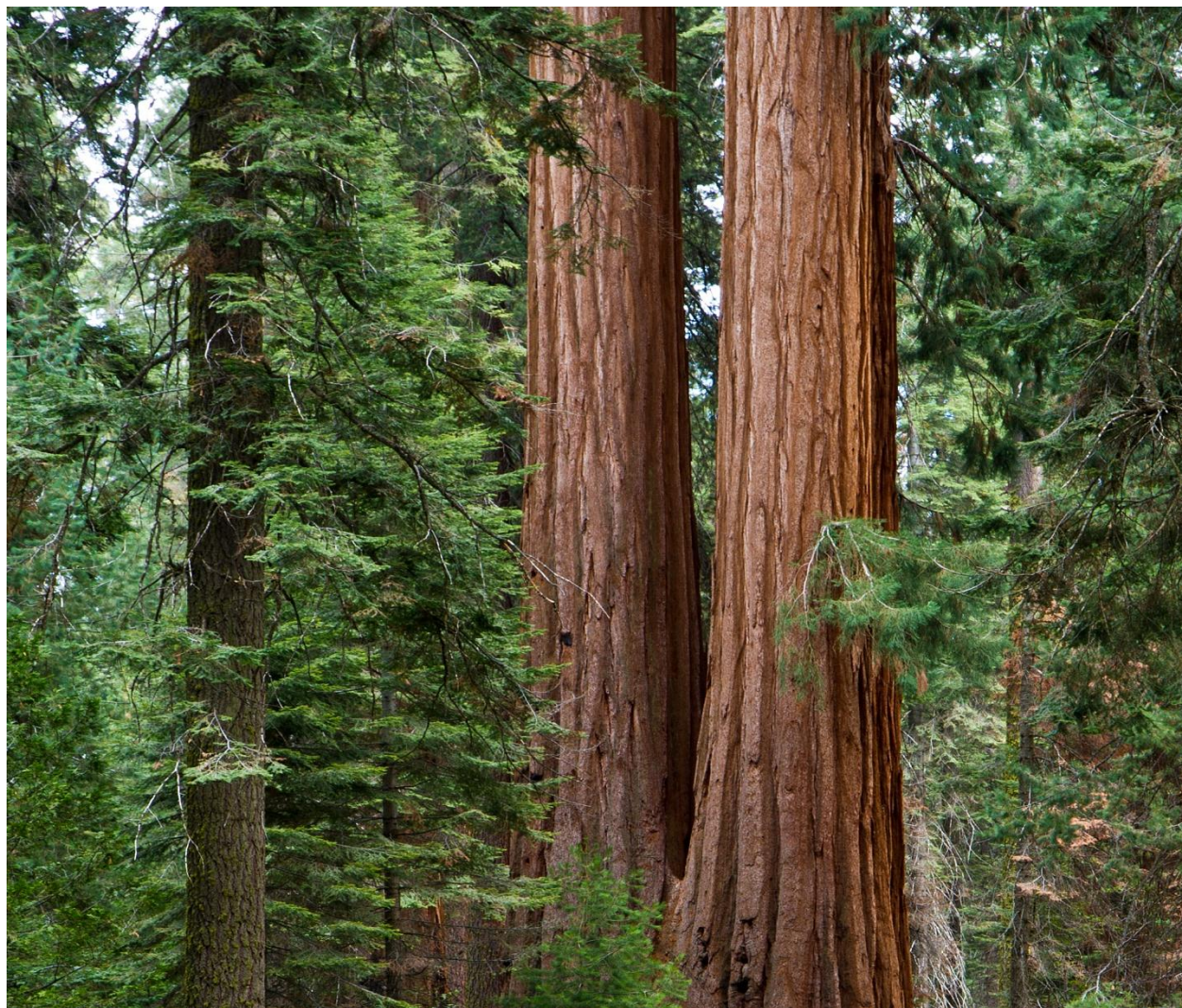




A Natural Resource Condition Assessment for Sequoia and Kings Canyon National Parks

Appendix 6 - Water Quality

Natural Resource Report NPS/SEKI/ NRR—2013/665.6



ON THE COVER

Giant Forest, Sequoia National Park
Photography by: Brent Paull

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Appendix 6 - Water Quality

Natural Resource Report NPS/SEKI/ NRR—2013/665.6

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U.S. Department of the Interior
National Park Service
Natural Resource Stewardship and Science
Fort Collins, Colorado

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Scope of analysis

Montane water systems are barometers of both natural and human induced change (Baron et al. 2009, Elser et al. 2009). By reviewing the past and current status of both rivers and lakes in Sequoia and Kings Canyon National Parks (SEKI) we have evaluated trends in concentrations of chemical solutes that can serve as indicators for anthropogenic pollution and establish a baseline to be used to evaluate environmental change. The suite of chemical solutes included major anions and cations, nutrients (nitrate and phosphate), chemicals of concern (mercury and representative pesticides); water temperature is also included.

Our approach involves examining spatial and temporal trends in different water quality parameters (see Table 1 for a list of these parameters). For locations with elevated concentrations (i.e. with concentrations significantly higher than mean concentrations), we first considered historical use patterns or local geologic explanations. Exogenous sources were considered for any chemical solute concentration that could not be explained. After establishing temporal and spatial patterns, we chose indicator locations, four streams and three lakes that have a temporal record of the longest duration a minimum of 14 different parameters measured, and at least 100 records per year. These were used to evaluate any systematic change in water quality parameters. As not all parameters are measured in all locations, we have indicated when we have had to deviate from this general analysis approach. The NRCA report for the Rocky Mountain national park has recently been completed (Theobald et al. 2010). We compare lake data to the trends they observed for alpine lakes.

There are well-known examples of anthropogenic impacts on watersheds and ecosystems. Among these are the impacts of phosphate fertilizers and pesticides, nitrates and ammonia from the agriculture industry in the San Joaquin Valley (SJV), and acid rain (Whiting et al. 1989, Murdoch and Stoddard 1992, Lovett 1994, Marchetto et al. 1995, Clow and Sueker 2000, Turk et al. 2001, Sullivan et al. 2005, Saros et al. 2011, Vicars and Sickman 2011). Among the greatest concerns in SEKI are acid rain, and mercury (Heyvaert et al. 2000, Clow et al. 2002, Krabbenhoft et al. 2002, Sanders et al. 2008), and pesticide deposition (McConnell et al. 1998, Luo et al. 2008, Bradford et al. 2010). These are all exogenous factors that involve atmospheric transport from sources outside SEKI. By performing a more comprehensive analysis using available literature, it is possible to develop a more complete picture of the state of the resources.

Atmospheric deposition of acids and nutrients are known to produce conditions in lakes, streams, and other water bodies that affect aquatic organisms (Murdoch and Stoddard 1992, Lovett 1994). Burning sulfur-containing fuels and the production of NO_x in internal combustion engines can produce sulfuric and nitric acids, respectively, after interactions with other oxidizers (such as ozone) and water in the environment. Wind-blown fertilizers containing nitrate, ammonia, and phosphorus have been shown to be carried for miles from croplands (Kirchmann and Witter 1989, Kratzer and Shelton 1998, Krauter et al. 2002) to high elevation where they deposit on trees, grass and rocks, or fall in rain and snow (Stoddard 1987, Stohlgren et al. 1991, Zhang et al. 2002, Ohte et al. 2004, Fenn et al. 2010, Vicars et al. 2010, Saros et al. 2011). For several decades, the concentrations of nutrients and alkalinity have been measured in samples collected from streams and lakes in Sequoia and Kings Canyon National Parks. These exogenous factors are not necessarily toxic themselves, but in sufficient quantities, they can have significant

negative effects on surface waters (Jorgensen and Postgate 1982, Beller et al. 2004, Bodelier and Laanbroek 2004, Nydick et al. 2004).

Numerous studies have been undertaken over several decades, and the data from many of these efforts have been compiled in the Sierra Nevada (SIEN) database, a collaborative effort between the National Park Service and the United States Geological Survey (Heard et al. 2008, Mutch et al. 2008). The combined data sets provide more than a snapshot of the parks. The studies that comprise the database span over 50 years with samples collected in over 900 locations inside the parks and in the national forest lands nearby. Using the complete set of almost 500,000 records, it is possible to begin to determine whether trends are emerging for various water quality indicators. In some cases, it may be possible to distinguish between local geochemical effects due to local bedrock or groundwater and exogenous anthropogenic factors. The value of the SIEN database is enhanced when used in conjunction with the Western Airborne Contaminants Assessment Project (WACAP) (Landers et al. 2003). The WACAP database surveys more contaminant parameters in more media than SIEN, however, it does not have the same temporal or spatial extent; data were collected from 2003 to 2006. WACAP extends the assessment also as a biological assessment. The short three-year period over which WACAP data were collected makes it difficult to assess trends. Furthermore, the limited spatial coverage limits our ability to distinguish local effects from park-wide effects, i.e., endogenous versus exogenous factors.

Here we attempt to gather the available information in order to provide a current assessment of the parameters that have the most potential for impact on the resources in SEKI. Spatial and temporal analysis is needed to determine whether the levels are significant and whether conditions are improving or deteriorating. In some cases, parameters are also used provide insight for interpretation of the impact of other parameters. When possible, long-term trends are evaluated in reference lakes and streams. Geographic Information Systems (GIS) data are used to explain the occurrence of anomalies. Data collection methods have varied for different parameters in time window, frequency, and location. These differences in some cases have been helpful and in others interpretation of data is more challenging. Our experiences in performing data analysis are helpful in making recommendations for future monitoring. We hope the current analysis aids making management decisions for the long term benefit of SEKI.

Critical questions

Spatial patterns

What do standard water quality parameters indicate concerning SEKI?

Is there a correlation of elevation with changes in water quality?

Where are nutrients present?

Are these nutrients endogenous or exogenous?

Where are contaminants present?

Are these contaminants endogenous or exogenous?

Temporal patterns

How do standard water quality parameters change over time? Improving or not?

How do nutrient levels change over time? Improving or not?

How do contaminant levels change over time? Improving or not?

Data sources and types used in analysis

Two databases were the main sources of information in our analysis. Parameter data were extracted from the Sierra Nevada (SIEN) database compiled from multiple studies over several decades by the USGS and NPS (Mutch et al. 2006). The original Access database file was available through the Sequoia/Kings NPS website, but is no longer linked. We converted the Access database to a standard MySQL 4.1 database which provided a more robust query capability. The database design was unchanged; only one auto-incremented integer field was added to each table to ensure a unique key was present for each record. A second source of information was the Western Airborne Contaminants Assessment Project (WACAP) database (Landers et al. 2003). These data were collected over a limited number of years, contained records for 20 National Parks, and covered a broad array of factors from water to vegetation and animals. Consequently, typically there were fewer records for each parameter in WACAP compared to the SIEN database. We used WACAP records related to toxic metals and pesticide contamination.

For any given water parameter, there are multiple studies, sample types, methods, and units of measurement. For example, there were 13 different categories (parameter codes, or pcodes) of database records related to 'nitrate'. Some pcodes described samples processed through different procedures such as with and without filtration. Other pcodes were used for various aggregated pcodes for the same parameter, or for combinations with multiple parameters. Many pcodes may describe limited studies, and contain relatively few records (less than 10 to a few hundred records); others may contain thousands of records. Since data records were frequently limited, aggregated pcode records were frequently used with units converted as necessary to a single form. For example, nitrate values expressed as mg L^{-1} of nitrate were converted to mg L^{-1} of nitrogen and combined with other values selected through other pcodes. Whenever possible, checks such as mass balance and charge balance were performed to support the validity of aggregation. Aggregation of data was performed in the SIEN database, and the methods for aggregation were described mathematically. When available and appropriate, these pcodes were chosen.

We also checked to determine whether multiple values were reported for a given parameter using the same water sample. In cases where records with different parameter codes were produced from the same water samples, the values were averaged since it was not clear which one should be used. In this way, we ensured that each sample provides at most one value to be further processed. The database records also contained a field to indicate whether a value was deemed below the detection limit, or known to be less than the value recorded. Records marked as inaccurate were excluded from averaging when inclusion would skew results. In some cases, exclusion could lead to large over-estimates of parameter values. In these cases, the values at the limit of detection were used. This value was chosen because parameter values often varied over two or more orders of magnitude above the detection limit.

Elevation records were missing for some sample sites in the SIEN database. There were over 12,000 water samples taken from over 900 sites. The site locations were identified using decimal degrees of latitude and longitude and UTM coordinates. UTM coordinates were used to obtain elevations for all sample sites from a USGS 30-m resolution digital elevation model (Gesch 2006). Where elevation values were recorded in the database, the database values and the USGS values were compared. All values were in close agreement (less than 10 m average difference). Consequently, we are confident the elevation values obtained externally for sample sites lacking elevation records in the database are accurate. These elevation comparisons also allowed us to identify elevation values in the database that were not converted from feet to meters. In such cases, the USGS elevation values were used.

When possible, long-term trends are evaluated in reference lakes and streams. Geographic Information Systems (GIS) data are used to explain the occurrence of certain anomalies. Data collection methods have varied for different parameters in time window, frequency, and location.

Reference conditions

Reference lakes and streams were used to look for trends in parameters. These sample sites were selected for long-term measurements and relatively high frequency of data collection each year. Three lake sites and four stream sites were selected as the standard reference set (Figure 1). An additional stream site was selected as an alternative if insufficient data were available in the standard reference set for a given parameter. The lake sites range from 2807 to 3218 m altitude (average 2950 m). The reference stream sites range from 1000 m to above 3000 m, with one additional stream site used when necessary at 250 m.

Mean values were calculated. Median values are reported to provide an indication of the deviation of parameter values from a normal distribution.

In order to evaluate the condition of the resources in Sequoia and Kings Canyon National Parks, we need to know not only what the condition was like at a point in time, but also how conditions may be changing over time. Parameter measurements from different water body types can have very different distributions. Elevation differences in a single water body type may also shift value distributions. Parameter values can have a strong dependence on seasonal factors such as snow melt, i.e. the volume of flow and the quantity of dissolved material in the water. Finally, local geochemical factors can potentially influence parameter values. These factors all can contribute to significant systematic errors potentially skewing results and leading to false conclusions.

The SIEN database contains almost 500,000 records relating to water samples collected from 1951 to 2005. Most water bodies were studied only for part of the period covered by the database, usually not longer than 20 years, and often only for about 5 years. The SIEN database contains records from over 900 different sample locations distributed over the Parks and the national forest. However, few of these sites were consistently measured multiple times during the

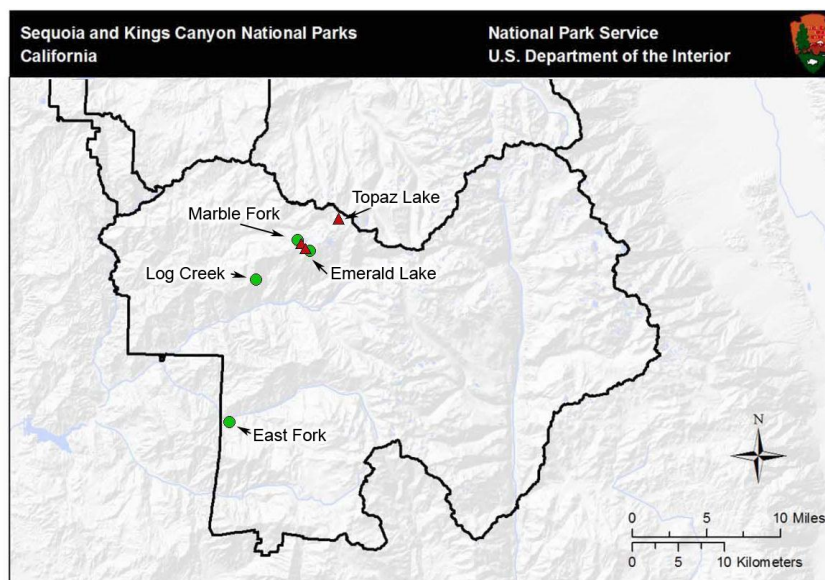


Figure 1. Standard reference sites for determining the parameter reference condition and trend evaluation. Streams are green circles, and lakes are red triangles. Reference sites are named. Emerald lake is indicated by three symbols. Emerald lake inflow is the stream to the southeast of the lake itself, indicated by the adjacent red triangle. The Emerald Lake outflow is the red triangle to the northeast of Emerald Lake. The Emerald Lake outflow waters flow downslope to the Marble Fork sample site. The additional non-standard site, Three Rivers (not shown), is located outside the park boundary upstream from the large lake (blue) at the lower left.

year continuously for decades. When considering the most relevant water quality indicators, lake and stream sites in the SIEN database having the most samples collected per year for one or more decades were selected.

Water samples reported in the database all had fields reporting date, time, and location of collection. Parameter values were viewed as plots in chronological order. We observed that certain water types at different elevations were evidently studied for periods of years, off and on, inconsistently. Parameter values were also viewed seasonally. Sometimes large seasonal variations were relatively consistent from year to year, with some variations that could be related to wet versus dry years.

After examining the SIEN database for water body type, elevation, number of samples, and length of time studied, we selected three lakes and five streams as our reference set. These had the most records per year for the most water parameters, with samples collected over the longest period of time. Although we know there is a strong seasonal influence on parameter values, we lacked a sufficient quantity of data to restrict values in the reference evaluation to a specific window of days within the calendar year. Furthermore, due to interannual variability in climate, the seasonal variation may be significantly shifted by several weeks. Some parameters can vary by an order of magnitude or more in a few weeks, thus it is difficult to assign a fixed window for parameter evaluation that yields parameter values with less variation (lower standard deviation). However, we do attempt to indicate the degree of seasonal effects in the aggregated data set.

Most of the reference set of lakes and streams are within the Marble Fork of the Kaweah. These are Topaz Lake, Emerald Lake inflow, Emerald Lake, Emerald Lake outflow, and Marble Fork. Log Creek is in the Middle Fork. Another site is East Fork. Finally, Three Rivers is below the confluence of these tributaries. However, we regard Three Rivers to be potentially strongly influenced by local and upstream human activities. Consequently, the Three Rivers site is usually unreported except in cases where data are lacking from other sites. We consider the Emerald Lake outflow to reflect the characteristics of the lake more than an ordinary stream, thus we include it in the lake category. This determination is supported by a comparison of Emerald Lake and its outflow by Sickman, et al. (Sickman et al. 2003). The lake sites are at an elevation near 3000 meters. The streams vary in elevation from about 500 meters to 3000 meters.

Additional reference sites for contaminants

The WACAP database covers multiple parameters in living organisms, sediments, snow and water. Both databases contain information regarding numerous parameters ranging from ions, to metals, and pesticides. However, WACAP samples were collected only from 2003 to 2006. Consequently, these data cannot be used to evaluate trends. A possible exception is the WACAP sediment data. Sediment cores were collected from two lakes in SEKI. The core layers were dated by ^{210}Pb and parameter values measured in these layers. The dated layers extended back to almost 1000 years ago. A concern is the degree of mixing of the sediment layers due to factors such as snow avalanche or bioturbation. These factors would tend to blur the actual level of the parameter for a given period. As a result, sediment-derived values may not be useful to evaluate parameter trends.

Bradford, et al., measured pesticides in high elevation lakes representing four different regions around Kings National Park (Bradford et al. 2010). These sites were over 30 miles from the sources of pesticide usage in the San Joaquin Valley, on two different latitudes. The lake sites were separated from each other by 20 miles. There were not accessible by established trails. Pesticide levels were collected over 5 months in 2003 at approximately weekly frequency. In this way, acute and chronic effects were evaluated.

None of the pesticide data sources were multi-year studies. WACAP does have sediment core sample data with pesticide levels measured within dated layers. However, through bioturbation or disturbances of sediments through avalanche, pesticide levels seem to be present in layers prior to use, and persisting at high levels after discontinuance of use. Thus, these core samples cannot be taken as reliable indicators of pesticide residue remaining after deposition at the year corresponding to the sample dating measurement. There are no long term studies of pesticide deposition reported in the SIEN and WACAP databases. Bradford, et al., measured collected samples for pesticide testing over 5 months in 2003 (Bradford et al. 2010). Numerous samples were collected which provided a clear picture of temporal factors involved in pesticide deposition, however, these were not long term studies of the type that would be needed to determine a trend in certain pesticide levels.

Spatial and temporal analyses

Various water quality parameter values were measured with different numbers of samples, at different sample sites. A comparison of selected parameters from lakes (Table 1) and streams (Table 2) in SEKI indicates sample number can vary by more than two orders of magnitude. Sample sites are distributed non-randomly in SEKI, over-representing some areas, and completely missing others. These values do not take into consideration seasonal, temporal, elevational, or local geochemical factors. A comparison of the mean values with the median values indicates the data do not fall into a normal distribution. It is expected parameter impacts can be better understood by examining the dependence of the parameter values on these additional factors.

Table 1. Selected water parameter values from SIEN database for SEKI lakes

Parameter	Number of samples (sites)	Mean $\pm$ s.d. (median)	Min	Max
ANC ($\mu\text{eq L}^{-1}$)	176 (26)	22.77 $\pm$ 20.58 (15.48)	0.19	150
Ca ²⁺ (mg L ⁻¹)	3345 (76)	0.42 $\pm$ 0.46 (0.38)	0	9
Cl ⁻ (mg L ⁻¹)	3345 (76)	0.11 $\pm$ 0.29 (0.08)	0	13.1
DO (mg L ⁻¹)	18 (13)	7.68 $\pm$ 1.19 (7.85)	5.8	10
K ⁺ (mg L ⁻¹)	3345 (76)	0.1 $\pm$ 0.09 (0.1)	0	1.18
Mg ²⁺ (mg L ⁻¹)	3345 (76)	0.04 $\pm$ 0.04 (0.04)	0	1.6
Na ⁺ (mg L ⁻¹)	3345 (76)	0.23 $\pm$ 0.17 (0.24)	0	3.56
NH ₄ ⁺ (mg L ⁻¹)	2401 (51)	0.01 $\pm$ 0.15 (0)	0	5.29
NO ₃ ⁻ (mg L ⁻¹)	2883 (35)	0.05 $\pm$ 0.09 (0.03)	0	2.52
Pb ($\mu\text{g L}^{-1}$)	9 (1)	10 $\pm$ 0 (10)	10	10
pH	2967 (67)	6.2 $\pm$ 0.3 (6.2)	4.5	8.6
PO ₄ ³⁻ (mg L ⁻¹)	3345 (76)	0.0012 $\pm$ 0.0065 (0)	0	0.1
SO ₄ ²⁻ (mg L ⁻¹)	3345 (76)	0.29 $\pm$ 0.84 (0.26)	0	29.8
SpC ($\mu\text{S cm}^{-1}$)	2975 (62)	5.31 $\pm$ 4.71 (4.5)	1.1	108
T (°C)	421 (52)	8.88 $\pm$ 6.81 (8.3)	-1	24.5
Turbidity (NTU)	78 (31)	1.17 $\pm$ 1.99 (0.43)	0	12

Table 2. Selected water parameter values from SIEN database for SEKI streams

Parameter	Number of samples (sites)	Mean $\pm$ s.d. (median)	Min	Max
ANC ($\mu\text{eq L}^{-1}$)	1051 (148)	309.09 $\pm$ 227.41 (269.73)	0.19	2298
Ca ²⁺ (mg L ⁻¹)	5627 (274)	4.07 $\pm$ 6.03 (2.86)	0	108
Cl ⁻ (mg L ⁻¹)	5627 (274)	0.71 $\pm$ 1.36 (0.32)	0	22.8
DO (mg L ⁻¹)	651 (41)	9.92 $\pm$ 1.49 (9.8)	5.2	15.5
Hg ($\mu\text{g L}^{-1}$)	61 (8)	0.53 $\pm$ 1 (0.2)	0	7
K ⁺ (mg L ⁻¹)	5627 (274)	0.54 $\pm$ 0.58 (0.4)	0	5.23
Mg ²⁺ (mg L ⁻¹)	5627 (274)	0.49 $\pm$ 0.64 (0.28)	0	9.53
Na ⁺ (mg L ⁻¹)	5627 (274)	2.49 $\pm$ 2.81 (1.91)	0	23
NH ₄ ⁺ (mg L ⁻¹)	3212 (132)	0.01 $\pm$ 0.06 (0)	0	2.01
NO ₃ ⁻ (mg L ⁻¹)	3445 (101)	0.06 $\pm$ 0.33 (0)	0	8.47
Pb ²⁺ ($\mu\text{g L}^{-1}$)	58 (8)	9.31 $\pm$ 14.94 (4)	0	60
PO ₄ ³⁻ (mg L ⁻¹)	5627 (274)	0.0061 $\pm$ 0.0201 (0.0032)	0	0.91
pH	4381 (256)	7.2 $\pm$ 0.6 (7.2)	4.8	10.2
SO ₄ ²⁻ (mg L ⁻¹)	5627 (274)	1.01 $\pm$ 2.5 (0.22)	0	44.2
SpC ($\mu\text{S cm}^{-1}$)	4586 (267)	50.13 $\pm$ 42.11 (39)	0.91	461
T (°C)	3604 (260)	9.5 $\pm$ 5.14 (9)	0	32.1
Turbidity (NTU)	476 (78)	2.9 $\pm$ 10.7 (0.55)	0	170

Standard water quality parameters assess the ordinary conditions of water, and do not directly address toxicity associated with contamination. Nevertheless, temperature, pH, and dissolved oxygen are factors that may impact species survival either directly, or by creating conditions in which other factors may impact survival or reproduction. As conditions change, the distribution of populations may change, usually driven by shifting survival and reproductive advantages among competitive species. High nutrient levels, low, or changes in nutrient amounts can also affect population distributions. Nutrients such as phosphorous and nitrogen compounds may be exogenous or endogenous in origin. There are concerns that atmospheric deposition of nutrients derived from the agriculture industry may be impacting SEKI. Pesticides used in agriculture are capable of being carried long distances from the point of use, and may be impacting sensitive species even at concentrations below the chronic exposure limits established by the US Environmental Protection Agency (US EPA) (USEPA 1980c, b, a). Industrial sources of toxic metals may also be carried long distances and be deposited in the National Parks (Schuster et al. 2002, Dastoor and Larocque 2004, Streets et al. 2005, Vicars and Sickman 2011). Metal toxicity can be dependent on water hardness (USEPA 2009b). Some nutrients potentially affect pH, which in turn can affect the toxicity of ammonium, and aluminum, for example (USEPA 1988, 2009a).

Standard water parameters

Acid Neutralizing Capacity (ANC)

Alkalinity as carbonate and bicarbonate in lakes within areas lacking soil comes from weathered rock (Meixner et al. 2004a). Oxidized combustion products of sulfur and nitrogen produce acids that can potentially affect surface water chemistry (Bytnerowicz et al. 2002), for example, reducing ANC. Sulfate as sulfuric acid is a major constituent of acid rain, mainly occurring in the eastern United States downwind of coal-fired power plants. Sulfur scrubbing has reduced the production of SO_2 which later oxidizes to sulfuric acid in the presence of water. Nitric acid is another potential constituent of acid rain derived from fuel combustion at high temperature and pressure in which N_2 and O_2 recombine to produce NO_x , the sum of NO and NO_2 (USEPA 2008). Like sulfur dioxide conversion to sulfuric acid, NO_2 is converted to nitric acid by oxidation in the presence of water (Enhalt 1981). Technological improvements have reduced the amount of NO_x produced by internal combustion engines; however, in newer automobiles more nitrogen oxides are converted to ammonium (Fenn et al. 2010).

Atmospheric carbon dioxide dissolves in water and forms carbonic acid. Unbuffered water naturally has a pH of about 5.5 due to equilibrium with atmospheric carbon dioxide. Episodic acidification of high-elevation Sierra Nevada lakes due to nitric and sulfuric acid deposition has been investigated, and none was observed (Leydecker et al. 1999, Meixner et al. 2004a). The concern is these acids can reduce the pH of poorly buffered water below 5. The minimum pH in most SEKI lakes is approximately 5.5 (Bradford et al. 1994), except where natural geochemistry lowers the pH in a few small lakes (Figure 2) located near Mt. Pinchot in Kings National Park (Bradford et al. 1998). Long term trends seem to indicate stable pH in SEKI lakes (Whiting et al. 1989). The main source of ANC is the dissolution of weakly basic rocks (e.g. carbonates). Other processes can also contribute to alkalinity such photosynthesis (Schindler 1981) and production of certain nitrogen species (Portielje and Lijklema 1995).

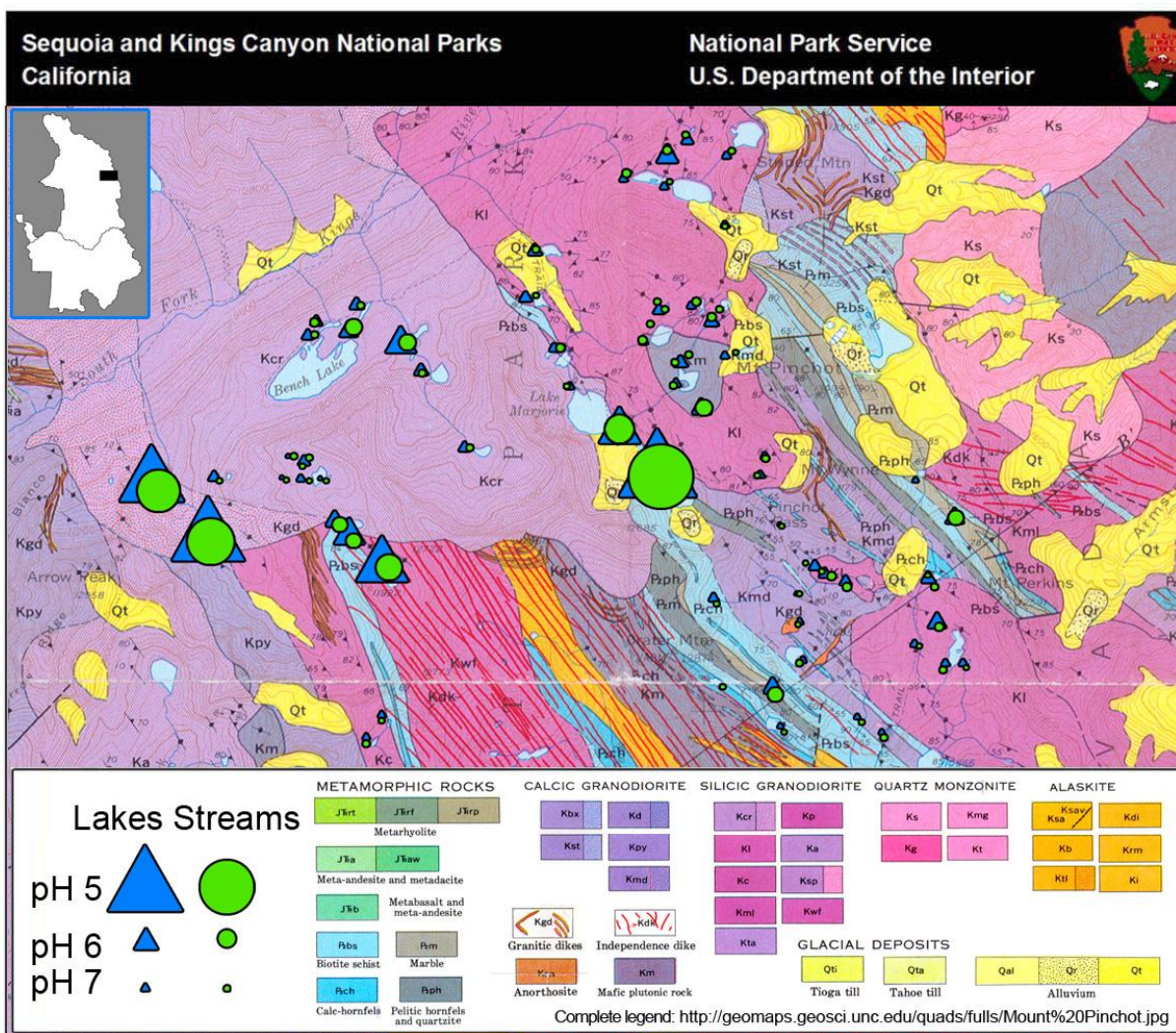


Figure 2. Mean pH of lakes and streams in Mt. Pinchot region of Kings National Park. The geologic map is the Mt. Pinchot quad available from the University of North Carolina (Caudill et al.).

Nitrogen fixation converts diatomic nitrogen dissolved in the water to ammonium. Reduction of nitrogen can lead to an increase in alkalinity. However, only certain organisms are capable of nitrogen fixation. These species may not be present in higher elevation lakes, streams, and soils, if soil is indeed present. The expected ratio of carbon, nitrogen and phosphorus is 106:16:1 (G. E. Likens et al. 1981), based on the composition of marine plankton. Both carbon and nitrogen potentially are captured from the atmosphere. In many cases, phosphorus may be the limiting nutrient.

Mean values of ANC and SO_4^{2-} concentrations in the SIEN database are shown in Figures 3 and 4. ANC and SO_4^{2-} appear to vary in opposite directions with elevation. Sulfate does not contribute to ANC, but may impact alkalinity as sulfuric acid derived from sulfides in rock, or

atmospheric deposition. The decreasing concentration of SO_4^{2-} with decreasing elevation might suggest that SO_4^{2-} is adsorbed as it flows downstream. However, it is more likely that the reduction in SO_4^{2-} concentration is a dilution effect downstream with SO_4^{2-} originating at higher elevation. Higher levels of sulfate are deposited at lower elevation in SEKI (Bytnerowicz et al. 2002). Williams, et al., note that soils are better able to take up sulfate in contrast with bare rock (Williams et al. 2001). Under anoxic conditions, bacteria can reduce SO_4^{2-} to H_2S ; however, this process has not been observed to significantly reduce the concentration of sulfate (Schindler 1981). Water originating at lower elevation tends to have lower sulfate concentration than water originating at higher elevation.

The Rocky Mountain

Condition Assessment (RMCA) found ANC at much higher levels in ROMO lakes than were found in SEKI. Mean ANC in ROMO lakes was $87.3 \mu\text{eq L}^{-1}$. Many of the SEKI lake catchments are bare rock with minimal soil in contrast to ROMO with forests reflecting different elevations, lodgepole, aspens, and alpine tundra with vegetation growing in various soils to high elevation. The mean pH of ROMO alpine lakes was 6.7, ranging between 5.7 and 8.3. The ROMO mean pH for lakes is approximately 0.5 pH units higher than the mean pH of 6.2 in SEKI lakes (Table 1).

