Sierra Nevada Network Lake Monitoring Protocol

SOP 4. Quality Assurance Project Plan (QAPP)

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Prepared by Andrea M. Heard and James O. Sickman

Revision History Log

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1. Introduction

The Sierra Nevada Network's (SIEN) Quality Assurance Project Plan (QAPP) follows the State of California's Surface Water Ambient Monitoring Program's (SWAMP) QAPP guidelines. The Sierra Nevada Network, by adhering to SWAMP's QAPP criteria, strives to insure SIEN Lake Monitoring data are compatible with the SWAMP program. This QAPP also meets the National Park Service-Water Resources Division quality assurance and quality control requirements (Irwin 2006).

We would like to acknowledge Roy Irwin for his detailed guidance described in Part B Lite (Irwin 2006). Significant portions of this QAPP were adapted from three other monitoring programs. The Network wishes to acknowledge these sources:

- Cooprider, M. 2004. Quality Assurance Project Plan for the San Francisco Bay Area Network Water Quality Monitoring Program. U.S. Department of the Interior, National Park Service. 32 pages.
- O'Ney, Susan. 2005. Standard Operating Procedure #7: Quality assurance/quality control procedures, Version 1.0. *In*: Regulatory water quality monitoring protocol, Version 1.0, Appendix E. Bozeman (MT): National Park Service, Greater Yellowstone Network.
- Pucket, M. 2002. Quality Assurance Management Plan for the State of California's Surface Water Ambient Monitoring Program (SWAMP). California Department of Fish and Game, Monterey, CA. Prepared for the State Water Resources Control Board, Sacramento, CA. 145 pp.

1.1. Distribution List and Contact Information

The Quality Assurance Project Plan (QAPP) is to be distributed to and retained by the Network's Physical Scientist (Lake Protocol Lead), Coordinator, and Data Manager and park staff that comprise the Water Resources Working Group (Table SOP 4.1).

Table SOP 4.1. QAPP distribution list.

Name	Affiliation
Andi Heard, Physical Scientist	Sierra Nevada Network
Alice Chung-MacCoubrey, Network Coordinator	Sierra Nevada Network
SIEN Data Manager	Sierra Nevada Network
Danny Boiano, Aquatic Ecologist	Sequoia/Kings Canyon National Parks
Annie Esperanza, Air Quality Specialist	Sequoia/Kings Canyon National Parks
Jim Roche, Hydrologist	Yosemite National Park
Harold Werner, Wildlife Ecologist	Sequoia/Kings Canyon National Parks

1.2. Project and Task Organization

Sierra Nevada Lake Monitoring is one of several long-term monitoring protocols for the Sierra Nevada Network (SIEN), Inventory and Monitoring Program (I&M). The individual responsible for managing the Lake Monitoring protocol, the Protocol Lead, is the Sierra Nevada Network Physical Scientist (Table SOP 4.2 and Figure SOP 4.1). Long-term implementation, which includes data collection, management, analysis, reporting, and information dissemination, will primarily be the responsibility of SIEN personnel with assistance from Yosemite and Sequoia and Kings Canyon National Parks and National Park Service-Water Resources Division. The Water Resources Work Group, which has been very active in advising and contributing to protocol development, will continue to be involved in decisions and monitoring implementation.

Table SOP 4.2. Project roles and responsibilities.

Name	Roles and Responsibilities
Physical Scientist (SIEN)	Protocol lead: Oversee collection of monitoring data and data management; analyzes data; write reports; maintain and coordinate any revisions for the protocol, including QAPP
Water Working Group (SEKI and YOSE)	Water Resources Work Group: Provide technical guidance; coordinate with protocol lead on park-level logistics; assist in disseminating information as appropriate; provide review and evaluation.
Network Coordinator (SIEN)	Program Lead: Coordinate with protocol lead on I&M program-level requirements (e.g. reporting, education/outreach) and integrating lake monitoring with the Vital Signs Program.
Data Manager (SIEN)	QA and Data Manager: Coordinate with protocol lead on I&M program-level data management requirements; assist with data collection processes and validation; upload database to NPS-WRD and CEDEN; provide technical support for database and data analysis procedures
Hydrologist (NPS-WRD)	Advisory role/technical assistance
Logistics Technician (SIEN)	Provide logistical support for field sampling; adhere to QAPP when organizing or conducting field sampling
Field Crews (SIEN)	Conduct field sampling and data entry in accordance with protocol and QAPP procedures.

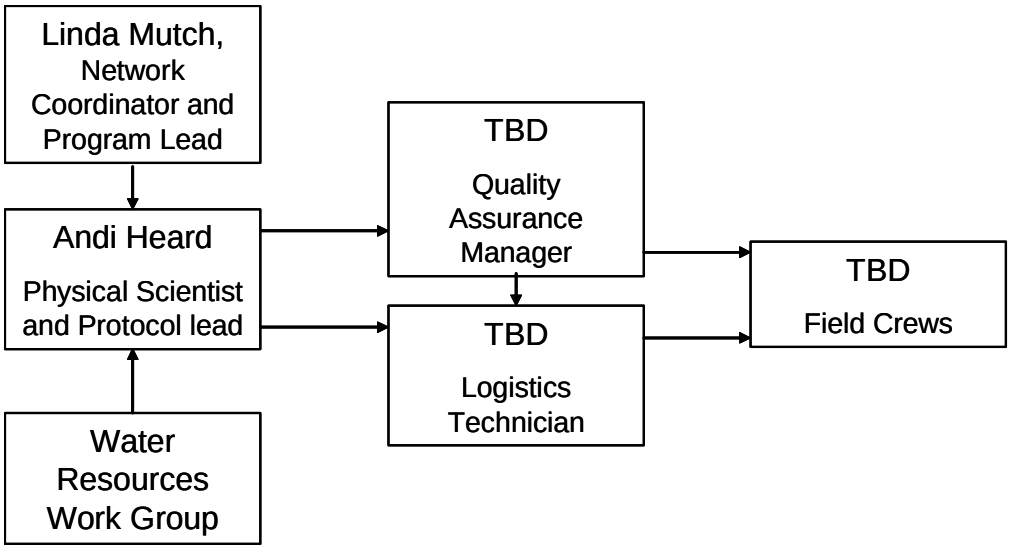

Figure SOP 4.1. Organizational chart showing lines of project management and reporting responsibilities under the QAPP.

1.3. Problem Definition and Background

National Park Service (NPS) Management Policies (National Park Service 2001) and recent legislation (National Parks Omnibus Management Act of 1998) require that park managers know the condition of natural resources under their stewardship and monitor long-term trends in those resources in order to fulfill the NPS mission of conserving parks unimpaired. The federal Clean Water Act and California's Porter-Cologne Water Quality Control Act, direct agencies to protect and enhance California's water resources. The NPS has developed an Inventory & Monitoring program to fill in knowledge gaps in baseline data about natural resources in parks and to design and implement long-term monitoring of vital signs that will enable managers to develop broad-based, scientifically sound information on the current status and long term trends in the composition, structure, and function of park ecosystems.

To improve the efficiency of an inventory and monitoring program, the NPS created networks of parks that are linked by geography and shared natural resource characteristics. There are 32 networks nationwide. The Sierra Nevada Network includes the following NPS administered units in California: Devils Postpile National Monument, Sequoia and Kings Canyon National Parks, and Yosemite National Park, all located on the west slope of the Sierra Nevada.

Sierra Nevada Network parks protect over 4,500 lakes and ponds, numerous other ephemeral water bodies, and thousands of kilometers of rivers and streams that have some of the highest water quality in the Sierra Nevada. High-elevation lakes are critical components of the parks' ecosystems, popular visitor destinations, and habitat for aquatic and terrestrial organisms including declining amphibian species. Lake ecosystems were selected for monitoring because they are valued for their ecological importance, recreational opportunities, and importance to regional water supplies. Moreover they are threatened by multiple stressors, and are sensitive to change. Lakes are habitat for two amphibian species that are candidates for listing as endangered under the federal Endangered Species Act—Sierran yellow-legged frog and Yosemite toad.

