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Up-Stream Dissolved Oxygen TMDL Project Quality Assurance Project Plan

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1. Title and Approval Page

Up-Stream Dissolved Oxygen TMDL Project Quality Assurance Project Plan

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Second Edition: Dominic Gregorio, SWRCB, 2001

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3. Distribution List

All group leaders, and technical advisors will receive copies of this Quality Assurance Project Plan (QAPP) , and any approved revisions of this plan. This QA plan will be available to any interested party by requesting a copy from Dr. William T. Stringfellow, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, MS 70A-3317, Berkeley, CA 94720, (wstringfellow@lbl.gov).

4. Project Organization

This QAPP is for the Up-Stream San Joaquin River DO TMDL Research Team as described in the CALFED Directed Action Proposal "Monitoring and Investigation of the San Joaquin River and Tributaries Related to Dissolved Oxygen, March 13, 2002" and related documents described in CBDA Ecosystem Restoration Program Recipient Agreement ERP-02D-P63. The objective of the project is to provide information on the sources of algae and nutrients on the San Joaquin River (SJR) and to conduct a mass balance on algae on the SJR above the Stockton Deep Water Ship Channel.

4.1. Management

The Project Manager is Joseph McGahan representing the San Joaquin Valley Drainage Authority (SJVDA). The Lead Principal Investigator (PI) is William Stringfellow of Lawrence Berkeley National Laboratory (LBNL) and the University of the Pacific (Pacific) in Stockton, CA. The Project Manager and the Lead PI will be responsible for organization and implementation of the QAPP in cooperation with the other PIs on the project as described in Recipient Agreement ERP-02D-P63 and the associated sub-contracts.

4.2. Team Leaders

The Monitoring Team Leader is William Stringfellow, who will be coordinating sample collection and field maintenance activities. The Modeling Team Leader is Russ Brown of Jones & Stokes. The Special Studies Team leader is Gary Litton of UOP.

4.3. Data Managers

Data management activities will be led by the Project Manager and the Monitoring Team Leader in cooperation with the Modeling Team Leader and Karl Jacobs of the California Department of Water Resources Interagency Ecological Program (DWR-IEP). Each project participant (Section 4.5) will have a role in entering and reviewing data generated by their respective research units and may participate in the overall review and interpretation of the data.

4.4. Quality Assurance Personnel

Laboratories at University of California at Davis (UC Davis), Pacific, LBNL, and US Geological Survey (USGS) will be generating results for this project. Laboratory QA will be overseen by Sharon Borglin at LBNL and by Gary Litton at Pacific. Randy Dahlgren will oversee laboratory QA at UC Davis. Carol Kendall will be responsible for QA oversight at USGS. Field QA will be overseen by Joe McGahan and William Stringfellow with the assistance of Nigel Quinn, Lowell Ploss, and participating water and irrigation districts.

4.5. Project Participants & Technical Advisors

A detailed description of participant qualifications and facilities can be found in the CALFED Directed Action Proposal "Monitoring and Investigation of the San Joaquin River and Tributaries Related to Dissolved Oxygen, March 13, 2002" (www.sjrdotmdl.org).

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5. Problem Definition/Background

5.1. Problem Statement

This project is focused on understanding the sources of oxygen-consuming materials, particularly algae, in the SJR upstream of the Stockton Deep Water Ship Channel (DWSC). The purpose of this study is to provide a comprehensive understanding of the sources and fate of oxygen-consuming materials in the SJR watershed. This study will provide stakeholders in the SJR basin an understanding of the baseline conditions of the basin, provide input for an allocation decision, and provide the stakeholders with a tool for measuring the impact of any water quality management program that may be implemented in response to the DO-TMDL requirements.

Previous studies have identified algal biomass as the most significant oxygen-demanding substance in the SJR upstream of the DWSC. Algal biomass is not a conserved substance, but grows and decays in the SJR; hence, characterization of oxygen-demanding substances in the SJR is inherently complicated and will require an integrated effort of extensive monitoring, scientific study, and modeling. This study includes a coherent and comprehensive study of algal growth dynamics in the SJR and will identify sources of algal nutrients to the SJR.

5.2. Project Objectives

Objective 1: Establish a comprehensive monitoring program to characterize the loading of algae, other oxygen-demanding materials, and nutrients from individual tributaries and sub-watersheds of the upstream SJR.

Objective 2: Characterize the transformation and fate of algae and other oxygen-demanding materials between their sources in the watershed and the Stockton Deep Water Ship Channel (DWSC).

Objective 3: Characterize the fate of nutrients and the impact of nutrients on algal growth between their sources in the watershed and the DWSC.

Objective 4: Characterize the temporal variability of water quality parameters on a daily and seasonal basis.

Objective 5: Provide input and calibration data for water quality modeling associated with the low DO problems in the SJR watershed, including modeling on the linkage among nutrients, algae, and low DO.

Objective 6: Provide stakeholder confidence in the information that will be used to support the DO TMDL allocation and implementation process.

5.3. Intended Usage of Data

Data will be collected for use by local stakeholders, scientific agencies, and other interested parties. Specific uses of data are described in the CALFED Directed Action Proposal "Monitoring and Investigation of the San Joaquin River and Tributaries Related to Dissolved Oxygen, March 13, 2002" and related documents described in CBDA Ecosystem Restoration Program Recipient Agreement ERP-02D-P63. The primary use of the data will be in regional water quality models and scientific publications.

