

UC Davis - US Forest Service Grazing Allotment Water Quality Monitoring Quality Assurance Project Plan (QAPP)

Submitted by:

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Background/Objective

There is substantial concern that microbial and nutrient pollution by cattle on public lands degrades water quality, threatening human and ecological health. Given the importance of clean water on multiple-use landscapes, additional research is required to document and examine potential water quality issues across common resource use activities. During the 2011 grazing-recreation season, we will conduct a cross sectional survey of water quality conditions associated with cattle grazing and/or recreation on 12 public lands grazing allotments in California. Our specific study objectives are to 1) quantify fecal indicator bacteria (FIB; fecal coliform and *E. coli*), total nitrogen, nitrate, ammonium, total phosphorus, and soluble-reactive phosphorus concentrations in surface waters; 2) compare results to a) water quality regulatory benchmarks, b) recommended maximum nutrient concentrations, and c) estimates of nutrient background concentrations; and 3) examine relationships between water quality, environmental conditions, cattle grazing, and recreation.

Water Sample Collection

Sample collection will be conducted by UC Rangelands staff and/or US Forest Service staff. All participants will be trained in sample collection (e.g., bottle labeling, sample handling, data recording) to assure consistency and data quality. A standard data collection sheet will be used.

On the day of sampling, at each sample site planned for that day, a single 500 mL water sample will be collected with a sterile plastic bottle in the morning and delivered to the appropriate laboratory location within 6 hours of collection time.

UC Laboratory Locations

- UC Rangelands Laboratory, UC Davis, Room 1223, Plant and Environmental Sciences Building (PES), University of California, Davis, (530) 754-8766

Field Water Sample Collection Protocol

1. Travel to the farthest sample site (in terms of time) from the laboratory location and work back from there.
2. At each site:
 - a. Label 250 mL sample bottle with sample site ID, and date and time of sample collection.
 - b. Record sample site ID, date and time of collection, and any notable observations at time of collection on the chain of custody form.
 - c. Collect sample using methods described in section 7.1 Fecal Indicator Bacteria of the National Field Manual for the Collection of Water Quality Data (https://water.usgs.gov/owq/FieldManual/Chapter7/7.1_ver2.1.pdf). Refer to the point-sampling methods section on page 26 which describes how to collect a hand-dipped sample.
 - i. Collect sample from a well-mixed area of the main reach of the stream.
 - ii. Minimize sediment disturbance during collection.
 - iii. Fill the 250 mL sample bottle allowing 2 to 3 cm of headspace.
 - iv. Tightly recap sample bottle.
 - v. Place bottle on ice in cooler.
 - vi. Note any relevant observations on chain of custody form (e.g., high stream flow, water turbidity, livestock present, or presence of recreation).
 - vii. If you have to sample stagnant, non-flowing pools (if the stream has stopped flowing at the sample site), take the sample and note that the site is stagnant on the chain of custody form.
3. If any site is not collected for any reason, note that it was not collected and a detailed reason (e.g., vehicle emergency, road was impassible, site dry, etc.) on the chain of custody form.

4. Deliver sample to laboratory location within 6 hours of collection time.
5. Document sample handoffs on the chain of custody form.

Monitoring and Analysis Objectives

Table 1 lists the constituents which will be measured at all sample sites during the summer grazing-recreation season of 2011. We anticipate sample collection to commence in May 2011 and end in November 2011. Sample frequency will be monthly. Standard accepted methods were used to collect and analyze water samples.

Table 1: Constituents to be monitored and respective methods of determination.

Parameter	Method
Fecal Coliform, Total	SM 9222 D: Membrane Filter Technique for Members of the Coliform Group
<i>E. coli</i>	SM 9222: Direct Membrane Filtration with CHROMagar <i>E. coli</i> , CHROMagar Microbiology
Total Nitrogen	Yu, Z.S., R.R Northrup; R.A. Dahlgren. 1994. Determination of Dissolved Organic Nitrogen using Persulfate Oxidation and Conductimetric Quantification of Nitrate-Nitrogen. Communications in Soil Science and Plant Analysis. 25:3161-3169. Total nitrogen (non-filtered sub sample) is determined as nitrate, using the Griess reagent method following persulfate oxidation.
Nitrate	Doane, T.A. and Horwath, W.R. 2003. Spectrophotometric Determination of Nitrate with a Single Reagent. Analytical Letters. 36:2713-2722. Spectrophotometric method based on Griess reagents for a filtered sub-sample.
Ammonium	Verdouw, H; van Echteld, C.J.A.; Dekkers, E.M.J. 1977. Ammonia Determination Based on Indophenol Formation with Sodium Salicylate. Water Research. 12:399-402. Spectrophotometric method based on a reaction of filtered sub-sample with phenol and hypochlorite, in which a blue colored indophenol is formed.
Total Phosphorus	SM 4500-P.D: Stannous Chloride Method on unfiltered sub-sample.
Phosphate	SM 4500-P.D: Stannous Chloride Method on filtered sub-sample.