The Sierra Nevada Network Lake Monitoring protocol monitors status and trends in lake water chemistry, hydrology, and amphibians in Sequoia, Kings Canyon, and Yosemite National Parks. The I&M program strongly emphasizes data management and dissemination of information. Park managers and scientists are the primary users of these data. Information will be used to manage park natural resources, educate the public about the ecological condition of the parks, and meet government reporting requirements. Data and information are made available to researchers, state and federal agencies, and the public.

1.4. Project and Task Description

Monitoring objectives are broken into two Tasks: 1) monitoring of "Extensive Lakes", which are set of 76 low intensity monitoring sites sampled at a broad spatial scale and 2) monitoring of "Index Lakes", which are a set of four lakes sampled more intensively. The target population from which our sample lakes are randomly selected includes all Sierra Nevada Network lakes. Lakes are defined as water bodies greater than or equal to 1 ha in surface area *and* greater than or equal to 2 m at maximum depth. Four index sites were judgmentally selected from the target population and include: Emerald Lake (Sequoia), an un-named lake in Dusy Basin (Kings Canyon), Maclure Lake (Yosemite), and an unnamed lake below Kuna Peak (Yosemite). *Please refer to the protocol narrative for a map of the target population and index sites.*

The Sierra Nevada Network's monitoring objectives are:

1.4.1. Task 1, Extensive Lakes

- Detect long-term trends in lake water chemistry for Sierra Nevada Network lakes by measuring:
    - Temperature, pH, specific conductance, dissolved oxygen, acid neutralizing capacity (ANC)
    - Major ions: Ca, Na, Mg, K, Cl, SO_4
    - Dissolved inorganic nitrogen (DIN), dissolved organic nitrogen (DON), total dissolved nitrogen (TDN), particulate nitrogen (PN), total nitrogen (TN)
    - Total dissolved phosphorus (TDP), particulate phosphorus (PP), total phosphorus (TP)
    - Particulate carbon (PC)

- Detect long-term trends in trophic condition of SIEN lakes, using the following nutrient ratios as chemical indicators of trophic status: PN:PP, DIN:TP, and TN:TP.
- Characterize Sierra Nevada Network lakes
- Determine the proportion of Sierra Nevada Network lakes with chemical characteristics above/below threshold values for selected constituents.

1.4.2. Task 2, Index Sites:

- Detect intra- and inter-annual trends in lake water chemistry for Sierra Nevada Network index lakes by measuring:
    - Temperature, pH, specific conductance, dissolved oxygen, acid neutralizing capacity
    - Major ions: Ca, Na, Mg, K, Cl, SO_4

  - Dissolved inorganic nitrogen, dissolved organic nitrogen, total dissolved nitrogen, particulate nitrogen, total nitrogen
  - Total dissolved phosphorus, particulate phosphorus, total phosphorus
  - Particulate carbon

- Detect long-term trends in trophic condition of index sites, using the following nutrient ratios as chemical indicators of trophic status: PN:PP, DIN:TP, and TN:TP.
- Characterize Sierra Nevada Network index site outlet flows.
- Determine if index sites are above/below threshold values for selected constituents.
- Detect intra- and inter-annual trends in lake level and outflow for Sierra Nevada Network index sites.

Note: Ammonium ion concentrations will not be assessed in water samples because of expected delays collecting water samples from remote lakes and previous studies indicating that ammonium levels are virtually always at or below the MDL for ammonium.

1.4.3. Schedule

Lake protocol development occurred in concert with the Vital Signs Monitoring Plan over a several year period. The protocol will be peer-reviewed during fall/winter 2007-2008 (Table SOP 4.3). Sampling begins in summer 2008 and, in the spirit of long-term monitoring, is expected to continue indefinitely. Program personnel will produce annual summary reports and a comprehensive synthesis and trend analysis report every four years. Protocol implementation success will be thoroughly reviewed by Network staff, the Water Work Group, and Science Committee following the first field season. Thereafter, the program will be formally reviewed and evaluated every 5 years, starting in FY13.

Table SOP 4.3. Long-term monitoring timetable.

Event	**FY07**	**FY08**	**FY09**	**FY10**	**FY11**	**FY12**	**FY13**	**FY14**
Develop protocol and QAPP	X							
Finalize protocol and peer-review		X						
Collect monitoring data		X	X	X	X	X	X	X
Initial review after first field season			X					
Produce annual summary report			X	X	X	X	X	X
Produce comprehensive synthesis and trend report						X		
Program review and evaluation							X	

Index lakes are sampled once per month from approximately May-October (actual dates are dependent on accessibility and timing of the spring flows) (Table SOP 4.4). Data are collected at extensive sites every year in August and September; however, with the rotating panel design individual sites are sampled every one or three years (*see protocol narrative for sample design, including description of the rotating panel design*). Data analysis and reporting are completed during the winter and early spring months.

Table SOP 4.4. Monitoring—monthly schedule.

Event	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep
End of season wrap-up	■											
Field data entry	■											
Lab results received						■						
Data analysis/reporting					■	■	■					
Pre-season field prep							■	■				
Index site sampling									■	■	■	■
Extensive site sampling											■	■

1.5. Quality Objectives and Criteria for Measurement Data

Adapted from O'Ney (2005).

Data quality objectives (DQOs) specify the kinds of data needed to fulfill the objectives of a water quality monitoring project. They ensure that the data collected will provide adequate information for making a decision. They require careful consideration during the planning and design of a sampling program (sampling site selection, sampling frequency, duration of sampling, water quality variable selection, etc.). The following are general DQOs for SIEN lake monitoring:

- All data shall be of a known and documented quality. The level of quality required for each specific monitoring project shall be established during the initial planning stages of the project and will depend upon the data's intended use. Two major measurements used to define quality are accuracy and precision.
- All data shall be comparable. Data shall be produced in a similar and scientific manner. The use of the standard methodologies for sampling, calibration, auditing, etc., found in the protocol narrative and accompanying Standard Operating Procedures (SOPs) should achieve this goal.
- All data shall be representative of the parameters being measured with respect to time, location, and the conditions from which the data are obtained. The use of the standard methodologies contained in the SOPs should insure that the data generated are representative.

- The protocol narrative and the SOPs must be dynamic to continue to achieve their stated goals as techniques, systems, concepts, and project goals change.

Specific measurement quality objectives (MQOs) were identified *a priori* and revised in the first years of implementation. These include target method detection limits (MDL), minimum level of quantitation (ML), method quantitation limits (MQL), and alternative measurement sensitivity (AMS). Precision, bias, completeness and representativeness objectives were also identified. These objectives were considered when selecting field measurement equipment and contract laboratories for chemical analyses. Detection condition definitions are:

Method detection limit is the minimum level of analyte that can be detected with 99% confidence that the analytical response is greater than zero. Defined as 2 SD above minimum quantifiable signal. The MDL is calculated using EPA methods.

Minimum level of quantitation is the level of analyte that can be routinely detected and quantified in a real matrix without qualification. Defined as 8 SD above minimum quantifiable signal or as 3.18x the MDL.

Method quantitation limit is the lowest non-zero point included in the initial calibration.

Alternative measurement sensitivity is the range of measurement precision uncertainty based on a sample size of seven samples (non-blanks) and 99% confidence.

Values for MDL, ML, MQL and AMS for all chemical analyses are summarized in Table SOP 4.5 along with the specified analytical procedures to be used for each constituent.

Table SOP 4.5. Measurement quality objectives.