6. Project Description

6.1. General Overview of Monitoring

The Up-Stream San Joaquin River DO TMDL Research Team is monitoring water quality in the San Joaquin River watershed. The project involves both research and monitoring. This Quality Assurance Project Plan (QAPP) was developed from quality assurance and quality control guidelines in *Quality Assurance Management Plan for the State of California's Surface Water Ambient Monitoring Program* (Puckett 2002); *Standard Methods for the Examination of Water and Wastewater* (APHA 1998); Chapter 1 of *SW-846 On-Line Test Methods for Evaluating Solid Wastes Physical/Chemical Methods* (USEPA 1992); and guidelines for monitoring plans available on the State of California's Surface Water Ambient Monitoring Program (SWAMP) website (www.swrcb.ca.gov/swamp/qapp.html).

Table 6.1 summarizes the monitoring design, including the physical, chemical and biological parameters to be measured and the frequency of measurement. Continuous monitoring for flow will be utilized where possible to gather higher quality information concerning hydraulic variability in the study region.

Table 6.1 Summary of Monitoring Design

Parameter	Type of monitoring	Frequency of monitoring
Flow	F	C
Temperature	F	C
Dissolved Oxygen	F	C
pH	F	C
Conductivity	F	C
Turbidity	F	C
Fluorescence (chlorophyll)	F & L	C

Parameter	Type of monitoring	Frequency of monitoring
Biochemical Oxygen Demand (10-Day)	L	B
Carbonaceous and Nitrogenous Biochemical Oxygen Demand (10-Day)	L	B
Soluble Biochemical Oxygen Demand (10-Day)	L	S
Chlorophyll <i>a</i>	L	B
Pheophytin <i>a</i>	L	B
Total Organic Carbon	L	B
Dissolved Organic Carbon	L	B
Volatile Suspended Solids	L	B
Total Suspended Solids	L	B
Total Nitrogen	L	B
Nitrate and Nitrite Nitrogen	L	B
Ammonia Nitrogen	L	B
Orthophosphate, Soluble	L	B
Total Phosphate	L	B
Metals	L	S

Codes for Table 6.1: **Type:** F: field analysis, L: in-house lab analysis. **Frequency:** C: Continuous at some sites, bimonthly (twice per month) or less at other sites; B: Bimonthly at some sites or less at other sites; S: Sample collection as part of special studies only.

6.2. Manual & Continuous Field Measurements

Where applicable, field procedures will conform to standards described in Appendix E "Procedures for Conducting Routine Field Measurements in SWAMP" (Puckett 2002) available from the Surface Water Ambient Monitoring Program (SWAMP) web-site (<http://www.swrcb.ca.gov/swamp/qapp.html>). Field data will be checked in the field by the senior technician before leaving the station. If any questions arise about a measurement, replicate measurements will be made to confirm original result before leaving station for next sample point.

Field measurements will be made with handheld probes (e.g., YSI 6600) or continuously deployed monitoring devices (e. g. Starflow Doppler Flowmeter). Handheld probes will be calibrated the day before each use and calibrations will be checked upon return from the field. Continuous monitoring devices will be calibrated and deployed according to the manufacturer's specifications. On-going field confirmation (QC) of continuous measurements will be performed using replicate sampling for laboratory analysis, manual stream ratings, and standardized instruments, as required.

Flow measurements will be made in a variety of ways at different locations. Where feasible, redundant devices will be deployed for flow measurement (e.g., Starflow units and bubbler stage measurement devices). Many stations will have continuous monitoring of flow with data recorded at 15 minute or hourly intervals. Continuous flow and water quality monitoring equipment will be installed according to manufacturer recommendations and will be subject to a routine calibration and maintenance schedule. Flow will be measured at structures, such as bridges, culverts, and weirs. Where weirs are utilized, rating tables based on standard engineering weir equations will be developed.

6.3. Grab Sample Collection and Handling

Whenever safely possible, the collector will sample from a bridge or other structure and samples will be taken approximately in mid-stream. Samples will be depth integrated when necessary. If it is necessary to wade into the water, the sample collector stands downstream of the sample, taking a sample upstream. If the collector disturbs sediment when wading, the collector will wait until the effect of disturbance is no longer present before taking the sample.

Samples collected in the field will be transported to LBNL, Pacific, and UC Davis for analysis. All analyses will be run within the allowed holding time applicable to the preservation method used (Table 6.2). Additionally, a 1-liter composite water sample from selected sites will be filtered through pre-combusted glass fibers for isotope and fatty acid analysis. Filters will be wrapped in foil, frozen, and sent to the USGS stable isotope lab in Menlo Park for isotopic analysis of the particulates. The filtered water sample will be divided into smaller bottles, chilled or frozen (as needed), and sent to the USGS lab for other isotopic analyses. Filters for fatty acid analysis will be frozen until analyzed.

