



Sierra Nevada Network Lake Monitoring 2008 and 2009 Summary Report

Natural Resource Data Series NPS/SIEN/NRDS—2012/357



ON THE COVER

Sampling on McGee Lake, Kings Canyon National Park
Photograph by: L. Belt

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All manuscripts in the series receive the appropriate level of peer review to ensure that the information is scientifically credible, technically accurate, appropriately written for the intended audience, and designed and published in a professional manner.

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Executive Summary

The Sierra Nevada Network (SIEN) monitors high-elevation lakes throughout Sequoia, Kings Canyon, and Yosemite National Parks as part of the National Park Service's Inventory and Monitoring (I&M) Program. The purpose of I&M Program is to develop and provide scientifically sound information on the current status and long-term trends in the composition, structure, and function of park ecosystems, and to determine how well current management practices are sustaining those ecosystems. SIEN monitors long-term trends for a suite of ecological indicators as part of the following monitoring efforts: lakes, rivers, high-elevation white pines, wetlands, birds, and climate.

Lake ecosystems were selected for monitoring because they are 1) valued for their ecological importance, contribution to Wilderness character, recreational opportunities, and importance to regional water supplies, 2) threatened by multiple stressors, and 3) sensitive to environmental change. The Lake Monitoring program incorporates two of SIEN's high priority indicators---water chemistry and surface water dynamics. The water chemistry objectives were the primary driver of the monitoring design, with the hydrologic objectives second in priority. In addition, we collect limited amphibian survey information at our lake sites that are used by the parks and cooperators to supplement ongoing research and monitoring. The amphibian information is beyond the scope of this report.

The 2008 and 2009 field seasons marked the first two seasons of SIEN's Lake Monitoring Program. In this report we provide a general evaluation of how well the protocol performed in its first years and present the 2008 and 2009 water chemistry results.

Our first two field seasons were very successful. We were able to visit all extensive and index sites on time and within budget. Twenty-five extensive sites were sampled for water chemistry each year and index sites were sampled monthly from June through October. We had strong, level-headed, and thorough field sampling crews who completed sampling with an excellent safety record. However, the hydrologic sampling of index lakes proved to be more of a challenge due to technical and budget constraints. We determined current project funding cannot support the amount of time required to train field crews on datalogger operation and for crews to be trained on and perform discharge measurements. As a result, the recommendation is to discontinue outflow stage and discharge monitoring and instead monitor lake level and water temperature, which are easier to measure.

Summary statistics are presented for the network as a whole and for each park for the 18 water chemistry measures that we monitor. Time series graphs are presented for the four sites that we sample on a more frequent schedule. A few points of interest are highlighted including lower observations of nitrate concentrations in Yosemite compared to Sequoia and Kings Canyon. This difference is likely attributed to lower rates of atmospheric deposition in Yosemite. Sequoia and Kings Canyon, Sequoia in particular, have higher deposition rates due to air patterns that concentrate pollutants in the southern Central Valley. Consistent with lower nitrate concentrations in Yosemite, we also see a higher proportion of lakes where nitrogen is the limiting nutrient. More in depth analyses and discussion will be included in the comprehensive reports which will be produced every four years.

Introduction

The purpose of the Inventory & Monitoring (I&M) Program is to develop and provide scientifically sound information on the current status and long-term trends in the composition, structure, and function of park ecosystems, and to determine how well current management practices are sustaining those ecosystems. As part of the National Park Service's (NPS) effort to "improve park management through greater reliance on scientific knowledge," a primary role of the Inventory and Monitoring Program is to collect, organize, and make available natural resource data and to contribute to the National Park Service's institutional knowledge by facilitating the transformation of data into information through analysis, synthesis, and modeling.

The I&M Program's goals are accomplished through park-wide inventories and a long-term monitoring program. In establishing a service-wide natural resources inventory and monitoring program, the National Park Service created networks of parks that are linked by geography and shared natural resource characteristics. Working within networks improves the efficiency of inventory and monitoring because parks are able to share budgets, staffing, and other resources to plan and implement an integrated program. The Sierra Nevada Network (SIEN) includes four NPS units: Devils Postpile National Monument (DEPO), Sequoia and Kings Canyon National Parks (SEKI)—two distinct parks managed as one unit, and Yosemite National Park (YOSE).

Sierra Nevada Network parks are located on the western slope of the Pacific Crest in the Sierra Nevada Mountains and span seven major watersheds (**Figure 1**). These watersheds, from north to south, are the Tuolumne, Merced, San Joaquin, Kings, Kaweah, Tule, and Kern. Runoff from these watersheds drains into the San Francisco Bay/ Sacramento–San Joaquin Delta in the north and the Tulare Lake Basin in the south. Sierra Nevada Network parks protect over 4,500 lakes and ponds 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. They are chemically dilute and characterized as oligotrophic, especially in the sub-alpine and alpine basins where there is sparse vegetative cover, shallow soils, and small contributing area. Despite the low productivity, these lakes still support a variety of flora and fauna. Aquatic wildlife include amphibians, fish (primarily non-native), macro-invertebrates, zooplankton assemblages, and micro-crustaceans (Boiano et al. 2005). However, they are subjected to stressors that have the potential to adversely affect them. The stressors of greatest concern are air pollution, climate change, non-native invasive species, and localized visitor impacts. Lakes are good indicators of aquatic and terrestrial ecosystem condition because they reflect changes within the larger watershed. Changes detected in high-elevation lakes can be an early indication of change that may eventually occur at other ecosystem types and elevations (Seastedt et al. 2004). Sierra Nevada lakes are especially sensitive to environmental change because the waters are very dilute (Eilers et al. 1989) and thus small changes can result in pronounced ecological effects. Prior research suggests that increased nitrogen and phosphorus inputs are contributing to changes in nutrient cycles and shifts in phytoplankton communities (Goldman et al. 1993, Sickman et al. 2003).

The Network monitors lake ecosystems because they are 1) valued for their ecological importance, contribution to Wilderness character, recreational opportunities, and importance to regional water supplies, 2) threatened by multiple stressors, and 3) sensitive to environmental change. The Lake Monitoring program incorporates two of SIEN's high priority vital signs---water chemistry and surface water dynamics. The water chemistry objectives were the primary driver of the monitoring design, with the hydrologic objectives second in priority. In addition, we collect limited amphibian survey information at our lake sites that are used by the parks and cooperators to supplement ongoing research and monitoring. The amphibian information is beyond the scope of this report.

The 2008 and 2009 field seasons marked the first two seasons of SIEN's Lake Monitoring Program. The purpose of this annual report is to: 1) provide a general evaluation of how well the protocol performed in its first years and 2) present the 2008 and 2009 water chemistry results. Future data summary reporting will occur on an annual basis and reports will typically be available for each field season the following spring. Comprehensive reports will be published every four years and include more detailed analyses and discussion, including trend analyses. An abbreviated description of the methods is provided in this report, and detailed information and methods for SIEN's Lake Monitoring program are found in Heard et al. (2008).

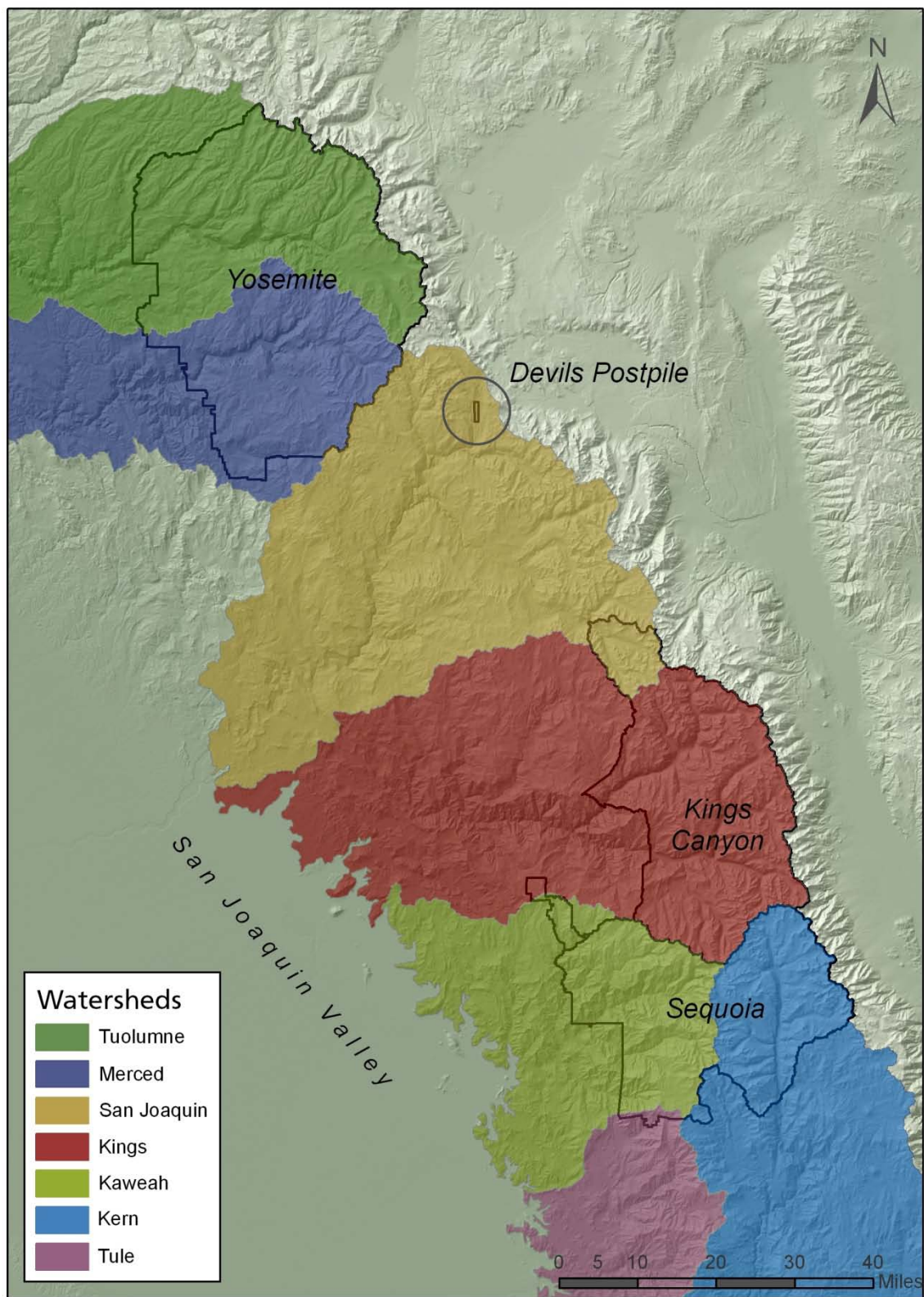


Figure 1. SIEN Parks and watersheds.

We monitor 18 water chemistry measures at each sampling station and as a result have an abundance of results to disseminate. The report format is structured so that it balances providing a succinct report to managers while at the same time increasing accessibility and documentation of the larger data set. The main body of the report includes summary information and detailed information only for specific measures of high interest. Detailed data summaries and graphs for water chemistry measures are available in Appendix A.

The measures I have chosen to highlight in this report are temperature, specific conductance, pH, acid neutralizing capacity (ANC), the suite of nitrogen fractions (nitrate, total dissolved nitrogen, and particulate nitrogen), and nutrient ratios.

Temperature, specific conductance, and pH are three of the four Inventory and Monitoring core parameters. Water temperature is a master variable controlling many physical, chemical, and biological lake processes, including lake stratification and mixing, reaction rates, dissolved oxygen concentrations, algal productivity, and health and reproduction of aquatic life. Lake water temperature is particularly sensitive to climate change.

Specific conductance is the measure of a waters' ability to conduct an electrical current and provides a broad measure of the amount of ions in a water sample. More dilute lakes, those with low specific conductance measurements, are most sensitive and susceptible to effects from stressors such as atmospheric deposition and visitor use. A change detected in specific conductance, especially in the dilute lakes of the Sierra Nevada, may indicate a change in the concentration of other major ions or nutrients of interest.

pH is the measure of hydrogen ion activity, which in dilute solutions, such as Sierra Nevada lakes, is roughly equivalent to the hydrogen ion concentration. pH controls many chemical and biological lake processes. It is sensitive to change from acidic inputs and depressions in acid neutralizing capacity.

ANC is the measure of a waters' capacity to neutralize acid. At the pH of most Sierra Nevada lakes ANC is composed primarily of the bicarbonate ion. Lakes with low ANC concentrations are more susceptible to acidification. In the Sierra Nevada, decreases in ANC are typically observed during spring snowmelt, when high streamflows dilute ANC concentrations. ANC depression also occurs during 'dirty' summer and fall storm events, when high concentrations of acids are washed into receiving waters.

The network has emphasized nutrient monitoring in high-elevation lakes. In particular, effects of atmospheric nitrogen deposition—a primary Sierra Nevada stressor—on both aquatic and terrestrial habitats, are of high interest to management and science and one of the primary reasons for selecting lakes for monitoring. Increases in nitrogen can lead to lake eutrophication and acidification and shifts in nutrient limitation (Sickman and Melack 1998, Baron et al. 2000, Elser et al. 2009b). Nitrogen and phosphorus are the primary limiting nutrients in Sierra Nevada lakes, although micronutrients such as iron and molybdenum can also be limiting. A 1999 re-survey of the Environmental Protection Agency's Western Lakes Study sites indicates that a high proportion of lakes in the Sierra Nevada are N-limited (Sickman 2001). Therefore, increased nitrogen inputs are likely to have a regional scale effect on phytoplankton growth and lake productivity. This is in contrast to the widely accepted paradigm that phosphorus is the limiting nutrient in freshwater lake ecosystems (Schindler 1974). Phosphorus can often be limiting in lake ecosystems because there is not as great a supply compared to nitrogen. Higher N supplies are

attributed to the nitrogen fixing abilities of cyanobacteria and blue-green algae and the more mobile nature of nitrate compared to phosphorus. Nitrate is a mobile anion that readily leaches into receiving waters, while phosphorus binds tightly to soil particles and moves into receiving waters primarily via erosion processes. Despite the ubiquitous supply of atmospheric nitrogen and presence of N-fixing phytoplankton, N-limitation does occur in freshwater lakes, especially in oligotrophic lakes where low N-fixation rates have been observed (Vitousek et al. 2002).

Increased productivity and shifts in nutrient limitation from N to P limited lakes is of concern because it can lead to changes in phytoplankton assemblages (Nydick et al. 2004). It is hypothesized that phytoplankton species that thrive in P-limited lakes are poorer food quality for zooplankton and, therefore, cascading effects through the food web may be observed (Elser et al. 2009a). Nydick et al. (2004) observed a decrease in zooplankton species following N enrichment, although further research is needed.

Redfield and dissolved inorganic nitrogen to total phosphorus (DIN:TP) ratios are good indicators of nutrient limitation and can be used to monitor changes in trophic status (Sickman 2001, Sickman et al. 2003). The Redfield ratio is the well established ratio of average C:N:P found in ocean phytoplankton and is 106:16:1 (Redfield 1958). Although based on internal nutrient concentrations in oceanic phytoplankton, it is applicable to freshwaters. Deviations from the N:P ratios are used to infer nutrient limitation---a ratio less than 10 indicates intracellular N deficiency and a ratio greater than 30 indicates intracellular P deficiency. In between 10 and 30 are intermediate and indicate either N or P limitation.

The availability of extracellular nutrients in the water column is also a good indicator of nutrient limitation and method for monitoring changes in trophic status over time. DIN:TP ratios are used to estimate nutrient limitation in lake ecosystems. (Morris and Lewis 1988, Sickman 2001, Bergstrom 2010). DIN:TP represents the extracellular concentrations of N and P that are bioavailable to phytoplankton (Morris and Lewis 1988). The primary source of N for phytoplankton is dissolved inorganic – nitrate and ammonium, whereas, P sources are both dissolved and particulate (i.e. TP). For DIN:TP a mass ratio less than 0.6 indicates N limitation and greater than 4 indicates P limitation. In between 0.6 and 4 are intermediate and may indicate either N or P limitation.

Monitoring Objectives

The lake monitoring design consists of two site types: 1) *extensive sites*, which are probabilistically selected and sampled once every 1-4 years and, 2) *index sites*, which are judgmentally selected and sampled multiple times each year. The two site types address slightly different monitoring objectives.

The Sierra Nevada Network lake monitoring objectives, separated by site type, are:

Extensive sites:

1. Detect long-term trends in lake water chemistry for Sierra Nevada Network lakes by measuring:
 - a. Temperature, pH, specific conductance, dissolved oxygen, acid neutralizing capacity (ANC)
 - b. Major ions: Ca, Na, Mg, K, Cl, SO₄

- c. Dissolved inorganic nitrogen (DIN), dissolved organic nitrogen (DON), total dissolved nitrogen (TDN), particulate nitrogen (PN), total nitrogen (TN)
 - d. Total dissolved phosphorus (TDP), particulate phosphorus (PP), total phosphorus (TP)
 - e. Particulate carbon (PC)
2. Detect long-term trends in trophic condition of SIEN lakes, using the following nutrient ratios as chemical indicators of trophic status: PN:PP and DIN:TP.
3. Characterize Sierra Nevada Network lakes.
4. Determine the proportion of Sierra Nevada Network lakes with chemical characteristics above/below threshold values for selected constituents.

Index sites:

1. Detect intra- and inter-annual trends in lake water chemistry for Sierra Nevada Network index lakes by measuring:
 - a. Temperature, pH, specific conductance, dissolved oxygen, ANC
 - b. Major ions: Ca, Na, Mg, K, Cl, SO₄
 - c. Dissolved inorganic nitrogen, dissolved organic nitrogen, total dissolved nitrogen, particulate nitrogen, total nitrogen
 - d. Total dissolved phosphorus, particulate phosphorus, total phosphorus
 - e. Particulate carbon
2. Detect long-term trends in trophic condition of index sites, using the following nutrient ratios as chemical indicators of trophic status: PN:PP and DIN:TP.
3. Characterize Sierra Nevada Network index site outlet flows.
4. Determine if index sites are above/below threshold values for selected constituents.
5. Detect intra- and inter-annual trends in lake level and outflow for Sierra Nevada Network index sites.

Methods

Monitoring Sites

Our monitoring design includes two types of sites that we sample: 1) *index sites*, which are judgmentally selected and sampled multiple times each year and, 2) *extensive sites*, which are probabilistically selected and sampled once every 1-4 years.

Data collected at index sites enable SIEN to answer objectives at a finer temporal scale and examine intra-annual patterns. Since index sites are sampled more frequently and focused on an individual site, we expect to detect trends for index sites sooner and with higher power than at extensive sites (i.e., network scale). Index sites were sampled once a month from approximately June through September. Although it is not possible to make network-wide statistical inferences from these more intensively collected data, these data will inform results observed at extensive sites. The network originally selected four index sites that were monitored during the 2008-2009 sampling period. The index sites have since been changed and reduced to two due to funding constraints, however, in this report we present data collected at the original sites during 2008 and 2009. These sites are:

- *Emerald Lake*, in Sequoia National Park, is one of the most thoroughly studied sub-alpine lakes in the world, with over 25 years of research and monitoring that continues through present day. It has high exposure to pollutants from the Central Valley and therefore, is an early warning indicator for other less-exposed lakes in the parks. The lake contains introduced trout and may provide habitat for tree frogs.
- *Dusy Basin*, in Kings Canyon National Park, is located on the northeastern area of the park just west of the Pacific Crest. There has been very little water chemistry data collected for lakes in Kings Canyon or on the eastern side of SEKI. This site has amphibian populations. It currently contains non-native fish, but is proposed by the park as a fish removal restoration site.
- *Maclure Lake*, in Yosemite National Park, is located in the upper Lyell Fork of the Tuolumne watershed. This lake was selected because it has been identified as especially sensitive to atmospheric N deposition based on chemical and physical characteristics. It has low specific conductance (< 10 uS/cm) and ANC concentrations (< 50 ueq/l) and moderate to high nitrogen concentrations. The watershed is granitic, sparsely vegetated, and receives above average precipitation. The lake is fishless.
- *Kuna Peak Lake*, in Yosemite National Park, is also located in the upper Lyell Fork of the Tuolumne watershed, across the canyon from Maclure Lake. This site was selected for its amphibian populations and practical access. The lake is fishless.

Data collected at extensive sites can be used to make network-wide inferences on status and trend. The target population for inference on water chemistry in Sierra Nevada Network lakes includes all lakes in the network that are greater than or equal to 1.0 hectare in area *and* greater than or equal to 2.0 m in depth. The population is sampled during the late ice-free season—August and September. Late summer and fall sampling is a better indicator of lake trophic condition. Nutrient concentrations during the growing season are good indicators of N or P saturation and changes in limiting nutrient status.

The membership design for the extensive sites is a generalized random tessellation stratified (GRTS) design. The GRTS design employs a systematic sampling approach along a randomly ordered sequence of location addresses to obtain a spatially balanced probability sample (Stevens Jr. and Olsen 2003, Stevens Jr. and Olsen 2004). The GRTS design incorporates variable probability sampling. SIEN inclusion probabilities are based on a cost-surface model that computes relative travel times to sites based on factors such as the presence of trails, vegetation type, and slope angle (Frakes et al. 2007). Lakes that are quicker to access (i.e. closer to trails and trailheads or accessed via ‘easier’ cross country terrain) have a higher probability of being selected.

The temporal sampling structure is a serial augmented panel design where sites are either visited annually or on an alternating schedule (e.g. once every 4 years). We are sampling a total of 25 lakes per year across the network. Thirty-two percent of the annual resources are allocated to the annual panel (1-0) and the remaining to the (1-3) panels. This translates to 8 lakes per year in panel (1-0) and 17 lakes per year for the (1-3) panels. We will have sampled a total of 76 different lakes after one complete rotation of the panel design. We sampled panels 1 and 2 in 2008 and panels 1 and 3 in 2009 (**Figure 2**).

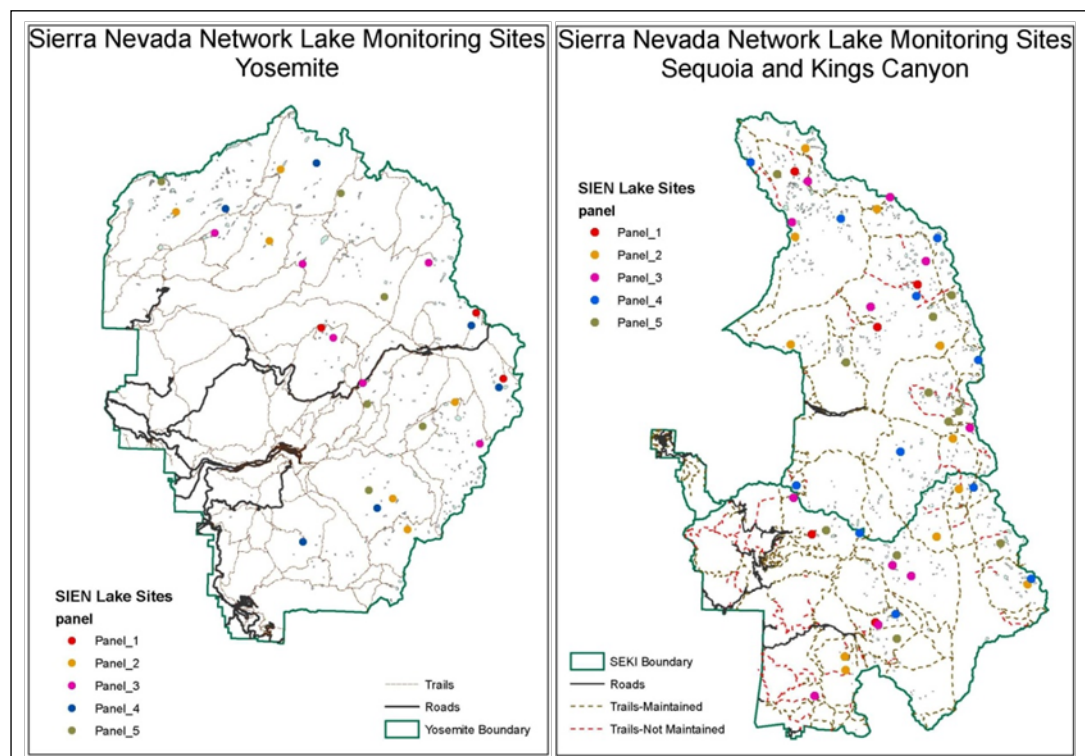


Figure 2. Sierra Nevada Network extensive monitoring sites.