High-elevation lakes contain little alkalinity (Melack et al. 1985, Whiting et al. 1989, Bradford et al. 1994). Melack, et al., found that 70% of the high elevation lakes studied had alkalinities below $90 \mu\text{eq L}^{-1}$ (Melack et al. 1985). Furthermore, water chemistry was strongly dependent on

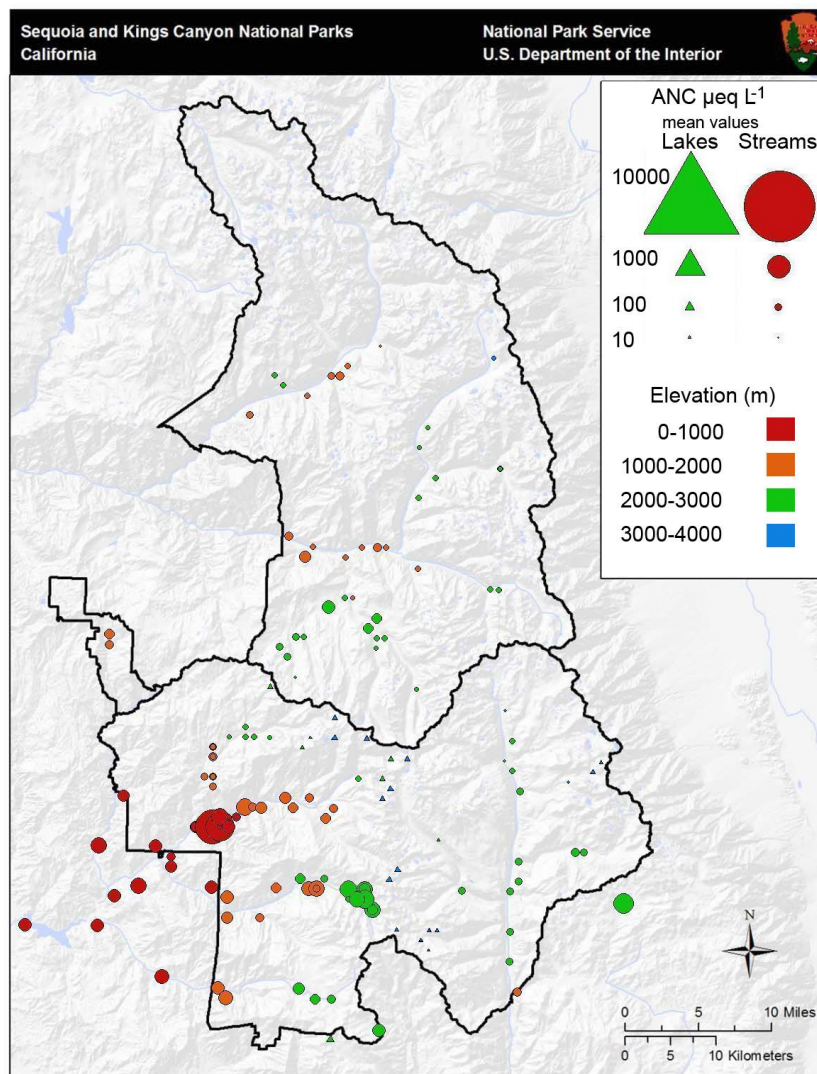


Figure 3. Mean Acid Neutralizing Capacity. Lakes are triangles, streams are circles, values are proportional to area. Elevation bands (1000 m) are represented by different colors.

the bedrock through which waters pass that feed high elevation lakes. The pH of these lakes can drop significantly with the addition of acids. Atmospheric dry and wet acid deposition has been a historic concern, with significant impact in eastern states. Lakes with higher alkalinity can neutralize more acid, and these are typically located below 3000 m elevation or in basins containing roof pendants or calcite inclusions in granitic rocks (Meixner et al. 2004b). A long-term study of Emerald lake coupled with a hydrologic model of the basin indicates acid deposition is not as important in affecting ANC as rock weathering rates, which depend more on the amount of precipitation (Meixner et al. 2004a).

High-elevation waters originate from rain and snow falling on bare rock. Stoddard found the seasonal variation of alkalinity depended on the weathering of granodiorite around Gem Lake (Stoddard 1987). The Sierra Nevada formed from uplifted marine sediments with granitic intrusions (plutons) in a process that started over 200 million years ago (Saleeby 1979, Notholt 1980, Filippelli and Delaney 1996, Holloway et

al. 1998, Stevens and Greene 1999, Hopson and Pessagno 2005, Snow and Scherer 2006). These marine layers were transformed to metamorphic rock approximately 100 million years ago, and remnants remain above the igneous granite and diorite in SEKI. These formations, typically found on ridge tops, are called 'roof pendants'. Water from melting snow and rain flows through fissures in rocks such as marble, shale, schist, and dissolves minerals from them. Depending on local lithology and hydrology, the mineral content of alpine lakes can vary considerably, even within a small geographic area, e.g. two pairs of lakes with very different properties separated by 25 and 100 m (Bradford et al. 1998).

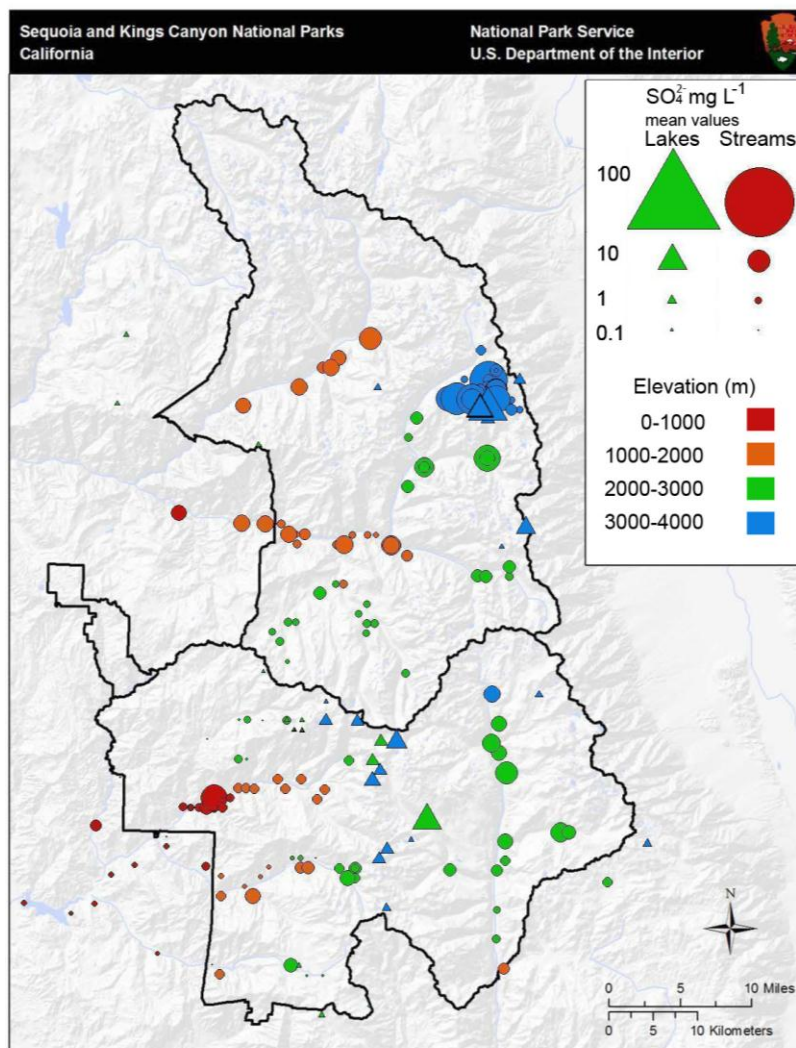


Figure 4. Mean sulfate concentration. Lakes are triangles, streams are circles, values proportional to area. Elevation bands (1000 m) are represented by different colors.

A clear example of a high-elevation geochemical source of sulfate is the high-elevation lake region on the east side of Kings Canyon National Park, the cluster of larger blue circles and triangles in Figure 4. These are naturally acidic lakes (Bradford et al. 1994, Bradford et al. 1998, Leydecker et al. 1999). The source of sulfuric acid is the oxidation of naturally occurring sulfides (Whiting et al. 1989, Bradford et al. 1998), likely pyrite in granitic rocks and metamorphic terranes, consistent with the elevated local concentration of aluminum (see *Aluminum* in Toxic Metals). Bytnerowicz, et al., contrast the low levels of sulfur deposition in the Sierra Nevada including SEKI, with high concentrations occurring in eastern states (Bytnerowicz et al. 2002). Sulfate concentrations can reach 20 to 30 mg L⁻¹. Interspersed are other lakes and streams with far lower SO₄²⁻ concentrations, comparable to most other high elevation lakes and streams. This observation is consistent with Bradford, et al., analysis that atmospheric deposition is not the source acidity these lakes (Bradford et al. 1994). Whiting, et al., note the presence of metamorphic rock in this region (Figure 2), and believe the high concentration of sulfate to originate from these geological sources, since the amount of atmospheric deposition observed in this basin cannot account for the observed concentration of sulfate (Whiting et al. 1989).

The mean sulfate concentration in ROMO lakes is 2.7 mg L⁻¹, approximately ten times that in SEKI lakes, which had a mean sulfate level of 0.29 mg L⁻¹. However, the mean pH in ROMO lakes was higher than SEKI lakes. If atmospheric deposition is the source of sulfate in ROMO, as sulfuric acid, then the higher ANC in ROMO lakes must be neutralizing the acid. SEKI lakes have much less ANC. In contrast, sulfuric acid produced from local rocks is not effectively neutralized in the SEKI lakes discussed above.

The reference lakes and streams for our analysis were selected for the most records available in the SIEN database for a majority of water parameters (see Reference conditions). Not all parameters were measured at each reference site. Many of our selected reference sites had no ANC records. Nevertheless, a long-term set of ANC measurements in one reference stream seems to indicate a relatively constant amount of alkalinity in the Middle Fork of the Kaweah from 1953 to 1988. The slight decrease in ANC from the 1950s through the 1970s was not confirmed by later measurements. There is greater uncertainty due to low numbers of samples collected in later years. There were no more than 2 samples taken per year from 1979 to 1988, compared to 11 to 14 samples per year collected from 1952 to 1969.

There is an apparent peak in acidity in higher elevation reference lakes and streams in the late 1980s that subsequently fell to levels below those preceding the peak (Figure 5). We found no significant long term trends of altered pH of reference lakes and streams. ANC increases over 30-fold flowing from high to low elevation. Although altered pH is not evident from the existing data, there is a lack of frequent ANC measurements over a long period of time in multiple reference locations.

Relatively low concentrations of sulfate were measured in the high elevation reference lakes and streams (Figure 5D and E), however the sulfate concentrations were higher at lower elevation in the Log Creek and East Fork sites. As shown in Figure 4, higher sulfate concentrations were measured at sites along the Middle Fork and East Fork of the Kaweah at some locations. Most of the East Fork has low sulfate concentrations, as does the Kaweah exiting the Park. These observations are consistent with SO₄²⁻ originating from multiple sources at higher elevation

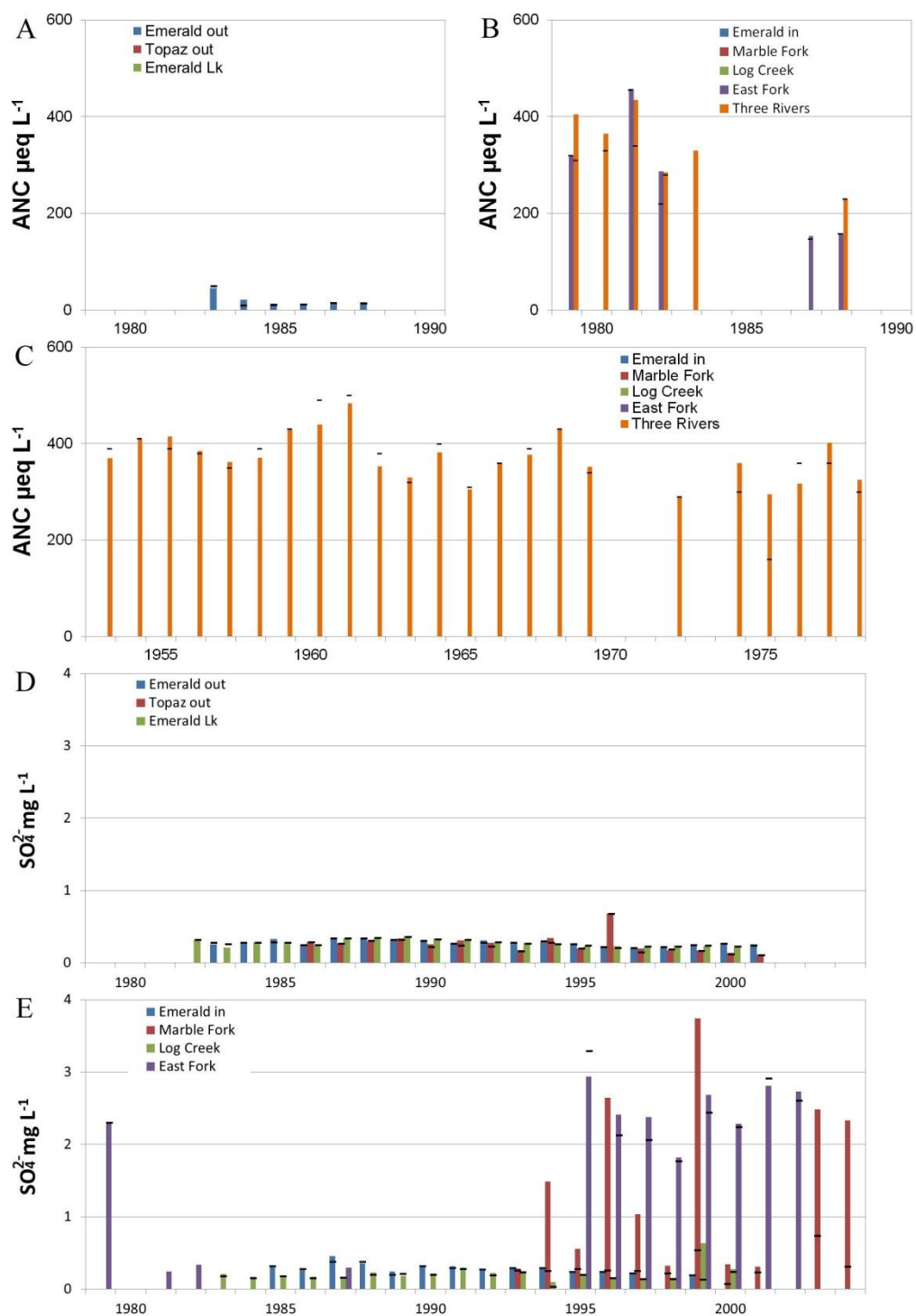


Figure 5. Comparison of ANC and SO_4^{2-} mean values in reference lakes and streams. Only one lake of three reference sites had ANC records (A). Stream ANC is shown for the same period (B). Stream ANC records were available in one stream several decades earlier (C).

subsequently diluted at lower elevation. High elevation lakes having low ANC would be the most sensitive to sulfuric acid deposition. Measurements of pH in reference lakes and streams (Figure 6) and elsewhere in SEKI (Figure 7) are more consistent with alkalinity levels, and very localized areas of pH lower than expected in unbuffered water. Sulfate in reference lakes was low (Figure 5D). Reference streams included Log Creek and the East Fork with significantly higher sulfate concentrations than the higher elevation lakes in this case (Figure 5E). For these reference sites, the observed sulfate concentration remained approximately constant from 1982 through 2002.

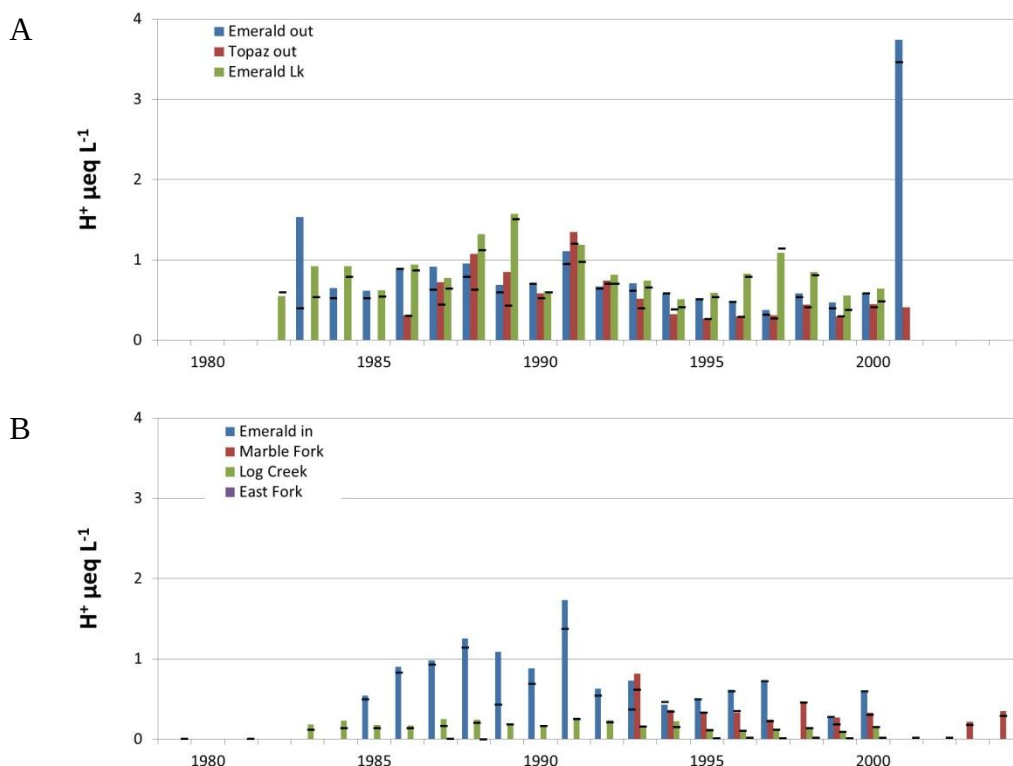


Figure 6. Mean hydrogen ion concentrations in reference lakes and streams. Median values are shown as dark horizontal bars. Note Emerald out in 2001: N2001=8, average N=62 for all years.

Acidification facilitates biological extraction of minerals (Landeweert et al. 2001). Reduced pH can increase the solubility of aluminum which is known to be toxic to some embryos and larva. Although acidification is considered a threat to amphibians, a study of three species did not find any correlation of water pH with numbers of amphibians present at sites with very different conditions. Higher aluminum concentrations were observed in the acidic lakes of eastern KNP (v.i. *Aluminum* in Toxic Metals).

Dissolved oxygen

Mixing and re-aeration are important for distributing oxygen through water. Oxygen is also produced through photosynthesis during daylight hours, and consumed through respiration at night. In some lakes, photosynthesis may be more prevalent in a layer well below the surface (Sadro et al. 2011a). These conditions are marked by an increase in dissolved oxygen in a depth

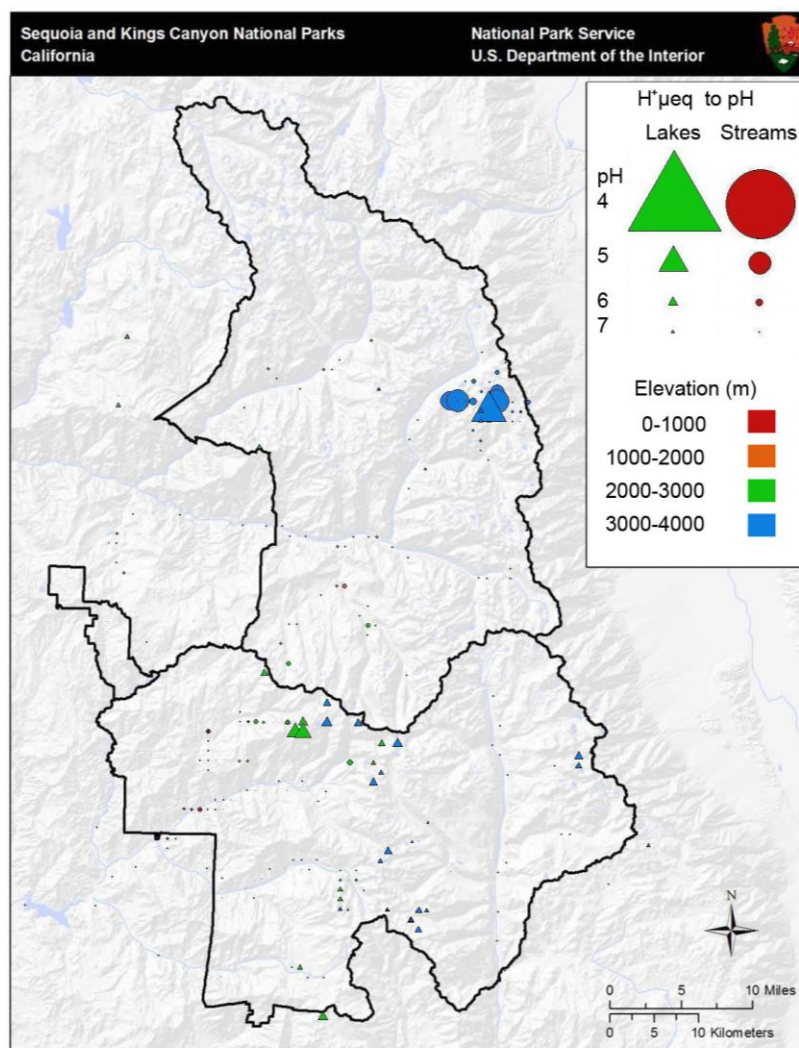


Figure 7. Mean pH measured in SEKI. Lakes are triangles, streams are circles, values proportional to area. Elevation bands (1000 m) are represented by different colors. Symbol size is proportional to μeq of H^+ . See also Figure 2.

al. 2011a, Sadro et al. 2011b). During the period of lake stratification, the epilimnion did not deviate much from 100% saturation. The metalimnion often had the highest DO concentrations throughout the water column, corresponding to sub-surface chlorophyll-a maximum. And although the benthos was consistently heterotrophic, DO within the hypolimnion remained near saturation in the 10-m deep lake.

Mixing as a source of oxygen is consistent with the observation of minimum DO lower in lakes compared with streams. However, additional monitoring is needed to determine whether nutrient enrichment is occurring. Collection of nutrient data could identify where action may be taken in response to unfavorable trends before adverse conditions develop. Lakes in SEKI are most at risk of low DO, especially during winter months where stream flows are near minim, ice-cover

band below the surface. Dissolved oxygen can be depleted by eutrophication, leading to an overgrowth of algae.

Dissolved oxygen (DO) was measured in SEKI mostly at sites on the Kaweah Middle and East Forks. The minimum DO was measured in summer to fall during low flow months. In SEKI, the DO did not fall below the minimum standard 5 mg L^{-1} , except for one datum slightly below the limit. Figure 8 shows the minimum DO occurs in streams from August through October. DO data for SEKI lakes are sparse; however, an apparent minimum occurs about the same time. The minimum DO appears to be significantly lower for lakes than for streams. Studies investigating the ecosystem metabolism of Emerald Lake measured DO at diel time scales over the ice free seasons of 2007 – 2009 (Sadro et

prevents photosynthesis, and respiration is the dominant metabolic pathway. There is very little data on DO in lakes, especially during winter months when under-ice minima are most likely to occur. Monitoring DO in lakes is important to properly assess their condition and identify potential risks currently existing or that may develop in the future.

Temperature

The seasonal temperature peaks for streams in July and in August for lakes (Figure 9). The maximum temperature for streams is 15 °C and 16 °C for lakes. The minimum temperature for streams is 4 °C occurring in December, and less than 1 °C in lakes occurring in January. Because of the lack of long term data sets and profiles for the lakes, no significant trends could be identified. Lake stratification can occur in winter because fresh water has a maximum density at about 4 °C.

Temperature changes are greatest at higher elevations where ice forms over lakes in winter, rocks absorb sunlight and raise the

temperature of shallow lake waters. These conditions provide a wide range of environments that can support a variety of organisms that may be adapted to local conditions. Some of these

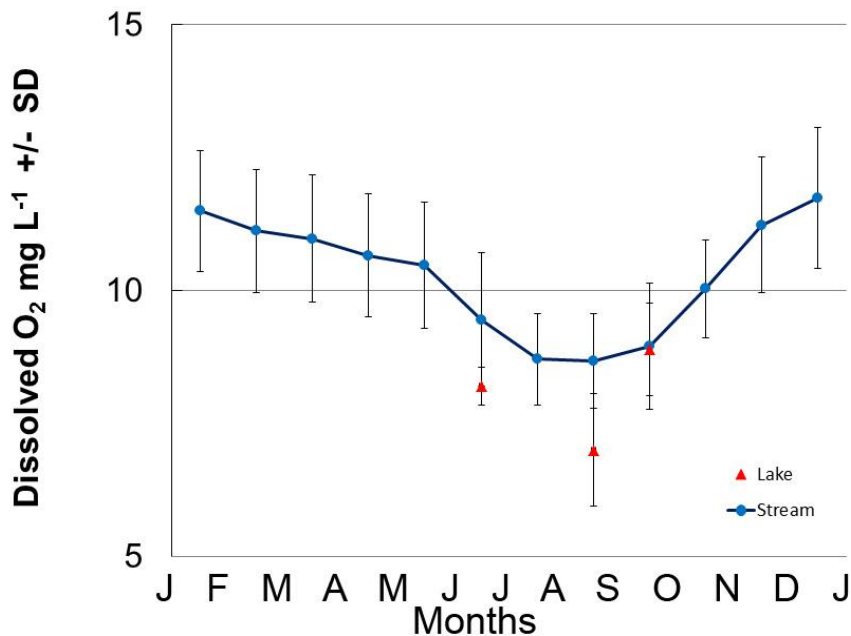


Figure 8. Seasonal mean dissolved oxygen concentration. Lakes are red triangles, streams are blue circles.

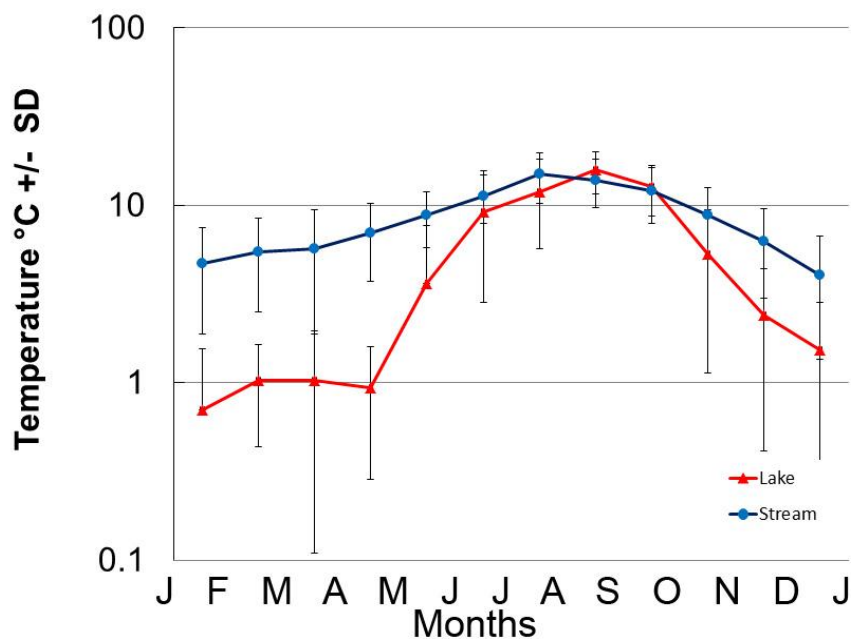


Figure 9. Seasonal mean water temperature with standard deviation. Lakes are red triangles. Streams are blue circles.

organisms may be more sensitive than others to temperature changes, and may not have sufficient mobility to seek alternative locations that are more suitable. Different species are adapted for survival within a range of environmental conditions.

The mean temperature of ROMO lakes at an average elevation of 3260 m was 9.5 °C, ranging from 1.7 to 19 °C from mid-July to late October. Figure 9 shows SEKI lakes have approximately the same mean temperature as ROMO lakes during the same period of time.

Specific conductance

Specific conductance is a measure of ionic strength in water and inversely as an indicator of dilution. Ion content varies seasonally, in general terms, ionic content is more dilute in spring during snow melt, and more concentrated in early fall as water flow is minimized. When runoff derived from melting snow is minimal, water properties are more strongly influenced by groundwater contributions and biological contributions stimulated by higher temperatures and more sunlight. Ions mainly originate from weathering of rock (Stoddard 1987) and contact with soil (Meixner et al. 2004b). Some are deposited through atmospheric transport and fall as dust, in rain or snow, or otherwise adhere to surfaces (Fenn et al. 2010).

Figure 10 shows specific conductance (SpCond) with features similar to ANC. This observation is not surprising since the highest concentration anions contributing to specific conductance are bicarbonate, carbonate, and sulfate. High elevation sites generally have low SpCond. SpCond increases as water flows downstream to lower elevations. Certain locations have higher SpCond that subsequently

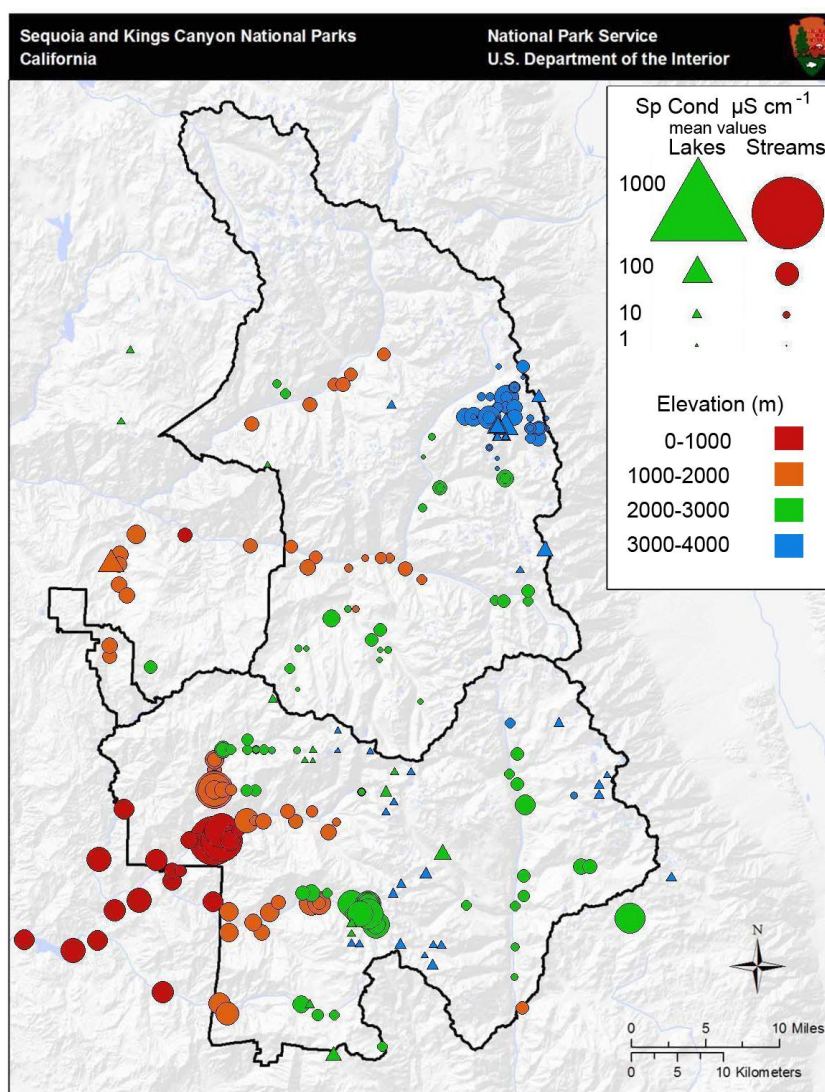


Figure 10. Mean specific conductance. Lakes are triangles, streams are circles, values proportional to area. Elevation bands (1000 m) are represented by different colors.

appears to be later diluted by other water joining the stream. Such areas are near Mineral King, the SNP Headquarters, the acidic lakes region of KNP, and the upper Kern. The higher SpCond observed in more remote locations may be due to mineral leaching from metamorphic rock. The lower elevation locations may have higher SpCond either due to anthropogenic causes or a large influx of groundwater which is especially likely given the impermeable granitic plutons underlying SEKI and the significant elevation change over a short distance in the location.

The mean SpCond in ROMO lakes is $21.0 \mu\text{S cm}^{-1}$, approximately 4 times the mean SpCond of SEKI lakes. In both ROMO and SEKI, the SpCond is mainly due to ANC bicarbonate, carbonate, and cations. In other words, low SpCond corresponds to low ANC, and low hardness as well, or the combined concentration of Mg^{2+} and Ca^{2+} (see below).

Turbidity

Increased turbidity can be due to higher amounts of suspended sediments, dissolved colored humic substances, or algae. The presence of algae can be measured by quantifying chlorophyll in the water sample. Unfortunately, there are no records containing chlorophyll concentration data for SEKI in the SIEN database.

Turbidity records in the SIEN database indicate that high-elevation lakes have turbidity higher than the surrounding streams (Figure 11). It is important to resolve these different contributions to turbidity in order to determine whether turbidity is due to algal growth or fine suspended particulates.

Nutrients

Nitrate, ammonium, and phosphorus are transported as particulates

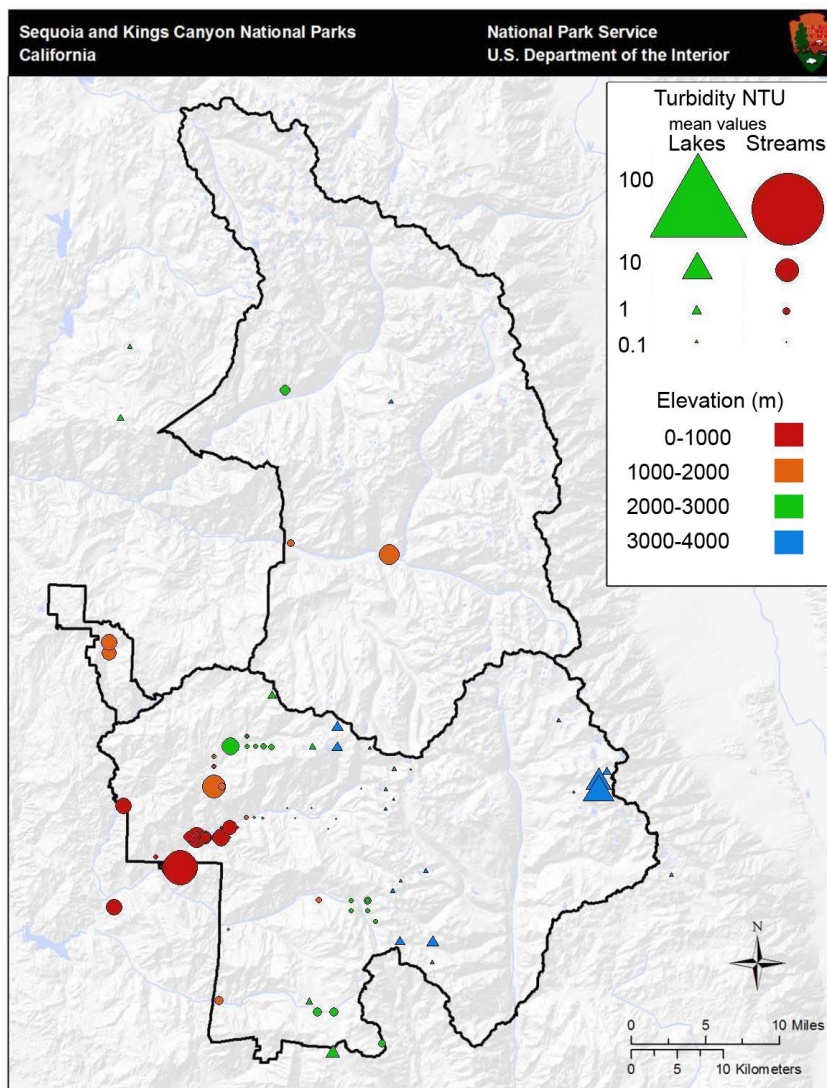


Figure 11. Mean turbidity. Lakes are triangles, streams are circles, values proportional to area. Elevation bands (1000 m) are represented by different colors.

or dissolved in water droplets (clouds) through the atmosphere and deposited dry or in precipitation (King Jr. et al. 1998). HNO_3 , HNO_2 and ammonia may be transported in a vapor phase at higher concentrations than particulates (Bytnerowicz et al. 2002). These nutrients are used for crop production in the San Joaquin valley can potentially support abnormal growth of algae and bacteria that can threaten other aquatic life in high elevation lakes and streams (Vicars and Sickman 2011), and reduce biodiversity (Das et al. 2008). Some species of cyanobacteria produce toxins that can impact not only the aquatic species in the lake, but also the non-aquatic species feeding around the lake margins (Mez et al. 1998, Graham et al. 2008). Anaerobes convert nitrate to ammonium, reduce metals, produce methane (Bodelier and Laanbroek 2004) and hydrogen sulfide (Jorgensen and Postgate 1982).

Nitrogen and phosphorus are typically of limited availability in granitic rocks. Weathered granites contain higher levels of nitrogen (Stevenson 1962). Extrusive igneous rocks may contain reduced nitrogen. Carbonate rocks (e.g. limestone or karst), may contain phosphates, and apatite inclusions are possible in igneous rock. Metamorphic rocks derived from marine sediment are found in the Sierra Nevada (Stevens and Greene 1999). Sierra Nevada bedrock has been investigated as the source of nitrate (Holloway et al. 1998). Nitrogen was found in phyllite, slate, biotite schist, metavolcanic breccia, and greenstone at 250 to 1000 mg N kg⁻¹. Moreover, nitrate concentrations measured in water samples correlated with bedrock lithology where the samples were collected. Several of these rock types are known to be present in roof pendants within SEKI.