Table 6.2 : Summary of Sampling and Handling Requirements (from APHA 1998)

Determination	Container	Min. sample size	Preservation	Recommended Hold	Regulatory hold
Biochemical Oxygen Demand	P, G	1000	Refrigerate	6 h	48 h
Carbonaceous and Nitrogenous Biochemical Oxygen Demand	P, G	1000	Refrigerate	6 h	48 h
Soluble Biochemical Oxygen Demand	P, G	1000	Refrigerate	6 h	48 h
Chlorophyll <i>a</i>	P, G	500	Unfiltered, dark, refrigerate Filtered, dark, freeze	24 – 48 h 28 d	
Pheophytin <i>a</i>	P, G	500	Unfiltered, dark, refrigerate Filtered, dark, freeze	24 – 48 h 28 d	
Total Organic Carbon	G	100	Refrigerate or H ₃ PO ₄ to pH < 2	7 d	28 d
Dissolved Organic Carbon	G	100	Refrigerate or H ₃ PO ₄ to pH < 2	7 d	28 d
Volatile Suspended Solids	P, G	200	Refrigerate	48 h	7 d
Total Suspended Solids	P, G	200	Refrigerate	48 h	7 d
Total Nitrogen	P, G	500	Refrigerate	7 d	28 d
Nitrate and Nitrite Nitrogen	P, G	200	Refrigerate	1 – 2 d	28 d
Ammonia Nitrogen	P, G	200	Refrigerate	48 h	28 d
Orthophosphate, soluble	P, G	100	Refrigerate	48 h	
Total Phosphate	P, G	100	Refrigerate	48 h	
Metals	P, G	1000	HNO ₃ to pH < 2 or freeze	6 months	6 months

P, plastic; G, glass

6.4. Sample Handling & Custody Procedures

Chain of Custody (COC) documents will be generated for monitoring samples. The COC form identifies the sample location, sample number, date and time of collection, sampler's name, and method used to preserve sample (if any). It also indicates the date and time of transfer, and the name and signature of the sampler and the sample recipient. In cases where the sample remains in the custody of the monitoring organization, then the field data notes may be allowed to double as the chain of custody form.

6.5. Sample Analysis

Each analytical laboratory (UC Davis, Pacific, LBNL, USGS) will have Standard Operating Procedures (SOPs) for all routine analysis methods. The SOP insures continuity in the analysis, reporting and QC monitoring of the data. The SOP outlines in detail the reagents, standards, apparatus, instrumentation and exact procedure for carrying out each analytical method. The SOP is prepared by the analyst in collaboration with the QA Personnel. A copy is placed in the analysis area and a master copy is kept on file. Daily laboratory work at the bench level is carried out according these documents.

Sample analysis methods are briefly described below. The methods listed below are the methods currently utilized for water quality analysis on the San Joaquin River and its tributaries (State and Federal funded projects), as well as samples analyzed for the Surface Water Ambient Monitoring Program (SWAMP) on surface waters in the San Joaquin River watershed. We will maintain consistent methods between the past five years of data and those collected as part of the proposed project. Any description here is for information only, the analytical SOP will describe the procedures used for analysis.

Biochemical oxygen demand (BOD) will be analyzed by Standard Method (SM) 52101 B with a modification for measurement of oxygen demand at 10 days rather than 5 days. Previous studies in the SJR have used 10-day BOD analysis (BOD₁₀) as a standard procedure and this data set will be consistent with prior studies. BOD₁₀ will be measured without seed, as in previous studies. The positive controls (CC, LCS, MS) for BOD₁₀ will utilize a standard solution of glucose/glutamic acid. Initial and final dissolved oxygen will be measured using calibrated DO meters. DO meters will be calibrated each day of use or more frequently if necessary. Duplicate measurements will be made every 20 analysis and blanks will consist of dilution water alone.

Total organic carbon (TOC) will be measured by high temperature combustion according to SM 5310 B. Dissolved organic carbon will be measured on split samples after filtration through a GF/F glass fiber filter (or equivalent) by the same method.

Total suspended solids (TSS) and volatile suspended solids (VSS) will be analyzed by SM 2540 D and E, respectively.

Chlorophyll-*a* (chl-*a*) and pheophytin-*a* (pha-*a*) will be extracted and analyzed using spectrophotometric absorption (SM 10200H). Alternative and supplementary measurements will also include EPA Method 466.0 (In-Vitro Determination of Chlorophylls) and the high performance liquid chromatographic method (EPA Method 447.0 or SM 10200H).

To assess the phytoplankton community, analysis of samples will follow EPA Standard Operating Procedure LG401. Briefly, a two-stage analysis is conducted using a modification of the Utermohl method (Utermohl 1958). For non-diatom algae, samples are settled in plankton chambers and then identified and enumerated with an inverted microscope. Later, diatoms species are identified and enumerated from a cleaned diatom preparation using a standard compound microscope. Species will be identified using standard taxonomic references for algae.

To assess the grazing community, water samples will be taken at each station using a Schindler-Patalas trap fitted with 63 um and 153 um mesh plankton nets to sample macro- and mesozooplankton, respectively. Samples will be taken at 2 m depth intervals, starting at 1 m below the surface, and proceeding to the bottom. Microzooplankton will be sampled by pumping water into a carboy while raising the water inlet hose from bottom to surface. Sample preservation will follow US EPA SOP LG402 (USEPA 2002). Enumeration of zooplankton species will follow the Utermohl method (Utermohl 1958), in which organisms are concentrated by settling in cylindrical chambers, and counted/identified with an inverted microscope, yielding estimates of the number of organisms per cubic meter of water. Alternatively, in samples containing high levels of sediment, Sedgewick-Rafter Counting Cells will be employed to count larger zooplankton, and Palmer Counting Cells will be used to

count smaller cells. Sediment samples will be taken at each station with a Ponar grab to assess the benthic macroinvertebrate community. Organism identifications will be performed using standard references for aquatic invertebrates and protozoa. Estimation of zooplankton biomass at a given sample site will be based on estimating the dry weight of zooplanktonic Crustacea by length-weight regressions (Dumont et al. 1975).

