination of results through publications, presentations, and our website. There is not a specific decision that will be made as a result of the data collected under this project. These data will be subsequently used and analyzed by other organizations for numerous purposes.

Limitations in the data will be identified by flagging data as noted in Section 22 and by inclusion of metadata when sharing data with other users. Statistical analyses may include tests for outliers, correlations, and trends. Data will be presented in reports that include tables, charts, and/or maps to illustrate trends, relationships, and anomalies.

The project has been designed to include a sufficient number of sampling locations and events to generate water quality data necessary to achieve the project's goals and produce the measurable results listed above. Uncertainty regarding the data will be addressed with data verification and validation procedures as indicated in Sections 22 and 23 above. The project needs sufficient numbers of data points, as represented by the completeness data quality objective, in order to do trend analyses, identify areas of concern within the watershed, and assess management practices. A failure to achieve the completeness objective could mean an inability to provide these assessments.

Another listed goal of this project is to improve coordination with CCAMP. This project has been designed to improve the quality of our data through attainment of SWAMP data acceptability criteria. Our project monitors water bodies of concern along the Central Coast and is designed to complement CCAMP and other monitoring data. Some of our monitoring stations are the same as or near existing CCAMP sites. These stations will supplement existing CCAMP data. Others are not currently in the CCAMP database. These stations will increase the breadth of the CCAMP database. Data will be submitted in a SWAMP-compatible format allowing for easy integration into the CCAMP database and subsequent use.

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G. APPENDICES

Appendix I: Standard Operating Procedures (SOPs)

Elkhorn Slough National Estuarine Research Reserve
Monthly Water Quality Monitoring Program

Standard Operating Procedures
Field Collection of Water Samples for Analysis of Conventional Constituents
(ESNEER SOP #1)

Revision Date: November 7, 2005

INTRODUCTION

The purpose of this document is to provide the Standard Operating Procedures (SOPs) associated with the collection of water samples for analysis of conventional constituents for the Monthly Water Quality Monitoring Program administered by the Elkhorn Slough Foundation (ESF) and the Elkhorn Slough National Estuarine Research Reserve (ESNERR). This document also outlines the criteria for site selection, field measurements, sample handling, and quality assurance.

SUMMARY OF METHODS

Staff members transport appropriate equipment to the field where they record water quality parameters and collect water samples according to the protocols described here. Samples are placed on ice, secured, and transported to the contracting laboratory. Procedures described in this SOP are modifications of those listed in the *SWAMP Standard Operating Procedures (SOP's) and Recommended Methods for Field Sample Collection* (Puckett 2002).

SAMPLING PREPARATION

1. Coordinate with contracting laboratory:
    a. Arrange for the appropriate number of bottles (usually done when dropping off samples at the previous sampling event).
    b. Notify laboratory when samples will be delivered.
    The primary contracting laboratory from December 1991 to present is the Monterey County Consolidated Chemistry Laboratory (831.755.4516; contact: Gerry Guibert, Laboratory Manager). For QAQC purposes we also contract with Moss Landing Marine Laboratories (MLML) for nutrient analysis and for laboratory space and equipment to do duplicate "in-house" analyses (831.771.4400; contact: Kenneth Coale, Director) and with the University of California, Santa Cruz, also for duplicate nutrient analyses (831.459.4926; contact: Marc Los Huertos, Ph.D.).
2. Sign out vehicle(s) at least one week in advance; notify ESF and ESNEER staff via email if >1 vehicle to be used
3. Sign out YSI and sonde at least one week in advance
4. Sign out cell phone, if needed
5. Sign out digital camera

6. Prepare and print forms and labels
   a. Labels for sample collection containers (not needed for MCCCL samples)
   b. Data collection forms
   c. Chain of Custody (COC) form
7. Label sample containers (for other than MCCCL samples)
8. Calibrate sonde within 24 hours of the sampling event (see ESNERR SOP #2: YSI 6000 and 6600 Multi-Parameter Water Quality Monitor (sonde) Pre- and Post-Sampling Calibration Check)
9. Verify files are set up in YSI for each sample location (see ESNERR SOP #2)
10. Check battery levels in sonde and YSI; recharge/replace as necessary
11. Gather necessary equipment listed below

Field Equipment and Supplies

- Clipboard
- Pen (waterproof ink)
- Permanent marker
- Data collection forms in sufficient number to record all collections (attached at the end of this document)
- Chain of custody form(s) (1 form for each laboratory being used) (attached at the end of this document)
- Digital camera
- Cell phone
- Extra blank bottle labels for in-field edits
- YSI 6000 and 6600 Multi-Parameter Water Quality Monitor (sonde) with connecting cable
- Damp towel to wrap around sonde between sites
- Spare batteries for camera and sonde
- 32-250 mL clean polyethylene sample collection bottles with lids, pre-labeled, plus extras as needed for QA sampling*
- Cooler with ice
- 5-gallon bucket (optional for bridge collection)
- 1-gallon polyethylene sample collection container
- 100m of rope (optional for bridge collection)
- Bottle dipping device
- Squirt bottle
- 5 gallons of water for between site rinses of equipment
- 1 roll utility tape
- Short tide stake
- GPS (optional)

*MCCCL provides clean sample bottles for use with samples going to their lab. The bottles have a label affixed that must be written on with indelible ink (“ESF,” station name, date, time, sample number if greater than one, and name of technician who collected samples). If the

samples are not for MCCCL, sample bottles will need labels made and affixed prior to entering the field.

Safety Equipment and Considerations

- Watertight tall rubber boots
- Rubber gloves – elbow length
- Hand disinfectant (waterless wipes or gel)
- Orange road cones

Personnel will receive appropriate training prior to entering the field. Personal protective gear should be worn appropriately to prevent injury and illness from hazards at the sample site. Utilize hand disinfectant after contact with potential pathogens. Park the vehicle a safe distance from the road's edge. Place orange road cones along the road preceding truck and/or the area from which you are sampling to alert traffic. If working at the back of the truck, move as far away from traffic as possible.

SAMPLING PROCEDURES

Pre-sampling Quality Assurance/Quality Control

On the day of sampling prior to entering the field, the YSI 6000 and 6600 Multi-Parameter Water Quality Monitor (sonde) are calibrated. Pre- and post-deployment standards outlined in the *YSI 6-Series Multi-Parameter Water Quality Monitor Standard Operating Procedure* (NERR 2000) were adapted to formulate the ESNERR YSI 6000 and 6600 Multi-Parameter Water Quality Monitor (sonde) Pre- and Post-Sampling Calibration Check – ESNERR SOP #2). Results from the pre-deployment calibration are logged on the Pre- and Post-Sampling Calibration Check Log (included in ESNERR SOP #2).

Site Photographs

A photograph of the site should be taken at each sampling event. The photograph should be taken from the site where the sample was collected looking upstream. Photographs may be taken of anything of note at the site, especially factors that may affect water quality. Record the picture number on the data collection form for the corresponding site.

Field Measurements and Sample Collection

Sample collection occurs at historically established locations. Special consideration should be taken to ensure sampling occurs at the same area of each site at each collection event to provide continuity over time. GPS measurements are taken at each site as it becomes active in the monitoring network. If you are unsure about the sampling location, bring a GPS unit and verify location prior to sampling.

Sample Collection

1. Unscrew the lid to the sample container immediately prior to sample collection being careful not to touch the inside of the bottle, its lip, or the cap. Polyethylene sample containers are used. Sample containers should be pre-labeled with the site name, date, time, sample number (if greater than 1), and sampler's name prior to collection.
2. Grab samples may be collected from a bridge or from the shore either directly into sample containers or using a polyethylene container/bucket.
3. Stand facing the current or tide. Try not to disturb the bottom sediment. Triple rinse the collection container with sample water. Collect the sample from in front of you facing against the current at a mid-depth level. Try to keep uncharacteristic debris out of the sample. Transfer to sample container if appropriate. Cap the sample immediately.
4. Place directly into a cooler filled with bagged ice.
5. If no sample is taken at a site, include an explanation on the field collection data form.

Field Measurements

1. Connect the sonde to the YSI by screwing in the place the cable ends. Remove the sonde cap and screw on the sonde cage. Place sonde in bucket with grab sample or in sample water at site as close as possible to where sampling occurs. Turn the YSI power on. Electronically connect to the sonde by pressing the "↵" button. The display will verify your connection.
2. Allow the system to stabilize for 90 seconds . To record a measurement, press "↵" then navigate to the proper file name representing the appropriate site. Press "↵" to log a sample. Log one measurement, making sure the system has stabilized before logging the sample.
3. Manually log a reading from the display on the field data collection form. Include the tide staff reading (if present), temperature, conductivity, salinity, dissolved oxygen as a percent and in ppm, pH, turbidity, and chlorophyll. Be sure to write the parameters in the correct location.
4. Disconnect the electronic connection between the sonde and YSI by navigating to "sonde run" in the main menu and pressing "↵". The display will verify you have disconnected. Turn YSI power off. Remove the sonde from the sample area (or bucket).
5. Rinse sonde with water between samples. Wrap in a damp towel to transport to the next site. Leave cable connection intact during transport between sites. Protect the sonde and YSI from vibrations during transport as much as possible.

Field Observations

On the field data collection form, record the water conditions when the sample is taken. Visually assess the site for other factors that may affect water quality; record on the field data collection form.

Diel Sampling Events

Diel samples may be collected per the method outlined above. They may also be collected using a peristaltic pump and clean polyethylene tubing (ISCO sampler) at the discretion of the Water Quality Scientist. All other procedures in this SOP are applicable to diel sampling events.

Sample Handling

In the field, all samples will be packed in wet ice or frozen ice packs during shipment so that they will be kept at approximately 4˚C. Samples will be kept out of direct sunlight as much as possible. Samples will be shipped in insulated containers. All caps and lids will be checked for tightness prior to shipping. All samples will be handled, prepared, transported and stored in a manner so as to minimize bulk loss, analyte loss, contamination, or biological degradation. Sample containers will be clearly labeled with an indelible marker.

Ice chests without latches will be sealed with tape before shipping. Samples will be placed in the ice chest with enough ice to completely fill the ice chest. COC forms will be placed in an envelope and taped to the top of the ice chest or placed in a plastic bag and taped to the inside of the ice chest lid. It is assumed that samples in tape-sealed ice chests are secure whether being transported by staff vehicle, by common carrier, or by commercial package delivery.

Chain-of-custody procedures require that possession of samples be traceable from the time the samples are collected until completion and submittal of analytical results. A complete chain-of-custody form will accompany the transfer of samples to the analyzing laboratory. The contracted laboratory receives the original COC form; a copy is given to the staff member relinquishing the samples. The copy of the COC is stored with the field data sheets. COC forms are provided by MCCCL. A sample is included at the end of this document. It contains the project name, billing information, name of sampler, type of samples, date and time samples were collected, sample identification names, type of analyses to be performed, relinquishing signature, and the receiving signature.

All samples should reach the laboratory within 24 hours of the time of the first sample collection. Maximum holding times prior to specific analyses are below. MCCCL prefers samples arrive by 15:00. Samples will be preserved in the laboratory as appropriate according to the contracted laboratory's protocol for each requested analyses.

The receiving contract laboratories will follow sample custody procedures outlined in their QA plans. Laboratories will maintain custody logs sufficient to track each sample submitted and to analyze or preserve each sample within specified holding times. Contract laboratory QA plans are on file with the respective laboratory.

All samples remaining after successful completion of analyses will be disposed of properly. It is the responsibility of the personnel of each analytical laboratory to ensure that all applicable regulations are followed in the disposal of samples or related chemicals.

Sampling Requirements

Parameter	Sample Container	Sample Volume (Per Laboratory)*	Immediate Processing & Storage	Maximum Holding Time
Temperature (°C)	Probe analysis	N/A	Store on electronic data recorder & field data log	N/A
Conductivity (mS/cm)	Probe analysis	N/A	Store on electronic data recorder & field data log	N/A
Salinity (ppt)	Probe analysis	N/A	Store on electronic data recorder & field data log	N/A
DO%	Probe analysis	N/A	Store on electronic data recorder & field data log	N/A
DO (mg/L)	Probe analysis	N/A	Store on electronic data recorder & field data log	N/A
pH	Probe analysis	N/A	Store on electronic data recorder & field data log	N/A
Turbidity (NTU)	Probe analysis	N/A	Store on electronic data recorder & field data log	N/A
Chlorophyll a (μg/L)	Probe analysis	N/A	Store on electronic data recorder & field data log	N/A
Nitrate	Polyethylene	50 mL	Store at 4°C	48 hours
Nitrite	Polyethylene	50 mL	Store at 4°C	48 hours
Ammonia	Polyethylene	50 mL	Store at 4°C (acidified by laboratory upon transfer)	48 hours (28 days after acidification)
Phosphate	Polyethylene	50 mL	Store at 4°C	48 hours

*Samples are usually collected in a single 250 mL bottle then split at the laboratory. Collection volume allows for laboratory QA procedures.

POST-SAMPLING

Equipment

Return vehicle; complete check-in sheet. Check in cell phone. Return boots if checked out; rinse with water prior to storage. Empty ice chests after delivery. Store with lid open so that any remaining water evaporates. Return other miscellaneous supplies to their proper storage area.

Clean the sides and body of the sonde probes, but do not clean or remove dirt from the probe tips or optics until after the post-sampling calibration check has been completed (see ESNERR SOP #2). After this has been completed, rinse the sonde completely. Fill pH probe nipple with pH 4

buffer solution and place carefully over the pH probe. Fill sonde cap with a small amount of de-ionized water (<0.5 inch) and place over the probes. Store upright.

Connect the YSI to its battery recharger and leave until battery charge is at its maximum.

Electronic data download

- Connect the YSI 650 MDS to the PC with its cable using the normal sonde connection slot on the back of the PC.
- Turn the hand unit on.
- Open the EcoWatch program on the PC. Click on the highlighted sonde connection icon in the top toolbar and select the com port "COM1." The hand unit is now connected to the EcoWatch program.
- On the hand unit use the down arrow to scroll to "File." Press the "↵" button (enter).
- Scroll to "Upload to PC" and press the "↵" button (enter).
- Scroll to "MONTHLY.dat" and press the "↵" button (enter). You will receive a "send_frame" message on the hand unit.
- The EcoWatch program on the PC will prompt you with the message "File MONTHLY.dat exists. Overwrite?" Select "Yes". You will see the file downloading on the PC. This will take a few minutes.
- Open the downloaded file in EcoWatch (file, open, navigate to file name).
- Export the file as a CSV (file, export, cdf). Save in the c:\monitor\monthly\station files\2005 folder. Save the file as "monthly_MMDDYY".
- Open the file in Excel. Save as "monthly_MMDDYY."

Post-sampling calibration check

Visually inspect the sonde, probes, and membranes for signs of damage or malfunction. Complete the post-sampling calibration check per the protocol outlined in the Pre- and Post-Sampling Calibration Check SOP (see ESNERR SOP #2). Record findings in the Pre- and Post-Sampling Calibration Check Log (see ESNEER SOP #2). Complete needed any maintenance and record on the Equipment Repair Log (see ESNERR SOP #2).

QA of electronic data

Compare electronic data with field sheets. Note any deviations between electronic and manually recorded values. Verify that parameters have been logged in the correct location on the data sheets.

Digital Camera and Site Photographs

Photographs are downloaded into the ESNERR Monthly Water Monitoring Program database (c:\monitor\monthly wat qual\Monthly Photos) using the camera's USB cable found in the camera box. A folder is created in this directory titled with the month, day, and year the sampling even occurred. Photographs are placed in the new folder then renamed with the three-

letter site code and six-digit date (ex.: APN082405). Check the battery status on the camera. Replace batteries if needed. Return camera for proper storage.

QUALITY ASSURANCE

Field Replicates

Field replicates will be collected at a rate of 5% of total samples collected within 12 months. This is roughly equivalent to two field replicates per sampling event. Field replicates will be used to assess method precision and total variability.

Field Blanks

Field blanks will be required during random field audits conducted by the Water Monitoring Coordinator. If the analyses of the field blank demonstrate acceptable performance, field blanks will not be required until the next random audit. If the results are not acceptable, field blanks will be required at a rate of 5% until the next satisfactory field audit.

Chain of Custody Forms

When samples are transported to the contract laboratory(ies) a completed Chain of Custody Form must accompany them. The form will list all samples collected and the analyses to be performed on each. Special instructions for the laboratory will also be included. Procedures outlined under "Sample Handling" above will be adhered to at all times.

REFERENCES

National Estuarine Research Reserve (NERR) System-Wide Monitoring Program (SWMP). 2000. YSI 6-Series Multi-Parameter Water Quality Monitor Standard Operating Procedure. Version 3.0. National Oceanic and Atmospheric Administration: Washington, DC.

Puckett M. 2002. Quality Assurance Management Plan for the State of California's Surface Water Ambient Monitoring Program: "SWAMP". 1st Version. Prepared for the California State Water Resources Control Board: Sacramento, CA.

Field Data Collection Form
ESNERR Monthly Water Quality Monitoring Program

Date	
Lower High Tide Ht / Time	m /
Higher High Tide Ht / Time	m /
Lower Low Tide Ht / Time	m /
Higher Low Tide Ht / Time	m /

Time	
% Cloud Cover / Time	% /
Wind Speed	m.p.h.
Wind Direction	
Field Technician(s)	

Precipitation now?	
Date of last precip.	
Amount of last precip.	
Salinas River open?	

Samp. Order	# Samp. Coll.	Photo	Time	Station Name	Station ID	Tide Staff	Temp °C	Cond mS/cm	Salinity ppt	DO %	DO mg/L	pH	Turb NTU	Chl μg/L	Water Cond.
Notes:															
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ENVIRONMENTAL ANALYSIS REQUEST FORM

MONTEREY COUNTY CONSOLIDATED CHEMISTRY LABORATORY
1270 NATIVIDAD ROAD, RM 15
SALINAS, CA 93906

Phone (831) 755-4516 Fax (831) 755-4652

Shaded areas for laboratory use only

Client Name: **Water Resources Agency**	Report Attention: **Sue Shaw**	
Address: **893 Blanco Rd.**	Copy to:	
City, State, Zip: **Salinas, CA 95031**	Phone: **X 4860**	Fax:

Collected by (Print & Sign): **Sue Shaw**	Received by:	Date & Time:
Relinquished by:	Received for Laboratory:	Date & Time:

Lab Number	Sample ID (Sweeps #)	Sample Location	Collection Date & Time	Sample type	Requested analyses
	ESF-1	SKIPPERS		Recreational Water	NO3, P-ORTHO, NH3-N
	ESF-2	RES. BRG.		Recreational Water	NO3, P-ORTHO, NH3-N
	ESF-3	S. MARSH		Recreational Water	NO3, P-ORTHO, NH3-N
	ESF-4	STRAWBERRY		Recreational Water	NO3, P-ORTHO, NH3-N
	ESF-5	KIRBY		Recreational Water	NO3, P-ORTHO, NH3-N
	ESF-6	UPPER POND		Recreational Water	NO3, P-ORTHO, NH3-N
	ESF-7	MID POND		Recreational Water	NO3, P-ORTHO, NH3-N
	ESF-8	LOWER POND		Recreational Water	NO3, P-ORTHO, NH3-N
	ESF-9	HUD LDG E		Recreational Water	NO3, P-ORTHO, NH3-N

Lab Number	Sample ID (Sweeps	Sample Location	Collection Date & Time	Sample type	Requested analyses
	ESF-10	HUD LDG W		Recreational Water	NO3, P-ORTHO, NH3-N
	ESF-11	CARNEROS		Recreational Water	NO3, P-ORTHO, NH3-N
	ESF-12	STRUVE RD.		Recreational Water	NO3, P-ORTHO, NH3-N
	ESF-13	BACK BENNETT		Recreational Water	NO3, P-ORTHO, NH3-N
	ESF-14	EAST BENNETT		Recreational Water	NO3, P-ORTHO, NH3-N
	ESF-15	JETTY		Recreational Water	NO3, P-ORTHO, NH3-N
	ESF-16	ML RD N		Recreational Water	NO3, P-ORTHO, NH3-N
	ESF-17	ML RD S		Recreational Water	NO3, P-ORTHO, NH3-N
	ESF-18	N. POTRERO		Recreational Water	NO3, P-ORTHO, NH3-N
	ESF-19	S. POTRERO		Recreational Water	NO3, P-ORTHO, NH3-N
	ESF-20	MONT DUNE WAY		Recreational Water	NO3, P-ORTHO, NH3-N
	ESF-22	SAL RVR BRG		Recreational Water	NO3, P-ORTHO, NH3-N
	ESF-23	MORO COJO		Recreational Water	NO3, P-ORTHO, NH3-N
	ESF-24	TEMBLADERO		Recreational Water	NO3, P-ORTHO, NH3-N

[ ] Other comments:

Elkhorn Slough National Estuarine Research Reserve
Monthly Water Quality Monitoring Program

Standard Operating Procedures
YSI 6000 and 6600 Multi-Parameter Water Quality Monitor (sonde)
Pre- and Post-Sampling Calibration Check
(ESNERR SOP #2)

Revision Date: March 13, 2006

INTRODUCTION

The purpose of this document is to provide the Standard Operating Procedures (SOPs) associated with the pre- and post sampling calibration checks of the YSI 6000 and the 6600 Multi-Parameter Water Quality Monitor (sonde) used to collect water quality monitoring data for the Monthly Water Quality Monitoring Program administered by the Elkhorn Slough Foundation (ESF) and the Elkhorn Slough National Estuarine Research Reserve (ESNERR). This document also includes a copy of the log forms used in this process.