					Precision	Bias		
Measure	**Method**	**MDL**	**ML**	**AMS**	**RPD**	***Check Samples***	***Spike Recovery***	**Completeness**
Core parameters								
Temperature	Thermistor	-	-	0.1 oC	±0.15 °C	-	-	95%
Specific Conductance - field	Conductivity meter (1 cm cell)	-	-	0.1 uS/cm	±0.5 us/cm	-	-	95%
Specific Conductance - lab	Conductivity meter (0.1 cm cell)	-	-	0.01 uS/cm	±0.1 uS/cm	-	-	95%
pH - lab	pH meter w/ Ross electrode	-	-	0.01 pH unit	±0.2 ph unit	-	-	95%
Dissolved oxygen - field	YSI DO meter	-	-	0.2 mg/l	±0.5 mg/l	-	-	95%
Nitrogen								
Nitrate	Ion chromotography (EPA Method 300.1)	*0.3 umol/L*	*0.95 umol/L*	-	5%	*±10%*	*80-120%*	95%
Nitrite	Ion chromotography (EPA Method 300.1)	*0.3 umol/L*	*0.95 umol/L*	-	5%	*±10%*	*80-120%*	95%
Dissolved organic nitrogen	TDN - (nitrate+nitrite)	-	-	-	-	-	-	95%
Total dissolved nitrogen	Valderrama (1981): Persulfate digestion followed by EPA Method 353.4	0.5 umol/L	2 umol/L	-	20%	*±10% or ± 0.040 uM*	*80-120%*	95%
Particulate nitrogen	Elemental Analyzer (EPA Method 440.0)	-	-	-	-	-	-	95%
Phosphorus								
Total dissolved phosphorus	Valderrama (1981): Persulfate digestion followed by EPA Method 365.5	0.05 umol/l	0.2 umol/L	-	20%	*±10% or ± 0.040 uM*	*80-120%*	95%
Particulate phosphorus	Valderrama (1981): Persulfate digestion followed by EPA Method 365.5	-	-	-	-	-	-	95%
Carbon								
Particulate carbon	Elemental Analyzer (EPA Method 440.0)	0.1 umol/L	0.4 umol/L	-	-	-	-	95%
Major Ions								
Calcium	*Inductively coupled plasma (ICP) (EPA Method 200.7) using modifications in Dombek (2009) and Mirishige and Kimura (2008)*	0.2 umol/L	0.8 umol/L	-	5%	*±10%*	*80-120%*	95%
Sodium	*Inductively coupled plasma (ICP) (EPA Method 200.7) using modifications in Dombek (2009) and Mirishige and Kimura (2008)*	0.2 umol/L	0.8 umol/L	-	5%	*±10%*	*80-120%*	95%
Magnesium	*Inductively coupled plasma (ICP) (EPA Method 200.7) using modifications in Dombek (2009) and Mirishige and Kimura (2008)*	0.2 umol/L	0.8 umol/L	-	5%	*±10%*	*80-120%*	95%
Potassium	*Inductively coupled plasma (ICP) (EPA Method 200.7) using modifications in Dombek (2009) and Mirishige and Kimura (2008)*	0.2 umol/L	0.8 umol/L	-	5%	*±10%*	*80-120%*	95%
Chloride	Ion chromotography (EPA Method 300.1)	0.3 umol/L	0.95 umol/L	-	10%	*±10%*	*80-120%*	95%
Sulfate	Ion chromotography (EPA Method 300.1)	*0.3 umol/L*	*0.95 umol/L*	-	5%	*±10%*	*80-120%*	95%
ANC	Gran titration (Rounds et al 2006)	0.5 umol/L	2 umol/l	-	-	-	-	95%

MDL: Method detection limit; ML: Minimum level of quantitation; MQL: Method quantitation limit; AMS: Alternative measurement sensitivity; RPD: Relative percent deviation

Representativeness expresses the degree to which data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, a process condition, or an

environmental condition. Representativeness of the data is dependent on the sampling locations, sample timing, sample design, and the sampling procedures adequately representing the true condition of the sample site or target population. Sampling locations, sampling of relevant media (water, sediment, or biota), use of only approved/documented analytical methods, and a statistically sound sample design will determine if the measurement data does represent the conditions at a single investigation site or for the larger target population to the extent possible. Sampling schedules will be designed with respect to frequency, locations, and methodology in order to maximize representativeness, where possible and applicable.

SIEN's sites are selected using two methods: 1) judgmental selection for index sites and 2) probabilistic selection for extensive sites. Sampling methods at the index sites will maximize representativeness for each site. The probabilistic sample design and methods for extensive sites will maximize representativeness to the target population (i.e. SIEN lakes). Samples are collected at different 'sampling stations'—lake outlet and mid-lake (epilimnion and hypolimnion) locations. Samples are representative of these individual sampling locations. The more 'mixed' a lake is the more representative an individual sample will be of the larger water body.

An important aspect of representativeness for SIEN lakes is the verification of holding times for samples. Owing to the remote locations of the target lakes, samples must spend several days, un-refrigerated while in transit back to the laboratory. In addition, since much of the chemistry will be performed by laboratories outside of the Network Parks, additional delays are expected during sample shipping. Sample holding times, specific to waters from Sierra Nevada lakes, have been developed by Sickman and Melack (1989) (Figure SOP 4.2). The SEIN Lake Monitoring Protocol specifies routine holding times for all water quality constituents that are consistent with those developed for Emerald Lake.

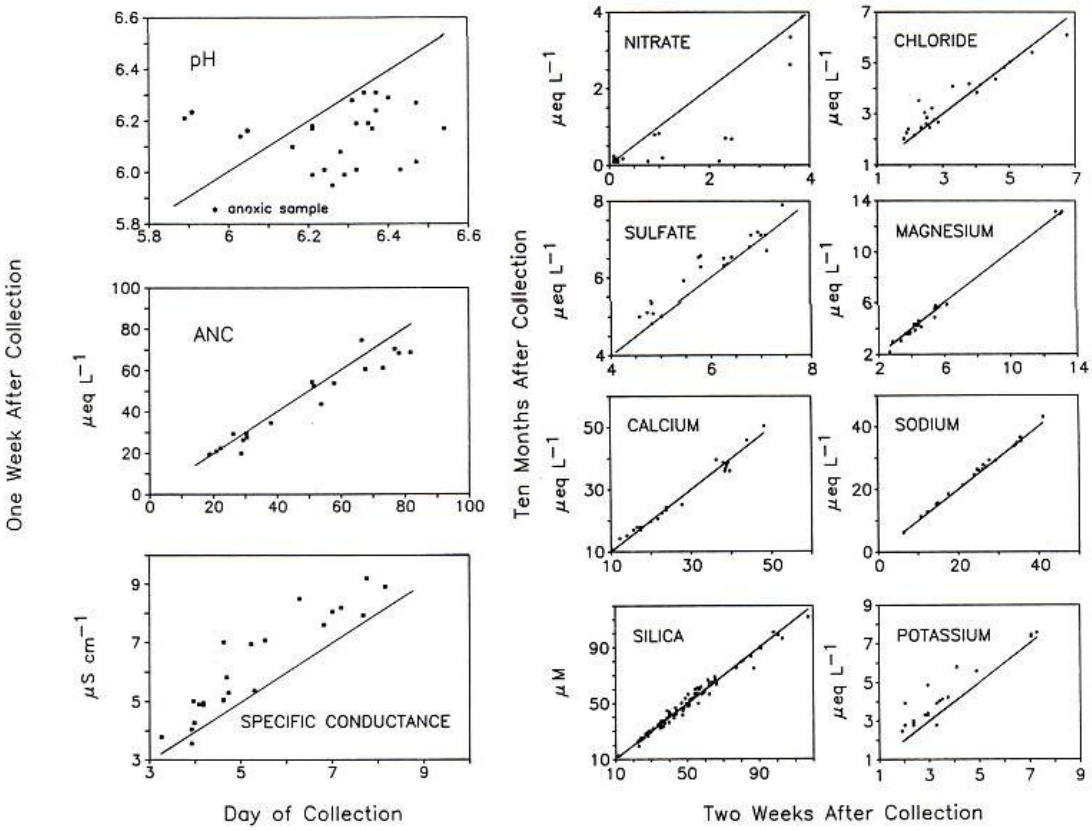

Figure SOP 4.2. Holding time tests for Emerald Lake.