Data and Sample Collection

Sampling was conducted by two field crews with support from SIEN, SEKI, and YOSE staff. In 2008, the Yosemite crew was composed of one GS-4 and one GS-5 and the Sequoia/Kings crew was composed of two GS-5's and a GS-3 student hire that helped for part of the season. The lake monitoring workload does not provide a full season of work for a summer crew; therefore, we shared crews with each of the parks. The Yosemite crew worked approximately 50% for Lakes

and 50% for Yosemite Hydroclimate monitoring. The Sequoia and Kings Canyon crew worked approximately 50% for Lakes and 50% of the time on Sequoia and Kings Canyon amphibian restoration projects.

In 2009, the Yosemite crew was composed of one GS-5 and one GS-6 and the Sequoia/Kings crew composed of two GS-5's. The Yosemite crew worked approximately 50% for Lakes and 50% for Yosemite Hydroclimate monitoring. The Sequoia and Kings Canyon crew worked approximately 50% for Lakes and 50% for a UC Riverside – SIEN collaborative research project. The current crew has one GS-6 as a result of logistics associated with sharing a crew with Yosemite staff. This is an exception and future crews will be composed of all GS-5's per the budget outlined in the lakes protocol.

Crews collected field observations, *in situ* water quality measurements, water samples (filtered and unfiltered), and particulate filter samples (**Table 1**) (**Figure 3**). Crews followed standard water quality sampling procedures, which are described in Heard et al. (2008). Sampling is conducted at both index and extensive sites. All lakes are sampled at the outlet. Index and [1-0] panel lakes are also sampled at mid-lake. A mid-lake sample is collected from the epilimnion, 1 m below the surface and if the lake is stratified, a second sample is collected from the hypolimnion.



Figure 3. Collecting an outlet sample at Emerald Lake.

Table 1. Observations and measures collected at SIEN lakes.

Data Collection Type	Measure
Field observations	Weather, lake photo, fish presence
In situ water quality measures	Water temp, specific conductance, dissolved oxygen, pH
Water samples-unfiltered	pH, acid neutralizing capacity, specific conductance
Water samples-filtered	Dissolved inorganic nitrogen, dissolved organic nitrogen, total dissolved nitrogen, total dissolved phosphorus, calcium, sodium, magnesium, potassium, chloride, sulfate
Particulate filter samples	Particulate nitrogen, particulate phosphorus, particulate carbon
Hydrologic data	Stage, qualitative outlet discharge

Hydrologic sampling is conducted at index sites only. Solinst levelloggers were installed at the end of the 2008 season at 3 of the 4 index sites---Kuna Peak, Maclure, and Dusy. Emerald lake is gaged by the University of California.

Field and Laboratory Methods

Field and laboratory instrumentation and methods were chosen based on their suitability for dilute water samples and use in previous studies of Sierra Nevada lakes. With the exception of field measurements of in-situ temperature, dissolved oxygen, and specific conductance, all other

analyses were conducted by the University of California, Riverside. Methods and quality assurance and quality control (QA/QC) were conducted in accordance with Heard et al. (2008) (**Table 2**).

In situ measurements were made using YSI-85 sondes. In the laboratory, a lab-grade conductivity meter equipped with a $K=1.0\text{ cm}^{-1}$ cell was used. Laboratory pH was measured with a high quality, laboratory pH meter equipped with an Orion-Ross combination electrode. Acid neutralizing capacity of samples was measured by Gran Titration (Gran 1952). All field and laboratory instruments were calibrated using manufacturer's direction using NIST-traceable standards, where feasible.

Major anions plus nitrate and nitrite were measured using chemically suppressed ion chromatography on a Dionex ion chromatograph (Hautman and Munch 1997). Major cations were measured using inductively coupled plasma (Martin and Brockhoff 1994) with modifications described in Morishige and Kimura (2008) and Dombek (2009).

Particulate carbon, nitrogen, and phosphorus were collected on Pall A/E glass fiber filters that were pre-combusted at 500°C for 3 hours. Particulate C and N were measured on a high-temperature elemental analyzer. Particulate P and total dissolved P were measured according to Valderrama (1981) followed by EPA Method 365.1 (O'Dell 1993b). TDN was analyzed according to Valderrama (1981) followed by EPA Method 353.2 (O'Dell 1993a).

Table 2. Analytical methods and 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 chromatography (EPA Method 300.1)	0.3 umol/L	0.95 umol/L	-	5%	±10%	80-120%	95%
Nitrite	Ion chromatography (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 chromatography (EPA Method 300.1)	0.3 umol/L	0.95 umol/L	-	10%	±10%	80-120%	95%
Sulfate	Ion chromatography (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

Data Analysis

Data analyses in this report address Monitoring Objective 3, which is to characterize Sierra Nevada lakes for extensive and index sites. The remaining objectives will be addressed once we have ample years of data for trend analyses and have established thresholds.

Extensive Sites

Summary statistics (mean, standard error, lower confidence interval (CI), upper CI, min, and max) were computed for extensive sites in 2008 and 2009. Methods incorporate the GRTS neighborhood variance estimator (Stevens Jr. and Olsen 2003) and censored data approaches (Helsel 2005). Box plots were graphed for each measure by year. Outlet sample results were used for extensive site summary statistics as these are collected at all extensive sites and thus allow for better comparison across sites. Descriptive statistics and box plots were calculated in the R environment (R Development Core Team 2011) and using methods described in Starceovich and Heard (2008). Specific conductance and nitrate concentration spatial patterns were mapped using ArcGIS.

Nutrient ratios were calculated by site to assess nutrient limitation. Two ratios were used---the Redfield ratio (PN:PP) and DIN:TP. Ratios are presented spatially using maps created in ArcGIS. Nutrient limitation was inferred from the ratios using the following criteria: For Redfield a molar ratio less than 10 indicates intracellular N deficiency and a ratio greater than 30 indicates intracellular P deficiency. Ratios between 10 and 30 are intermediate and may indicate either N or P limitation. For DIN:TP a mass ratio less than 0.6 indicate N limitation and greater than 4 indicates P limitation. Ratios in between 0.6 and 4 are intermediate and may indicate either N or P limitation.

Index Sites

2008 and 2009 water chemistry results were graphed for each site as a time series scatter plot using Sigma Plot.

Quality Assurance and Quality Control

Quality assurance and quality control methods and criteria were followed as described in the Quality Assurance Project Plan (Heard and Sickman 2008). Completeness was determined by calculating the proportion of stations sampled to the total expected per the protocol. Field aspects of the program were assessed using field duplicates and blanks. Relative percent difference (RPD) was used to compare field duplicates:

$$RPD = [ABS(replicate1 - replicate2)/(AVG \text{ of replicates 1 and 2})]*100$$

The mean deviation from zero was calculated for each measure using field blank results.

Quality assurance and quality control for laboratory analyses were evaluated by the University of California, Riverside and summarized in a report submitted to SIEN (Appendix B).

Results

Extensive Sites

Extensive site samples were collected for panels one and two in 2008 and one and three in 2009. Sampling was conducted in August and September of both years. Summary statistics (mean, standard error, lower CI, upper CI, min, and max) were computed for each measure by year network- wide (**Table 3** and **Table 4**) and by park (**Table 5 - Table 8**). Results are also presented as box plots for each measure by year. Box plots for measures of high interest (temperature, pH, ANC, specific conductance, NO₃, TDN, and PN) are highlighted in the main body of the report (**Figure 4** and **Figure 5**) and discussed below. (*Refer to Appendix A for box plots of all 18 measures by year*). Specific conductance and nitrate spatial patterns for the combined 2008 and 2009 data were mapped by park (**Figure 6** and **Figure 9**).

The mean lake water temperature (standard error) in 2008 was 15.8 (0.83) °C and ranged from 5.2 to 23.9 °C. The mean lake water temperature in 2009 was 16.1 (0.83) °C and ranged from 10.9 to 22.8 °C. The mean specific conductance in 2008 was 12.84 (1.916) µS/cm and ranged from 3.40 to 89.7 µS/cm. The mean specific conductance in 2009 was 9.36 (0.94) µS/cm and ranged from 4.5 to 22.3 µS/cm. Mean ANC in 2008 was 60.6 (2.35) µequ/l and ranged from 7.49 to 129 µequ/l. Mean ANC in 2009 was 62.4 (2.33) µequ/l and ranged from 15.7 to 151 µequ/l. The mean nitrate concentration in 2008 was 2.52 (0.832) µM and ranged from below detection to 8.90 µM. The mean nitrate concentration in 2009 was 6.99 (0.1.12) µM and ranged from 0.30 to 11.80 µM. Mean total dissolved N in 2008 was 9.32 (0.823) µM and ranged from 4.02 to 15.6 µM. Mean total dissolved N in 2009 was 9.49 (0.1.12) µM and ranged from 1.63 to 29.7 µM. Mean particulate N in 2008 was 24.1 (2.33) µg/l and ranged from 0.27 to 93.5 µg/l. Mean particulate N in 2009 was 20.2 (1.69) µg/l and ranged from 4.80 to 69.4 µg/l.

DIN:TP ratios (mass) ranged from 0.13 to 77 and PN:PP ratios (molar) ranged from 0.10 to 62 (**Figure 10** and **Figure 11**). In Yosemite, PN:PP ratio results indicate that 8 sites were N limited, 0 P limited, and 10 intermediate. The DIN:TP ratio results indicate 12 sites were N limited, 2 P limited, and 1 intermediate. In Sequoia and Kings Canyon PN:PP results indicate that 16 sites were N limited, 3 P limited, and 12 intermediate. DIN:TP ratio results indicate 12 sites were N limited, 10 sites were P limited, and 9 intermediate (**Table 9**).

Table 3. Summary Statistics for 2008 SIEN extensive sites.

Measure	Mean	SE	Lower CI	Upper CI	n	Min	Max
<u>Core parameters</u>							
Temperature	15.8	0.863	14.4	17.3	25	5.2	23.9
Specific Conductance - field ($\mu\text{S}/\text{cm}$)	12.3	1.92	9.2	15.5	25	0.0	92.0
Specific Conductance - lab ($\mu\text{S}/\text{cm}$)	12.84	1.916	9.69	16.00	25	3.4	89.7
pH - lab	6.31	0.182	6.01	6.61	25	5.83	6.70
Dissolved oxygen (%)	60	1.5	58	63	24	31	82
<u>Nitrogen</u>							
Nitrate (μM)	2.52	0.832	1.16	3.89	25	< 0.100	8.90
Total dissolved nitrogen (μM)	9.32	0.823	7.96	10.7	25	4.02	15.6
Particulate nitrogen ($\mu\text{g}/\text{l}$)	24.1	2.33	20.2	27.9	24	0.27	93.5
<u>Phosphorus</u>							
Total dissolved phosphorus (μM)	0.063	0.006	0.053	0.0739	25	< 0.033	0.129
Particulate phosphorus (μM)	0.182	0.075	0.060	0.305	24	0.118	0.331
<u>Carbon</u>							
Particulate carbon ($\mu\text{g}/\text{l}$)	228.1	27.25	183.2	272.9	24	2.8	605.6
<u>Major Ions</u>							
Calcium (μM)	38.7	3.62	32.8	44.7	25	7.04	316
Sodium (μM)	24.1	1.67	21.4	26.9	25	8.53	73.4
Magnesium (μM)	4.13	1.13	2.27	5.98	25	0.65	29.8
Potassium (μM)	5.33	0.44	4.60	6.06	25	1.53	11.9
Chloride (μM)	4.31	0.669	3.21	5.41	25	0.600	11.8
Sulfate (μM)	19.9	3.60	13.9	25.8	25	1.50	290
ANC ($\mu\text{equ}/\text{l}$)	60.6	2.35	56.7	64.5	25	7.49	129

Table 4. Summary statistics for SIEN 2009 extensive sites.

Measure	Mean	SE	Lower CI	Upper CI	n	Min	Max
<u>Core parameters</u>							
Temperature	16.1	0.83	14.8	17.5	24	10.9	22.8
Specific Conductance - field ($\mu\text{S}/\text{cm}$)	8.0	1.0	6.3	9.7	23	0.0	21.6
Specific Conductance - lab ($\mu\text{S}/\text{cm}$)	9.36	0.94	7.82	10.9	25	4.50	22.3
pH - lab	6.36	0.27	5.92	6.80	25	5.70	7.12
Dissolved oxygen (mg/l)	8.0	1.1	6.3	9.7	23	0.0	21.6
<u>Nitrogen</u>							
Nitrate (μM)	6.99	1.12	5.15	8.83	25	0.30	11.80
Total dissolved nitrogen (μM)	9.49	1.12	7.65	11.4	25	1.63	29.7
Particulate nitrogen ($\mu\text{g}/\text{l}$)	20.2	1.69	17.4	23.0	25	4.80	69.4
<u>Phosphorus</u>							
Total dissolved phosphorus (μM)	0.059	0.008	0.046	0.071	25	0.012	0.149
Particulate phosphorus (μM)	0.084	0.059	0.000	0.181	25	0.051	0.130
<u>Carbon</u>							
Particulate carbon ($\mu\text{g}/\text{l}$)	256.1	6.044	246.1	266.0	25	94.5	830.7
<u>Major Ions</u>							
Calcium (μM)	23.4	1.84	20.4	26.5	24	7.22	73.3
Sodium (μM)	23.7	1.56	21.1	26.3	24	7.08	51.5
Magnesium (μM)	3.33	0.64	2.28	4.38	24	1.24	11.65
Potassium (μM)	4.88	0.69	3.74	6.02	24	1.75	10.3
Chloride (μM)	2.62	0.46	1.86	3.37	25	1.10	5.64
Sulfate (μM)	6.72	1.00	3.44	10.01	25	0.21	44.04
ANC ($\mu\text{equ}/\text{l}$)	62.4	2.33	58.6	66.2	25	15.7	151

Table 5. Summary statistics for YOSE 2008 extensive sites.

Measure	Mean	SE	Lower CI	Upper CI	n	Min	Max
<u>Core parameters</u>							
Temperature	19.5	0.957	17.9	21.1	9	11.6	23.9
Specific Conductance - field ($\mu\text{S}/\text{cm}$)	11.5	3.33	6.02	17.0	9	0.01	92
Specific Conductance - lab ($\mu\text{S}/\text{cm}$)	8.09	1.08	6.32	9.86	9	3.40	23.40
pH - lab	6.21	0.255	5.79	6.63	9	5.83	6.51
Dissolved oxygen (%)	53	2.1	50	57	9	31	82
<u>Nitrogen</u>							
Nitrate (μM)	*	*	*	*	9	0.10	4.30
Total dissolved nitrogen (μM)	9.86	1.04	8.14	11.6	9	4.75	15.16
Particulate nitrogen ($\mu\text{g}/\text{l}$)	28.8	4.20	21.9	35.7	9	5.83	93.5
<u>Phosphorus</u>							
Total dissolved phosphorus (μM)	0.071	0.010	0.054	0.088	9	0.033	0.129
Particulate phosphorus (μM)	0.182	0.117	0.000	0.375	9	0.118	0.331
<u>Carbon</u>							
Particulate carbon ($\mu\text{g}/\text{l}$)	228	5.84	218	237	9	2.77	426
<u>Major Ions</u>							
Calcium (μM)	20.5	1.87	17.4	23.6	9	7.04	67.9
Sodium (μM)	24.0	1.76	21.1	26.9	9	8.53	45.1
Magnesium (μM)	3.09	0.78	1.81	4.37	9	0.65	13.1
Potassium (μM)	5.04	0.85	3.74	6.44	9	1.53	11.9
Chloride (μM)	2.51	0.66	1.41	3.61	9	0.60	5.70
Sulfate (μM)	4.65	1.28	2.55	6.75	9	2.00	46.0
ANC ($\mu\text{equ}/\text{l}$)	54.9	2.90	50.1	59.7	9	17.2	109

* 8 of 9 samples were below detection

Table 6. Summary statistics for SEKI 2008 extensive sites.

Measure	Mean	SE	Lower CI	Upper CI	n	Min	Max
<u>Core parameters</u>							
Temperature	13.8	0.96	12.3	15.4	16	5.2	17.5
Specific Conductance - field ($\mu\text{S}/\text{cm}$)	13.5	2.3	9.7	17.4	16	0.6	84.8
Specific Conductance - lab ($\mu\text{S}/\text{cm}$)	15.5	2.38	11.6	19.4	16	4.6	89.7
pH - lab	6.36	0.197	0.03	6.68	16	5.86	6.70
Dissolved oxygen (%)	65	1.4	62	67	15	40	79
<u>Nitrogen</u>							
Nitrate (μM)	2.30	1.04	0.58	4.01	16	0.10	8.90
Total dissolved nitrogen (μM)	9.01	0.93	7.5	10.5	16	4.02	15.6
Particulate nitrogen ($\mu\text{g}/\text{l}$)	20.5	2.45	16.4	24.5	15	0.27	48.9
<u>Phosphorus</u>							
Total dissolved phosphorus (μM)	0.06	0.005	0.052	0.069	16	0.033	0.103
Particulate phosphorus (μM)	0.18	0.063	0.078	0.286	15	0.153	0.267
<u>Carbon</u>							
Particulate carbon ($\mu\text{g}/\text{l}$)	228	34.6	171	284	15	47.1	606
<u>Major Ions</u>							
Calcium (μM)	48.8	4.51	41.4	56.2	16	9.28	316
Sodium (μM)	24.2	1.99	20.9	27.5	16	9.24	73.4
Magnesium (μM)	4.70	1.39	2.40	6.99	16	1.08	29.8
Potassium (μM)	5.45	0.69	4.30	6.58	16	2.23	10.3
Chloride (μM)	5.31	0.79	4.00	6.61	16	1.20	11.8
Sulfate (μM)	28.2	4.48	20.9	35.6	16	1.50	290
ANC ($\mu\text{equ}/\text{l}$)	63.7	2.68	59.3	68.1	16.0	7.49	129

Table 7. Summary statistics for YOSE 2009 extensive sites.

Measure	Mean	SE	Lower CI	Upper CI	n	Min	Max
<u>Core parameters</u>							
Temperature	17.2	1.0	15.5	18.9	8	10.9	20.8
Specific Conductance - field ($\mu\text{S}/\text{cm}$)	8.4	1.29	6.30	10.6	9	4.40	21.6
Specific Conductance - lab ($\mu\text{S}/\text{cm}$)	8.66	1.23	6.65	10.68	9	4.50	22.30
pH - lab	6.27	0.341	5.70	6.83	9	5.74	7.04
Dissolved oxygen (mg/l)	6.0	0.56	5.0	6.9	6	4.4	9.0
<u>Nitrogen</u>							
Nitrate (μM)	*	*	*	*	9	0.30	9.51
Total dissolved nitrogen (μM)	9.50	1.68	6.73	12.3	9	2.98	29.7
Particulate nitrogen ($\mu\text{g}/\text{l}$)	14.7	1.57	12.1	17.6	9	4.80	26.0
<u>Phosphorus</u>							
Total dissolved phosphorus (μM)	0.052	0.094	0.000	0.206	9	0.027	0.116
Particulate phosphorus (μM)	0.081	0.052	0.000	0.167	9	0.059	0.091
<u>Carbon</u>							
Particulate carbon ($\mu\text{g}/\text{l}$)	186	5.52	177	195	9	94.5	328
<u>Major Ions</u>							
Calcium (μM)	20.0	2.21	16.3	23.6	9	7.22	60.5
Sodium (μM)	22.7	2.05	19.4	26.1	9	7.08	48.5
Magnesium (μM)	3.33	0.85	1.94	4.73	9	1.40	11.7
Potassium (μM)	5.00	0.98	3.39	6.61	9	1.75	10.3
Chloride (μM)	2.84	0.63	1.80	3.87	9	1.10	5.64
Sulfate (μM)	5.9755	1.85	2.901	9.01	9	0.21	44.0
ANC ($\mu\text{equ}/\text{l}$)	58.0	3.40	52.4	63.6	9	15.7	126

* 8 of 9 samples were below detection

Table 8. Summary statistics for SEKI 2009 extensive sites.

Measure	Mean	SE	Lower CI	Upper CI	n	Min	Max
<u>Core parameters</u>							
Temperature	15.657	0.9384	14.1	17.2	16	11.9	22.8
Specific Conductance - field ($\mu\text{S}/\text{cm}$)	7.8	1.2	5.8	9.7	15	0.0	20.6
Specific Conductance - lab ($\mu\text{S}/\text{cm}$)	9.75	1.033	8.1	11.5	16	5.2	21.2
pH - lab	6.41	0.296	5.93	6.90	16	5.70	7.12
Dissolved oxygen (%)	6.216	0.8801	4.77	7.69	13	0.4	10.9
<u>Nitrogen</u>							
Nitrate (μM)	5.19	1.31	3.04	7.342	16	0.30	11.76
Total dissolved nitrogen (μM)	9.49	1.09	7.70	11.3	16	1.63	22.8
Particulate nitrogen ($\mu\text{g}/\text{l}$)	23.3	2.05	19.9	26.6	15	5.0	69.4
<u>Phosphorus</u>							
Total dissolved phosphorus (μM)	0.070	0.016	0.045	0.096	16	0.012	0.149
Particulate phosphorus (μM)	0.085	0.073	0.000	0.204	16	0.051	0.130
<u>Carbon</u>							
Particulate carbon ($\mu\text{g}/\text{l}$)	295	7.31	283	307	16	126	831
<u>Major Ions</u>							
Calcium (μM)	25.5	2.13	22.0	29.0	15	9.94	73.3
Sodium (μM)	24.3	1.71	21.5	27.1	15	9.67	51.5
Magnesium (μM)	3.33	0.70	2.17	4.48	15	1.24	7.7
Potassium (μM)	4.80	0.72	3.62	5.98	15	2.32	9.7
Chloride (μM)	2.50	0.490	1.69	3.3	16	1.24	4.54
Sulfate (μM)	7.18	1.72	4.36	10.0	16	0.35	42.9
ANC ($\mu\text{equ}/\text{l}$)	64.8	2.33	61.0	68.6	16.0	39.0	151

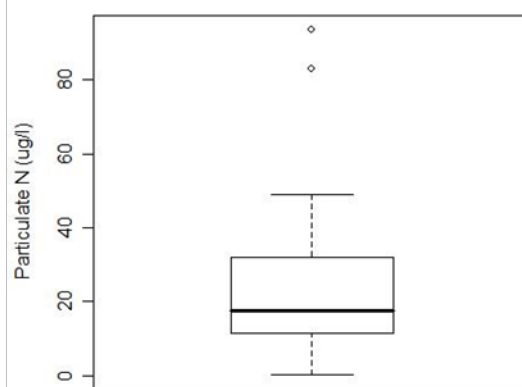
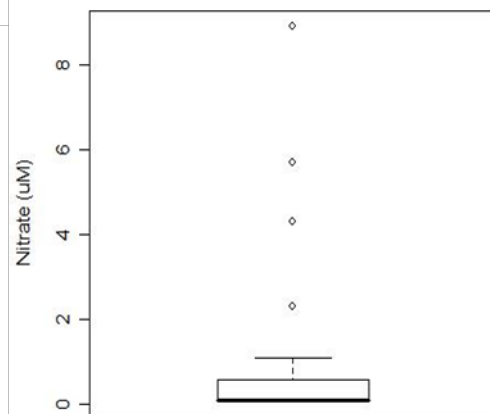
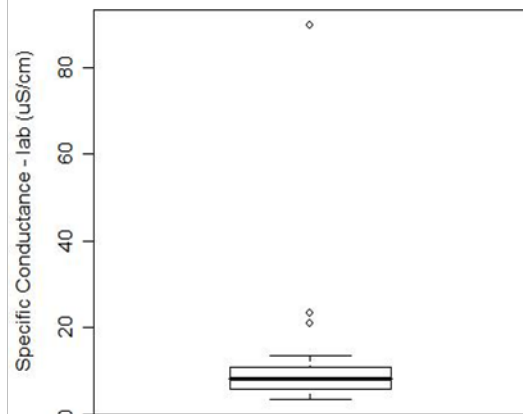
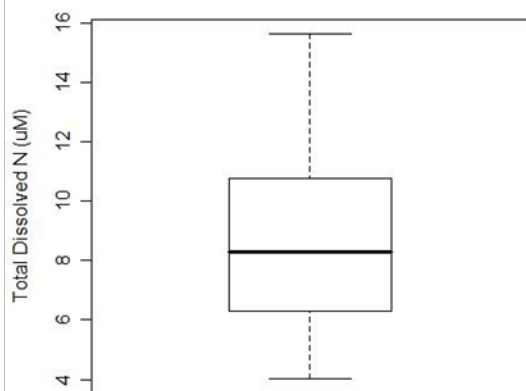
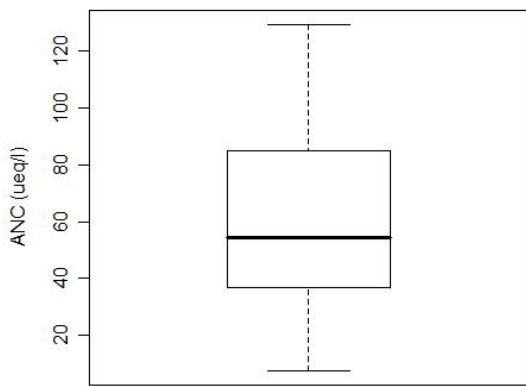
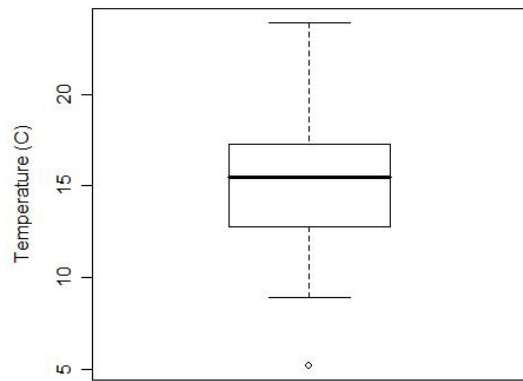


Figure 4. Box plots for selected measures from 2008 extensive sites. Concentrations below the MDL are plotted at the detection limit. The bold line inside the box is the median, the bottom and top of the box are the 25th and 75th percentiles, respectively, the whiskers (or lines extending from the box) reach to the minimum and maximum values omitting outliers, and dots are outliers.