SUMMARY OF METHODS

Probes are calibrated prior to sampling utilizing purchased standards to optimize instrument performance. Probes are checked against standards after sampling. Results are recorded on the Pre- and Post-Sampling Calibration Check Log. Repairs are made prior to sampling and logged. Pre- and post-deployment standards outlined in the *YSI 6-Series Multi-Parameter Water Quality Monitor Standard Operating Procedure* (NERR 2000) were adapted to formulate this SOP.

PRE-SAMPLING CALIBRATION

The instrument should be visually inspected for any cracked or damaged components. Repairs are documented as outlined below. During the calibration of the probes note any readings outside of acceptable range. You must determine the cause of the problem (see YSI Environmental Operations Manual for assistance if needed), correct the problem, and recalibrate the probe before deploying the instrument. Standards are purchased from a scientific supply house and must not be expired. Previously used standards may be used to rinse probes but must not be used to calibrate. Discard and replace all expired standards.

Record the date, time, and your initials on the calibration log (attached at the end of this document). Calibration should occur within 24 hours of the sampling event.

Connecting the Sonde to the EcoWatch Program

1. Attach the sonde to the stand.
2. Connect the cable to the top of the sonde. When removing the top sonde cap check for signs of fouling or water leakage.
3. Open the EcoWatch program on the PC.
4. Click on the highlighted sonde connection icon in the top toolbar.
5. Select the com port COM 1. The sonde is now connected to the EcoWatch program.
6. Deselect the "wait for DO" option.
7. Select "8-Advanced" from the main menu (if no menu appears, type "menu").
8. Select "3-Sensor."
9. Select "8-Wait for DO" so that this parameter is turned off (no asterisk appears beside it).
10. Select DO charge and pH mV to show up on the report.
11. "Escape" to the main menu.
12. Select "6-Report."
13. Select "B-DOChrg" (asterisk should appear beside it).
14. Select "F-pH mV" (asterisk should appear beside it).
15. Select "2-Calibrate" from the main menu. You are now ready to start calibrating specific parameters:

Conductivity/Salinity

1. Select "1-Conductivity" from the calibration menu.
2. Select "1=SpCond".
3. Enter a specific conductivity of "53."
4. Fill the appropriate container with the jar labeled "53 ms/cm^2" and hold the filled container so that the conductivity probe is immersed.
5. When the conductivity value has stabilized on the screen, hit "enter" and record the value on the calibration log.
6. Hit "enter" again.

Dissolved Oxygen

1. Select "2=Dissolved Oxy" from the calibration menu.
2. Select "1-DO%."
3. Enter the barometric pressure as read by the handheld YSI meter. Record the barometric pressure on the calibration log.
4. Fill the sonde cap with a small amount of de-ionized water and place loosely over probes.
5. When the DO% value has stabilized, hit "enter" and record both the DO% value and the DO charge value on the calibration log. The DO charge should be between 25 and 75.
6. Perform the DO warm-up test:
    a. Start a discrete sampling ("1-Run" from the main menu, "1-Discrete sample", then "1-Start sampling") with the sonde cap filled with a small amount of de-ionized water. If the %saturation is at or above 100% and then drifts down (or slightly up) to 100%, the probe is functioning properly. If the %saturation is very low or negative and then climbs to 100%, the probe is failing due to reverse polarity of the electrodes. If this happens, the probe is either in dire need of a reconditioning or will need to be replaced. Record either pass/fail on calibration

log. Do not take the probe into the field if it fails this test. The data will not be valid.

7. Check the membrane integrity by pressing gently on one side of the membrane with a pencil eraser; replace the membrane if bubbles or other abnormalities are noted.
    a. Remove the rubber o-ring from the probe. Discard the old membrane. Check the probe contacts for signs of fouling. If fouling is present, dry the probe completely. Scour it lightly with special sandpaper circles (about the pressure of a match strike along the length of the contact NOT across). Brush off any debris. Fill with KCl probe solution. Place a new membrane over the probe tightly. No bubbles can be present. Replace the o-ring. Carefully cut away excess membrane from below the o-ring with a utility knife. The oxygen probe needs to rest for a minimum of 6 hours (12 hours is optimal) after the membrane is changed to allow the probe to stabilize electro-chemically. Re-calibrate after this time interval before taking the sonde into the field.

ISE1 pH

1. Select “4-ISE1 pH” from the calibration menu.
2. Select “2-2 point”.
3. Enter the first pH as “7.”
4. Fill the appropriate container with the jar labeled pH 7 clean” and hold the filled container so that the pH probe is immersed. Handle the pH probe with care as it breaks easily.
5. When the pH value has stabilized hit “enter” and record both the pH value and the pH mV value on the calibration log. The value should be 0 $\pm$40mV.
6. Enter the second pH as “10” at the prompt.
7. Fill the appropriate container with the jar labeled “pH 10 clean” and hold the filled container so that the pH probe is immersed.
8. When the pH value has stabilized hit “enter” and record both the pH value and the pH mV value on the calibration log. The value should be -180 $\pm$40mV.
9. Subtract the pH 7 mV value from the pH 10 mV value to determine the span between the pH 7 and 10 values. Record this on the calibration log. The span should be between 165 and 180.

Optic-T Turbidity-1636

1. Select 5-Optic-T Turbidity-1636” from the calibration menu.
2. Select “2-2 point”.
3. Enter the first turbidity value as “0.”
4. Fill the appropriate container with de-ionized (DI) water and hold the container so that the turbidity probe is immersed.
5. When the turbidity water has stabilized hit “enter” and record the value on the calibration log.
6. Enter the second turbidity as “100” when prompted. (Note: the extended deployment sondes calibrate at 123).
7. Fill the appropriate container with the jar labeled “100 NTU clean” and hold the container so that the turbidity probe is immersed.

8. When the turbidity value has stabilized hit “enter” and record the value on the calibration log.

Chlorophyll a

1. Select “6-Optic-C Chlorophyll” from the calibration menu.
2. Select “1-Chl µg/L.”
3. Select “1-1-point.”
4. Enter “0.”
5. Fill the appropriate container with de-ionized (DI) water and hold the container so that the chlorophyll probe is immersed (orange tip).
6. When the value has stabilized hit “enter” and record the value on the calibration log.

Temperature

The temperature probe does not require calibration.

Depth

1. Select “3-Pressure-Abs” from the calibration menu.
2. Enter the depth in meters you wish to calibrate to. Note: Offset is automatically calculated using current barometric pressure in the NERR electronic calibration worksheet. Use the electronic worksheet to calculate the appropriate depth to calibrate to depending on the current barometric pressure.
3. When the value has stabilized hit “enter” and record the value on the calibration log.

Battery Voltage

Check the battery voltage from “4-Status” in the main menu. If the battery voltage is less than 10 volts, replace the batteries. A diagram on the sonde illustrates how the batteries should be loaded. Be sure the inner red o-ring is not folded and is in its proper place before closing the compartment. O-rings can be lubricated with a small amount of silicone gel if they are dry.

DO Gain

1. At the main menu select “8-Advanced.”
2. Select “1-Cal constants.”
3. Select “2-DO gain.”
4. Record this value on the calibration log. The DO gain should be between 0.8 and 1.7.

Cell Constant

1. At the main menu select “8-Advanced.”
2. Select “1-Cal constants.”
3. Select “1-Cond.”
4. Record this value on the calibration log under “Cell Constant.” This value should be between 4.6 and 5.45.

Date and Time

1. “Escape” to the main menu.
2. Select “4-Status.”
3. Select 2 for date and 3 for time.

4. Mark the appropriate column on the calibration log to verify this has been checked.

Final Steps

1. Turn the "wait for DO" option back on:
    a. "Escape" to the main menu.
    b. Select "8-Advanced."
    c. Select "3-Sensor."
    d. Select "8-wait for DO" so that it is turned on (asterisk appears beside it).

De-select the DO charge and pH mV to show up on reports:

1. "Escape" to the main menu.
2. Select "6-Report."
3. Select "B-DOChrg" and "F-pH mV" so that both are turned off (no asterisk appearing beside them)

Discard used standards (or save to rinse probes).

Disconnect the sonde. Replace the top metal screw cap.

STORAGE

Store upright with the pH probe covered (pH nipple filled with pH 4 solution) and the lower sonde cap attached containing a small amount of de-ionized water.

If the sonde is to be used immediately, do not apply the pH nipple. Attach the sonde cage rather than the sonde cap. Wrap the sonde in a damp towel. Transport to the field protected from vibrations.

YSI 650 MDS FILE SETUP

1. Prior to entering the field, check that the YSI hand unit is set correctly so that data may be stored by individual station names.
2. Connect the YSI 650 MDS to the sonde using the cable.
3. Using the up/down arrows, scroll to "Sonde run" and press the "↵" button (enter). You will see the devices connecting.
4. Using the up/down arrows, scroll to "Log one sample" and press the "↵" button (enter). You will see a list of station names. If the station names appear in black, the YSI is set up OK. You may press the "escape" button until the devices disconnect, turn the unit off, and disconnect the cables. If the station names appear in gray, there is a mismatch between the parameters that are being logged and those appearing on the screen. Follow the steps below:
    a. From the main menu, scroll to "Sonde menu" and press the "↵" button.
    b. Scroll to "Report" and press the "↵" button. Make sure the following parameters are selected (circle is filled):

i. Date
ii. Time hh:mm:ss
iii. Temp C
iv. Sp Cond mS/cm
v. Sal ppt
vi. DO sat %
vii. DO mg/L
viii. DO chrg
ix. Depth meters
x. pH
xi. pH mV
xii. Turbid NTU
xiii. Chl ug/L
xiv. Fluor %FS
xv. Battery volts

c. To press the "↵" button to select or deselect parameters (circle filled = selected). If the wrong parameters are selected, a type mismatch will occur, and the YSI will not log samples electronically!

5. Once you have selected verified the parameters are correctly selected, escape to the main menu and repeat steps 1 – 3 to verify station names now appear in black.

FIELD DATA UPLOAD

1. Connect the YSI 650 MDS to the PC with its cable using the normal sonde connection slot on the back of the PC.
2. Turn the hand unit on.
3. Open the EcoWatch program on the PC. Click on the highlighted sonde connection icon in the top toolbar and select the com port "COM1." The hand unit is now connected to the EcoWatch program.
4. On the hand unit use the down arrow to scroll to "File." Press the "↵" button (enter).
5. Scroll to "Upload to PC" and press the "↵" button (enter).
6. Scroll to "MONTHLY.dat" and press the "↵" button (enter). You will receive a "send_frame" message on the hand unit.
7. The EcoWatch program on the PC will prompt you with the message "File MONTHLY.dat exists. Overwrite?" Select "Yes". You will see the file downloading on the PC. This will take a few minutes.
8. Open the downloaded file in EcoWatch (file, open, navigate to file name).
9. Export the file as a CSV (file, export, cdf). Save in the c:\monitor\monthly\station files\2005 folder. Save the file as "monthly_MMDDYY".
10. Open the file in Excel. Save as "monthly_MMDDYY."

POST-SAMPLING CALIBRATION CHECK

1. Record the date, time, and your initials on the calibration log (attached at the end of this document).
2. Clean the sides and body of the probe with water but do not clean or remove dirt from the probe tips or probes.
3. Connecting the Sonde to the EcoWatch program:
    a. Attach the sonde to the stand.
    b. Connect the cable to the top of the sonde. Check the top connection for signs of water leakage.
    c. Open the EcoWatch program on the PC.
    d. Click on the highlighted sonde connection icon in the top toolbar.
    e. Select the com port COM 1. The sonde is now connected to the EcoWatch program.
4. Check the sonde, probes, and DO membrane for any visible signs of damage, fouling, or malfunction; note on the calibration log.
5. De-select the "Wait for DO" option:
    a. Select "8-Advanced" from the main menu.
    b. Select "3-Sensor."
    c. Select "8-Wait for DO" so that this parameter is turned off (no asterisk beside it).
    d. "Escape" to the main menu.
6. Begin discrete sampling:
    a. Select "1-Run" from the main menu.
    b. Select "1-Discrete sample."
    c. Select "1-Start sampling."
7. Record post-sampling values:
    a. Fill the appropriate container with the appropriate standard and hold over the appropriate probe so that the probe is immersed.
    b. When the variable you are testing has stabilized, record the value in the post-sampling row of the calibration log. Be sure to record the battery charge and the depth. DO% values may also be recorded from the last uploaded out-of-water data points for an additional check.
    c. Post-sampling values should include:
        i. Conductivity
        ii. Barometric pressure
        iii. Dissolved oxygen (%)
        iv. Dissolved oxygen warm-up test
        v. pH (2 point)
        vi. Turbidity (2 point)
        vii. Chlorophyll a (1 point)
        viii. Battery charge
        ix. Depth
8. Escape to the main menu when done.
9. Disconnect the sonde from the connecting cable and replace the screw cap.
10. Return sonde to the shed sink and thoroughly clean all probes.

11. Replace the DO membrane if needed or make any other necessary repairs, logging them on the Equipment Repair Log.
12. Return cleaned sonde to stand. Fill pH probe nipple with pH 4 buffer solution and place carefully over the pH probe.
13. Fill the lower sonde cap with a small amount of de-ionized water and place over probes. Store upright.

EQUIPMENT REPAIR

All equipment should be carefully checked before and after sampling for signs of maintenance needs. Extra probes and parts for the sonde are stored on hand (see John for access to these). Consult John or Kristy prior to undertaking any repair/replacement work. The YSI 6-Series Environmental Operations Manual details repair procedures (YSI 2002). This manual can be found in the ESNERR offices (see John or Kristy). Major repair work requires shipment to the manufacturer. Note any replacement of probes or other maintenance work on the Equipment Repair Log (sample attached at the end of this document). Use the electronic version of the Equipment Repair Log; it is the most current version. Equipment for this program is shared with other programs. Therefore, one central log for all programs is necessary. This log is stored at c:\monitor\probe and sonde inv.xls.

REFERENCES

National Estuarine Research Reserve (NERR) System-Wide Monitoring Program (SWMP). 2000. YSI 6-Series Multi-Parameter Water Quality Monitor Standard Operating Procedure. Version 3.0. National Oceanic and Atmospheric Administration: Washington, DC.

YSI Incorporated. 2002. YSI Environmental Operations Manual: 6-Series. Yellow Springs, OH.

Calibration Log
ESNERR Monthly Water Quality Monitoring Program
Hand Held YSI

Sonde ID: 01F1278AA **pH S/N:** 02AIII **Turb S/N:** Y3997 **DO S/N:** 00D0850A **Cond S/N:** 04A0190I **Chl S/N:** 0Y1256

Type	Date	√ per SOP& Tech Initial	Sp Cond 53	DO	DO Chrg	pH 7	pH 7	pH 10	pH 10	Turb 0 (DI)	Turb 100	Chl 0 (DI)	Baro Press	Depth	DO Gain	Cell Const	DO Warm-Up Test	DO Mem Test	Bat.	√Date & Time
Units			mS/ cm	%			mV		mV	NTU	NTU	μg/L	Mm Hg	m			P/F	P/F	V	
Acceptable Range			(Cell Const)	(DO Chrg)	25 – 75	(pH mV)	0 ± 50	(pH mV)	- 180 ± 50	±10	±10	±10	-	-	0.8 – 1.7	4.6 – 5.45	P	P	≥10	
Pre-Calibration																				
Notes																				
Post-Sampling																				
Notes																				
Pre-Calibration																				
Notes																				
Post-Sampling																				
Notes																				
Pre-Calibration																				
Notes																				
Post-Sampling																				
Notes																				

Updated 09/28/2005

Equipment Repair Log
ESNERR Monthly Water Quality Monitoring Program

SONDES				
Type	Serial Number	Date Received	Age (years)	Notes
PROBES				
Type	Serial Number	Date Received	Age (years)	Notes
MISC.				
Type	Serial Number	Date Received	Age (years)	Notes

Updated 10/04/2005

Monterey County Consolidated Chemistry Laboratory's Standard Operating Procedure for Nitrate Analysis (MCCCL SOP #1)

DETERMINATION OF INORGANIC ANIONS BY ION CHROMATOGRAPHY (EP A METHOD 300.0) USING THE DIONEX DX-80 ION ANALYZER

PRINCIPLE

This method determines the following inorganic anions: fluoride, chloride, nitrite, bromide, nitrate, phosphate and sulfate.

A small volume of sample (approx. 1 ml) is loaded into the ion chromatograph. The injection valve injects 10 ul of the sample into the flow of eluent. The eluent (a NaHC03 - Na2C03 solution) flows continuously through the IC and serves as a carrier for the 10 ul of sample and facilitates in the separation process.

The anions of interest are separated using suppressed conductivity detection, and are identified and quantified by comparing data to those obtain from a standard solution. The major parts of the system are the liquid eluent, high pressure pump, sample injector, guard column, the separator column, the chemical suppressor and the conductivity detector. The guard column protects the separator column, which separates the anions based on their size and charge. The function of the suppressor is to chemically reduce the background conductivity of the electrolytes in the eluent, and to convert the sample anions into a more conductive form. The detector then detects the conductivity of the solution, which varies depending on the concentrations of the anions (higher conductivity indicates a greater concentration of the anion).

SAMPLE CRITERIA

The holding times for drinking water samples are as follows:

Fl^-	28 days
Cl^-	28 days
NO_2^-	48 hours
NO_3^-	48 hours
$SO4^-$	28 days
Br^-	28 days

Samples submitted for IC testing routinely should be run within 48 hours of collection, especially for nitrite and nitrate. If testing needs to be delayed, the sample can be preserved with sulfuric acid; preserved samples can be held for up to 28 days and the nitrate results reported as combined Nitrate/Nitrite. Any samples not tested within specified holding times should be identified on the worksheet.

Samples bottles dedicated for IC testing only are placed on the IC bench. As soon as a sample is setup, place it on the white tray for easier storage. After 6 weeks the containers should be emptied and discarded. Nondedicated samples (i.e. those also submitted for additional testing) should be returned to the designated cart after IC testing.