Comparability can be discussed in terms of comparability of data within a project or between projects. Comparability within a project expresses whether analytical conditions are sufficiently uniform for each analytical run and between analytical runs to insure that all of the reported data will be consistent. In a laboratory setting, comparability would typically be measured by running certified reference materials or standards at the beginning and end of an analytical run and over several analytical runs.

Comparability between projects is a qualitative term that expresses the measure of confidence that one data set can be compared to another and combined for decision or analysis purposes. The comparability of data produced by SIEN is predetermined by the commitment of its staff and contracted laboratories to use standardized methods, where possible, including EPA approved analytical methods, or documented modifications thereof which provide equal or better results. Measurements are made according to standard procedure, or documented modifications which provide equal or better results. In addition, while selecting analytical methods for the SEIN program we sought to maintain consistency with previous and ongoing studies of Sierra Nevada Lakes. Table SOP 4.6 contains a summary of analytical methods used by the most extensive monitoring programs of Sierran lakes to date.

Overall, the projects listed in Table SOP 4.6 used identical or very similar methodologies. For example, dissolved inorganic nitrogen, chloride and sulfate were all measured by EPA Method 300.1 – ion chromatography (IC), with slight differences in instrumentation. The major exception to consistency, was the use of IC for base cation analyses by the US Forest Service. Unpublished inter-laboratory comparisons of cations in Sierra Nevada lakes measured by IC, atomic absorption spectrophotometry (AA) and inductively coupled plasma (ICP) have demonstrated that AA and ICP produce similar divalent cation concentrations on duplicate samples. In contrast, divalent cation concentrations measured by IC are not consistent with AA and ICP values (J. Sickman, UC Riverside and D. Clow, US Geological Survey, unpublished data). Thus for the SEIN protocol, only AA or ICP methods will be used for base cation analyses.

Completeness. The completeness of data is the percentage of data that are valid and available for use compared to the total potential data. Ideally, 100% of the data would be available. However, in reality, data become unavailable due to unexpected field conditions, contamination, insufficient sample volume, or samples broken in shipping. Therefore, 95% data completeness is required by SIEN for data usage in most cases.

SOP Table 4.6. Summary of analytical methods used in previous surveys and monitoring programs in the Sierra Nevada.

	Analytical Procedures by Monitoring Program				
Comparability	**Lakes**			**Streams**	
Measure	**USFS-LAKES**	**WLS-99**	**UCSB-Tokopah**	**Yose-VERP**	**Seki Watershed**
Core parameters					
Temperature	Certified thermometer	YSI-Thermistor	YSI-Thermistor	Electronic thermometer	YSI-Thermistor
Specific Conductance- field	na	YSI-1 cell constant	YSI-1 cm cell constant	Conductivity meter	YSI-1 cell constant
Specific Conductance- lab	PC-Titrate Cond. Meter 4310	YSI-0.1 cell constant	YSI-0.1 cm cell constant	Conductivity meter	YSI-0.1 cell constant
pH	PC-Titrate (by Man Tech corp)	Ross Orion Electrode	Ross Orion Electrode	pH meter	Ross Orion Electrode
Dissolved oxygen-field	na	YSI-DO meter	YSI-DO meter	Electronic meter/probe	YSI-DO meter
Nitrogen					
Nitrate + nitrite	IC w/ separator column (APHA 1998a)	Dionex IC with AS4A	Dionex IC with AS14A	USGS/NWQL 1979 (nitrate and nitrite)	Dionex IC with AS4A
Dissolved organic nitrogen	na	TDN-DIN	TDN-DIN	na	TDN-DIN
Total dissolved nitrogen	na	Valderama (persulfate boric acid digestion)	Valderama 1981 (persulfate boric acid digestion)	USGS/NWQL 2754	Valderama (persulfate boric acid digestion)
Particulate nitrogen	na	High temperature elemental analysis	High temperature elemental analysis	na	High temperature elemental analysis
Phosphorus					
Total dissolved phosphorus	na	Valderama (persulfate boric acid digestion)	Valderama 1981 (persulfate boric acid digestion)	USGS/NWQL 2331	Valderama (persulfate boric acid digestion)
Particulate phosphorus	na	Valderama (persulfate boric acid digestion)	Valderama 1981 (persulfate boric acid digestion)	na	Valderama (persulfate boric acid digestion)
Carbon					
Particulate carbon	na	High temperature elemental analysis	High temperature elemental analysis	na	High temperature elemental analysis
Major Ions					
Calcium	IC w/ monovalent/ divalent column	Flame Atomic Absorbence Spectrophotometry	Flame Atomic Absorbence Spectrophotometry	na	Flame Atomic Absorbence Spectrophotometry
Sodium	IC w/ monovalent/ divalent column	Flame Atomic Absorbence Spectrophotometry	Flame Atomic Absorbence Spectrophotometry	na	Flame Atomic Absorbence Spectrophotometry
Magnesium	IC w/ monovalent/ divalent column	Flame Atomic Absorbence Spectrophotometry	Flame Atomic Absorbence Spectrophotometry	na	Flame Atomic Absorbence Spectrophotometry
Potassium	IC w/ monovalent/ divalent column	Flame Atomic Absorbence Spectrophotometry	Flame Atomic Absorbence Spectrophotometry	na	Flame Atomic Absorbence Spectrophotometry
Chloride	IC w/ separator column (APHA 1998a)	Dionex IC with AS4A	Dionex IC with AS14A	na	Dionex IC with AS4A
Sulfate	IC w/ separator column (APHA 1998a)	Dionex IC with AS4A	Dionex IC with AS14A	na	Dionex IC with AS4A
ANC	Gran 1952	Gran 1952	Gran 1952	na	Gran 1952
Other parameters measured	NH4, SRP, Fl, Si, Al, Hg	Si, SRP, DOP, NH4	Si, SRP, DOP, DOC, NH4	TP, ecoli, total petrolium hydrocarbons	Si, SRP, DOP, NH4

USFS-LAKES: Project LAKES, USFS long-term lake monitoring program in Sierra
WLS-99: 1999 resurvey of selcted EPA WLS lakes conducted by Clow et al.
Yose-VERP: Yosemite Visitor Experience and Resource Protection monitoring program
UCSB-Tokopah: UC Santa Barbara long-term research and monitoring
SEKI-watershed: Watershed research conducted by SEKI from approximately 1983-2000

Precision, Bias, and Accuracy The precision, bias, and accuracy of data are determined by particular actions of the analytical laboratory and field staff.

Precision is a measure of the reproducibility of a measurement when an analysis is repeated. It is reported in Relative Percent Difference (RPD) or Relative Standard Deviation (RSD).

Two types of precision are evaluated during the project: analytical precision and process precision. Analytical precision refers to measurements of replicate samples during an analytical procedure at a 5% frequency. Process precision refers to duplicate samples collected in the field and run through the entire sample handling and analytical procedure (i.e., Field Duplicates). Field Duplicate samples are collected at a 5% frequency during both Task 1 and 2. Target values for analytical precision are summarized in Table SOP 4.5.

Accuracy of an analysis is a measure of how much of the constituent actually present is determined. An assessment of accuracy has to factor in both precision and bias. EPA has clarified that accuracy is "a measure of the overall agreement of a measurement to a known value". Accuracy includes a combination of random error (precision) and systematic error (bias) components that are due to sampling and analytical operations. EPA recommends using the terms "precision" and "bias," rather than "accuracy," to convey the information usually associated with accuracy. Therefore**,** what is estimated for each sample batch or each QC sample is systematic error (bias) rather than accuracy.