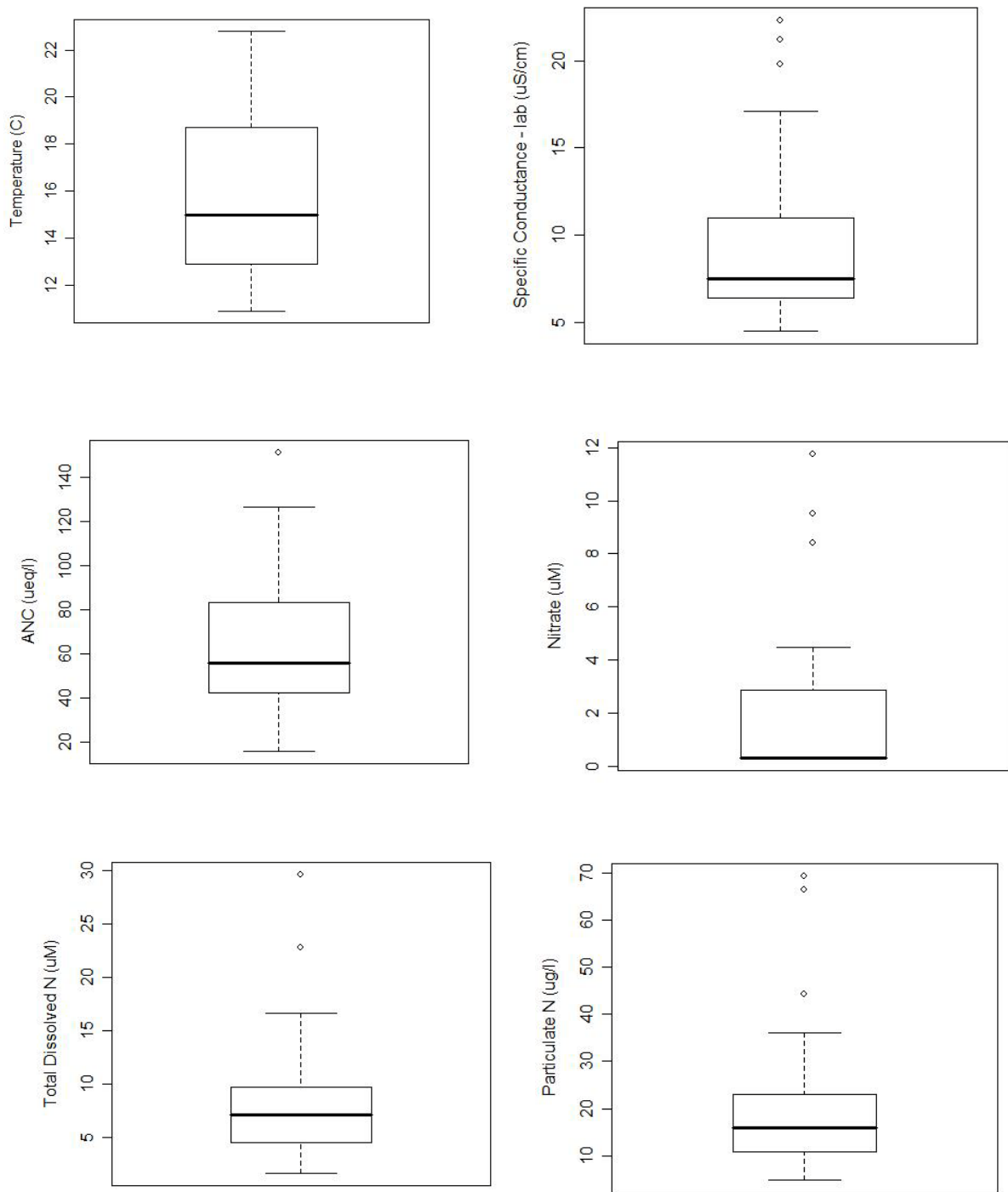


Figure 5. Box plots for selected measures from 2009 extensive site data.

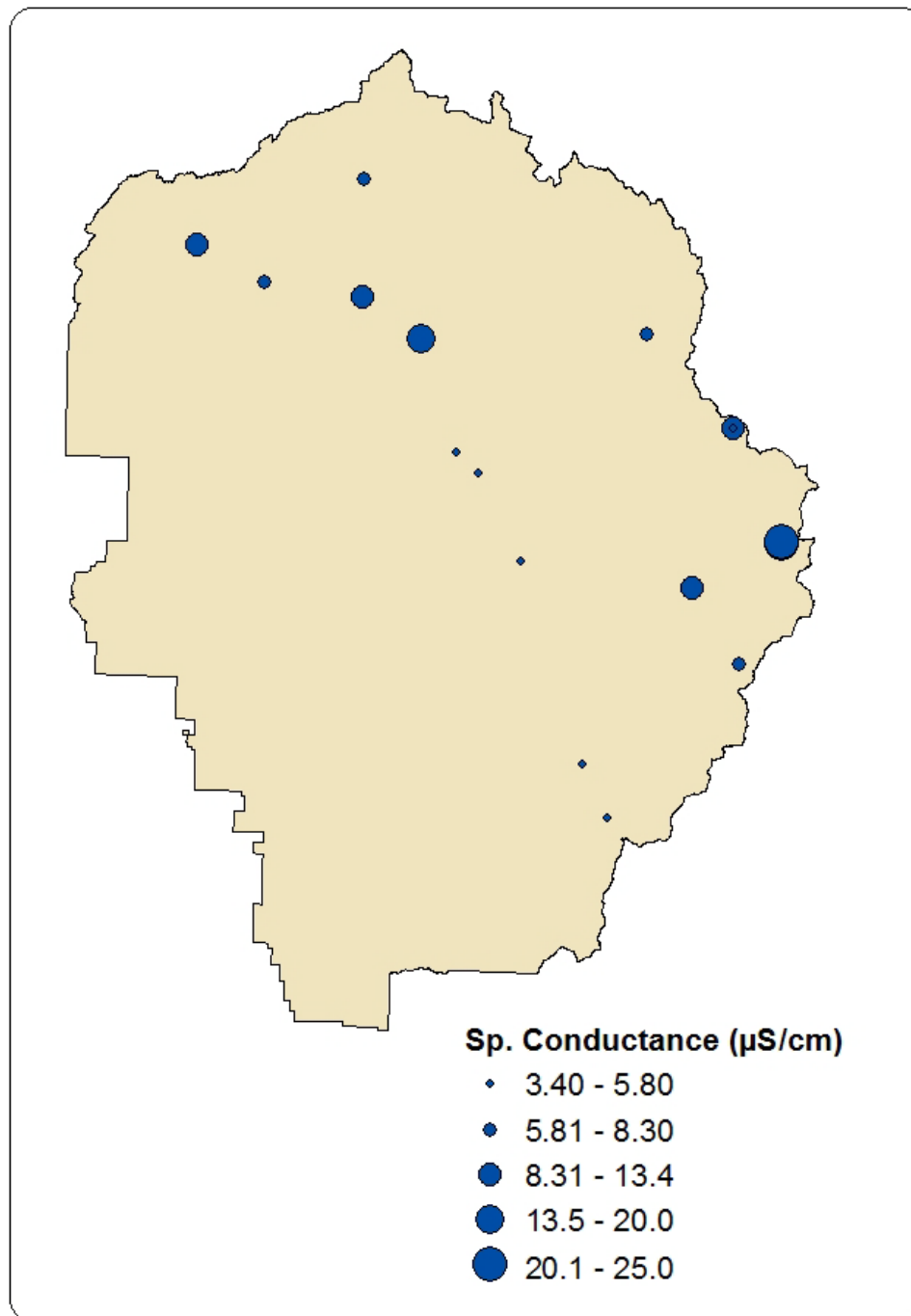


Figure 6. 2008 and 2009 specific conductance results across Yosemite National Park.

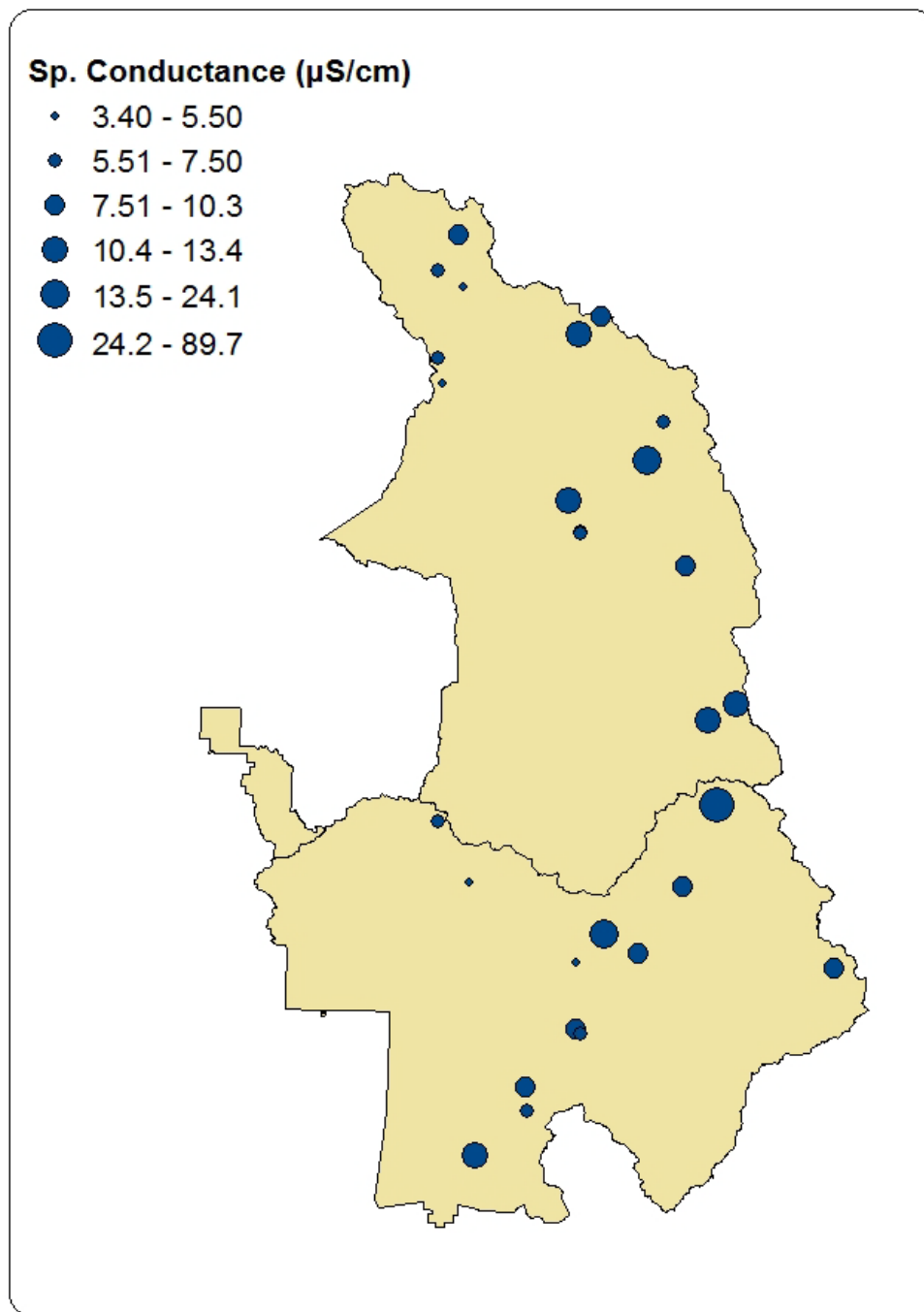


Figure 7. 2008 and 2009 specific conductance results across Sequoia and Kings Canyon National Parks.

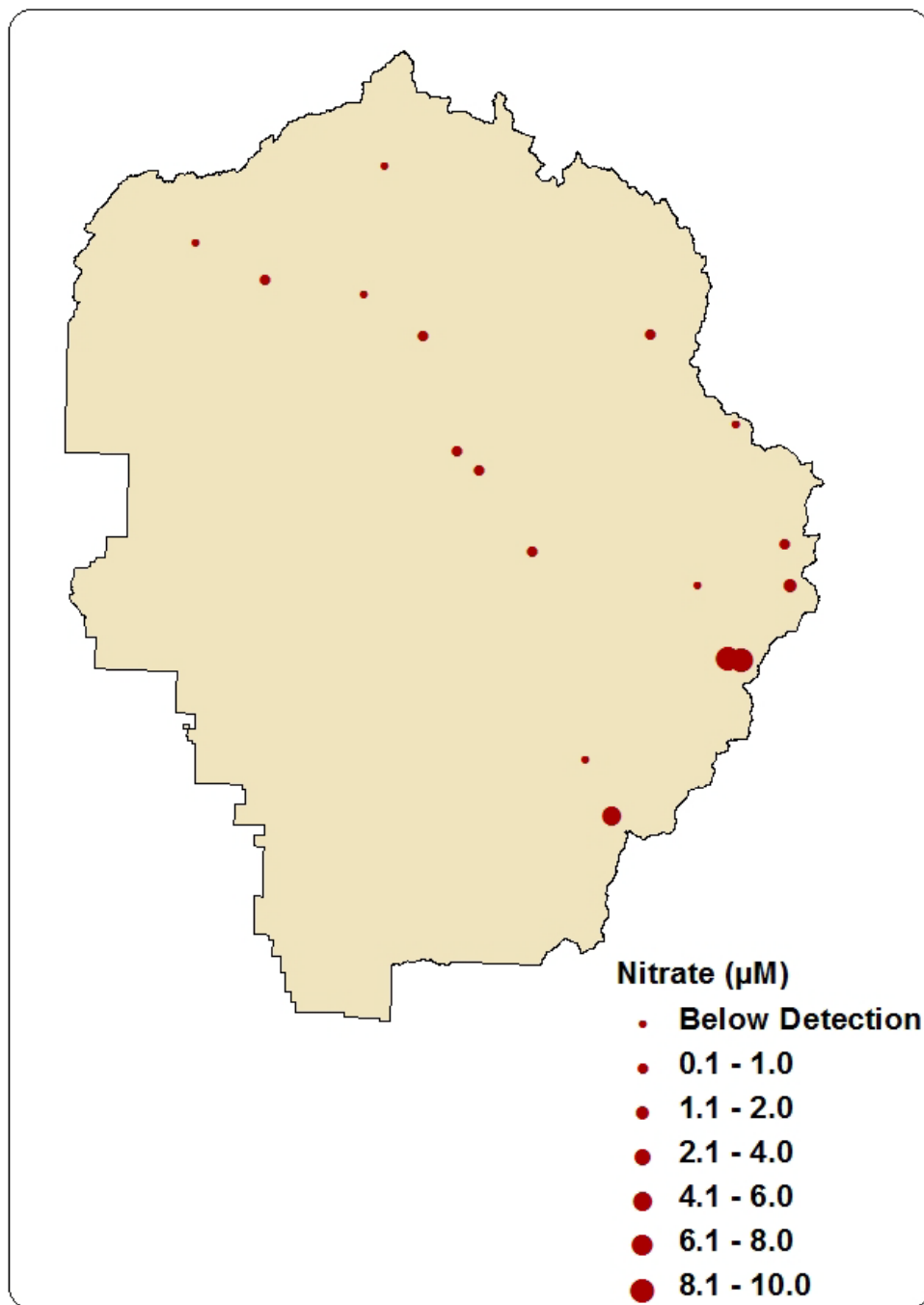


Figure 8. 2008 and 2009 nitrate concentrations across Yosemite National Park.

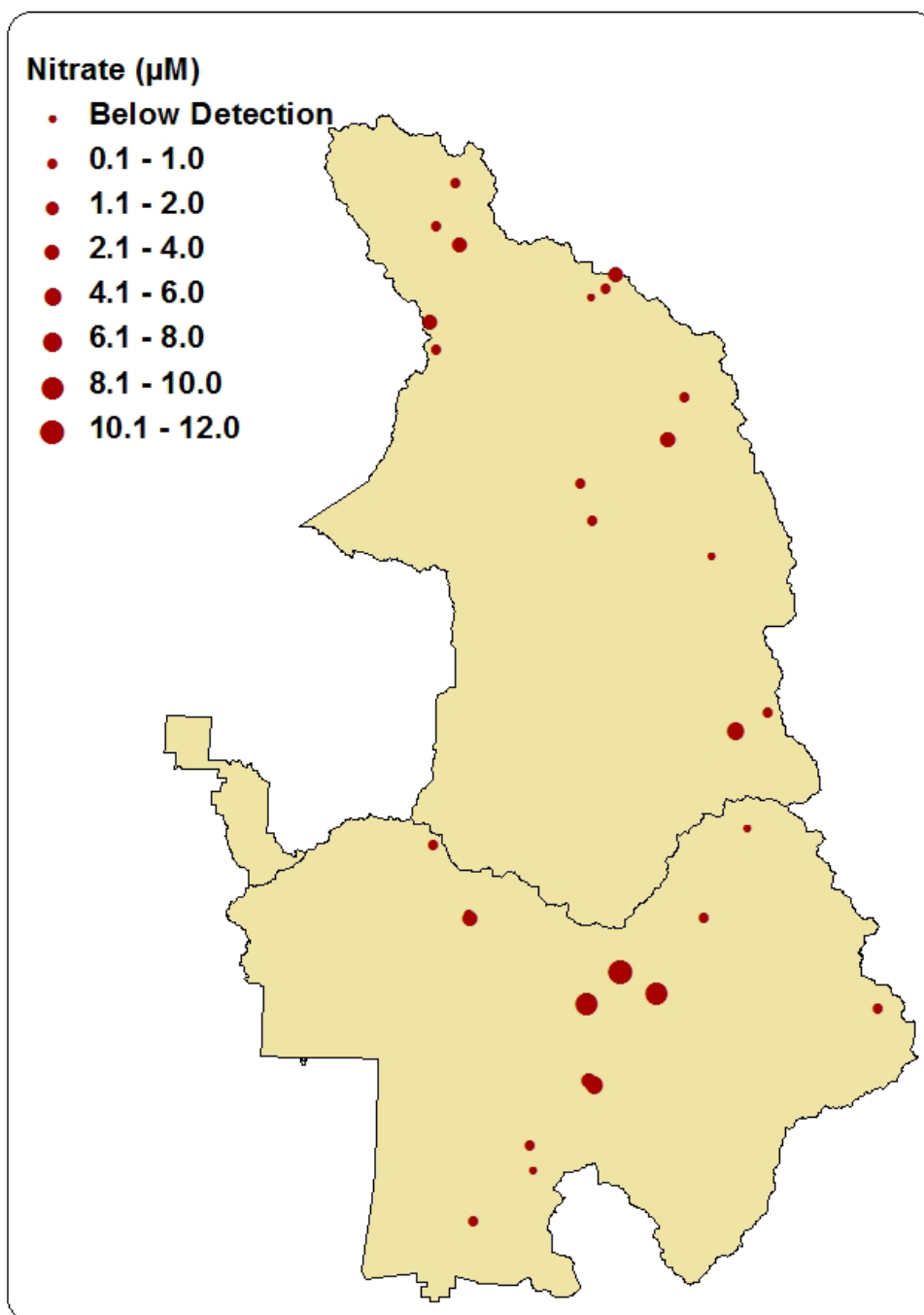


Figure 9. 2008 and 2009 nitrate concentrations across Sequoia and Kings Canyon National Parks.

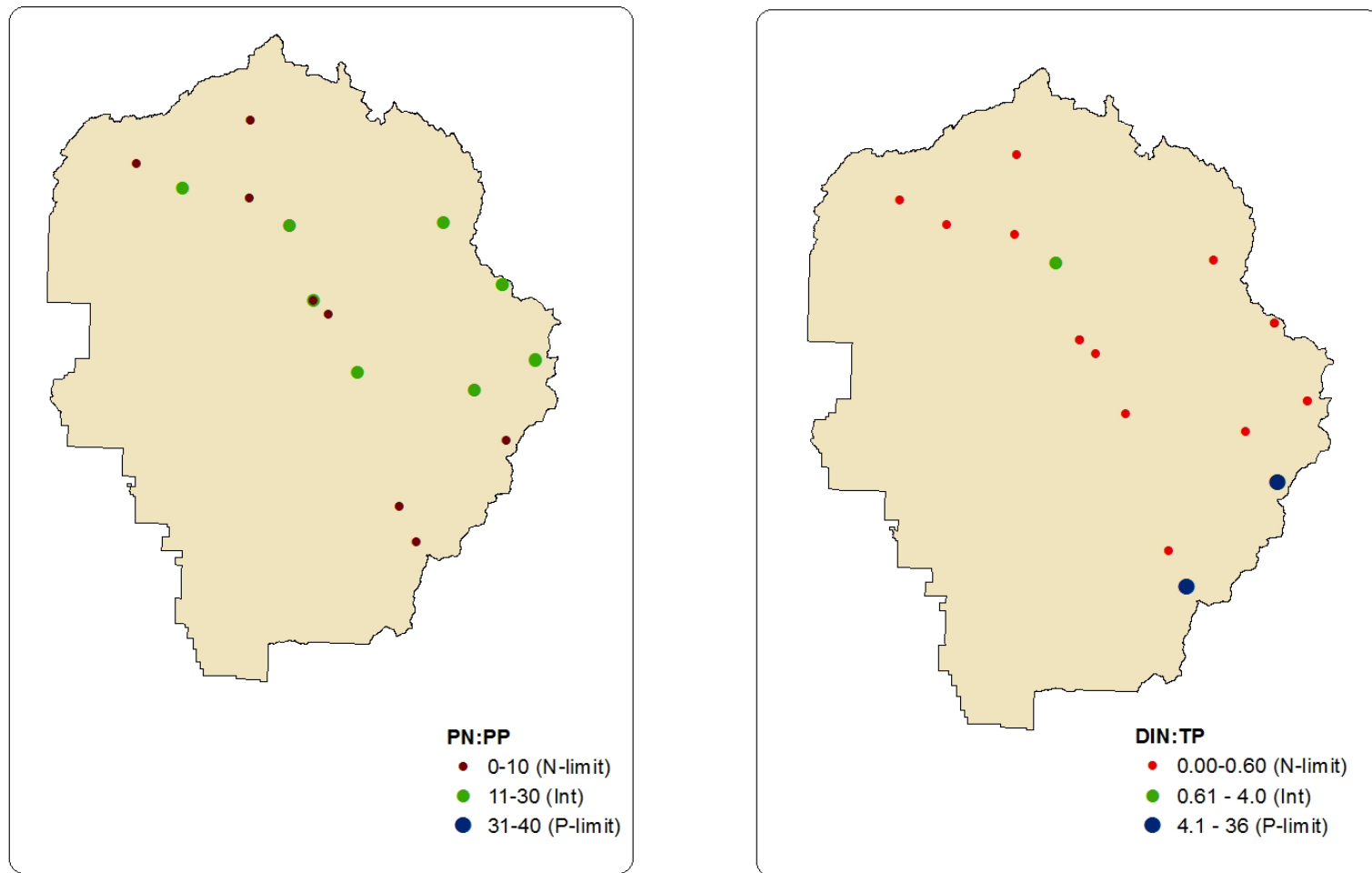


Figure 10. 2008 and 2009 PN:PP and DIN:TP ratios for Yosemite National Park. Red indicates N-limitation, green indicates intermediate limitation (N or P), and blue indicates P-limitation.