QUALITY ASSURANCE

Operator competency - Ion chromatography may be performed only by analysts who have been trained and who have demonstrated competency with the procedure. One check consists of preparing the calibration standards and calibrating the I.C. An r-value of 0.995 or higher (correlation coefficient of 99.95%) in the linear fit type must be attained for each analyte of interest. Another way to demonstrate competence is to run a minimum of four replicate analyses of an independently prepared sample. Each analyte of interest in the sample should have a known concentration between 5 and 50 times the MDL.

Blank - A blank consisting of nanopure water should be included at the beginning of each run. The results for the blank must be below the MDL for each analyte.

Control standard(s) - Controls representing two concentration levels for each analyte (ICMIX HIGH & ICMIX LOW) must be analyzed as described below. The source of the analytes used to prepare these controls must be different from the source used to prepare the calibration standards. *An ICMIX HIGH stock solution of the 7 anions with the following final concentrations:*

Anion	Final Cone	Preparation in 500 ml volumetric flask
Fl-	20 ppm	10 ml of 1000 ppm Fl std
C1-	100 ppm	50 ml of 1000 ppm Cl std
NO2	65.5 ppm	10 m1 of 1000 ppm NO2-N std
Br-	20 ppm	10 ml of 1000 ppm Br std
NO3	100 ppm	50 ml of 1000 ppm NO3 std
PO4	100 ppm	50 ml of 1000 ppm PO4 std
SO4	100 ppm	50 ml of 1000 ppm SO4 std

should be kept on hand. Use this undiluted at the beginning of the run and after every tenth sample. Each week, prepare an ICMIX LOW solution from the ICMIX HIGH solution as follows: to mark with nanopure water. Record date made in the IC logbook under Quality Control. Run the IC LOW at the beginning of the days run and after every 10th sample after the IC HIGH. The percent recovery for each anion should be between 90 and 110%.

Duplicate spikes - Duplicate spikes should be run after every tenth sample. The spike should not be less than four times the MDL, and it should increase each anion concentration by more than 25% of the background value. A suitable spike can be prepared by adding one part ICMIX HIGH to three parts sample. The average percent recovery for each anion should be between 80 and 120%. The duplicate spikes should be within 10% of each other. Record average percent recovery of spikes and duplicate percent difference on worksheets. Note: if the concentration of the spike is less than 25% of the background concentration, the spike recovery should not be calculated.

If any of the above control criteria are not met, do not report sample results until the problem has been resolved.

External controls & chart analysis - In addition to the control standards tested with each batch of samples, an external reference standard (i.e. SPEX IC standard or WS proficiency sample) should be tested on a quarterly basis; however we like to run one at the end of each run. Furthermore, nitrate control values should be entered into the UPC program and a printout generated for review by the principal analyst each quarter.

CALIBRATION FOR GOUNDW ATER (DRINKING WATER AND MONITORING WELLS):

Calibration for groundwater samples is described below. Calibration should be performed whenever: 1) controls are out of range; 2) a new batch/lot of eluent/regenerant is made or 3) when a column, suppressor or detector is changed.

1. Prepare 1/10, 1/100, 1/1000 dilutions of the calibration standard ordered from Dionex, which contains 20 mg/l fluoride, 100mg/l chloride, 100 mg/L nitrite, 100 mg/L bromide, 100 mg/l nitrate, 200 mg/L phosphate and 100 mg/l sulfate.

2. Run calibration standards beginning with the highest dilution (1/1000) first.

3. Create calibration sequence: File - New - Sequence - Standards - Next. Skip section on Choosing Timebase - name the sequence *calibMMDDYEAR* and initials - Next - Done.

4. Add sequence to batch file before starting

5. After all four calibration standards have been ran, check the calibration curve.

a) Double click on any of the calibration standards (Cal Std 1). You will get a chromatograph
b) Click on Calibration Plot icon, upper right comer or click on VIEW - Calibration Plot. You will see a graph of the first analyte along with the correlation coefficient percentage for each analyte. Only anaytes with percentage of 99.95 or greater are acceptable. Generally try for a 99.98% for an average of all seven analytes to pass quality control checks. See the principle analyst if the result is a lesser value.
c) The mean retention times and detection range are automatic on the DX-80 Ion Analyzer and can not be changed or edited.

PREPARE MDL STUDY

The Method Detection Limit is the lowest concentration of a substance that can be identified with accuracy and confidence by a certain method or analysis.
1) Prepare a Cal Std 1 level each analyte separately using the secondary standards (not Dionex mix)

2) Make seven replicates of this dilution and run through the Ion Analyzer under the Unknown Method.

3) Collect data and calculate the standard deviation for the seven replicates. Multiply the standard deviation values by 3.143. This number will be the Method Detection Limit.

GENERATE BACKLOG REPORT:

1) On a network computer - not the Instrument computer. Double click on LAB WORKS icon. Enter password. Click on OK. Click on backlog. Click on analysis code. Click on OK. Type in #ICANION. Click on OK. Click on display report. Click on print. Click on exit until you are out.

2) Check the clipboard to see if a worksheet has been initiated listing samples that need repeat testing; if so, append worksheet with samples on backlog report.

a) Account for all specimens on backlog report
   i) Samples may have been tested in a previous run but not recorded. Record these results and give to the clerk.
   ii) If a sample appears on the backlog but needs to be tested by a different method (i.e. wastewater), inform the clerk so that the analysis ordered can be modified.

b) Include any "new" samples on the I.C. bench that have not yet been entered into the computer.

SAMPLE PREPARATION

Groundwater (drinking water and monitoring wells) should be filtered through 0.45 um membrane filters before injection:

1) Rinse the syringe once with the sample water. Then fill syringe with about 10 ml of sample water.
2) Filter a minimum of 2 ml of sample through the 0.45 membrane into a labeled autosampler vial discarding the first few drops.
3) Place autosampler cap on vial and press down using the provided tool. Make sure the cap goes in straight and remove any air bubbles seen in the vial (invert or knock gently).
4) Place sample in autosampler rack. The order in the rack must match that on the schedule.
Note: If you suspect the result of a sample to be above that of the calibration standard for an analyte, make an appropriate dilution. Check by measuring conductivity - anything greater than 700 uS will need to be diluted.
5) Include duplicate spikes for every 1dh sample. Add 1 part ICMIX high to 3 parts filtered sample. Then IC HIGH, LRB, IC LOW. The laboratory reagent blank (LRB) is necessary to minimize carry over as the IC low is 100 times less than the High. Double check any samples where analyte concentrations are low after a high sample to verify analyte is even detected.

Samples which may contain high concentrations of chloride or organic contaminants (Carmel Area Wastewater District and ESF), are run on the DX-100 and require additional filtering through Dionex OnGuard Ag, Dionex OnGuard H, and Dionex OnGuard P filters before injection. See supplemental procedures.

SYSTEM START-UP:

1) Ensure the **eluent** bottle is at least 1/4 full. If it is less, depending on size of run, prepare new eluent (and regenerant):

a) Prepare 2 liters of a final eluent concentration of 8.0 mM Sodium Carbonate and 1.0 mM Sodium Bicarbonate by diluting one Dionex AS 14A Eluent Concentrate bottle (pIN 057060) into two 1L-volumetric flasks. Bring each to volume (1000 ml) with nanopure water. Makes 2 liters.

b) Use the designated filter/vacuum flask, a filter funnel, a clean 0.45um membrane filter, and a large magnetic stir bar to degas the eluent. Pour the eluent into the filter funnel and turn on the vacuum. Set the magnetic sticker at medium to high speed. Once all the eluent has been filtered, keep the vacuum and magnetic stirrer on for 15-20 minutes, allowing the eluent to degas.

c) Turn off the magnetic stirrer and the vacuum. Remove the filter funnel. Carefully decant the degassed eluent into the eluent bottle, without aerating. Make sure the cap is on tightly, and the tubes are securely attached.

2) Whenever new eluent is prepared, new regenerant must also be made.

a) Prepare 2 liters of a final anion regenerant concentration of 72 mN Sulfuric Acid by adding one Dionex Anion Regenerant Concentrate bottle (PIN 057559) to two liters of nanopure water.

b) Mix in the regenerant in the designated filter flask using the stir bar and degas for 15-20 minutes.

c) Turn off the magnetic stirrer and the vacuum. Remove the filter funnel. Carefully decant the degassed regenerant into the REGEN bottle, without aerating. Make sure the cap is on tightly, and the tubes are securely attached.

DX-80 OPERATION

1) Turn on nitrogen gas cylinder (main knob only), autosampler (rear right hand comer), ion analyzer (rear panel right hand side) and computer.

2) Double click on Peaknet to open computer program. **File - Panels\Dionex DX-80 System** for the Control Panel.

3) Under the DX-80 Status click on **CONNECT** to connect analyzer to computer

4) Turn on the pump by clicking the **ON** button on the DX-80 Control Panel. **Prime** the pump by turning the pump head waste valve knob counter clockwise and leaving it open for about 5 seconds. Close the pump valve knob by turning clockwise until secure. After changing to new eluent, it is a good idea to leave pump valve open until all air bubbles have been purged - look for the air bubbles coming out the eluent bottle until it reaches the waste line at the pump. This will allow any air bubbles to be pumped to waste instead of through the columns.

5) Allow the system to **equilibrate** for 30 minutes minimum, generally one hour if new eluent is used. Once ready, the **operating pressure** should be 2000+- 300 psi (usu 2100 psi); and the operating **total conductivity** background should be < 30 uS (usually 25.00uS). You can offset the background and zero the reading by clicking the Autozero button on the Control Panel.

6) To begin a run, create a sequence worksheet by clicking on **File - New - Sequence**. (May have to do this twice if worksheet is not already open.)

a. It will then prompt you to choose Standard or Unknowns. Choose **Unknowns - Next**
b. Skip **next** screen where it prompts you to specify timebase,
c. **Estimate** number of unknowns (you can always add or delete samples from sequence when done.
d. Fill out file name you wish to save the file We save under ***MMDDYEAR*** and **initials**: (05052002tl) and press **enter**.
e. Press **Done** when prompted to exit wizard.
f. A worksheet will appear where sample identifications can be added after the calibration data (line #5). Follow printed worksheet - first include a *blank, ic low, ic high, lrb,* then the samples. Note for the first set, the lrb is listed as a sample. *Duplicate spikes* are required for every 10th sample or a minimum of 10% of samples. Finish off sequence with a known quality control standard, usually a proficiency standard such as *WS 60* or Ultra QC and another blank (LRB).
g. Change *dilution factor* if sample was diluted; default is one. Save by pressing the SAVE icon (floppy disk).

7) To start the run - click on **Batch - Edit - Add** - double click on the newly created sequence, or the one you want run - then **Start** to begin.

8) Make sure autosampler vials are in order and the green light is on 'Run' not 'Hold'.

9) Record date, total conductivity and pressure in the log notebook at which the run has started.

10) During or after the run, verify that the blank and QCs (IC HIGH, IC LOW, IC CHECK) are within range. If not stop the run by clicking on **Batch - Stop - after current sample**, and notify principal analyst to investigate and solve the problem before resuming the run.

REPORTING RESULTS

1) When run is complete the analyst performing the run is responsible for recording and reporting results. Review each chromatogram to verify that the peaks were properly identified. Retention times may shift if there was a sudden change in pressure. Changes to the peak name can be made by a right click on the peak and choosing the correct analyte then save.

2) The results are found on the worksheet next to the sample ill and can be exported to an excel file for accuracy calculation:

a) Click on any sample cell- i.e. ic low, cell will be outlined.
b) Click on **File - Batch Report - Export** (unclick the Printout option- computer is not connected to any printer) - **Excel file format**
c) For sheets to be exported, choose only **"Summary - INJ vs. Area, Ht, Amt."** Unclick the Integration, Calibration, Peak analysis, Summary-INJ vs. Anion, and Audit Trail options as they are extra and rarely needed for our purpose.
d) Click on **Finish** then **OK** on batch menu. Status will appear and when transfer is complete, press **OK** to exit.

3) To copy exported file onto a floppy, right click on Start icon on lower left screen and choose EXPLORE for Windows Explorer. Under **C:\Chromel\Export** folders are the files just exported. Highlight the correct sequence and drag to **A:** drive to copy file. (Make sure you have a floppy disk inserted).

4) Open exported file under an EXCEL program - the instrument computer does not have one so use a network computer. You will see three types of charts: first- Sample vs. Area, second- Sample vs. Height, and third - Sample vs. Amount. Copy all of the **Sample vs. Amount** table to an old/previous excel file.

5) The Excel Results worksheet is permanently saved under **G:\Laboratory\Data\Water\IC Data\2002** under the correct month. It is also saved in Tess' computer under **C:\My Documents\IC Data** and correct year and month. Easiest way to create the worksheet is to open a previously saved file (of the same year and month) and then cut and paste the data. There are two worksheets in each file, one for the complete results, the other for the raw data (the Sample vs Amount table exported from peaknet).

a) Before any changes are made, save the file under a new name: MMDDYY and initials
b) On RAW worksheet, delete old table and replace with recently ran sequence data. Add a column between Sample ill and Fluoride Amount for the dilution factor.
c) Change Date Analyzed and Analyst if applicable. Calibrations are generally done once a month with the most recent noted under Date of Calibration - change if necessary.
d) Copy and paste data results from raw worksheet onto Results worksheet under correct sample name. Use the **Paste Special option - Values** - to retain similar fonts on results worksheet. **% Recoveries** will be automatically calculated as will % Differences, and Averages for the duplicate spikes but references to certain cells may need to be changed for the correct result.
e) Verify that all QC are accurate before entering into labworks.

6) For drinking water, results should be recorded as ND - Not Detected for levels below DLR (Detection Limit for Reporting) as follows:

a) Fluoride 0.1 mg/L
b) Nitrate 2.0 mg/L
c) Sulfate 0.5 mg/L
d) Bromide 0.1 mg/L
e) Chloride, Nitrite, Phosphate 1.0 mg/L

f) Record values above 1 mg/L to the whole number. Enter only the nitrate control values into the computer using the UPC program. Instructions for the UPC are in supplemental procedures. Print graph is any controls are out of range and give to the principal analyst. Note on the worksheet the date completed and initials. Record the duplicate spikes and calculate the spike difference and actual spike recovery.

g) Any samples with readings above the calibration range (20 mg/L fluoride, 100 mg/l chloride, nitrite, bromide, nitrate, sulfate, and 200 mg/l phosphate) needs to be diluted and repeated in the next run. List these samples on a new worksheet with the appropriate dilution and place the worksheet on the clipboard.

7) Do not report results if control/spike values do not fall within limits (refer to section on quality control). If controls, spikes, etc. are out of range, notify the principal analyst. If controls are within limits, date and initial the worksheet and give the worksheet to the clerk for data entry. When the worksheet and backlog are returned place them in the binder.

SHUTDOWN

After the run is complete the Ion Analyzer can be shut down. The IC should be shut down on weekends if the system is not in operation on Friday night so as not to damage the suppressor unit:

1) On the Control Panel screen of Peaknet - turn **OFF** pump and **DISCONNECT** DX-80
2) Close Peaknet.
3) Turn off DX-80, autosampler and close nitrogen cylinder valve.

PREVENTIVE MAINTENANCE:

1) Each quarter, replace the bed supports on guard column
2) Maintain the following spare parts. These items are considered consumables:
    a) Anion Refill Kit (Part No. 057069) contains 4 bottles each of AS14A eluent and anion regenerant concentrate.
    b) AS14A anion separator column, 3 mm (Part No. 056901)
    c) AS 14G anion guard column (Part No. 056899)
    d) AMMS III suppressor (part No. 056751)
    e) DS5 Detection Stabilizer (Part No. 057290T)

DOS AND DON'TS

* Try to make additions, changes, and deletions to the sequence during the middle of a run and then save immediately. If the changes are not saved immediately, the program may get confused on which sequence to use and will freeze. If this happens, wait until the current sample is completed, turn off all equipment and wait for about 15 minutes before restarting.

* Be gentle when loading samples onto the autosampler, especially the first rack. If racks are installed too roughly, conveyor belt may get stuck and samples will not be injected in the proper sequence.

REFERENCES:

1) DX-80 Ion Chromatograph with SRS Control Operator's Manual, Dionex Corporation, 2002.
2) Methods for the Determination of Inorganic Substances in Environmental Samples, Method Number 300.0, Determination of Inorganic Anions by Ion Chromatography, John D. Pfaff, U.S. Environmental Protection Agency, 1993.
3) Standard Methods, 18th Edition, 1992. Part 4110.

Originally written by: Johanna Rosen for DX-100
Date: 12-96
Updated by: Theresa Lam for DX-80 Ion Analyzer
Date: 05-02

Monterey County Consolidated Chemistry Laboratory's Standard Operating Procedure for Ammonia Analysis (MCCCL SOP #2)

Nitrogen, Ammonia
EPA 350.3 (Potentiometer, Ion selective Electrode)

Scope and Application:

1. This method is applicable to the measurement of ammonia-nitrogen in drinking, surface and saline waters, domestic and industrial wastes.

2. This method covers the range from 0.03 to 1,400 mg NH3-N/L. Color and turbidity have no effect on the measurement, thus, distillation may not be necessary.

Summary of Method:

1. The ammonia is determined potentiometrically using an ion selective ammonia electrode and a pH meter having an expanded millivolt scale or a specific ion meter.

2. The ammonia electrode uses a hydrophobic gas-permeable membrane to separate the sample solution from an ammonium chloride internal solution. Ammonia in the sample diffuses through the membrane and alters the pH of the internal solution, which is sensed by a pH electrode. The constant level of chloride in the internal solution is sensed by a chloride selective ion electrode which acts as the reference electrode.

Sample Collection/Handling:

1. Collect 250 ml of sample in a screw capped plastic bottle.

2. Specimens that are to be tested within 24 hours should be store in the refrigerator at 4°C. Preserve samples high in organic and nitrogenous matter, and any other samples for a prolonged period, by lowering pH to 2 or less with concentrated H_2SO_4 (2 ml concentrated H_2SO_4/L).

Interferences:
1. Volatile amines act as a positive interference.

2. Mercury interferes by forming a strong complex with ammonia. Thus the samples cannot be preserved with mercuric chloride.

Reagents:

1. 10 N NaOH:

Use the fume hood; be careful of the heat generated on the addition of the NaOH to the water. Dissolve 200.0 g NaOH (use top loader balance) in a 500 ml beaker filled with approximately 400 ml of deionized water. Transfer solution to a 500 ml Class A volumetric flask and fill to mark using deionized water.

2. Ammonium Chloride stock Solution (1 ml = 1.0 mg):

Use Ricca Chemical Company Nitrogen Standard, Cat. No. 5455, 1 ml = 1 mg Ammonia N (Baxter Scientific).

3. Standards:

Make-up the following standards in 100 ml Class A volumetric flasks; add the required amount of standard to the flask and bring to mark with deionized water. Use the adjustable pipetor to add NH3-N. Mark each flask with the concentration, date made, outdate of 24 hours, and
initial.

Standard in 100 ml vol. flask	Ammonium Chloride Working Standard
0.1 mg/L NH_3-N	0.01 ml
1.0 mg/L NH_3-N	0.10 ml
10.0 mg/L NH_3-N	1.0 ml

4. 0.02 M Ammonium Chloride Solution (used to condition electrode) :

Dissolve 1.07 g NH_4Cl (use toploader balance) in a 1L Class A volumetric flask containing deionized water. Mix and fill to mark; transfer to plastic bottle. Label bottle with "0.02 M Ammonium Chloride Solution (Electrode conditioner), date made, expiration date of 6 months, and initial.

Controls:
1. Run a deionized water blank. The reading should be less than 0.05 mg/L NH_3^--N.

2. Run every tenth specimen in duplicate. The results should fall within 20% of each other. There should be a minimum of one duplicate per run.