Systematic error/bias will be measured in each analytical run at a 5% frequency, by adding a known amount of the constituent to a portion of the sample and determining how much of this spike is then measured, and, running a certified reference material at a 5% frequency. Bias will be reported as percent recovery and percent agreement with the certified value. 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. Target values for analytical bias are summarized in Table SOP 4.5.

It is the responsibility of the program manager to verify that the data are representative while the analytical data's precision, accuracy, and comparability are mainly the responsibility of the laboratory supervisor. The program manager also has prime responsibility for determining that the 95% data completeness criteria are met or for justifying acceptance of a lesser percentage.

1.6. Special Training and Certifications

1.6.1. Field

Proper and consistent training for personnel is a critical aspect of quality assurance. Detailed training requirements are outlined in SOP 2 (Safety) and SOP 3 (Staff Training).

The Protocol Lead/Network Physical Scientist will have an educational background in biological, chemical, and/or physical sciences and specialized experience in water quality or closely related aquatic sciences. Field crews will have at least one individual with an educational background and/or field experience in biological, chemical, and/or physical sciences. Extensive site field crews will also have at least one individual with strong wilderness and backpacking skills.

All personnel will be trained in the lake sampling protocol at the level appropriate for their position. The Protocol Lead is ultimately responsible for training field crews and ensuring consistency, to the extent possible, between crews and years. He/she may delegate portions of the training to experienced technicians or park professional staff that are well-versed and have hands-on experience with the Lake Monitoring protocol. Safety will be emphasized throughout the training. The Protocol Lead and employee supervisors (if not the Protocol Lead) are responsible for ensuring adequate safety training (*see SOP #2: Safety*).

1.6.2. Laboratory

The contract laboratories used for chemical analyses will have in place, training procedures for all analysts to insure data meet our targets for completeness, precision, and bias. Documentation for these training procedures is mandatory for each contract laboratory and will be submitted in writing to the Protocol Lead. Both the QA Manager and the Protocol Lead will evaluate these procedures.

1.7. Documentation and Records

The following documents, records, and electronic files are expected to be produced:

- Lake Monitoring Protocol, Standard Operating Procedures (includes QAPP), and supporting documents
- Field forms and notebooks
- Chain-of-custody forms
- GPS sampling location electronic files
- Digital photographs
- Laboratory chemical analysis results-electronic spreadsheet or database
- Datalogger output files
- Water quality and streamflow database
- Annual summary reports
- Synthesis and trend analysis reports
- Publications
- Contracts and agreements
- Personnel records

The primary depository for paper records will be in the Inventory and Monitoring office at Ash Mountain, Sequoia National Park. The primary depository for electronic files will be on the Sequoia and Kings Canyon National Parks network in the Inventory and Monitoring file directory structure. Electronic copies of documents, records, etc. will be made available to staff stationed in other parks via the SIEN I&M Internet and Intranet sites and local park networks. Copies of paper documents will also be stored as needed in satellite offices. Electronic records will be backed-up in accordance with procedures outlined in the SIEN Data Management Plan (Cook and Lineback 2007).

The Protocol Lead is responsible for disseminating the QAPP, including revisions as they occur to those listed in Table SOP 4.2. Electronic copies are e-mailed or mailed on a CD to recipients

identified in section A3. Hardcopies are sent on request. In addition, the current copy will be posted to SIEN web pages.

2. Data Generation and Acquisition

2.1. Sampling Design and Logistics

Our network, along with others working in large mountainous landscapes, struggled with the trade-offs between in-depth temporal sampling and an ability to make inferences across the landscape. SIEN lakes, for the most part, are located in the remote Wilderness areas of Yosemite, Sequoia, and Kings Canyon. Access, logistics, and safety were prominent considerations throughout the development process. An additional and equally important requirement, was a sampling design that would address both trend and status objectives. Balancing these trade-offs, we settled on a design that is comprised of two site types: 1) *extensive sites*, which are probabilistically selected and sampled once every 1-3 years and, 2) *index sites*, which are judgmentally selected and sampled multiple times each year. To address the extensive site objectives, the type of design we are implementing is a spatially-balanced, probabilistic, split-panel design. Extensive sites are sampled once in August or September. Index sites, which are sampled 1/month from May-October, were selected using criteria such as accessibility, existing monitoring or research, and specific management concerns. Sampling will be conducted at the lake outlet and at mid-lake (this varies by site type and panel). Please refer to the Lake Protocol Narrative for a detailed description of the sample design and sampling schedule.

2.1.1. Site Replacement

If a site is inaccessible or determined to be unsafe to access in anyway, the field crew will not sample the site.

In the case of index sites, if the barrier is temporary (e.g. from high streamflows, weather) crews will resume sampling once the site is safe to access again. If inaccessibility is deemed to be long-term, the Water Resources Work Group will meet and select a replacement index site.

In the case of extensive sites, if the barrier is temporary (e.g. weather), that site will not be sampled for that year, but sampling will continue the next time the site is scheduled for sampling. There will be a gap in the dataset for that year. If inaccessibility is deemed to be long-term (e.g. a route to a site is determined to be unsafe), the site will be replaced with the next site from the list of selected sites. Sites are selected using a general randomized tessellation stratified (GRTS) sample (Stevens Jr. and Olsen 2004). GRTS samples assure spatial balance by recursively subdividing the parks, drawing the sample, and then reversing the ordering. The final result is a list of lakes such that any contiguous set achieve a high degree of spatial balance. Because the design is spatially-balanced a site may be replaced without compromising statistical integrity.

2.1.2. Sources of Bias or Misrepresentation

The Lake Monitoring protocol clearly defines the areas of inference for each site type and sampling station. Misrepresentation should be minimized as long as assumptions and areas of inference continue to be clearly stated.

There are sources of bias in the sample design. We are selecting lakes using a cost-surface model to apply unequal probability inclusions. Trend analyses in the context of panel designs cannot incorporate variable probability sampling. When testing trend it must be assumed that sites had

equal chance of being selected. The results are trend estimates that are biased towards lakes that are quicker to access.

Sources of bias during data acquisition include bias from field instrumentation (e.g., DO and temperature meter) and bias in laboratory instrumentation.

2.2. Sampling Methods

All measurements and sampling techniques associated with monitoring activities will be conducted according to the SOPs outlined in the SEIN Lake Monitoring Protocol narrative.

2.3. Sample Handling and Custody

Proper sample handling procedures for water, sediment, and biological samples are provided in Table SOP 4.7. This table provides a summary of the size and composition of required sample containers, laboratory storage conditions, and maximum storage times for water and filter samples. In the field, all samples will be kept as cool as possible and in the shade since transporting frozen ice packs and coolers into remote field sites is impractical. During shipment to contract laboratories, samples will be shipped with refrigerant packs in insulated containers. 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 have computer generated labels printed on water-proof paper.

Lakes in the Sierra Nevada are extremely dilute, thus extraordinary care must be taken to not contaminate the samples with sweat or oils from finger tips. SOP #8 describes a series of precautions that will be used during field collection. Similarly, the filters and sample containers themselves can introduce significant levels of contaminants into samples if not properly prepared.

Only brand new, Nalgene, high density polypropylene (HDPE) bottles will be used for water sampling. The bottles will be rinsed once with 18 megaohm deionized water (DIW) and then filled to the brim with DIW. Bottles will be soaked for seven days and re-rinsed three times with DIW. They will then be air dried and capped. Clean bottles will be stored in clearly marked containers to avoid confusion with unclean bottles.

Two types of filters will be used to collect water and seston samples from the lakes and were chosen on the basis of their cleanliness and prior use in other Sierra Nevada lake studies. Polycarbonate filters from Nuclepore have been shown to have the lowest leachable solutes of any commercially available water filter and have been used with success by many of the research studies listed in Table SOP 4.6. For seston samples, we will use 47 mm Pall (Gelman) A/E filters. These filters are used around the world for collection of lake seston samples and the vast majority of seston data from Sierra Nevada lakes are based upon their use. The filters will be pre-combusted in a high-temperature furnace for 3-hours at 500 °C to reduce background levels of C,N and P. These glass fiber filters have a nominal pore size of one micron (1 µm).