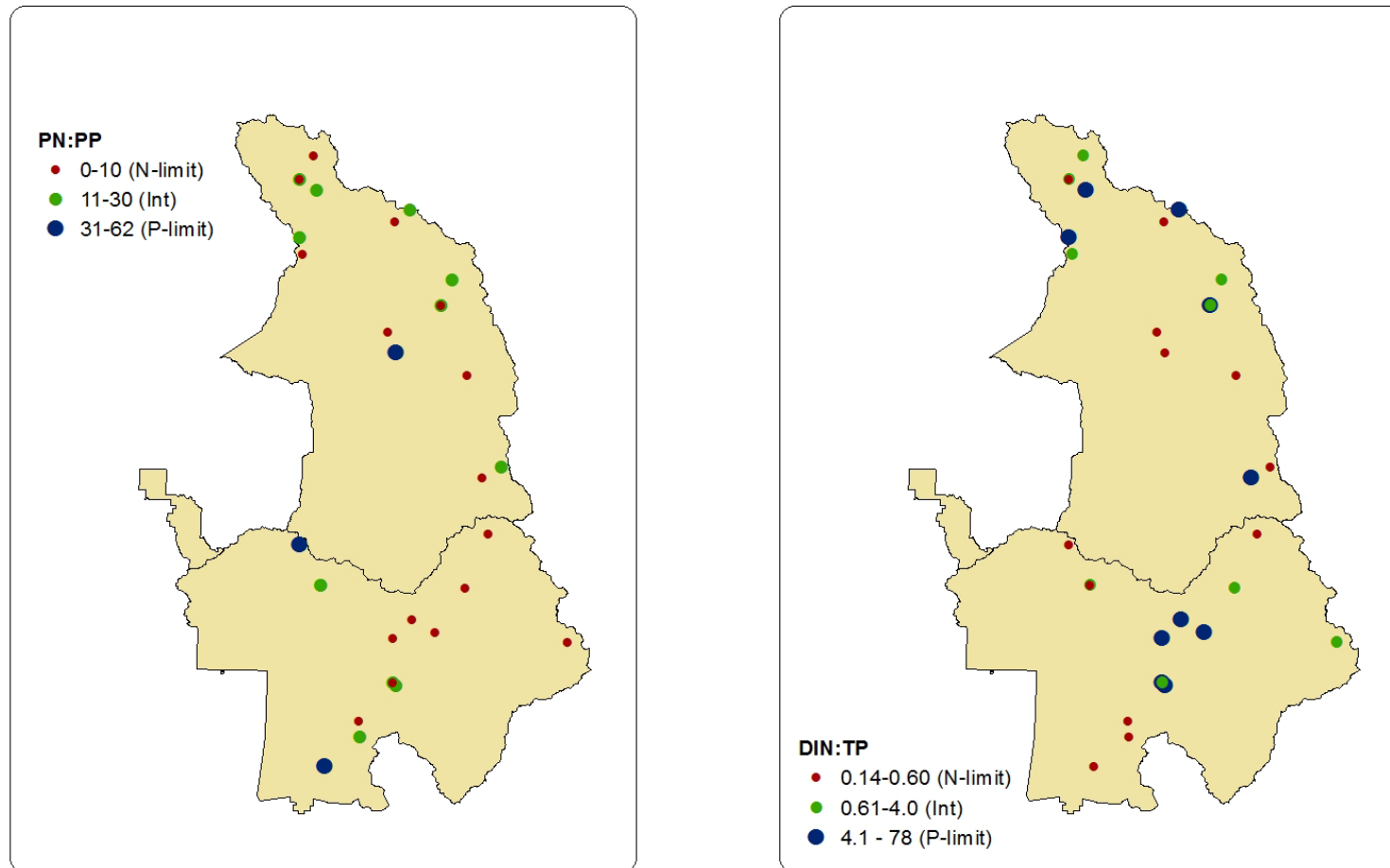


Figure 11. 2008 and 2009 PN:PP and DIN:TP ratios for Sequoia and Kings Canyon National Parks. Red indicates N-limitation, green indicates intermediate limitation (N or P), and blue indicates P-limitation (Note in some cases symbols overlap).

Table 9. Nutrient ratios and inferred nutrient limitation for extensive sites (Int=intermediate limitation).

StationName	StationCode	SampleDate	PN:PP (molar)	Limitation	DIN:TP (mass)	Limitation
Lake Basin	S001-Out	9/6/08	4.0	N	3.0	Int
Lake Basin	S001-Out	8/21/09	15.3	Int	7.6	P
McGee	S002-Out	9/24/08	7.9	N	0.2	N
McGee	S002-Out	9/14/09	20.4	Int	1.8	Int
Spring Lake	S003-Out	9/17/08	3.6	N	2.8	Int
Spring Lake	S003-Out	9/2/09	11.5	Int	11.5	P
Aster	S004-Out	9/24/08	22.3	Int	0.2	N
Aster	S004-Out	10/2/09	19.7	Int	0.6	Int
Upper State	S005-Out	9/7/09	61.6	P	0.6	N
Finger Basin	S006-Out	8/21/08	0.1	N	0.7	Int
Sky Blue Lake	S007-Out	8/25/08	6.7	N	0.9	Int
West Spur Vidette	S008-Out	8/20/08	3.9	N	13.4	P
Lower Dusy	S009-Out	8/7/08	3.6	N	0.1	N
Upper Horse Creek	S010-Out	9/21/08	18.1	Int	0.2	N
Kern Point	S011-Out	8/23/08	7.6	N	1.2	Int
Little South America	S012-Out	8/22/08	6.3	N	0.2	N
Darwin Bench	S013-Out	9/23/08	2.6	N	1.5	Int
Mosquito Lakes	S015-Out	9/21/08	10.0	N	0.3	N
Little Window Peak	S016-Out	9/8/08	6.5	N	0.2	N
Upper Basin	S017-Out	8/20/09	17.0	Int	0.8	Int
Evolution Basin	S018-Out	9/15/09	15.2	Int	20.5	P
Cyclamen	S019-Out	9/3/09	13.9	Int	18.6	P
Twin Lake	S020-Out	9/10/09	31.0	P	0.5	N
Horseshoe	S021-Out	9/6/09	9.7	N	0.4	N
Reinstein Lake	S022-Out	9/16/09	10.9	Int	9.2	P
Nine Lakes	S023-Out	9/17/09	8.3	N	77.8	P
Kearsarge Lake	S024-Out	8/29/09	29.7	Int	0.5	N
Bishop Pass	S025-Out	8/25/09	11.2	Int	6.9	P
Hockett	S026-Out	8/12/09	36.4	P	0.3	N
Kaweah Basin	S027-Out	9/2/09	5.6	N	48.2	P
Lippincott	S051-Out	9/18/08	7.8	N	17.1	P
Spillway	Y001-Out	9/16/2008	25.6	Int	0.1	N
Spillway	Y001-Out	9/10/2009	13.5	Int	0.2	N
Upper Granite	Y002-Out	9/15/2008	27.9	Int	0.2	N
Upper Granite	Y002-Out	9/21/2009	12.6	Int	0.3	N
Ten Lakes	Y003-Out	9/18/2008	8.2	N	0.1	N
Ten Lakes	Y003-Out	8/12/2009	13.6	Int	0.5	N
Edna	Y004-Out	9/5/2008	3.5	N	16.0	P
Tilden	Y005-Out	8/19/2008	5.6	N	0.2	N
Saddle Puddle	Y006-Out	9/6/2008	16.3	Int	0.1	N
Breeze	Y007-Out	8/20/2008	6.7	N	0.2	N
Adair	Y008-Out	9/4/2008	7.7	N	0.2	N
Kendrick	Y009-Out	8/22/2008	6.3	N	0.3	N
Tenaya	Y010-Out	9/20/2009	12.0	Int	0.3	N
Table Lake	Y011-Out	8/19/2009	22.7	Int	0.7	Int
Lyll Fork Lake	Y012-Out	8/25/2009	3.7	N	36.4	P
Upper Falls Creek	Y013-Out	10/6/2009	12.3	Int	0.3	N
South Fork Cathedral	Y014-Out	8/13/2009	8.4	N	0.4	N
McCabe	Y015-Out	8/17/2009	18.3	Int	0.3	N

Index Sites

Our four index sites, Maclure, Kuna Peak, Dusy Basin, and Emerald, were sampled once a month from approximately late-June/early-July through late-September/early-October in 2008 and 2009. Results for temperature, specific conductance, nitrate, total dissolved nitrogen, and particulate nitrogen are presented. *Refer to Appendix A for results for all 18 measures.*

Lake temperatures at the index lakes ranged from 0.2 to 24.3 °C (**Figure 12 a**). Temperatures were higher at Dusy and Emerald compared to Kuna Peak and Maclure. Dusy and Emerald are typically ice-free several weeks prior to Kuna Peak and Maclure and, therefore, warm earlier in the season. Temperatures were typically lowest during the early season sampling and then peaked in late July into August. Temperatures decreased again into September.

Specific conductance ranged from 4.2 to 13.8 $\mu\text{S}/\text{cm}$ (**Figure 12 b**). Specific conductance was highest at Maclure and Kuna Peak followed by Dusy and then Emerald. Values varied by site and over time. There are not any pronounced patterns, with the exception of slight increase over the 2008 season. There is a notable spike in Maclure specific conductance values (from 9.7 to 13.8 $\mu\text{S}/\text{cm}$) in late September.

Acid neutralizing capacity values ranged from 6.2 to 71.2 $\mu\text{eq}/\text{l}$ (**Figure 13 a**). ANC was highest at Maclure and Dusy followed by Emerald and Kuna Peak. ANC typically increased over the season at all sites. In late September 2008, decreases were observed in the final samples of the season.

Nitrate concentrations ranged from below the method detection limit to 16.1 μM (**Figure 13 b**). Typically, concentrations were highest at Maclure and then in decreasing order Emerald, Kuna Peak and Dusy Basin. Nitrate was highest in the June and July samples and then decreased in the late season samples, with the exception of Maclure in 2009. Early season nitrate concentrations were higher in 2009 compared to 2008.

Total dissolved nitrogen concentrations ranged from 3.7 to 20.8 μM (**Figure 14 a**). Similar to nitrate, concentrations were highest at Maclure followed by Emerald, and then Kuna Peak or Dusy Basin. 2008 TDN concentrations were quite variable by site and over time. In 2009 there was a consistent decrease in TDN at all sites observed from late June to early August. Followed by an increase at 3 of the 4 sites, that varied in magnitude by site. TDN at Kuna Peak continued to decrease throughout the 2009 season.

Particulate nitrogen ranged from 4.4 to 81.8 $\mu\text{g}/\text{l}$ (**Figure 14 b**). At Emerald, PN increased throughout the growing season during both years. There was little change observed at Dusy over time. Maclure and Kuna Peak had notable high PN concentrations (81.8 and 78.1 $\mu\text{g}/\text{l}$) in late July of 2008 that decreased prior to early September. Little change was observed at either site during the 2009 season.

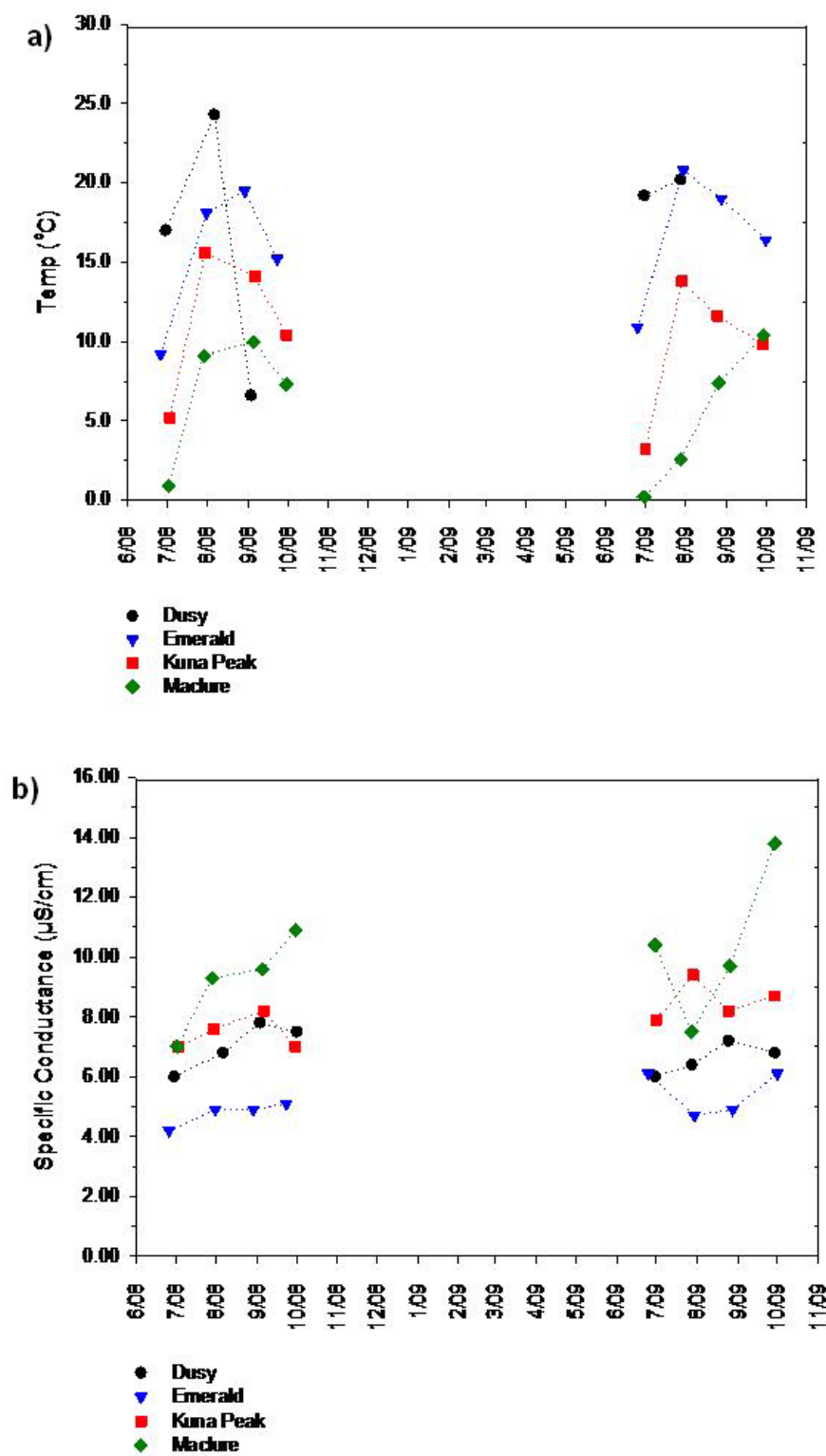


Figure 12. 2008 and 2009 temperature and specific conductance results for SIEN index sites.

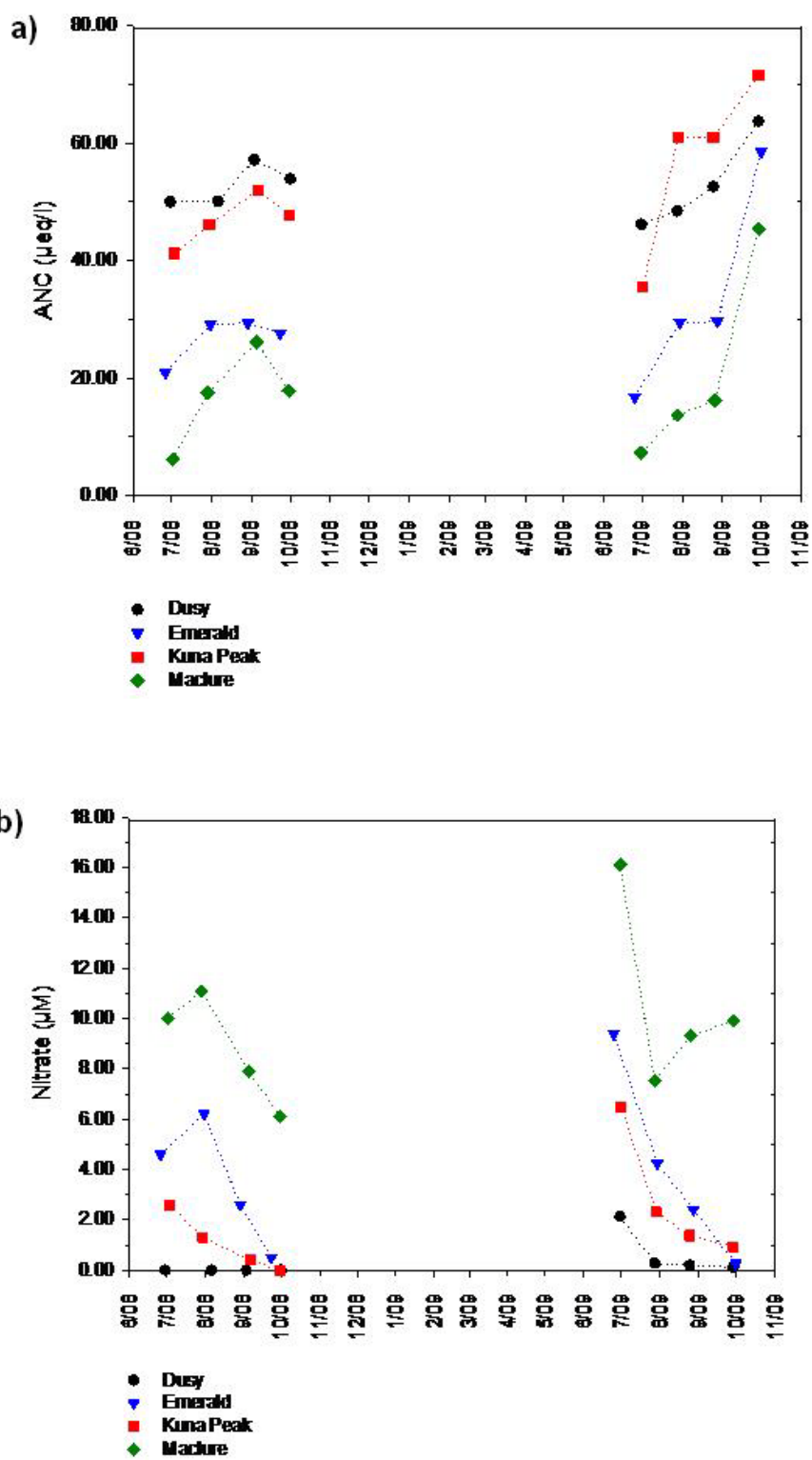


Figure 13. 2008 and 2009 ANC and nitrate results for SIEN index sites.

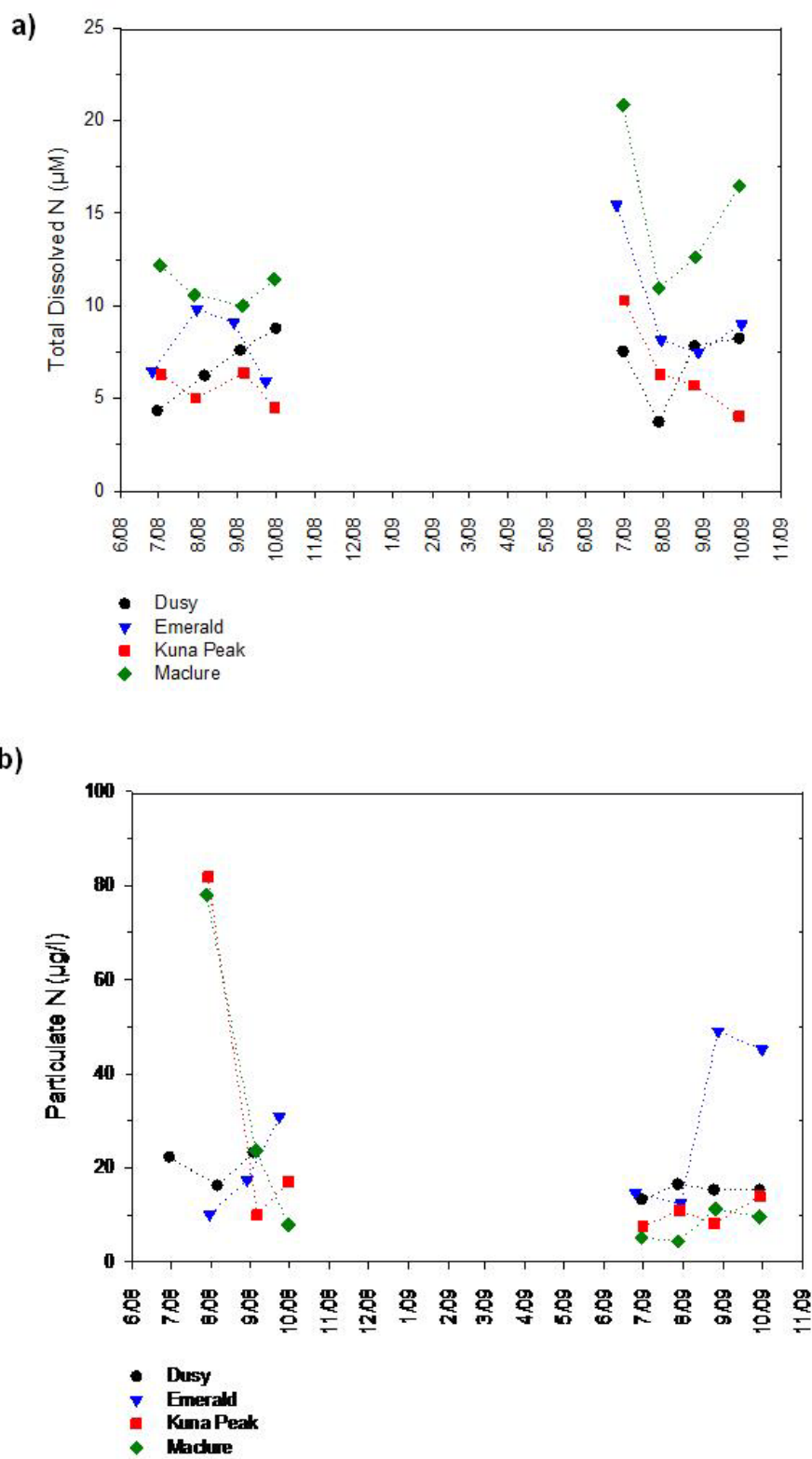


Figure 14. 2008 and 2009 TDN and PN results for SIEN index sites.

Quality Assurance and Quality Control

Quality assurance and quality control results for field assessments are presented in **Table 10** and **Table 11**. The field QA/QC assessments include percent completeness, relative percent difference (RPD) for field duplicates, and deviation from zero for field blanks. For some measures, an absolute criteria is used instead of RPD when concentrations are low (**Table 2**). Refer to Appendix B for laboratory QA/QC results.

Table 10. QA/QC results for 2008 field measures ('Meets Criteria' indicates it met the absolute criteria).

Measure	Completeness (%)	Field Duplicates (Mean RPD)	Field Blanks (Mean deviation from 0 uM)
<u>Core parameters</u>			
Temperature	98	NA	NA
Specific Conductance - field (µS/cm)	100	NA	NA
Specific Conductance - lab (µS/cm)	100	8.0	3.60
pH - lab	100	3.6	NA
Dissolved oxygen (mg/l)	92	NA	NA
<u>Nitrogen</u>			
Nitrate (µM)	100	59.3	0.00
Total dissolved nitrogen (µM)	100	15.3	1.41
Particulate nitrogen (µg/l)	85	5.4	0.04
<u>Phosphorus</u>			
Total dissolved phosphorus (µM)	100	Meets Criteria	0.03
Particulate phosphorus (µM)	85	26.7	0.16
<u>Carbon</u>			
Particulate carbon (µg/l)	85	14.7	14.80
<u>Major Ions</u>			
Calcium (µM)	100	4.4	0.32
Sodium (µM)	100	3.1	2.54
Magnesium (µM)	100	5.2	0.10
Potassium (µM)	100	14.4	0.40
Chloride (µM)	100	56.2	0.50
Sulfate (µM)	100	5.9	0.20
ANC (µequ/l)	100	32.9	7.20

Table 11. QA/QC results for 2009 field measures ('Meets Criteria' indicates it met the absolute criteria).