Because zooplankton are microscopic, the possibility of contamination of samples is great. Laboratory rooms where raw samples are transferred will be maintained in a clean environment. Techniques similar to those used for sterile experiments (bacteriological plating, etc.) will be employed to minimize the risk of cross contamination of samples. Disposable plastic ware will be used when feasible. Where they cannot be used, plastic and glassware will be rinsed in high purity water after each sample.

Nitrate and ammonium concentrations are determined on samples filtered through a 0.45 mm Nuclepore membrane filter (filters are pre-rinsed with sample). Nitrate and ammonium are quantified simultaneously using an automated membrane diffusion/conductivity detection method (Carlson, 1978, 1986; Carlson et al., 1990). The method allows for analysis of high ionic strength solutions without dilution of samples. This method has excellent detection limits. Under standard operating conditions for river waters from the Central Valley the limit of detection is approximately 10 ppb. This limit of detection results in very few "less than detection" values for Central Valley river waters. Recovery of ammonium and nitrate is >95% within the concentration range of Central Valley river waters. Repeated analyses of analytical standards have a coefficient of variation (CV) consistently <5%. Alternatively, nitrate and nitrite will be analyzed by the Cadmium Reduction Method (adapted from SM 4500-NO₃-E) and ammonia will be quantified by the Nessler Method.

Alternative methods for nitrogen compounds include measurement of nitrate, nitrite and total ammonia with ion specific electrodes (SM 4500 D) and the measurement of nitrite by SM 4500 B (Ultraviolet Spectrophotometric Method) and ammonia by SM 4500 C.

Total nitrogen will be determined on non-filtered samples. Total nitrogen is determined conductimetrically (as described above) following persulfate oxidation (Yu et al., 1994). Oxidation is conducted using a 1% persulfate oxidant concentration, a sample:oxidant ratio of 1:1 (V/V), and heating in an autoclave. The limit of detection is about 50 ppb N. This detection level is low enough to quantify total nitrogen in all of the Central Valley river waters. Recovery of total nitrogen is statistically identical to the Kjeldahl total nitrogen method in a comparison study conducted by UC Davis utilizing several reagent grade, organic nitrogen compounds. Quantification of nitrogen is by the automated membrane diffusion/conductivity detection method (Carlson, 1978, 1986; Carlson et al., 1990).

Ortho-phosphate is determined on samples filtered through a 0.45 mm Nuclepore membrane filter (filters are pre-rinsed with sample). The Stannous Chloride method is the preferred method for this analysis (SM 4500 P.D). The limit of detection for this method is approximately 3 ppb P in clean water using a 1 cm cell for measurement. We have the ability to utilize a 5 cm cell to lower the limit of detection; however, we find that the 1 cm cell is sufficient for most Central Valley river waters. Alternatively, *ortho*-phosphate and total phosphorous will be quantified by the Ascorbic Acid Method (adapted from SM 4500-P-E).

Total phosphorus is determined on non-filtered samples. Total P is measured by the Stannous Chloride" method following persulfate digestion as described above for the total N procedure. The limit of detection for this method is about 5 ppb P using a 1 cm cell for measurement.

General metals will be analyzed by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) according to EPA Method 6020. Samples will be digested using nitric acid according to SM 3030 D. If necessary, the more rigorous digestion using HNO₃ + HCl (SM 3030 F) will be performed. Following digestion the samples will be filtered through a 0.45 um filter prior to analysis.

This project will characterize BOD isotopic composition in the SJR and tributaries. The methods listed below are used by USGS for isotopic, elemental, concentration, and optical analysis of San Joaquin River water and dissolved constituents.

The isotopic and elemental composition (d¹⁵N, d¹³C, d³⁴S, C:N, and C:S) of bulk particulate organic matter (POM) are determined on samples filtered through a pre-combusted 0.7 micrometer GF/F filter. The filter is freeze-dried, homogenized, and acidified prior to analysis. We will also isolate different size fractions of POM from a few samples using centrifugation and Ludox separations to better characterize pure, undegraded phytoplankton when the rivers contain significant amounts of non-algal POM (i.e., during winter). All POM samples are combusted in a Carlo Erba elemental analyzer and the gases are measured using an interfaced Micromass Optima or IsoPrime stable isotope ratio mass spectrometer (IRMS) (e.g., Kendall et al., 2001). The precision of analyses (1s) is ±0.15‰ for d¹³C and d¹⁵N and ±0.5‰ for d³⁴S.

A few POM samples will be analyzed for ^{14}C activity to quantify contributions of old detrital carbon (sample preparation as described above for POM elemental and isotopic composition). These samples are combusted to CO_2 in sealed, evacuated quartz tubes containing CuO as an oxygen source (Buchanan and Corcoran, 1957; Frazer and Crawford, 1963). The CO_2 is then cryogenically purified and sealed in ampoules for transport to the Center for Accelerator Mass Spectrometry (CAMS) at Lawrence Livermore National Laboratory (LLNL). There, the CO_2 samples are converted to graphite (Lowe and Judd, 1987) and analyzed for ^{14}C activity on a tandem accelerator mass spectrometer. Analytical precision is $\pm 1\%$.