3. After the tenth specimen has been run in duplicate, a third aliquot of the specimen is spiked with 50 uL of the stock ammonium standard (1 mg/ml). If there is not enough sample left for the third aliquot, dilute the remaining sample 1:2 with deionized water; record the dilution value on the worksheet. Run the spiked sample.

Calculations:

Value of spiked sample - Average of duplicitous = Recovery in mg/L NH_4^--N. (corrected for dilution)

The recovery should fall within 0.4 to .6 mg/L NH_4^--N. If the value falls outside these limits (80 to 120% of the added spike) repeat the spike control. If there is not enough specimen left, use the next specimen available.

Equipment:

Storage of Electrode:

Between measurements, the electrode can be stored wet or dry.

1. For short term storage, up to one week, it is best to store the electrode in 0.02 M ammonium chloride solution (without added NaOH).

2. For long term storage, drain the internal solution, rinse the body and cap with distilled water, and store disassembled unit dry.

3. Use of the electrode in non-aqueous media can wet the membrane, promote penetration of the sample liquid into the electrode, and results in electrode failure. Aqueous solutions containing surfactants can do likewise. For such samples, it is best to measure ammonia with the electrode suspended above the sample in a closed system.

4. For best performance, change the internal filling solution (Cat. No. 13-620-803) every 2-3 weeks.

Electrode Assembly:
1. Using the bottle of Ammonia Internal Fill Solution provided, fill the membrane cap one-half full (approximately 1 ml).

2. Screw the membrane cap onto the electrode body. Make a tight "0" ring seal.

3. Add approximately 2 ml more filling solution through the fill hole in the electrode body. Tap the electrode gently to dislodge any air bubbles in solution.

4. Soak the newly assembled electrode in 0.02 M ammonium chloride (with no base added) for two hours prior to use. Label the electrode with the date filled and initial.

Instrument Calibrations:

1. Connect the electrode plugs to terminal 2 of the ISI meter.

2. Rinse electrode with deionized water to remove soaking solution.

3. Measure 100 ml of each standard using a graduated cylinder. Pour sample into 150 ml beaker containing a magnetic stir bar set at a low spin rate. Immerse the electrode into the solution at an angle of approximately 20°, and then add one ml of 10 N NaOH.

4. Select electrode number 2 by pressing button marked "Electrode" - be sure display indicates "E2".

5. Press "Mode" key, then press the up "Arrow". Press this until the display reads "Concentration".

6. Press "Enter" key.

7. Press "Cal" key. The display reads "Manual Calibration".

8. Press "Enter" key. The display reads "Cations".

9. Press "Enter" key. The display reads "NH_4^+". If not use the arrow key to select "NH_4^+".

10. Press "Enter" key. The display reads "mg/L".

11. Press "Enter" key. The display reads "Enter Conc. Std. 1".

12. Press "Enter" key. The display will read "001. 00E-1 mg/L". This indicates the 0.1 mg/L NH_4^+ for standard one.

13. Immerse the electrode in the first standard and add one ml of 10 N NaOH. start stirrer. After the electrode has soaked in the first standard for at least five minutes, press "Enter" key.

14. The display will show a millivolt reading until the electrode is stable. Then the display will read "Enter standard number 2".

15. Press "Enter" key. The display will read 001.00 E 0 mg/L NH_4^+". This indicates the 1.0 mg/L NH_4^+ standard.

16. Rinse electrode with deionized water, blot dry, and immerse in standard 2 (1.0 mg/L NH_4^-). Add 1 ml of 10 N NaOH (make sure stirrer is set at correct speed).

17. After the electrode has soaked in the second standard for approximately two minutes press "Enter". The display will show a millivolt reading until the electrode is stable, the display will change to "Enter Standard number 3".

18. Press "Enter" key and the display will indicate 001.00 E 1 mg/L NH4T. This indicates the 10.0 mg/L NH_4^+ standard.

19. Rinse electrode with deionized water blot dry, and immerse in standard 3 (10.0 mg/L NH_4^+). Add 1 ml of 10 N NaOH (make sure stirrer is set at correct speed).

20. After the electrode has soaked in the third standard for approximately two minutes press "Enter". The display will show a millivolt reading until the electrode is stable, the display will change to "Enter Standard number 4".

21. We are using three standards so press "Cal" key at this point. The calibration is complete.

Calibration Check:

When you have completed the calibration of the ISE meter, check the calibration.

1. Press the "Cal" key. Press the up "Arrow" key until the display indicates "Calibration Review". Press "Enter".

2. Use the up "Arrow" key until the display indicates the word "Linear" or "Nonlinear".

3. Press the up "Arrow" again. The display will show the correlation coefficient. continue pressing the key and the display will indicate the millivolts for each standard. Record the readings on the worksheet.

4. If the calibration is non-linear or the correlation coefficient is less than 0.995, re-calibrate.

5. The calibration is acceptable when the correlation coefficient is 0.995 or better and linear.

6. To read samples, press "Mode" key and select the concentration mode. Press "Enter key".

Procedure:

1. Measure 100 ml of deionized water and pour into a 150 ml beaker with stir bar. Immerse rinsed electrode at proper angle, start stir bar, and add 1 ml of 10 N NaOH.

2. Let the electrode stabilize, read, and record results on the worksheet. The blank should read less than 0.05 mg/L NH_4^-. If reading is greater, repeat the blank.

3. Rinse the electrode. Measure out 100 ml of sample and pour into a 150 ml beaker. Immerse electrode at proper angle, start stir bar, and add 1 ml of 10 N NaOH.

4. Let the electrode stabilize, read, and record results on the worksheet.

5. Rinse electrode and continue with samples.

Calculations:

The concentration will display in mg/L.

Reporting:

1. Report results to nearest 0.05 mg.

2. Results less than 0.1 mg/L are reported as "Less than 0.05 mg/L of Ammonia Nitrogen (NH_4^+-N)".

3. Report results "_____ mg/L of Ammonia Nitrogen (NH_4^--N)".

References:

1. Package insert "Ammonia Ion Selective Electrode", Fisher Scientific, Part No. 69494, Ammonia ISE, Published 7-87.

2. "Method for Chemical Analysis of Water and Wastes", EPA- 600/4-79-020, Revised March 1983, pages 350.3-1 to 350.3.2.

3. "Standard Methods for the Examination of Water and Wastewater", 18th Edition, 1992, pages 4-81 to 4-82.

Written by: David Perez
Date: March 1993

Approved by: _____
Chemist

Monterey County Consolidated Chemistry Laboratory's Standard Operating Procedure for Phosphate Analysis (MCCCL SOP #3)

Total Phosphorous and Orthophosphate SM 4500-P E

Ascorbic Acid Method

Scope and Application: These methods cover the determination of specified forms of phosphorus in drinking, surface, and saline water, domestic and industrial wastes. Method is usable in the 0.01 to 1.00 mg P/L range.

Summary of Method: Ammonium molybdate and antimony potassium tartrate react in an acid medium with dilute solutions of phosphorus to form an antimony-phospho-molybdate complex. This complex is reduced to an intensely blue-colored complex by ascorbic acid. The color is proportional to the phosphorus concentration.

Only orthophosphate forms a blue color in this test. Polyphosphate and some organic phosphorus compounds may be converted to the orthophosphate form by sulfuric acid hydrolysis. The rest of the organic phosphorus compounds are converted to the orthophosphate form by persulfate digestion.

Sample Collection/Handling: A minimum 250 ml of sample must be collected in a glass or plastic bottle. If the sample cannot be tested within 48 hours of collection, preserve the sample with 0.5 ml concentrated sulfuric acid (0.5 ml is equal 2 ml of acid per liter of sample) and refrigerate at 2-80C for up to seven days.

Filter samples: Samples must be filtered and transferred to an acid rinsed plastic bottle stored in the Chemistry room (cardboard box labeled "Phosphorus Test")

1. Insert a 47 mm diameter, 0.45 urn filter into a two piece (clear top with white bottom) Gelman funnel. Place the assembly in a 1,000 m1 vacuum flask. Vacuum switch located in the media room. Rinse filter with 100 ml of DI water before use to remove trace phosphorus.

2. Filter 250 ml of sample through the filter. Occasionally several filters will need to be used before enough specimen is filtered.

3. Rinse the flask and filter with deionized water between specimens.

Glassware: Contamination of glassware is a serious problem in performing this test. To avoid contamination, the glassware must be acid washed. Commercial detergents should never be used to clean the glassware. Once washed, store all glassware in cardboard box labeled "Glassware for Phosphorus Testing". Glassware used for phosphorus testing should be initially cleaned as follows:

1. Make a 50% HCL solution by carefully adding 50 ml of concentrated HCI to 250 ml beaker containing 50 ml of deionized water. Use fume hood and wear goggles. Be careful of the heat generated by the mixture.

2. Wash the glassware by pouring 10 to 15 ml of the 50% acid solution into each beaker, graduated cylinder, and test tube used in the test. Carefully swirl the acid so that all the inside surfaces come into contact with acid.

3. Let the acid sit in the glassware for five minutes before pouring the acid back into the original 250 ml beaker. Re-use the acid to wash all the equipment. After the glassware has been cleaned, neutralize the acid and flush down the drain with plenty of water.

4. Thoroughly rinse the acid washed glassware with deionized water.

5. To remove the last traces of phosphorus, wash each piece of glassware with 10 to 15 ml of "combined reagent" by wetting the inner surface of the glassware with the reagent. Reuse the reagent by transferring the reagent into the next piece of glassware, until each piece has been rinsed. Discard the used reagent.

6. Thoroughly rinse the reagent washed glassware with deionized water.

7. The specially cleaned glassware should only be use for this test. Once it has been cleaned, the glassware need only be rinsed with deionized water before it can be reused.

8. If the glassware becomes contaminated with phosphorus, re-clean as described above in steps 1 to 6.

Reagents: Use specially cleaned glassware that has been dedicated to this test Record source, lot number, final concentration date made/expiration and preparer in reagent prep log book.

1. 1 N Sulfuric Acid (H2SO4) - See Reagent Preparation Manual

2. 5 N Sulfuric Acid (H2SO4):
   a. Carefully add 35 ml of concentrated sulfuric acid to a 250 ml Class A volumetric flask filled three quarter full with deionized water. Allow to cool.

   b. Bring to mark with deionized water. Transfer to plastic bottle, label with "5 N H2SO4", date made, outdate of 1 year, and initial. Store in Acid Cabinet located below the hood.

3. Sulfuric Acid Solution (H2SO4):

a. Carefully add 75 ml of concentrated sulfuric acid to a 250 ml Class A volumetric flask filled half full with deionized water. Allow to cool.

b. Bring to mark with deionized water. Transfer to plastic bottle, label with "10.8 N H2SO4", date made, outdate of 1 year, and initial. Store in Acid Cabinet located below the hood.

4. 1 N Sodium Hydroxide (NaOH) - See Reagent Preparation Manual.

5. 10 N Sodium Hydroxide (NaOH):

a. Carefully weigh out 100 g of NaOH pellets using the top loader balance.

b. Dissolve by stirring in beaker with 200 ml of deionized water; let cool. Add the solution to a 250 ml volumetric flask. Carefully add deionized water to mark. Transfer to a plastic bottle, label with "10 N NaOH", date made, outdate of 1 year, and initial. Store on prepared reagent shelf.

6. Antimony Potassium Tartrate Solution:

a. Weigh out 0.6858 g of antimony potassium tartrate using the analytical balance. Dissolve in a 250 volumetric flask containing approximately 200 ml of deionized water. Fill to mark.

b. Transfer to dark glass stoppered bottle, label with" Antimony Potassium Tartrate Solution", date made, outdate of six months, and initial. Store in refrigerator at 2 to 8 degree C.

7. Ammonium Molybdate Solution:

a. Weigh out 109 of ammonium molybdate using the top loader balance. Dissolve in a 250 ml volumetric flask containing approximately 200 ml of deionized water. Fill to mark.

b. Transfer to plastic bottle, label with" Ammonium Molybdate Solution", date made, outdate of six months, and initial. Store in refrigerator at 2 to 8 degrees C.

8. Ascorbic Acid:

a. Weigh out 1.76 g of ascorbic acid using the digital balance. Dissolve in a 100 ml volumetric flask containing approximately 75 ml of deionized water. Fill to mark.

b. Transfer to plastic bottle, label with" Ascorbic Acid", date made, outdate of one week, and initial. Store in refrigerator at 2 to 8 degrees C.

9. Potassium persulfate, reagent grade.

10. Phosphorus Solutions

Stock Phosphorus (50mg/l)

a. Dry 0.25 g of potassium dihydrogen phosphate for 4 hours at 105 degree C. Immediately weigh out 0.2197 g of potassium dihydrogen. If the dried reagent cannot be weigh out immediately, store in a desiccator until ready to use.

b. Transfer to a 1,000 ml Class A volumetric flask, bring to volume with deionized water. Transfer to acid washed plastic bottle. Label with "Potassium Dihydrogen Phosphate, 0.2197 g/L", date made, outdate of6 months, and initial.

Standard Phosphorus Solution (0.50 mg/l)
a. Using a Class A pipette, transfer 5 ml of Stock Phosphorus to a 500 ml Class A volumetric flask.

b. Dilute to mark with deionized water. Label with "Standard Phosphorus Solution", date made, outdate of 24 hours, and initial.

Blank and standards: (Prepare six standards plus a blank)

Using volumetric pipettes, transfer the following amounts of Standard Phosphorus Solution (0.50mg/l) to 100 ml volumetric flasks. Bring to volume with deionized water.

ml of Standard	Phosphorus Solution Concentration in mg/L
0.0	Blank
10.0	0.05
20.0	0.10
40.0	0.20
60.0	0.30
80.0	0.40
100.0	0.50

11. "Working Reagent":

Reagents must be at room temperature and be added in the order given below. The 300 ml of working reagent is sufficient for 35 samples (controls and samples) for both orthophosphate and total phosphate.

a. Using a 100 ml graduated cylinder, measure out 150 ml (50 ml/100 ml) of 5 N sulfuric acid. Pour into 500 ml flask.

b. Using a 25 ml graduated cylinder, measure out 15 ml (5 ml/100 ml) of antimony potassium tartrate solution. Add the reagent to the 500 ml flask. Mix by swirling.

c. Using a 100 ml graduated cylinder, measure out 45 ml (15 ml/100 ml) of ammonium molybdate solution. Add the reagent to the 500 ml flask. Mix by swirling.

d. Using a 100 ml graduated cylinder, measure out 90 ml (30 ml/100 ml) of ascorbic acid. Add the reagent to the 500 ml flask. Mix by swirling.

e. If turbidity forms, shake and let stand for a few minutes. The working reagent is good for 8 hours.

12. Spiking solution: Use commercial std such as Lab Chem Inc. LC18600-7 (50ppm) Add 500ul of spike to a 50ml sample or 250ul to a 25ml sample for a concentration of 0.50 mg/l.

Quality Control

1. Use two external reference standards, selecting controls from any of the following sources EPA, ERA, SPEX or Analytical Product Group. The values for the controls are located in the "True Values" QC binder in the chemistry bookshelf.

2. Run both controls after the blank and standards. Thereafter, run one control after every ten samples, alternating between the two controls. Record percent recovery and verify results are within acceptable range. Reanalyze previous ten samples when results are out of range.

3. Run every tenth specimen as a duplicate spike. The recovery should be 80 to 120% for drinking water and 75-125% for waste water with precision within 20% of each other. If these limits are exceeded results are invalid. Analysis should be repeated after corrective action is taken and documented on worksheet.

4. Calibration requires six concentrations plus the blank. The minimum correlation coefficient is 0.995 with a zero intercept. Digest standards for total phosphorus.

5. Samples are not to be reported and must be reanalyzed when QC failures occur. Document all corrective action on worksheets.

Sample log-in:
Using a worksheet record the blank, standards, controls, and samples. Make sure to include each control (after every tenth specimen) and duplicate spike. Prepare separate worksheets for orthophosphate and total phosphate if necessary.

Sample Digestion (Total Phosphate):
To test for total phosphate the sample must digested and heated for several hours to convert all forms of phosphorus to orthophosphate before testing. Use specially cleaned glassware that has been dedicated to this test.

1. Using a 50 ml graduated cylinder, transfer 50 ml of sample to a 50 ml beakers. Note: If orthophosphate testing is required, also transfer a 25 ml portion to a specially cleaned 50 ml screw cap tube. These samples can be tested for orthophosphate while sample is digested for total phosphate.

2. Add 0.5 g potassium persulfate using the properly labeled "scoop", to each specimen. Note: The scoop holds 0.5 g, so use one scoop for each sample.

3. Using the 5 ml adjustable pipettor, add 1.0 ml of 10.8 N H2SO4 to each beaker.

4. Place the beakers on a hot plate set at 3 on the dial. Heat the samples until approximately 10 ml of sample remain (approximately 2 hour). Note: The specimens on the center of the hot plate will evaporate faster than the specimens on the outer edges. Remove each specimen as it reaches the proper volume.

5. While the specimens are heating, continue with the first set of test tubes that were set aside in step a, starting with step b below.

6. After all the specimens have cooled, add 1 ml of 10 N NaOH to each specimen. Use the adjustable 5 ml pipettor.

7. Dilute to 30 ml with distilled, add one drop phenolphthalein indicator solution, and neutralize to a faint pink with NaOH.

8. Adjust all the samples before continuing with the procedure. Pour each sample into a 50 ml graduated cylinder marked TC (to contain). Bring up to 50 ml with deionized water. Mix the sample by pouring the sample back and forth between the graduated cylinder and the beaker. Measure out a 25 ml portion of the sample and pour into a properly numbered 50 ml screw capped tube. Save the rest of the specimen in the beaker for dilution, if needed.

Spectrophotometer set-up:
The spectrophotometer needs a 20 minute warm up period before it can be used. The power switch is located on the front panel in the lower right hand side of the instrument.

To enter standards for a new calibration curve:

Total phosphorus & Orthophosphate

1. Turn power on; await completion of self test.

2. Enter wavelength 880nm. Then press "Go to"

3. After the 30 minute warm up period, press "Conc" to measure concentration.

4. Insert blank into sample holder.

5. Press "Second Function", then "Zero". Remove blank.

6. Press "Select". The display will begin to scroll through options, when the display shows Standards, press "Enter".

7. Display shows Linear Fit Y/N, press "Yes".

8. Display shows Standards Y/N, press "Yes".

9. Display shows Put Thru 0 Y/N, press "Yes".

10. Display shows # STDS, enter 4, press "Enter".

11. Display shows STD 1. Place first standard in sample holder, press "Enter". Remove standard. Enter the value of the standard. Continue with the last three standards; rinse the cuvet out between samples with a few ml of the sample you are going to read next.

12. After the last standard has been entered, the printer will show the "Slope Intercept and Correlation Coefficient".

13. The correlation coefficient should be greater than 0.995. If it is not, repeat the readings of the standards.

14. If after repeat readings either of the two parameters are out of range, consult with the Chemist.

15. The standard information can be saved for future use by pressing "Save Test". Number will be assigned to saved test; record number on worksheet along with calibration values.

To set up instrument using stored calibration curve:

1. Press "Select." The display will scroll through options. When "Load Test" is displayed, press "enter."

2. When the display screen indicates "test number" enter the number for PO4 (refer to test numbers taped to spectrophotometer.

3. When the display screen asks "save current" enter "no."

4. The spectrophotometer will load previous calibration. Set zero absorbance by inserting blank (deionized water with developing reagent), pressing "second function" key and pressing "zero" key.

5. Make sure spectrophotometer is set to read concentration (vs. absorbance)

Procedure:

The spectrophotometer needs a 30 minute warm up period before it can be used. Turn on spectrophotometer before proceeding.