Nitrogen- and phosphorus-containing fertilizers are applied to crops in the San Joaquin valley. Kratzer and Shelton conducted a water quality study of the San Joaquin valley from 1965 through 1985 (Kratzer and Shelton 1998). During this period, approximately 180,000 tons of nitrogen were used annually in Fresno, Tulare, Kings, and Kern counties. At the same time, approximately 27,000 tons of phosphorus were applied annually. Tens of thousands of tons of manure containing nitrogen and phosphorus are also produced in two of these counties and a few others farther north. Nitrogen contamination from manure usually affects groundwater and downstream surface water. Krauter, et al., note that half of the ammonia releases in California come from fertilizer applied in the four counties listed above (Krauter et al. 2002). They estimate 2.4% of fertilizer tonnage is released as ammonia into the air. The fraction of urea and organic nitrogen in manure converted to ammonia depends on decomposition conditions. Kirchmann, and Witter, found that less than one percent of nitrogen was volatilized as ammonia during acidic anaerobic decomposition of agricultural waste, in contrast with 9 to 44% of nitrogen under alkaline aerobic conditions (Kirchmann and Witter 1989). Bytnerowicz, et al., found ammonia and nitric acid are deposited in SEKI at levels that decrease significantly with elevation (Bytnerowicz et al. 2002). The authors concluded that atmospheric deposition of these nutrients could significantly impact forests and meadows; however, these nutrients could not be detected in stream outflows. Nutrients associated with particulates peaked just below 2000 m, in amounts less than the gaseous nutrient peak levels at 500 m.

Nitrogen

Atmospheric deposition of nitrate, ammonia, and ammonium (in particulate matter) has been measured in SEKI after transport great distances from their sources (Bytnerowicz et al. 2002, Fenn et al. 2010, Saros et al. 2011). The majority of this material is deposited at lower elevation in forests and meadows. Isotopic studies indicate the majority of nitrate is acquired through

biological activity in soils (Sickman et al. 2001, Ohte et al. 2004). Stoddard found the seasonal variation of alkalinity depended on the weathering of granodiorite around Gem Lake (Stoddard 1987). Calculations based on ionic proportions expected from bedrock were most consistent with observations. Nitrate ions were not included because nitrate was not expected from the bedrock around Gem Lake.

Metamorphic rocks, derived from marine sediments, are found in SEKI (Saleeby 1979), and elsewhere in California (Stevenson 1962, Dahlgren 1994, Holloway et al. 1998, Stevens and Greene 1999, Holloway and Dahlgren 2002, Holloway and Smith 2005). These rock types are known to contain inorganic nitrogen that can leach into surface water. In some locations, nitrate derived from bedrock may account for 30 to 50% of total soil nitrate in a California oak woodland, and in the Mokelumne greater than 90% of nitrate flux originates from 10% of the basin with nitrogen-containing metamorphic rock (Holloway and Dahlgren 2002).

Mean levels of nitrate observed in SEKI surface waters are not explained solely by atmospheric deposition, since higher levels of nitrate are not consistently observed at lower elevation (Figure 12). Two sites of much higher nitrate concentration were found. These locations are associated with human and animal activity. In KNP, a historic unrestricted grazing area existed where the mean nitrate was over 9 mg L^{-1} . In SNP, the second site with mean nitrate at approximately 4 mg L^{-1} is located just inside the park boundary and associated with a parking lot and public toilets. Some of the highest levels

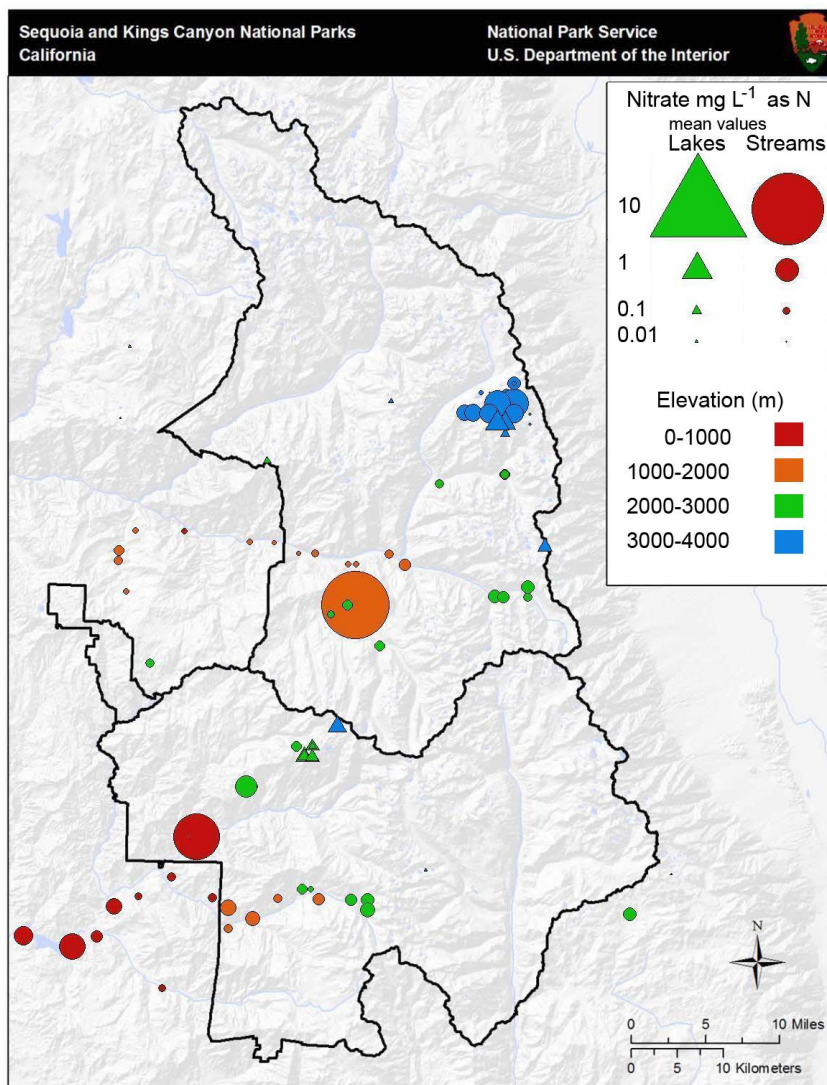


Figure 12. Mean nitrate concentration. Lakes are triangles, streams are circles, values proportional to area. Elevation bands (1000 m) are represented by different colors.

of nitrate observed were above 3000 m in KNP near Mt. Pinchot, in the same region where high sulfate and the lowest pH values were measured. As noted above, the presence of metamorphic rock can cause water parameters to diverge from those expected in basins composed of granitic rock. SIEN database records indicate nitrate concentrations vary by two orders of magnitude within a small geographic region with limited soil. Areas with high nitrate concentrations can be located near areas with low nitrate concentrations, and may have little soil. These observations are most consistent with rock as the source of inorganic nitrogen, rather than atmospheric deposition or nitrogen fixation.

In the Mt. Pinchot region of KNP where high nitrate concentrations were observed, ammonium levels are low (Figure 13). Nitrification of ammonium occurs in aerobic conditions, and denitrification occurs in anoxic conditions (Downes 1988, Dahlgren 1994). Depending on the

dissolved oxygen concentration, ammonium can be converted to N_2O , NO_2^- , and NO_3^- . The concentration of inorganic nitrogen compounds in water is of concern also due to their known toxicity to vertebrates and invertebrates (Camargo et al. 2005).

Ammonium concentrations peak in the spring and fall to a minimum at peak snow melt in lakes; however, streams maintain a relatively constant concentration during the year; the reverse trend from nitrate. Clow, et al., observed similar behavior in Loch Vale, Colorado (Clow and Sueker 2000). This phenomenon could be explained by nitrification versus denitrification depending on the concentration of dissolved oxygen. SIEN database records indicate the highest ammonium concentrations (0.1 mg

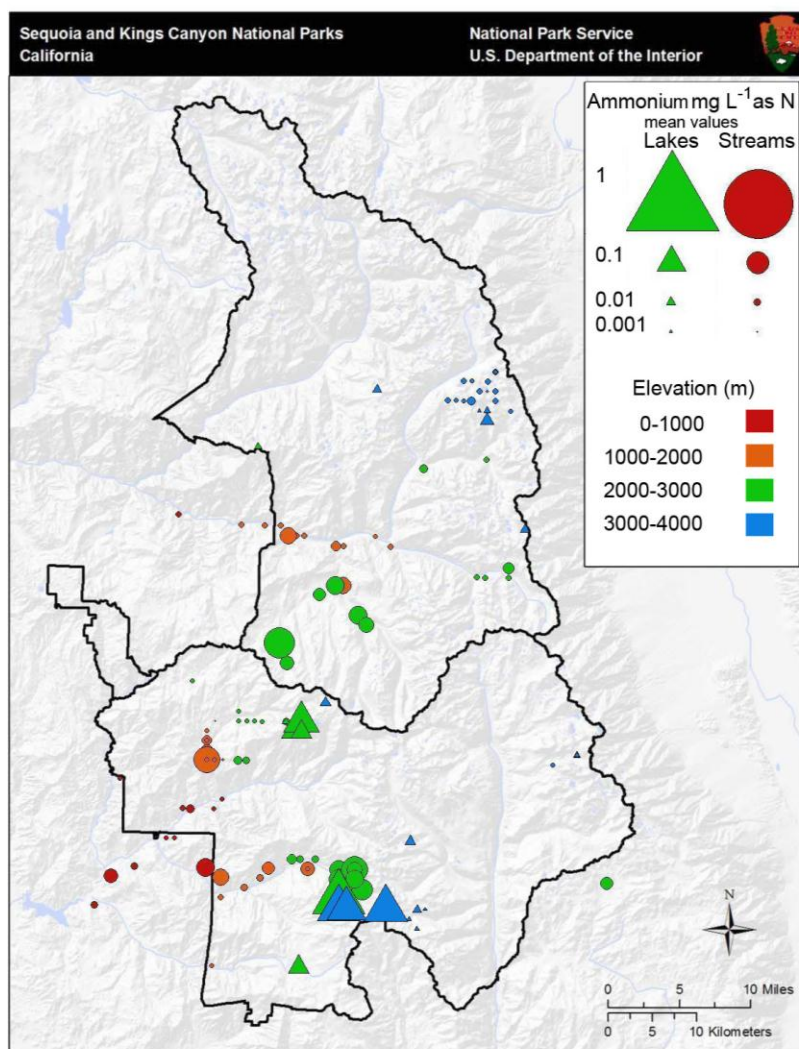


Figure 13. Mean ammonium concentration. Lakes are triangles, streams are circles, values proportional to area. Elevation bands (1000 m) are represented by different colors.

L⁻¹) occurred in lakes before snow melt (see Appendix). The pre-snowmelt ammonium peak suggests either there is a region of hypoxic conditions in lakes during winter, or microbial nitrification is slow due to low water temperature. The mean inorganic nitrogen concentration rises during September and October in both lakes and streams during peak temperature and minimum flow. Although snowpack ammonium concentrations can exceed nitrate, ammonium export downstream from snowpack was negligible (Sickman et al. 2003).

The highest ammonium concentrations observed in SEKI occurred in the Mineral King area in the southern border region of SNP (Figure 13). This area has metamorphic rock, however, it was also the center of mining activity and the area is still inhabited. Sites where water samples were collected are located at elevations above the inhabited areas. Ammonium concentrations downstream of the sample sites and inhabited areas are lower.

SIEN database records from reference lakes and streams indicate no significant trend of altered nitrate levels from 1983 to 2003 (Figure 14). Topaz Lake appears to have an episode of high nitrate; however, the median values are all comparable. The solitary high nitrate mean value for Marble Fork in 2001 is probably not representative since it was calculated from only two observations that year, far lower than any other year. Similarly, reference lakes and streams do not exhibit any trend for altered ammonium concentration over the same period (Figure 15).

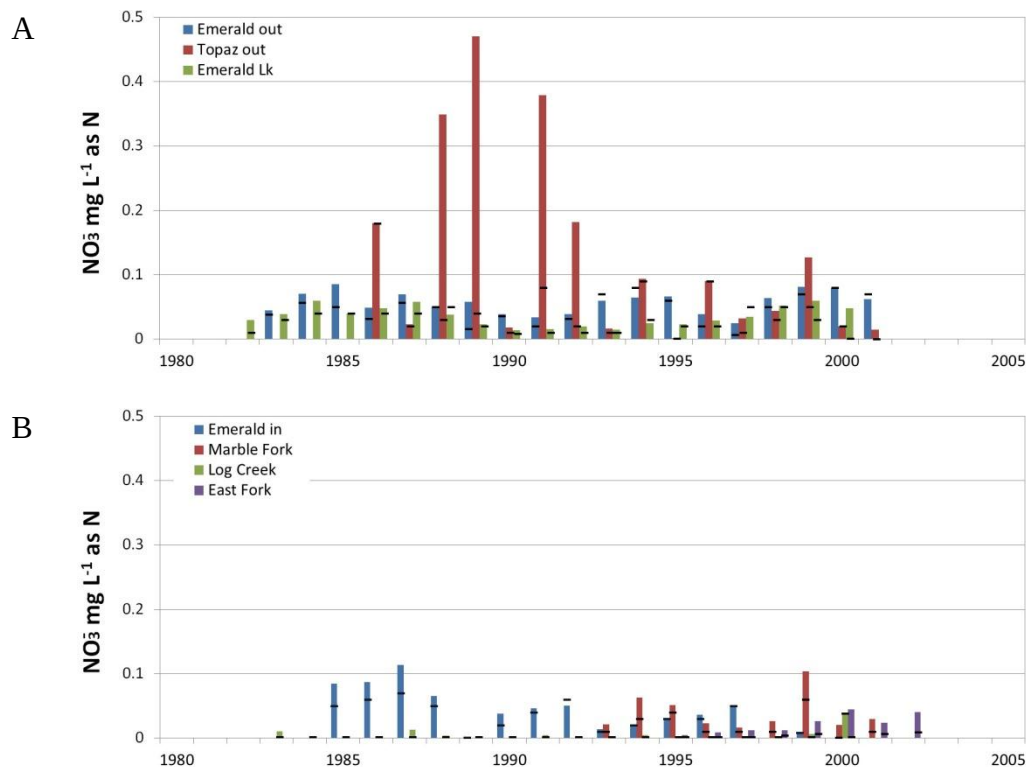


Figure 14. Mean nitrate concentrations in reference lakes and streams from 1982 to 2002. Median values are shown as dark horizontal bars. Note: Topaz out N₁₉₈₆=1, average N=13 for all years.

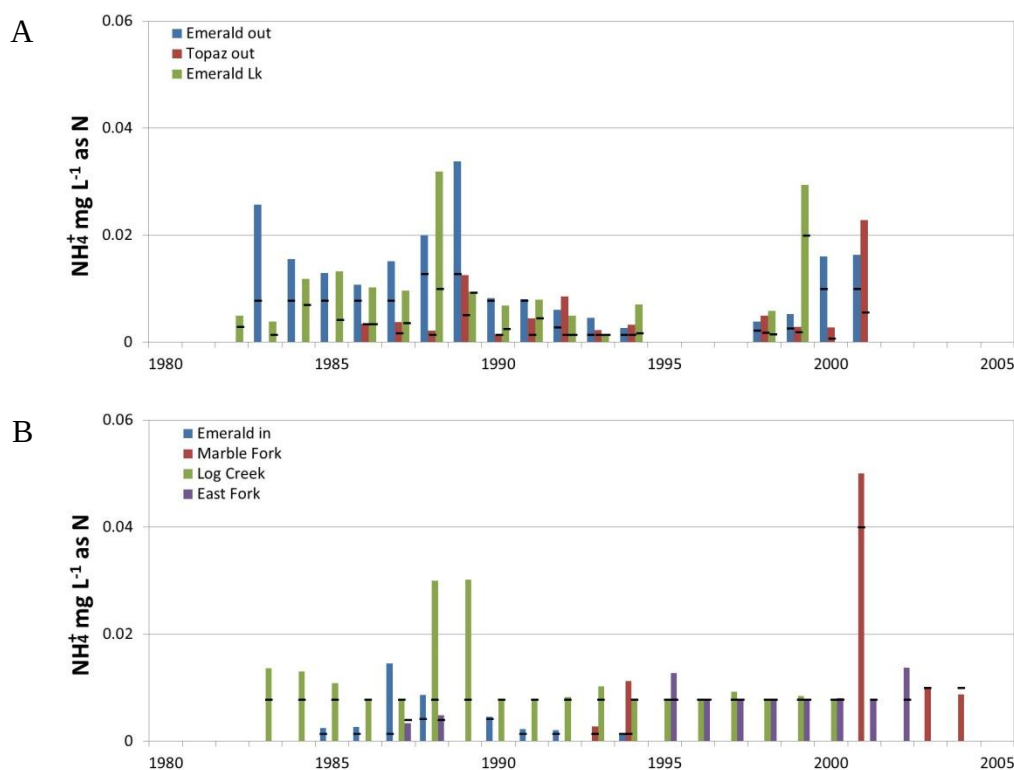


Figure 15. Mean ammonium concentrations in reference lakes and streams from 1982 to 2002. Median values are shown as dark horizontal bars. Note Marble Fork in 2001: $N_{2001}=2$, average $N=32$ for all years.

The presence of ammonium can interfere with the digestion and conversion of methane to CO_2 by methanotrophic bacteria (Bodelier and Laanbroek 2004). In an oligotrophic lake, additional nitrogen can stimulate methanotrophs; however, in eutrophic waters, dissolved oxygen can be depleted leading to reduction of methanotrophs and increased methane emission. The addition of phosphorus, when limiting, can stimulate methanotroph growth.

The mean concentrations of nitrate and ammonium in ROMO lakes were higher than SEKI. For nitrate, ROMO lakes had a mean nitrate concentration of 0.5 mg L^{-1} ranging between 0 and 7.4 . ROMO nitrate level in lakes was approximately an order of magnitude higher than SEKI lakes. ROMO lakes had a mean ammonium concentration of 0.03 mg L^{-1} ranging from 0 to 0.6 mg L^{-1} , about 3-fold higher than SEKI lakes.

Phosphorus

High levels of nitrate may not lead to algal or bacterial overgrowth of lakes if another nutrient, typically phosphorus, is limiting (Sickman et al. 2003). Phosphorus may leach from rock. Many karst formations around the world contain apatite, or karst phosphorite. Carbonate fluorapatite is the final stage in P capture in marine sediments (Filippelli and Delaney 1996). Apatite is also found in granitic rock (Gasquez et al. 2005).

The highest concentrations of phosphorus measured in SEKI water were located around Mineral King and the Kaweah Middle Fork basin lakes and the river itself (Figure 16). This higher

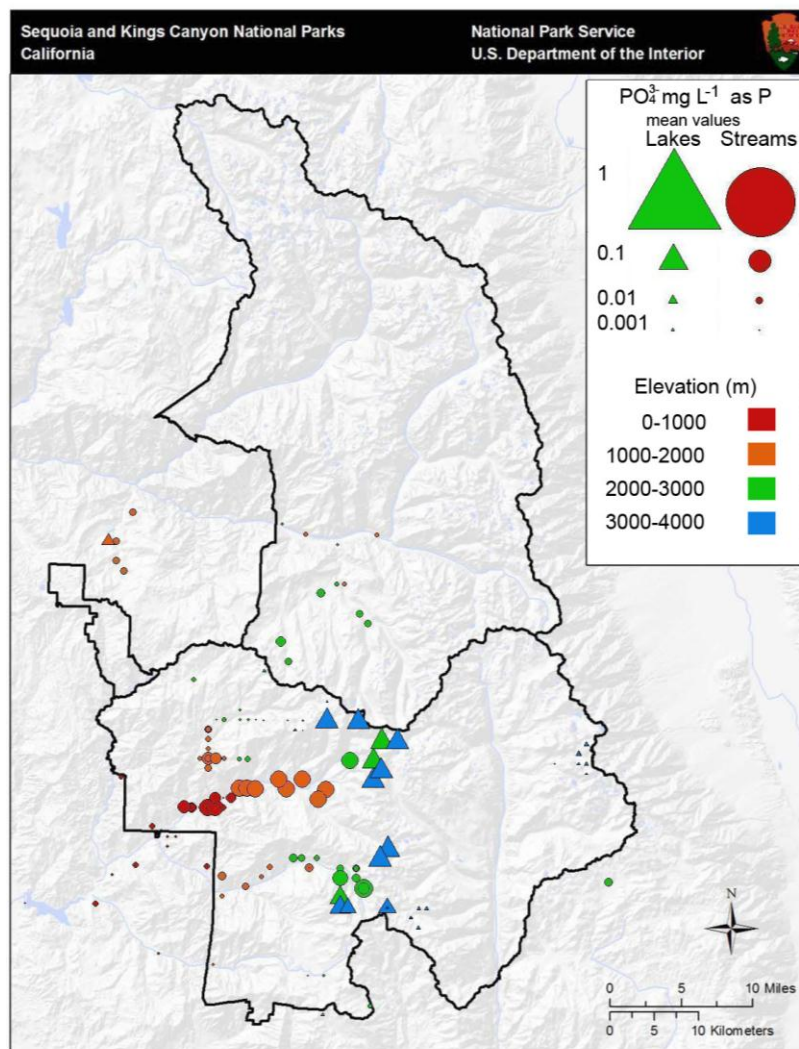


Figure 16. Mean phosphate concentration. Lakes are triangles, streams are circles, values proportional to area. Elevation bands (1000 m) are represented by different colors.

data indicate phosphorus levels have increased slightly (approx. 0.1 to 0.2% per year) over the preceding 150 years in Emerald Lake and in Pear Lake over the preceding 800 years.

Penn, et al., found phosphorus is seasonally mobile in sediments depending on factors including pH, dissolved oxygen, and the presence of Fe^{3+} or Ca^{2+} (Penn et al. 2000). In anoxic conditions and lower pH, phosphorus is most readily released from Onondaga Lake (NY) sediments, and very poorly released under oxic conditions.

Reference lakes and streams do not indicate any consistent trend for altered phosphorus concentration (Figure 17). Most mean values are comparable, and all median values are roughly the same. The Kaweah East Fork has higher P than other reference sites. The P concentration in the Kaweah Middle and South Forks seems to fall as elevation decreases.

phosphate concentration is consistent with the presence of roof pendant metamorphic rock in part of SNP. The concentrations of P are approximately 10-fold higher in the Kaweah Middle Fork than any other streams except for the Kaweah South Fork near Mineral King.

Phosphorus is limiting when the N is more than 15-20 times the concentration of P. Sickman, et al., found Emerald Lake was at times N-limited or P-limited from 1983 to 1999 depending on factors such as the amount of precipitation in a given year (Sickman et al. 2003). They determined the largest reservoir of P is lake sediments and soils around Emerald Lake. Atmospheric deposition and export are approximately balanced. WACAP sediment core

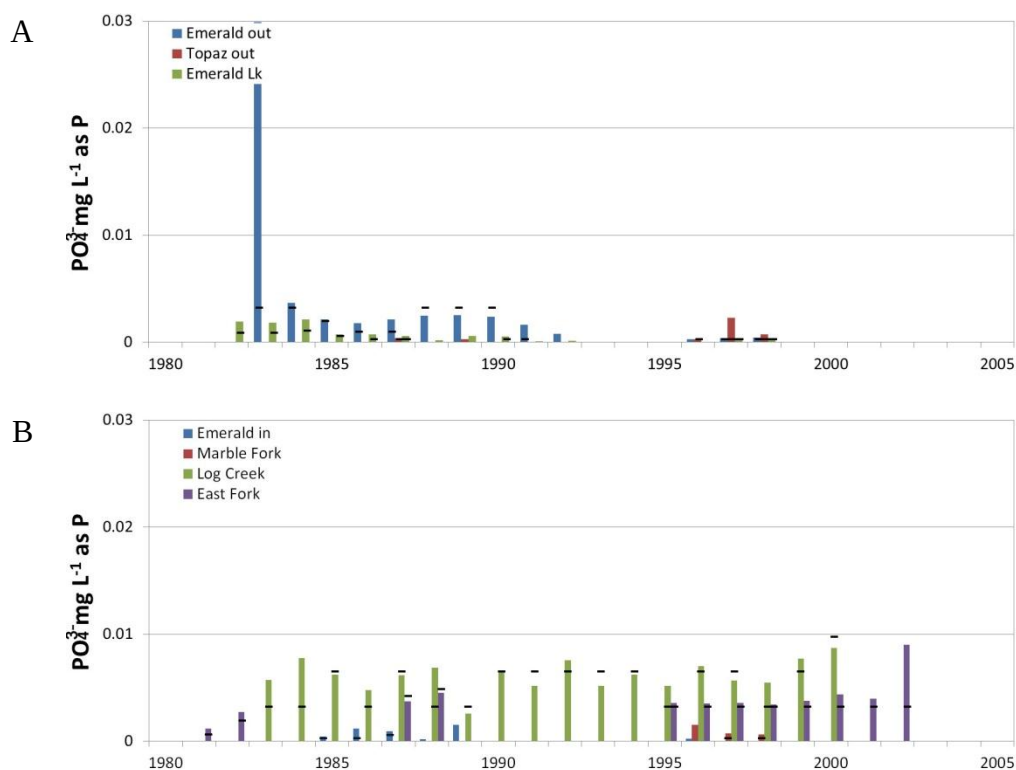


Figure 17. Mean phosphate concentrations in reference lakes and streams from 1982 to 2004. Median values are shown as dark horizontal bars. Note Emerald out in 1982: $N_{1982}=30$, average $N=65$ for all years.

The ratio of nitrogen to phosphorus in water determines whether nitrogen from the air is fixed by microbes (Vitousek et al. 2002). If nitrogen is limiting in water, certain species of cyanobacteria can outgrow other organisms and quickly raise the level of dissolved inorganic nitrogen. In studies of nutrient additions to Canadian lakes, Schindler found that a lake fertilized for 6 years with an N:P ratio of 14:1 by weight was dominated by a green alga and no nitrogen fixation was detected (Schindler 1981). However, when the ratio was changed to 5:1, a bluegreen alga never before seen in that lake appeared, and nitrogen fixation contributed 14% of the nitrogen in the lake. Anoxic conditions produced in lakes containing dense bluegreen algae resulted in the death of trout before they could be harvested. However, the addition of ammonium nitrate to phosphorus-rich lakes dominated by bluegreen algae allowed other species of aquatic plants to grow, and eliminated fish kills.

Pesticides

Pesticides are man-made toxins that are not naturally present in SEKI lakes and streams at any elevation. The concern is pesticides can be very slow to degrade and bioaccumulate. The US Environmental Protection Agency (US EPA) has designated a number of substances as priority pollutants, including pesticides. Studies of toxicity on vertebrates, invertebrates and plants have served as the basis for establishing limiting concentration allowable for acute and chronic exposure. In SEKI, some of these priority pollutants are exogenous man-made and deposited, others may be natural and leaching from local terrain.

The SIEN database contained records of pesticide measurements in five streams, however, only one of these sites reported pesticide residues above the detection limit. Bradford, et al. (Bradford et al. 2010), measured pesticide levels in 2003 over a period of five months in four lakes distributed around the border of KNP. None of the reported pesticides was applied in the mountains during 2003. Consequently, the only source of pesticides was airborne transport from application sites in the San Joaquin Valley. Pesticide levels in sample sites reflected application peaks with a lag of one to two weeks.

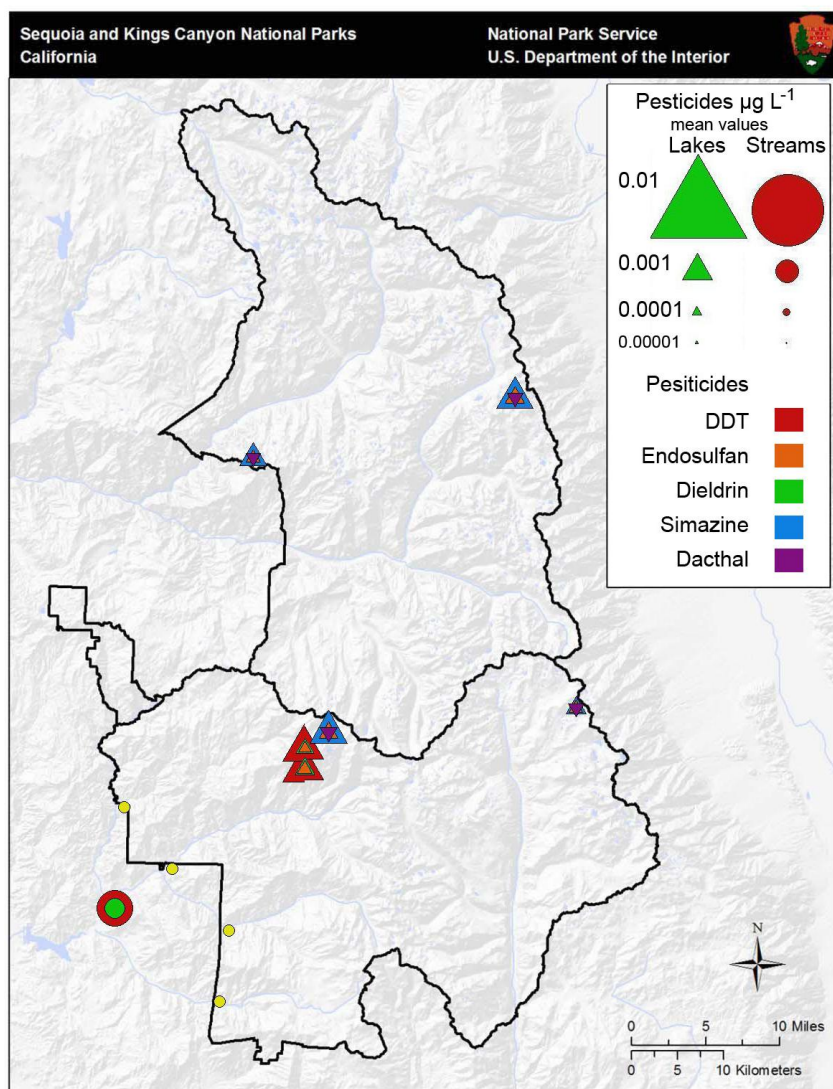


Figure 18. Mean concentration of several pesticides. Lakes are triangles, streams are circles, values proportional to area. Different pesticides are represented by different colors. DDT has two isomers, o,o'-DDT (left half) and o,p'-DDT (right half). The yellow circles are stream sites tested with no pesticides found above the detection limit.

The Western Airborne Contaminant Assessment Project (WACAP) attempted to provide a broad assessment of water quality and contaminant presence in 20 National Parks in 9 western states (Landers et al. 2003). Pesticide residues were measured in water, snow, lake sediments, vegetation, fish, and mammals. However, in SEKI, the water related samples consisted of sediment cores from two lake sites as shown in Figure 18, Emerald and Pear Lake. Core sections were dated by the decay of ^{210}Pb (Robbins and Edgington 1975, Appleby and Oldfield 1978). The WACAP studies attempted to detect numerous pesticides, however, only a few were found at levels above the detection limit. The pesticides found above detection limits in SEKI sites were DDT, endosulfan, Aldrin (or related Dieldrin), Simazine, and Dacthal. The apparent absence of other pesticides may be

due to less abundant use, or more rapid degradation.

Records in the WACAP database reported DDT levels in lakes distinguishing between o,p'-DDT and p,p'-DDT, however SIEN records did not. Similarly, endosulfan reported in WACAP was endosulfan I and endosulfan II, whereas the SIEN database reported endosulfan sulfate. Bradford, et al., reported the sum of endosulfan I and II. Consequently, we report endosulfan with no distinction between subtypes (Figure 18).

Pesticides detected in sediment cores of Emerald Lake and Pear Lake in SEKI were found layers dated prior to the first use of these pesticides. It appears pesticides must diffuse through sediments or be transported via biological activity or other means. These are high elevation lakes and can be subject to avalanches and rock falls, i.e. major mixing events. .

DDT

DDT is a chlorinated hydrocarbon insecticide. It was first synthesized in Germany in 1874. Beginning in the 1940s, it had widespread use over a span of 30 years. In the United States, DDT use peaked in the 1959, and was discontinued for use in agriculture in 1972. The two main degradation products are DDE and DDD (USEPA 1980b). DDT has poor solubility in water, and accumulates in fatty tissue. Consequently, bioaccumulation is a concern in predatory species at higher trophic levels, e.g. ducks, and especially raptors. Biological concentration factors (BCF) are calculated based on body mass. BCF values normalized to lipid content indicate a typical 20,000-fold concentration increase in fatty tissue from the environment, with over 50 percent of the DDT-like content often composed of DDE. The one reported chronic toxicity study for freshwater fish indicated an LC_{50} of $0.74 \mu\text{g L}^{-1}$ over the lifecycle of the fathead minnow. No studies of chronic toxicity in invertebrates were reported. However, invertebrates generally were more sensitive to DDT than fish in acute toxicity studies. US EPA established $0.001 \mu\text{g L}^{-1}$ for p,p'-DDT as the Criterion Continuous Concentration (CCC), i.e. the amount allowed for chronic exposure in fresh water taking into consideration health effects on humans and wildlife (USEPA 2009b).

The levels of DDT in lake sediments appear to rise through 2002 in Emerald Lake (Figure 19). Simple diffusion seems unlikely as an explanation for the continued increase in DDT concentration observed after the 1970s. It is unlikely that DDT levels increased through illegal use. The DDT, Aldrin, and Simazine concentration values reported in the WACAP database records multiplied by a constant factor are identical, i.e. each pesticide data set maintains constant ratios with respect to the others. This relationship strongly suggests the levels of these pesticides were not independently determined. Consequently, these database records do not demonstrate increasing levels of DDT in SEKI to 2002, but are likely an artifact of the analytical method that did not distinguish between these pesticides. The reported DDT levels are comparable at the Emerald Lake, Pear Lake, and Three Rivers sample sites in the SIEN and WACAP databases.

Although DDT was first used in the United States in the 1940s, DDT in Pear Lake is reported to be present in a sediment layer dated to 1925 at a concentration comparable to that found in another layer dated to the 1960s. DDT was also reported in an Emerald Lake sediment layer

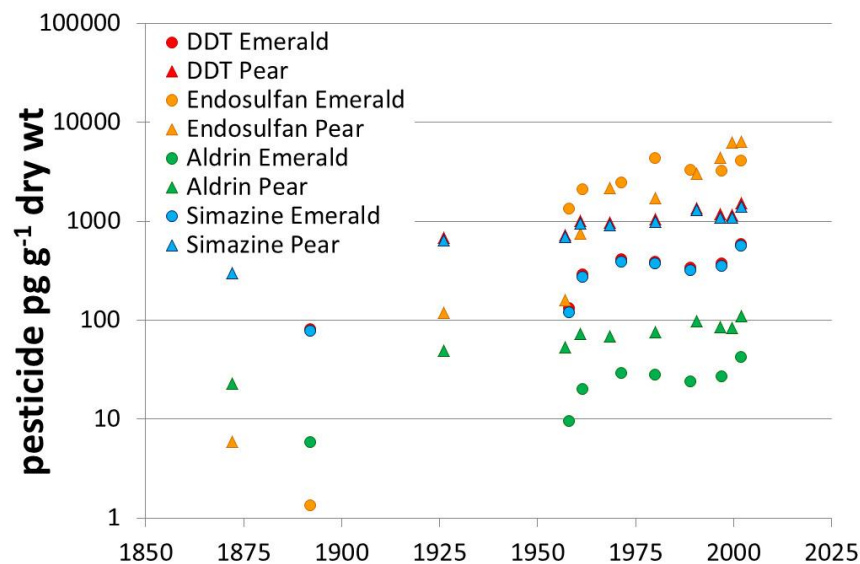


Figure 19. Pesticide concentrations in sediments of Pear Lake and Emerald Lake. Pear Lake samples are triangles, Emerald Lake samples are circles. Note the DDT and Simazine data points are almost coincident.