Water d^{18}O is determined on unfiltered samples. Samples are analyzed using an automated $\text{CO}_2\text{-H}_2\text{O}$ equilibration method (Epstein and Mayeda, 1953; Kendall and Coplen, 2001). CO_2 gas is equilibrated with the water and then analyzed on a Finnigan MAT 251 or Micromass IsoPrime IRMS. Precision of d^{18}O analyses is better than $\pm 0.1\text{‰}$.

Ultraviolet absorption spectra of unfiltered water samples are measured from 310 to 210 nanometers wavelength with a Perkin-Elmer Lambda 3B spectrophotometer (Standard Method 5910). Organic structures in the dissolved organic carbon (DOC), such as conjugated and aromatic species, absorb UV light at characteristic wavelengths, and thus the spectra yield information about the type and abundance of organic species within DOC.

Dissolved organic carbon (DOC) concentration and d^{13}C measurements are determined on water samples filtered through a Polysulfone GD/X syringe filter, which includes graded density Multigrade GMF 150 (10:1 mm) and Grade GF/F (0.7 mm) prefilters. The samples are stored chilled in pre-combusted, amber vials containing a droplet of 85% phosphoric acid. Samples are analyzed using an automated OI TOC analyzer interfaced with a Micromass IsoPrime IRMS (St. Jean, 2003). This method first acidifies water samples to remove dissolved inorganic carbon (DIC), then analyzes the concentration and d^{13}C value of CO_2 obtained from persulfate oxidation of DOC. Precision of d^{13}C analyses is $\pm 0.3\text{‰}$.

Dissolved inorganic carbon (DIC) concentration and d^{13}C measurements are determined on water samples filtered through a Polysulfone GD/X syringe filter, which includes graded density Multigrade GMF 150 (10:1 mm) and Grade GF/F (0.7 mm) prefilters. The samples are stored chilled in pre-combusted, clear vials containing 5-10 mg of copper sulfate (as a bactericide). Samples are analyzed using an automated OI TOC analyzer interfaced with a Micromass IsoPrime IRMS (St. Jean, 2003). This method acidifies water samples, then analyzes the concentration and d^{13}C value of CO_2 obtained. Precision of d^{13}C analyses is $\pm 0.3\text{‰}$.

The isotopic composition of dissolved nitrate (d^{15}N and d^{18}O) is determined on water samples filtered through 0.2 mm syringe filters (0.45 mm filters may be used for pre-filtering sediment-laden water). The samples are stored frozen in pre-cleaned, HDPE bottles. Samples are analyzed using an automated version of a new microbial denitrifier method (Casciotti et al., 2002; Sigman et al., 2001). This method uses microbes to convert dissolved nitrate to N_2O gas, which is then analyzed on a Micromass IsoPrime IRMS. Precision of analyses is $\pm 0.4\text{‰}$ for d^{15}N and $\pm 0.8\text{‰}$ for d^{18}O .

The d^{15}N value of ammonium is determined on water samples filtered through a pre-combusted 0.7 mm GF/F filter. The samples are stored frozen in bottles with solid plastic lids. Ammonium ion in the samples is converted to ammonia gas at elevated pH and temperature, and the ammonia is trapped on an acidified GF/F filter (Holmes et al., 1998; Sebilo et al., 2004). Sample filters are combusted in a Carlo Erba elemental analyzer and the resulting N_2 gas is measured for d^{15}N using an interfaced Micromass Optima or IsoPrime stable isotope ratio mass spectrometer (IRMS) (e.g., Kendall et al., 2001). Precision of d^{15}N analyses is $\pm 0.4\text{‰}$.

The d^{15}N value of dissolved organic nitrogen (DON) is determined on water samples filtered through a Polysulfone GD/X syringe filter, which includes graded density Multigrade GMF 150 (10:1 mm) and Grade GF/F (0.7 mm) prefilters. The samples are stored chilled in pre-combusted, amber vials containing a droplet of 85% phosphoric acid. DON d^{15}N is determined by combining the persulfate oxidation method for converting total dissolved nitrogen to nitrate (Bronk et al., 2000; Solorzano and Sharp, 1980) with the microbial denitrifier method for d^{15}N analysis of nitrate (discussed above) (Knapp et al., submitted).

The d^{18}O value of phosphate is determined on dissolved inorganic phosphate (DIP) precipitated from water samples, which is purified and converted to silver phosphate (Karl and Tien, 1992; McLaughlin et al., 2004). The silver phosphate is converted (via pyrolysis) to CO gas, which is analyzed for d^{18}O on a Micromass IsoPrime IRMS. Precision of d^{18}O analyses is $\pm 0.3\text{‰}$.

7. Data Quality Objectives

Minimum acceptable data quality objectives (DQOs) for analytical techniques used in this project are summarized in Tables 7-1. Most methods used in this project (see Section 6) exceed the DQOs in Table 7-1 and the DQOs listed in Table 7-1 are intended to set minimum acceptable standards. These DQOs were derived from the SWAMP QA Management Plan (Puckett 2002) and guidelines for monitoring plans available on the SWAMP website (<http://www.swrcb.ca.gov/swamp/qapp.html>). Whenever possible, the methods with greater sensitivity and lowest detection limit will be employed as the primary methods. Methods with lesser sensitivity and higher detection limits will be used for samples known to contain high concentrations of analytes, field confirmations, or as back-up methods in the case that the primary methods are not available or functioning properly for a particular sampling event.