Laboratory Quality Control

Accuracy describes how close the measurement is to its true value. Accuracy is the measurement of a sample of known concentration and comparing the known value against the measured value. The accuracy of chemical measurements will be checked regularly. A standard is a known concentration of a certain solution. Standards can be purchased from chemical or scientific supply companies. The concentration of the standards should be within the mid-range of the equipment. All field and laboratory instrumentation will be calibrated to manufactures specifications twice a year. Accuracy for bacteria will be determined by analyzing a positive control sample twice annually. A positive control is similar to a standard, except that a specific discreet value is not assigned to the bacterial concentrations in the sample. This is due to the fact that bacteria are alive and capable of mortality and reproduction. Instead of a specific value, an approximate target value of the bacterial concentration is assigned to the sample by the laboratory preparing the positive control sample.

Comparability is the degree to which data can be compared directly to similar studies. To insure comparability of the results of this project with others, we will be using standardized methods and/or peer-reviewed published scientific methods for all constituents.

Completeness is the fraction of planned data that must be collected in order to fulfill the statistical criteria of the project. Volunteer data will not be used for legal or compliance uses. There are no statistical criteria that require a certain percentage of data. However, it is expected that 80% of all measurements could be taken when anticipated. This accounts for adverse weather conditions, safety concerns, and equipment problems. We will determine completeness by comparing the number of measurements we planned to collect compared to the number of measurements we actually collected that were also deemed valid. An invalid measurement would be one that does not meet the data quality objectives. Completeness results will be checked monthly. This will allow us to identify and correct problems.

Precision describes how well repeated measurements agree, assuming that the constituent of concern is uniformly distributed between the duplicate samples. The evaluation of precision for all field and laboratory determined constituents will be determined

twice a year from repeated measurements taken by either different staff on the same sample or the same staff analyzing split samples. Precision for bacterial parameters will be determined by having the same analyst complete the procedure for laboratory duplicates of the same sample. At a minimum this should be done once per lab batch, or run duplicates on a minimum of 5% of the samples if there are over 20 samples run per lab batch. The results of the duplicates should be within the 95% confidence limit of its pair. The 95% confidence limit for raw plate counts are obtained from Standard Methods 9222 Table 9222.II and section 6.c.

Representativeness describes how relevant the data are to the actual environmental condition. The technical advisory personnel will actively participate in sample design development, training, and assessment of representativeness of the resulting data. Bias (lack of representativeness) can occur if:

- Samples are taken in a stream reach that does not describe the area of interest (e.g., below agricultural source sample is collected below a city and the agricultural source),
- Samples are taken in an unusual habitat type (e.g. a stagnant backwater instead of in the flowing portion of the creek),
- Samples are not analyzed or processed appropriately, causing conditions in the sample to change (e.g. bacteria concentrations not determined within 24 hours of collection).

Representativeness and resulting bias will be controlled via appropriate sample sites selection and sample collection (as described in this document and the project’s Monitoring Plan.

The Method Detection Limit is the lowest possible concentration the instrument or equipment can detect. This is important to record because we can never determine that a pollutant was not present, only that we could not detect it. Sensitivity is the ability of the instrument to detect one concentration from the next. Detection Limits and Sensitivities are noted in Table 2.

Table 2: Data quality objectives for project constituents

Parameter	Units	Detection Limit	Sensitivity	Precision	Accuracy	Completeness
Fecal Coliform, Total	cfu/100 ml	1	1	Split sample within 95% confidence limit of the other*	Split positive spike within 0.7 log ₁₀ of expected value	80%
<i>E. coli</i>	cfu/100 ml	1	1	Split sample within 95% confidence limit of the other*	Split positive spike within 0.7 log ₁₀ of expected value	80%
Total Nitrogen	mg/l	0.02	0.01	±0.2 (<2.0) ±20% (>2)	±0.2 (<2.0) ±20% (>2)	80%
Nitrate	mg/l	0.01	0.005	±0.2 (<2.0) ±20% (>2)	±0.2 (<2.0) ±20% (>2)	80%
Ammonium	mg/l	0.01	0.005	±0.2 (<2.0) ±20% (>2)	±0.2 (<2.0) ±20% (>2)	80%
Total Phosphorus	mg/l	0.005	0.002	±0.2 (<2.0) ±20% (>2)	±0.2 (<2.0) ±20% (>2)	80%
Phosphate	mg/l	0.005	0.002	±0.2 (<2.0) ±20% (>2)	±0.2 (<2.0) ±20% (>2)	80%

Training Requirements

All UC and USFS staff will be fully trained on all aspect of their duties associated with sample collection and laboratory analysis. Trainings will occur on-site in the field and laboratory in a hands-on approach. Project staff will conduct multiple collections and analyses and meet the data quality objectives described above. Field and laboratory safety training will also be conducted monthly (<http://ehs.ucdavis.edu>).