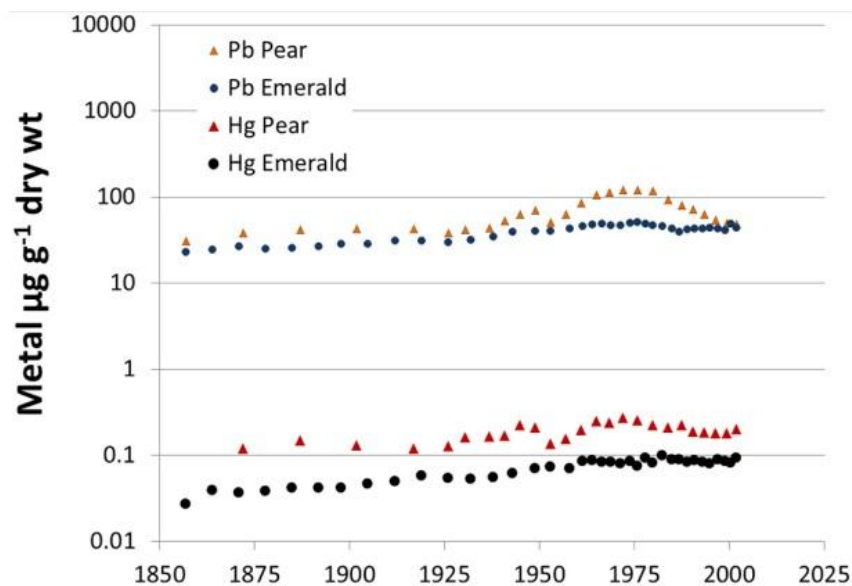


Figure 20. Lead and mercury concentrations in sediments of Pear Lake and Emerald Lake. Pear Lake samples are triangles, Emerald Lake samples are circles. Lead values are in gold and navy, mercury samples are in red and black.

dated to 1892 at a concentration comparable to another layer dated to 1961. It appears DDT must be mobile in lake sediment.

The concentrations of lead in the same sediment cores may help understand the limitations of the data (Figure 20). Emerald Lake is located near Pear Lake, adjacent to each other at nearly the same elevation. Pear Lake has a large broad Pb^{2+} peak around 1975, whereas Emerald Lake has almost no peak. Bioturbation should be comparable in both lakes. In contrast to Pear Lake, snow avalanches at Emerald Lake are associated with steep terrain to lake level (Leydecker et al. 2001). Avalanches pushing through the winter ice may disturb lake sediments. Physical disturbance of Emerald Lake sediment appears to be a more likely explanation for the consistent difference between all Emerald and Pear Lake sediment records examined.

DDT is found at greater than 4.0 ng g^{-1} in fish lipid fraction within ROMO. The levels are higher on the east side of ROMO, consistent with atmospheric deposition

from local sources near an urban area. WACAP data indicate the mean mercury level in the lipid fraction of SEKI fish is a little above 6 ng g⁻¹ in 20 fish taken from 2 lakes.

Simazine

Simazine, a herbicide and algaecide, is in the triazine class first used in 1956, with almost one million tons used per year on fruit and nut crops in California (USEPA 2006). It is moderately soluble in water (3.5 mg L⁻¹ at 20 °C), and is sufficiently volatile that significant atmospheric deposition occurs many miles from the point of use. It may accumulate in a microlayer on the water surface where photodegradation can occur (Pease and Nguyen 2005). Simazine is persistent in anoxic conditions such as aquatic sediments and soils. The half-life in aquatic sediments is estimated to be 664 days. Simazine is not listed as a priority pollutant by EPA.

Simazine was detected in Emerald and Pear lake sediments at approximately 10⁻⁶ mg L⁻¹ (Figure 19). Bradford, et al., found Simazine at slightly lower average levels in all four lakes. Although the Simazine concentrations reported in the SIEN database were orders of magnitude below the expected toxic level, Bradford, et al., demonstrate the acute nature of pesticide deposition. Lake levels of pesticides increase in days or weeks following pesticide application in the agricultural areas of the San Joaquin Valley. Pesticide levels may rise rapidly; however, the measured pesticide quantities quickly return to low levels. The peak Simazine concentration never exceeded 4 x 10⁻⁶ mg L⁻¹ in the four lakes. Consequently, Simazine appears to be well below the levels of concern at the sites tested in SEKI. However, these sites are located at relatively high elevation. If deposition is higher at lower elevations, then the impact of Simazine could be more significant in some locations. Simazine may have a greater impact on sensitive species than suggested by the acute and chronic effects studies described below.

Fish kills have been evaluated by US EPA. They concluded the level of Simazine required in water for fish kill is 1 part per million. However, a toxic effect on endocrine function in male salmon has been reported at 0.1 parts per billion (µg L⁻¹). Native rainbow and Kern golden trout are related species (genus *Oncorhynchus*) and may have similar sensitivity to Simazine.

US EPA studies confirm Simazine has low toxicity in freshwater fish and invertebrates; with an estimated acute toxicity LC₅₀ greater than the solubility of Simazine in water. Fish kills due to Simazine occur indirectly. At a Simazine concentration lethal to phytoplankton and other photosynthetic organisms, fish death occurs as a result of an acute drop in dissolved oxygen, and not any direct toxic effect on fish. However, a study of Atlantic salmon indicated disruption of male response to female pheromones as low as 0.1 µg L⁻¹ Simazine. Although there are no studies demonstrating chronic toxicity of Simazine in fish or invertebrates, a related compound, Atrazine, has been shown to produce endocrine-related effects in frogs.

Endosulfan

Endosulfan is a cyclodiene insecticide, commonly used around the world on cotton, coffee, and tea crops. It is produced with two isomers (I and II), not stereoisomers. They are metabolized by various bacteria, plants, and animals mainly to endosulfan sulfate (USEPA 1980c, 2010). It is unknown which if either isomer is more toxic; they likely interconvert spontaneously, with ratios dependent on steric factors. These three compounds are practically insoluble in water, and have a high potential for accumulation. EPA currently lists these three forms of endosulfan as priority pollutants.

In 2010, US EPA decided to phase out the use of Endosulfan in the United States. Depending on the use type, last use dates in the United States range from 2012 to 2016 (Keigwin 2010). US EPA documents indicate endosulfan is more toxic to freshwater fish than to invertebrates. Other studies indicate temperature impacts toxicity. For example, endosulfan had three-fold higher toxicity in rainbow trout at 10 °C compared to 1.5 °C. One freshwater plant study demonstrated *Chlorella*, an alga, was able to tolerate very high concentrations of endosulfan (2000 µg L⁻¹) with some growth inhibition. US EPA established 0.056 µg L⁻¹ for Endosulfan as the CCC (USEPA 2009b).

The WACAP database records show endosulfan was detected in the water of Emerald and Pear Lakes at less than 0.0005 µg L⁻¹. In the four lakes studied by Bradford, et al., the acute levels of endosulfan never exceeded 0.002 µg L⁻¹. As an approximate baseline, 12 out of 20 measurements were below 0.0001 µg L⁻¹ in samples collected from June to October 2003. Although studies are limited, acute endosulfan levels in SEKI at high elevation have come within one order of magnitude below the EPA recommended limits of chronic exposure.

Aldrin - Dieldrin

Dieldrin and Aldrin are related chlorinated hydrocarbons that interconvert in soils and through liver action. Dieldrin is produced by oxidation of Aldrin. Dieldrin is estimated to be one order of magnitude more toxic to fish than Aldrin. Dieldrin is acutely toxic as low as 0.5 µg L⁻¹ for freshwater aquatic organisms. The chronic toxicity is comparable, about one order of magnitude lower concentration, or approximately 0.05 µg L⁻¹. EPA set the MCL for Dieldrin averaged over 24 hours at 0.0019 µg L⁻¹ in fresh water, and the level should never exceed 0.71 µg L⁻¹. Aldrin MCLs were set slightly higher.

Aldrin is naturally converted to Dieldrin in the environment, both are listed by EPA as priority pollutants. Most uses of both pesticides were discontinued in 1974 and all uses in 1987 (USEPA 2001). Dieldrin is one of the most stable cyclodiene insecticides (Schatzow 1980). US EPA established 0.056 µg L⁻¹ as the CCC for Dieldrin (USEPA 2009b). Dieldrin concentrates in fatty tissue. Salmonid fish are particularly sensitive, indicating the native rainbow and Kern golden trout are at risk. Regular consumption of contaminated fish may pose a human health risk.

Dieldrin and Aldrin were found below 0.001 µg L⁻¹ in SEKI lakes, as reported in the SIEN and WACAP databases, approaching the EPA CCC limit. These levels were measured more than twenty years ago; however, Dieldrin is persistent. Although it may be altered by some species of bacteria, Dieldrin establishes equilibrium concentrations in sediment, water, and biota, maintaining stable levels at a given location. Given the limited amount of sampling, it is possible that Dieldrin may have established an equilibrium concentration in some locations harmful to biota. Additional information is needed.

WACAP data indicate Dieldrin was found in ROMO fish lipid fraction at 0.09 µg g⁻¹, and in SEKI fish at 0.06 µg g⁻¹. In both ROMO and SEKI, the respective values were determined from a total of 20 fish taken from two lakes.

Toxic metals

Several metals are listed by US EPA as priority pollutants. These include mercury, lead, zinc, copper, and cadmium. Other metals not listed as priority pollutants may also be toxic to biota in SEKI. Many of these metals either leach from rock. Some metal pollutants are known to be deposited in forests through atmospheric transport (Rea et al. 2001). These include mercury, lead, zinc, cadmium, copper, and aluminum, and have among the highest flux. The solubility of metals bound in lake sediments can be affected by the presence or absence of dissolved oxygen in and near the sediment surface (Gantzer et al. 2009).

Mercury

Mercury is listed as a priority pollutant by US EPA. Mercury is naturally present in California mineral deposits as cinnabar, and gold ore (USEPA 2003). Today, mercury is only produced as a secondary product of gold mining. All mercury ore mines have been closed. It is preferable to recover mercury from gold mining rather than leave it in the tailing to contaminate surface and ground waters. Former mercury mining areas are heavily contaminated, such as New Almaden and Clear Lake. Elsewhere, mercury contamination has occurred through local use for industrial purposes. Mercury is transported through the atmosphere and deposited in remote areas including SEKI. Deposited inorganic mercury can be converted to methylmercury which is readily taken up by organisms.

Mercury metal is very poorly soluble in water, and has very low vapor pressure (USEPA 1980e). Mercurous (Hg^+) salts are not very soluble, and are much less toxic than mercuric (Hg^{2+}) salts which are very soluble. In some locations, surface waters can naturally contain mercury as high as $70 \mu\text{g L}^{-1}$ (USEPA 2007c). The normal ambient Hg in the atmosphere is about 20 ng m^{-3} . Methylmercury is produced by bacteria and fungi in the upper layers of sediments and suspended organic matter, acting on the mercuric ion. The mercuric ion is produced from mercury metal (Hg^0) through interactions with organic matter. Hg^0 is also oxidized to Hg^{2+} in the atmosphere within water droplets. Bacterial production of dimethyl mercury ($(\text{CH}_3)_2\text{Hg}$) is favored over monomethyl mercury (CH_3Hg^+) in high pH environments. Dimethylmercury is more volatile. Microbial resistance to Hg toxicity involves demethylation of methylmercury to Hg^{2+} . A wide variety of bacteria and fungi reduce Hg^{2+} to the metal.

US EPA established $0.77 \mu\text{g L}^{-1}$ (total Hg) for mercury and methylmercury as the Criterion Continuous Concentration (CCC) (USEPA 2009b). The CCC is based on measurements of total recoverable metal (USEPA 1996). It assumes a fraction is adsorbed to particulate material and the remainder is dissolved, and a translation factor is applied. US EPA states the CCC based on total metal may not be sufficiently protective if a large fraction of total mercury is methylmercury.

Mean mercury levels in SEKI taken from the SIEN database are shown in Figure 21 and 22A. The highest levels were found in Three Rivers, an inhabited area outside of SNP. These samples were collected from 1973 through 1987, usually two to three times per year. The mean value of $0.85 \mu\text{g L}^{-1}$ is above the CCC. However, Figure 22A shows the mean mercury level remained below the CCC after 1982. Much higher mercury values were measured at Three Rivers between 1974 and 1978 in 3 of the 5 years. Figure 20 shows Hg levels at various dated layers in sediment cores taken from Emerald Lake and Pear Lake in SNP as reported in the WACAP database. The mercury levels appear to peak during the 1970s and decrease to the present in Pear Lake. This

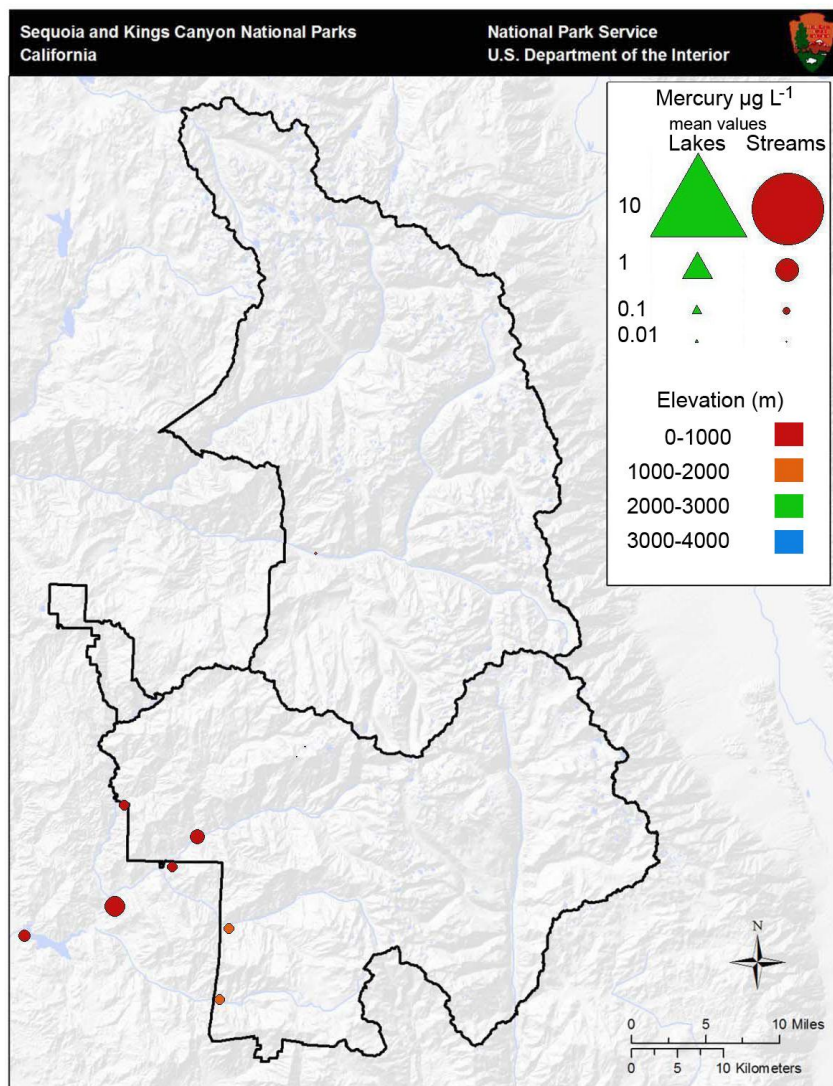


Figure 21. Mean mercury concentration. Lakes are triangles, streams are circles, values proportional to area. Elevation bands (1000 m) are represented by different colors. Two higher elevation sites, located near the Marble Fork just below the KNP boundary, were derived from snow measurements taken from WACAP records. One site in KNP had much lower Hg levels.

trend is almost identical to the world mercury production over the last century (Schuster et al. 2002).

There is concern that mercury produced in Asia could reach SEKI, transported as vapor, adsorbed to dust, or carried in water droplets. Recent modeling by Dastoor and Larocque (Dastoor and Larocque 2004) suggests mercury is deposited within a few hundred to a few thousand miles of the location where it is produced. These results suggest most mercury produced in China and Japan is not transported as far as California, and that mercury produced within the state is the major source of mercury deposited in SEKI. However, metallic mercury deposition may be higher in forests through leaching into foliage (Rea et al. 2001).

In 1995, the current standards were developed based on studies of acute and chronic effects on aquatic species. There were few chronic studies of mercury performed. The CCC value was based on studies of invertebrates. For vertebrates, no chronic studies were performed. Instead, a mean acute-chronic ratio was applied to the acute studies to estimate the appropriate chronic levels. The acute species mean values are approximately 240 and 275 $\mu\text{g L}^{-1}$ for Rainbow trout and Coho salmon, respectively. The estimated chronic value is approximately 0.4 $\mu\text{g L}^{-1}$, which is lower than the CCC (see above). Thus, the established CCC may not adequately protect these species. These limited studies and the levels of mercury measured at sites in SEKI suggest mercury is potentially impacting sensitive species in SEKI, and more monitoring is needed.

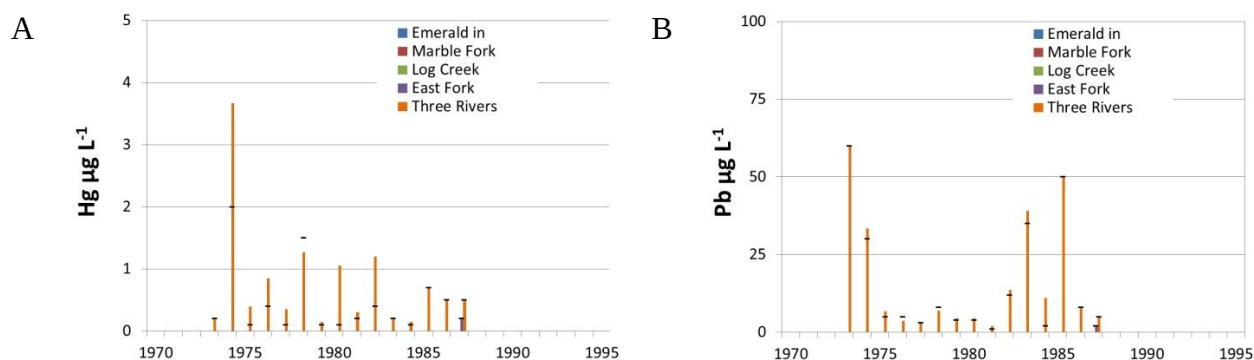


Figure 22. Mean mercury concentration (A) and mean lead concentration (B) measured in reference streams in SEKI. Median values are shown as dark horizontal bars.

The Pear Lake sediment data also are in general agreement with measurements taken from Three Rivers as described above (Figure 17). Emerald Lake mercury measurements from sediments do not exhibit any significant peak as observed in Pear Lake. This difference may be explained by snow avalanches at Emerald Lake producing disturbances of lake sediments (discussed above). Only total mercury was reported in the SIEN database. Shanley, et al., observed that methylmercury maintained a constant ratio with total mercury in diverse streams sampled repeatedly, suggesting a common origin for both mercury and methylmercury (Shanley et al. 2008). Measurements of total mercury may be adequate for routine assessment. However, in studies of toxicity or bioconcentration, it may be necessary to know the mercury concentration in forms most readily taken up by organisms, e.g. methylmercury versus mercury metal.

Mean mercury levels at other locations in the Kaweah basin were within one half of one order of magnitude below the CCC. Most of these sites were at an elevation under 1000 m. Mercury data were collected between 1971 and 1994. In KNP, far lower levels of mercury were measured at one site. Nutrients may support the growth bacteria and fungi that could mobilize mercury from sediment layers, convert mercury metal to mercuric ion, and subsequently into methylmercury. As noted above, methylmercury is more likely to be produced in slightly acidic water, which is found at higher elevation. Krabbenhoft, et al., found that high elevation lakes with lower pH and oligotrophic condition did not produce as much methylmercury as might be predicted (Krabbenhoft et al. 2002). They note major producers of methylmercury are sulfate reducing bacteria, growing in anoxic or low dissolved oxygen conditions. The three limiting factors in methylmercury production are sulfate, a carbon substrate, and Hg^{2+} . These factors may become non-limiting at lower elevation. Mercury in 'natural waters' is expected to be less than 10 ng L^{-1} . SIEN records indicate only one site in KNP has been tested for mercury, and few sites above 1000 m in SNP have mercury data. Additional testing is needed to accurately assess the potential impact of mercury in SEKI.

WACAP data indicate mercury in fish in ROMO is $0.07 \mu\text{g g}^{-1}$ for a total of 20 fish taken from two lakes. The corresponding data for SEKI is $0.11 \mu\text{g g}^{-1}$ wet weight for 20 total fish also taken from two lakes. Two factors that could account for the slightly higher mercury levels in SEKI compared with ROMO may be closer proximity to urban sources of mercury and being located more frequently downwind from such sources.

Lead

Lead is a priority pollutant. Lead entering ordinary surface waters from natural sources is not readily transported, because free lead forms insoluble compounds as a sulfide, with sulfate, and carbonate, or may be adsorbed by iron compounds (USEPA 1980d). When not in one of these forms, lead solubility varies strongly with pH from 0.001 mg L^{-1} at pH 9.0 to $10,000 \text{ mg L}^{-1}$ at pH 5.5. Lead is deposited as dust and in precipitation after being transported through the atmosphere, often great distances from the source.

Studies of vertebrates and invertebrates demonstrated acute and chronic lead toxicity can be reduced by more than 90% as water hardness increases (Ca^{2+} and Mg^{2+} content) (USEPA 1984) due to cation competition (USEPA 2007b). Other ions such as hydroxide, and carbonate may also reduce toxicity. US EPA established the CMC for lead as $65 \text{ } \mu\text{g L}^{-1}$, and the CCC as $2.5 \text{ } \mu\text{g L}^{-1}$, in water having a hardness of 100 mg L^{-1} (USEPA 2009b). The dependence of lead toxicity on hardness is shown in Figure 23.

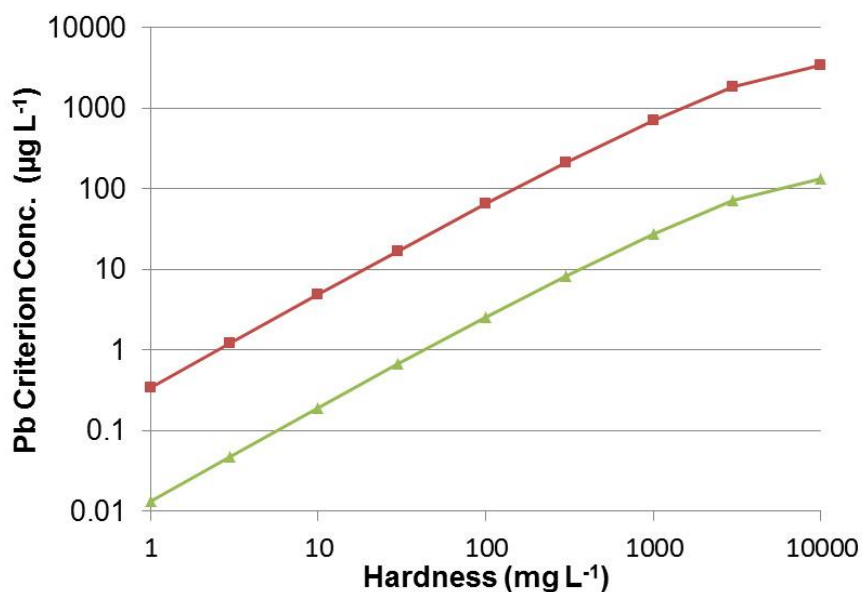


Figure 23. Acute and chronic lead toxicity dependence on hardness, mg L^{-1} as CaCO_3 . The criterion maximum concentration (CMC, acute toxicity) is red. The criterion continuous concentration (CCC, chronic toxicity) is green. Curves produced from equations provided by the US Environmental Protection Agency (USEPA 1996).

The standard US EPA CMC and CCC are defined at 100 mg L^{-1} hardness as CaCO_3 . However, hardness in SEKI rarely reaches 100 mg L^{-1} (Figure 24). SEKI lakes typically have 4 mg L^{-1} of hardness, and streams have approximately 20 mg L^{-1} . Low hardness may allow lead to produce toxic effects well below the standard CMC and CCC (Figure 23). The corrected CMC and CCC for lakes at 1 mg L^{-1} hardness would be approximately $0.33 \text{ } \mu\text{g L}^{-1}$ and $0.01 \text{ } \mu\text{g L}^{-1}$, respectively. Streams are somewhat protected by

hardness at 10 mg L^{-1} , with estimated CMC and CCC at $4.9 \text{ } \mu\text{g L}^{-1}$ and $0.19 \text{ } \mu\text{g L}^{-1}$, respectively. Consequently, atmospheric deposition in SEKI could deliver metals, some of which would have higher toxicity due to the low hardness concentrations in SEKI lakes and streams.

Lead was found in SEKI lake sediment cores (Figure 20) and water samples collected from streams (Figure 25), and is reported as mean lead levels from SIEN database records. The highest levels were found in Three Rivers, an inhabited area outside of SNP. These samples were collected from 1973 through 1987, usually two to three times per year. The highest

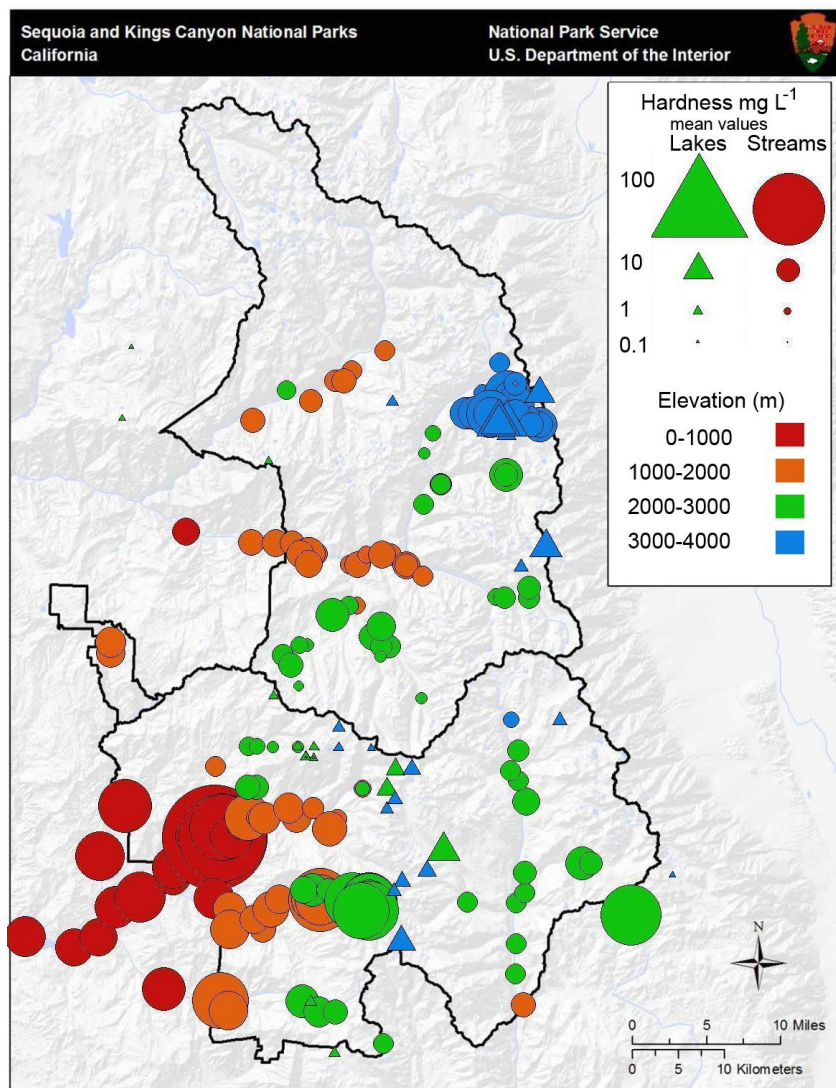


Figure 24. Mean hardness, mg L^{-1} as CaCO_3 in SEKI. Lakes are triangles, streams are circles, values proportional to area. Colors indicate the elevation band where the sample was collected.

measurements taken from Three Rivers as described above. In addition, the Pear Lake sediment data suggest that lead deposition from atmospheric transport may be decreasing, perhaps due to the removal of lead from gasoline. It is difficult to assess the impact of lead in SEKI with the limited data available.

mean lead concentration, $15 \mu\text{g L}^{-1}$ measured at Three Rivers, was 6-fold above the CCC. Most of the other low elevation mean values were also above the CCC. Figure 19B shows the mean and median lead levels were consistently above the CCC, sometimes by more than an order of magnitude. However, since SEKI waters are relatively soft, the calculated lead CCC values using local average hardness range from 0.01 to $0.59 \mu\text{g L}^{-1}$ in SEKI (see Toxic metals in Assessment).

Lead levels were measured in dated layers of sediment cores taken from Emerald Lake and Pear Lake in SNP, as reported in the WACAP database (Figure 20). Viewed over time, lead levels appear to peak during the 1970s and decrease to the present in Pear Lake. These data are in general agreement with

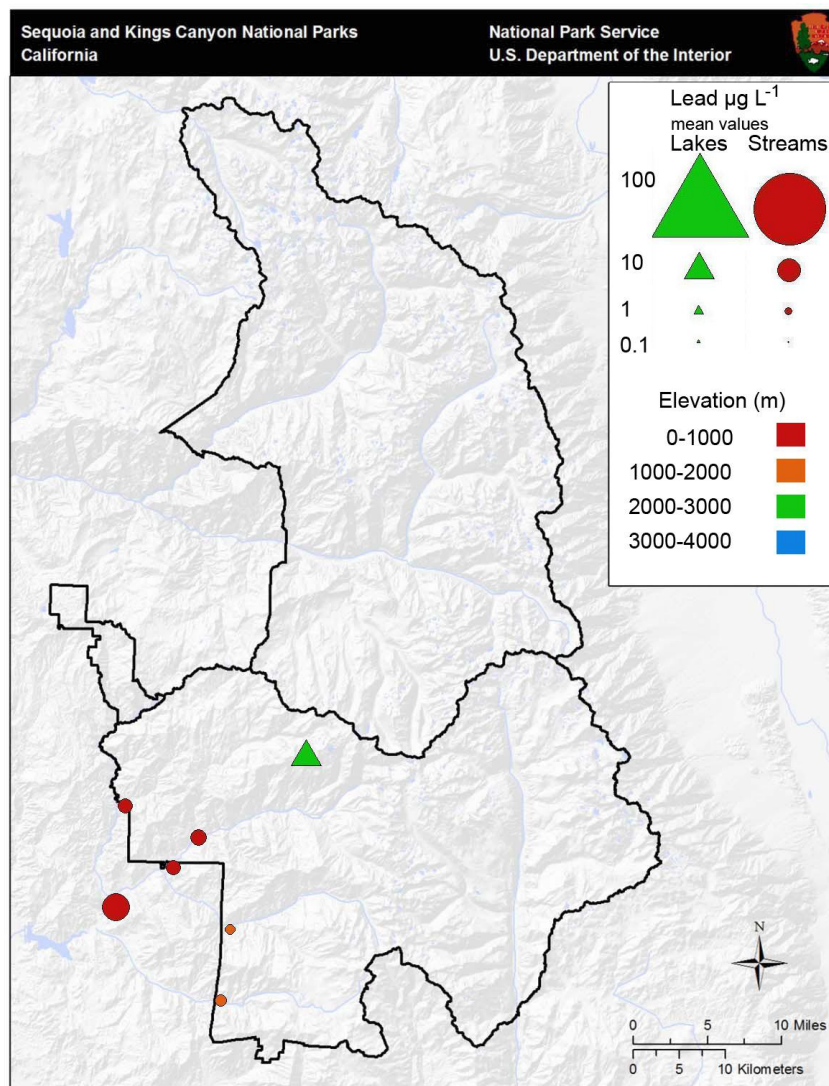


Figure 25. Mean lead concentration. Lakes are triangles, streams are circles, values proportional to area. Elevation bands (1000 m) are represented by different colors.

Aluminum

Aluminum is a non-priority pollutant as defined by US EPA (USEPA 2009b). Federal standards for aluminum specify a pH range of water from 6.5 to 9.0 based on hydrogen ion standards to protect organisms. The CMC and CCC for aluminum are $750 \mu\text{g L}^{-1}$ and $87 \mu\text{g L}^{-1}$, respectively, as total recoverable metal. US EPA uses acid soluble aluminum to determine total recoverable aluminum. Figure 7 shows the pH values measured in SEKI in various lakes and streams. It is apparent that several high elevation lakes are well below pH 6.5. The SIEN database records indicate 38% of lakes and 6% of streams had mean pH measurements below pH 6.5. These are natural pH values, and not the result of acid rain.

Some Al levels reported in the SIEN database are above the CCC and CMC. However, these samples were collected at pH values below 6.5 and often in unfiltered water samples (Figure 26). Aluminum solubility increases under acidic conditions (USEPA 1988) and basic conditions,

aluminum also forms. polymers with hydroxide ions (Parks 1972). In SEKI, 21% of lakes in the SIEN database had mean pH below pH 6.2. The highest concentrations of aluminum were found in the most acidic lakes and streams (Figure 26). Furthermore, SIEN data are consistent with the dependence of aluminum solubility on pH (Figure 27). No inference can be made regarding toxicity for samples having a pH outside the range specified for the CCC.

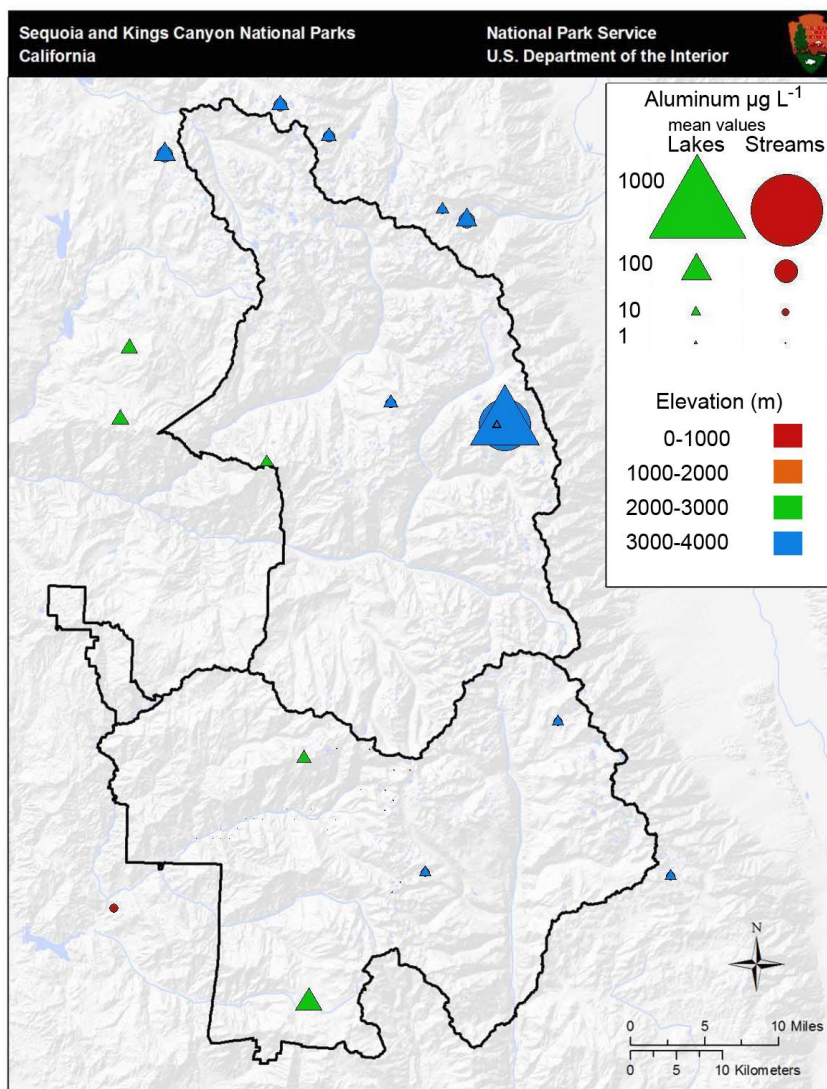


Figure 26. Mean Aluminum concentration. Lakes are triangles, streams are circles, values proportional to area. Elevation bands (1000 m) are represented by different colors.

There is an apparent temporal trend of increasing aluminum concentration in the SIEN reference lakes and streams (Figure 28). The SIEN records indicate the aluminum concentration is rising in the slightly acidic water of Emerald Lake compared with the neutral Kaweah River at Three Rivers, with higher ANC. However, the median values of aluminum for reference sites never exceeded the CCC. Additional monitoring is needed to determine whether there is a trend in aluminum and identify possible toxic effects of aluminum on sensitive species.