1. Using a 50 ml graduated cylinder, measure 25 ml of the blank (dH20), calibration standards, controls, samples, and duplicate spikes to a correspondingly numbered 50 ml screw capped test tube (use dedicated tubes). Note: For measurement of total phosphate, transfer 50 ml of the sample to a numbered 50 ml beaker and digest as described above. After the samples have been digested, pH adjusted, and brought back to 50 ml volume, take 25 ml and test as described below.

2. Add 4 ml of working reagent to the first tube of the run (blank). Immediately vortex sample and start clock that has been set for 15 minutes.

3. Continue with the controls, adding reagent and vortexing. Wait 15 minutes and zero the blank and read the controls before pro ceding. If the control results are satisfactory, reset timer for 15 minutes and add reagent to samples. Maintain a steady pace of approximately 30 seconds between specimens.

4. At the end of 15 minutes but before 30 minutes have passed, read the first sample. Read the next sample thirty seconds later. Maintain the 30 second interval between each specimen. Rinse the cuvet out with a small portion of the specimen you are going to read next.

5. Record concentration on worksheet; make sure to match up sample numbers (in margin of worksheet) with the numbers on the 50 ml tubes.

6. After recording all the orthophosphates on the worksheet, rinse the tubes out with deionized water and ready them for use in the total phosphate portion of the test.

After both tests have been completed rinse out all the glassware used in the Phosphorus test with deionized water. Let the glassware dry and store in the properly marked box.

Calculations:
Spectrophotometer will display phosphorus concentration in mg/L. Record results on

worksheet and multiply results by the dilution factor. Record final results on right side of worksheet as "P, mg/L."

Reporting:

All results expressed as "P, mg/L". Report to nearest 0.01 mg. The detection limit for reporting purposes is 0.03 mg/L. Report all results with less than 0.03 mg/L P as NOT DETECTED. The MDL of 0.03 mg/l should be on report. Report results as Orthophosphate or Total Phosphorus. See figure 1 for analytical scheme for differentiation of phosphorus forms.

1. "Methods for Chemical Analysis of Water and Wastes", EPA- 600: 4-79-020, March 1983, pages 365.1-1 to 365.1-7.

2. "Standard Methods for the Examination of Water and Wastewater", 18th Edition, 1992.

3. "Water Analysis Handbook", Hack Company, 1989.

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Chemist

Elkhorn Slough Reserve
Monthly Nutrient Monitoring Program
Standard Operating Procedures
And Quality Control Guidelines

ESNERR SOP/QA Guidelines for Nutrient Analyses Performed at MLML

Prepared 2005

Standard Operating Procedures for Elkhorn Slough Reserve
Monthly Nutrient Monitoring Program

Purpose

The National Estuarine Research Reserve System (NERRS) conducts large-scale water quality monitoring for the purposes of increasing understanding of the nation's estuarine waters and contributing to effective coastal zone management. The NERRS System-Wide Monitoring Program (SWMP) tracks short-term variability and long-term changes in coastal ecosystems represented in the reserve system. The initial phase of the reserve's SWMP began in 1996. This phase focused on monitoring a suite of physical water quality and atmospheric information. As part of a recent enhancement to water quality monitoring, the reserve system began monitoring nutrients and chlorophyll levels in 2002. The current monitoring program for nutrients and chlorophyll consists of two separate but complimentary components, they are the monthly grab and the diel sampling programs**.**

The purpose of this document is to provide the operating procedures and chemical reagents used in the Elkhorn Slough Reserve monthly nutrient monitoring program. This program monitors the concentrations of nitrite, nitrate, dissolved inorganic nitrogen, ammonia, phosphate, and chlorophyll at four locations within the slough on a monthly basis.

SAMPLING PROTOCOLS

Monthly Grab Samples: Basic Protocol

Grab samples are taken monthly at the four principal, long-term continuous monitoring stations (YSI deployment stations). A grab sample is defined as a single sample taken at a specific location over a short period of time (typically seconds). Each of the four stations is considered shallow and well mixed, thus two samples are taken sequentially as close to the datasonde as possible. 250 ml amber Nalgene bottles are rinsed three times with water to be sampled. Sample bottles are filled and capped then stored in a dark iced cooler. Temperature, dissolved oxygen, pH, salinity, and turbidity are taken at the time of sampling. Samples are collected between +3 hrs before slack low water and slack low water. No distinction is made between neap and spring tide conditions. Samples are collected and filtered the same day as the diel samples are collected.

Diel Samples: Basic Protocol

Diel samples are taken from the South Marsh site that has been a long-term continuous monitoring station since 1995 and monitored through telemetry since July 2004. Twenty four samples are collected with an ISCO 6712 over a lunar day at 1 hour and 2 minute intervals at the same depth as the water mass sampled by the datasonde. Due to the use of ISCO auto samplers, ambient water rinses of the sample containers are not possible. However, ISCO auto sampler tubing is rinsed with ambient water prior to a sampling event. ISCO is filled with ice at time of deployment usually 6-10 hours prior to initiation of the program.

Glassware and Sample Bottle Care
Sample bottles are rinsed three times with distilled water and then three times with sample water. Once a month all glass and plastic ware that is used in either chemical analysis or as sample bottles or filtrate bottles are washed in 10% hydrochloric acid then rinsed five times in Milli-Q water. ISCO bottles are filled with 500 mls of sample and grab samples are taken in 250 ml amber Nalgene bottles.

LABORATORY ANALYSIS

Filtration
All samples are filtered prior to chemical analysis. A vacuum is used at low pressure to prevent cell rupture. Moss Landing Marine Labs has historical data from Elkhorn Slough and Monterey Bay for nutrients and chlorophyll analysis in which 25 mm diameter Whatman GF/F filters (pore size 0.7 μm) were used. To keep with these data samples for this program are filtered using these same filters.

Chlorophyll analysis:
In order to save time and filters each sample (60 mls) is filtered once the filter is then removed and placed in 90% acetone) in 15 ml plastic capped disposable culture tubes. These are then stored in the freezer in the dark for a minimum of 24hrs. The filtrate is then used for nitrate/phosphate analysis using an Alpkem analyzer and nitrite and ammonia using an Ocean Optics spectrophotometer.

Nutrient analysis:
60mls of sample is measured in a 3 times DI water rinsed graduated cylinder and poured into the filter apparatus. After filter has been removed and placed in aqueous acetone the filtrate is then used to rinse out a dry pre-rinsed in DI water 60 ml amber bottle 3 times. The remaining filtrate is poured in the 60 ml bottle. 10 ml aliquots are then placed in dry pre-rinsed scintillation vials for ammonia analysis and pre rinsed 60 ml glass test tubes for nitrite analysis. Filter flasks and apparatus are rinsed 3 times in DI water and shaken dry in preparation for the next sample.

Chlorophyll analysis
After an minimum of 24 hrs, the glass disposable culture tubes are removed from the freezer filters are removed and sample is spun down at 5000 rpm for 1 minute to draw down any particles floating in solution that may interfere with chlorophyll measurements. Special care is made to keep the samples in the dark during this process. Samples are equilibrated to room temperature prior to analysis. A modified single step method is used with a Turner Designs TD-700 flourometer with 436 and 680 nm filters.

Reagents: Aqueous acetone – Mix 90 parts acetone with 10 parts DI water.

Procedure:
- Filter know volume of sample through 25 mm Whatman GF/F filter.
- Submerge filter into acetone in plastic capped disposable culture tubes filled with 5-8 mls acetone depending on estimated chl-a concentration.

- Place test tubes in freezer for a minimum of 24 hours prior to analysis.
- After 24 hours remove filter from test tubes and centrifuge for 1 minute at 5000 rpm to clear acetone of filter particles.
- Place test tube in Turner Designs TD-700 flourometer and read RFU (relative flourometry unit).

Notes:
Obtain current calibration coefficient from Moss Landing Marine Labs Biological Oceanography Lab prior to analysis. This lab calibrates their TD-700 flourometer on a quarterly basis by diluting a chl-a standard verifying the concentration with HPLC.

Ammonia Determination – Spectrophotometer (640 nm)

Reagents

Phenol solution – Dissolve 20g crystalline analytical reagent grade phenol in 200 ml of 95% v/v ethyl alcohol.

Sodium Nitroprusside solution – Dissolve 0.5 g of sodium nitroprusside $Na_2Fe(CN)_5NO$ $2H_2O$ in 100 ml of de-ionized water. Store in amber bottle, which is stable for one month.

Alkaline Reagent – Dissolve 100 g of sodium citrate and 5 g of sodium hydroxide (analytical grade) in 500 ml of de-ionized water. Solution is stable indefinitely.

Sodium hypochlorite solution- Use a commercial solution of bleach (unscented) with at least 5.25 % hypochlorite.

Oxidizing solution – Mix 40 ml of alkaline reagent and 10 mls of sodium hypochlorite solution. Keep this solution capped while not in use and prepare fresh every day.

Procedure:

- Add 10 ml of sample to a 20 ml scintillation vial from a 10 ml graduated cylinder.
- Add 0.4 ml of phenol solution swirl then sequentially 0.4 ml of sodium nitroprusside solution and 1 ml of oxidizing solution mixing after each addition.
- Allow sample with reagents to stand covered (cap screwed on) in dark for at least one hour.
- Read the extinction at 640 nm in a 1cm path length cell and determine concentration from a graph of absorbance vs concentration.

Nitrite Nitrogen

The determination of nitrite is based on the reaction of nitrite with an aromatic amine (sulfanilamide hydrochloride) to form a diazonium compound, which then couples with a second aromatic amine (NED) to form an azo dye. The absorbance is measured at 540 nm.

Reagents Preparation

Sulfanilamide: Dissolve 10 g sulfanilamide in 1 L of 10% HCl.

NED: Dissolve 1 g NED N-(1-Napthyl)ethylenediamine dihydrochloride) in 1 L 18 ohm water. Store in an amber plastic bottle in the refrigerator.

Procedure

- Add 10 ml of sample to clean plastic vial.
- Add 0.2 ml Sulfanilamide solution. Swirl.
- Wait 2-8 min.
- Add 0.2 ml NED. Swirl.
- Read absorbance at 543nm in a 10cm cell, between 10 minutes and 2 hrs after last addition.

Nitrate + Nitrite Nitrogen

The following procedure was developed by MBARI (Sakamoto et al., 1990). The determination of nitrate is based on the quantitative reduction of nitrate to nitrite by copper-coated cadmium metal in a 24 inch open tubular cadmium reactor (OTCR). The resulting nitrite and any nitrite originally present in the seawater sample is then determined by measuring the absorbance (543 nm) of the azo dye as in the nitrite procedure.

Manifold configuration

Sample (226 μl/min) and imidazole buffer (385 μl/min) merge and then nitrogen gas is injected at 118 μl/min. The analyte stream passes through a 5-turn mixing coil and then through a 24" cadmium coil. The stream then merges with sulfanilamide (74 μl/min), passes through a 10-turn mixing coil, and then merges with NED (74 μl/min). After passing through a 10 turn mixing coil, the stream is de-bubbled (287 μl/min) and then re-bubbled (118 μl/min) and then passes through a 1.5 cm flow-cell with bubble gating. A damping time of 2 seconds and a standard calibration setting of 1.0 is used.

Reagent preparation

0.1M Imidazole buffer - Dissolve 6.81 g imidazole in approximately 900 ml DI water in a 1 L bottle. Add 19 ml of 10% HCL and dilute to 1L with DI water. This reagent can be stored at room temperature. The pH of this buffer should be about 7.5.

Sulfanilamide – Dissolve 10 g sulfanilamide in 1 L of 10% HCL. Store in the refrigerator.
Working sulfanilamide reagent – Add Brij-35 at a rate of 1 ml Brij-35 per 100 ml sulfanilamide reagent.

NED- Dissolve 1g NED (N-(1-Napthyl)-ethylenediamine dihydrochloride in 1 L DI water. Store in an amber plastic bottle in the refrigerator.

2% (w/v) cupric sulfate – Dissolve 20 g cupric sulfate pentahydrate in 1 L DI water.

Buffered copper solution – Mix 20 ml imidazole reagent (no Brij-35) and 20 ml 2% cupric sulfate.

OTCR Activation

- Using a syringe, draw buffered coppered solution into the OTCR. Let sit for 5 minutes and then repeat again.
- Draw imidazole buffer into the coil and leave filled with buffer. Do not introduce air into the OTCR during this process.
- When necessary, reactivate the OTCR by filling the reactor with buffered copper solution only once and then flushing it with stock imidazole buffer. Make the buffered copper solution fresh before use.

Notes
The conditions of the reduction reaction must me adjusted so that nitrate is quantitatively converted to nitrite and not reduced further. The efficiency of the reaction is dependent on the pH of the solution and the activity of the metal surface. At the buffered reaction pH of 7.5, nitrate should be quantitatively reduced to nitrite with no further reduction. By calculating a nitrate calibration factor for the high nitrite standard and comparing this factor versus the calibration factor for the nitrate standards, column reduction efficiency can be estimated. The efficiency should be between ~95-100%. Over reduction can be detected by comparing the value of the high nitrite standard with and without the cadmium coil in-line, taking into account any nitrate present in the nitrite standard.

Reactive Phosphorus
The following procedure was developed by MBARI (Sakamoto et al., 1990). The determination of reactive phosphorus (phosphate) is based on reaction with an acidified molybdate reagent to yield a phosphomolybdate complex. This complex is then reduced with hydrazine sulfate to produce highly colored blue compound. Antimony is not used in this analysis (see note one). The absorbance is measured at 820 nm and a 2 ml heating bath set at 55 degrees C is used to accelerate the reaction.

Manifold Configuration
Sample (642 µl/min) and ammonium molybdate (37 µl/min) merge and then air is injected at 118 µl/min.After passing through a 5-turn mixing coil, the stream merges with hydrazine sulfate (37 µl/min). The stream then passes through another 5-turn mixing coil, a 2 ml heading bath set at 55 degrees C, and a 10-turn mixing coil. The stream is de-bubbled at 482 µl/min and then passes through a 30 mm flow cell. A damping time of 1 second and a standard calibration setting of 4.5 are used.

Reagent preparation
2% (v/v) Ultrawet 60 L – Mix 1 ml ultra wet 60 L (available from Sigma and Alpkem) in 50 ml DI water.

Ammonium molybdate – Dissolve 27 g ammonium molybdate in 250 ml DI water. Slowly and with mixing, add 427 ml concentrated sulfuric acid to 540 ml DI water in a pyrex beaker. Allow the acid solution to cool and then slowly add the acid solution to the molybdate solution and make up to 1 L. This reagent is stable at room temperature.

Working molybdate reagent – Dilute the above stock solution 1:1 with DI water. Add 1 ml of 2% Ultrawet solution per 40 ml reagent. Prepare daily.

Hydrazine sulfate – dissolve 6.4 g dihydrazine sulfate in 1 L DI water. Store in the refrigerator in a brown bottle. If dihydrazine sulfate is difficult to obtain, hydrazine sulfate can be substituted. If hydrazine sulfate is used instead of dihydrazine, dissolve 10.15 g hydrazine sulfate in 1L DI water. Store in the refrigerator in a brown bottle.

Working hydrazine sulfate – add 200 µl Aerosol-22 to 40 ml hydrazine reagent. Prepare daily.

Notes

Previous methods for the determination of reactive phosphorus have commonly used the addition of potassium antimony tartrate, which increases the reaction rate but also results in significant tailing and carryover. By eliminating the antimony, smearing of the signal is greatly reduced and the baseline remains stable over the course of a day. Since no antimony is used, the analytical wavelength is 820 nm and it is necessary to heat to 55-60 degrees C.

Do not add SDS to these reagents, as it is incompatible with the hydrazine reagent. Do not add Brij-35 to the reagents as it interferes with the reaction. The Ultrawet 60 L and aerosol 22 were chosen as wetting agents because they were effective, compatible with the reagents, and commercially available.

To depress the interference of silicate, the final reaction pH must be less than 1. Interference with silicate can be detected from the standard analyses.

Quality Control Program

In order to insure accuracy of these nutrient data, the following quality control procedures have been implemented.

- Blanks are run for all analysis by adding all reagents to deionized water in order to calculate amount of absorbance due to the reagents themselves.
- A calibration curve is also run for all analysis. Five to six known standards are made in a range to bracket the expected range of concentrations of the samples during that month. A graph of absorption vs concentration is created and is redone if the r^2 is below 0.995.
- As previously noted one field replicate is collected sequentially in the field at the same time and place. These are analyzed as separate samples to assess the variability of the station being sampled.
- Laboratory replicates are also conducted in which sub-samples are taken from the same sample bottle in order to assess the variability in the laboratory method. 10% of the samples are duplicated in the laboratory.
- Absorption replicates of standards are also performed in order to assess the drift over time of the spectrophotometer in the duration of reading all the samples. A drift correction is applied only if drift is greater than 5%.
- Standard reference materials are also diluted to a concentration within the standard curve being used and analyzed in order to quality control sample preparation process and verify calibration curve.
- Matrix spikes are performed by adding 100 µl of diluted standard reference material to the sample. Spikes are added to samples that total concentration will not exceed the highest standard concentration in the standard curve. A new calibration curve is done if spike recovery is less than 90% or greater than 110%. 10% of the samples are spiked in the laboratory each month.

REFERENCES:

Sakamoto C, Friederich G, Codispoti L. 1990. MBARI Procedures for Automated Nutrient Analysis Using a Modified Alpkem 300 Rapid Flow Analyer. MBARI Technical Report #90-2.

Shennan Laboratory at the University of California, Santa Cruz's Standard Operating Procedures for Nitrate Analysis

STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF NITRATE/NITRITE BY FLOW INJECTION ANALYSIS

By Kristy Morris, Shennan Lab, Environmental Studies Department, UCSC.

1.0 SCOPE AND APPLICATION

1.1 This method provides a procedure for the determination of nitrate/nitrite in surface or wastewater

1.2 This method is modified from the US APHA Standard Methods for the Examination of Water and Wastewater, 20th Edition, Proposed Method 4500-NO_3^- Cadmium Reduction Flow Injection Method and the EPA approved QuikChem® Method 10-107-04-1-J

2.0 SUMMARY OF METHOD

2.1 Nitrate is quantitatively reduced to nitrite by passage of the sample through a copperized cadmium column. The nitrite (reduced nitrate plus original nitrite) is then determined by diazotizing with sulfanilamide followed by coupling with N-(1-naphthyl)ethylenediamine dihydrochloride. The resulting water soluble dye has a magenta color which is read at 520 nm. Nitrite alone also can be determined by removing the cadmium column.

2.2 The measuring range of the method is 0.1 – 10.0 mg N/L and the detection limit is 0.012 mg N/L

3.0 DEFINITIONS

3.1 Stock Standard Solution (SSS)- A solution prepared in the laboratory using reference materials purchased from a reputable commercial source.

3.2 Laboratory reagent blank (LRB)- An aliquot of reagent water (Milli-Q) or other blank matrices that are treated exactly the same as the sample including exposure to all glassware, equipment, solvents, reagents, internal standards and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, reagents or apparatus.

3.3 Field duplicates- Two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Provide measure of the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.

3.4 Quality Control Sample (QCs) - It is a solution of known concentration obtained from a source external to the laboratory to check laboratory performance.

3.5 Matrix Spike samples- Matrix spike samples are samples to which known quantities of a solution with one or more well-established analyte concentrations have been added. These samples are analyzed to determine the extent of matrix interference or degradation on the analyte concentration during sample processing and analysis.

4.0 INTERFERENCES

4.1 Residual chlorine can interfere by oxidizing the cadmium column.

4.2 Low results would be obtained for samples that contain high concentrations of iron, copper, or other metals. In this method, EDTA is added to the buffer to reduce this interference.

4.3 Samples that contain large concentrations oil and grease will coat the surface of the cadmium. This interference is eliminated by pre-extracting the sample with an organic solvent.

