APPENDIX D

Quality Assurance Project Plan (QAPP)

For

Restoration of Riparian Habitat and Assessment of Riparian Corridor Fencing and Other Watershed Best Management Practices on Nutrient Loading and Eutrophication of Crowley Lake, California

Hereinafter referred to as "Crowley Watershed Restoration QAPP"

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Crowley Watershed Restoration QAPP
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QUALITY ASSURANCE AND CONTROL PROCEDURES

An investigation of surface water chemistry requires a strong quality assurance (QA) plan for sampling and analysis. Our QA plan is comprised of rigorous field and laboratory quality control (QC) procedures. We implement a QA program to ensure the integrity of precipitation and surface water samples collected in the field and to produce reliable analytical data for samples analyzed in the laboratory.

Our QA procedures include the following components: Identical instruments are used and adherence to standardized data collection procedures and field protocols are emphasized with the field staff at all sites. Procedural variability in the field is assessed by replicate samples and by means of field blanks. In the laboratory, blanks include deionized water processed through plastic bottles, filters, and buckets, which assess contamination.

FIELD METHODS

Tributary Sampling

All apparatus and bottles used in surface water sampling are soaked in deionized water (DIW) for several days and then rinsed 4 times with DIW. Our experience has shown that acid washing does little to clean the bottles and increases the risk of sample contamination. Filtered samples are filtered in the field with plastic syringes fitted with Gelman A/E filters (1 micron) which are rinsed with at least 150 ml of sample water. For the biweekly sampling all samples with the exception of Benton Crossing are "grab" samples taken at a well-mixed location in the stream such as the outlet of a culvert. Samples at Benton Crossing will be integrated across the river with a DH-48 sampler. During longitudinal sampling a decision will be made at each field location as to the uniformity of samples collected. If there is any consideration of mixing problems, such as immediately downstream of Big Springs, the integrating sampler will be used. Two field blanks are also prepared each sampling trip. These consist of DIW carried into the field and filtered and treated exactly like a sample. Samples are kept cool and in the dark during transport. For long-term storage, samples are frozen.

Dissolved oxygen (DO) and temperature will be measured at each sampling location using a YSI Model 57 meter with combination DO and temperature probe

Lake Sampling

The approximate locations of five sampling locations have been identified in the Scope of Work. Stations are located in each major section of the lake and vary in depth between 8 and 25 m. On the first lake sampling date, final locations will be selected and locations recorded by GPS. GPS will be used on subsequent sampling trips to relocate sampling locations within 25 m.

In situ profiles of water temperature, conductivity, dissolved oxygen, and photosynthetically available light will be determined at each station at 1-m intervals. Temperature and conductivity will be measured with a high-precision, conductivity-temperature-depth profiler (CTD) (Sea-Bird Electronics, model Seacat SBE 19). The CTD is deployed with a free-fall rate of ~0.25–0.35 m s^{-1} and records temperature and conductivity every 0.5 seconds. The CTD sensors are very stable and are calibrated once per year by Sea-Bird Electronics. In situ light will be measured with a LI-COR light meter (model LI-250) equipped with a submersible PAR light sensor (LI-COR, model LI-192S). Dissolved oxygen concentration will be measured with a Yellow Springs Instrument temperature-oxygen meter (YSI, model 58) and probe (YSI, model 5739). The LI-COR meter and sensor are calibrated annually by LI-COR Inc and while a saturated air calibration is conducted prior to each use in the field the oxygen electrode will also be calibrated annually against Miller titrations of Crowley Lake water (Walker *et al.* 1970). In addition to the in-situ light profiles, water transparency will also be assessed using a 20-cm Secchi disk.

Samples collected for the analysis of nutrient fractions will be treated identically to those collected from the tributaries (see above). Samples for chlorophyll *a* analysis will be filtered through a 120-micron net filter to remove macrozooplankton and kept cool and in the dark during transport to the laboratory. Zooplankton samples will be collected with a plankton net (1 m x 0.30 m diameter, 120 μm Nitex mesh) towed vertically through the water column and immediately preserved with 5% formalin in lake water.

MTBE

Babcock Laboratories of Riverside, California will perform MTBE analyses. Prior to each lake sampling date, for each sampling location on the lake, Babcock will provide two 40-ml sample tubes containing small amounts of HCl, and a 40-ml field blank tube containing acidified DIW. At each sampling location the tube is held under the surface of the lake by hand and the cap is removed underwater allowing the tube to fill. The tube is recapped immediately with no airspace. The field blank is carried along on the sampling trip but otherwise not uncapped or handled. All sample tubes will be shipped the same day or the next day to Babcock. All analyses will be performed within 9 days of sampling. Babcock will employ EPA Method 8260A for analysis with a reporting limit of 1 ppb of MTBE. As MTBE use in California is being discontinued it is not anticipated that these results will be used for regulatory action. Therefore, no chain-of-custody will be required.