In deciding on a pore size for the polycarbonate filters used for water sampling we considered both the standard 0.45 µm and 1.0 µm porosities. Dissolved constituents in water are most commonly defined as those that can pass through a 0.45 µm filter, although smaller sizes, e.g., 0.2 and 0.1 µm, are often used in studies of natural organic matter and trace metals. However, we have chosen to use 1.0 µm filters for two reasons. One of our goals is to quantify total nitrogen

and total phosphorus in lake water by summing TDN+PN and TDP+PP, respectively. If we chose to use a 0.45 µm water filter, then we would neglect to measure the N and P content of water particles in the range of 0.45 to 1.0 µm. Secondly, UC researcher have collected the largest and most extensive datasets on Sierra Nevada lake chemistry using 1.0 µm polycarbonate filters.

Chain-of-custody procedures are described in SOP 6 (Chain-of-custody).

Table SOP 4.7. Summary of sample handling requirements.

Measurement	Field Method	Container Type	Storage	Max holding time
Core parameters				
Temperature	YSI-thermistor	n/a	4°C refrigeration	n/a
Specific Conductance- fld	YSI-conductivity meter (1 cm cell constant)	n/a	n/a	n/a
Specific Conductance- lab	unfiltered	125 ml HDPE Bottle	4°C refrigeration	7-days
pH	unfiltered	125 ml HDPE Bottle	4°C refrigeration	Recommended 48 hours Maximum 7-days
Dissolved oxygen-fld	YSI-DO meter	n/a	n/a	n/a
Nitrogen				
Nitrate+nitrite	Filtration through 1.0 µm polycarbonate	125 ml HDPE Bottle	4°C refrigeration	30 days
Dissolved organic nitrogen	TDN-DIN	n/a	n/a	n/a
Total dissolved nitrogen	1.0 µm polycarbonate	60 ml HDPE Bottle	"-20 °C freezer	6 months
Particulate nitrogen	Filtration onto 47 mm Pall A/E filter	Polystyrene Petri dish	"-20 °C freezer	6 months
Phosphorus				
Total dissolved phosphorus	Filtration through 1.0 µm polycarbonate	60 ml HDPE Bottle	"-20 °C freezer	6 months
Particulate phosphorus	Filtration onto 47 mm Pall A/E filter	Polystyrene Petri dish	"-20 °C freezer	6 months
Carbon				
Particulate carbon	Filtration onto 47 mm Pall A/E filter	Polystyrene Petri dish	"-20 °C freezer	6 months
Major Ions				
Calcium	Filtration through 1.0 µm polycarbonate	125 ml HDPE Bottle	4°C refrigeration	60 days
Sodium	Filtration through 1.0 µm polycarbonate	125 ml HDPE Bottle	4°C refrigeration	60 days
Magnesium	Filtration through 1.0 µm polycarbonate	125 ml HDPE Bottle	4°C refrigeration	60 days
Potassium	Filtration through 1.0 µm polycarbonate	125 ml HDPE Bottle	4°C refrigeration	60 days
Chloride	Filtration through 1.0 µm polycarbonate	125 ml HDPE Bottle	4°C refrigeration	30 days
Sulfate	Filtration through 1.0 µm polycarbonate	125 ml HDPE Bottle	4°C refrigeration	30 days
ANC	unfiltered	125 ml HDPE Bottle	4°C refrigeration	7-days

2.4. Analytical Method and Field Measurement Requirements

Detection limits may be affected by instrument sensitivity or by bias due to contamination or matrix interferences. In all cases, results cannot be reported for values less than the Method Detection Limit (MDL). Data falling between the MDL and minimum level of quantitation (ML) are considered “semi-quantitative” and can be presented as greater than zero. They are detected but not quantifiable and can be given a flag of DNQ (detected, not quantifiable). The ML is equal to some multiple of the MDL. Censored data will be presented as less than or greater than the ML in order to compare it to water quality criteria (Irwin 2006).

The SIEN Lake Program will follow the same guidelines as the SWAMP program and STORET for recommended use of detection and quantification limits. Result quality codes for CEDEN and STORET are assigned to individual results in the database. The following are CEDEN result quality codes *(Refer to Sierra Nevada Network Database User's Manual for corresponding STORET codes)*: Values below the Method Detection Limit (MDL) are to be reported as ND = not detected and the actual MDL value is recorded. Values between the MDL and the ML (or quantification limit) will be reported as the actual measured value, with a flag that is carried all the way through data storage, handling, and reporting. The flag is DNQ = detected, not quantifiable. Values above the ML (or quantification limit) are deemed as acceptable values without reservation, and are shown as the actual measured value, and assigned a result quality code of 'Detected and Quantified'. In general, laboratories should strive to meet target reporting limit recommendations for undetected analytes (Table SOP 4.5).

In most water quality investigations, MDLs are considerably lower than water quality objectives, however analyte levels in Sierra Nevada lakes are often at or below the MDL. The MDL levels specified in Table SOP 4.5 are in many cases below those typically reached in commercial analytical laboratories and to be attained, special analytical techniques must be followed. For example, to attain a detection limit below <1 µmol L^{-1} for chloride, nitrite, nitrate and sulfate, sample injection loops of 250 µl are required; most commercial laboratories use a 50 µl sample loop. Thus, a primary criterion for selecting contract laboratories for the SIEN Program will demonstrated experience in analyzing dilute water samples from areas such as the Sierra Nevada and Rocky Mountains.

2.5. Laboratory Quality Control Requirements

The approaches required to meet data quality objectives will include laboratory matrix spikes, laboratory method blanks, calibration standards, laboratory- and field-duplicated samples, and sample holding time tests. The definition and use of each of these types of quality control samples are explained further below. Laboratories providing analytical support for chemical analyses will have the appropriate facilities to store, prepare, and process samples and appropriate instrumentation and staff to provide data of the required quality within the time period dictated by the project. Laboratories will be able to provide information documenting their ability to conduct the analyses with the required level of data quality. Such information will include results from inter-laboratory calibration studies, and summary data of internal QA/QC checks, and results from certified reference material analyses. Laboratories will also provide a laboratory QA plan and Analytical Methods Manual,

2.5.1. Measurement Quality Objectives (MQOs)

Completeness: Completeness is the amount of data collected compared against the expected amount. For the SIEN Program we have established a data completeness level of 95%.

Precision: Precision is the reproducibility of an analytical method. Each laboratory is expected to maintain records for use by analysts in monitoring the overall precision of certified reference materials and natural samples. Within each analytical run, measurements of precision will be performed at a 5% frequency (i.e., one duplicate for every 20 samples) or at least once if the run contains less than 20 samples. Both certified reference material and natural samples will be used in measurements of precision. The relative percent difference (RPD) will be calculated for each

analyte of interest and recorded and compared to values shown in Table SOP 4.5. Use of both synthetic and natural samples for precision measurements will help identify matrix interferences.

Laboratory Method Blank: Laboratory method blanks (also called extraction blanks, procedural blanks, or preparation blanks) are used to assess laboratory contamination and instrument background during all stages of sample preparation and analysis. An appropriate number of laboratory blanks will be done at the beginning and throughout each analytical run.

Matrix Spike Recovery: A laboratory fortified sample matrix (commonly called a matrix spike, or MS) will be used both to evaluate the effect of the sample matrix on the recovery of the compound(s) of interest and to provide an estimate of analytical precision. Recovery is the accuracy of an analytical test measured against a known analyte addition to a sample. These QA samples will be done in duplicate. Sample matrices will include both certified reference materials and natural water samples. Comparison of recoveries in synthetic and natural samples will allow identification of matrix interferences. These QA samples will be done at least once or at a 5% frequency in each analytical run.