Measure	Completeness (%)	Field Duplicates (Mean RPD)	Field Blanks (Mean deviation from 0)
<u>Core parameters</u>			
Temperature	97	NA	NA
Specific Conductance - field ($\mu\text{S}/\text{cm}$)	98	NA	NA
Specific Conductance - lab ($\mu\text{S}/\text{cm}$)	100	6.6	1.50
pH - lab	100	2.4	NA
Dissolved oxygen (mg/l)	88	NA	NA
<u>Nitrogen</u>			
Nitrate (μM)	100	103.0	0.05
Total dissolved nitrogen (μM)	100	55.4	0.01
Particulate nitrogen ($\mu\text{g}/\text{l}$)	100	25.9	5.22
<u>Phosphorus</u>			
Total dissolved phosphorus (μM)	100	Meets Criteria	0.01
Particulate phosphorus (μM)	100	33.3	0.07
<u>Carbon</u>			
Particulate carbon ($\mu\text{g}/\text{l}$)	100	55.7	9.87
<u>Major Ions</u>			
Calcium (μM)	99	2.2	0.18
Sodium (μM)	99	8.7	0.02
Magnesium (μM)	99	1.7	0.02
Potassium (μM)	99	15.4	0.03
Chloride (μM)	100	38.0	0.16
Sulfate (μM)	100	10.4	0.00
ANC ($\mu\text{equ}/\text{l}$)	100	6.3	68.40

Discussion

Field Seasons

Our first two field seasons were very successful. We were able to visit all extensive and index sites on time and within budget. We had strong, level-headed, and thorough field sampling crews who completed sampling with an excellent safety record. We found that two crews of two are the best combination to complete sampling safely, efficiently, and within budget. It is desirable to have a third crew member for some of the SEKI mid-lake sampling sites because they must hike additional gear (e.g., boats, hand pumps, pfd's and more) to remote sites. Lakes Basin, States Lake, and McGee Lake were identified as sites to sample with a crew of three. However, hiring a three person crew for the season to accomplish this is not necessary. We found it is better to use SIEN staff or the Yosemite based crew to assist on these trips. We are also considering increasing our use of food and gear caches to lighten the crew loads. The Yosemite mid-lake sites are less rigorous hikes and very doable with a two person crew.

We found that the allotted time and budget as described in Heard et al. are appropriate for index and extensive site water chemistry and amphibian sampling. However, the hydrologic sampling of index lakes proved to be more of a challenge due to technical and budget constraints. Kuna Peak and Dusy outlets have multiple channels that wind through alpine-wetland areas and are not well constrained making it a challenge to collect reliable stage and discharge measurements. Maclure's outlet is a good site for a gaging station as it flows through a well-defined and tall rock channel immediately downstream of the lake. We found it challenging to revisit and download the dataloggers. We determined that current project funding cannot support the amount of time required to train field crews on datalogger operation and for crews to be trained on and perform discharge measurements. Stage and discharge are not presented in this report due to the challenges of collecting these data.

Initially, we were optimistic that the budget constraints could be overcome by leveraging with the Rivers protocol, which would have a strong hydrologic component. However, due to the recent prioritization of monitoring protocols by the Steering Committee and the need to scale back most protocol budgets, the Rivers monitoring will have a limited field component and will not require a field crew. As a result, our recommendation is to discontinue outflow stage and discharge monitoring and instead monitor lake level and water temperature, which are easier to measure.

Water chemistry

The purpose of the annual reports is to document the field season, summarize data, and disseminate results to park managers and other interested audiences. Therefore, the reports do not include a detailed discussion of the year's results. A more comprehensive report with detailed analysis and discussion will be produced every four years, in sync with completion of a full panel rotation. However, we have selected a few points to highlight in the 2008 and 2009 report:

Nitrate Variability: Nitrate concentrations vary across the network. Lower concentrations were generally observed in Yosemite (**Figure 8** and **Figure 9**). This difference is likely attributed to lower rates of atmospheric deposition in Yosemite. Sequoia and Kings Canyon, Sequoia in particular, have higher deposition rates due to air patterns that concentrate pollutants in the

southern Central Valley. These pollutants, which include nitrogen oxides produced from agricultural, urban, and industrial sources travel from the San Francisco Bay Area and down the Central Valley, where they collect on the western edge and rise into the parks (Landers et al. 2008). This additional nitrogen is then deposited in the parks as wet and dry deposition. Other factors that can contribute to nitrate variability across the network include watershed area, in-lake processes, and watershed characteristics such as vegetation cover and type, geology, and soils.

Despite lower mean nitrate concentrations in Yosemite, the highest concentration measured in our 2008 and 2009 sampling was at Maclure Lake (16.1 μM). Maclure was selected because it has been identified as especially sensitive to atmospheric deposition based on chemical and physical characteristics, location, and moderate to high lake nitrate concentrations. The watershed is granitic, sparsely vegetated, and receives above average precipitation and thus higher N inputs. There is also a glacier, located in the upper watershed, that drains into Maclure. Saros et al. (2010) have found that glacier fed lakes typically have high nitrate concentrations.

Index site results are useful for understanding both inter- and intra-annual patterns in lake chemistry. Within a season, high nitrate concentrations in the early season that decrease over the summer and fall are consistent with previous research and monitoring in the parks. Nitrate typically peaks during spring snowmelt when it is flushed out of the watershed and into receiving waters. The decrease early in the season is attributed to decreased snowmelt rates and then later in the season to biological uptake of N (Melack et al. 1998).

Nutrient Ratios: Two indicators, PN:PP and DIN:TP were used to assess nutrient limitation in SIEN lakes. The results---if sites were limited by N, P, or were intermediate---varied depending on which nutrient ratio was used (**Table 9**). The Redfield ratio is a well established criteria used to assess nutrient limitation in oceanic and lake ecosystems (Wetzel 2001). Intracellular ratios are strong indicators of nutrient limitation because limitation is best determined by the internal cell quota compared to the minimum quota required for growth (Reynolds 2006). However, Morris and Lewis (1988), in assessing multiple indices of nutrient limitation determined that DIN:TP was typically a better indicator of nutrient limitation in lake ecosystems. They found that PN:PP may not accurately represent intracellular levels of N and P because it includes all particulate matter. The extracellular ratio, DIN:TP, best represents the fractions of N and P available to phytoplankton. In a study specific to Sierra Nevada lakes, Sickman (2001) also found that DIN:TP was a better indicator of nutrient limitation.

DIN:TP results indicate that Yosemite has a lower proportion of P limited lakes and higher proportion of N limited lakes compared to Sequoia and Kings Canyon. This is consistent with the generally lower nitrate observed across Yosemite sites and may be a result of lower atmospheric N deposition. These differences suggest that atmospheric N deposition may have already contributed to shifts from N to P limitation at sites with high deposition. Although further analyses are needed as there are multiple factors (e.g. watershed characteristics) that can explain variations in nutrient limitation. Shifts in the major limiting nutrient are a fundamental ecosystem change (Vitousek 2004) and is of high concern even though cascading and long-term effects are not yet well understood.

High concentrations in Lake S012: Mean values are higher in 2008 than 2009 for specific conductance (12.3 compared to 8.0 $\mu\text{S}/\text{cm}$), calcium (38.7 compared to 23.4 μM), and sulfate (19.9 compared to 6.72 μM). This is at least partially attributed to exceptionally high concentrations from one site, Lake S012. Lake S012 is a small lake located in the upper Kern watershed adjacent to Lake South America. Field and lab specific conductance values at S012 are 89.7 and 84.8 $\mu\text{S}/\text{cm}$, respectively. Calcium and sulfate concentrations are 12.7 and 27.8 μM , respectively. Consistency between field and lab specific conductance values suggests that these high concentrations are valid and not from sample contamination. It is uncertain why these values are high—further investigation of the surrounding geology and water chemistry of adjacent lakes is suggested.

Quality Assurance and Quality Control

We met the completeness criteria for all but a few measures. We did not meet the 95% criteria for DO in both 2008 and 2009. This is a combined result of not having enough field probes when we have three crews in the field and having problems with the probe in the field. We should consider purchasing another YSI-85 if we anticipate occasionally having three crews in the field at once. In order to mitigate issues with the probe in the field we should consider increasing training, focusing on trouble shooting, and send the probes to YSI for routine maintenance and calibration on an annual or bi-annual schedule. Completeness criteria were not met for particulate samples in 2008. Due to logistical and training constraints we did not implement particulate sampling until after the first index site sampling. We also underestimated the amount of particulate samples needed and as a result were short at the end of the season. We recommend having an abundance of extra particulate filters at the office and field. Filters are prone to being blown away during processing – we underestimated how many we would lose this way. It is especially high when training new crew members.

Field duplicate RPD results were higher than expected for some measures, especially nitrate, TDN, potassium and chloride. High RPD's for nitrate and TDN are at least partially explained by the low concentrations. A small (and acceptable) difference when concentrations are low results in a high RPD. This is discussed in the laboratory QA/QC report where recommendations were made to add an absolute criterion for TDN and TDP that can replace the RPD when concentrations are low. We recommend considering doing this for nitrate as well.

High chloride and potassium RPD's suggest a source of contamination during field sampling. Field blank results were also slightly higher for chloride and potassium compared to the other cations. The bleach used during the decontamination procedure is one source of chloride contamination, although we would expect sodium to be higher as well. Other sources include contamination during sample collection and processing and carry-over in the cubitainers from previous sites. In order to minimize future contamination and variability between samples we recommend additional emphasis be put on proper sample handling during training. In addition, crews should increase rinsing of cubitainers between sampling locations.

The University of California, Riverside (UCR) and the Sierra Nevada Network worked collaboratively to improve and streamline the analytical aspects of the lake monitoring protocol. UCR made several recommendations that SIEN will be implementing. The most significant recommendations are summarized below. Refer to Appendix B for details. Laboratory recommendation highlights:

- Cation analysis: UCR recommends modifying EPA Method 200.7 by incorporating methods described in Morishige and Kimura (2008). This modified method increases the sensitivity of the analysis and lowers the detection limit.
- Particulate C, N, and P: UCR recommends adjusting the measurement quality objectives for particulate carbon, nitrogen, and phosphorus to better reflect limitations in estimating MDL's, precision, and bias for particulate samples. It is not possible to do a true laboratory replicate, spike a filter sample, run a representative check sample, or calculate a highly accurate MDL. Therefore, we recommend that the protocol does not have strict precision and bias criteria for these measures. Spike samples are impossible to run for PC, PN, and PP so they will not be included in the analysis. An updated version of *Table 8: Analytical methods and measurement quality objectives*, in the SIEN Lake Monitoring Protocol Narrative, that reflects these recommendations is included in Appendix B.
- UCR recommends incorporating two measures of bias. One measure for standard check samples and one for spike recoveries.
- UCR recommends changing the MDL's for sulfate, nitrate, and nitrite from 0.200 μM to 0.300 μM because the original target MDL's are unrealistic given typical instrumentation.

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Appendix A: Water Chemistry Results

This appendix presents 2008 and 2009 extensive site and index site chemistry results for all 18 measures.

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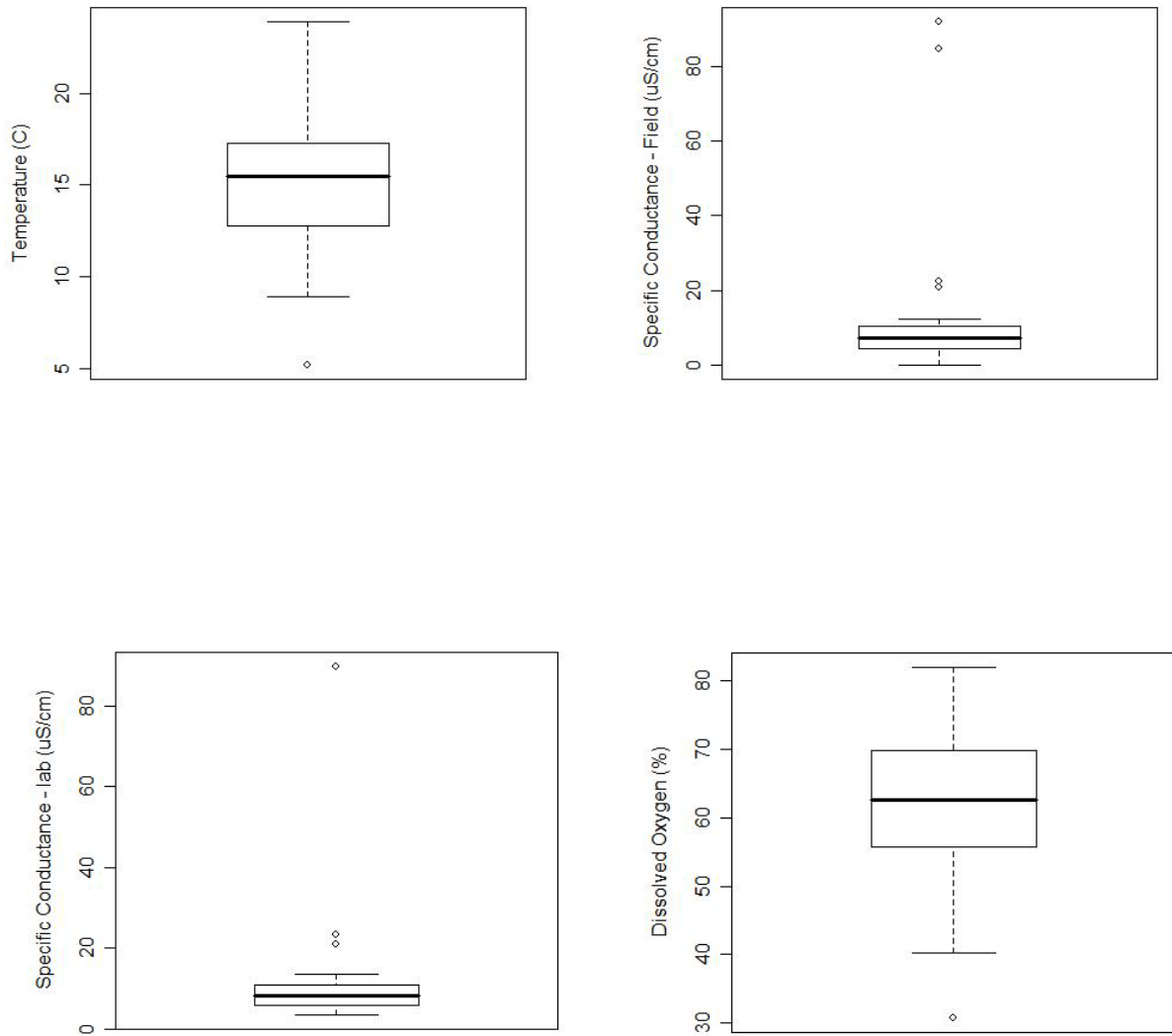


Figure A.15. Box plots for temperature, field and lab specific conductance, and dissolved oxygen from 2008 extensive site data. The bold line inside the box is the median, the bottom and top of the box are the 25th and 75th percentiles, respectively, the whiskers (or lines extending from the box) reach to the minimum and maximum values omitting outliers, and dots are outliers.

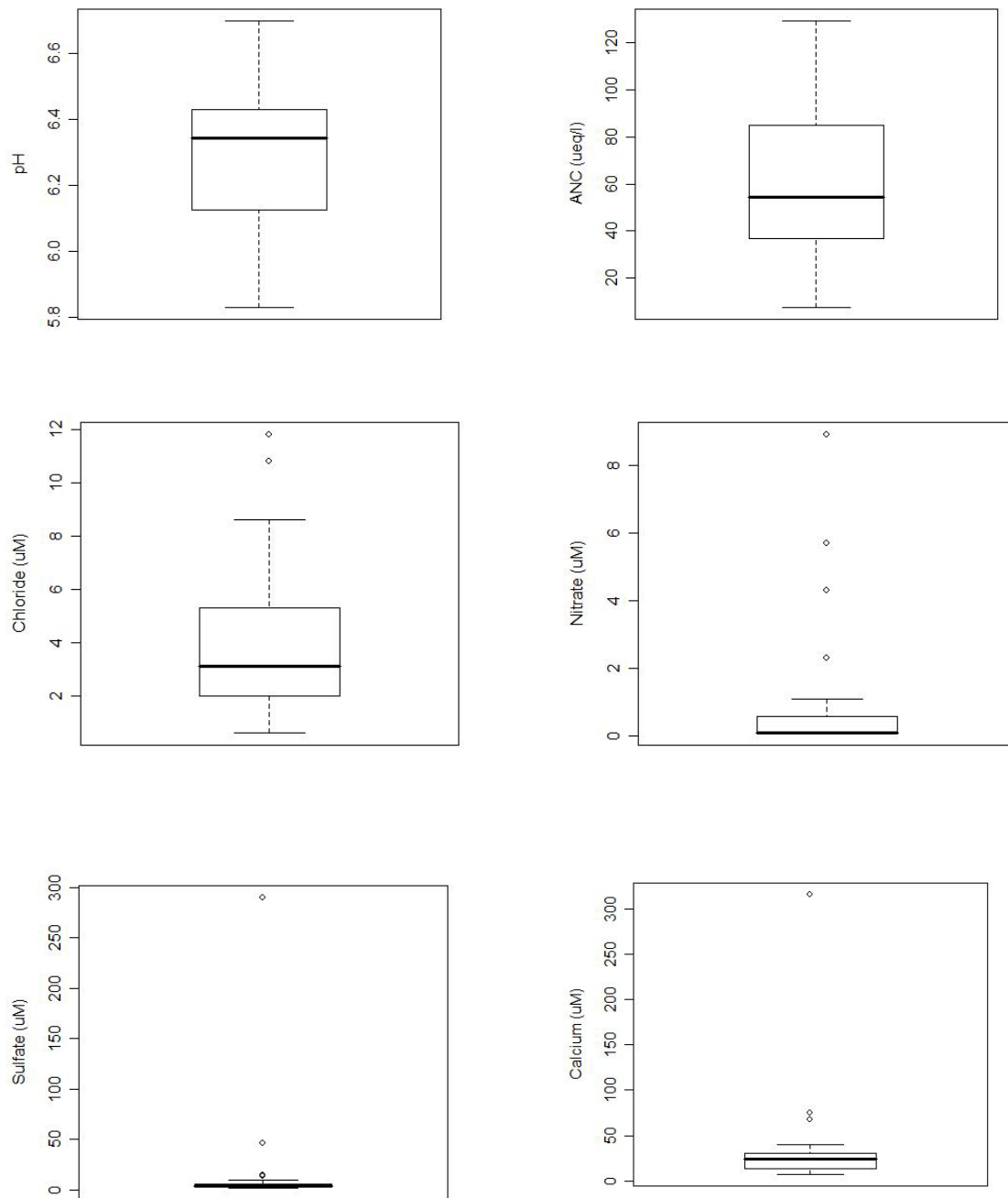


Figure A.16. Box plots for pH, ANC, chloride, nitrate, sulfate and calcium from 2008 extensive site data.

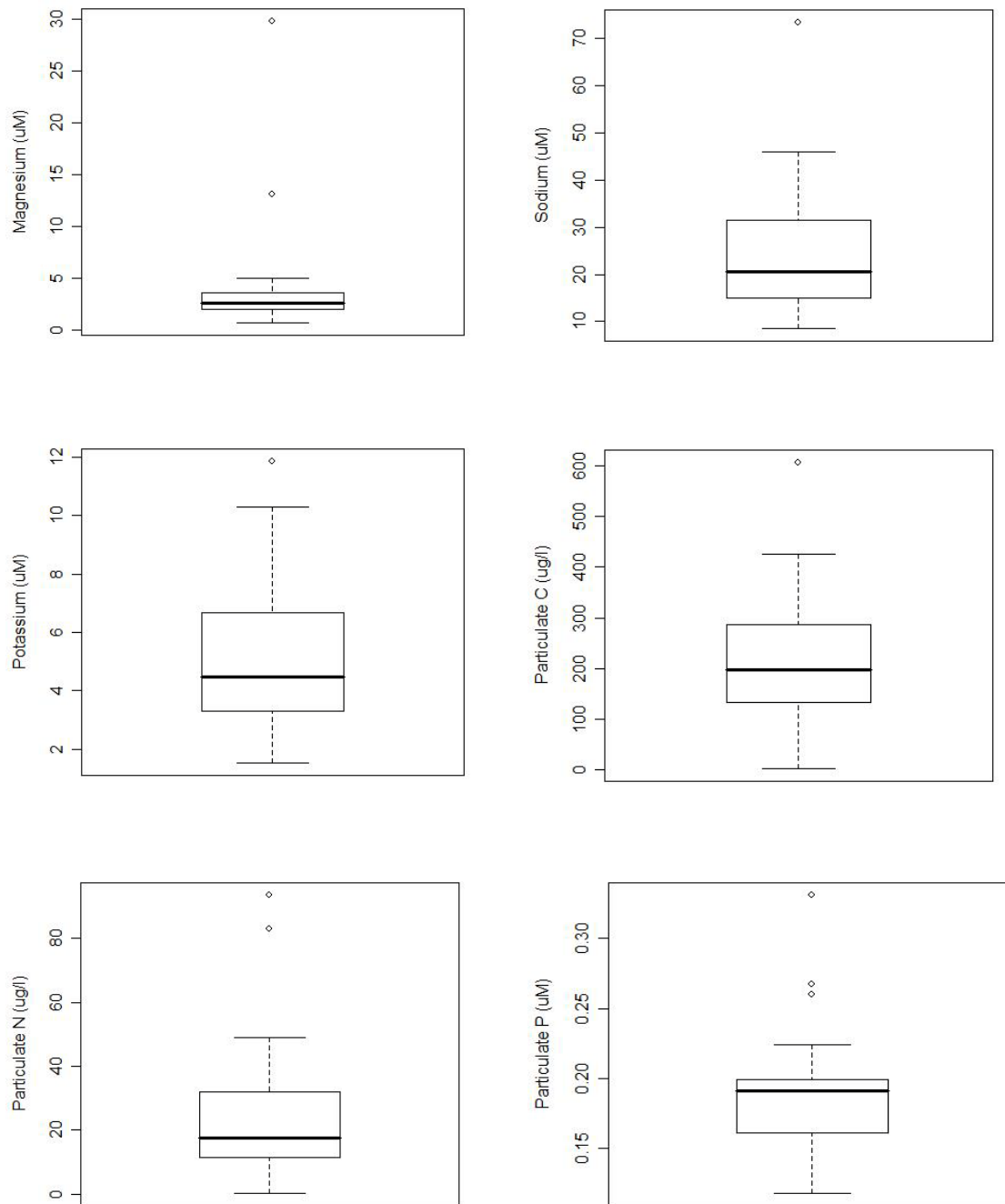


Figure A.17. Box plots for magnesium, sodium, potassium, particulate C, particulate N, and particulate P from 2008 extensive site data

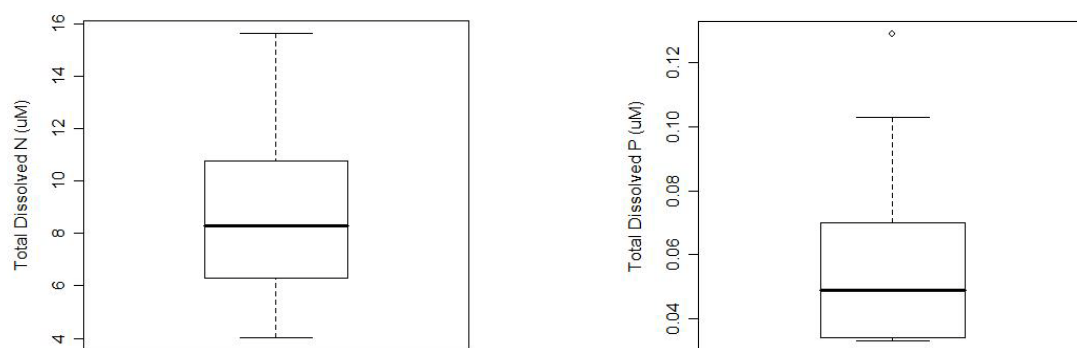


Figure A.18. Box plots for total dissolved N and P from 2008 extensive sites.