Continuous monitoring devices will be calibrated and deployed according to the manufacturer's specifications and field confirmation will be performed using methods such as manual flow ratings, grab sampling (for laboratory analysis), and QC measurements with standardized instruments.

Table 7-1: Minimum Acceptable Data Quality Objectives for Methods.

Parameter	Method/ Range	Units	Detection Limit	Sensitivity	Precision ¹	Accuracy ²
Flow	Continuous	cfs	5.0	2.0	± 5%	± 5%
Temperature	Continuous or Handheld	° C	-5	0.5 ° C	± 0.5 ° C	± 0.5 ° C
Dissolved Oxygen	Continuous or Handheld	mg/l	0.5	0.1	± 0.6 (<2) ± 20%	± 10%
pH	Continuous or Handheld	pH units	2.0	0.1	± 0.2 units	± 0.2 units
Conductivity	Continuous or Handheld	µS/cm	10	10	± 5%	± 10%
Turbidity	Continuous or Handheld	NTUs	1.0	0.5	± 20%	± 20%
Fluorescence (chlorophyll)	Continuous or Handheld	%	1.0	0.1	± 20%	± 10%
Biochemical Oxygen Demand	Laboratory	mg/l	1.0	0.1	± 20%	± 20%
Chlorophyll a	Laboratory	µg/l	2.0	0.1	± 20%	± 20%
Pheophytin a	Laboratory	µg/l	2.0	0.1	± 20%	± 20%
Total Organic Carbon	Laboratory	mg/l	0.2	0.1	± 0.6 (<2) ± 20% (>2)	± 20%
Dissolved Organic Carbon	Laboratory	mg/l	0.2	0.1	± 0.6 (<2) ± 20% (>2)	± 20%
Volatile Suspended Solids	Laboratory	mg/l	5.0	1.0	± 20%	± 20%
Total Suspended Solids	Laboratory	mg/l	5.0	1.0	± 20%	± 20%
Total Nitrogen	Laboratory	mg/l	0.05	0.01	±0.2 (<1.0) ±20% (>1)	±20%
Nitrate and Nitrite Nitrogen	Laboratory	mg/l	0.05	0.01	±0.5 (<2.0) ±20% (>2)	± 20%

Parameter	Method/ Range	Units	Detection Limit	Sensitivity	Precision ¹	Accuracy ²
Ammonia Nitrogen	Laboratory	mg/l	0.05	0.01	±0.2 (<1.0) ±20% (>1)	± 20%
Orthophosphate, soluble	Laboratory	mg/l	0.07	0.01	±0.2 (<1.0) ±20% (>1)	± 20%
Total Phosphate	Laboratory	mg/l	0.07	0.01	±0.2 (<1.0) ±20% (>1)	± 20%
Metals	Laboratory	mg/l	0.07	0.01	±0.2 (<1.0) ±20% (>2)	± 20%

¹The precision objectives apply to duplicate and split samples or in-field QC checks. ²Accuracy applies to calibration check samples, laboratory control samples and other measurements of samples of known concentration where the known value is compared against the measured value.

8. Quality Control Procedures

For continuous field measurements, QC will consist of independent measurements made with calibrated handheld instruments. Other quality control exercises will include execution of mass balance analysis by the Modeling Team to identify problem areas and data gaps in the overall analysis of the basin.

Quality control samples will be analyzed to ensure valid data are collected. Depending on the parameter, quality control samples will consist of calibration check standards, laboratory control samples, matrix spikes, and analytical blanks (Table 8.1). In addition, other quality control exercises such as analysis of performance test standards, will be conducted once a year to verify the proper working order of equipment and determine whether the data quality objectives are being met. For most analyses, the QC objectives described in Table 8.1 will apply.

Table 8.1. Analytical Quality Control Samples

QC Type	Definition	Frequency	Used to Evaluate	Limits	Corrective Action
Calibration Check (CC)	Standard solution from the same vendor or source as the calibration curve at a concentration in the center of the calibration curve.	Every analytical batch or at least every 20 samples.	Accuracy Comparability	80 –120% or Table 7.1	Analysis can not proceed unless the CC passes.
Laboratory Control Sample (LCS)	Standard solution from a different vendor or source than that of the calibration check in a clean water matrix.	Every analytical batch or at least every 20 samples.	Accuracy Comparability	80 –120% or Table 7.1	Perform instrument maintenance and prepare new standard solution if necessary.
Matrix spike & Matrix spike duplicate (MS/MSD)	Standard solution with compounds of interest spiked into a representative sample matrix.	Every 40 samples.	Precision Accuracy Comparability	80 –120% or Table 7.1	If LCS passes, result may reflect matrix interference and may be reported with qualification.

QC Type	Definition	Frequency	Used to Evaluate	Limits	Corrective Action
Sample Duplicates (Duplicates)	Replicate or split sample matrix	Every 20 samples.	Precision Comparability	80 –120% or Table 7.1	If LCS passes, result may reflect sample variability and may be reported with qualification.
Surrogate	The addition of a non-occurring substituted compound to the sample matrix.	Inorganics: Not Applicable. Organics: every sample if available.	Precision Comparability	75 –125%	Rerun sample. If second result is not within limits, report with qualifier.
Instrument or Analytical Blank (IB or AB)	Clean water matrix, free of analyte. Analyzed in same manner as samples.	Every analytical batch or at least every 20 samples.	Accuracy		In some cases, target compound values may be subtracted out, in other analyses target compounds present in blank must be flagged as contamination and may not be subtracted out.