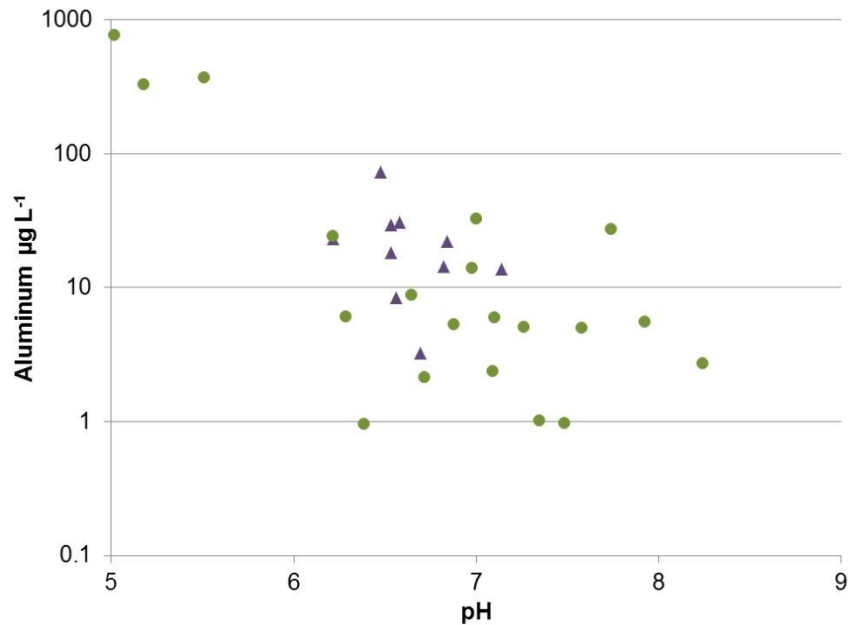


Figure 27. Mean aluminum concentration in SEKI lakes and streams. Lakes are triangles, and streams are circles.

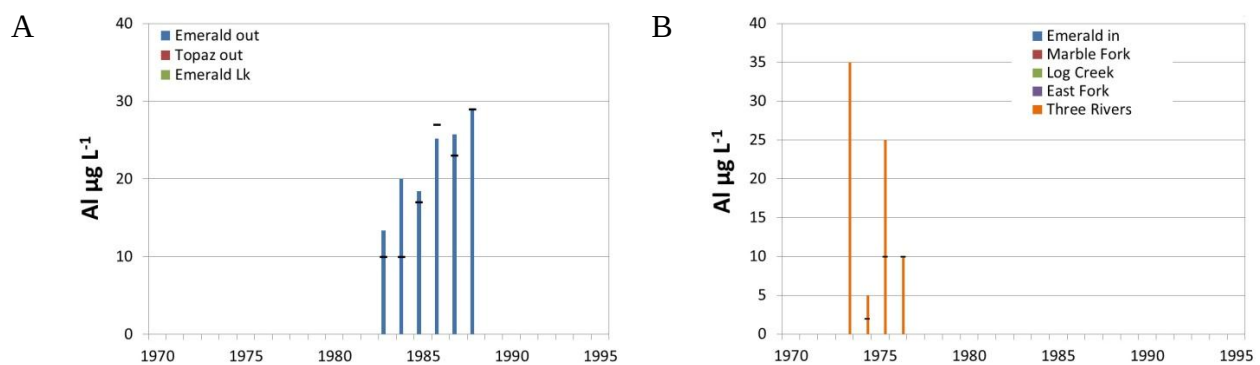


Figure 28. Mean aluminum concentration in SEKI reference lakes (A) and streams (B). Median values are shown as dark horizontal bars.

Zinc

Zinc is a priority pollutant. The CMC and CCC for zinc are hardness dependent, both $120 \mu\text{g L}^{-1}$ at 100 mg L^{-1} hardness. SIEN records indicate virtually all of the concentrations reported are well below the standard CCC. However, when hardness values in SEKI are considered, the corrected CMC and CCC for lakes at approximately 4 mg L^{-1} hardness would be $7.7 \mu\text{g L}^{-1}$, each. Streams with an approximate hardness of 20 mg L^{-1} would have CMC and CCC at $30 \mu\text{g}$

L^{-1} , each. Consequently, reliably measured zinc concentrations in streams are approximately at the CCC, with individual measurements exceeding the limit. Lake values are mostly unreliable, however one reliable site indicated zinc levels well above the CCC. Some species are more sensitive to zinc than others. However, locations with abnormally high zinc concentrations more likely reflect the local geology, which would make zinc an indigenous factor. In such cases with potentially toxic chronic zinc levels, it is reasonable to conclude indigenous native species capable of tolerating zinc were selected long ago.

Mean zinc levels at 10 to $20 \mu g L^{-1}$ were found in waters of SEKI south of the Kings River, on the Marble Fork of the Kaweah, and at Three Rivers. Low levels of zinc were detected in the Kaweah above the Marble Fork and in the high elevation lakes in this catchment (Figure 29).

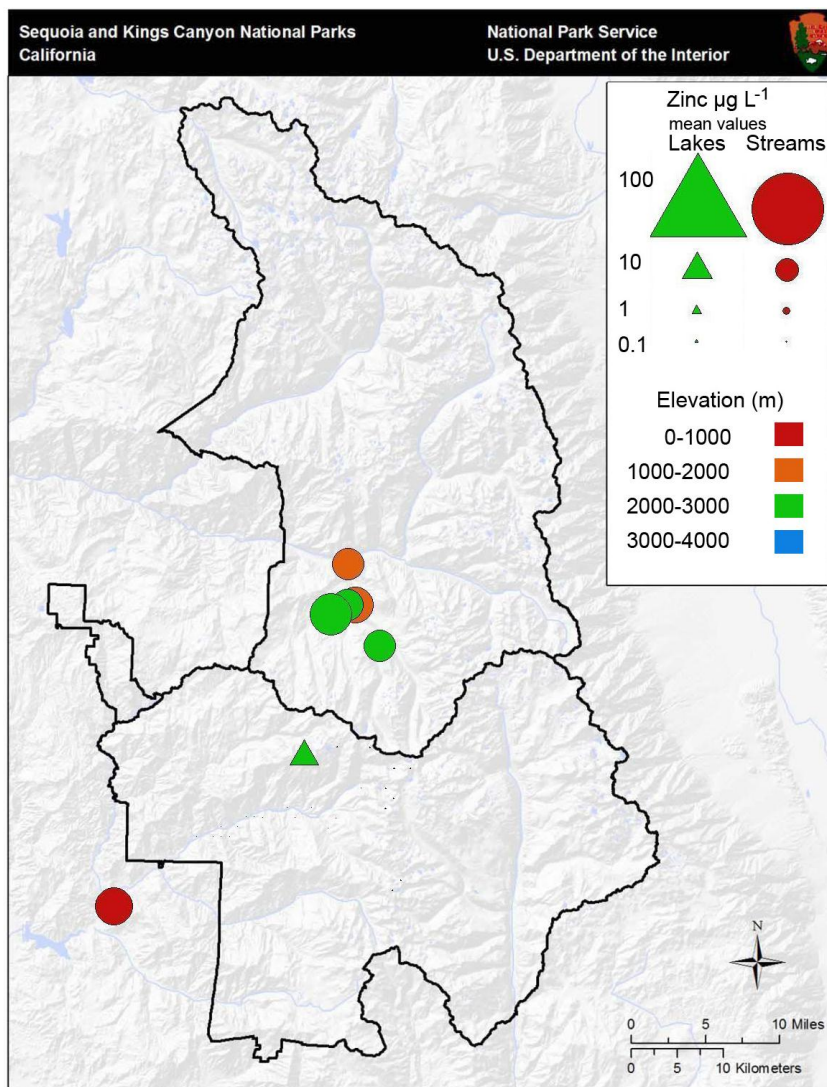


Figure 29. Mean zinc concentration. Lakes are triangles, streams are circles, values proportional to area. Elevation bands (1000 m) are represented by different colors.

Copper

Copper is listed as a priority pollutant by the US EPA. The CMC and CCC for copper are hardness dependent; however, copper toxicity is being re-evaluated using a Biotic Ligand Model (BLM) (USEPA 2007a) that seeks to set copper toxicity standards based on more detailed and variable factors.

Using the standard EPA hardness dependent equations for copper, the CMC and CCC are $13 \mu g L^{-1}$ and $9 \mu g L^{-1}$, respectively at $100 mg L^{-1}$ hardness. For SEKI streams at $20 mg L^{-1}$ hardness, the CMC and CCC would be approximately $2.9 \mu g L^{-1}$ and $2.3 \mu g L^{-1}$. For SEKI lakes, at $4 mg L^{-1}$ hardness, the values converge, both being $0.6 \mu g L^{-1}$.

Copper between about 1 and 10 $\mu\text{g L}^{-1}$ was found in waters of SEKI south of the Kings River, on the Marble Fork of the Kaweah, and at Three Rivers. Low levels of copper were detected in the Kaweah above the Marble Fork and in the high elevation lakes in this catchment (Figure 30). SIEN records indicate virtually all of the copper concentrations reported from SEKI sites are well below the standard CCC, and most are below the CCC corrected for hardness. Since only 23 streams and 10 lakes were represented, additional measurements would help in determining the potential impact of copper more accurately.

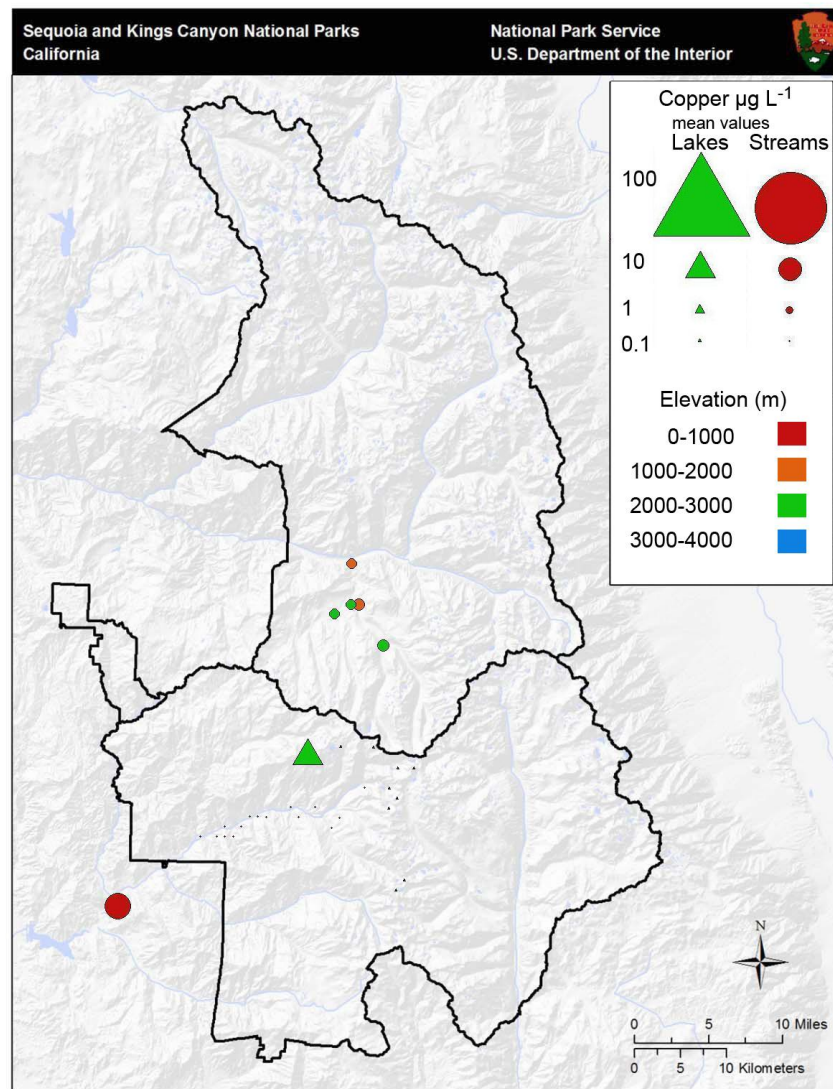
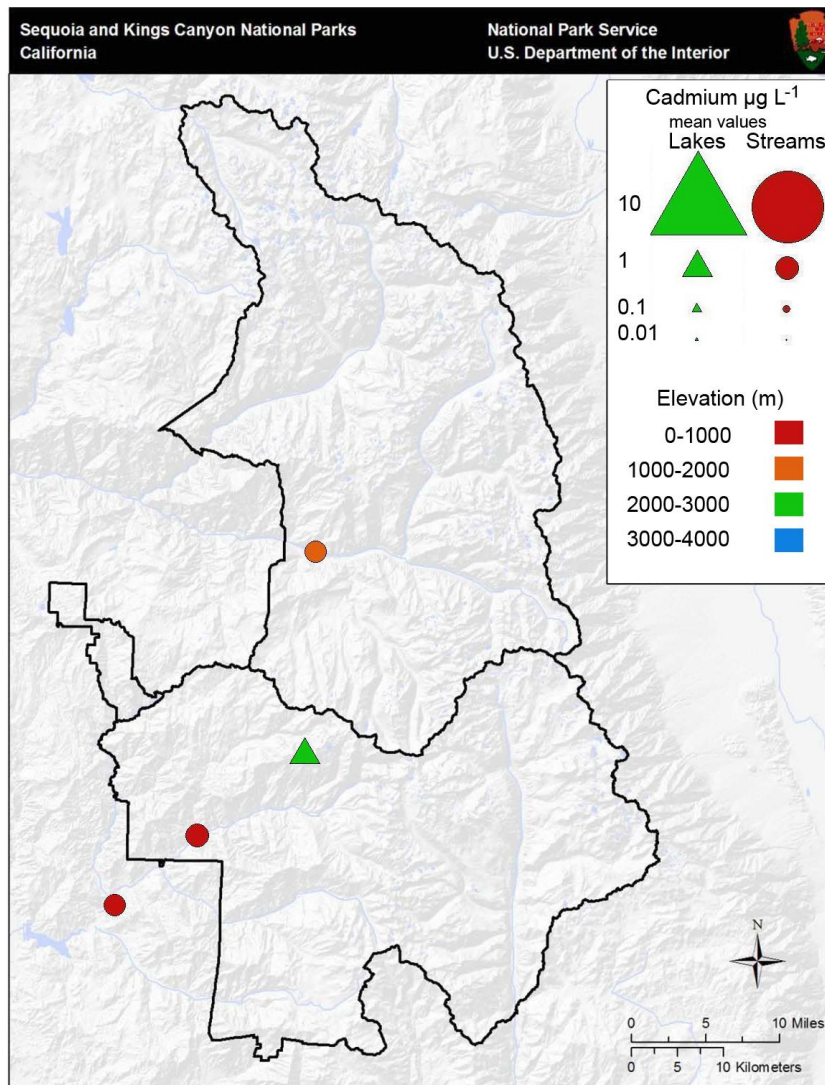


Figure 30. Mean copper concentration. Lakes are triangles, streams are circles, values proportional to area. Elevation bands (1000 m) are represented by different colors.

Cadmium

Cadmium is a priority pollutant. The CMC and CCC for cadmium are hardness dependent, the CMC and CCC are 2.0 $\mu\text{g L}^{-1}$ and 0.25 $\mu\text{g L}^{-1}$, respectively at 100 mg L^{-1} hardness. SIEN records indicate virtually all of the concentrations reported are well below the standard CCC. However,

when hardness values in SEKI are considered, the corrected CMC and CCC for lakes at approximately 4 mg L^{-1} hardness would be $0.09 \text{ } \mu\text{g L}^{-1}$ and $0.03 \text{ } \mu\text{g L}^{-1}$, respectively. Streams with an approximate hardness of 20 mg L^{-1} would have CMC and CCC at $0.42 \text{ } \mu\text{g L}^{-1}$, and $0.08 \text{ } \mu\text{g L}^{-1}$.



SIEN records indicate virtually all of the concentrations reported are well below the standard CCC. Cadmium at $1 \text{ } \mu\text{g L}^{-1}$ was found in waters of SEKI near the Kings River, on the Marble Fork of the Kaweah, and at Three Rivers (Figure 31). These streams contain Cd at more than an order of magnitude above the CCC corrected for hardness. Given the limited measurements for cadmium, further measurements of this priority pollutant will be needed to assess the effects on biota in SEKI.

Figure 31. Mean cadmium concentration. Lakes are triangles, streams are circles, values proportional to area. Elevation bands (1000 m) are represented by different colors.

Analysis Uncertainty

For many water-quality parameters, samples were collected from different water bodies and at different elevations in separate periods of time. In many cases, lower-elevation streams were studied from 1951 through 1970. Higher-elevation lakes became a focus of study for several years and higher-elevation streams studied in a separate period of years. As a result, relatively few locations were consistently evaluated for long periods of time. Also, because sites within certain elevation bands were studied exclusively for many years at a time, there is a strong correlation of elevation with time, introducing systematic error. Consequently, it is important to deconvolute the time and elevation dependencies of parameter variation. It is also important to consider seasonal variation when estimating trends. Mean values and standard deviations are reported for lakes and stream separately by month of the year.

From evaluation of parameter values, and plots of mean values at the sample locations on a map of the Sequoia and Kings Canyon National Parks, we can determine that there are some locations with distinct catchment properties as well as local differences. It is important to determine whether these anomalies are produced by local conditions or whether they are produced by exogenous factors that may be anthropogenic. We have attempted to correlate some of the observations of these anomalies with known geochemistry using Geographic Information Systems (GIS) data layers indicating the bedrock type in the vicinity of the anomalies. For example, it is known that there are areas of karst within the parks that can be a source of carbonate, calcium, and phosphate. Roof pendants (Filippelli and Delaney 1996, Stevens and Greene 1999, Snow and Scherer 2006) in the Parks can be sources of minerals and salts, for example nitrate, that do not occur in granitic rocks making up the majority of the high elevation terrain.

It is evident from SIEN database records that some parameters samples could not be measured accurately or at all in the concentration ranges necessary to assess the impact of the parameter. This limitation is likely due to insufficient technical capability, since lowest measured values often decreased over time. For the parameters in this challenging category, the SIEN records often indicate sample values are known to be less than the indicated value, or below the detection limit. In these cases, determining whether the parameters exceed critical levels has not been possible or estimates were calculated with higher relative error.

Interactions with other focal resources

As discussed above, atmospheric deposition is the only source for pesticides in SEKI, and a significant source of nutrients and toxic metals. There is also the potential of acid deposition in sensitive low alkalinity lakes at high elevation which could result in a significant reduction in pH. It now appears that this latter concern is unwarranted due to the policies enacted by the state of California to severely restrict coal-fired power plants from operating. Toxic metals are also released from burning coal. However, an analysis of mercury transport via the atmosphere indicates that coastal cities appear to be significant sources of mercury, and likely of other metals as well. Lead was released in large quantities via automobile exhaust when lead was a component of gasoline. Since removing lead from gasoline in the mid-1980s, a major source of

the toxic metal has been eliminated. Multiple potential stressors have been significantly reduced through policy decisions.

Agriculture is a potential source of nutrients, pesticides, and metals. Organomercury compounds were used historically as fungicides in rice crops, including the Sacramento Valley in California. Large volumes of nitrate, ammonia, and phosphorus may be transported from the SJV to SEKI. Pesticides are not used in SEKI, and must be transported and deposited wet or dry from the atmosphere.

Water-quality parameters change significantly as water flows from high to low elevation where it exits SEKI. A clear example is alkalinity, as described above. These changing characteristics of water can have potentially impact organisms that depend on this resource for survival. Aquatic organisms must survive in the waters they inhabit, and have limited options to seek out alternative places to feed and reproduce. Atmospheric deposition of exogenous substances will change the water chemistry of these high elevation aquatic systems and resulting ecosystem changes should be monitored.

Stressors

Air Quality

Air quality was considered a significant potential stressor impacting water quality and biota in SEKI. Atmospheric deposition of acids, nutrients, toxic metals, and pesticides, has been known to occur and in some cases have negatively impacted the natural environment in various regions of the United States.

Measurements of pH in SEKI lakes and streams have not indicated any widespread impact of exogenous acids. The most sensitive high elevation lakes have low alkalinity and are most sensitive to acid deposition. However, in most cases lake pH reflects equilibrium with atmospheric CO₂. Local geochemistry seems to be sufficient to explain observed pH anomalies (Figure 2).

Nitrogen and phosphorus nutrients are known to be carried from the San Joaquin Valley to SEKI; however at least nitrogen deposition tends to be heaviest at lower elevation (Bytnerowicz et al. 2002, Fenn et al. 2010). Local nitrogen fixation can exceed the rate of deposited nutrients (Schindler 1981); nitrogen does not accumulate in catchments (Sickman et al. 2003), and increased atmospheric nitrogen deposition is not expected to profoundly impact nitrate concentrations at least at higher elevations (Meixner et al. 2004a). In the Sierra Nevada, nitrogen compounds are known to leach into water contacting metamorphic rock derived from marine sediments, and have been identified as the major source of nitrates in some watersheds (Holloway et al. 1998, Holloway and Smith 2005). There are local sources of phosphorus such as karst that result in localized elevated levels, especially around Mineral King (Figure 16).

Pesticides appear to have potentially severe impact on sensitive species in SEKI. Pesticides used in agriculture in the San Joaquin Valley are deposited in SEKI (Bradford et al. 2010). Not all pesticides pose a risk for SEKI, such as Simazine. However, certain pesticides that persist and have toxic or reproductive effects are being discontinued, or already have been. Nevertheless, in many cases, these substances persist in sediments and the food chain for decades. There has been insufficient monitoring to accurately assess the impact of pesticides in SEKI, however the studies that have been performed indicate levels of certain pesticides are in the range that can have significant negative effects.

Toxic metals impacting SEKI can originate in local rock, or may be deposited from the atmosphere after being transported long distances. Because of the dilute nature of SEKI high elevation water bodies, toxic metals such as Pb²⁺ are of concern at low levels. Species may be more sensitive to toxic metals in SEKI due to the low levels of hardness in SEKI water. Several priority pollutant metals, such as Cu and Zn, have not been adequately sampled. There are inadequate data for other toxic metals in the SIEN database.

WACAP records indicate lead, mercury, and cadmium were found in lake sediments. Metal levels were measured in dated sediment layers. The levels seem to form a broad peak in the undisturbed Pear Lake sediment with the highest levels occurring between 1970 and 1985 (see Toxic metals in Appendix). Other metals measured in the same Pear Lake core layers, manganese, copper, zinc, iron, and nickel, do not show similar broad peaks. Emerald Lake has

sediments likely disturbed by avalanches; the corresponding broad peak for lead is barely perceptible. It seems unlikely that leaching from rock would increase the concentration of some metals and not others only for a few decades. These results seem to indicate that significant exogenous metals were deposited in SEKI likely through atmospheric transport.

Climate Change

Clearly, climate changes could have a profound effect on water quality in SEKI. It is likely the effects of climate change would be detectable as temporal trends observed in parameters such as pH, temperature, and alkalinity. Despite an abundance of measurements within SEKI, a lack of long-term data from single sites prevented us from drawing any conclusions regarding trends. Regular monitoring at multiple representative fixed locations, frequently during the year, and over multiple decades is necessary to obtain the data required to assess climate impacts.

Assessment

In the SIEN database, 12,676 samples were collected from 802 sites. Of these, 466 sites were placed in the twelve SEKI HUC 10 units based on UTM coordinates (Figure 32). These sites are only marginally well distributed around SEKI, with an average of 38.8 +/- 39.2 sites in each HUC 10 unit. The minimum is 8, and the maximum is 136 sites, median 24.5.

Ideally, samples would be collected frequently over a long period of time at all sites, and all parameters would be measured in every sample. Very few sites had regular sample collection over many years, measuring a wide range of parameters. Typically, a limited set of parameters was measured in each sample.

Consequently, the number of samples for any given parameter could be very different from the number collected in another HUC 10 unit, or compared to a second parameter measured in the same HUC 10 unit.

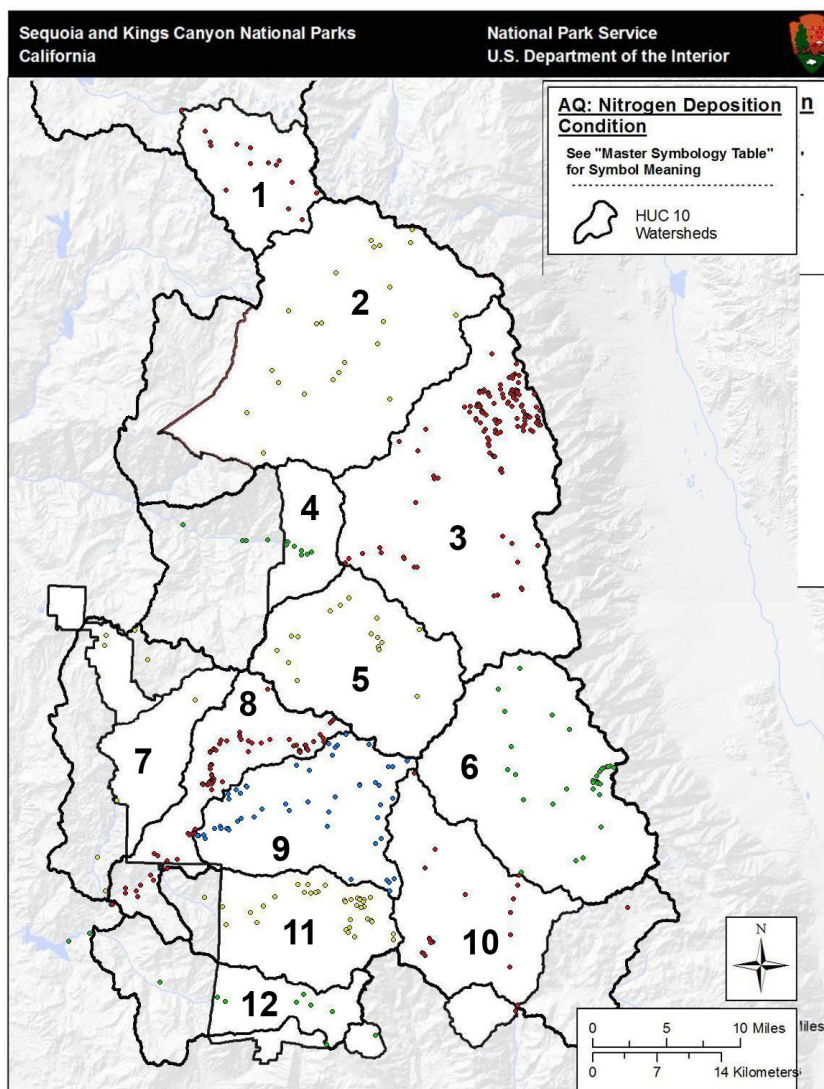


Figure 32. All water sample sites in SIEN database located in SEKI HUC 10 units. Colors indicate sites in different HUC 10 units. Numbers indicate a convenient HUC 10 unit numbering scheme used in data tables, not the actual designations.

We selected certain parameters as representative of three condition categories. These were standard water parameters, nutrients, and contaminants. Some parameters do not have clear minimum or maximum values that would likely be exceeded. For example, water temperature could reasonably vary from 0 to 40 °C. There is no clear standard for comparison. Although a specific temperature range may be appropriate for the survival or reproduction of certain species, this issue is beyond the scope of this assessment. In contrast, mercury toxicity studies do indicate toxicity for a broad range of species. Mercury is not utilized in any biological process, and is

purely a toxic contaminant. Whereas, different temperature ranges provide alternative habitat conditions for different distributions of organisms to which they are more or less adapted.

We assigned a condition assessment for each HUC 10 unit in SEKI based on the number of samples, the level of a parameter compared to a critical level, whether there was a significant trend of improvement or degradation, and the confidence level of the assignments. Sample numbers varied over three orders of magnitude for some parameters. Sample number was “low” when less than 50 samples were measured in a HUC 10 unit, “medium” from 50 to less than 500, and “high” for 500 and above, and served to indicate the confidence of the assessment. Trends were calculated using fractional years to account for the sample date, estimated by linear regression (Equation 1).

$$\begin{aligned} &\text{Linear Regression estimate of the Slope} \\ \text{Slope} &= \{ \sum(x_i * y_i) - [\sum(x_i) * \sum(y_i)] / N \} / \{ \sum(x_i^2) - [\sum(x_i)]^2 / N \} \end{aligned} \quad \text{Eq. 1}$$

Mean year and level, and rate of change were determined for each parameter in each HUC 10 unit in which data were available. The standard error of the slope was used (Equation 2) to determine the confidence of the trend (Equation 3).

$$\begin{aligned} &\text{Slope Standard Error} \\ \text{SE}_{\text{slope}} &= \text{sqrt} [\sum(y_i - \hat{y}_i)^2 / (n - 2)] / \text{sqrt} [\sum(x_i - \bar{x})^2] \end{aligned} \quad \text{Eq. 2}$$

$$\begin{aligned} &\text{Slope Confidence} \\ \text{Conf}_{\text{slope}} &= \text{ABS} [\text{Slope}] / 3\text{SE}_{\text{slope}} \end{aligned} \quad \text{Eq. 3}$$

When the estimated slope had an absolute value greater than three standard errors, the trend confidence was greater than 95% non-zero. These significant trends were used in conjunction with mean levels to further assess the condition. In other words, a significant trend was used to indicate whether a parameter condition was improving, not changing, or declining. HUC 10 units with trends with confidence values less than 1 were reported as not changing.

Individual parameter assessments were “good”, “moderate”, or “poor”. Since these are somewhat subjective, we attempted to apply uniform rules to make these determinations. A “good” condition indicates the parameter level is in an acceptable range and the trend is either improving, or there is no change. A unit could still be deemed “good” if a significant trend indicates the level would remain within the acceptable range in 2011. Consequently, a marginally deteriorating parameter could still be deemed “good”. A “poor” condition indicates the parameter mean level is outside the acceptable range and not improving. Other conditions were deemed “moderate”.

The combined assessment was calculated using weighted averages of individual HUC 10 assessments. A unit with no data was excluded from the calculation. A “good” condition valued as 1, “moderate” as -1, and “poor” as -3. To these values, a weighting factor was multiplied to take into account the individual confidence. Individual assessments with “low” sample number were weighted 1, “medium” were weighted 2, and “high” were weighted 3. A similar calculation was performed to determine the combined trend. The individual trends were valued with “improving” as 1, “no change” as 0, and “declining” as -2. The same weighting factors used in

the combined assessment were used to account for differences in sample number in the combined direction calculation. The combined confidence was the average of the confidence weighting factors.

The combined assessment and direction also depended on the combined confidence score. A unit could be deemed “poor” only with a “medium” or “high” confidence (combined confidence score >2), otherwise the worst assessment would be “moderate”. This check balances the strong negative value of a “poor” individual rating in the combined assessment. The combined direction score was “improving” if the overall direction score was greater than 1, “declining” if the score was less than -0.25, and “no change” otherwise. Thus, multiple individual “declining” ratings at low confidence would be required to trigger a combined “declining” direction assessment. Similarly, multiple “improving” ratings for a given HUC 10 at low confidence would be needed to trigger an overall “improving” direction assessment.

Most of the toxic metals assessed are listed as “priority pollutants” by US EPA, and were rated “moderate” when the levels approached within one order of magnitude of the Criterion Continuous Concentration (CCC) limit. Many of the CCC levels are hardness dependent. Hardness was calculated for each HUC 10 unit. Since there is no standard for hardness itself, hardness was not included in the overall standard water quality assessment. However, the mean hardness for each HUC 10 unit was used to calculate the CCC, for each metal with hardness-dependent toxicity, in each unit (Table 3).

Table 3. Hardness data for HUC 10 units

HUC 10 ¹	Mean ²	Water samples collected		N	From	To
		Trend ²	Conf. ³			
1	0.94	-0.025	0.79	15	1978	2004
2	2.43	-0.113	0.87	20	1979	2004
3	4.80	0.074	1.40	81	1978	2004
4	5.82	0.049	0.45	23	1974	2004
5	2.68	-0.417	1.00	12	1974	1985
6	3.49	0.124	0.19	14	1978	1993
7	27.08	1.387	0.61	9	1970	1987
8	1.59	-0.338	10.11	2006	1951	2004
9	6.24	0.060	1.81	651	1978	2000
10	10.07	-0.372	0.24	16	1969	1993
11	11.99	-0.238	7.30	854	1968	2002
12	9.99	-0.971	0.65	24	1974	1987

¹ Arbitrary numbering of the HUC10 regions in SEKI. See Figure 32

² Mean units mg as CaCO₃ L⁻¹, trend units mg as CaCO₃ L⁻¹ y⁻¹

³ Values greater than 1 indicate trend confidence greater than 95%

Standard water quality parameters

The standard water-quality-parameter combined assessment is based on the individual assessments of ANC, DO, and pH. The mean values, trends, and number of water samples and time frame of sampling in each HUC 10 unit are shown in Table 4. Figure 33 shows four units have “moderate” condition assessments. Three units are “declining”, and two of these have high

confidence, based on thousands of records for individual parameters. However, both the ANC and pH standards defined by US EPA may not be appropriate for high elevation lakes and streams. The alkalinity standard is a minimum of almost $200 \mu\text{eq L}^{-1}$. This level is easily achieved in lower elevation lakes and stream in SEKI. It appears the standard is appropriate for lower elevations, and is not appropriate for water bodies having naturally low alkalinity. In lakes and streams with low alkalinity, the pH can easily be determined by dissolved atmospheric CO_2 , i.e. the pCO_2 . Under these conditions, a pH between 5.5 and 6.0 is expected. However, the US EPA pH standard is 6.5 to 9.0. Given naturally low alkalinity, it appears the minimum pH standard also is not appropriate for SEKI. If the ANC standard were lowered to $20 \mu\text{eq L}^{-1}$ and the minimum pH lowered to 5.5, only one “moderate” unit would remain. The remaining units would be assessed as “good”.

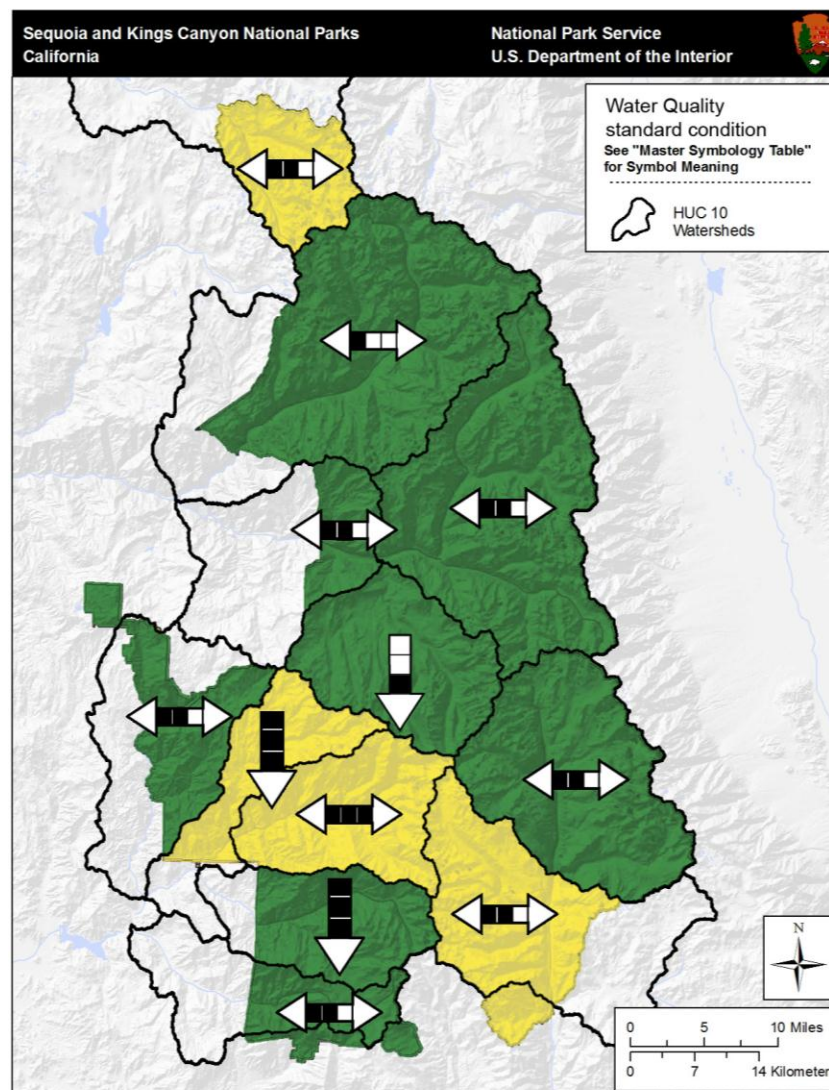


Figure 33. Standard water quality condition assessment.