Travel Blanks: The purpose of the travel blank is to determine if there is any cross-contamination of volatile constituents between sample containers. Travel blanks are not required for other analytes, but are encouraged to be utilized for other analytes as possible and appropriate.

Holding Time Tests: During each field season, duplicate samples will be collected at three lakes during performance of Task 2. The lakes chosen will be sampled on the final day of a field trip so that they can be rushed back to the laboratory. One set of replicates will be held for the standard holding times under standard storage conditions that are specified in Table SOP 4.7. The other set of duplicates will be stored at room temperature for 7 days then held for the standard holding times under standard storage conditions before analysis. All chemical analyses will be conducted on the duplicate samples and the results will be compared statistically to determine if 7 days of storage results in significantly different analyte concentrations.

Equipment Blanks (done in lab prior to field work): To insure that equipment used during sampling does not contaminate samples, the device is filled with DI water or DI water is pumped through the device, transferred to sample bottle(s), preserved (if appropriate) and analyzed by the lab.

Field Duplicates: Duplicate samples will be collected for all parameters at an annual rate of 5% of total samples to be collected within a given year's monitoring plan. These duplicate samples will be done in addition to the duplicate used for the holding time tests. The duplicate sample will be collected in the same manner and as close in time as possible to the original sample.

Field Blanks: A field blank is designed to assess potential sample contamination levels that could occur during field sampling and sample processing. Field Blanks (DI water) are taken to the field, transferred to the appropriate container, preserved (if appropriate), and otherwise treated the same as the corresponding sample type during the course of a sampling event. Field blanks for water quality constituents should be conducted upon initiation of sampling, and if field blank performance is acceptable, further collection and analysis of field blanks for these

other media and analytes need only be performed on an as-needed basis, or during field performance audits.

2.6. 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, when possible, 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. Refer to SOPs and Users Manuals for specific instructions.

Field Equipment - All field equipment that has manufacturer-recommended schedules of maintenance will receive preventive maintenance according to that schedule. Other equipment used only occasionally will be inspected for availability of spare parts, cleanliness, battery strength, etc. at least monthly and especially prior to being taken into the field. Common spare parts which should be available include, but are not limited to: batteries; DO membranes; tubing; replacement probes. After use in the field, all equipment will be re-checked for needed maintenance. The Crew Lead is responsible for testing, inspecting, and maintaining equipment.

Laboratory Equipment - Electronic laboratory equipment usually has recommended maintenance prescribed by the manufacturer. These instructions will be followed as a minimum requirement. Due to the cost of some laboratory equipment, back up capability may not be possible. But all commonly replaced parts will have spares available for rapid maintenance of failed equipment.

A separate log book will be maintained for each type of field and laboratory equipment. All preventive or corrective maintenance will be recorded. The total history of maintenance performed will be available for inspection during a systems audit.

2.7. Field Instrument/Equipment Calibration and Frequency

An instrument or device used in obtaining an environmental measurement must be calibrated by the measurement of a standard. Every instrument or device has a specialized procedure for calibration and a special type of standard used to verify calibration. See instrument manuals for further details. A log book will be kept to record dates of calibration and any equipment errors or failures, battery changes, changes of calibration solutions, and repair notes. The log book will also contain calibration methods, this schedule of inspections and calibrations, and a list of needed supplies and equipment. When a change in equipment occurs, overlapping measurements will be made using both the old and new equipment in order to document precision in reproducibility. Calibration frequency, acceptance criteria, and corrective actions for field meters are outlined in Table SOP 4.8.

Table SOP 4.8. Routine instrument inspections and calibrations.

Parameter	Calibration Frequency	Acceptance Criteria	Corrective Actions
Water temperature	Every 3 to 4 months, check calibration, annually, using a 5-point calibration against a certified thermometer	±1.0 ºC	Re-test with a different thermometer; repeat measurement
Specific conductance	Prior to field mobilization, at the field site, and calibration check at day's end; 10% of the readings taken each day must be duplicated or a minimum of 1 reading if fewer than 10 samples are read.	±5%	Re-test; check low battery indicator; use a different meter; use different standards; repeat measurement
Dissolved oxygen	Prior to field mobilization, at the field site, and calibration check at day's end	±10%	Re-enter altitude; re-test; check low battery indicator; check membrane for wrinkles, tears or air bubbles; replace membrane; use a different meter; repeat measurement

2.8. Inspection/Acceptance for 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. 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 supplies are not damaged. 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.

The Protocol Lead oversees procurement and inspection of field and local laboratory equipment. Responsibilities may be delegated to Logistics and Field Technicians. It is the responsibility of each staff person ordering to inspect the equipment and materials for quality. Required equipment is listed in individual SOPs. Contract laboratories are responsible for procurement and inspection of their equipment and materials.

2.9. Data Acquisition Requirements (Non-direct Measurements)

Primary analyses will be performed using data from the SIEN Lake Monitoring protocol. The SIEN Water Quality and Streamflow Database will only store data collected as part of the Vital Signs Monitoring Program. SIEN Lake protocol data includes data collected by pre-identified partners. These data may be imported into the data base to facilitate analyses and provide a comprehensive record of the project. Partner data must meet or exceed the same quality assurance and quality control standards as SIEN collected data.

Although non-direct measurements will not be used for core analyses, the use of these data is highly encouraged for SIEN planning efforts and data assessment/data interpretation activities, provided that these data were collected in projects which were supported by an approved QAPP, or at a minimum utilized approved and documented standard methods. SIEN staff must use their professional discretion for the use of such data for these purposes. These data are usually obtained in electronic format and should be inspected in their raw form by automated data editing procedures, where possible, before data reduction and interpretation are undertaken.

2.10. Data Management

The Sierra Nevada Network Data Management Plan provides the framework for lake monitoring data management procedures (Cook and Lineback 2007). Detailed procedures are described in the Lake Monitoring Protocol Narrative, SOPs, QAPP, SIEN Water Quality and Streamflow Database User's Manual, and database documentation.

3. Assessment and Oversight

3.1. Assessments and Response Actions

Proper and consistent use of equipment and methods is critical to maintaining the integrity of long-term monitoring data sets. The commitment to use approved equipment and approved methods when obtaining environmental samples and when producing field or laboratory measurements must have periodic verification that the equipment and methods are, in fact, being employed and being employed properly. Verification is accomplished by conducting periodic audits. The Protocol Lead is responsible for auditing field crews. Audits will be conducted at least once during the field season. If problems arise, the Protocol Lead should take one or more of the following actions, as appropriate:

- If sample integrity is compromised: Document issues in field forms and database.
- Re-train field technician(s) in deficient areas
- Modify sampling equipment or methods. Update protocol.

Quality control issues and response actions will be documented.

3.2. Reports to Management

Quality assurance is reported on annually as part of the annual summary reports. The Lake Protocol Lead is responsible for completing these summaries and reports. Reports will be distributed to NPS-WRD, Network staff, Resource Chiefs, and Water Resources Work Group. Reports will also be made available to interested spark staff and the public via the SIEN I&M web pages.

4. Data Validation and Usability

4.1. Data Review, Verification, and Validation

This section was excerpted from the Sierra Nevada Network Data Management Plan (Cook and Lineback 2007).

Data quality is appraised by applying verification and validation procedures as part of the quality control process. These procedures are more successful when preceded by effective quality assurance practices (i.e., planning). *Data verification* checks that the digitized data match the source data, while *data validation* checks that the data make sense. Although data entry and verification can be handled by personnel who are less familiar with the data, validation requires in-depth knowledge about the data.