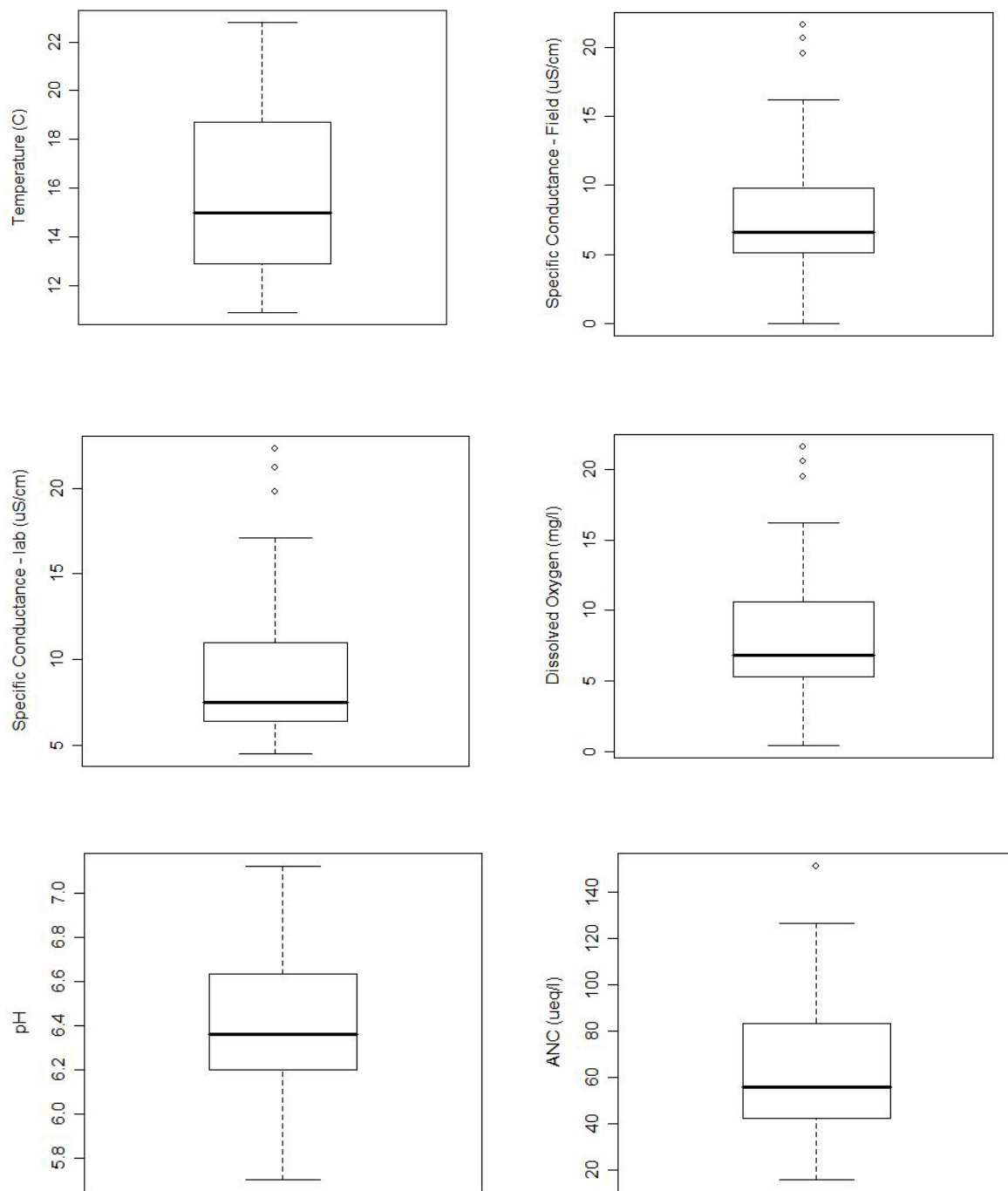


Figure A.19. Box plots for temperature, field and lab specific conductance, pH, and ANC from 2009 extensive sites.

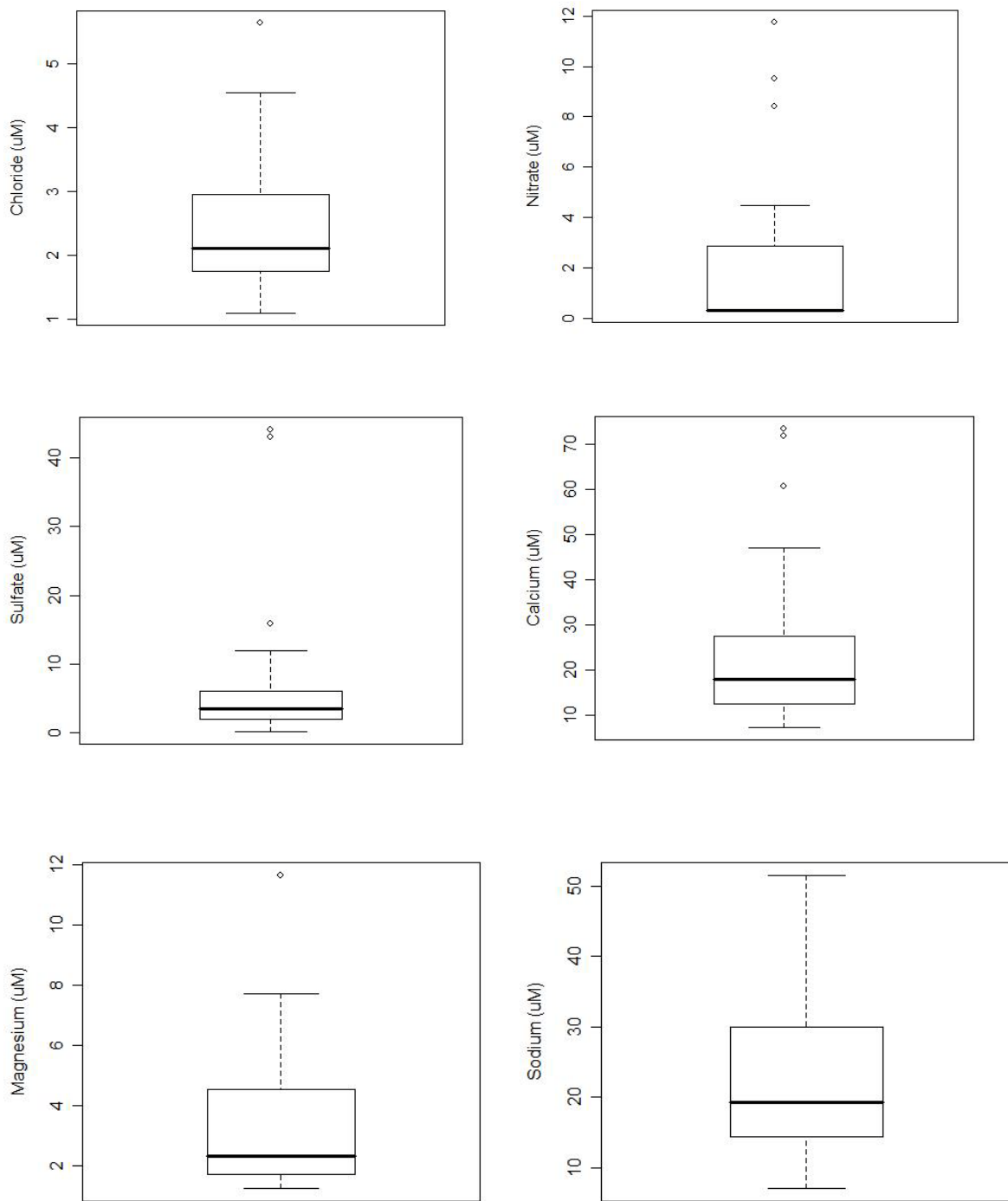


Figure A.20. Box plots for chloride, nitrate, sulfate, calcium, magnesium, and sodium from 2009 extensive sites.

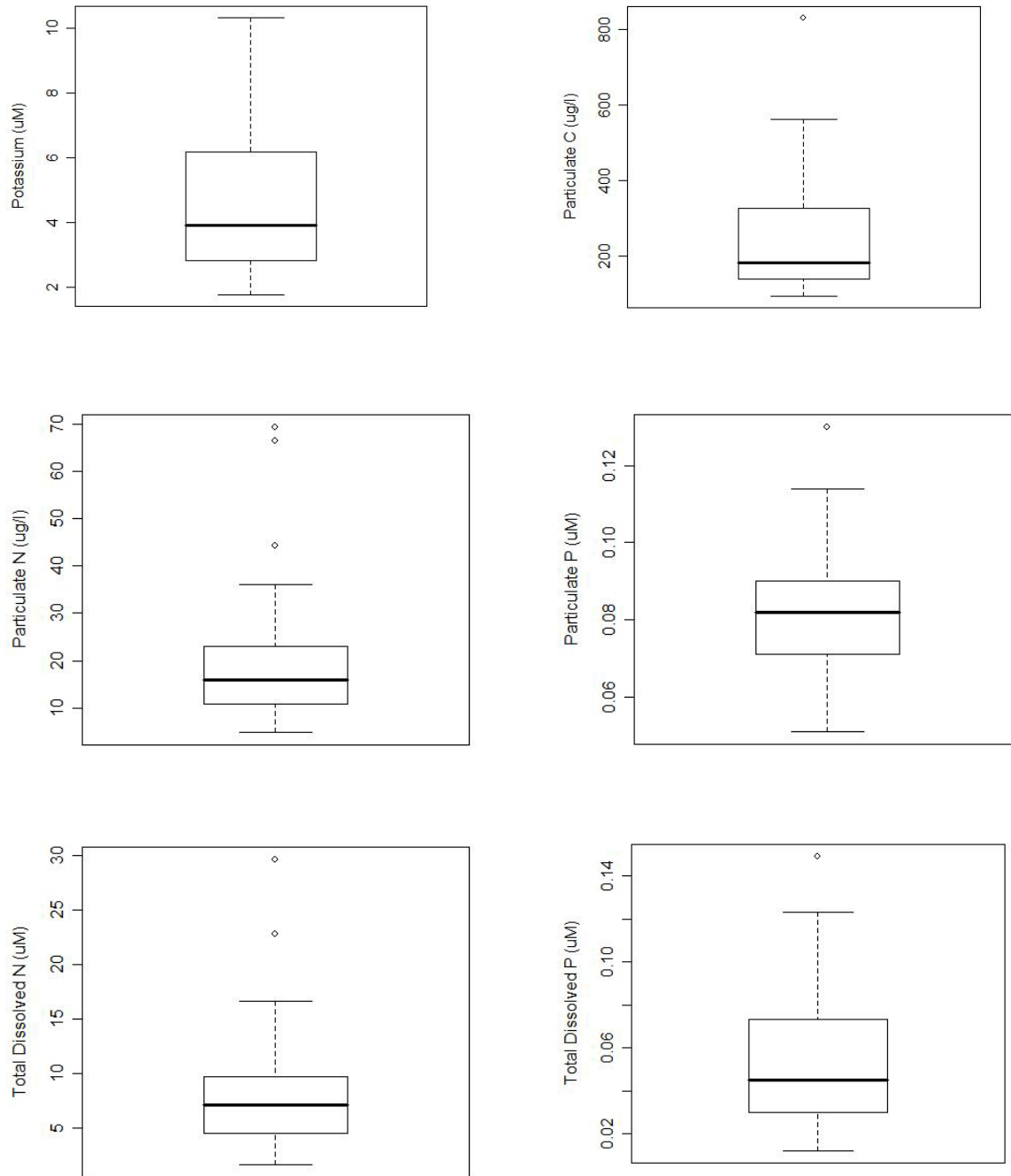


Figure A.21. Box plots for potassium, particulate C, particulate N, particulate P, total dissolved N, and total dissolved P from 2009 extensive sites.

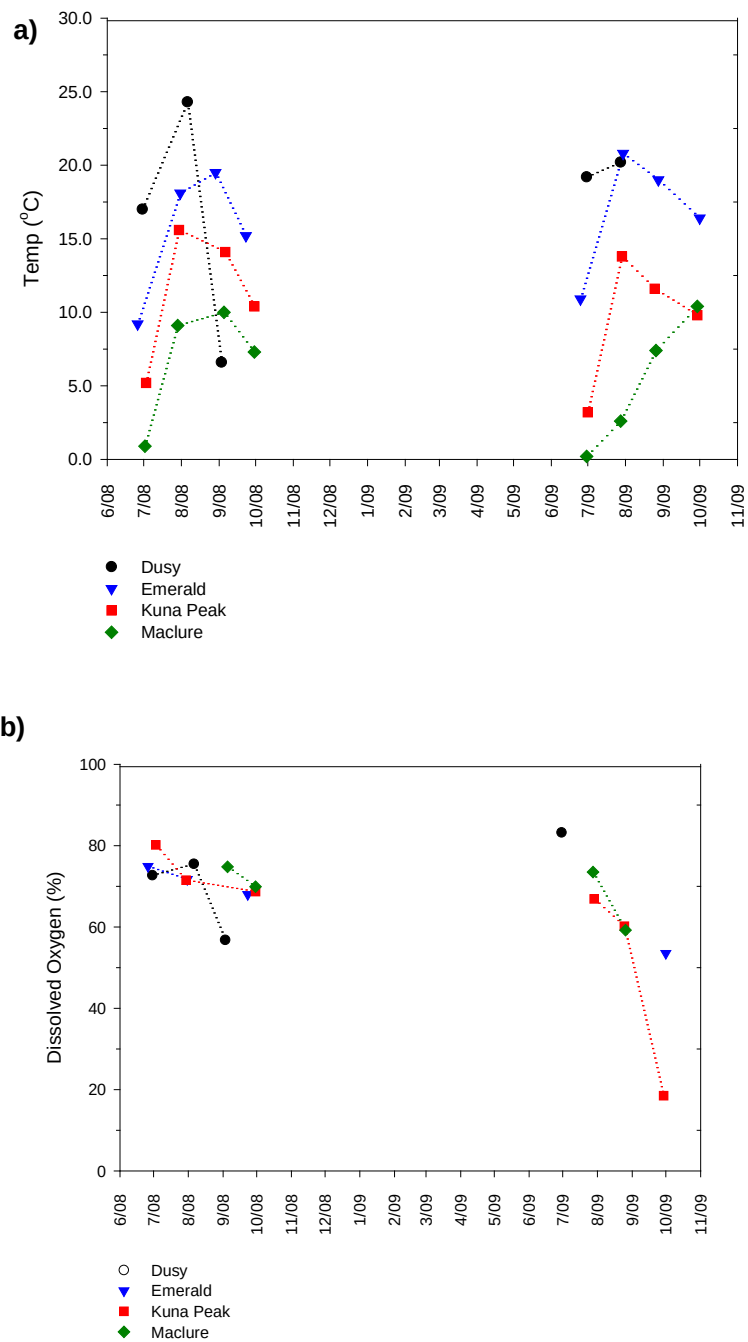


Figure A.22. 2008 and 2009 index site results for a) temperature and b) dissolved oxygen.

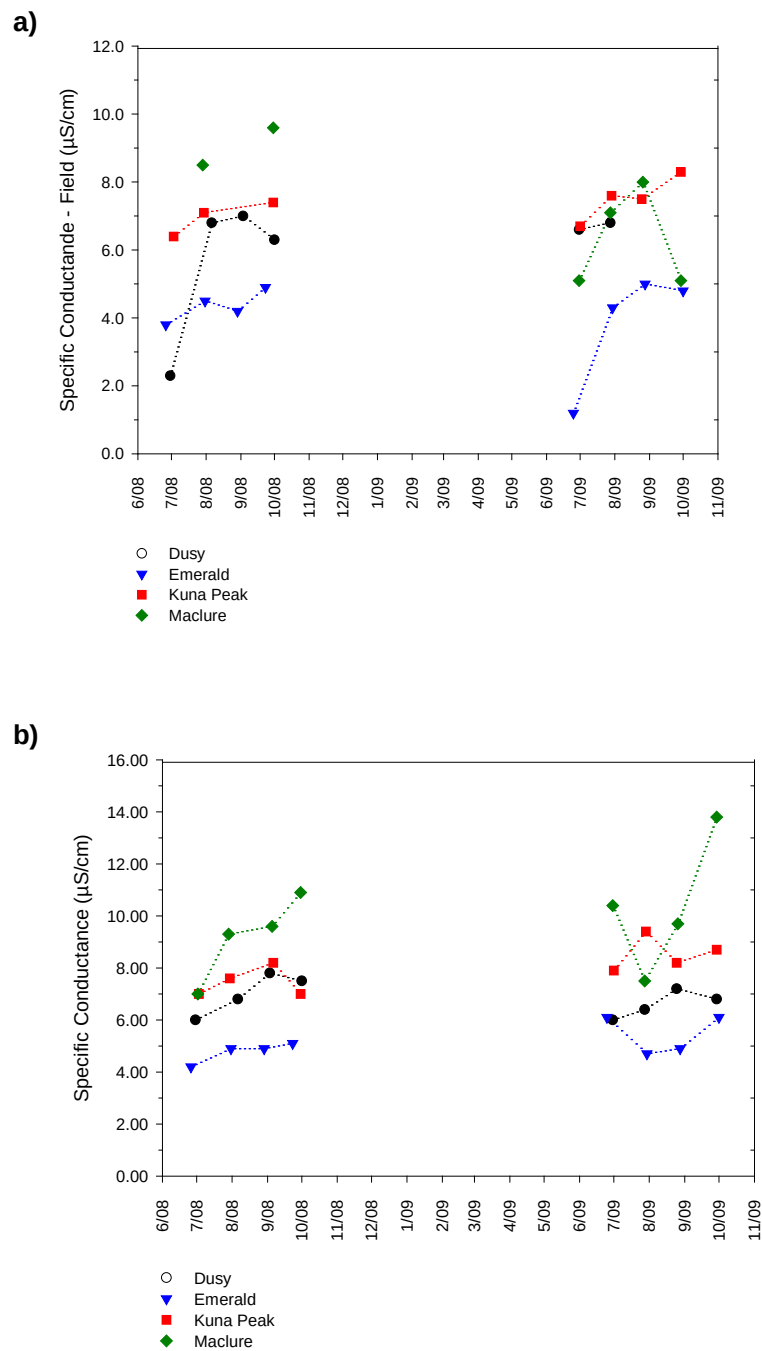


Figure A.23. 2008 and 2009 index site results for a) field and b) lab specific conductance.

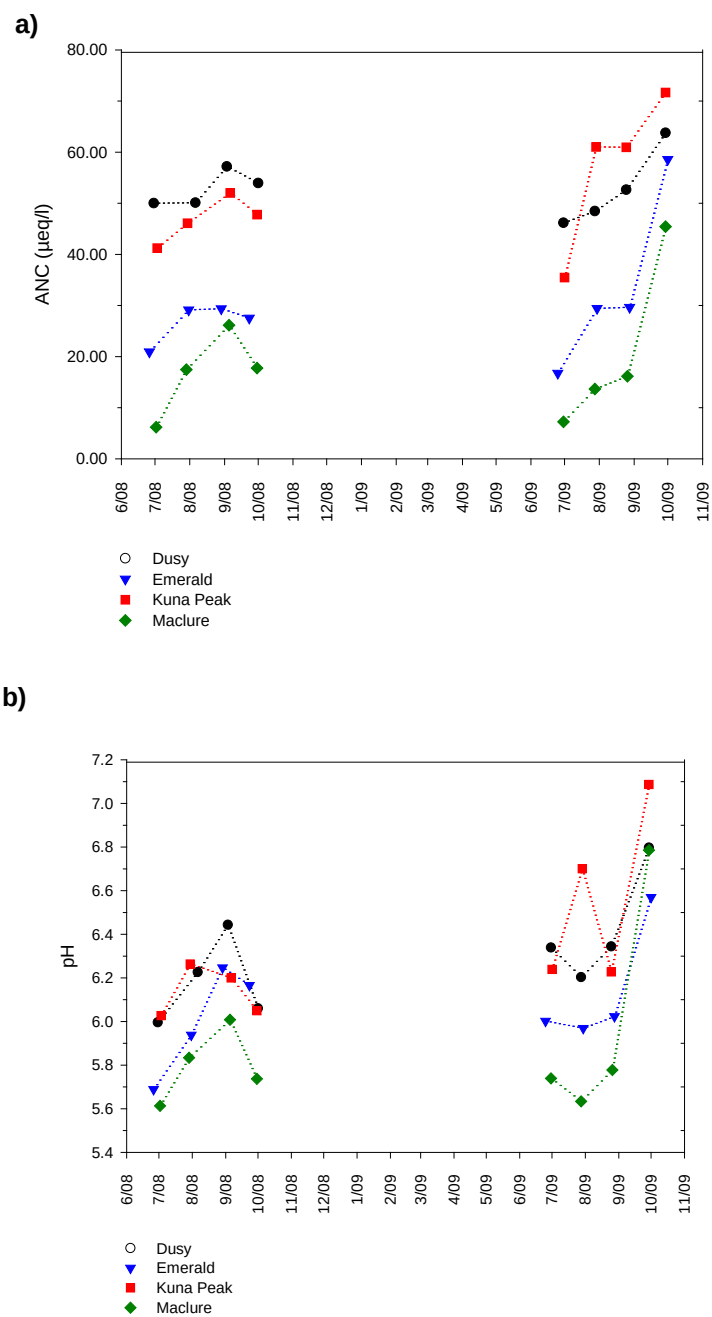


Figure A.24. 2008 and 2009 index site results for a) ANC and b) pH.

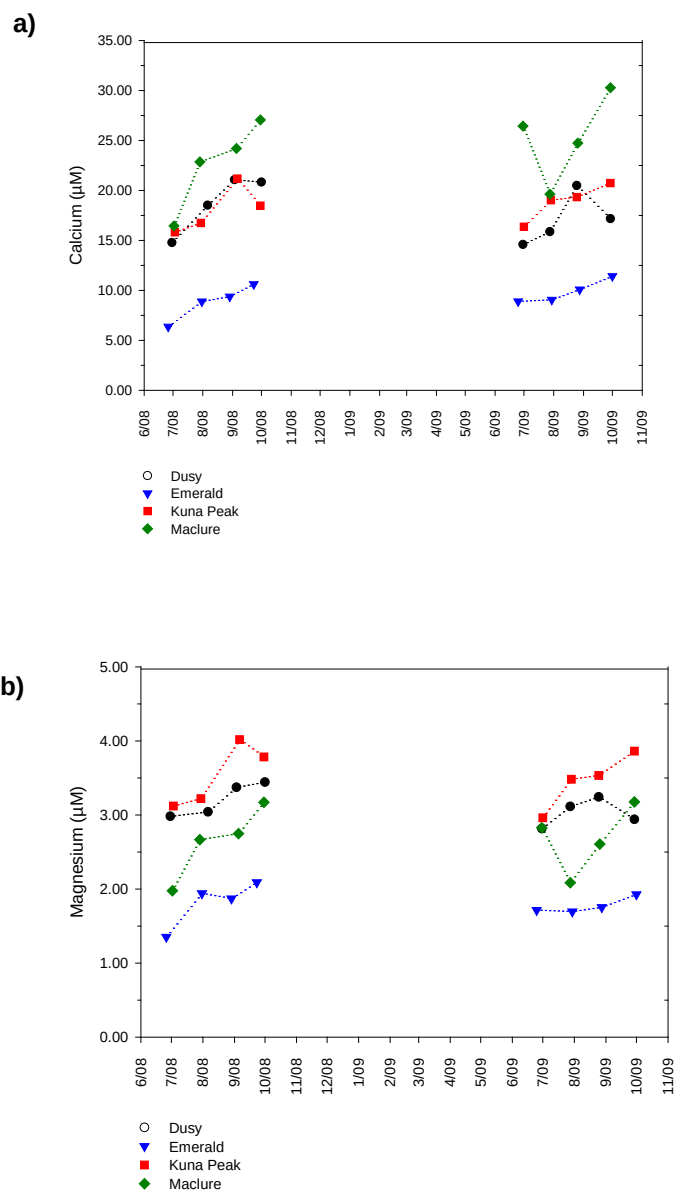


Figure A.25. 2008 and 2009 index site results for a) calcium and b) magnesium.