For all analyses, calibrations shall be performed in accordance with Method specific SOPs. For Inorganic analyses, calibrations will be performed if duplicate CCs or LCSs are out of compliance or at least every six months. For organic analyses, calibrations must be performed every six months or more frequently if necessary.

Performance check standards of verifiable concentrations shall be purchased at six month intervals to assess laboratory performance in a blind study. This allows the analyst to address any weaknesses and provides a quality check from a third source which is representative of an actual sample composition.

Approximately 5% of unknown samples are run as duplicates. Because the individual who prepares the samples for analysis (filtering & pouring off samples) is different from the individual doing the analytical analysis, all duplicate samples are effectively blind samples. Within an analytical run, we will reanalyze samples if duplicate samples are not within 20% of each other.

9. Method and Instrument Calibration

Instruments will be calibrated and reagents checked against standards. Standards will be purchased from a chemical supply company or prepared. Calibration records will be kept in the laboratory notebooks with the results of analyses. Separate calibration reports will be generated and kept in a calibration binder. Calibrations that are performed by monitors in the field are recorded on the field notebooks which will be archived. The frequency of calibration for field instruments is described in Table 9.1.

We utilize certified quality assurance standards for methods when commercially available. Certified “nutrient” and “minerals” standards containing nitrate, ammonium, and ortho-phosphate will be used in this study. Calibration Check (CC) Standards are run between calibration curves to insure accuracy and precision. For the total N and P methodologies, we digest reference standard to determine the recovery of the inorganic nutrient species.

Working standards are prepared fresh from dilution of a stock solution on at least a monthly basis. Standards are stored in a refrigerator and in the dark. All analytical standards are made from chemicals of known purity. A standard curve is then run from a series of standards which defines the working range of analysis. Where

possible, the standard curve is verified by running the certified reference standard. The standard curve is rejected if it does not determine the values of the certified reference standard within $\pm 10\%$.

Table 9.1 Field Instrument Calibration and Frequency

Conventional Water Quality Parameters		
Equipment Type	Calibration Frequency	Standard or Calibration Instrument Used
Temperature	Every sampling day	NIST calibrated or certified thermometer
Dissolved Oxygen meter	Every sampling day	At a minimum, water saturated air, according to manufacturer's instructions.
pH	Every sampling day	pH 7.0 buffer and one other standard (4 or 10).
conductivity	Every sampling day	Conductivity standard and distilled water.
Turbidity meter (nephelometer)	Every sampling day	High and low expected NTU values (e. g. 1.0 NTU standard and 20.0 NTU standard).
Fluorescence	Every sampling day	Solid standard if available, otherwise check against calibrated laboratory fluorometer. Reported Chl a levels are determined from Chl a measurement calibration curve.

10. Instrument/Equipment Testing, Inspection and Maintenance

A maintenance log is kept for each instrument or group of instruments. This log details the dates of instrument and sampling gear inspection, calibrations performed in the laboratory, battery replacement, the dates reagents and standards are replaced, and any problems noted with instruments, samplers, or reagents.

Before each use, thermometers are checked for breaks in the column. If a break is observed, alcohol thermometers will be placed in nearly boiling water so that the alcohol expands into the expansion chamber, and the alcohol forms a continuous column. In the case of mercury thermometers, the thermometer will be dipped in dry ice or liquid nitrogen to remove break. Electronic thermometers and non-certified thermometers will be verified for accuracy by comparing with a calibrated or certified thermometer.

For Dissolved Oxygen Meters, membranes and solutions should be replaced according to manufacturer's specifications. Membranes should be checked for bubbles after replacement. Before each use, DO meters are checked to see if they are clean and in good working order.

Before each use, conductivity and pH meters are checked to see if they are clean and in good working order. Conductivity and pH meters are calibrated daily or before each use as necessary. Conductivity standards and pH buffers are replaced at least annually. Conductivity standards are stored with the cap firmly in place and in a dry place kept away from extreme heat. Do not re-use pH or conductivity standards (i.e. use a fresh aliquot of standard to calibrate each instrument).

11. Reagent Inspection/Acceptance Requirements

Upon receipt, buffer solutions, standards, and other reagents will be inspected for leaks or broken seals, and to compare the age of each reagent to the manufacturer's recommended shelf-life.

All other sampling equipment will be inspected for broken or missing parts, and will be tested to ensure proper operation.

Before usage, thermometers are inspected for breaks. Breaks can be eliminated by heating or cooling (see Section 10). If not, they will be returned to the manufacturer.

Reagents are replaced before they exceed manufacturer's recommended shelf life. These shelf lives are typically one to two years. However, specific replacement dates can be determined by providing the reagent lot number to the manufacturer. Reagent replacement dates are noted in the equipment maintenance logs and laboratory notebooks.

12. Documentation and Records

All laboratory and field notebooks will be legible and neatly kept. Each page and entry will be identifiable as to date, project, subject, sample or site location, author and other requirements described in the SOP for keeping notebooks and other records.

All field results will be recorded at the time of completion in field notebooks and in field data sheets or instantaneously captured in an electronic form. Field data will be reviewed for outliers and omissions before leaving the sample site. Field technicians will follow a SOP for collection, entry, duplication, distribution, and archiving of field data. Copies of data sheets and relevant notebook pages will be made upon return from each field trip and filed in three ring binders. Field data sheets and notebooks will be stored in hard copy form at Pacific and LBNL. Field data sheets are archived for at least five years from the time they were collected. If data entry is ever performed at another location, duplicate data sheets will be used, with the originals remaining at the headquarters site. Hard copies of all data as well as computer back-up disks are maintained for at least five years. All raw data are held for a minimum of five years.