Validation is the process of reviewing computerized data for range and logic errors and may accompany data verification only if the operator has comprehensive knowledge of the data and subject. More often, validation is a separate operation carried out after verification by a project specialist who can identify generic and specific errors in particular data types. It is essential that we validate all data as truthful and do not misrepresent the circumstances and limitations of

collection. Invalid data commonly consist of misspelled species names or site codes, wrong dates, or out-of-range errors in parameters with well defined limits (e.g., pH). More interesting and often puzzling errors are detected as unreasonable metrics (e.g., stream temperature of 70°C) or impossible associations (e.g., a tree 2 feet in diameter and only 3 feet high). These types of erroneous data are called *logic errors* because they produce illogical (and incorrect) results. The discovery of logic errors has direct, positive consequences for data quality and provides important feedback to the methods and data forms used in the field. Histograms, line plots, and basic statistics can reveal possible logic and range errors.

4.2. Verification and Validation Methods

4.2.1. Verification

The Lake Protocol will follow guidelines for data verification outlined in the Sierra Nevada Network Data Management Plan (Cook and Lineback 2007):

- Project leaders are responsible for specifying in the project protocol one or more of the data verification methods available and ensuring proper execution. At the discretion of the project leader, additional verification methods may be applied.
- Data verification is carried out by staff thoroughly familiar with data collection and entry.
- All records (100%) will be verified against original source data.
- A subset of randomly selected records (10%) will be reviewed after initial verification by the project leader. If errors are found, the entire data set will be verified again.
- A record of the verification process for each dataset, including number of iterations and results, will be prepared by the project leader as part of formal metadata generation.
- Spatial data collected as part of the project will be viewed in a GIS and visually inspected for accuracy (e.g., points located outside park boundaries, upland locations occurring in water).

The method we are using to verify the lake chemistry and streamflow data is *visual review after data entry*. Upon completion of data entry, all records are printed and compared with the original values from the hard copy. Errors are clearly marked and corrected in the database as soon after data entry as possible. The review is performed by someone other than the person keying the data or by two technicians---one reading from the original data and one checking the entered data.

Additional data verification methods include calculating summary statistics and identifying duplicate or omitted records. For example, the number of known constant elements, such as the number of sampling sites or dates per sample can be evaluated. The SIEN Water Quality Databases has built in controls to prevent duplicate records. Specific queries must be performed to identify missing records.

4.2.2. Validation

The Lake Protocol will follow guidelines for data validation outlined in the Sierra Nevada Network Data Management Plan (Cook and Lineback 2007):

- Project protocols will address a process for data validation that includes at least one of the available methods.

- Corrections or deletions as a result of data validation require notations in the original paper field records about how and why the data were changed, with the editor's initials.
- Modifications of the field data will be clear and concise while preserving the original data entries or notes (i.e., no erasing).
- Validation efforts will also include a check for the completeness of a data set since field sheets or other sources of data could easily be overlooked.
- Use of automated routines and/or data summary and visualization (e.g., histograms, line plots, and basic statistics) will be maximized to identify possible logic and range errors.
- Use of database programming will be maximized to control data entry. This will be achieved via the use of lookup tables and/or field-type design in a database (e.g., yes/no field-types).

We use the following three validation methods:

1) *Data entry application programming.* Certain components of data validation are built into data entry forms. This method is essentially part of the database design. Not all fields, however, have appropriate ranges known in advance. Caution must be exercised when using lookup tables to constrain variable values. Values occurring outside the range set by a lookup table (established during database design) may not always be invalid. As part of data validation procedures, the project leader is responsible for correct use of lookup tables or other automated value range control.

2) *Outlier Detection.* According to Edwards (2000), "the term outlier is not (and should not be) formally defined. An outlier is simply an unusually extreme value for a variable, given the statistical model in use." Any data set will undoubtedly contain some extreme values, so the meaning of 'unusually extreme' is subjective. The challenge in detecting outliers is in deciding how unusual a value must be before it can (with confidence) be considered 'unusually' extreme.

Data quality assurance procedures should not try to eliminate outliers. Extreme values naturally occur in many ecological phenomena; eliminating these values simply because they are extreme is equivalent to pretending the phenomenon is 'well-behaved' when it is not. Eliminating data contamination is perhaps a better way to explain this quality assurance goal. When an outlier is detected (via GIS, database, graphic, and statistical tools for ad-hoc queries and displays), the possibility of contamination will be evaluated and noted.

3) *Other exploratory data analyses.* Palmer and Landis (2002) suggest calculations for assessments of precision, bias, representativeness, completeness, and comparability may be applicable and, for certain types of measurements, evaluation of detection limits may also be warranted. Normal probability plots, Grubb's test, and simple and multiple linear regression techniques may also be used (Edwards 2000).

4.2.3. Roles and Responsibilities

Table SOP 4.9. Verification and validation responsibilities and frequencies. Adapted from O'Ney (2005).

Procedure	Verified by	Frequency	Purpose
Crew training	Protocol Lead	Annually	Verifies that project staff are qualified to perform the work to be done.
Field data collection audit	Protocol Lead	Annually	Verifies that SOPS and QAPP are followed for sample collection
Quality control samples	Crew Lead & Protocol Lead	Each sampling event	Verifies the correct number of blanks, spikes, and replicates are collected.
Calibration	Crew Lead	Each sampling event	Verifies field instruments have been calibrated correctly and calibration has been documented in the log book.
Calibration corrective action	Protocol Lead	Monthly	Verifies that the appropriate action is taken if the calibration/log fail to meet acceptance criteria
Sample preservation and handling	Field tech/ laboratory	Each sample batch	Verifies sample integrity (temp, preservation, chain-of-custody)
Instrument inspection and maintenance	Crew lead	Monthly or before long trips	Verifies that all sampling equipment is in proper operating condition and log books maintained
Data entry	Techs	w/in 5 days of data entry; 100% of records	Verifies records against original source.
Data entry	Protocol Lead	End of season; 10% of records	Verifies data were entered correctly and procedures for verifying, documenting, and correcting data errors were followed.
Raw data validation	Field crew/ Laboratory/ Protocol Lead	Each sample batch	Validates data through data summaries and identifying anomalies
Chain-of-custody documentation	Tech shipping samples	Each sample batch	Verifies that complete chain-of-custody exists before shipping to the lab.
Chain-of-custody documentation	Protocol Lead	10% throughout season	Verifies that complete chain-of-custody exists for the sample.
QA/QC sample analysis	Protocol Lead/ Laboratory	Annually	Quantifies data quality through analysis of blanks, spikes, and replicate data.
QC Result Documentation	Protocol Lead	Annually	Documents effectiveness of QC measures and makes recommendations for improvement
Data validation	NPS-WRD	Annually	Validate data before uploaded to Storet
Document location and format of computer files	Data Manager	Annually	Verifies that the location, format, media, and platform of computer files are part of project records.

4.2.4. Resolution Process

Concerns, issues, or errors identified during the verification and validation process are brought to the attention of the crew lead and to the protocol lead as soon as is possible. The protocol lead identifies, initiates, and follows-up on the effectiveness of the corrective actions. Decisions to

discard or flag data are the responsibility of the protocol lead. Examples, of error correction procedures are:

- If identified immediately, take a second measurement or sample
- Correct data entry errors on field forms by putting a line through the error, documenting, and initialing the change.
- Correct data entry errors in the database and document in the database log book.
- Flag data in the database with qualifying codes.
- Evaluate if any changes in the protocol would decrease errors.

4.3. Reconciliation and User Requirements

Any data that do not meet DQO will not be used. If data quality issues arise, a determination will be made on whether the error was caused by equipment failure or operator error. If additional staff training, equipment repair, or minor revisions to the protocol or SOPs do not correct the problem, then the DQOs will be re-evaluated for feasibility of attainment. If they are determined to be unattainable, then they will be modified or the use of the parameter(s) in question will be evaluated. In some cases, a parameter may be eliminated if no reasonable/acceptable DQOs can be attained.

Limitations on data are conveyed to users through thorough metadata documentation, most of which is contained in the database and therefore, will travel with the data. Users can also access the protocol, which describes the sample design and methods, via the SIEN websites or by contacting the network directly.

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