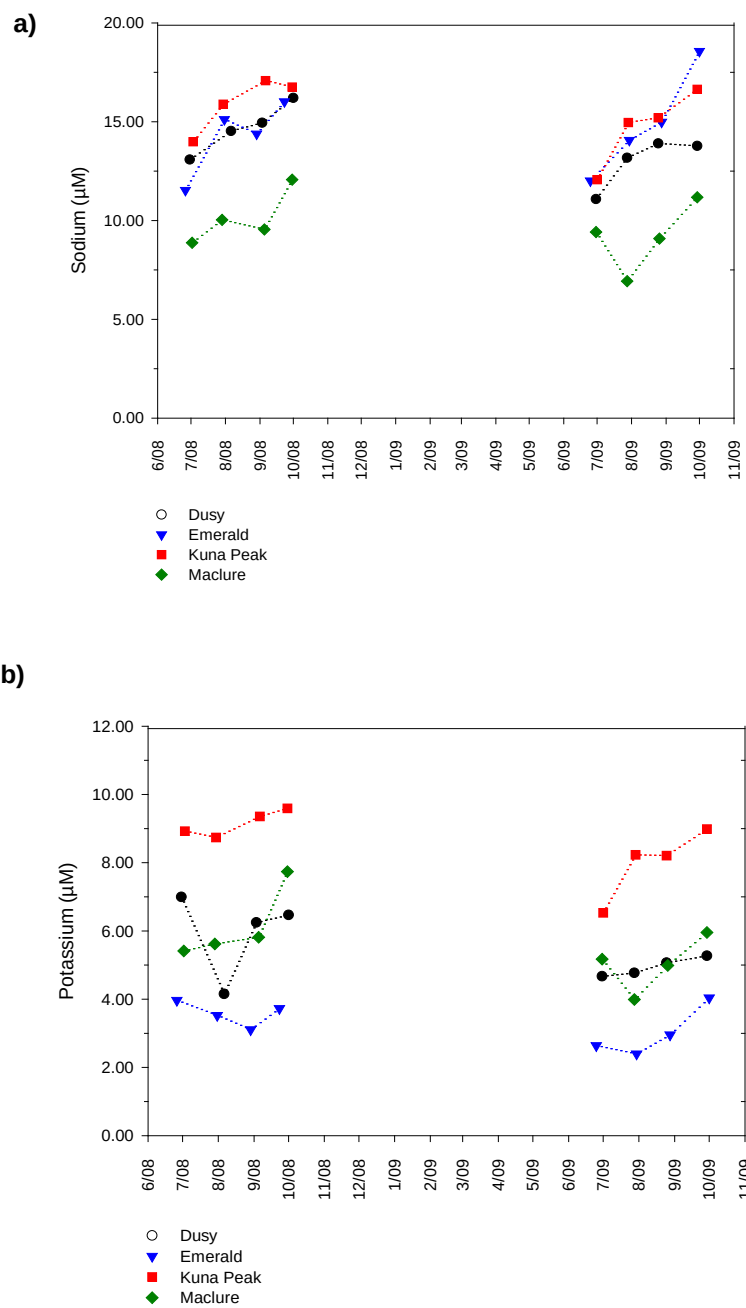
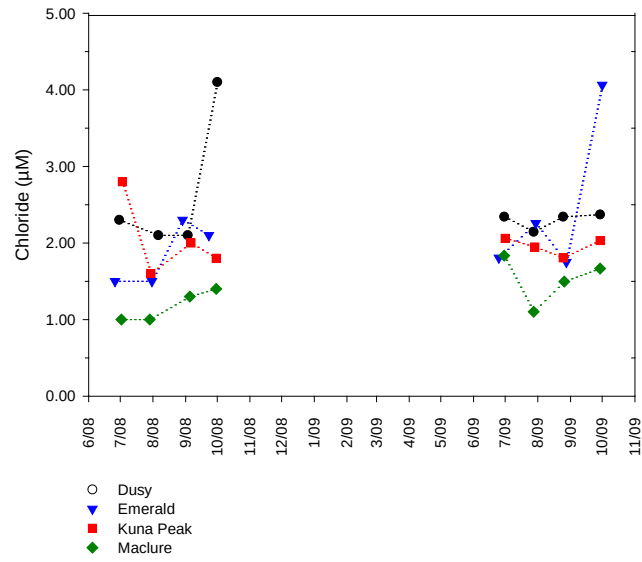


Figure A.26. 2008 and 2009 index site results for a) sodium and b) potassium.

a)



b)

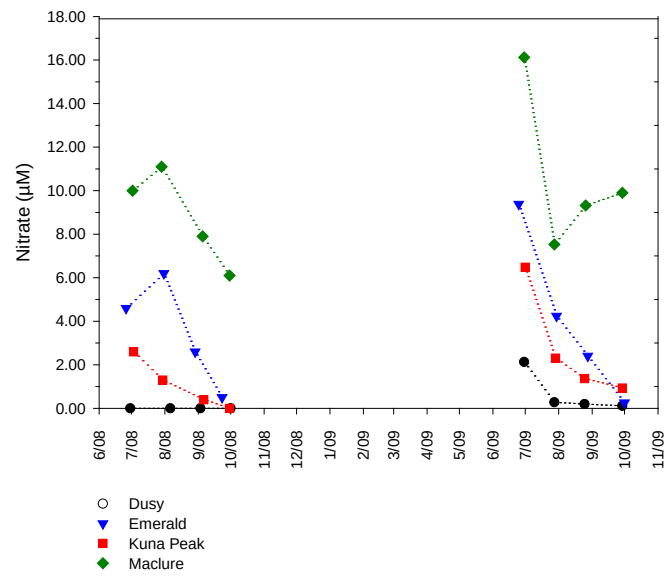


Figure A.27. 2008 and 2009 index site results for a) chloride and b) nitrate.

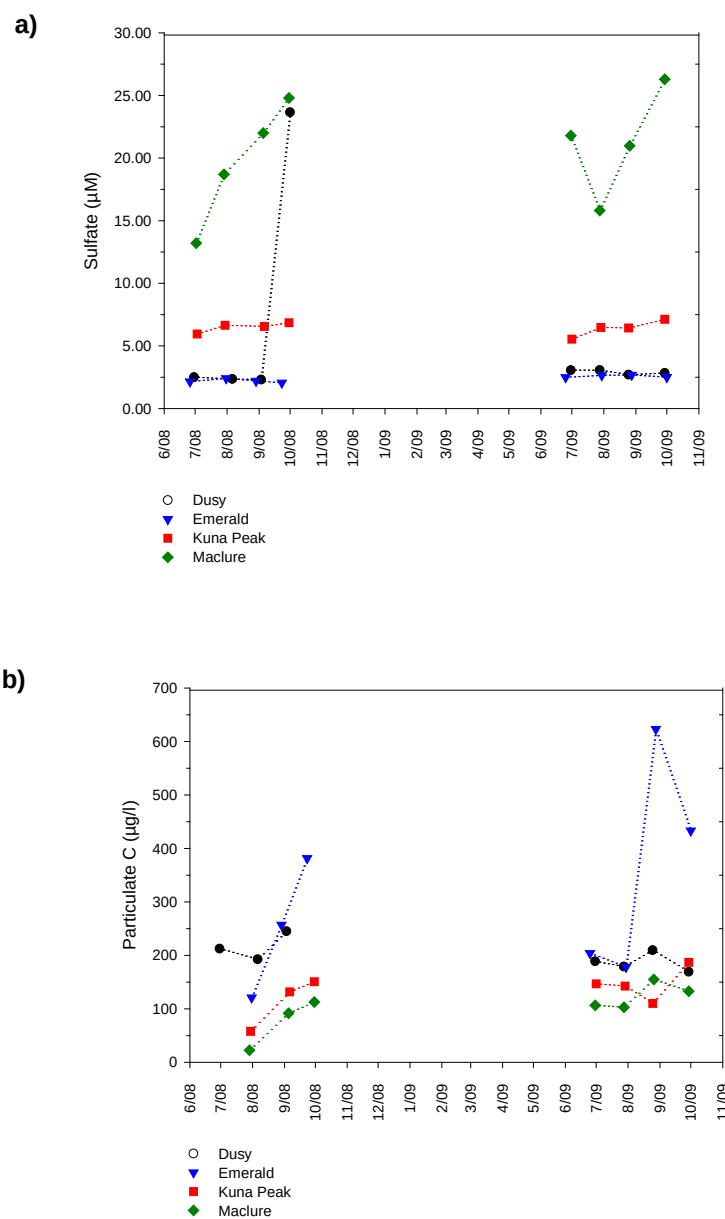


Figure A.28. 2008 and 2009 index site results for a) sulfate and b) particulate carbon.

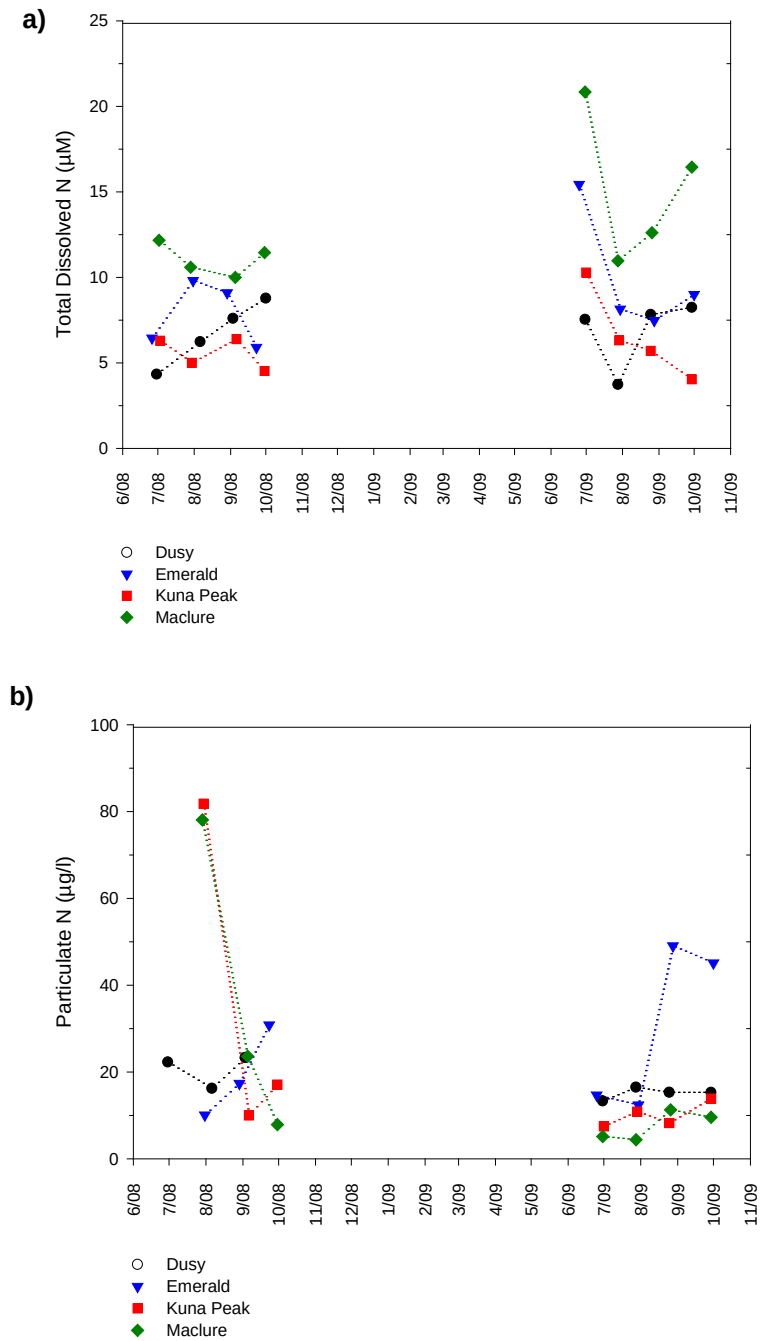


Figure A.29. 2008 and 2009 index site results for a) total dissolved N and b) particulate N.

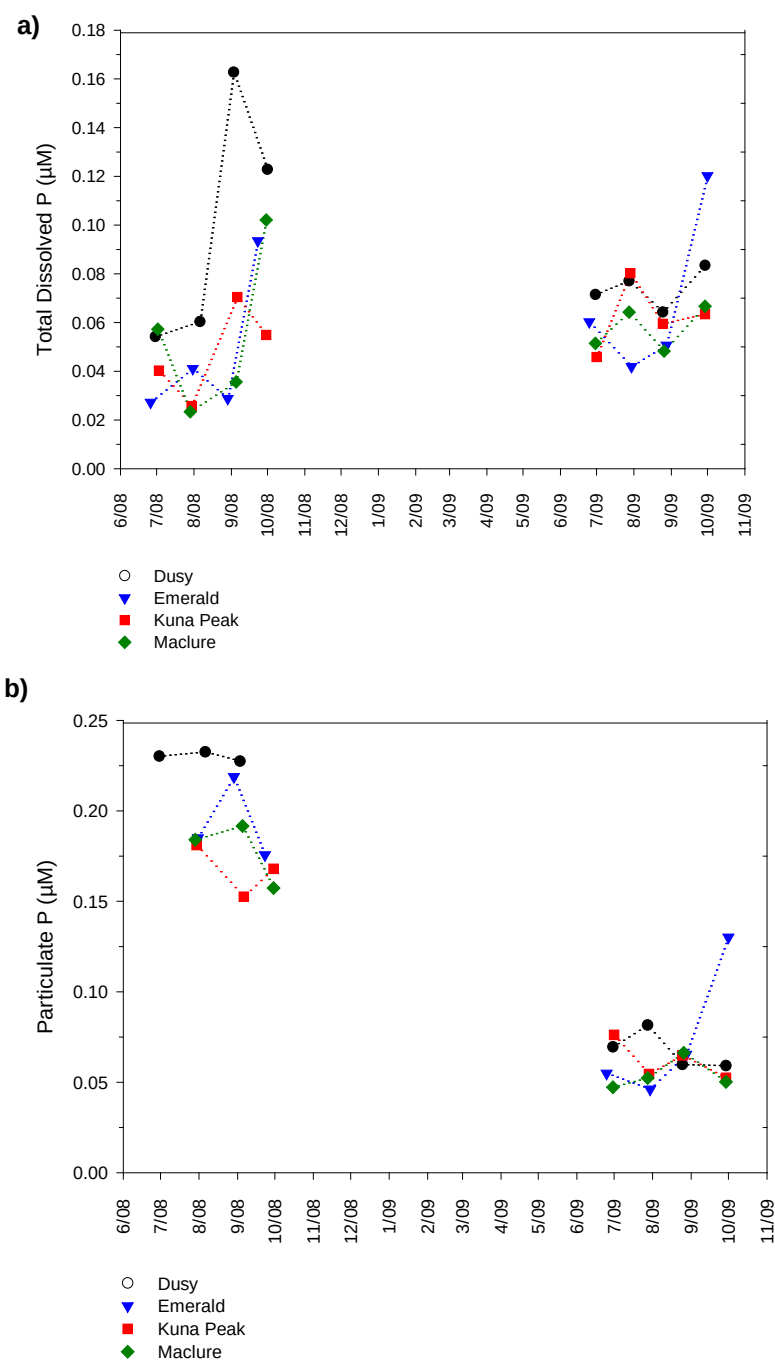


Figure A.30. 2008 and 2009 index site results for a) total dissolved P and b) particulate P.

Appendix B:

Quality Assurance and Quality Control Report for the Sierra Nevada Network Lake Monitoring Chemistry Samples

Submitted by: University of California, Riverside
August 20, 2010
CESU Agreement: H8R07080001
Primary Contact: Dr. James Sickman

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Introduction

The purpose of this report is to summarize the quality assurance and quality control results for the Sierra Nevada Network lake monitoring 2008 and 2009 chemistry data and to make recommendations for improving the protocol. The University of California, Riverside and the Sierra Nevada Network worked cooperatively to analyze samples, improve methods, and streamline procedures and processes. This report supplements the data provided to the network in Excel spreadsheets. In this report we:

- Summarize the quality assurance and quality control data for the 2008 and 2009 data,
- Make recommendations for improving the protocol as it relates to analytical methods,
- Discuss laboratory costs and workload.

Quality Assurance and Quality Control

Quality assurance and quality control procedures were followed as described in Heard et al. (2008). Some of our recommendations, which are discussed in *Section 3: Recommendations*, are incorporated into the interpretation and discussion of these results, including revised criteria. We decided to analyze the qa/qc data with the revised criteria so there would be consistency across years. If there are additional changes or revisions are not accepted, the data can always be re-evaluated.

Specific Conductance, pH, and ANC

Specific conductance was measured using a Symphony VWR SR601C meter and VWR probe ($K = 1.0 \text{ cm}^{-1}$). pH and ANC were measured using a Symphony VWR SR601C meter and Ross electrode that was calibrated with pH 4.01 and 10.00 buffers. The instrument was checked with a known HCl solution that must be within ± 0.02 pH units of the theoretical value.

Anions

Anions were analyzed using ion chromatography (EPA Method 300.1). In 2008 samples were run at UC Santa Barbara due to technical difficulties with the IC at UCR. In 2009, technical issues were resolved and the anions were run at the UCR lab. Samples were run on a Dionex IC with an AS19 column and an AG19 guard column using a 50 μl injection loop. Precision was assessed by computing relative percent differences of laboratory replicates. Bias was assessed by comparing measured values with the certified values for SPEX NIST certified standards and by measuring the percent recovery for laboratory spiked samples.

Precision measurements for the 2009 samples were all within the 5% (sulfate, nitrate, nitrite) and 10% (chloride) criteria (Figure 1). Relative percent differences ranged from 0.0-2.4% for sulfate, 0.0-3.7% for chloride, 0.4-1.7% for nitrate, and 0.0% for nitrite. Check sample were also all within the $\pm 10\%$ range (Figure 2). Percent differences between the measured and theoretical value ranged from -3.8–5.6% for sulfate, -5.0-3.0% for chloride, -7.0-4.0% for nitrate, and -4.0-1.0% for nitrite. Spike recoveries were within the 80-120% criteria with the exception of two samples (Figure 3). One nitrate spike only had a 73% recovery and one sulfate spike only had a 64% recovery. Percent recoveries ranged from 64-103% for sulfate, 91-103% for chloride, 73-107% for nitrate, and 100-110% nitrite. Method detection limits met SIEN's revised MDL

criteria (Table 1). Nitrate and sulfate did not meet the original detection limit criteria. (*Refer to Section 3.4 for discussion on MDL criteria*).

Cations

Cations were analyzed using inductively coupled plasma (ICP-AES) (EPA Method 200.7). Precision measurements for the 2008 potassium and magnesium samples were within the 5% criteria. RPD's for potassium ranged from .3-2.3% and for magnesium from .5-4.7%. However, calcium ranged from 0-7.2% with two calcium samples that slightly exceeded criteria and sodium ranged from 1.7-28.6% with one measurement that greatly exceeded criteria (Figure 4). Potassium and magnesium check samples were also within the +/- 10% range. Potassium ranged from -2.8 – 5.9% and magnesium ranged from -1.4 – 0.4%. Calcium and sodium exceeded the criteria. Calcium ranged from 58.2-60.7% and sodium ranged from 9.1 – 18.7% (Figure 5). Spike recoveries were within the 80-120% criteria with one exception with calcium (Figure 6). Spike recoveries ranged from 74-114% for calcium, 93-102% for potassium, 100-101% for magnesium, and 93-116% for sodium. Method detection limits for the sodium and potassium did meet SIEN criteria, but were too high for calcium and magnesium (Table 1).

The 2008 cation qa/qc results were not as good as they need to be. The calcium check sample results were especially poor. In addition to the check samples we include in the run, the staff research associate running the ICP includes additional check samples within all of his runs. These samples were well within in the criteria and ranged from -1.0 to -0.5% difference for all four cations. All of our calcium check samples were higher than expected. As a result, we concluded that the flasks used to make the check samples were contaminated with calcium. We purchased new flasks that will be used exclusively for SIEN cations in future years. In 2009 we made adjustments to the cation methods which improved our detection limits and qa/qc sample results. (*Refer to Section 3.1*).

Precision measurements for the 2009 samples were all within the 5% criteria (Figure 7). RPD ranged from 0.07-1.77% for calcium, 0.04-1.81% for potassium, 0.22-1.47% for magnesium, and 0.04-2.35% for sodium. Check sample were also all within the +/- 10% range (Figure 8). Percent differences between the measured and theoretical value ranged from 4.2-6.2-% for calcium, -0.7-0.6% for potassium, 2.5-5.1% for magnesium, and -3.9 – (-2.7)% for sodium. Spike recoveries were within the 80-120% criteria (Figure 9). Spike recoveries ranged from 96-105% for calcium, 102-104% for magnesium, and 95-98% for sodium, and were 99% for all samples for potassium. Method detection limits met SIEN criteria (Table 1).

Total Dissolved Nitrogen and Phosphorus

Total dissolved nitrogen (TDN) and total dissolved phosphorus (TDP) were analyzed using a persulfate digestion followed by EPA Method 353.4 and 365.5, respectively.

Precision measurements for the 2008 samples were within the 10% criteria. The 2008 TDN and TDP samples were run in three batches. The average precision for TDN for each batch was 9.0%, 1.3%, and 5.0%. The average precision for TDP for each batch was 1.3%, 0.3%, and 0.5%. Accuracy was not measured in 2008, but incorporated into the 2009 procedures. Method detection limits were computed as 3 times the standard deviation of the blank plus the mean blank. They ranged between 0.5 and 2.32 µM for TDN and 0.006 and 0.052 µM for TDP (Table 1). The MDL for the first batch of TDN was unusually high due to higher than normal blank

results. In the future, the MDL's will be computed using the methods described in the SIEN's revised QAPP.

Precision measurements for 2009 samples were within the 10% criteria, with one exception. TDN and TDP samples were run in two batches. The average precision for TDN for each batch was 7.8% and 5.7%. The average precision for TDP for each batch was 5.8% and 13.7%. Spike recoveries for the 2009 samples were within the 80-120% criteria. Average recovery for TDN was 116% and 111% for each batch and for TDP was 109% and 103% for the each batch. Method detection limits were computed as 3 times the standard deviation of the blank plus the mean blank. They ranged between 0.18 and 0.94 μM for TDN and 0.018 and 0.021 μM for TDP (Table 1). In the future, the MDL's will be computed using the methods described in the SIEN's revised QAPP.

Particulate Carbon and Nitrogen

Particulate carbon and nitrogen (PC and PN) samples were analyzed on a Thermo Electron Flash EA 1112 in 2008 and on a Costech elemental analyzer in 2009. Multiple 2008 PN samples were below the MDL. As a result, SIEN increased the amount of water filtered to 1000 ml in 2009. In addition, we ran the 2009 samples on a more sensitive instrument with lower MDL's. As a result, nearly all 2009 samples were above detection. We will run future samples, which will be filtered at higher volumes, on the Thermo Electron Flash EA 1112. As discussed in the recommendations below, we are not reporting on precision and bias for the particulate samples (*Refer to Section 3.2*).

Particulate Phosphorus

Particulate phosphorus was analyzed using a persulfate digestion followed by EPA Method 365.5.

As discussed in the recommendations below, we are not reporting on precision and bias for the particulate samples (*Refer to Section 3.2*). Although duplicate filters were run for approximately 5% of the samples. RPD's for these results ranged from 4.5% - 12.6% across both years. Method detection limits were computed as three times the standard deviation of the blank plus the mean blank. As discussed below, there are limitations with calculating an MDL for particulate samples. An estimated MDL was computed using soluble reactive phosphorus standards. MDL's were calculated by batch and ranged between 0.002 and 0.006 μM , assuming one liter of water was filtered through the sample filter (Table 1).

Charge and Conductance Balances

Charge and conductance balances were used to evaluate the internal consistency of the 2008 and 2009 data sets. Charge balances are used to evaluate the accuracy of the ionic concentrations and determine if all major constituents present in the sample have been measured. They are calculated as a percent ion difference, which is the absolute value of the sum of positive ions minus the sum of negative ions divided by the sum of positive ions plus the sum of negative ions. Charge imbalances greater than 20% indicate a potential problem with the sample data that may warrant rerunning the sample. Conductance balances are the theoretical conductance divided by the measured conductance. Theoretical conductance is the calculated conductance of the sample

based on the concentrations of all ions in the solution. Measured conductance is the specific conductance of the sample measured directly in the laboratory. If the conductance balance equals one then all major ions have been accounted for and measured without bias. Ratios less than one indicate that some ion concentrations were underestimated and ratios greater than one indicate that some ion concentrations were overestimated.

We provided SIEN with the charge and conductance calculations and results in an Excel spread sheet. In the 2008 data set four samples exceeded the 20% criteria and in the 2009 data set all samples were within the 20% criteria for the charge balances. The 2008 conductance balance results, with the exception of three samples, were between 0.78 and 1.17 with a mean of 0.97. There were two samples collected at different visits from the Dusy Index site that had ratios of 1.45 and 1.47. The high ratios are likely the result of overestimated sulfate concentrations (47.3 and 41.7 ueq/L respectively). Upper Granite had a ratio of 1.73. It is not clear from the data, which ions are overestimated. SIEN might consider re-analyzing anions and/or cations for these three samples. In 2009 ratios ranged from 0.71-1.13 with a mean of 1.02. The lowest ratio was from the June Emerald Lake outflow sample. It is possible the ANC is underestimated, but it is not entirely clear which ion(s) are underestimated.