4.4 Sample turbidity may interfere. Turbidity can be removed by filtration through a 0.45 µm pore diameter membrane filter prior to analysis.

5.0 HEALTH AND SAFETY

5.1 Lab safety- Safety glasses are required for all laboratory analysis. Use gloves to avoid skin irritation from contact with reagents and work under the fume hood when possible (See section 9.3-NH_4Cl buffer preparation). Please refer to the Material Data Safety Sheets (MSDS) file for any other information about personnel protective equipment and other safety considerations. In particular, the following chemicals

have the potential to be highly toxic or hazardous, for detailed explanation consult the MSDS.

5.1.1 Sodium Hydroxide

5.1.2 Hydrochloric acid

5.1.3 Ammonium hydroxide

5.1.4 Phosphoric acid

5.1.5 Sulfanilamide

5.1.6 N-(1-naphthyl)ethylenediamine dihydrochloride (NED)

5.1.7 Chloroform Sodium nitrite

5.1.8 Cadmium

5.2 Chemical hygiene- Hazards of the chemicals used in this method were discussed in the previous section. Please refer to the MSDS file for any further questions concerning a chemical's toxicity and the necessary safety precautions.

5.3 Waste Disposal-Excess reagents, samples and method process wastes should be characterized and disposed of in an acceptable manner and in accordance with the UCSC EHS hazardous waste identification checklist. Laboratory analysts should consult the Laboratory Manager before disposing of potentially hazardous wastes.

6.0 PERSONNEL/ TRAINING/ RESPONSIBILITIES

6.1 General Responsibilities- This method is restricted to use by or under the supervision of the analyst experienced in the method. Each analyst must be trained and able to read and understand the SOP.

6.2 Laboratory analysts: it is the responsibility of analysts/technicians to;

6.2.1 Read and understand the SOP and follow it as written.

6.2.2 Produce quality data the meets all of the laboratory requirements.

6.2.3 Complete the required demonstration of proficiency before performing this procedure without supervision

6.2.4 Repeat the required initial demonstration of proficiency each time a modification is made to the method.

6.3 Laboratory managers: it is the responsibility of the laboratory manager to:

6.3.1 Ensure that all analysts have the technical ability and have the adequate training required to perform this procedure.

6.3.2 Ensure that all analysts have completed the required demonstration of proficiency before performing this procedure without supervision.

6.3.3 Produce quality data that meets all laboratory requirements.

7.0 RELATED DOCUMENTS

7.1 SOP for the handling of hazardous materials

7.2 SOP for preparing Standards and QCs

8.0 APPARATUS AND MATERIALS

8.1 Balance- analytical, capable of accurately weighing to the nearest 0.0001g

8.2 Glassware- Class A volumetric flasks and pipettes as required. Samples may be stored in plastic or glass

8.3 Flow injection analysis equipment designed to deliver and react sample and reagents in the required order ratios.

8.3.1 Sampler

8.3.2 Multichannel proportioning pump

8.3.3 FIA Manifold

8.3.4 Absorbance detector

8.3.5 Data acquisition system

8.4 Millipore Cadmium-Copper reduction Column

9.0 REAGENTS AND STANDARDS

9.1 Deionized water (Milli-Q) for the preparation of all solutions

9.2 15N NaOH solution- In a 250 mL volumetric flask, add 150 g NaOH very slowly to 200mL deionized water. Stir until dissolved and dilute to volume. Cool and store in a plastic bottle.

9.3 NH_4Cl buffer, pH 8.5- In a 1L volumetric flask, dissolve 85.0g NH_4CL and 1.0g $Na_2EDTA \cdot 2H_2O$ in about 800 ml of deionized water (Milli-Q). Adjust to a pH 8.5 with 15N NaOH solution (section 9.2) **CAUTION: Fumes! USE THE HOOD**

9.4 Sulfanilamide color reagent- In a 1L volumetric flask add approximately 600mL DI water (Milli-Q). Then add 100ml H_3PO_4, 40.0 g sulfanilamide and 2.0g NED (N-(1-napthyl) ethylenediamine dihydrochloride). Shake to wet and stir to dissolve for 30 minutes. Dilute to the mark and invert to mix. Store in a dark bottle. This solution is stable for one month.

9.5 Matrix spike solution- A combined Matrix spike solution is prepared from 1000 mg/L stock standard solutions of each of the following analytes: NO_3^-, PO_4^{-3}, NH_4^+ to provide the following concentrations in the final solution: 100mg/L NH_4^+, 100mg/L PO_4^{-3} and 250 mg/L NO_3.

9.6 Matrix Spike sample –add 200uL of Matrix spike solution prepared in Section 9.5 to 50mL of sample (This will add 0.996 mg/L NO_3^- to the sample).

10.0 SAMPLE COLLECTION. PRESERVATION AND STORAGE

10.1 Collect a minimum 100 mL grab sample. Use sample bottles that have been cleaned in phosphate free detergent and acid rinsed. Rinse sample bottle and cap in sample 3 times prior to taking the sample. Insert the sample bottle just below the water surface with the mouth of the bottle facing upstream and fill bottle taking caution not to disturb the bottom sediment. If analysis can be made within 24 hours, the sample should be filtered through a 45um syringe filter and preserved in the refrigerator. When samples must be stored for more than 24 hours, they should be preserved with sulfuric acid (2 mL 5.6M H_2SO_4 per Liter). **Caution:** Samples must not be preserved with mercuric chloride or thiosulfate because this will degrade the cadmium column.

11.0 PROCEDURE

11.1 Prepare reagents as per Section 9.0. Prepare Standard and Quality Control Solutions as per SOP for preparing Standards and QCs. QCs are prepared with the following NO_3^- concentrations:

QC1 = 0.5 mg/L

QC2 = 7.5 mg/L

QC 3 =10mg/L

11.2 Follow procedures outline in Operating the Lachat Autoanalyser document.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Calibration is done by injecting standards. The data system will then prepare a calibration curve by plotting response versus standard concentration. Sample concentration is calculated from the regression equation

12.2 Report only those values that fall between the lowest and highest calibration standards. Samples exceeding the highest standard should be diluted and reanalyzed.

12.3 Report results in mg N/L as NO_3^-

13.0 QC/ QA CRITERIA

13.1 An LRB is performed at the beginning and end of each run or for 5% of samples, whichever is more frequent. The LRB should be less than the detection limit for this method (DL = 0.114 mg/L).

13.2 QCs are performed at the beginning and end of each run or for 5% of samples, whichever is more frequent. QC samples should be within ± 10% of the known value.

13.3 The RSD of the replicate measurements should be within ± 15%.

13.4 A set of duplicate samples are analyzed for each run and duplicate measurements should be within ± 15%.

13.5 A set of field duplicate samples are analyzed for each run and duplicate measurements should be within ± 15%.

13.6 A matrix spike solution is performed for every run and the percent recovery of the matrix spike should be 100± 15%.

The cadmium column efficiency should be determined as least weekly. Before running samples or after a stopped run:

1. Calibrate with nitrate standards
2. Run a known concentration of nitrite (NO_2) standard as N.
3. Run a matching concentration of NO_3 as N.

The column efficiency can be determined by the equation: $E = \frac{[NO_3]}{[NO_2]} \times 100$

Where: E= column efficiency

$[NO_3]$ = concentration of nitrate standard
$[NO_2]$ = concentration of nitrite standard

If the efficiency is less than 90% the column should be replaced

Shennan Laboratory at the University of California, Santa Cruz's Standard Operating Procedures for Phosphate Analysis

STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF DISSOLVED ORTHOPHOSPHATE BY FLOW INJECTION ANALYSIS

By Kristy Morris, Shennan Lab, Environmental Studies Department, UCSC.

14.0 SCOPE AND APPLICATION

14.1 This method provides a procedure for the determination of orthophosphate in drinking, ground and surface waters, and domestic and industrial wastes. In this method the sample is filtered through a 0.45 um pore size filter, therefore the result is termed dissolved orthophosphate.

14.2 The method is based on reactions that are specific for the orthophosphate (PO_4^{3-}) ion.

14.3 This method is modified from the US APHA Standard Methods for the Examination of Water and Wastewater, 20th Edition, Proposed Method 4500-P G.- Flow Injection Analysis of Orthophosphate and the EPA approved QuikChem® Method 10-115-01-1-P

15.0 SUMMARY OF METHOD

15.1 The orthophosphate (PO_4^{3-}) ion reacts with ammonium molybdate and antimony potassium tartrate under acidic conditions to form a complex. This complex is reduced with ascorbic acid to form a blue complex that absorbs light at 880 nm. The absorbance is proportional to the concentration of the orthophosphate in the sample.

16.0 DEFINITIONS

16.1 Stock Standard Solution (SSS)- A solution prepared in the laboratory using reference materials purchased from a reputable commercial source.

16.2 Laboratory reagent blank (LRB)- An aliquot of reagent water (Milli-Q) or other blank matrices that are treated exactly the same as the sample including exposure to all glassware, equipment, solvents, reagents, internal standards and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, reagents or apparatus.

16.3 Field duplicates- Two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory

procedures. Provide measure of the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.

16.4 Quality Control Sample (QCs) - It is a solution of known concentration obtained from a source external to the laboratory to check laboratory performance.

16.5 Matrix Spike samples- Matrix spike samples are samples to which known quantities of a solution with one or more well-established analyte concentrations have been added. These samples are analyzed to determine the extent of matrix interference or degradation on the analyte concentration during sample processing and analysis.

17.0 INTERFERENCES

17.1 Guard against contamination from reagents, water, glassware, and the sample preservation process. Glassware contamination is a problem in low-level phosphorus determinations-use phosphate free detergents.

17.2 Silica forms a pale blue complex that also absorbs at 880nm. This interference is generally insignificant as a silicate concentration of approximately 30mg SiO_2 /L would be required to produce a 0.005 mg P/L positive error in orthophosphate.

17.3 Concentrations of ferric ion greater than 60 mg/L cause a negative error due to competition with the complex for the reducing agent ascorbic acid. Treat samples high in iron with sodium bisulfite to eliminate this interference, as well as the interference due to arsenates.

17.4 Sample turbidity may interfere. Turbidity can be removed by filtration through a 0.45 µm pore diameter membrane filter prior to analysis.

18.0 HEALTH AND SAFETY

18.1 Lab safety- Safety glasses are required for all laboratory analysis. Use gloves to avoid skin irritation from contact with reagents and work under the fume hood when possible. Please refer to the Material Data Safety Sheets (MSDS) file for any other information about personnel protective equipment and other safety considerations. In

particular, the following chemicals have the potential to be highly toxic or hazardous, for detailed explanation consult the MSDS.

18.1.1 Sulfuric acid

18.2 Chemical hygiene- Hazards of the chemicals used in this method were discussed in the previous section. Please refer to the MSDS file for any further questions concerning a chemical's toxicity and the necessary safety precautions.

18.3 Waste Disposal-Excess reagents, samples and method process wastes should be characterized and disposed of in an acceptable manner and in accordance with the UCSC EHS hazardous waste identification checklist. Laboratory analysts should consult the Laboratory Manager before disposing of potentially hazardous wastes.

19.0 PERSONNEL/ TRAINING/ RESPONSIBILITIES

19.1 General Responsibilities- This method is restricted to use by or under the supervision of the analyst experienced in the method. Each analyst must be trained and able to read and understand the SOP.

19.2 Laboratory analysts: it is the responsibility of analysts/technicians to;

19.2.1 Read and understand the SOP and follow it as written.

19.2.2 Produce quality data the meets all of the laboratory requirements.

19.2.3 Complete the required demonstration of proficiency before performing this procedure without supervision

19.2.4 Repeat the required initial demonstration of proficiency each time a modification is made to the method.

19.3 Laboratory managers: it is the responsibility of the laboratory manager to:

19.3.1 Ensure that all analysts have the technical ability and have the adequate training required to perform this procedure.

19.3.2 Ensure that all analysts have completed the required demonstration of proficiency before performing this procedure without supervision.

19.3.3 Produce quality data that meets all laboratory requirements.

20.0 RELATED DOCUMENTS

20.1 SOP for the handling of hazardous materials

20.2 SOP for preparing Standards and QCs

21.0 APPARATUS AND MATERIALS

21.1 Balance- analytical, capable of accurately weighing to the nearest 0.0001g

21.2 Glassware- Class A volumetric flasks and pipettes as required. Samples may be stored in plastic or glass

21.3 Flow injection analysis equipment designed to deliver and react sample and reagents in the required order ratios.

21.3.1 Sampler

21.3.2 Multichannel proportioning pump

21.3.3 FIA Manifold

21.3.4 Absorbance detector

21.3.5 Data acquisition system

22.0 REAGENTS AND STANDARDS

22.1 Deionized water (Milli-Q) for the preparation of all solutions. To prevent bubble formation, degas carrier and buffer with helium for 1 minute.

22.2 Stock Ammonium Molybdate Solution- In a 1L volumetric flask, dissolve 40.0g ammonium molybdate tetrahydrate [$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$] in 800 mL DI(Milli-Q) water. Dilute to mark and stir for a minimum of four hours. Store in plastic and refrigerate. May be stored up to two months when refrigerated.

22.3 Stock antimony potassium tartrate solution- In a 1L volumetric flask, dissolve 3.0 g antimony potassium tartrate (potassium antimonyl tartrate hemihydrate $K(SbO)C_4H_4O_6\cdot H_2O$) in approxikmately 800 mL of water. Mix with a magnetic stirrer until dissolved and dilute to the mark. Store in a dark bottle and refrigerate. May be stored up to two months when refrigerated.

22.4 Molybdate color reagent- In a 1L volumetric flask, add approximately 500mL of DI water, then add 35.0 mL of concentrated sulfuric acid H_2SO_4 (**CAUTION: The solution will get very hot).** Swirl to mix. When it can bbe comfortably handled add 72.0 mL of stock antimony potassium tartrate solution (Section 9.3) and 213 mL

Stock Ammonium Molybdate Solution (Section 9.2). Dilute to mark and invert three times. Degas with heliumj. Prepare fresh weekly.

22.5 Ascorbic acid reducing solution, 0.33M- In a 1L volumetric flask dissolve 60.0 g granular ascorbic acid in approximately 700mL of DI (Milli-Q) water. Dilute to the mark and invert to mix. Add 1.0g dodecyl sulfate, sodium salt ($CH_3(CH_2)_{11}OSO_3Na$). Prepare fresh weekly. Discard if the solution becomes yellow. Do not use ascorbic acid powder.

22.6 NaOH-EDTA manifold rinse-Dissolve 65.0 g NaOH and 6.0 g Na_2EDTA in 1.0L

22.7 Matrix spike solution- A combined Matrix spike solution is prepared from 1000 mg/L stock standard solutions of each of the following analytes: NO_3^-, PO_4^{-3}, NH_4^+ to provide the following concentrations in the final solution: 100mg/L NH_4^+, 100mg/L PO_4^{-3} and 250 mg/L NO_3.

22.8 Matrix Spike sample –add 200uL of Matrix spike solution prepared in Section 9.7 to 50mL of sample (This will add 0.398 mg/L PO_4^{3-} to the sample).

23.0 SAMPLE COLLECTION. PRESERVATION AND STORAGE

23.1 Sample should be filtered through a 45um syringe filter immediately upon collection and samples must be refrigerated and analyzed within 48 hours.

24.0 PROCEDURE

24.1 Prepare reagents as per Section 9.0. Prepare Standard and Quality Control Solutions as per SOP for preparing Standards and QCs.

24.2 Calibration Standards are prepared in the following concentrations:

4 mg P/L , 2 mg P/L, 1 mg P/L, 0.5 mg P/L, 0 mg P/L.

24.3 QCs are prepared with the following PO_4^{3-} concentrations:

QC1 = 0.1 mg/L, QC2 =0.5 mg/L, QC 3 =1.5mg/L

24.4 Follow procedures outline in Operating the Lachat Autoanalyser document.

25.0 DATA ANALYSIS AND CALCULATIONS

25.1 Calibration is done by injecting standards. The data system will then prepare a calibration curve by plotting response versus standard concentration. Sample concentration is calculated from the regression equation

25.2 Report only those values that fall between the lowest and highest calibration standards. Samples exceeding the highest standard should be diluted and reanalyzed.

25.3 Report results in mg P/L.

26.0 QC/ QA CRITERIA

26.1 An LRB is performed at the beginning and end of each run or for 5% of samples, whichever is more frequent. The LRB should be less than the detection limit for this method (DL = 0.67ug P/L)[1].

26.2 QCs are performed at the beginning and end of each run or for 5% of samples, whichever is more frequent. QC samples should be within ± 10% of the known value.

26.3 The RSD of the replicate measurements should be within ± 15%.

26.4 A set of duplicate samples are analyzed for each run and duplicate measurements should be within ± 15%.

26.5 A set of field duplicate samples are analyzed for each run and duplicate measurements should be within ± 15%.

26.6 A matrix spike solution is performed for every run and the percent recovery of the matrix spike should be 100± 15%.

[1] APHA Standard Methods for the Examination of Water and Wastewater, 20th ed., p.4-149- 4-150, Method 4500 P G.

Shennan Laboratory at the University of California, Santa Cruz's Standard Operating Procedures for Ammonia Analysis

STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF DISSOLVED AMMONIA BY FLOW INJECTION ANALYSIS

By Kristy Morris, Shennan Lab, Environmental Studies Department, UCSC.

27.0 SCOPE AND APPLICATION

27.1 This method provides a procedure for the determination of ammonia in surface waters, and domestic and industrial wastes. In this method the sample is filtered through a 0.45 um pore size filter.

27.2 The method is based on reactions that are specific for ammonia ion.

27.3 This method is modified from the EPA approved QuikChem® Method 10-107-06-3-B

28.0 SUMMARY OF METHOD

28.1.1 Ammonia in the sample reacts with hypochlorite ions which are generated in situ by alkaline hydrolysis of sodium dicholorisocyanurate. This reaction forms monochloramine which then reacts with salicylate ions in the presence of sodium nitroprusside to form a blue, indophenol-type compound, measured colorimetrically at 660nm.

29.0 DEFINITIONS

29.1 Stock Standard Solution (SSS)- A solution prepared in the laboratory using reference materials purchased from a reputable commercial source.

29.2 Laboratory reagent blank (LRB)- An aliquot of reagent water (Milli-Q) or other blank matrices that are treated exactly the same as the sample including exposure to all glassware, equipment, solvents, reagents, internal standards and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, reagents or apparatus.

29.3 Field duplicates- Two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Provide measure of the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.

29.4 Quality Control Sample (QCs) - It is a solution of known concentration obtained from a source external to the laboratory to check laboratory performance.

29.5 Matrix Spike samples- Matrix spike samples are samples to which known quantities of a solution with one or more well-established analyte concentrations have been added. These samples are analyzed to determine the extent of matrix interference or degradation on the analyte concentration during sample processing and analysis.

30.0 INTERFERENCES

30.1 Magnesium interferes by forming a precipitate of magnesium hydroxide at the high pH values (>12) required for full color development. Trisodium citrate is used as a complexing agent to prevent this interference. At the concentration of trisodium citrate specified, the method will tolerate magnesium at concentrations normally encountered in most non-saline waters. The tolerance of the chemistry to magnesium can be increased, to deal with partially saline waters, by increasing the concentration of trisodium citrate in the reagents (up to the limit of solubility, which is 390 g/L)

31.0 HEALTH AND SAFETY

31.1 Lab safety- Safety glasses are required for all laboratory analysis. Use gloves to avoid skin irritation from contact with reagents and work under the fume hood when possible. Please refer to the Material Data Safety Sheets (MSDS) file for any other information about personnel protective equipment and other safety considerations. In particular, the following chemicals have the potential to be highly toxic or hazardous, for detailed explanation consult the MSDS.