Documentation and Records

Documents and records we expect to generate from this project include: field data sheets, a laboratory notebook (raw laboratory data, duplicate results, etc.), and chain of custody forms, and final data spreadsheets. Hard copies of all documentation and records will be stored in Room 1231 Plant and Environmental Sciences Building, UC Davis Campus, Davis, CA. All electronic copies of documentation and records, including data, will be stored on nightly backed up computers in 1231 Plant and Environmental Sciences Building. All documents and records will be made available for review by NCRWQCB and United States Forest Service representatives upon request, and in a reporting format appropriate to address the request. In general, data will be reported in tabular and graphical format with accompanying interpretive text.

All field data will be recorded at the time of collection using field data sheets. Field data sheets will be reviewed for outliers and omissions before leaving the field site. Field data sheets will again be reviewed and finally approved upon entry into the local database or spreadsheet. Upon collection, each water sample is assigned a unique identification number, which allows us to track it through the various stages of handling, preparation, analysis, data correction, and reporting. Analytical procedures and results will be recorded in a laboratory notebook along with records of all quality control samples. Results from individual analytical runs will be recorded in a laboratory notebook and entered in a spreadsheet (M.S. Excel). Field data sheets and laboratory notebooks are archived for 10 years. If data entry is ever performed at another location, duplicate data sheets will be used, with the originals remaining at the headquarters site. A chain of custody form will accompany each set of samples collected by an individual field data collector on each collection date, and will be stored in the laboratory notebook.

Instrument/Equipment Testing, Inspection and Maintenance

A maintenance log is kept for each instrument used in the study. The log details the dates of instrument and sampling gear inspection, calibrations performed in the laboratory, battery replacement, and any problems noted with instruments. Crucial spare parts for all equipment will be maintained at the appropriate work site (laboratory or field kit). Any problems identified with equipment will be corrected by the field data collectors, or laboratory analysts. If the problem cannot be corrected, the item will be returned to the manufacturer.

Inspection/Acceptance Requirements

All required reagents, equipment, or other supplies required for this project will be purchased new from reputable commercial sources (e.g., Fisher Scientific, Inc.). Upon receipt, reagents will be inspected by the project staff for leaks or broken seals, and will compare the age of each 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. Field data collectors are responsible for field equipment and standards, while laboratory analysts are responsible for laboratory items.

Data Management

All data and measurements for this project will be made directly by project staff following the project monitoring plans for each National Forest, and will meet the requirements detailed in this QAPP. Field data sheets are checked in the field by the field sample collection staff. Sample identification information and the chain-of-custody forms will be reviewed by project staff. Working with field and laboratory staff, the data manager will identify any results where sample holding times (8 hours) have been exceeded, sample identification information is incorrect, samples were inappropriately handled, or data quality objectives were not met. The data manager will bring such data to the attention of project leader for review, and will be "flagged" upon entry into the project spreadsheet.

The data manager will oversee the entering of data with the supervision of the project leader. Upon entering the data the data manager will archive the field data sheets. Data will be entered into a spreadsheet (MS Excel) compatible with CEDEN data reporting requirements. All electronic files will be stored on a computer which is automatically backed-up nightly. Following initial data entry the data manager will review electronic data, compare to the original field data sheets/laboratory notebooks and correct entry errors. After performing data checks and ensuring that data quality objectives have been met, data analysis will be performed to achieve the objectives of the project.

Assessment and Response Actions

Review of all field, laboratory, and data management activities is the responsibility of the project leader and the laboratory manager. The project leader and laboratory manager have authority to stop work if problems are found and implement corrective actions as required. All assessment information as well as corrective actions implemented will be reported to the project leader and laboratory manager. Training (as described above) will be utilized to correct any problems with data quality attributable to staff's implementation of procedures described above. Retraining will be scheduled as frequently as required to meet data quality objectives. All field and laboratory activities, field data sheets, laboratory notebooks, as well as maintenance logs may be reviewed as requested.

The project leaders are always actively engaged in the daily management of project staff, thus providing a continuum of oversight and assessment throughout the project. Field staff oversight will be the direct responsibility of the project leaders. Oversight and assessment of field staff performance and resulting data quality will occur in the field during at least 5% of the sample collection events conducted during the project. Field staff in need of performance improvement will be retrained on-site. The laboratory manager will be directly responsible for oversight and assessment of laboratory analysts. Oversight and assessment of laboratory staff performance and resulting data quality will occur in the laboratory during at least 5% of the sample analysis events conducted during the project.

Data Review, Validation and Verification

Data review, validation, and verification for this project will follow the guidelines provided by USEPA (2002, "Guidance on Environmental Data Verification and Data Validation", EPA QA/G-8, <http://www.epa.gov/quality/qs-docs/g8-final.pdf>). The project staff will collaborate on 2 data review, validation, and verification sessions per year. The project leader has final authority on data acceptance. They will also evaluate compliance with the data quality objectives as described above.