Atmospheric Sampling

Precipitation is measured at SNARL using a tipping-bucket rain gauge (Qualimetrics model 6011-B) connected to a solid-state data logger. The Los Angeles Department of Water and Power also measure precipitation at the Crowley Lake Dam. Precipitation samples are collected in polyethylene buckets using an Aerochemetrics wet/dry collector. Dry fall atmospheric inputs will be measured biweekly during the summer and monthly during the winter. Dry fall sampling buckets will be rinsed with 60 ml of DIW and analyzed for ammonium, SRP, nitrate, pH, and conductivity.

Stream Gauging

For the nutrient budget we will be relying on stream gauging data provided by the Los Angeles Department of Water and Power. All of the major tributaries have been gauged for upwards of 60 years with permanent flumes and stage recorders. For Hilton Creek, where the biweekly sampling is taking place at a location where the stream is divided, staff gauges will be installed below the highway in the 4 major channels. Rating curves for the staff gauges will be developed using a velocity-area method (Gore, 1996) employing a Marsh McBurney stream velocity meter.

For the longitudinal surveys stream gauging will take place at each sampling location to allow discrimination of dilution effects. Gauging will be done using a velocity-area method employing a Marsh McBurney stream velocity meter.

LABORATORY METHODS

For the purposes of this project DIW will be used to refer to filtered, deionized, reverse osmosis treated water. This is our primary washing and rinse water with a specific conductance of approximately 5 μS cm^{-1}. For reagent and standard preparation this water is further polished by ion exchange to a specific conductance of approximately 0.5 μS cm^{-1}.

Immediately following sample collection samples will be transported cold and in the dark to the Sierra Nevada Aquatic Research Laboratory for processing and analysis. pH measurements are done on unfiltered subsamples immediately upon return to the laboratory using a Fisher Acumet digital pH meter and Ross (Orion) combination electrode. The meter is calibrated in a two-point calibration with NRS-traceable buffers near room temperature. After calibration the accuracy of the calibration is checked using dilute solutions of HCl (10^{-4} and 10^{-5} N). The electrode is then rinsed with stirred DIW for several minutes before the pH of the quiescent sample is measured. Specific conductance of unfiltered subsamples are measured on a YSI Model 32 digital conductance meter (cell constant=1.0) corrected to 25°C. A 10^{-4} M KCl conductivity standard, which has a theoretical specific conductance of 14.7 μS cm^{-1} at 25°C is measured at the beginning of each laboratory session.

NH_4, SRP, and As will be analyzed on each duplicate field sample on the same day as collection. Remaining filtered field samples will be frozen and analyzed for NO_3 within two months of collection. Unfiltered samples for TN, TP , TDN, TDP, particulate P, and particulate C,H,N will be frozen upon return to the laboratory and kept frozen until analysis within two months of collection. TN, TP, TDN, and TDP may be analyzed in our laboratory at UCSB. If this is the case, frozen samples will be transported by car to UCSB and analyzed by one of our project staff who will transport them. The samples will never be out of our control and no chain-of-custody will be required. Table 1 shows the method employed and the detection limit for each nutrient analysis. Detection limits are reported as two times the standard deviation of replicate analyses. Detection limits for total and total dissolved fractions are more variable because of the digestion step.

Table 1 –Methods for Nutrient Analysis

Species	Method	Reference:	Detection Limit (μM)
NH_3+NH_4^+	phenol-hypochlorite colorimetric	Wetzel and Likens, 1991	0.30
SRP	phospho-molybdate colorimetric	Wetzel and Likens, 1991	0.06
NO_3	Cd reduction followed by azo dye colorimetric	Wetzel and Likens, 1991	0.20
TP	Valderrama (oxidation/phospho-molybdate)	Valderrama, 1981	0.4
TN	Valderrama (oxidation/Cd reduction/azo dye)	Valderrama, 1981	0.4
TDN	Valderrama (oxidation/Cd reduction/azo dye)	Valderrama, 1981	0.4
TDP	Valderrama (oxidation/phospho-molybdate)	Valderrama, 1981	0.4
As	As(V)→As(III) reduction/phospho-molybdate	Johnson, 1971	0.02
MTBE	EPA Method 8260A	EPA Manual SW846	1 ppb

We also employ independent (external) checks on the accuracy of our chemical analyses. Routine analyses of standard reference materials (SRM) from the National Bureau of Standards (NBS) and the U.S. Environmental Protection Agency (EPA) are performed. The SRM was synthetic rain-water with certified concentrations for major cations and anions. Another independent check on our chemical data involves participation in the U.S. Geological Survey's Analytical Evaluation Program and Environment Canada's LTRAP Audit. These are regular audits that test the quality and accuracy of the analytical procedures used in laboratories throughout the U.S. and Canada. These agencies distribute water samples to participating laboratories and participants submit their results to these agencies and are assigned a score based on how close their results come to the mean value obtained from all participants. Our laboratories have always scored well (good to excellent ratings) in these audits.

Upon return to the laboratory, chlorophyll samples will be filtered onto 47 mm Gelman A/E filters and kept frozen until the pigments are analyzed. Chlorophyll *a* concentrations will then be determined by acetone extraction and spectrophotometric absorption (Wetzel and Likens 1991).

Phytoplankton and zooplankton identification and relative composition will be determined by standard microscopy methods (Wetzel and Likens 1991) employing inverted and dissecting scopes and appropriate keys, respectively.

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