31.1.1 Sodium hydroxide

31.2 Chemical hygiene- Hazards of the chemicals used in this method were discussed in the previous section. Please refer to the MSDS file for any further questions concerning a chemical’s toxicity and the necessary safety precautions.

31.3 Waste Disposal-Excess reagents, samples and method process wastes should be characterized and disposed of in an acceptable manner and in accordance with the UCSC EHS hazardous waste identification checklist. Laboratory analysts should consult the Laboratory Manager before disposing of potentially hazardous wastes.

32.0 PERSONNEL/ TRAINING/ RESPONSIBILITIES

32.1 General Responsibilities- This method is restricted to use by or under the supervision of the analyst experienced in the method. Each analyst must be trained and able to read and understand the SOP.

32.2 Laboratory analysts: it is the responsibility of analysts/technicians to;

- 32.2.1 Read and understand the SOP and follow it as written.
- 32.2.2 Produce quality data the meets all of the laboratory requirements.
- 32.2.3 Complete the required demonstration of proficiency before performing this procedure without supervision
- 32.2.4 Repeat the required initial demonstration of proficiency each time a modification is made to the method.

32.3 Laboratory managers: it is the responsibility of the laboratory manager to:

- 32.3.1 Ensure that all analysts have the technical ability and have the adequate training required to perform this procedure.
- 32.3.2 Ensure that all analysts have completed the required demonstration of proficiency before performing this procedure without supervision.
- 32.3.3 Produce quality data that meets all laboratory requirements.

33.0 RELATED DOCUMENTS

33.1 SOP for the handling of hazardous materials

33.2 SOP for preparing Standards and QCs

34.0 APPARATUS AND MATERIALS

34.1 Balance- analytical, capable of accurately weighing to the nearest 0.0001g

34.2 Glassware- Class A volumetric flasks and pipettes as required. Samples may be stored in plastic or glass

34.3 Flow injection analysis equipment designed to deliver and react sample and reagents in the required order ratios.

- 34.3.1 Sampler
- 34.3.2 Multichannel proportioning pump

34.3.3 FIA Manifold

34.3.4 Absorbance detector

34.3.5 Data acquisition system

35.0 REAGENTS AND STANDARDS

35.1 Deionized water (Milli-Q) for the preparation of all solutions. To prevent bubble formation, degas carrier and buffer with helium for 1 minute.

35.2 Salicylate/ Citrate Mixed reagent- In a 1L volumetric flask, dissolve 34.0g sodium salicylate [salicylic acid, sodium salt, 2-$(HO)C_6H_4CO_2Na$] and 40.0 g trisodium citrate [sodium citrate, $C_6H_5Na_3O_7$] in approximately 700 mL of water. Then add 0.400g sodium nitroprusside [$Na_2Fe(CN)_5NO{\cdot}2H_2O$]. Stir to dissolve and dilute to mark with DI water. Transfer to an amber glass bottle. This reagent is stable for 2 weeks.

35.3 Sodium Dichloroisocyanurate (D.C.I.C)- In a 1L volumetric flask, dissolve 10.0 g sodium hydroxide (NaOH) in approxikmately 500 mL of water. Cool the solution to room temperature then add 0.80g sodium dichloroisocyanurate (D.C.I.C) [dichloro-triazine 2,4,6, (1H,3H,H)-trione sodium salt] to the solution. Mix with a magnetic stirrer until dissolved and dilute to the mark with DI water. Store in a dark bottle and refrigerate. Prepare fresh weekly.

35.4 Matrix spike solution- A combined Matrix spike solution is prepared from 1000 mg/L stock standard solutions of each of the following analytes: NO_3^-, PO_4^{-3}, NH_4^+ to provide the following concentrations in the final solution: 100mg/L NH_4^+, 100mg/L PO_4^{-3} and 250 mg/L NO_3.

35.5 Matrix Spike sample –add 200uL of Matrix spike solution prepared in Section 9.7 to 50mL of sample (This will add 0.398 mg/L NH_4^+ the sample).

36.0 SAMPLE COLLECTION. PRESERVATION AND STORAGE

36.1 Ammonia is volatile and will leave the sample slowly, even through polyethylene bottles. The samples should be stored on ice on return to the laboratory, refrigerated and analyzed within 24 hours. If this cannot be done, they should be frozen

unacidified for up to 28 days. If even this cannot be done the samples should be adjusted to a pH of 2 with sulfuric acid and refrigerated.

37.0 PROCEDURE

37.1 Prepare reagents as per Section 9.0. Prepare Standard and Quality Control Solutions as per SOP for preparing Standards and QCs.

37.2 Calibration Standards are prepared in the following concentrations:

2 mg P/L , 1 mg P/L, 0.5 mg P/L, 0.25 mg P/L, 0 mg P/L.

37.3 QCs are prepared with the following PO_4^{3-} concentrations:

QC1 = 0.1 mg/L, QC2 =0.5 mg/L, QC 3 =1.5mg/L

37.4 Follow procedures outline in Operating the Lachat Autoanalyser document.

38.0 DATA ANALYSIS AND CALCULATIONS

38.1 Calibration is done by injecting standards. The data system will then prepare a calibration curve by plotting response versus standard concentration. Sample concentration is calculated from the regression equation

38.2 Report only those values that fall between the lowest and highest calibration standards. Samples exceeding the highest standard should be diluted and reanalyzed.

38.3 Report results in mg N/L

39.0 QC/ QA CRITERIA

39.1 An LRB is performed at the beginning and end of each run or for 5% of samples, whichever is more frequent. The LRB should be less than the detection limit for this method (DL = 0.008 mg N/L as NH_4)

39.2 QCs are performed at the beginning and end of each run or for 5% of samples, whichever is more frequent. QC samples should be within ± 10% of the known value.

39.3 The RSD of the replicate measurements should be within ± 15%.

39.4 A set of duplicate samples are analyzed for each run and duplicate measurements should be within ± 15%.

39.5 A set of field duplicate samples are analyzed for each run and duplicate measurements should be within ± 15%.

39.6 A matrix spike solution is performed for every run and the percent recovery of the matrix spike should be 100± 15%.

Appendix II: Other ESNERR Forms

ESNERR Training Log

Monthly Water Quality Monitoring Program

Name of Trainee	Date	Scope of Training (circle all applicable)	Type of Training (circle one)	Satisfactory Completion? (circle one)	Instructor's Signature
		Water Sampling Field Measurements Equipment Calibration Laboratory Analyses	Initial Refresher	Yes No	
		Water Sampling Field Measurements Equipment Calibration Laboratory Analyses	Initial Refresher	Yes No	
		Water Sampling Field Measurements Equipment Calibration Laboratory Analyses	Initial Refresher	Yes No	
		Water Sampling Field Measurements Equipment Calibration Laboratory Analyses	Initial Refresher	Yes No	
		Water Sampling Field Measurements Equipment Calibration Laboratory Analyses	Initial Refresher	Yes No	
		Water Sampling Field Measurements Equipment Calibration Laboratory Analyses	Initial Refresher	Yes No	

Updated 09/22/2005

ESNERR Database Modification Log
Monthly Water Quality Monitoring Program

File Name	Staff Initials	Date	Tasks

Updated 10/11/2005

ESNERR Data Verification Checklist
Monthly Water Quality Monitoring Program

Records checked for completeness, correctness, and conformance/compliance

Date of Sampling Event:

Record	Verified	Verified with Corrections or Qualifications	Not Verified	Not Applicable	Comments
Field Data Collection Form					
Calibration Log					
Equipment Repair Log					
Chain-of-Custody Form					
Field Data Results					
Temperature					
Conductivity					
Salinity					
DO%					
DO mg/L					
pH					
Turbidity					
Chlorophyll a					
Laboratory Results					
Ammonia					
Nitrate					
Phosphate					
Laboratory QC Data					
Laboratory Blanks					
Standard Reference Materials (SRMs)					
Laboratory Duplicate					
Field Replicates					
Field Blanks					
Matrix Spikes					
Matrix Spike Replicates					
Inter-laboratory Exercises					

Verified by: **Date:**

Updated 03/15/2006

Appendix III: QA/QC Manuals

Quality Assurance/Quality Control Manual for Monterey County Consolidated Chemistry Laboratory

TABLE OF CONTENTS

ORGANIZATION AND RESPONSIBILITY

On October 11, 1988, the Monterey County Board of Supervisors, in Resolution No. 88-508, authorized the Director of the County Health Department and the General Manager of Monterey County Flood Control and Water Conservation District (MCFC&WCD) to consolidate laboratory services for their respective programs into one facility. A Laboratory Steering Committee, comprised of representatives from both agencies, was established for the purpose of providing the planning, operation, and future development of the Consolidated Environmental Laboratory.

Each year the Steering Committee develops a Memorandum of Agreement (MOA) that describes and confirms the services to be provided by the Health Department to the Water Resources Agency (formerly the Flood Control and Water Conservation District) and defines the responsibilities of each party. In addition to providing laboratory support for the Health Department and the Water Resources Agency, the Consolidated Chemistry Laboratory provides analytical services to the Monterey Regional Water Pollution Control District, the County Department of Public Works and numerous water supply systems and wastewater treatment facilities.

The Consolidated Environmental Laboratory is accredited by the State Department of to perform tests in the following fields: 1) microbiology of drinking water and waste water; 2) inorganic chemistry and physical properties of drinking water; 3) analysis of toxic chemical elements in drinking water; 4) wastewater inorganic chemistry, nutrients and demand; and 5) toxic chemical elements in wastewater. A list of analyses and methods used in the laboratory is included in Appendix A.

The following is a brief description of the staff support for the Consolidated Chemistry Laboratory:

1. Director - Plans, organizes and controls laboratory operations. Coordinates laboratory interactions with other programs in the Health Department. Administers laboratory budget, billing and purchasing. Develops laboratory policy and procedures and supervises staff.

2. Public Health Chemist - Principal analyst. Performs complex organic and inorganic chemical analysis, evaluates and implements laboratory methods, develops and maintains quality assurance, reports results and maintains records, purchases equipment and supplies, provides technical consultation to Environmental Health and Water Resources Agency. Trains analysts and documents competency

3. Water Quality Specialist- Performs broad range of professional scientific work related to water quality and environmental issues; is proficient in performing water quality analyses and managing the laboratory water quality database. Interpret and explain regulatory guidelines to clients.

4. Public Health Microbiologists - Assist Public Health Chemist in performing environmental analyses and providing oversight of quality assurance.

5. Laboratory Assistant - Prepares culture media and reagents, assists in the processing of specimens, performs low to moderately complex environmental analyses and clinical analyses where interpretation or medical judgment is not required.

6. Laboratory Helper - Washes and sterilizes glassware and supplies. Prepares and labels mailing containers and specimen collection kits. Accession laboratory specimens. Sterilizes and disposes infectious waste. Maintains stockroom.

7. Typist-Clerk II - Enters clients and laboratory results into computer. Prints reports/forms. Prepares billing statements; receives and accounts for payments. Distributes laboratory results, and maintains laboratory files.

QUALITY ASSURANCE OJECTIVES FOR MEASUREMENT OF DATA

Quality Assurance (QA) includes all aspects of laboratory operation that affect the accuracy and reliability of sample test results. In addition to quality control of the analytical test process, quality assurance practices include: 1) proper sample collection, receiving and holding, 2) proper maintenance of equipment, 3) accurate data reduction, validation and reporting; and, 4) periodic performance and systems audits.

CUSTODY, HOLDING AND DISPOSAL OF SAMPLES

Quality assurance includes proper labeling of samples, proper completion of the chain of custody/analysis request form, proper collection, preservation and storage of samples, proper accessioning of samples, and proper disposal of the sample.

1) Sample Collection/Labeling. Sample collection is a coordinated effort between the client and the laboratory. The laboratory will provide clients with appropriate sample containers and sample collection/ preservation instructions. The laboratory will also request duplicates and blanks according to client's sample plan requirements. All samples submitted for testing should be appropriately labeled. Sample containers provided by our laboratory have a suitable label which should be filled out at the time of sampling by the sample collector. The following information must be provided with all samples:

a) Sample identification - submitters identification of sample (e.g. well number)

b) Location - an address or brief description of the place the sample was taken.

c) Time and date taken.

d) Name of sample collector.

e) Any preservatives

2) Chain of Custody/Analysis Request Form. A Chain of Custody / Analysis Request form should accompany all samples (see Appendix B). The Chain of Custody / Analysis Request form must include the following information: submitter name and address; sample identification; location of sample collection; date & time of collection; sample type; analysis to be performed; signatures of persons involved in the collection and chain of possession; and inclusive dates of possession.

3) Sample Receiving. Laboratory personnel receiving samples should assure that samples are properly collected, labeled, and the Custody/Analysis Request form has been completed:

a) The laboratory assistant receiving the specimen must sign and date the Custody / Analysis Request form. Make sure that any special requests made by the client are recorded under the comments section of the form

b) Assign each sample a unique laboratory identification number. Place preprinted lab number on analysis request form and sample container.

c) Check that the samples meet the criteria described in Table 1006:1 Summary of Special Sampling or Handling Requirements in 18th ed. Of Standard Methods for the Examination of Water and Wastewater (Appendix C)

i) Samples should be collected in a suitable container; samples collected in bottles of unknown origin or questionable cleanliness should be brought to the attention of the Water Quality Specialist or the Public Health Chemist.

ii) Samples should be adequately labeled.

iii) Samples should be checked for proper preservative, holding time, and holding temperature.

iv) Samples should be adequately sealed. Notify public health chemist if there is evidence of leakage. Verify that adequate sample volume exists to perform requested analysis.

d) NOTE: Samples that are not properly identified or are otherwise unsuitable for testing (e.g. improperly preserved or exceeding holding/transport time) are recorded on the "Sample Invalidation Log" and the Water Quality Specialist or Public Health Chemist notifies the client. Samples not meeting collection/preservation criteria may be tested only if resampling is impossible; results from such samples must be qualified on the laboratory report by comments describing sample deficiency.

4) When the sample meets criteria for acceptance by the laboratory, required preservatives are added immediately and the sample is stored under conditions specified by the analytical method to be used. For samples requiring thermal preservation, a laboratory refrigerator and freezer is available. The temperature is maintained at 4 degrees and below -10°C respectively. Temperatures are monitored each day.

5) Chain of Custody/Analysis Request forms are given to the clerk to enter into a password protected computer laboratory information management system. Refer to "Water Sample Entry" in Clerical Manual for instructions on sample log-in.

6) Disposal of samples: Upon completion of all analyses, any remaining sample will be stored

for at least one month prior to disposal. Chain-of-Custody form, worksheets and lab reports are retained for five years.
NOTE: Longer retention of samples or data may be required when legal action is probable. The samples and any associated extracts or digests are disposed of following recommendations found in the book, Prudent Practices for Disposal of Chemicals from Laboratories, National Academy Press, Washington, D.C. 1983.

CALIBRATION PROCEDURES AND FREQUENCY

Calibration is the process for determining the correctness of the assigned values of the physical standards used or the scales of the measuring instruments. Calibration accuracy is critically dependent on the reliability of the standards used for the required comparisons. Only the highest quality chemicals are used to provide necessary standard solutions, and due care is exercised in their preparation. The concentrations of the calibration standards bracket the expected concentration of the analyte in the samples. No data is reported beyond the range of calibration of the methodology. The calibration data, when plotted graphically, is referred to as a calibration curve. The calibration must be done under the same instrumental and chemical conditions as those that will exist during the measurement process. The frequency of calibration depends on the accuracy requirements of the investigation and the stability of the instrument used for the measurements:

At a minimum, three different dilutions of the standard will be measured when an analysis is initiated. Correlation coefficient must be > 0.995. Reportable analytical results are those within the range of the standard dilutions used. Do not report values above the highest standard. The lowest reportable value is the Method Detection Limit (MDL), providing that the lowest calibration standard is less than 10 times the MDL.

1) Atomic Absorption Spectrophotometers - Two approaches are used to calibrate atomic absorption spectrophotometers. These methods are direct comparison and standard additions.

a) Direct comparison is the simple approach, and can be used with many instruments to give a direct readout of the concentration of an element in an unknown sample. To obtain good precision (e.g., 1-2% coefficient of variation), the absorbance levels measured must be about 0.1 to 0.6 units. Standard and sample solutions should be similar in bulk matrix constituents, particularly acid and salt content. Interference suppressants are used in all solutions when required. A number of standards (usually three to five in increasing concentration) as well as a blank, are prepared to cover the concentration range. A volume of type II reagent water with the same amounts of acids as the samples and standards) will be used for calibration blank. These solutions are run in absorbance to check linearity of the calibration curve.

b) The method of standard additions is used when samples contains severe matrix interference. In this case it is possible to add small amounts of conventional standard solutions, in increasing amounts, to aliquots of each sample. A calibration graph can then be constructed. This method will often be used in work with the graphite furnace.

2) UV -VIS Spectrophotometer - The calibration procedure for the UV –VIS spectrophotometer is similar to that for the A.A. spectrophotometers. An integration interval is not required as the signal is very stable. It is important to use blanks and allow at least 1/2 hour warm up time.

3) PH Meters - The proper calibration of pH meters requires the use of two buffer solutions and a thermometer. The two buffer solutions must cover the expected range of samples to be tested. A third buffer is used to confirm calibration. The pH meter should be calibrated each day. The temperature of the buffers must be entered into the meter.

4) Conductivity Meter - The conductivity meter does not require frequent calibration but should be checked against a known standard each day of use. Recalibrate when there is significant deviation with the value of the standard.

5) Ion Chromatograph- Calibration of the Ion Chromatograph is performed at least once each year and whenever: 1) Controls are out of range; or, 2) the column, suppressor or detector is changed.

6) Inductively Coupled Plasma/Mass Spectrometer - Calibration of the ICP-MS is performed every day of analysis and whenever controls are out of range. See SOP for more information.

ANALYTICAL PROCEDURES

The laboratory employs only methods approved by Environmental Laboratory Accreditation Program. Analysts must conduct sufficient preliminary tests using the methodology and typical samples to demonstrate competence in the use of the measurement procedure.

Each time an analytical procedure is performed controls are included and duplicate samples and known additions are tested to insure accuracy and precision. Results are not reported unless all controls are within acceptance limits referenced in Standard Methods 18th Edition, 1992.

To monitor reliability of analytical measurements, data is periodically obtained on detection limits, accuracy, precision and recovery.

ACQUISITION, REDUCTION, VALIDATION OF REPORTING DATA

The analytical chemist is responsible for describing and reporting the data in an appropriate manner. In order to insure the accurate transcription, calculation and reporting of analytical data, the chemist will adhere to the following quality assurance procedures.

1) Use documented procedures and record all significant experimental details in such a way that the measurements could be reproduced by a competent analyst at a later date.

2) All measurements are made so that results are representative of the matrix (soil, water, etc.) and conditions being measured.

3) Report data only to the number of significant figures consistent with their limits of uncertainty.

4) Report data with the proper units of concentration. Units should be chosen which clearly indicate whether the concentration is in terms of weight by weight, weight by volume or volume by volume. Unless otherwise specified, all data are calculated and reported in standard units to allow comparison with data reported by other laboratories.

5) The analytical methodology used will be cited. The raw data for each sample, along with reagent blanks, control, and spiked samples will be suitably identified if included in the report. If average values are reported, an expression of the precision, including the number of measurements, must be included.

6) The report should include date and place of sampling, sampling point, the name of the sample collector, identification as to type of sample, date and time of submittal to the lab, date of analysis, name of the analyst, and the result. Any conditions which may effect the interpretation of the data should be noted in the report.. All results will be reviewed by a Water Quality Specialist or Public Health Chemist before a final report is released.

7) Laboratory records will be retained in a permanent file for three years.

8) Retain samples for one month after issuing final report and retain data and documentary evidence for three years.