The percent ion difference was plotted against the ratio of calculated conductance to measured conductance (Figure 10 and Figure 11). These plots are useful in determining if there is any bias in the data set towards an under- or over-estimation of cations and/or anions. The 2008 plot indicates a bias towards underestimating an anion(s). This may be attributed to an underestimation of bicarbonate due to exceeding ANC holding times. The 2009 plot indicates there are no strong biases in the charge and conductance balances.

Recommendations

The University of California, Riverside and the Sierra Nevada Network have been working collaboratively to improve and streamline the analytical aspects of the lake monitoring protocol. In this section, we describe our recommendations for changes to SIEN's Lake Monitoring Protocol.

Cation methods

The SIEN Lake Monitoring Protocol calls for using one of two cation analysis methods, EPA Method 200.7 (inductively coupled plasma) or 200.9 (flame atomic absorption spectrophotometry). We ran the samples using EPA Method 200.7, but recommend a few modifications to this method to improve detection limits, precision, and bias. These modifications are based on a publication by Morishige and Kimura (2008) and methods used by the National Atmospheric Deposition Program (Dombek, 2009).

The 2008 samples and a preliminary run of the 2009 samples were analyzed on the ICP with the instrument set to detect ions in the radial view. Radial view, as opposed to axial view, is often used because it minimizes ionization interference, which for many samples results in improved precision and accuracy. However, radial view is not the most sensitive setting. Therefore, it works well for higher concentration solutions, but is not sensitive enough for SIEN's exceptionally dilute Sierra Nevada lake samples. We recommend analyzing the samples using the axial view, a more sensitive setting for the instrument. In order, to suppress ionization and minimize interference we recommend adding cesium to the samples as described in Morishige

and Kimura (2008) and Dombek (2009). The 2009 samples were run using this modified method. Each sample and standard contained 196 ppm Cs (0.2 ml of 10,000 mg/L cesium were added to 10 ml samples and standards) and a drop of concentrated nitric acid.

Particulate C, N, and P

We recommend adjusting the measurement quality objectives for particulate carbon, nitrogen, and phosphorus to better reflect limitations in estimating MDL's, precision, and bias for particulate samples. It is not possible to do a true laboratory replicate, spike a filter sample, run a representative check sample, or calculate a highly accurate MDL. Therefore, we recommend that the protocol does not have strict precision and bias criteria for these measures. Spike samples are impossible to run for PC, PN, and PP so they will not be included in the analysis. An updated version of *Table 8: Analytical methods and measurement quality objectives*, in the SIEN Lake Monitoring Protocol Narrative, that reflects these recommendations is included in this report (Table 2). There are some quality assurance and quality control procedures that the lab will continue to include as estimates of the detection limits, precision, and bias.

The lab will determine MDL's for PC and PN using known C and N quantities in a peach standard. Since the MDL is calculated using a solid and not a filtered sample, it is not as representative as a traditional water chemistry MDL calculation; however, it provides a good estimate. PP has similar limitations. An estimated MDL will be calculated using soluble reactive phosphorus standards. The MDL's will be calculated by the lab once and then only re-calculated if there is a change in methods or instrumentation. We also recommend reporting the MDL's in respect to μg of nitrogen or carbon on half a filter for PC/PN. PC/ PN filters are analyzed for weight of N or C by the half filter. The concentration is not measured directly by the instrument; it is calculated based on the amount of water filtered. We are comfortable recommending this less rigorous approach, because highly accurate MDL's are not as critical with particulate samples. Once an estimate is calculated, we can ensure the samples are well above the rough 'MDL' by filtering more water, which increases the concentrations on the filters. Based on the calculated MDL's and the 2008 PN concentrations we recommend SIEN change their protocol from filtering 500 ml of water per filter to 1000 ml per filter.

The lab will include peach and soluble reactive phosphorus check samples during PC/PN and PP runs, respectively, to help with internal quality assurance and quality control monitoring.

However, we do not recommend using the results of these check samples to report bias estimates. An acceptable and standardized approach does not exist.

The lab will run a percentage of replicate filter samples. However, since this requires running two different filters they are technically not laboratory replicates, and therefore, should not be reported as a true measure of laboratory precision.

Bias Measures

We recommend changing the bias criteria to better reflect the two primary measures of bias in the lab. The one criterion for bias that is currently in the protocol does not apply well to both measures. We recommend having one criterion for check samples and one for spike recoveries. In addition, we have made recommendations for the new criteria (Table 2). They are different for the two measures because they are reported differently and spike recoveries typically have a larger acceptable range than is expected from check samples.

Anions: Measured constituents and MDL's

The SIEN Lake Monitoring protocol requires the lab to measure dissolved inorganic nitrogen using ion chromatography to measure nitrate + nitrite. We propose SIEN change their protocol to measure and report in the database nitrate and nitrite as two separate ions. They are measured separately on the IC and by combining them the network will lose information. They may always be combined at a later date for data analysis and reporting.

We recommend changing the MDL's for sulfate, nitrate, and nitrite from 0.200 µM to 0.300 µM because the original target MDL's are unrealistic given the instrumentation at UC Riverside. These recommendations are reflected in the revised measurement quality objectives table (Table 2).

Holding times

Holding times were violated in both 2008 and 2009 (dates are reported with the data sets) due to delays in sample delivery to the UCR lab and delays in analysis caused by methods development. During the 2010 field season, SIEN and UCR will be streamlining the shipping and laboratory analysis processes to ensure we meet the holding time requirements in future years.

Laboratory Costs

We underestimated the laboratory costs for the 2008 and 2009 samples. Specifically, we underestimated the time it would take for the QA/QC reporting (i.e., developing detection limits, reporting QA/QC on a per sample basis) and the time it would take to adapt and streamline analytical methods specifically for SIEN (i.e., ICP-AES, IC, PC/PN analysis). Now that these additional tasks have been completed and incorporated into lab procedures, the contract is more in line with costs. However, in the spirit of collaboration, UCR will likely contribute 5-10% more annually than the agreements direct costs.

Literature Cited

- Dombek, T. (2009), Standard operating procedure for the determination of calcium, magnesium, sodium, potassium by inductively coupled plasma-optical emission spectroscopy, rev. 6.0 National Atmospheric Deposition Program, Central Analytical Laboratory, Champaign, IL.
- Heard, A. M., L. A. H. Starcevich, J. Sickman, M. G. Rose, and D. W. Schweizer (2008), Sierra Nevada Network lake monitoring protocol, National Park Service, Three Rivers.
- Morishige, Y., and A. Kimura (2008), Ionization interference in inductively coupled plasma-optical emission spectroscopy, *SEI Technical Review*(66), 106-111.

Tables

Table B.12. MDL and ML results for 2008 and 2009 data.

2008 Samples			
Measure	MDL	ML	AMS
Specific Conductance	-	-	.1 uS/cm
pH	-	-	.01 pH unit
ANC	not calculated	not calculated	-
Anions			
Nitrate	.100 uM	.318 uM	-
Nitrite	-	-	-
Chloride	.40 uM	1.272 uM	-
Sulfate	.10 uM	.318 uM	-
Cations			
Calcium	0.025 uM	0.080 uM	-
Potassium	2.17 uM	6.90 uM	-
Magnesium	0.082 uM	0.262 uM	-
Sodium	0.696 uM	2.21 uM	-
Nutrients - Total Dissolved			
Total dissolved nitrogen	0.63 uM	2.00 uM	-
Total dissolved phosphorus	0.63 uM	2.00 uM	-
Particulate Fractions			
Particulate nitrogen	0.48 ug/half filter	1.52 ug/half filter	-
Particulate carbon	3.06 ug/half filter	9.74 ug/half filter	-
Particulate phosphorus	0.006 uM	0.018 uM	-
2009 samples			
Measure	MDL	ML	AMS
Specific Conductance	-	-	.1 uS/cm
pH	-	-	.01 pH unit
ANC	not calculated	not calculated	-
Anions			
Nitrate	0.299 uM	0.951 uM	-
Nitrite	0.142 uM	0.452 uM	-
Chloride	0.219 uM	0.696 uM	-
Sulfate	0.210 uM	0.667 uM	-
Cations			
Calcium	0.031 uM	0.099 uM	-
Potassium	0.051 uM	0.162 uM	-
Magnesium	0.098 uM	0.312 uM	-
Sodium	0.043 uM	0.137 uM	-
Nutrients - Total Dissolved			
Total dissolved nitrogen	.18 uM	.572 uM	-
Total dissolved phosphorus	0.021 uM	.067 uM	-
Particulate Fractions			
Particulate nitrogen	.12 ug/half filter	.37 ug/half filter	-
Particulate carbon	1.86 ug/half filter	5.91 ug/half filter	-
Particulate phosphorus	.002 uM	0.006 uM	-

Table B.13. Revised measurement quality objectives table (changes are italicized and in red font).

Measure	Method	MDL	ML	AMS	RPD	<i>Check Samples</i>	<i>Spike Recovery</i>	Completeness
Core parameters								
Temperature	Thermistor	-	-	0.1 °C	±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								
<i>Nitrate</i>	Ion chromatography (EPA Method 300.1)	<i>0.3 umol/L</i>	<i>0.95 umol/L</i>	-	5%	<i>±10%</i>	<i>80-120%</i>	95%
<i>Nitrite</i>	Ion chromatography (EPA Method 300.1)	<i>0.3 umol/L</i>	<i>0.95 umol/L</i>	-	5%	<i>±10%</i>	<i>80-120%</i>	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%	<i>±10%</i>	<i>80-120%</i>	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%	<i>±10%</i>	<i>80-120%</i>	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	<i>Inductively coupled plasma (ICP) (EPA Method 200.7) using modifications in Dambek (2009) and Mirishige and Kimura (2008)</i>	0.2 umol/L	0.8 umol/L	-	5%	<i>±10%</i>	<i>80-120%</i>	95%
Sodium	<i>Inductively coupled plasma (ICP) (EPA Method 200.7) using modifications in Dambek (2009) and Mirishige and Kimura (2008)</i>	0.2 umol/L	0.8 umol/L	-	5%	<i>±10%</i>	<i>80-120%</i>	95%
Magnesium	<i>Inductively coupled plasma (ICP) (EPA Method 200.7) using modifications in Dambek (2009) and Mirishige and Kimura (2008)</i>	0.2 umol/L	0.8 umol/L	-	5%	<i>±10%</i>	<i>80-120%</i>	95%
Potassium	<i>Inductively coupled plasma (ICP) (EPA Method 200.7) using modifications in Dambek (2009) and Mirishige and Kimura (2008)</i>	0.2 umol/L	0.8 umol/L	-	5%	<i>±10%</i>	<i>80-120%</i>	95%
Chloride	Ion chromatography (EPA Method 300.1)	0.3 umol/L	0.95 umol/L	-	10%	<i>±10%</i>	<i>80-120%</i>	95%
Sulfate	Ion chromatography (EPA Method 300.1)	<i>0.3 umol/L</i>	<i>0.95 umol/L</i>	-	5%	<i>±10%</i>	<i>80-120%</i>	95%
ANC	Gran titration (Rounds et al 2006)	0.5 umol/L	2 umol/l	-	-	-	-	95%

Figures

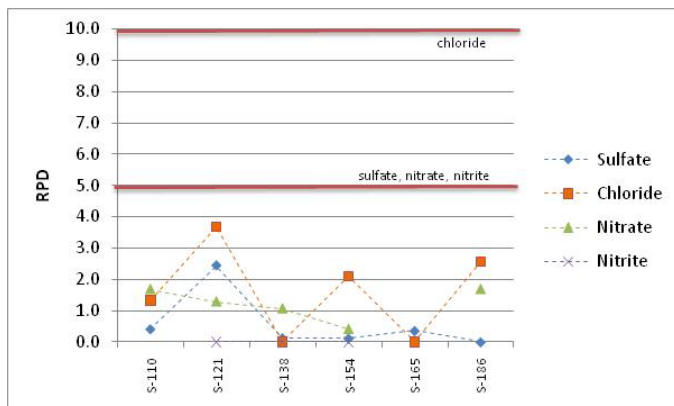


Figure B.31. 2009 anion precision results.

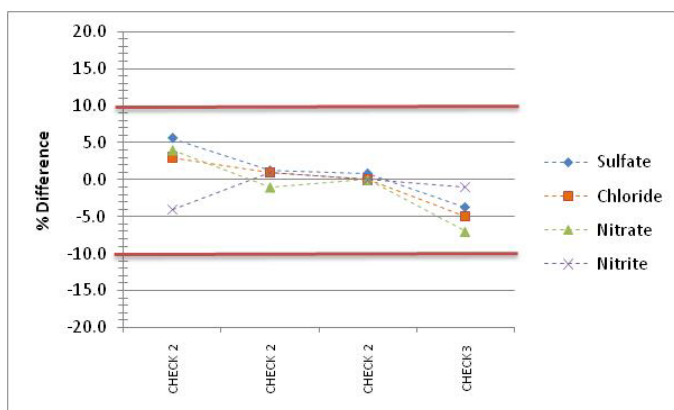


Figure B.32. 2009 anion check sample results.

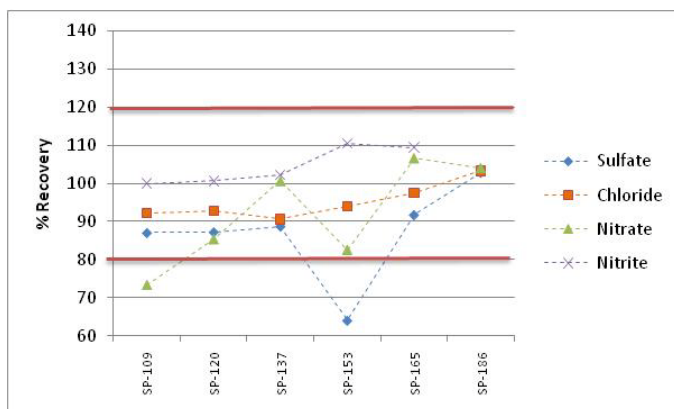


Figure B.33. 2009 anion spike recovery results.

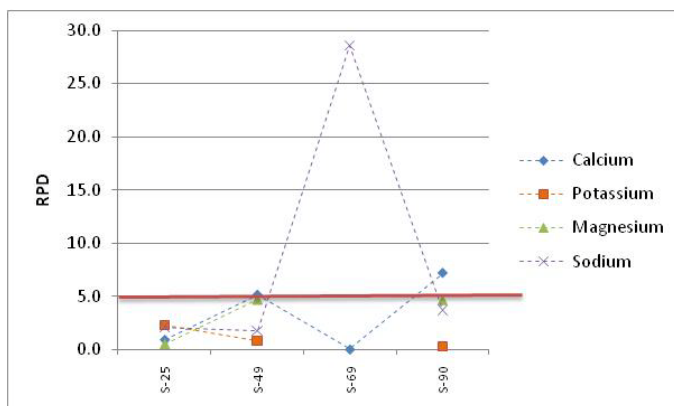


Figure B.34: 2008 cation precision results.

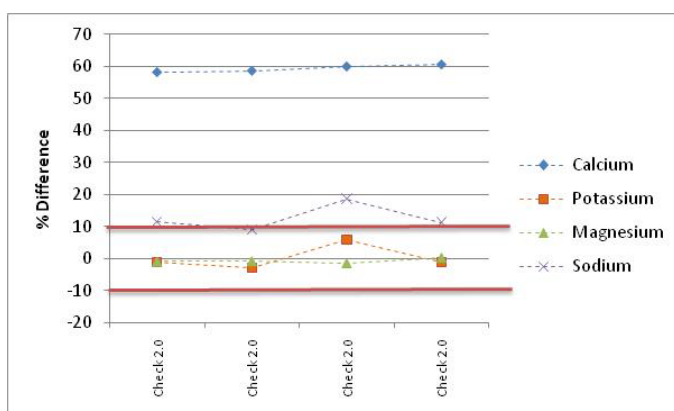


Figure B.35. 2008 cation check sample results.

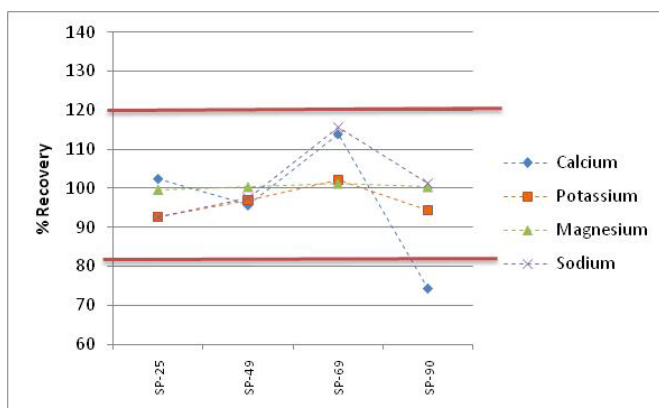


Figure B.36. 2008 cation spike recovery results.

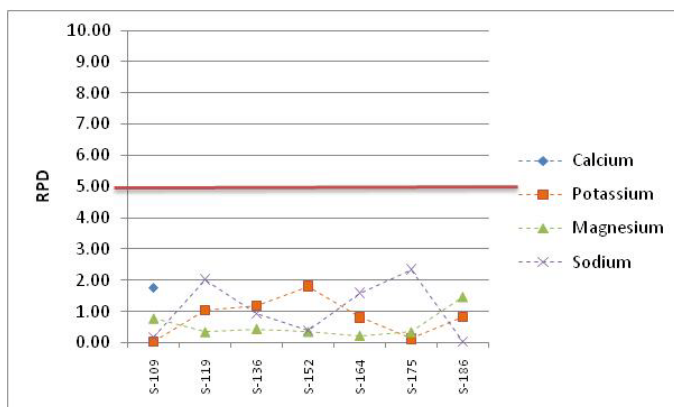


Figure B.37. 2009 cation precision results.

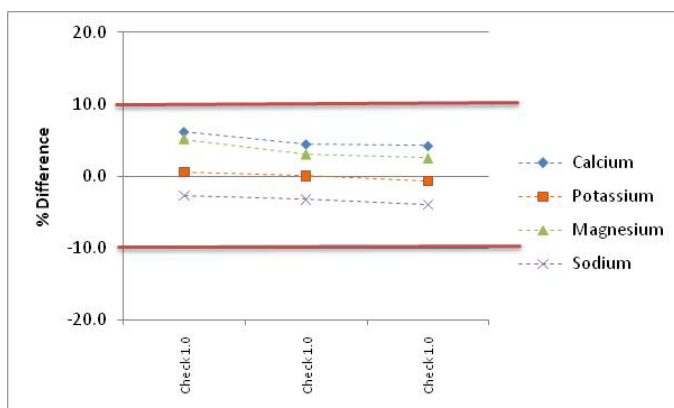


Figure B.38. 2009 cation check sample results.

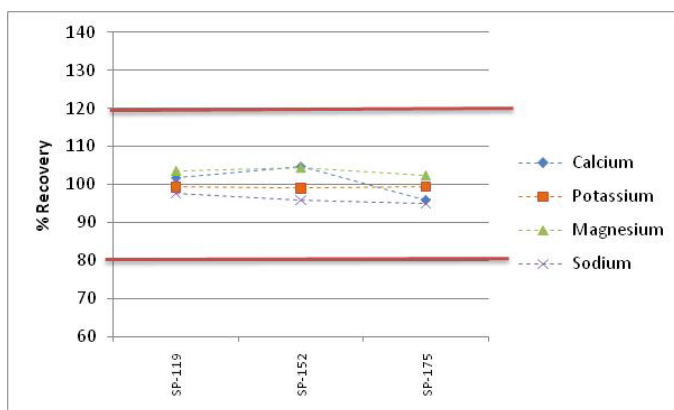


Figure B.39. 2009 cation spike recovery results.

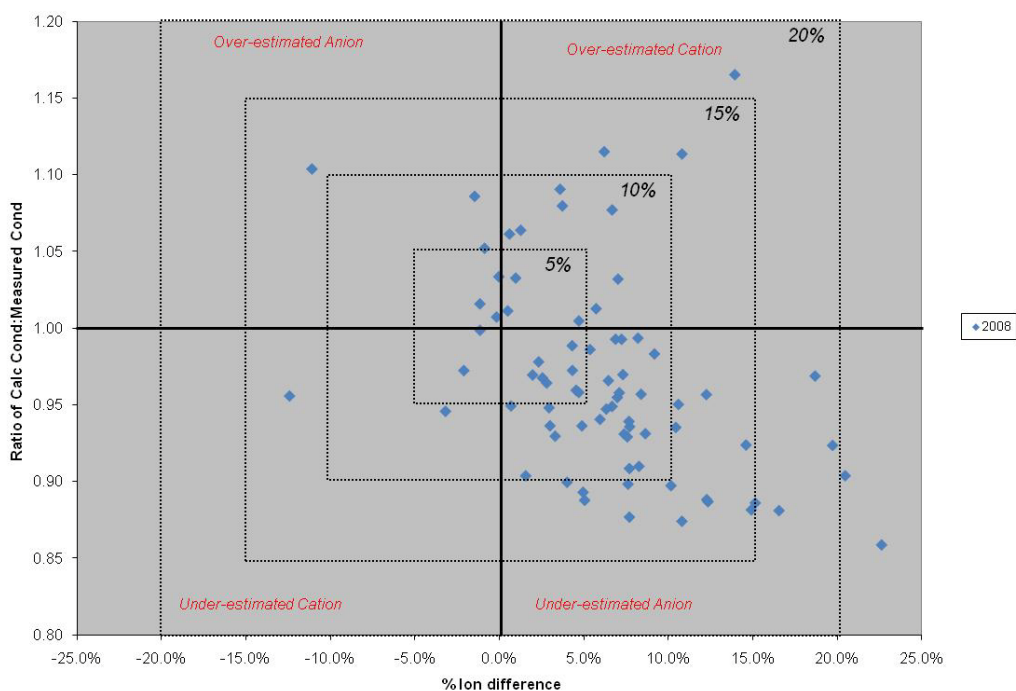


Figure B.40. Percent ion difference plotted against the ratio of calculated to measured conductance for the 2008 data set.

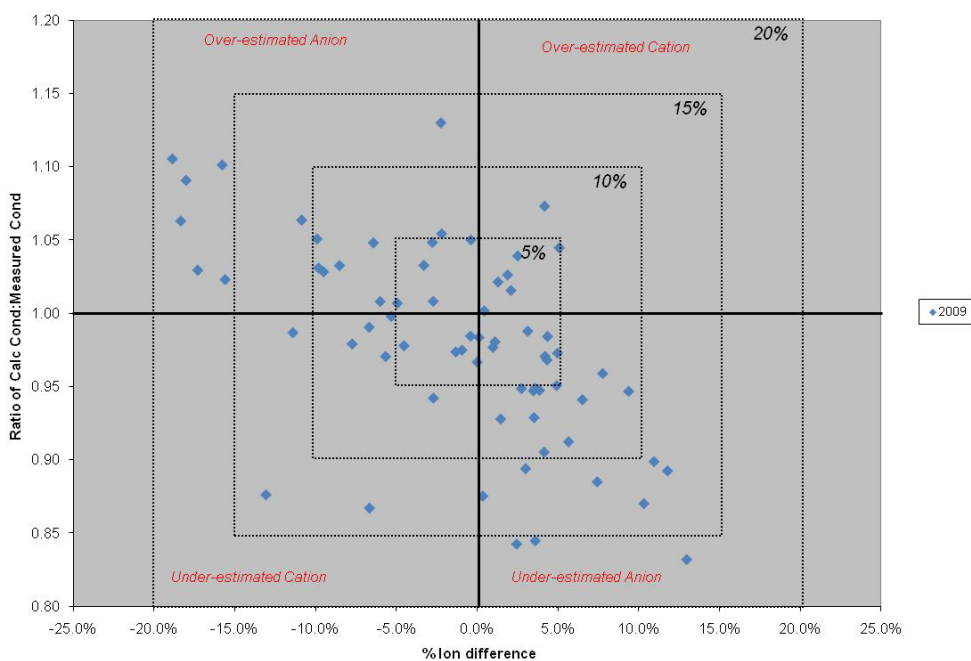


Figure B.41. Percent ion difference plotted against the ratio of calculated to measured conductance for the 2009 data set.

The Department of the Interior protects and manages the nation's natural resources and cultural heritage; provides scientific and other information about those resources; and honors its special responsibilities to American Indians, Alaska Natives, and affiliated Island Communities.

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