Upon receipt at the laboratories, samples are recorded in a log that includes project, submitter, sample type/description, storage/preparation needs, and the name of the person who logged the samples. Any lists or additional information sent with the samples are stored with the log (and in a computer in categorized folders if electronic files are sent). Each sample is assigned a unique identification number in a database, which allows us to track it through the various stages of preparation, analysis, data correction, and reporting.

Analytical procedures and results will be recorded in laboratory note books along with records of all calibrations and quality control samples. Laboratory technicians will follow a SOP for collection, entry, duplication, distribution, and archiving of laboratory data. Results from individual analytical runs will be written up in "Data Reports" and results entered in the local database or spreadsheet. Data reports will be stored in notebooks and copies of each data report will be compiled with the COC and filed.

All voucher collections, completed data quality control forms and maintenance logs will also be kept at Pacific and LBNL. The maintenance log details the dates of equipment inspection, battery replacement and calibrations, as well as the dates reagents and standards are replaced.

Flow data and other continuous data will be collected electronically via manual downloads at individual stations, or remotely via SCADA, modem, satellite, or web-based methods. Data will be collected, reviewed, compiled, and organized by project participants according to agreed SOPs for each type of data. Electronic data will be transferred to Pacific and LBNL for archiving.

13. Data Management

All data will be entered in the Field Notebook and a field data sheet (if used). Field data will be entered in spreadsheets or a local database upon return to the technicians home base.

Analytical results will be written directly in laboratory notebooks and also on a laboratory data sheet (if used). The results data will be entered by the analyst into the appropriate spreadsheet or local database. The analyst will identify any results where holding times have been exceeded, sample identification information is incorrect, samples were inappropriately handled, or calibration information is missing or inadequate. The analyst will verify sample identification information, review the chain-of-custody forms, and identify the data appropriately in the database. Stable isotopic data generated at USGS will be integrated with analytical and field data from LBNL, UC Davis, and Pacific using an access database created for that purpose by the DWR-IEP.

The QA Personnel will serve as data management coordinators. QA Personnel will review and archive the field and laboratory notebooks and data sheets. Data will be entered into a spreadsheet (MS Excel) or a database (MS Access) in a way that will be compatible with SWAMP database guidelines. Following initial data entry, QA Personnel will review electronic data, compare to the original data sheets and correct entry errors. After performing data checks, and ensuring that data quality objectives have been met, data will be forwarded to the Modeling Team, the Monitoring Team, and the Specials Studies Team for analysis.

14. Data Review, Validation and Verification

Field and laboratory data sheets or data files are reviewed on an on-going basis by the QA Personnel. At least annually, the Project Participants & Technical Advisors will determine if the data meet the Quality Assurance Project Plan objectives. Mass balance on salt and flow in San Joaquin River models will be used to help assess the accuracy of field data collection by comparing mass balance results between salts, nutrients, and algae. Project Participants & Technical Advisors will identify outliers, spurious results or omissions to the Monitoring Team leader. They will also evaluate compliance with the data quality objectives. They will suggest corrective action that will be implemented by the Monitoring Team leader. Problems with data quality and corrective action will be reported in final reports.

Most data are collected electronically so that data transfer errors are minimized. For those methods requiring hand entry of data, data are verified by graphical and observation techniques to spot outliers. For complete chemistry analysis, we use charge balance and solute/EC relationships to validate concentrations. For long-term monitoring programs, temporal data are plotted to look for inconsistent relationships in the data record. Prior to releasing the data, the laboratory manager/principal investigator independently examines the data.

15. Adaptive Management Plan

The scope of the project, characterization of an entire watershed, requires that the progress of the sampling and analysis program be reviewed to insure that the proper data is being collected and that data gaps are identified and addressed. A major mechanism for assessing data quality and completeness will be through model runs performed by the Modeling Team. The Modeling team is executing water quality models that are closing the mass balance on salt and flow in the SJR. Results of the model runs will help identify regions of the study area where more sampling or better quality control are needed. Additionally, data and analysis from this study will be presented to the DO TMDL Technical Working Group, which meets approximately every two months to review scientific and engineering programs related to resolving DO issues on the SJR. Review by the Technical Working Group will be used to help shape the adaptive management response to close data gaps.

If data do not meet the project's specifications, the following actions will be taken. First, the Project Participants & Technical Advisors will review the errors and determine if the problem is equipment failure, calibration errors, maintenance techniques, monitoring approach, or sampling techniques. They will suggest corrective action. If the problem cannot be corrected by training, revision of techniques, or replacement of supplies or equipment, then the Project Participants & Technical Advisors will review the DQOs and determine if the DQOs are feasible. If the specific DQOs are not achievable, they will determine whether the specific DQO can be relaxed, or if the parameter should be eliminated from the monitoring program. Any revisions to DQOs will be appended to this QA plan with the revision date and the reason for modification. The appended QAPP will be sent to the review panel that approved this plan. When the appended QAPP passes review, the data coordinator will ensure that all data meeting the new DQOs are entered into the database. Archived data can also be entered.

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Appendix A. Map of project study region