Table 4. Acid Neutralizing Capacity, Dissolved Oxygen, and pH assessment data for HUC 10 units

HUC 10 ¹	Parameter	Mean	Trend	Conf. ²	N	Water samples collected	
						From	To
1	ANC ^{3,6}	29.97	-	-	7	1978	1978
2		69.93	0.000	-	16	1968	1979
3		77.66	1.811	0.20	20	1978	1983
4		115.12	-1.547	0.56	21	1974	1981
5		88.09	-9.990	1.00	11	1974	1978
6		69.34	5.741	0.41	15	1978	1993
7		364.06	0.332	0.01	14	1970	1988
8		418.13	-6.375	3.08	192	1951	1993
9		74.66	-5.869	2.04	54	1978	1993
10		163.30	-14.869	0.49	23	1969	1993
11		453.35	-6.012	1.78	190	1968	1993
12		331.31	-18.529	1.12	23	1974	1988
1	DO ^{4,6}	-	-	-	-	-	-
2		-	-	-	-	-	-
3		-	-	-	-	-	-
4		10.03	0.016	0.32	36	1974	1981
5		-	-	-	-	-	-
6		4.80	-	-	1	1993	1993
7		8.20	-	-	5	1980	1980
8		10.12	-0.002	0.09	279	1951	1993
9		8.28	-0.092	1.89	34	1980	1993
10		7.64	-0.403	0.87	9	1969	1993
11		9.27	-0.285	3.91	262	1968	1993
12		9.82	0.018	0.14	22	1972	1988
1	pH ^{5,6}	6.78	-0.019	0.74	15	1978	2004
2		6.91	-0.005	0.36	25	1968	2004
3		7.00	0.003	0.60	213	1974	2004
4		7.13	0.003	0.58	50	1974	2004
5		6.73	0.050	0.94	25	1974	1985
6		6.96	-0.010	0.14	49	1978	1993
7		7.87	-0.011	0.22	33	1970	2003
8		6.36	-0.024	13.00	4500	1951	2004
9		6.86	0.005	1.45	1035	1978	2003
10		6.67	-0.094	2.59	71	1969	1993
11		7.62	0.013	9.48	1501	1968	2002
12		7.62	0.050	1.81	68	1972	1988

¹ Arbitrary numbering of the HUC10 regions in SEKI. See Figure 32² Values greater than 1 indicate trend confidence greater than 95%³ ANC minimum 20 mg as CaCO₃ L⁻¹, mean units $\mu\text{eq L}^{-1}$, trend units $\mu\text{eq L}^{-1} \text{y}^{-1}$ ⁴ DO minimum 5 mg O₂ L⁻¹, mean units mg O₂ L⁻¹, trend units mg O₂ L⁻¹ y⁻¹⁵ pH minimum 6.5, mean in standard pH units, trend units pH y⁻¹⁶ US EPA national water quality criteria (USEPA 2009b)

Nutrients

The combined water-quality-parameter assessment for nutrients is based on the individual assessments of NO_3^- , NH_4^+ , and PO_4^{3-} (actually, HPO_4^{2-} and H_2PO_4^-). The mean values, trends, and number of water samples and time frame of sampling in each HUC 10 unit are shown in Table 5. Figure 34 shows one unit has a “moderate” condition assessment. Three have a “declining” condition, based mainly on trends of significantly increasing PO_4^{3-} in these units. Two of the three have “medium” confidence and one has “low”. Upon closer examination, the two “medium” confidence units are barely above “low”, having 72 and 84 samples. In contrast, two units are improving with “high” confidence based on thousands of samples in each unit. These improving units are also have improving in NO_3^- levels, assessed with high confidence based on thousands of samples each. Relatively few nutrient records are available for KNP.

Table 5. Nutrients NO_3^- , NH_4^+ , and PO_4^{3-} assessment data for HUC 10 units

HUC 10 ¹	Parameter	Mean	Trend	Conf. ²	Water samples collected		
					N	From	To
1	NO_3^- ^{3,6}	0.02	0.001	0.82	8	1985	2004
2		0.02	-0.001	0.82	8	1985	2004
3		0.06	0.000	0.23	79	1974	2004
4		0.02	0.000	0.06	27	1974	2004
5		0.02	-0.002	1.11	13	1974	1985
6		0.04	0.028	0.67	6	1985	1993
7		0.03	-	-	1	1977	1977
8		0.03	0.000	3.51	3827	1951	2003
9		0.00	0.000	-	959	1983	2000
10		0.08	0.005	0.53	9	1969	1993
11		0.01	-0.002	7.38	1322	1968	2002
12		0.03	-0.007	0.38	15	1972	1985
1	NH_4^+ ^{4,6}	0.01	-	-	6	2004	2004
2		0.01	-	-	3	2004	2004
3		0.01	0.000	0.61	56	1974	2004
4		0.00	0.000	-	29	1977	1981
5		0.05	-	-	18	1974	1974
6		0.01	-	-	17	1984	1984
7		0.01	0.008	-	2	1987	1988
8		0.01	0.000	1.91	1479	1977	2003
9		0.03	-0.001	0.28	84	1983	1999
10		0.01	0.001	0.63	11	1969	1984
11		0.05	0.000	0.42	328	1968	2002
12		0.01	-0.001	0.33	3	1977	1987
1	PO_4^{3-} ^{3-5,6}	-	-	-	-	-	-
2		-	-	-	-	-	-
3		0.01	0.002	0.17	10	1974	1983
4		0.00	-0.001	0.66	43	1974	1983
5		0.01	-	-	8	1974	1974
6		0.00	0.005	2.93	84	1983	1993
7		0.01	0.000	1.15	32	1977	2003
8		0.00	0.000	3.90	2278	1973	2003
9		0.00	0.000	3.87	1004	1981	2003
10		0.00	0.000	0.19	89	1969	1993
11		0.01	0.000	4.41	1497	1968	2002
12		0.00	0.001	2.32	78	1973	1988

¹ Arbitrary numbering of the HUC10 regions in SEKI. See Figure 32² Values greater than 1 indicate trend confidence greater than 95%³ NO_3^- 16 x PO_4^{3-} limit is 0.065 mg as N L^{-1} , mean units mg as N L^{-1} , trend units mg as N $\text{L}^{-1} \text{y}^{-1}$ ⁴ NH_4^+ maximum is 4.16 mg as N L^{-1} , mean units mg as N L^{-1} , trend units mg as N $\text{L}^{-1} \text{y}^{-1}$ ⁵ PO_4^{3-} maximum 0.015 mg as P L^{-1} , mean units mg as P L^{-1} , trend units mg as P $\text{L}^{-1} \text{y}^{-1}$ ⁶ US EPA national water quality criteria (USEPA 2000, 2009b)

Nitrate was measured in all twelve HUC 10 units, three with high confidence. Nitrate is not listed as a priority pollutant by US EPA, although ammonium is. There is no CCC for nitrate, although it is regulated in drinking water. The main concern in SEKI is the potential for eutrophication. We used the US EPA recommended reference for nutrients in streams within nutrient ecoregion II (USEPA 2000) to set a limit for nitrate. The reference contains no criterion for nitrate. However, nitrogen and phosphorus levels are available for level III ecoregion 5 containing SEKI. The 25th percentile (P25) of total nitrogen reported in this region is 0.29 mg N L⁻¹, and the P25 of total phosphorus is 0.015 mg P L⁻¹. The ratio of nitrogen to phosphorus in algae is 16:1, and this ratio was used to determine our maximum limit for nitrogen, or 0.11 mg N L⁻¹. In SIEN records, nitrate comprises approximately 60% of total nitrogen. Although this value varies substantially seasonally (see Appendix), we used 60% of the total nitrogen limit, or 0.065 mg N L⁻¹ as the nitrate limit. There were two units with “moderate” condition; however, these had low confidence based on sample number. No units were deteriorating. Three were improving, and two of these were high confidence, each with more than one thousand samples. With low confidence in 8 of 12 units, it is not possible to exclude nitrate as a significant stressor in SEKI despite the current assessment.

Ammonium is a non-priority pollutant listed by US EPA, and has a CCC that can be calculated depending on pH and T, using a formula (Table 6) selected by the presence or absence of certain species or life stages (USEPA 2009a). Ammonia was measured in all twelve units. All were assessed as “good”. We assessed ammonium using an overall more stringent-SEKI CCC. This value was calculated using pH 7.5 and 10 °C, and evaluated to a maximum limit of 4.2 mg N L⁻¹. Individual CCCs for each unit calculated using HUC 10 mean pH and temperature values were higher in 10 of 12 units than the overall CCC we used. The overall CCC was not exceeded in any unit, and ammonium exceeded 1% of the CCC in only one unit. None of the units were deteriorating, and one was improving with high confidence. However, 8 of 12 units were sampled with low confidence. Consequently, it is difficult to exclude ammonium as a potential stressor in SEKI.

Table 6. Equations to calculate the CCC of ammonium and hardness dependent priority pollutant metals Pb, Cu, Zn, and Cd (USEPA 2009b). Hardness is the sum of Ca²⁺ and Mg²⁺ (mg L⁻¹).

Pollutant	CCC equation
NH ₄ ⁺ ¹	$0.814 * (0.0676 * (1 + 10^{(7.688 - \text{pH})})^{-1} + 2.912 * (1 + 10^{(\text{pH} - 7.688)})^{-1}) * \min(2.852, 2.26 * 10^{(0.028 * (25 - T))})$
Pb	$(1.46203 - \ln(\text{hardness})) * 0.145712 * e^{(1.273 * \ln(\text{hardness}) - 4.705)}$
Cu ²	$0.96 * e^{(0.8545 * \ln(\text{hardness}) - 1.702)}$
Zn	$0.978 * e^{(0.8473 * \ln(\text{hardness}) + 0.884)}$
Cd	$(1.101672 - \ln(\text{hardness})) * 0.041838 * e^{(0.7409 * \ln(\text{hardness}) - 4.719)}$

¹ US EPA CCC for mussels absent and early fish in early life states present (USEPA 2009a)

² The Biotic Ligand Model (BLM) is recommended to calculate the CCC for copper in fresh water (USEPA 2007b). The previously recommended CCC equation for copper was used instead to estimate the CCC, since the BLM-based CCC is not readily calculated.

Phosphorus was measured in 10 of 12 HUC 10 units in SEKI. Six of ten were sampled sufficiently to assess units with medium to high confidence. The maximum limit for phosphorus was taken from the US EPA recommended reference for nutrients in streams within nutrient ecoregion II (USEPA 2000), and was the P25 for total phosphorus in level III ecoregion 5 containing SEKI. This value was $0.015 \text{ mg P L}^{-1}$. Four units were “moderate” condition. Three of these were deteriorating, two with medium confidence, and one with low confidence. Seven units were “good” condition and two of these were improving with high confidence. Although the locations of the moderate condition units seem to be inconsistent with atmospheric deposition as the major source of phosphorus, the low confidence or absence of data in several units makes it difficult to exclude phosphorus as a stressor in SEKI.

When comparing the observed PO_4^{3-} levels in the HUC 10 units to the sum of nitrate and ammonium, it appears that three units have nitrogen levels 2 to 3 times the standard 16:1 N-P molar ratio. However, only one of these has high confidence. This excess nitrogen may have a geochemical source, possibly roof pendants, as discussed above. The other units have N:P very close to the standard ratio. With no widespread elevation of nitrogen over phosphorus, it appears exogenous nitrate and ammonium are not likely significant stressors. In fact, nitrogen can only have an impact if sufficiently high levels of phosphorus are available, otherwise P is a limiting nutrient. Phosphate is increasing significantly in three HUC 10 units, two of these have medium confidence and one has low confidence. Phosphate is decreasing in two units with high confidence, and nitrogen is also decreasing. These observations support a local origin for nutrients, or decreasing quantities of exogenous phosphorus. There is not enough information in database records to distinguish between exogenous nitrogen deposition and nitrogen fixation. Although the assessment indicates mostly good conditions regarding nutrients, given the limited coverage and duration of nutrient sampling in SEKI, it is not possible to exclude nutrients as significant stressors.

Toxic metals

The combined water-quality-parameter assessment for toxic metals is based on the individual assessments of Pb, Hg, Cu, Zn, and Cd. The mean values, trends, and number of water samples and time frame of sampling in each HUC 10 unit are shown in Table 7. Figure 35 shows six units with a “moderate” condition assessment. One has a “declining” condition, based mainly on trends of significantly increasing Cu and Zn in the units. Two units in northern KNP have no data. Toxic metal testing records in the SIEN database are limited in frequency, duration, and coverage of SEKI. However, in many units and for many of the metals examined here, the records indicate levels approaching or above the CCC calculated (Table 6) based on water hardness in each unit (Table 3).

Table 7. Priority pollutants Pb, Hg, Cu, Zn, and Cd assessment data for HUC 10 units

HUC 10 ¹	Parameter	CCC ²	Mean ³	Trend ³	Conf. ⁵	Water samples		
						N	From	To
1	Pb	0.03	-	-	-	-	-	-
2		0.10	-	-	-	-	-	-
3		0.19	-	-	-	-	-	-
4		0.18	0.00	0.000	-	12	1977	1981
5		0.14	-	-	-	-	-	-
6		0.15	-	-	-	-	-	-
7		1.17	1.52	-0.120	0.47	4	1987	2003
8		0.04	11.18	-0.890	0.80	46	1973	2003
9		0.22	0.08	-	-	1	2003	2003
10		0.77	-	-	-	-	-	-
11		0.47	2.00	-	-	3	1987	1987
12		0.20	2.00	-	-	3	1987	1987
1	Hg	0.77	-	-	-	-	-	-
2		0.77	-	-	-	-	-	-
3		0.77	-	-	-	-	-	-
4		0.77	0.00	0.000	-	12	1977	1981
5		0.77	-	-	-	-	-	-
6		0.77	-	-	-	-	-	-
7		0.77	0.20	-	-	3	1987	1987
8		0.77	0.47	-0.035	0.60	38	1973	1993
9		0.77	-	-	-	-	-	-
10		0.77	-	-	-	-	-	-
11		0.77	0.20	-	-	3	1987	1987
12		0.77	0.20	-	-	3	1987	1987

¹ Arbitrary numbering of the HUC10 regions in SEKI. See Figure 32

² Criterion Continuous Concentration calculated, US EPA national water quality criteria (USEPA 2009b)

³ Mean units $\mu\text{g L}^{-1}$, trend units $\mu\text{g L}^{-1} \text{y}^{-1}$

⁵ Values greater than 1 indicate trend confidence greater than 95%

Lead was measured in six of the twelve HUC 10 units in SEKI, in all cases with a sample number we defined as providing low confidence (N <50). In four of these units, the measured lead levels were well above the calculated CCC for lead in the unit. In one, the lead level was slightly below the CCC. In one, lead was not detected. Lead appears to be a significant stressor currently.

Mercury was measured in five HUC 10 units, all low confidence. In four of these units, the measured mercury levels were within an order magnitude below the fixed CCC for mercury. In one unit, mercury was not detected. Mercury appears to be a significant potential stressor. Given the limited sampling and detection technology available at the time the samples were processed, it is not possible to exclude that possibility that mercury is currently a significant stressor.

Copper was measured in nine HUC 10 units, all low confidence. In three of these units, the mean copper levels were well above the calculated CCC for copper in the unit. In one unit, copper was not detected. Copper appears to be a significant potential stressor in certain HUC 10 units. However, given the limited area with relatively high levels of copper detected, the source may be

geochemical, and the local biota should be adapted to it. Nevertheless, given the low sample frequency, duration, and spatial coverage, it is not possible to exclude an exogenous source of copper, and the potential of significant impact of copper toxicity on sensitive species.

Zinc was measured in eight HUC 10 units, all low confidence. In three of these units, the mean zinc levels were well above the calculated CCC for zinc in the unit. Zinc appears to be a significant potential stressor in certain HUC 10 units. However, given the limited area with relatively high levels of zinc detected, the source may be geochemical, and the local biota should be adapted to it. Nevertheless, given the low sample frequency, duration, and spatial coverage, it is not possible to exclude an exogenous source of zinc, and the potential of significant impact of zinc toxicity on sensitive species.

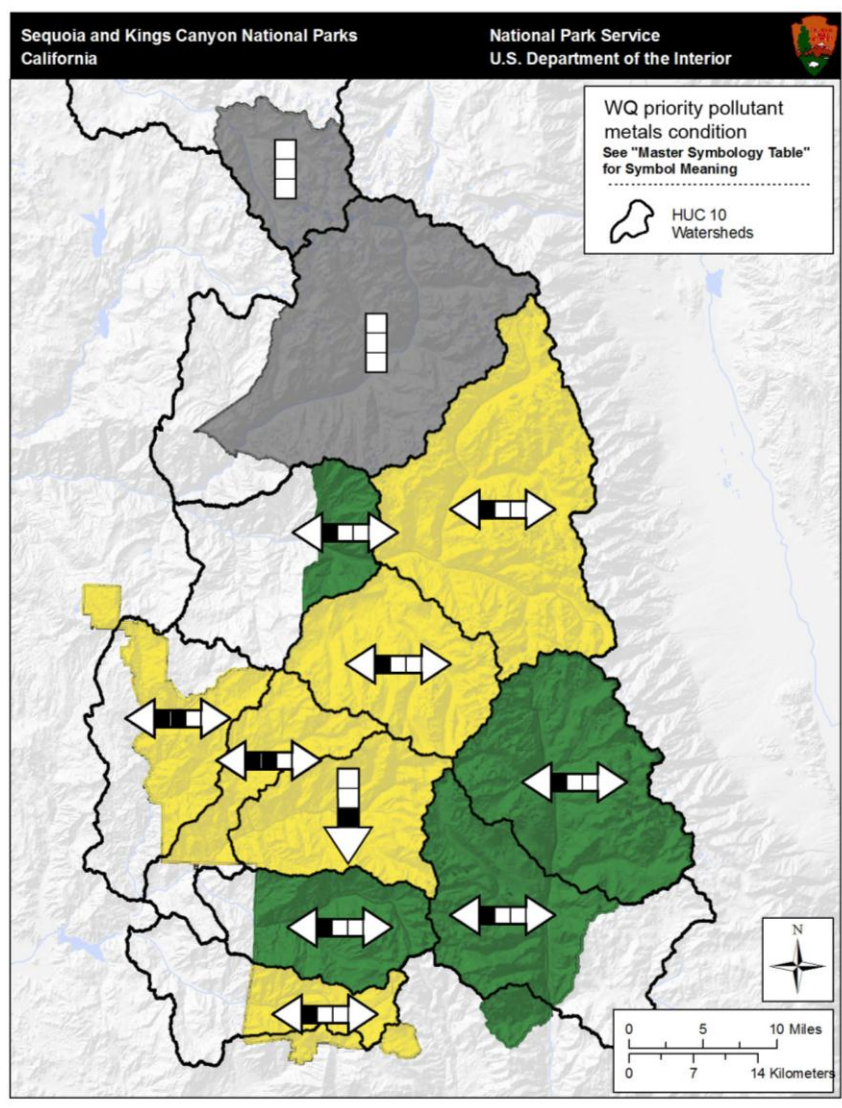


Figure35. Toxic metals water quality condition assessment

Cadmium was measured in four HUC 10 units, all low confidence. In two of these units, the mean cadmium levels were at or above the calculated CCC for cadmium in the unit. In one unit, cadmium was not detected. The limited frequency, duration, and spatial coverage of sampling makes statements regarding the general impact of cadmium on SEKI difficult. However, with half of the HUC 10 units having cadmium levels at or above the CCC suggests that additional sampling may be helpful in assessing the potential impact of this toxic metal on sensitive species.

Level of confidence in assessment

We have attempted to combine assessments for larger categories of water quality parameters by using a consistent set of rules for combining them. However, these rules themselves have not been rigorously tested with multiple sample data sets. They were tested for dependence on CCC changes, and other factors.

We decided to avoid assigning a “poor” condition assessment when low sample numbers were reported. We also attempted to avoid diluting a negative factor too much among other positive factors. Consequently, negative impacts were weighted more heavily and these were multiplied by confidence factors. In our method, a single strong negative could easily outweigh several weaker positives. These weighting factors seem to work well; however, this is a subjective determination.

We chose to lower the bar by one order of magnitude compared to the CCC in reporting a moderate condition for toxic metals, since in the cases of Pb, Hg, and Cd, there is no beneficial biological role. Otherwise the weighting factors were the same.

Gaps in understanding

There are significant seasonal effects on many water quality parameters. We had intended to use only the summer to fall data following snowmelt to avoid seasonal variation noise. However, the lack of data especially in the HUC 10 assessments required us to include winter data before snowmelt. Certain parameters did not exhibit as much seasonal variation, and more data from these could be retained.

In addition, seasonal variation is not consistent from year to year. There are differences in snow depth, the pattern of storms, temperature differences, etc. Consequently, it is not possible to select a specific date at which runoff snowmelt begins and ends. These effects also differ depending on the elevation of the sample site.

The geochemistry of the local terrain has been demonstrated to have a strong influence in certain locations within SEKI and elsewhere. At this time we do not fully understand the origin of certain nutrients and toxic metals, which is necessary to distinguish between geochemical and atmospheric sources of stressors.

It is clear that pesticides may have a significant impact on SEKI, however the data on these substances is very sparse. Reservoirs of certain persistent pesticides are expected to exist in anoxic acidic conditions, such as in lake sediments. We were able to examine records for only two SEKI lake sediment cores in the WACAP database, and one of these appeared to be altered by avalanche disturbance of the sediments.

It is not possible to assess potential impacts of climate with the current records in the database due to the lack of consistent frequent sampling at fixed locations for long duration. We cannot

fully distinguish between differences in climate, effects due to elevation differences, and geochemistry in the various catchments.

Recommendations for future study/research

Trend analysis is vitally important for understanding changing conditions in SEKI. Many water-quality studies have been conducted over the past 60 years in the Southern Sierra Nevada, however, few have produced data over a broad set of parameters obtained frequently during the water year, and spanning several decades. A dedicated effort could be undertaken to collect water samples perhaps once per week, or at least monthly, at specific sites representative of geochemistry, elevation, atmospheric deposition phenomena, biological, and other factors. If this effort spans several years to decades without interruption, excellent trend data could be obtained, and potential impacts of climate could be identified.

Differences in seasonal variation can be observed in data collected frequently in multiple years from the same locations during each year. Figure 36 shows an example of specific conductance data from two locations on the same stream, one at higher elevation. The samples were taken frequently for five years, and three years of data are shown. The two locations produce U-shaped curves, one above the other. The higher specific conductance curve was collected at lower elevation. This result is consistent with increasing alkalinity as water flows downstream in SEKI. The key observation is the striking differences between years. Runoff due to snowmelt occurring in spring dilutes streams and lakes, and results in lower specific conductance, after perhaps some pulses of mobilized ions. In two years, the peak of runoff occurred before 180 days (Figure 36A), and in one year, runoff peaked later (Figure 36B). It is also evident that the higher elevation peak in runoff occurred perhaps a month later than at lower elevation. Trends in flow, concentration, and timing of seasonal events must be identified in order to begin defining and documenting the extent of climate change, and begin to develop effective efforts to deal with it.

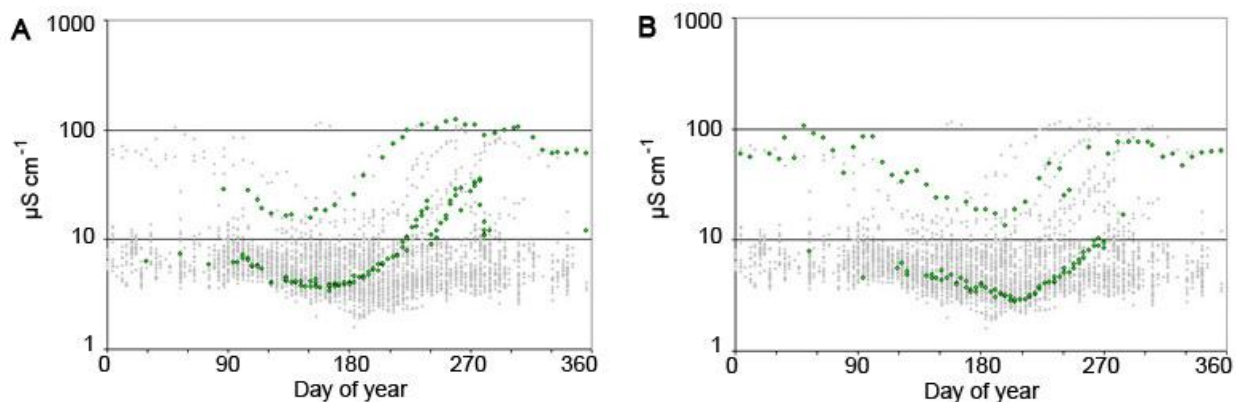


Figure 36. Seasonal variation of specific conductance. Gray points are all specific conductance data. Green points indicate measurements at two locations on the Marble Fork of the Kaweah at different elevations. The green points forming a lower conductance curve are from a high elevation lake outlet, and the higher conductance curve data are from a point farther downstream. Data were collected in successive years, 1997 (A), and 1998 (B). Gray points are all other data points.

Temperature is a water-quality parameter that could be measured continuously over long periods at relatively low cost, and a potentially good indicator of climate change effects on water bodies. Again, interannual variability can mask trends, making it important to continue measurements at key index sites over the long term. Both lakes and streams, particularly in headwater basins, should be included.

The impact of geochemistry on water quality is inadequately characterized. A database of mineral content in the catchments of SEKI would be helpful in determining whether toxic metals or nutrients are leaching from local rock, compounding the impact of atmospheric deposition. If geochemical data are not available, some sampling and analysis of mineral content could be required.

Toxic metals and pesticides appear to have the potential for significant impact on SEKI. A survey of these substances with additional sediment cores from lakes would be valuable in determining the location and potential reservoir of toxic metals and persistent pesticides that could be mobilized from lake sediments. Well-dated cores of undisturbed sediments are needed to chart the historic deposition and trends.

The SIEN and WACAP databases we used should be available as an online resource where queries are relatively simple. This work has just begun to explore the potential information contained within these databases. They should not be lost or used by only a limited number of people asking a narrow set of questions.

The data needed for long-term trend analysis can be gathered using relatively inexpensive sensors to record high-frequency temperature, conductivity, DO, and other water parameters. Additional data may be obtained using more traditional sampling methods at representative sites in lakes and streams. Such data, collected over several decades, would have very high value. This information is needed to determine trends of known and potential stressors in SEKI.

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Appendix

Standard Water Parameters

Acid neutralizing capacity

There were three independent ANC record sets in the SIEN database: 1) acid neutralizing capacity, water, unfiltered, fixed endpoint (pH 4.5) titration, field, mg L^{-1} as calcium carbonate; 2) alkalinity, water, filtered mg L^{-1} as calcium carbonate; and 3) acid neutralizing capacity, water, unfiltered, fixed endpoint (pH 4.5) titration, laboratory, mg L^{-1} as calcium carbonate.

Figure A1 shows low ANC is about one order of magnitude lower in lakes compared with streams. ANC decreases in streams seasonally, with the lowest values corresponding with peak snow melt.

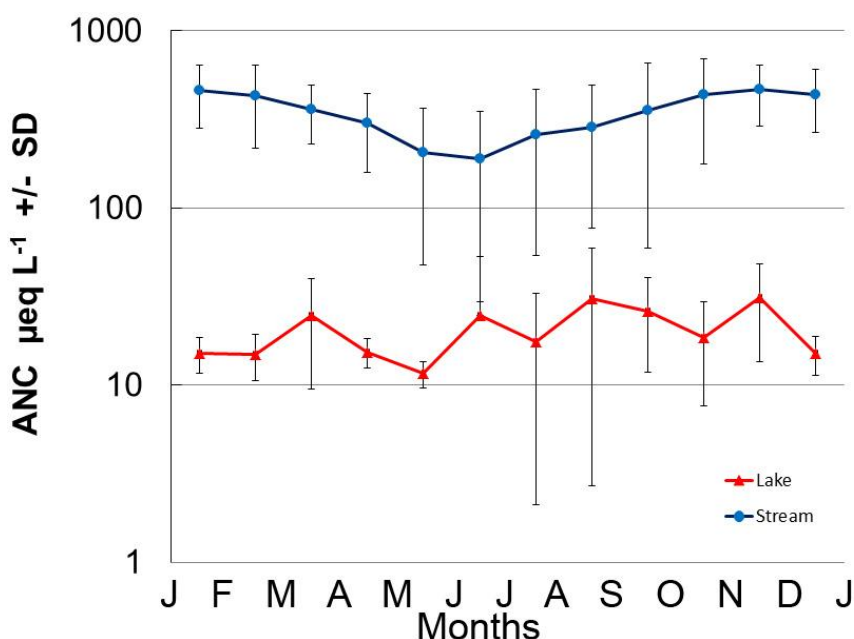


Figure A1. Seasonal variation of mean Acid Neutralizing Capacity (ANC) SEKI Lakes and Streams. ANC ($\mu\text{eq L}^{-1}$), 1951 to 1994. Seasonal mean ANC means and standard deviations were calculated. Lakes and lake outlets were combined as 'Lakes'. Rivers and creeks were combined as 'streams'.

pH

There were five independent pH record sets in the SIEN database: 1) pH, water, unfiltered, field, standard units; 2) pH, water, unfiltered, laboratory, standard units; 3) pH, field, standard units; 4) acidity, water, unfiltered, milligrams per liter as calcium carbonate; 5) acidity, water, unfiltered, heated, milligrams per liter as hydrogen ion. There was also a combined record: pH aggregated. The order of preference was (1), (3), (2) with a final total of 10,416 records. In the records for (1), (2) and (3), some were flagged to indicate errors. Instead of the aggregated set, we used the unflagged pH values to calculate a mean pH value.

Mean and median values of H^+ concentration were calculated for reference lakes and streams (Figure 6). There is no clear indication of a positive or negative trend in any lake or stream. However, there is some indication that the high elevation lakes and a creek feeding water into Emerald Lake were slightly more acidic during the 1980s than the 1990s. This variation would amount to a less than half of a pH unit, approximately 6.5 versus 6.2.

In SEKI lakes, the peak of pH occurs in late summer and fall, which corresponds to warmer temperatures and perhaps higher levels of photosynthesis (Figure A2). Carbon dioxide removed from water during photosynthesis raises pH. In streams the minimum pH occurs approximately during peak runoff during snow melt in June. Melted snow at high elevation would have the least alkalinity, and would dilute the water derived from soils at lower elevation which would have higher alkalinity. The highest pH in streams occurs in late fall, which could correspond with early precipitation leaching alkalinity from soils at lower elevations before precipitation falls predominantly as snow.

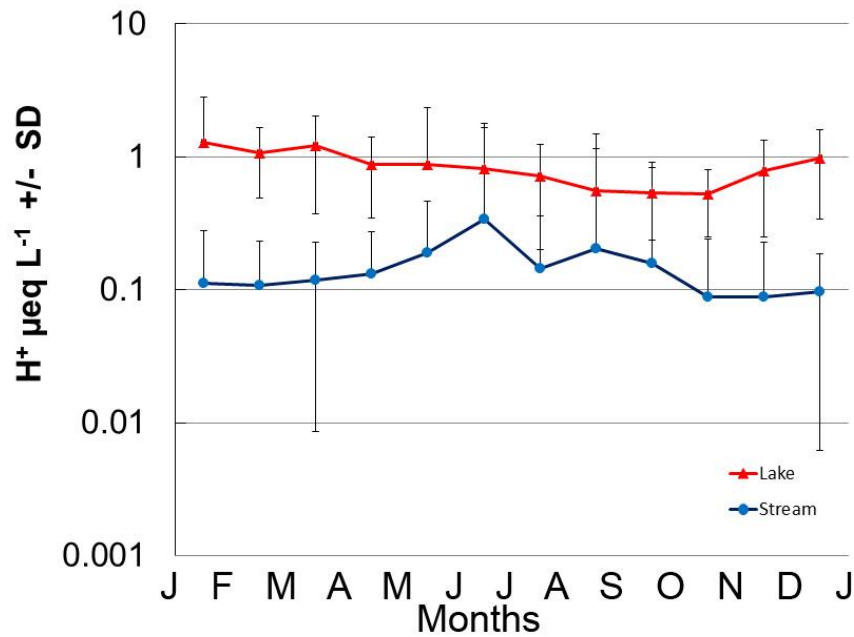


Figure A2. Seasonal variation of mean H^+ cation, concentration ($\mu\text{eq L}^{-1}$) in SEKI Lakes and Streams, 1951 to 2005. Seasonal mean H^+ concentrations and standard deviations were calculated. Lakes and lake outlets were combined as 'Lakes'. Rivers and creeks were combined as 'Streams'. Standard deviation values less than zero are not shown. Note, $1 \mu\text{eq L}^{-1}$ of H^+ is pH 6.

Temperature

There were two useful independent water temperature record sets in the SIEN database: 1) Temperature, water, degrees Celsius; 2) Temperature, water, degrees Fahrenheit. There was also a combined record: Temperature, water aggregated. The order was (1), (2) with (2) converted to Celsius, given a total of 5,718 records.

Seasonal lake and stream temperatures were calculated from SEKI site records grouped by month and water body type. Lakes have greater seasonal variation than streams and mean lake temperatures peak about one month later in the year than streams (Figure 9).

Reference lakes and streams sites show no clear trend of changing temperatures from 1980 through 2002 (Figure A3). Large variations can be attributed to low sample numbers. For example, East Fork in 1979 had mean and median values well above the values calculated in later years. There was only one sample in 1979 versus an average of 29 samples in later years.

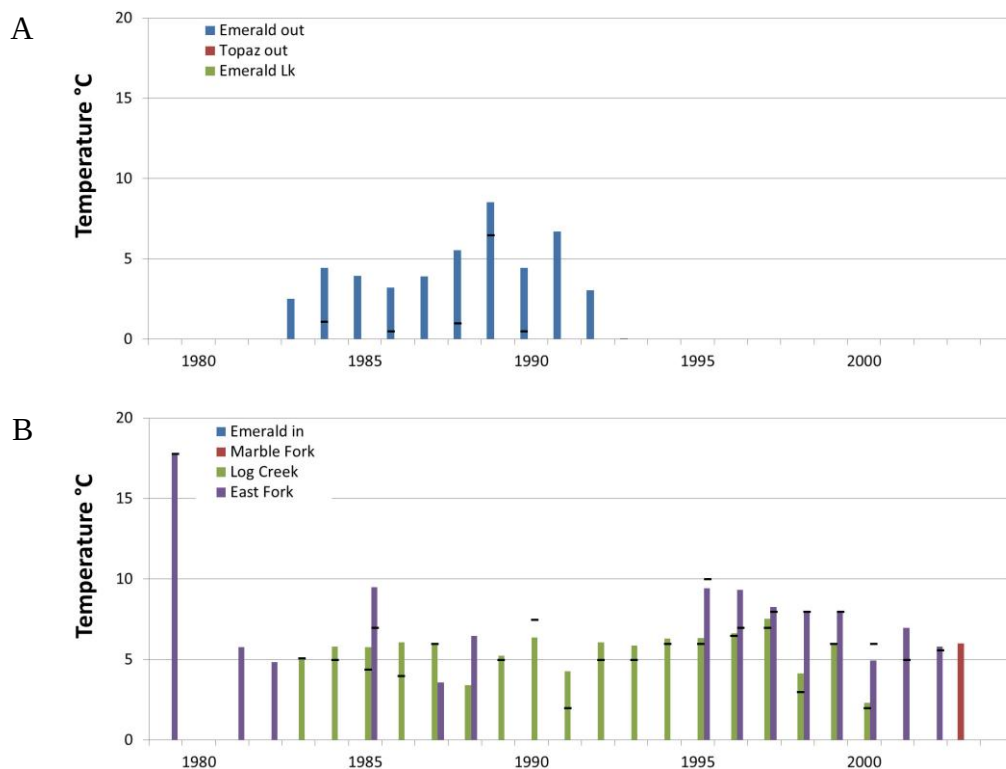


Figure A3. Mean temperature (°C) in reference site lakes (A) and streams (B). Median values are shown as dark horizontal bars.