INTERNAL QUALITY CONTROL

Quality Control (QC) may be defined as those measures undertaken in the laboratory to maintain the analytical testing process within acceptable limits of accuracy and precision.
The Quality Control Program consists of the following elements: documentation of operator competence, recovery of known additions, analysis of externally supplied standards, analysis of method blanks, and testing of replicate samples:

1) Operator competence The principal analyst is responsible for: 1) developing a standardized training syllabus for the methods employed in the laboratory; 2) assuring that test personnel are adequately trained; 3) assessing the competency of test personnel, and 4) maintaining documentation of training and competency of all test personnel.

a) Before test personnel are permitted to do reportable work, competency in performing the analysis is to be demonstrated. Commonly, the analyst performs replicate analysis under the supervision of the principal analyst. General limits for acceptable work are found in Standard Methods 18th Edition, 1992 in Table 1020:I.

b) After initial demonstration of competency, the principal analyst will assure test personnel maintain competency through testing internal or external proficiency test samples at least once each year.

2) With each batch of samples tested, controls will be tested to verify the accuracy of results as described below. Controls used with each method are outlined in Appendix D.

a) Recovery of known additions as part of all regular analytical protocols except titrimetric and gravimetric methods. Use known additions to verify the absence of matrix effects. Spiked samples shall be analyzed with a minimum frequency of ten percent of the samples per matrix per batch of samples. Spike recovery must be between 80-120% for potable water (75-125% for waste water). When a spike sample fails to meet this criteria, retest all samples following the last acceptable spike sample. Spike recovery calculated as % of the known addition recovered.

b) Analyze control standards with a minimum frequency of ten percent of the samples per matrix, per batch of samples. If there are less than 10 samples in a batch, at least one per matrix per batch must be analyzed. The concentration of the sample shall be within the working range of the method. Sources of these samples include but are not limited to: performance evaluation samples from the EPA, commercially available standards, or standards prepared in-house but from sources different from calibration standard. Control

standards must be within the published acceptance range (for external controls). If the control standard does not have a published acceptance range, recovery of the control should be within 10% of the known value. When a control standard fails to meet this criteria, retest all samples following the last acceptable control.

c) Method blanks will be analyzed with each batch of samples. The use of method blanks provides a measurement of laboratory contamination. Blanks cannot exceed the minimum detection level. See Appendix A.

d) Replicate samples will be analyzed with a minimum frequency of ten percent of samples per matrix, per batch of samples for drinking water. For wastewater the requirement is 5%. If there are less than ten samples per batch, at least one sample per matrix per batch must be analyzed. If the analyte is not detected, replicate matrix spike samples will be analyzed. The percent difference between replicate samples must be within 20% for potable water (25% for wastewater). When a replicate sample fails to meet this criteria, retest all samples following the last acceptable replicates. Duplicate % difference calculated as the difference as a percent of the mean. [100(X1-X2) / avg].

e) In addition to the control standards tested with each run, an external reference standard for each analyte will be tested at least once each quarter.

All of the quality assurance control procedures will be followed in the laboratory. All documentation for these checks should be available for inspection by laboratory management.

PREVENTIVE MAINTENANCE

As part of the QA plan, the laboratory has a comprehensive preventive maintenance program. Balances, spectrophotometers, and other instruments undergo routine maintenance and accuracy checks by a manufacturer's representative or by laboratory personnel as described below. All preventive maintenance performed in-house is documented on preventive maintenance forms. Instrument s which undergo routine professional maintenance have labels affixed to indicate date of last servicing. Manufacturer's instructions and service manuals are readily accessible.

Adequate spare parts are kept on hand to perform routine maintenance and minimize downtime. The spectrophotometers have maintenance contracts that provide for immediate servicing in the event of malfunction. Equipment records documenting preventive maintenance and emergency servicing/repairs are kept for a minimum of three years.

1) Thermometer/temperature-reading instruments: Accuracy of thermometers or recording instruments are checked annually against a certified National Bureau of Standards (NBS) thermometer or one traceable to NBS and conforming to NBS specifications. All thermometers a relabeled with date calibrated and correction factor.

2) Balance: Balance accuracy is verified each week using ASTM type 1 reference weights. Accuracy checks are documented on preventive maintenance chart. Balances are serviced and certified annually through a maintenance contract. Type 1 weights are re-certified at least every five years.

3) pH meter: pH meters are standardized with at least two NIST traceable standard buffers (pH 4.0, 7.0, or 10.0) and compensated for temperature before each series of tests. A third buffer is used to confirm calibration. Date buffer solutions when opened and discard buffer after expiration date on bottle. Buffers prepared from powders are replaced after four weeks.

4) Water deionization unit: Conductivity of the RO and Nanopure water is checked each month. A heterotrophic plate count on Nanopure water is also performed monthly. Filters are changed as indicated by conductivity readings and heterotrophic plate count. Records are maintained on preventive maintenance chart. Water is tested annually for bacteriologic quality and heavy metals.

5) Autoclave: Autoclave charts are used to document date, time, temperature and contents of each load. Chem-di indicators and heat sensitive tape are used with each load to identify materials that have been autoclaved; results are recorded on autoclave chart. Autoclave performance is checked each month with biological indicator (e.g. spore suspension). Autoclaves are serviced quarterly under maintenance contract. The accuracy of autoclave recording thermometer is checked annually. The autoclave operating temperature is monitored on a weekly basis.

6) Refrigerator: Temperatures are recorded daily and units defrosted and cleaned as needed. All media and reagents stored in the refrigerator are labeled.

7) Freezer: Temperatures are recorded daily. Identify and date materials stored. Defrost and clean semiannually; discard outdated materials.

8) Ultraviolet sterilization lamps: Unit is cleaned monthly by wiping lamps with a soft cloth moistened with ethanol. Test lamps quarterly with UV light meter and replace if they emit less than 70 % of initial output or if agar spread plates containing 200 to 250 microorganisms, exposed to the light for 2 minutes, do not show a count reduction of 99%.

9) Water bath: Fecal coliform water bath is checked twice daily. All other water baths are checked each day of use.

10) Incubator: Check and record temperature twice daily (morning and afternoon) on the shelf areas in use. Locate incubator where room temperature is in the range of 16 to 270 C.

11) Fume hoods/Biological Safety Cabinets: Fume hoods are checked once each month using a velometer; readings are recorded on preventive maintenance chart. Hoods and safety cabinets are certified annually through service contract.

PERFORMANCE AND SYSTEMS AUDITS

Corrective action is required when data is outside of predetermined limits for acceptability. The corrective actions can be triggered by the following quality assessment activities: Control Chart analysis; proficiency evaluation testing; and QA audits.

1) CONTROL CHART ANALYSIS:
The laboratory's quality assessment techniques will be used to maintain the precision and accuracy of all laboratory analyses within a state of statistical control. Precision and accuracy measurements are the best way to assess analytical performance. Precision is the degree of reproducibility of a particular analytical procedure. Accuracy is a measure of the agreement between an experimental determination and the true value.

a) PRECISION - Assess precision by replicate analysis, by repeated analysis of a stable standard, or by analysis of known additions to samples. Precision is specified by the standard deviation of the results. The formula for determining standard deviation (SD) is:

$$SD = \sqrt{\Sigma (X1-X)^2 / (N-1)}$$

Xl is the value of the individual measurements; X is the mean of all measurements for a given sample and N is the number of measurements.

The purpose of determining precision is to establish the typical variance of the method in the absence of any matrix influence. In the course of determining precision, there are two cases that indicate there is a problem with the precision data:

i) The measured values show wide variation from one to another for a given day.

ii) The measured values show little variance from one to another for a given day, but the mean and standard deviation show wide variation from one day to another.

If either of the above occurs, factors such as sample homogeneity, instrument calibration, or analyst error should be checked, documented, and corrected. The precision measurements should then be repeated.

b) ACCURACY - The best method to determine accuracy is to spike an aliquot of reagent water with a known amount of the constituent being measured and analyze the sample. The amount spiked should be at least five to ten times greater than the analytical detection limit.

To evaluate the data accuracy, the percent recovery of the spike must be determined. The formula for determining percent recovery is:

$$\% \text{ recovery} = [100(S - S\,1) / S2]$$

Where S is the concentration of the spiked sample; Sl is the concentration of the unspiked sample; S2 is the concentration of the spike added to the sample.

If the percent recovery deviates significantly from 100% and the method has not demonstrated significant bias, the problem must be detected and corrected prior to continuing the analysis. Sources of this problem include incorrect standard or spike solution concentration or a problem
in the procedural detection system.

Precision, accuracy, and detection limits for all methods used in the laboratory is comparable to values referenced in Standard Methods 18th Edition, 1992 and EPA Methods for Chemical Analysis of Water and Wastes, March 1983.

2) PERFORMANCE EVALUATION SAMPLES: The laboratory director is responsible for enrolling the laboratory in ELAP approved proficiency testing program(s) and assuring that proficiency testing is performed for all regulated tests. The principal analyst (Public Health Chemist) will conduct and document internal proficiency testing at least once a year for tests where proficiency testing is not available. Proficiency test samples are treated in the same manner as routine samples (i.e. tested the same number of times, tested using personnel who routinely perform testing, tested using routine methods and tested during patient testing).

3) QUALITY ASSURANCE AUDIT: The quality assurance program will be audited quarterly and any deviations from the program will signal corrective action to be taken. Quality assurance audit will be documented in a written report. The audit will include the following aspect:

a) Competency of test personnel must be evaluated annually and be documented

b) Evidence of the systematic use of control samples, replicate measurements and reference materials all in conjunction with control charts.

c) Proper labeling of reagents and samples.

d) Use of approved methods.

e) Results on blind samples.

f) Acceptable safety equipment and procedures.

g) Quality assurance reports generated on a regular basis.

h) Documentation on equipment performance and maintenance.

i) Training records.

j) All relevant files accessible and organized.

k) Laboratory personnel following good laboratory practices.

1) Laboratory personnel following good measurement practices

The Public Health Chemist will be responsible for initiating and documenting any corrective action necessary. Corrective action will be documented on the appropriate control chart, performance evaluation report, or QA audit report. No data shall be reported until the cause of the problem is located and corrected or the laboratory demonstrates the cause was a random event and no longer affects data. Although the elimination of events requiring corrective action may not be achieved, a reduction in the repetition of these events is the objective of this program. The audit would include the following:

REFERENCES FOR QUALITY ASSURANCE DOCUMENT

1) Standard Method for the Examination of Water and Wastewater, 18th edition, 1992.

2) Handbook for Analytical Quality Control in Water and Wastewater Laboratories. EPA-600j4-79-019, March 1979, USEPA.

3) Manuals for the Certification of Laboratories Analyzing Drinking Water Criteria and Procedures for Quality Assurance. EPA QAMS-005j80, Interim Guidelines, EPA-570j9-82-009, USEPA.

4) Methods for Chemical Analysis for Water and Waste. EPA-600j4-79-020, March 1983.

Written by: Gerry Guibert & David Holland

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Approved by: _____
(Laboratory Director's Signature)

APPENDIX A

ANALYTICAL METHODS FOR WATER ANALYSIS

PARAMETER	HOLD TIMES	METHOD REFERENCE	MDL	UNITS
Free Chlorine	.25 h; ASAP	SM 4500-CI G	0.02	mg/L
Total Chlorine	.25 h;ASAP	SM 4500-CI G	0.05	mg/L
Enterococcus	8 h	IDEXX	1/100	ml
Heterotrophic Plate Count	8 h	SM 9215 B	1	CFU
E. coli – MPN	6 h waste 8 h source 30 h potable	SM 9221 B	2/100	ml
Fecal Coliform – MPN	6 h waste 8 h source 30 h potable	SM 9221 B	1/100	ml
Total Coliform - MPN	6 h waste 8 h source 30 h potable	SM 9221 B	2/100	ml
Total Coliform – Quantitray	6 h waste 8 h source 30 h potable	SM 9223	1/100	ml
E. coli – Presence/Absence	30 h potable	SM 9223	1/100	ml
Total Coliform - PIA	30 h potable	SM 9223	1/100	ml
pH	.25 h; ASAP	EPA 150.1		pH units
Bicarbonate	ASAP {with pH)	SM 2320 B	10	mg/L
Calcium Carbonate	ASAP (with pH)	SM 2320 B	1	mg/L
Carbonate	ASAP (with pH)	SM 2320 B	1	mg/L
Solids	24 h	SM 2540 F	0.1	mL/L
Color Determination	48 h	SM 2120 B	2	CU
Odor	NS; 48 h (rec 6h)	SM 2150 B	1	TON
Turbidity	48 h	SM 2130 B	0.05	NTU
Nitrate	48 h	EPA 300.0	1	mg/L
Nitrite as (N)	48 h	SM 4500 NO2-B	10	ug/L
Total Dissolved Solids	7 d	SM 2540 C	5	mg/L
Total Suspended Solids	7 d	SM 2540 D	5	mg/L
Alkalinity	14 d	SM 2320 B 1	0	mg/L, CaCO3
Bromide	28 d	EPA 300.0	1	mg/L
Chloride	28 d	EPA 300.0	1	mg/L
Fluoride	8 d	EPA 300.0	0.02	mg/L
Sulfate	8 d	EPA 300.0	1	mg/L
Conductivity	28 d	SM 2510 B	1	umhos at 25C
Ammonia (N)	28 d	SM 4500 NH3 F	0.05	mg/L
Orthophosphate	NS; 28 d	SM 4500P E	0.03	mg/L
Total Phosphorus	28 d SM 4500 P E	0.03	mg/L	

PARAMETER	HOLD TIMES	METHOD REFERENCE	MDL	UNITS
Aluminum	6 months	EPA 200.8	5	ug/L
Antimony	6 months	EPA 200.8	0.5	ug/L
Arsenic	6 months	EPA 200.8	1	ug/L
Barium	6 months	EPA 200.8	0.5	ug/L
Beryllium	6 months	EPA 200.8	0.5	ug/L
Cadmium	6 months	EPA 200.8	0.5	ug/L
Chromium	6 months	EPA 200.8	5	ug/L
Copper	6 months	EPA 200.8	0.5	ug/L
Iron	6 months	EPA 200.8	50	ug/L
Lead	6 months	EPA 200.8	0.5	ug/L
Manganese	6 months	EPA 200.8	0.5	ug/L
Mercury	6 months	EPA 200.8	0.25	ug/L
Nickel	6 months	EPA 200.8	0.5	ug/L
Selenium	6 months	EPA 200.8	5	ug/L
Silver	6 months	EPA 200.8	5	ug/L
Thallium	6 months	EPA 200.8	0.5	ug/L
Zinc	6 months	EPA 200.8	5	mg/L
Calcium	6 months	EPA 200.8, 6020	0.05	mg/L
Magnesium	6 months	EPA 200.8, 6020	0.05	mg/L
Potassium	6 months	EPA 200.8,6020	0.05	mg/L
Sodium	6 months	EPA 200.8, 6020	0.05	mg/L
Hardness as CaCO3	6 months	SM 2340 B	1.0	mg/L
Boron	6 months	SM 4500 B B	0.1	mg/L

Appendix IV: Eutrophication Studies for PG & E Grant #20060387

Introduction

During the seven-month period where eutrophication data will be collected along with on-going water quality samples in fulfillment of the second ESNERR PGE grant (grant # 20060387), several additional parameters will also be assessed and added to the database as appropriate. These include percentage cover estimates of floating macro algal mats at the volunteer monitoring sites and laboratory analyses of chlorophyll a concentrations from water samples taken at these same locations. The goal for these two assessments will be to determine if there is a response of local macro algal or phytoplankton abundances to changes in local nutrient concentrations. The primary species that forms conspicuous floating algal mats in Elkhorn Slough is Ulva intestinalis (Zimmerman and Caffery 2002, Schaadt 2005), which can grow vegetatively in floating algal mats or by propagules attaching to hard substrate. In addition, surface and bottom-water dissolved oxygen concentrations will be measured over multiple 24-hr periods at a subset of the 26 monitoring locations to assess night-time water column hypoxia. The current ESNERR QAPP requires only monthly day-time dissolved oxygen concentration assessments, which can underestimate the extent of hypoxia possibly linked to elevated nutrient concentrations and eutrophication. The methods to be followed for the collection of these field and laboratory analyses are outlined below.

Methods

Macro algal assessments

At each of the established volunteer water quality monitoring locations, by-eye estimates of macro algal percent cover will be made on monthly intervals. In the course of monthly sampling operations established in the ESNERR QAPP, digital photographs are being collected at specified GPS locations. A visual survey will be made at each of these same locations to determine the percent cover in relation to the surface area of the water body in question. Only algal cover visible at the water surface that can be seen within a 10 m radius from the water's edge, closest to the sampling location will be included in estimates. Algae must be breaking the water surface, and benthic algae seen through the water column will be excluded from coverage estimates. Algae growing on mudflats above the water line will not be included. Sites will be sampled during the low slack-tide to ensure algae are not being pushed by tidal forcing. The total percent cover will be estimated for all species of algal pooled together that are observed under these conditions. Field percent cover sheets will be used to calibrate by-eye estimates made with each monthly sampling.

Accuracy of the by-eye estimates will be verified in a more detailed field survey conducted in May or June of 2009, when algal abundances tend to be highest in the Elkhorn Slough. Aerial photographs taken on an annual basis at this time will be compared with by-eye estimates made on the same sampling day at low tide to determine error. Field surveys will also be conducted at a subset of the 26 sites found to have more conspicuous algal cover (>10%). Macro algal percent cover will be determined by using stratified sampling of 1m2 quadrats along transects across each site. Percent cover estimates collected from the ground truthing survey will compared to by-eye estimates using linear regression, and the error from the linear regression will be applied to the final multivariate analysis.

Chlorophyll a assessments

Chlorophyll a concentration in Elkhorn Slough waters will be determined by use of YSI probes (YSI 6025 and YSI 6026)on the YSI 6600 EDS and V2 sondes. Simultaneously, discrete water samples will be collected in opaque brown bottles, kept in an iced dark cooler until filtered with in 12 hours of collection. YSI Chl probes will be calibrated using Dinelliella spp. that is grown up in F/2 media and then Chl a concentration will be determined as outlined in Jeffrey and Humphrey (1975) using spectrophotometry.. Readings will be determined in relative fluorescence units (RFU) for better accuracy. Detection limits will be calculated by three times the standard deviation of the lowest standard run at least seven separate times. Water samples will be filtered and extracted in 90% acetone, and run for chl a concentrations as detailed analysis in section 10200 H of Standard Methods for the Examination of Water and Wastewater Analysis. A modified single step method is used with a Turner Designs TD-700 flourometer with 436 and 680 nm filters for these samples. The results of the laboratory chl a analyses will be compared to probe detected in-situ chl a measurements. Chl a data will then be compared with nutrient concentrations measured in the same water sampling events for links representing eutrophication processes.

Hypoxia Assessments

Dissolved oxygen concentrations are currently being monitoring as part of the monthly water quality sampling plan executed at the 26 volunteer monitoring sites, outlined in the ESNERR QAPP. These same procedures for pre and post equipment calibrations, data acquisition and storage will be followed to collect night-time concentrations. However, in addition to the single monthly day-time dissolved oxygen concentration currently being measured, YSI Sondes will also be deployed for up to a lunar tidal cycle at selected sites to obtain a more detailed understanding of dissolved oxygen concentrations over time. The resulting data will be categorized into concentration-based groups representing oxic, hypoxic, or anoxic conditions. The raw data from these surveys will not be entered into the database as the data will be acquired every 15 minutes and will be too extensive, but the data will be made available in graphical and categorical form as part of final report and manuscript preparation. Further details of the methods used to account for drift over time and biofouling can be found in the protocols for the National Estuarine Research Reserve (NERR), system-wide monitoring program: http://cdmo.baruch.sc.edu/data_dissemination.html#NERR%20Water%20Quality%20Data.

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