Turbidity

There were five independent turbidity record sets in the SIEN database: 1) turbidity, water, unfiltered, Jackson turbidity units; 2) turbidity, water, unfiltered, milligrams per liter as silicon dioxide; 3) turbidity, water, unfiltered, nephelometric turbidity units; 4) turbidity, field nephelometric turbidity units, NTU; 5) turbidity, water, unfiltered, laboratory, nephelometric turbidity units. There was also an aggregated turbidity with a total of 775 records.

Mean turbidity in SEKI appears to have a strong elevational dependence (Figure 11). Most high elevation sites have low turbidity below 1 NTU. The turbidity increases as elevation decreases; however, mean turbidity did not typically rise above 10 NTU, still relatively low.

Seasonal turbidity in SEKI lakes and streams were lowest in late September and October when stream flows were lowest (Figure A4). During this time, finer suspended sediment particles might have an opportunity to settle. Peak stream turbidity occurred in December and January, corresponding to lower elevation rain. Lake turbidity was not measured during late fall, winter, and spring. A secondary peak in turbidity occurred in April, which may correspond to early snowmelt at lower elevation. Peak runoff does not necessarily cause higher turbidity, perhaps due to the presence of less soil at higher elevation.

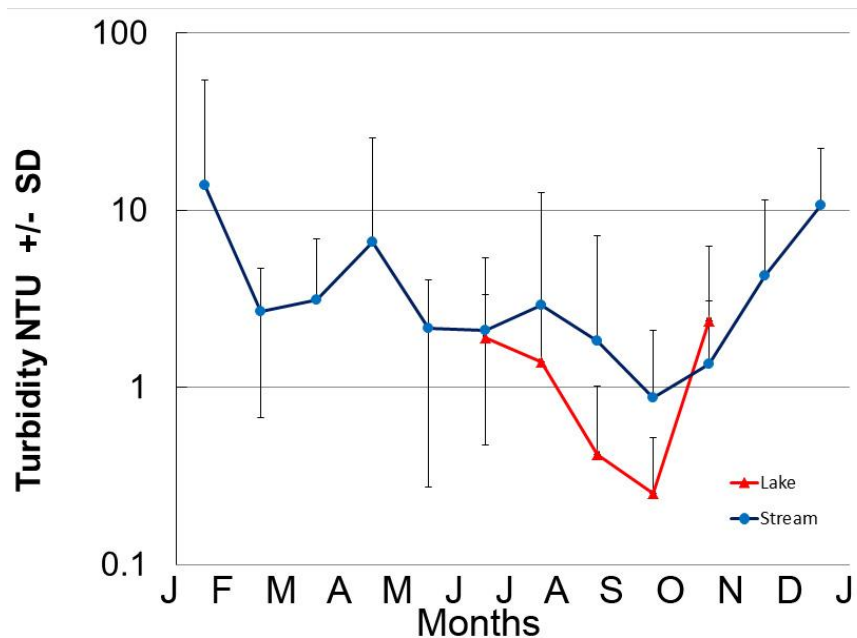


Figure A4. Seasonal variation of turbidity in SEKI streams and lakes, 1951 to 2004. Lakes and lake outlets were combined as 'lakes'. Rivers and creeks were combined as 'streams'.

Dissolved Oxygen

There were five independent Dissolved Oxygen (DO) record sets in the SIEN database: 1) turbidity, water, unfiltered, Jackson turbidity units; 2) turbidity, water, unfiltered, milligrams per liter as silicon dioxide; 3) turbidity, water, unfiltered, nephelometric turbidity units; 4) turbidity, field nephelometric turbidity units, NTU; 5) turbidity, water, unfiltered, laboratory, nephelometric turbidity units. There was also an aggregated turbidity with a total of 775 records.

Mean DO in SEKI appears to have very little elevational dependence (Figure A5). Some locations have DO levels between 5 and 7.5 mg L⁻¹, as indicated. Low DO is a seasonal effect stronger in lakes than in streams, occurring during the low flow months of summer. See *Dissolved Oxygen* in “Spatial and temporal analyses”.

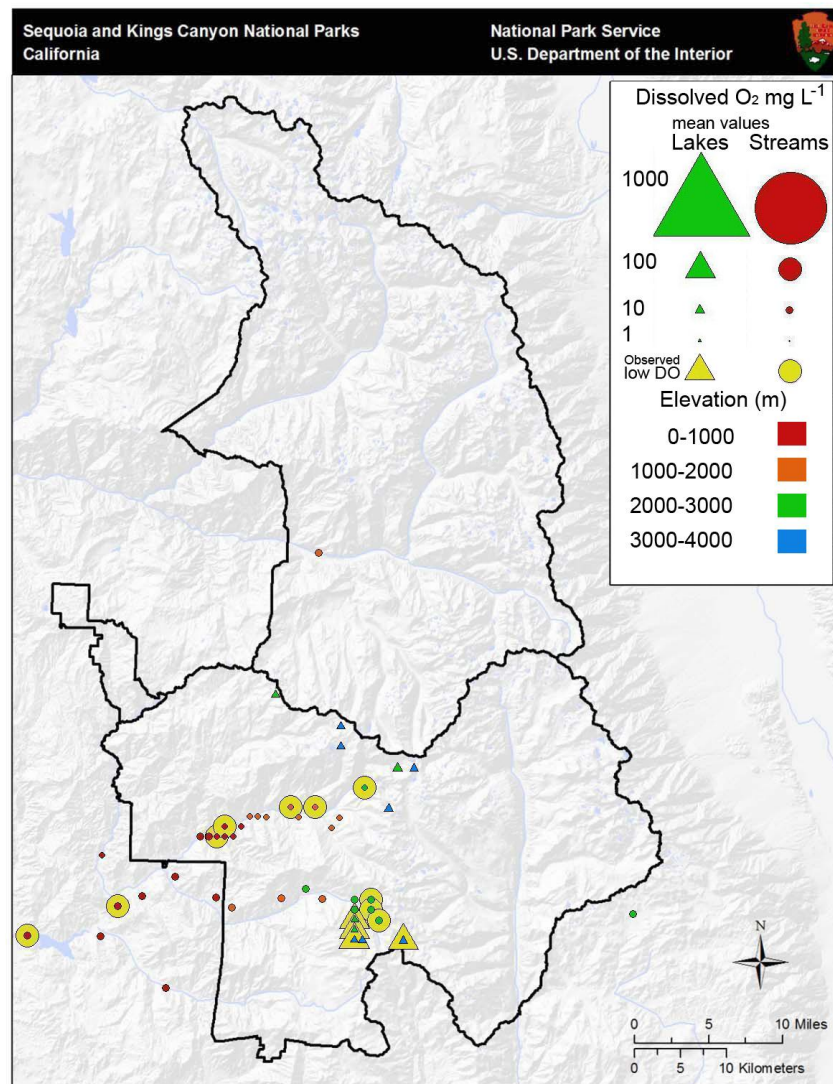


Figure A5. Mean dissolved oxygen measured in SEKI. Lakes are triangles, streams are circles, values proportional to area. Elevation bands (1000 m) are represented by different colors. Yellow circles and squares indicate one or more DO measurements at that site less than 7.5 mg L⁻¹.

Specific Conductance

There were four independent Specific Conductance (SpCond) record sets in the SIEN database: 1) specific conductance, water, unfiltered, field, microsiemens per centimeter at 25 degrees Celsius; 2) specific conductance, water, unfiltered, microsiemens per centimeter at 25 degrees Celsius; 3) specific conductance, non-temperature corrected, water, unfiltered, microsiemens per centimeter; 4) specific conductance, water, unfiltered, laboratory, microsiemens per centimeter at 25 degrees Celsius;. There was also an aggregated specific conductance record set produced from the above with preference order 1), 2), 4), and 3), with a total of 10994 records.

Specific conductance varies seasonally in a manner consistent with surface flow variation related to snow melt (Figure A6). Lake SpCond is approximately one order of magnitude lower than streams. There is very little seasonal variation of SpCond which suggests that ions in lakes enter during snow melt, and remain approximately constant through the year. In contrast, stream SpCond varies to a greater extent with the lowest values at approximately the same time as peak flow due to snow melt.

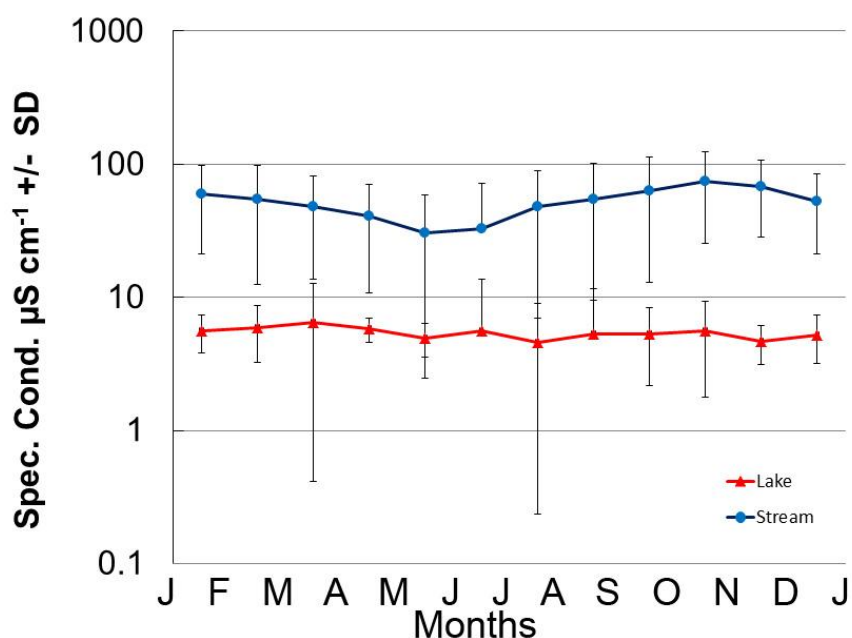


Figure A6. Seasonal variation of specific conductance in SEKI streams and lakes, 1951 to 2004. Lakes and lake outlets were combined as 'lakes'. Rivers and creeks were combined as 'streams'.

SEKI reference sites indicate consistently low SpCond in high elevation lakes, increasing as elevation decreases (Figure A7). Reference data for ANC is limited (not shown), but have essentially the same elevational dependence. A large fraction of the ions producing specific conductance are the same that produce acid neutralizing capacity.

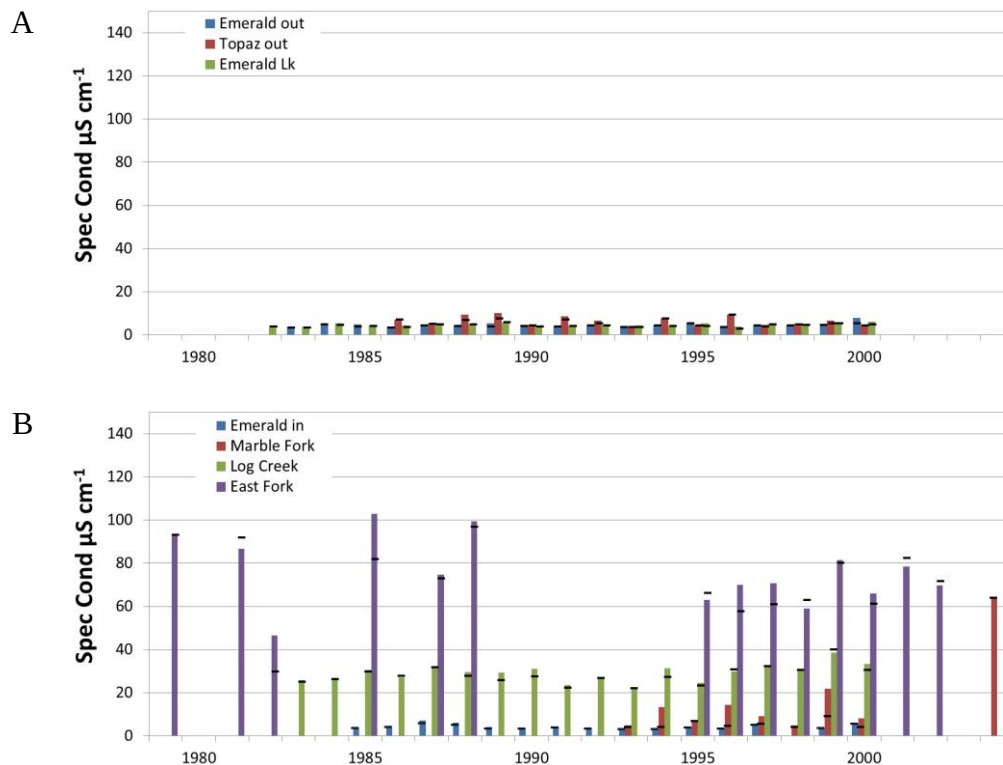


Figure A7. Mean specific conductance ($\mu\text{S cm}^{-1}$) in reference site lakes (A) and streams (B). Median values are shown as dark horizontal bars. Note Marble Fork 2004, $N_{2004}=2$, average N for all years is 65.

Calcium

There were three independent calcium record sets in the SIEN database: 1) calcium, water, unfiltered, milligrams per liter as calcium carbonate; 2) calcium, water, filtered, milligrams per liter; 3) calcium, water, filtered, micrograms per liter. There was also an aggregated calcium record set produced from the above with preference order 1), and 2), with a total of 8786 records.

Calcium concentrations in SEKI appear to have some dependence on elevation and local geochemistry (Figure A8). High elevation lakes have mean calcium concentrations about one order of magnitude lower than streams. Outside the Park, the Kaweah has lower calcium, suggesting possible dilution with groundwater. The highest concentration is near the SNP headquarters area.

The seasonal variation of calcium concentration in lakes and streams is limited (Figure A9). Lakes have calcium levels approximately one order of magnitude lower than streams. The decrease in calcium is likely due to dilution from snow melt.

Reference sites show a consistent elevational effect in calcium concentration with higher elevation lakes having much lower levels than lower elevation streams (Figure A10). There is no apparent trend indicating a change in calcium levels over time.

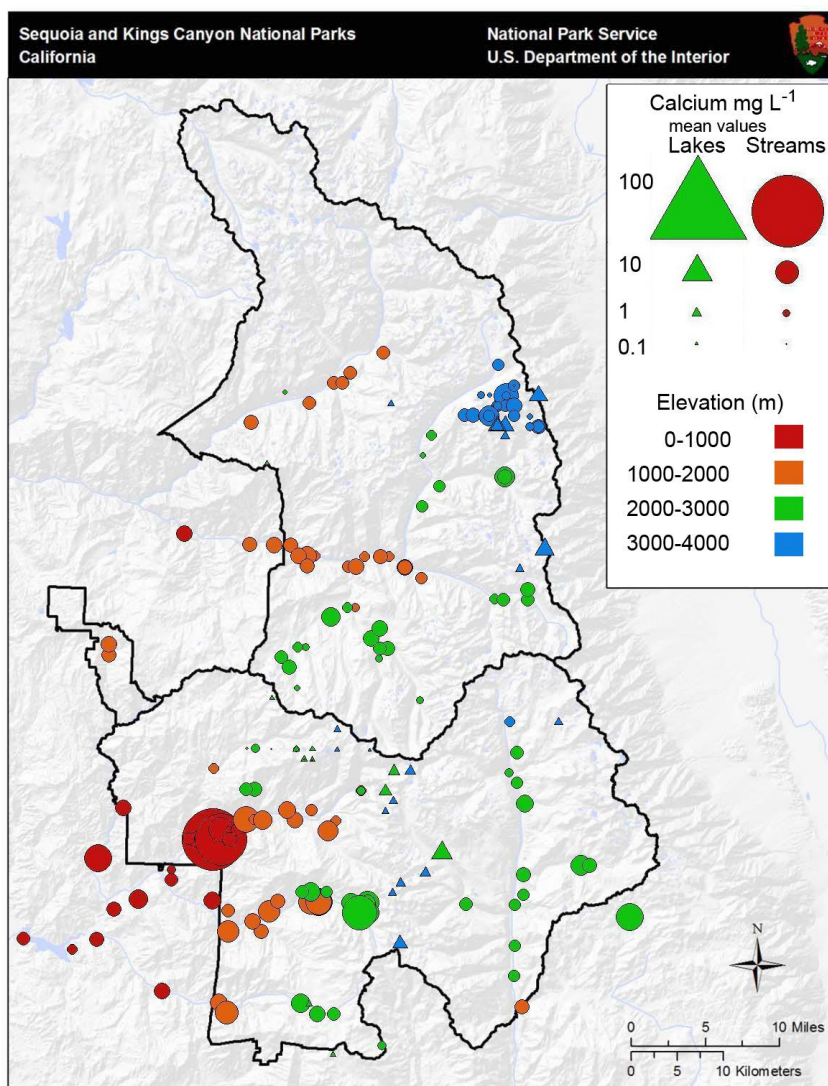


Figure A8. Mean calcium measured in SEKI. Lakes are triangles, streams are circles, values proportional to area. Elevation bands (1000 m) are represented by different colors.

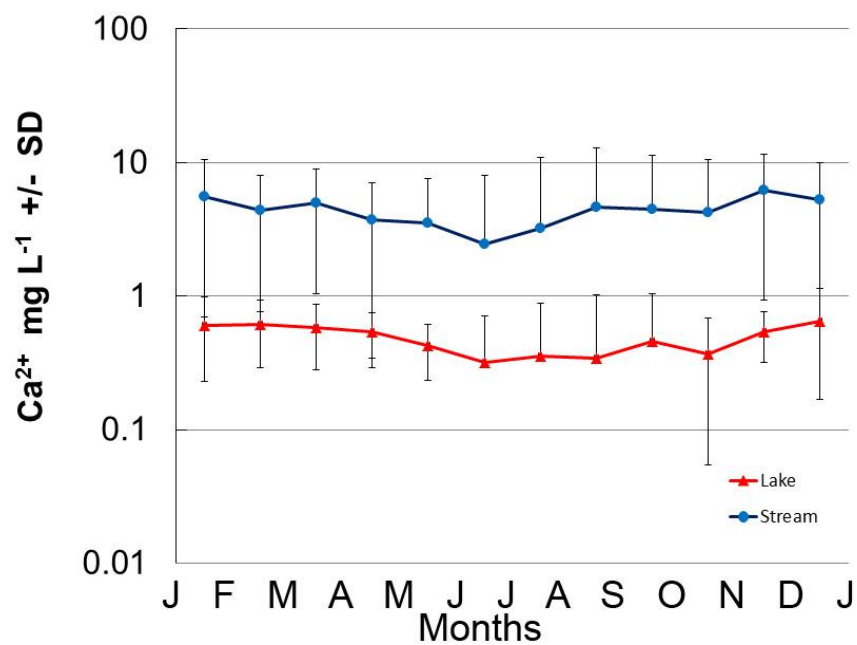


Figure A9. Seasonal variation of calcium in SEKI streams and lakes, 1951 to 2004. Lakes and lake outlets were combined as 'lakes'. Rivers and creeks were combined as 'streams'.

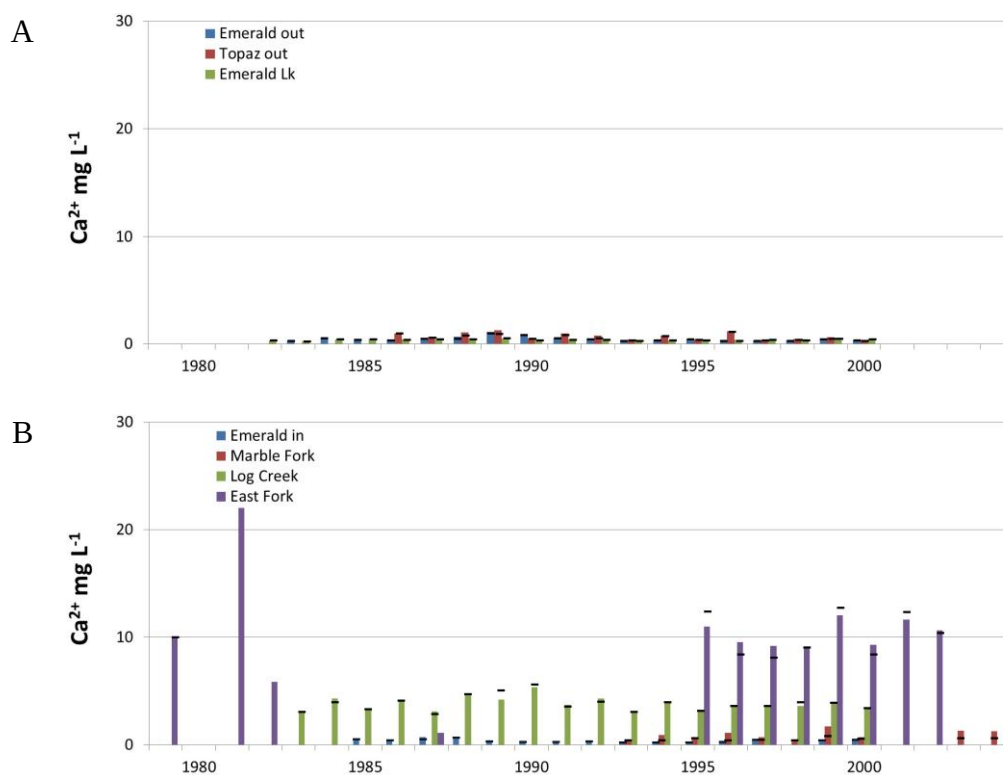


Figure A10. Mean calcium (mg L⁻¹) in reference site lakes (A) and streams (B). Median values are shown as dark horizontal bars.

Magnesium

There were two independent magnesium record sets in the SIEN database: 1) magnesium, water, filtered, milligrams per liter; 2) magnesium, water, filtered, micrograms per liter. There was also an aggregated magnesium record set produced from the above with a total of 8654 records.

Magnesium concentrations in SEKI seem to have some dependence on elevation and local geochemistry (Figure A11). High elevation lakes tend to have magnesium concentrations about one order of magnitude lower than streams. However, outside the Park, the Kaweah has a lower magnesium level, suggesting possible dilution with groundwater. The highest concentration is near the SNP headquarters area.

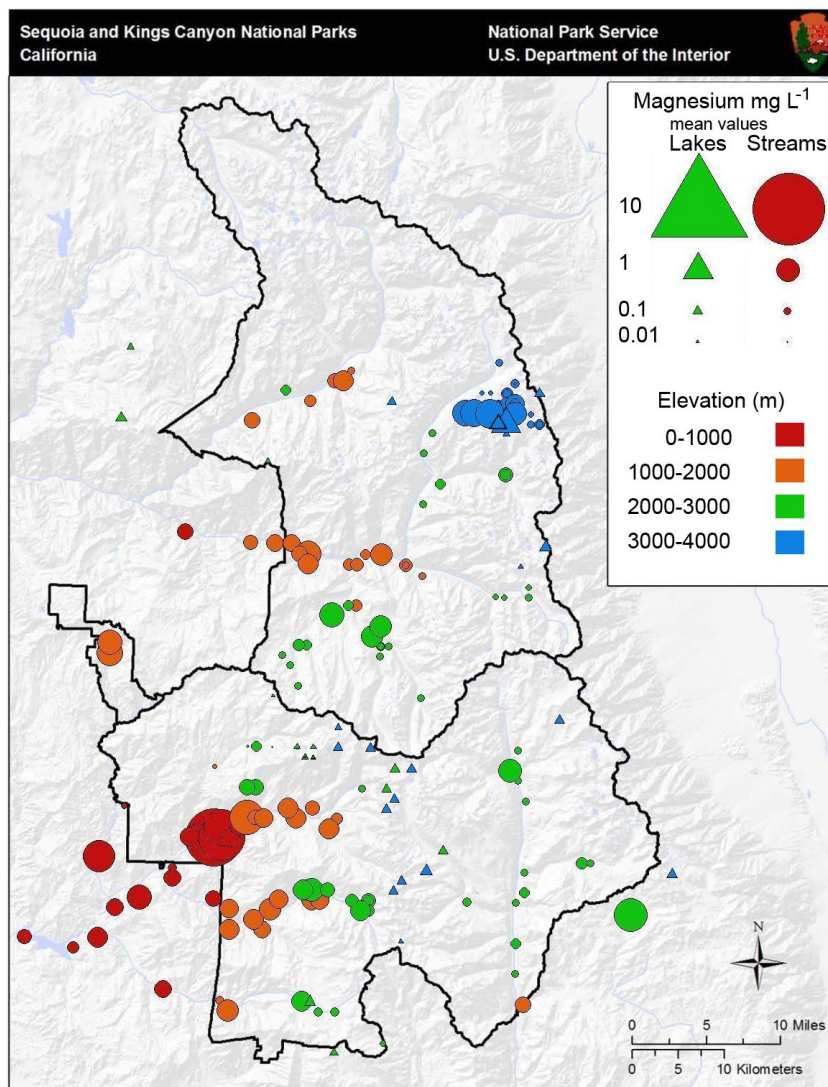


Figure A11. Mean magnesium measured in SEKI. Lakes are triangles, streams are circles, values proportional to area. Elevation bands (1000 m) are represented by different colors.

The seasonal variation of magnesium concentration in lakes is limited; however, streams have a seasonal decrease of about one half of an order of magnitude coinciding with snow melt (Figure A12). The decrease in magnesium is likely due to dilution from snow melt runoff.

Reference sites show a consistent elevational effect in magnesium concentration with higher elevation lakes having much lower levels than lower elevation streams (Figure A13). There is no apparent trend indicating a change of magnesium levels at any reference site over time.

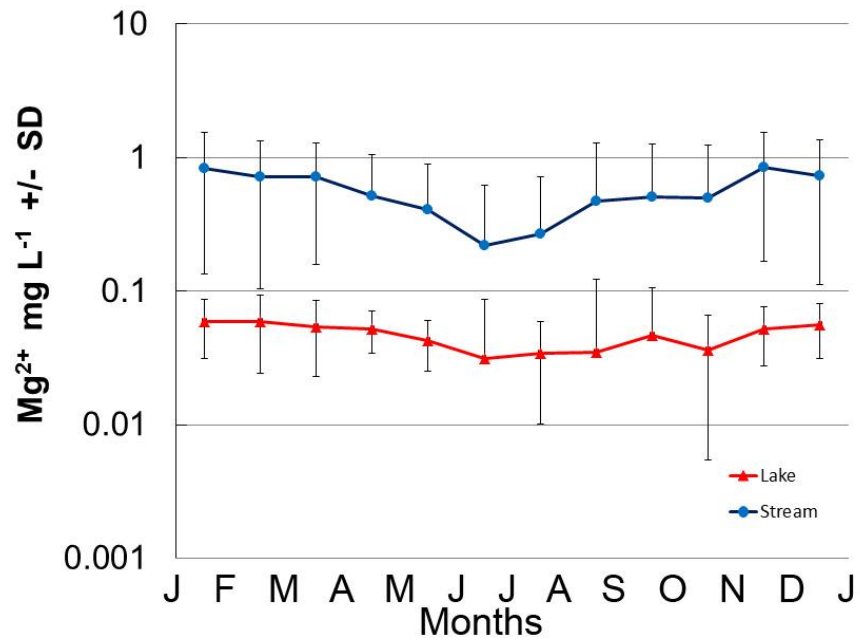


Figure A12. Seasonal variation of magnesium in SEKI streams and lakes, 1979 to 2004. Lakes and lake outlets were combined as 'lakes'. Rivers and creeks were combined as 'streams'.

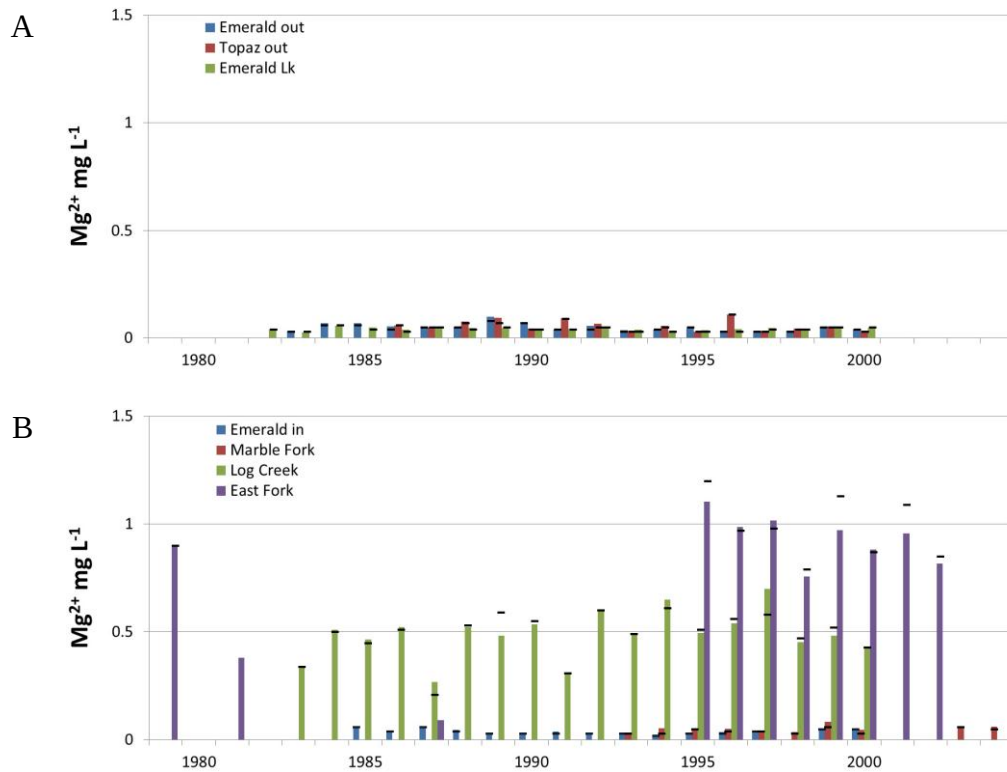


Figure A13. Mean magnesium (mg L^{-1}) in reference site lakes (A) and streams (B). Median values are shown as dark horizontal bars.

Sodium

There were two independent sodium record sets in the SIEN database: 1) sodium, water, filtered, milligrams per liter; 2) sodium, water, filtered, micrograms per liter. There was also an aggregated sodium record set produced from the above with a total of 8919 records.

Sodium concentrations in SEKI seem to have some dependence on elevation and local

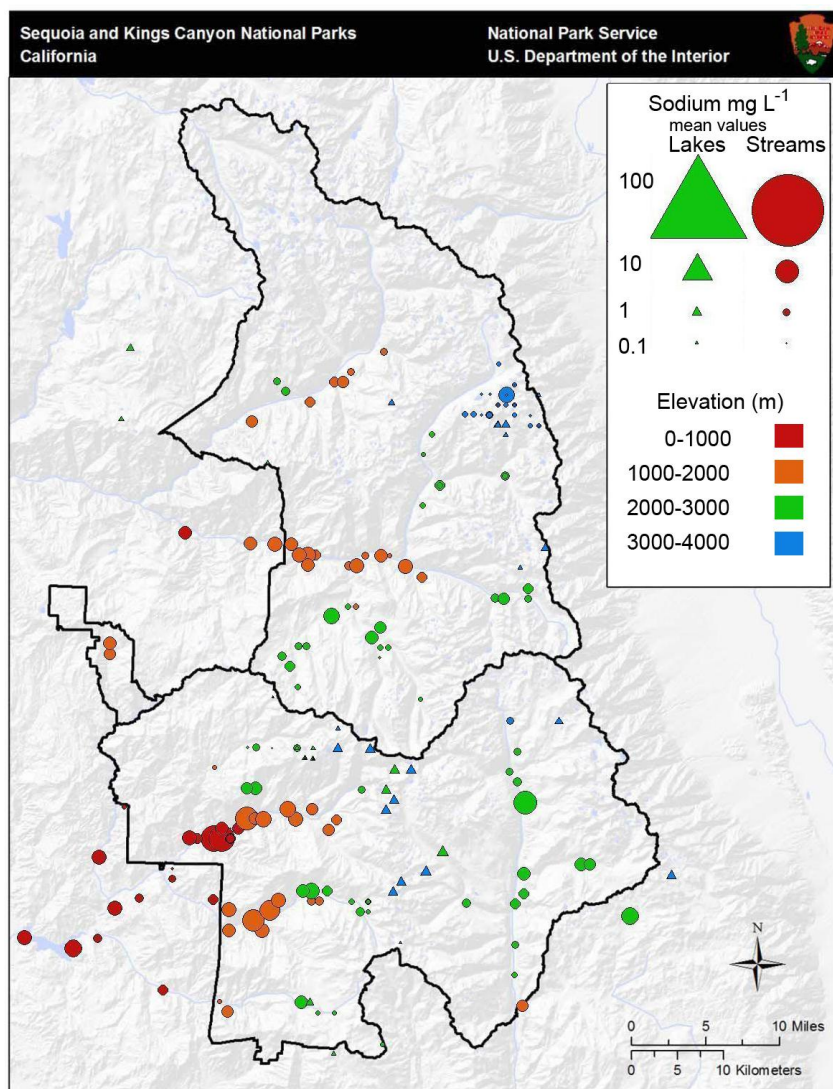


Figure A14. Mean sodium measured in SEKI. Lakes are triangles, streams are circles, values proportional to area. Elevation bands (1000 m) are represented by different colors.

elevation lakes having much lower levels than lower elevation streams (Figure A16). There is no apparent temporal trend indicating a change of sodium levels at any reference site. However, there may be more complex variations evident in lake reference sites that appear to be sinusoidal, and perhaps reflect changes in precipitation.

geochemistry (Figure A14). High elevation lakes tend to have sodium concentrations about one order of magnitude lower than streams. However, outside the Park, the Kaweah has a lower sodium level, consistent with possible dilution by groundwater influx. The highest concentration is near the SNP headquarters area, slightly higher than elsewhere on the Kaweah Middle Fork.

The seasonal variation of sodium concentration in lakes limited; however, streams have a seasonal decrease of slightly more than one half of an order of magnitude coinciding with snow melt (Figure A15). The decrease in sodium is likely due to dilution from snow melt runoff.

Reference sites show a consistent elevational effect in sodium concentration with higher

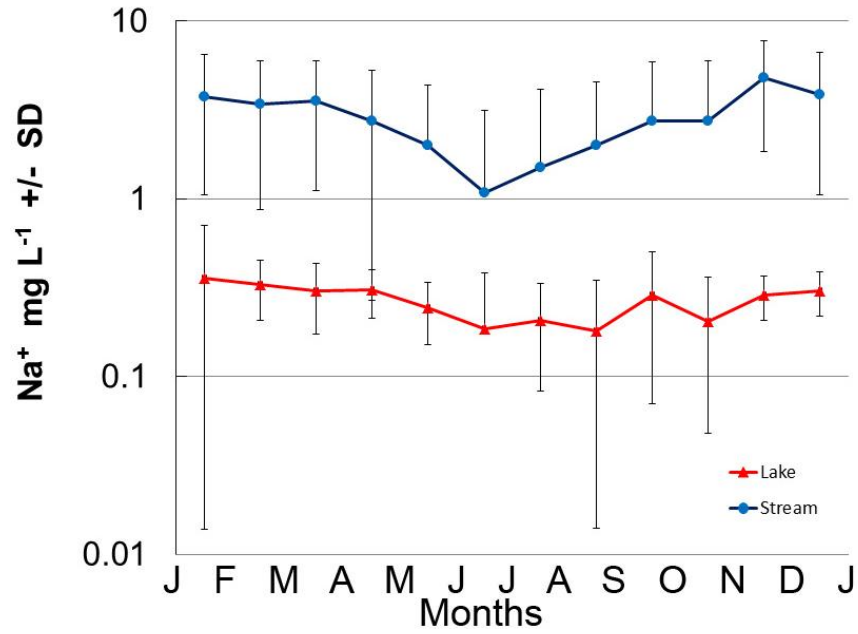


Figure A15. Seasonal variation of sodium in SEKI streams and lakes, 1979 to 2004. Lakes and lake outlets were combined as 'lakes'. Rivers and creeks were combined as 'streams'.

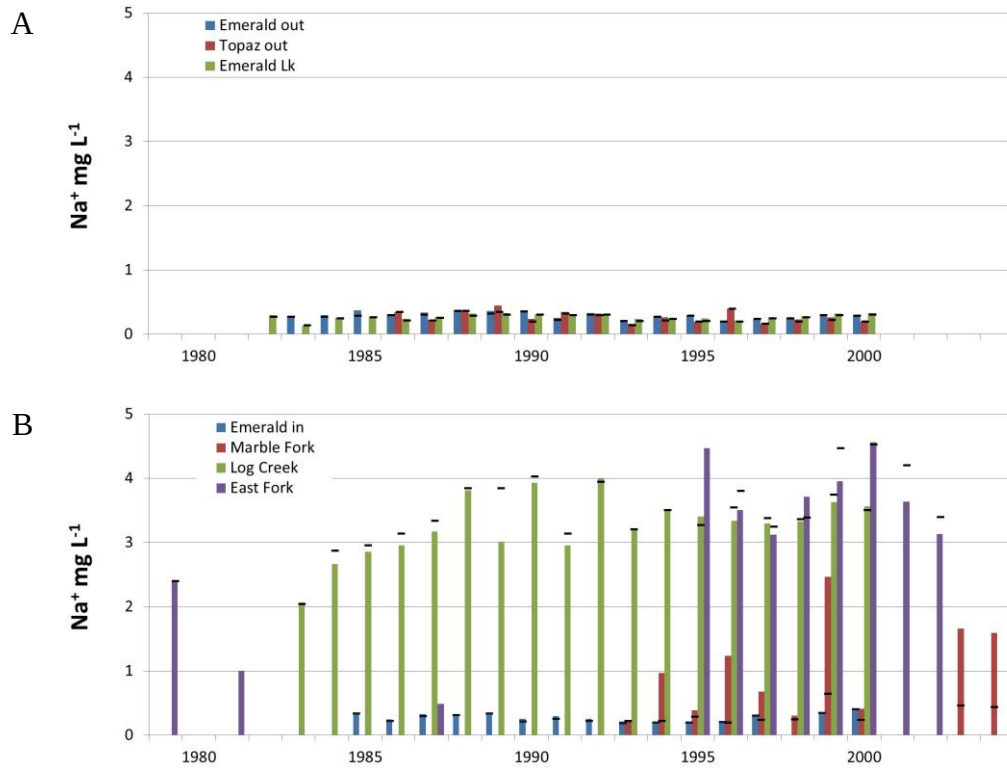


Figure A16. Mean sodium (mg L^{-1}) in reference site lakes (A) and streams (B). Median values are shown as dark horizontal bars.

Potassium

There were three independent magnesium record sets in the SIEN database: 1) potassium, water, filtered, milligrams per liter; 2) potassium, water, unfiltered, recoverable, milligrams per liter; 3) potassium, water, filtered, micrograms per liter. A fourth record set was, 4) potassium-40, water, filtered, picocuries per liter; however, that set was not used. There was also an aggregated potassium record set produced from the above with a total of 8621 records.

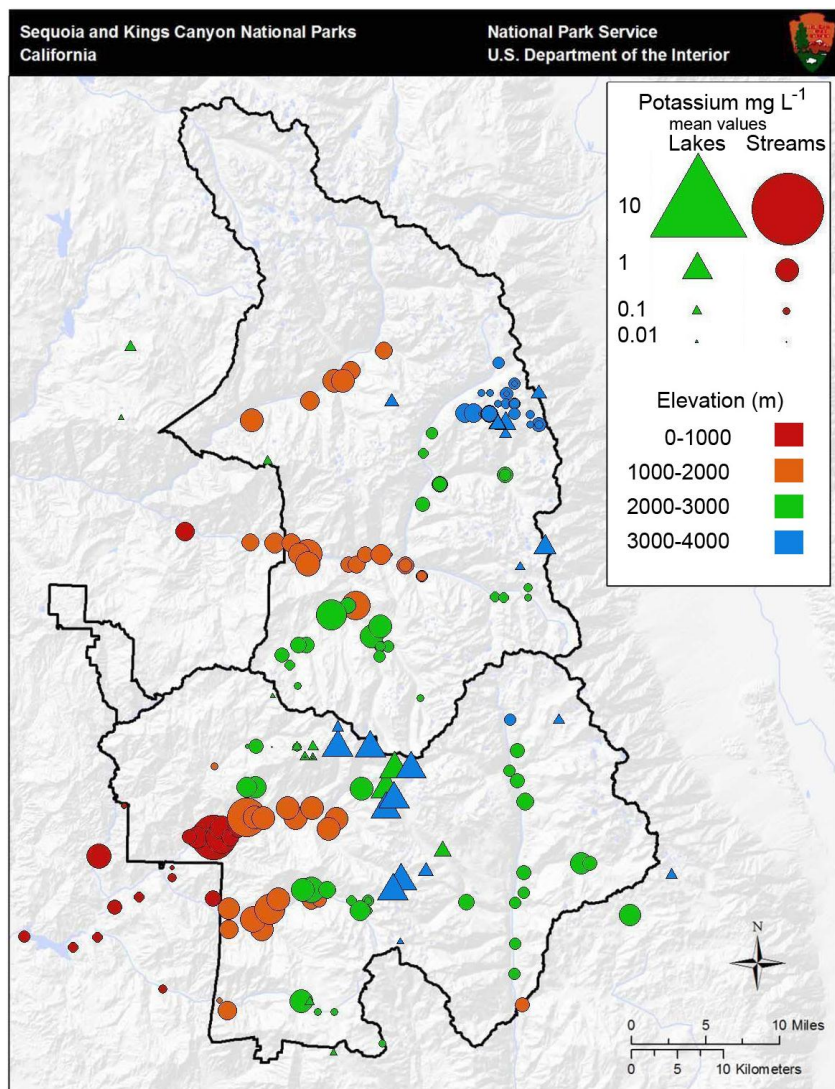


Figure A17. Mean potassium measured in SEKI. Lakes are triangles, streams are circles, values proportional to area. Elevation bands (1000 m) are represented by different colors.

A18). The decrease in potassium is likely due to dilution from snow melt runoff. The decrease in potassium concentration in lakes is delayed relative to streams, consistent with snow melting later at higher elevation.

Potassium concentrations in SEKI seem to have some dependence on elevation and local geochemistry (Figure A17). High elevation lakes tend to have potassium concentrations less than one order of magnitude lower than streams. Outside SNP, the Kaweah has a significantly lower potassium level, suggesting possible dilution with groundwater. The highest concentration is near the SNP headquarters area, a little higher than elsewhere on the Kaweah. Several lakes in SNP have relatively high potassium concentrations perhaps due to regional geochemistry.

The seasonal variation of potassium concentration in lakes is limited; however, streams have a seasonal decrease of about one half of an order of magnitude coinciding with snow melt (Figure

Reference sites show a consistent elevational dependence of potassium concentration with higher elevation lakes having much lower levels than lower elevation streams (Figure A19). There is no clear temporal trend indicating a change of potassium levels at any reference site.

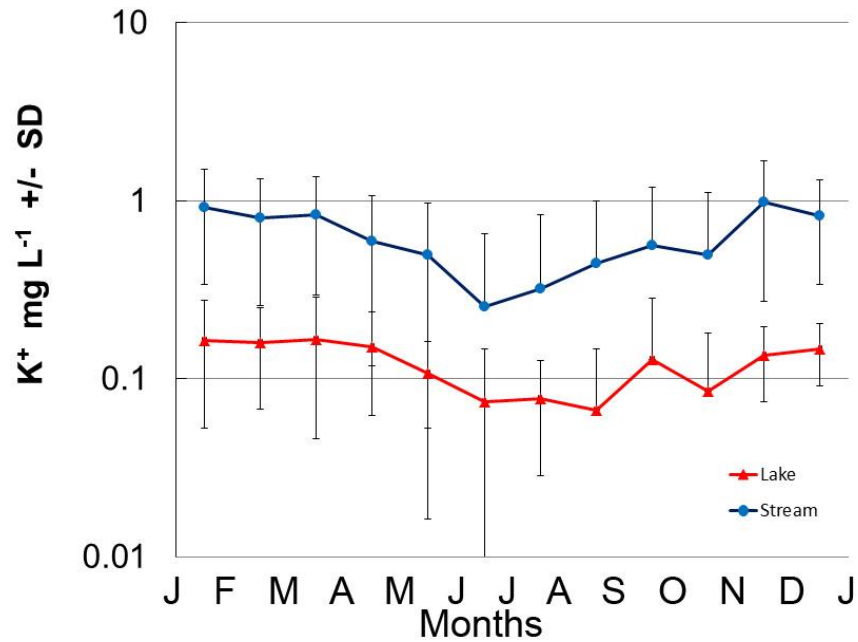


Figure A18. Seasonal variation of potassium in SEKI streams and lakes, 1979 to 2004. Lakes and lake outlets were combined as 'lakes'. Rivers and creeks were combined as 'streams'.

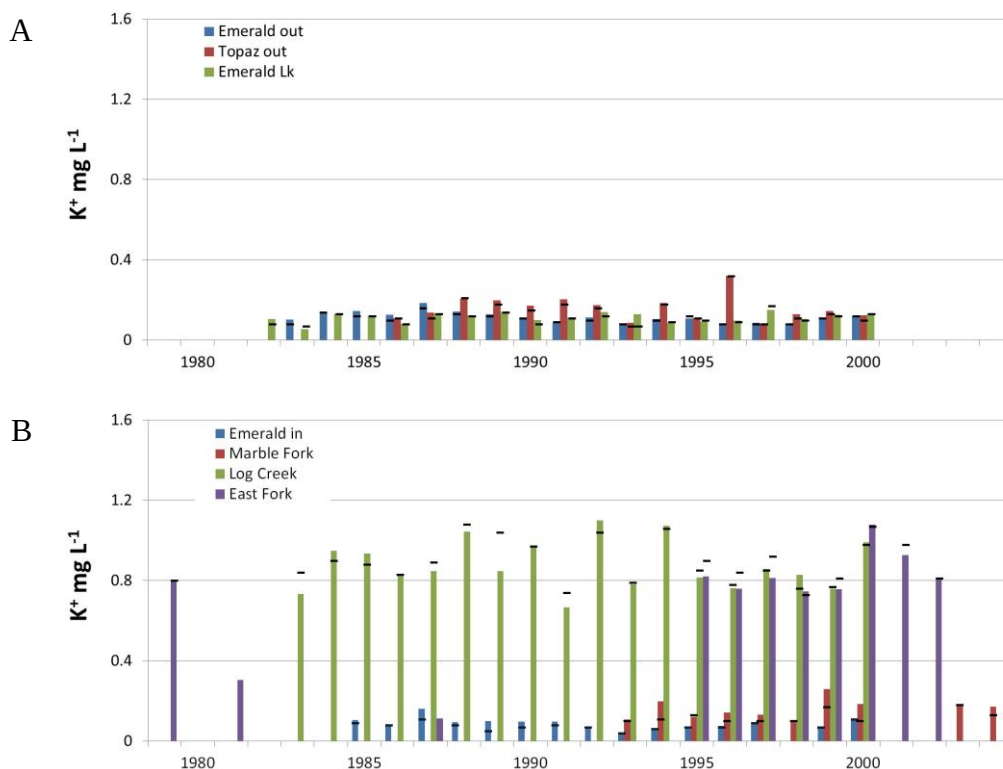


Figure A19. Mean potassium ($mg\ L^{-1}$) in reference site lakes (A) and streams (B). Median values are shown as dark horizontal bars. Topaz out $N_{1996} = 1$, $N_{avg} = 13$ for all years.

Chloride

There were three independent chloride record sets in the SIEN database: 1) chloride, water, filtered, milligrams per liter; 2) chloride, dissolved in water mg/L ; 3) chloride, water, filtered, micrograms per liter. There was also an aggregated chloride record set produced from the above with a total of 9074 records.

Chloride concentrations in SEKI seem to have some dependence on elevation and local geochemistry (Figure A20). High elevation lakes tend to have chloride concentrations roughly one half of one order of magnitude lower than streams. Outside SNP, the Kaweah has an increasing chloride level, consistent with a possible influx of groundwater. The highest concentration is near the SNP headquarters area. Several lakes in SNP have relatively high chloride concentrations perhaps due to regional geochemistry.

The seasonal variation of chloride concentration in lakes and streams a little more than one half of an order of magnitude coinciding with snow melt (Figure A21). The decrease in chloride is likely due to dilution from snow melt runoff. The decrease in chloride concentration in lakes is delayed relative to streams, consistent with snow melting later at higher elevation.

Reference sites show a consistent elevational dependence of chloride concentration with higher elevation lakes having much lower levels than lower elevation streams (Figure A22). There is no

apparent linear trend indicating a change of chloride levels at any reference site over time. However, there may be a dependence on other factors that vary from year to year.

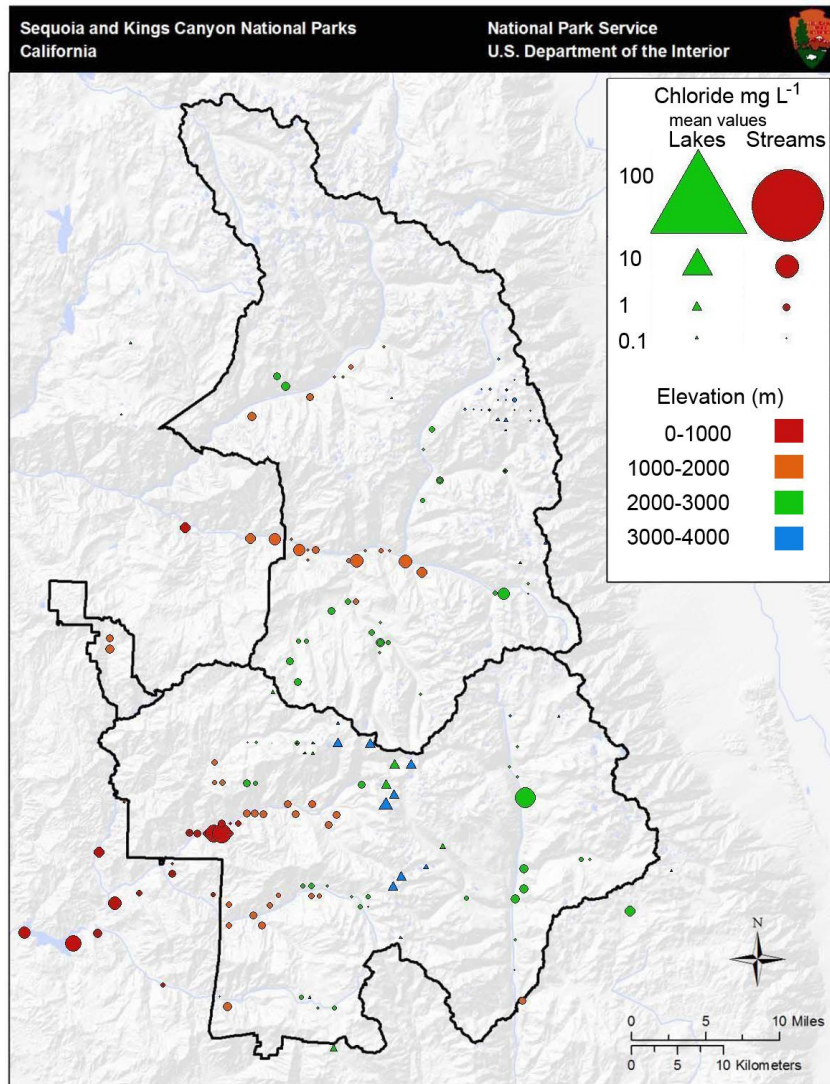


Figure A20. Mean chloride measured in SEKI. Lakes are triangles, streams are circles, values proportional to area. Elevation bands (1000 m) are represented by different colors.

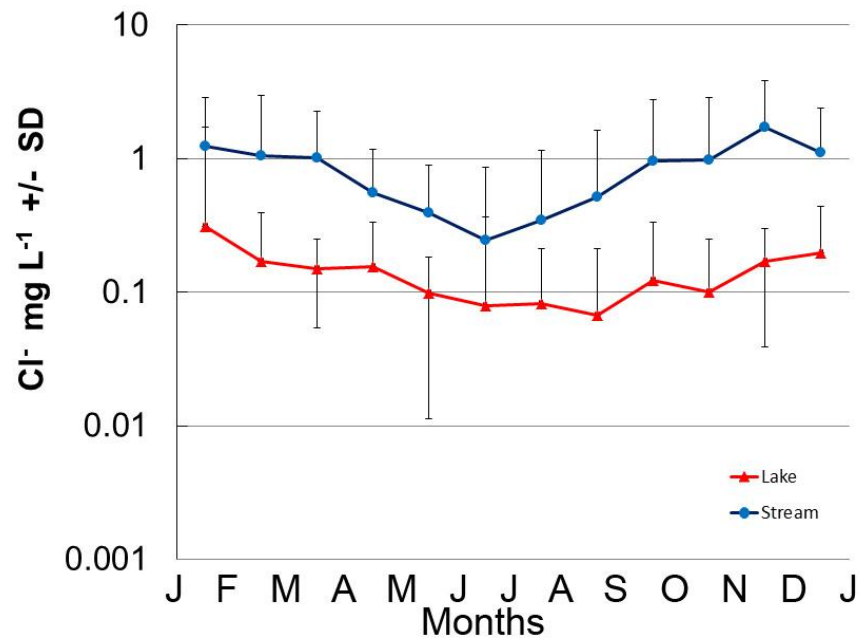


Figure A21. Seasonal variation of chloride in SEKI streams and lakes, 1979 to 2004. Lakes and lake outlets were combined as 'lakes'. Rivers and creeks were combined as 'streams'.

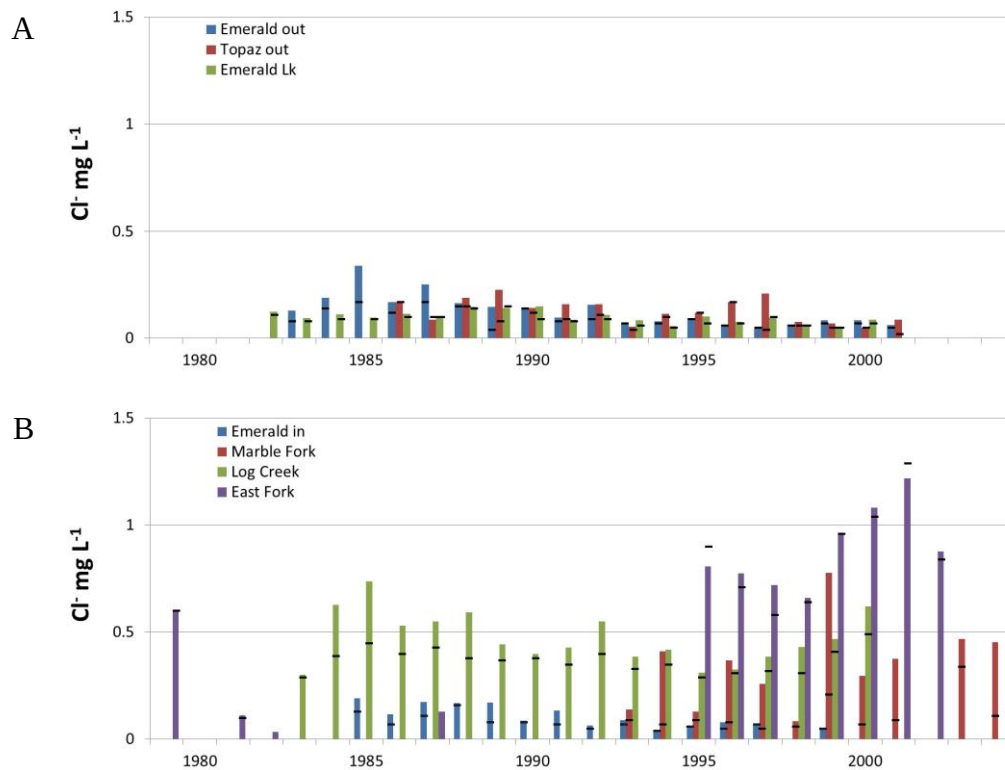


Figure A22. Mean chloride (mg L^{-1}) in reference site lakes (A) and streams (B). Median values are shown as dark horizontal bars.

Sulfate

There were five independent sulfate record sets in the SIEN database: 1) sulfate as S whole water, mg / L; 2) sulfate, water, filtered, milligrams per liter; 3) sulfate, water, unfiltered, milligrams per liter; 4) sulfate, water, filtered, micrograms per liter; 5) sulfate, water, filtered, uncorrected, milligrams per liter. There was also an aggregated chloride record set produced from the above with a total of 8780 records.

The seasonal variation of sulfate concentration in lakes and streams seems to be unchanged by snow melt (Figure A23). Sulfate concentrations increase as surface flow decreases in late summer to fall.

With the exception of Log Creek, reference sites show a consistent elevational dependence of sulfate concentration with higher elevation lakes having much lower levels than lower elevation streams (Figure A24). Log Creek may originate in a region with different geochemistry, adding less sulfate to the water. There is no apparent linear trend indicating a change of sulfate levels at any reference site over time.

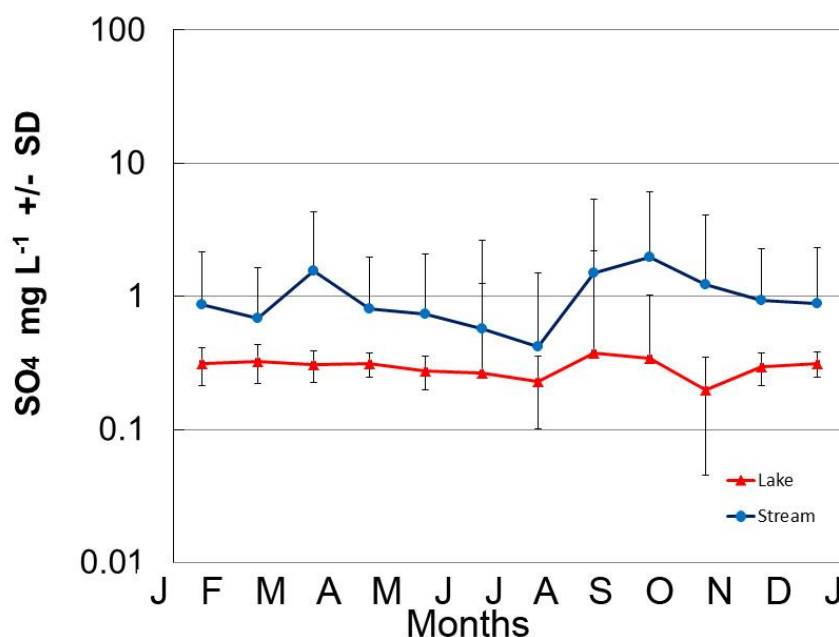


Figure A23. Seasonal variation of sulfate in SEKI streams and lakes, 1979 to 2004. Lakes and lake outlets were combined as 'lakes'. Rivers and creeks were combined as 'streams'.

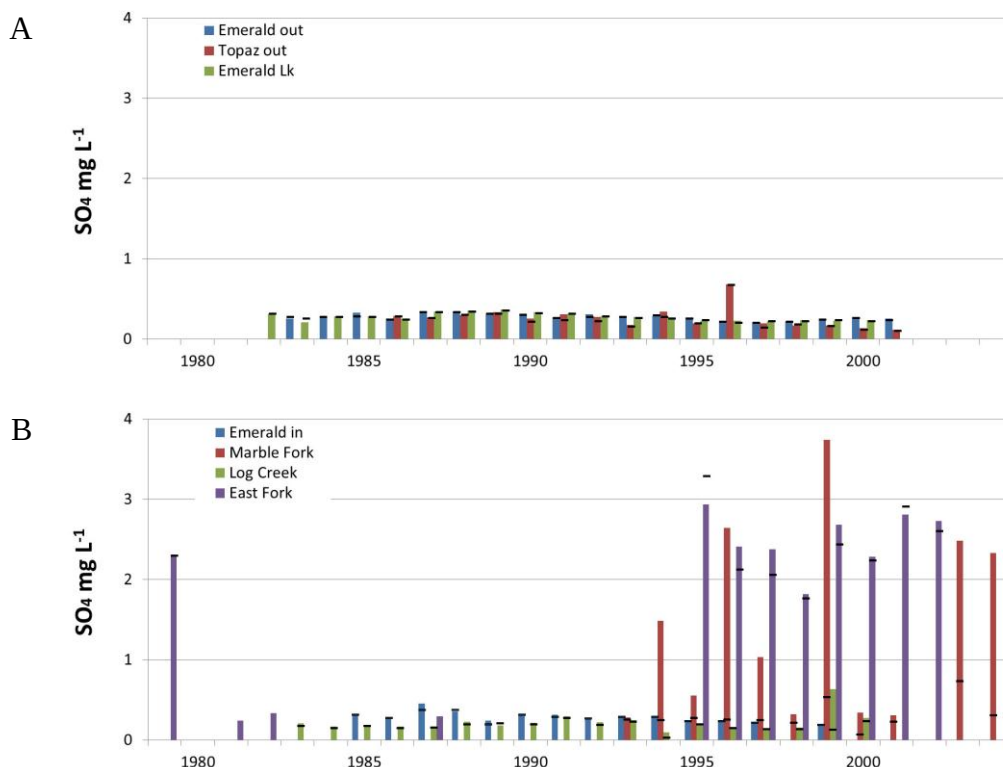


Figure A24. Mean sulfate (mg L^{-1}) in reference site lakes (A) and streams (B). Median values are shown as dark horizontal bars.

Nutrients

Nitrate

There were five independent nitrate record sets in the SIEN database: 1) nitrate, water, filtered, milligrams per liter as nitrogen; 2) nitrate, water, unfiltered, milligrams per liter as nitrogen; 3) nitrate, water, unfiltered, milligrams per liter; 4) nitrate, water, filtered, milligrams per liter; 5) nitrate, water, filtered, micrograms per liter. There was also a combined record: nitrate aggregated as N. However, this record set included records containing nitrite measurements combined with nitrate. The nitrite contributions were removed using nitrite records (not listed). The final aggregated nitrate set had a total of 9678 records. We used the combination of (1) and (4) with a total of 8000 records. 2232 had flags indicating levels were known to be lower, indicating detection limitation. Consequently, some of the lowest mean values reported for lakes could be slightly lower. However, the primary interest is in the high levels of nitrate.

Seasonal variation of mean nitrate concentrations in lakes and streams indicate a winter peak of nitrate for streams and a spring peak of nitrate for lakes (Figure A25). The minimum nitrate levels occur in early summer for streams, just following peak runoff, and the minimum for lakes occurs in late summer for lakes, following the end of snow melt and prior to early fall rain.

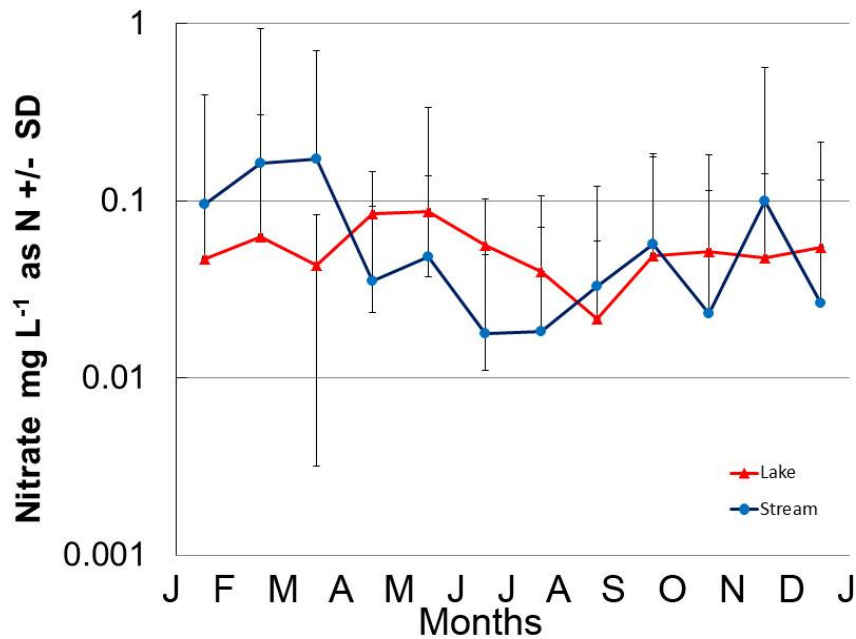


Figure A25. Seasonal variation of mean nitrate, concentration (mg L^{-1} as N) in SEKI Lakes and Streams, 1951 to 2005. Seasonal mean nitrate concentrations and standard deviations were calculated. Lakes and lake outlets were combined as 'Lakes'. Rivers and creeks were combined as 'Streams'. Standard deviation values less than zero are not shown.

Ammonium

There were six independent ammonium record sets in the SIEN database: 1) ammonia, water, filtered, milligrams per liter as nitrogen; 2) ammonia, water, unfiltered, milligrams per liter as nitrogen; 3) ammonia, unionized, milligrams per liter as N; 4) ammonia unionized, water, unfiltered, calculated, milligrams per liter as N; 5) ammonia, water, unfiltered, milligrams per liter as NH_4 ; 6) ammonia, water, filtered, milligrams per liter as NH_4 . Other record sets included organic nitrogen. There was also a combined record: ammonia aggregated as N combined in order of preference as (1), (6), (2), and (5). The final aggregated ammonia set had a total of 7676 records. We used the combination of (1) and (4) with a total of 7676 records. 4351 had flags indicating levels were known to be lower, indicating detection limitation. Consequently, some of the lowest mean values reported could be somewhat lower. However, the primary interest is in the high levels of ammonia.

Seasonal variation of mean ammonia concentrations in lakes and streams indicate a winter peak of ammonia for lakes (Figure A26). The peak of ammonia for streams is in early fall. The minimum ammonia levels occur in early summer for lakes, just following ice cover melting, peak runoff, and during peak insolation. The minimum for streams occurs in early winter.

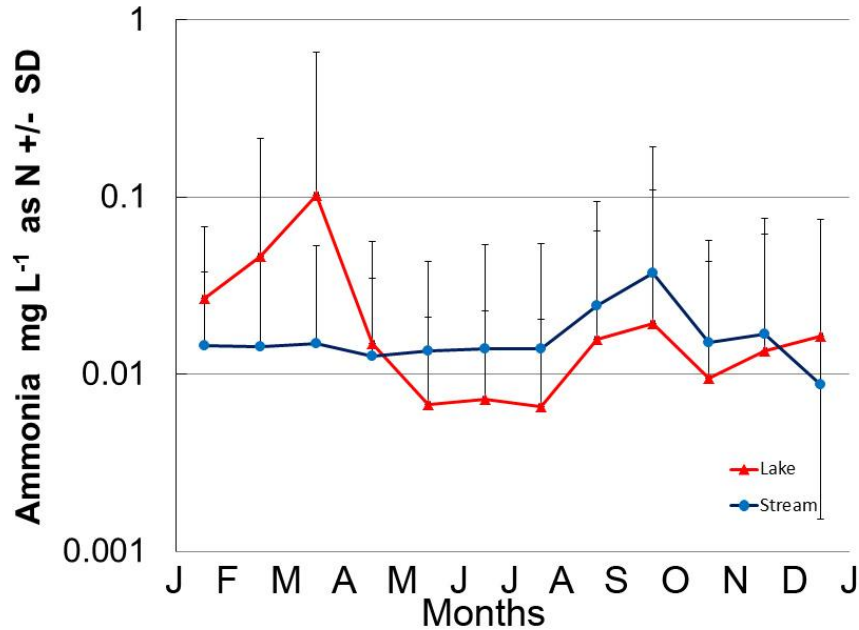


Figure A26. Seasonal variation of mean ammonium, concentration (mg L^{-1} as N) in SEKI Lakes and Streams, 1951 to 2005. Seasonal mean ammonia concentrations and standard deviations were calculated. Lakes and lake outlets were combined as 'Lakes'. Rivers and creeks were combined as 'Streams'. Standard deviation values less than zero are not shown.

Phosphorus

There were ten significant independent phosphorus record sets in the SIEN database: 1) phosphate, water, unfiltered, milligrams per liter; 2) phosphate, water, filtered, milligrams per liter; 3) orthophosphate, water, filtered, milligrams per liter; 4) phosphorus, water, total recoverable micrograms per liter; 5) phosphorus, water, unfiltered, milligrams per liter; 6) phosphorus, water, filtered, milligrams per liter; 7) orthophosphate, water, filtered, milligrams per liter as phosphorus; 8) orthophosphate, water, unfiltered, milligrams per liter as phosphorus; 9) phosphorus, water, unfiltered, milligrams per liter as phosphate; 10) orthophosphate, water, filtered, micrograms per liter. Other record sets had less than 10 records. There were also two combined records: The first was orthophosphate aggregated as P combined in order of preference as (7), (2), (3), (8), and (1). The final aggregated ammonia set had a total of 5753 records. The second was total phosphorus aggregated as P combined in order of preference as (5), (9), and (4). This aggregated record set contained 889 records. We used the first aggregate set.

Seasonal variation of mean phosphorus concentrations in lakes and streams indicate a winter peak concentration for streams, and a fall peak concentration for lakes (Figure A27). The minimum phosphorus levels occur in spring, during peak runoff. The low level for lakes begins a little earlier during winter while they are covered with ice.

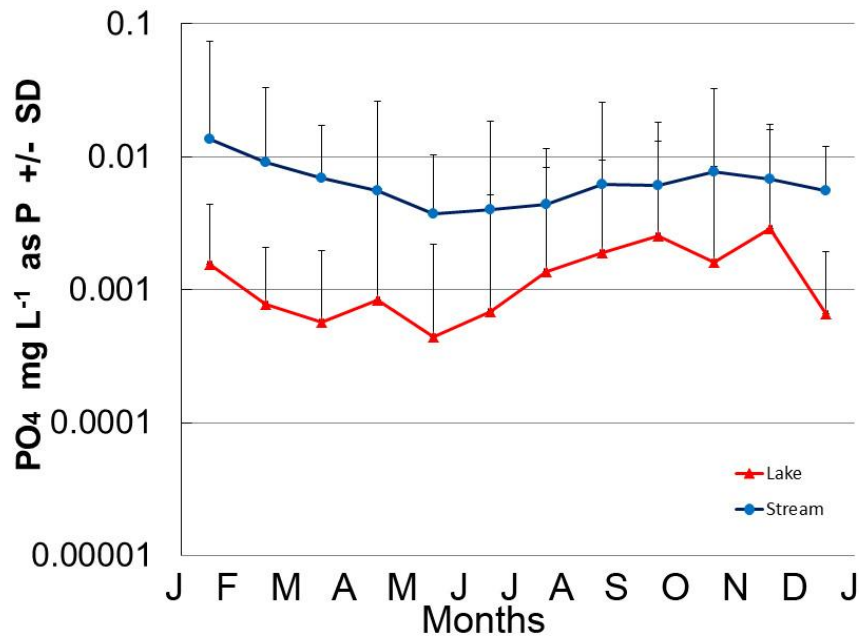


Figure A27. Seasonal variation of mean phosphorus, concentration (mg L^{-1} as P) in SEKI Lakes and Streams, 1969 to 2002. Seasonal mean P concentrations and standard deviations were calculated. Lakes and lake outlets were combined as 'Lakes'. Rivers and creeks were combined as 'Streams'. Standard deviation values less than zero are not shown.

Toxic Metals

Mercury

There were three mercury record sets in the SIEN database: 1) mercury, water, filtered, milligrams per liter; 2) mercury, suspended sediment, recoverable, milligrams per liter; 3) mercury, water, unfiltered, recoverable, milligrams per liter. We aggregated the three mercury record sets from the above with a total of 240 values, 47 flagged as below the detection limit.

The seasonal variation of the mercury concentration in streams shows a decrease in levels consistent with a peak in snowmelt occurring around June (Figure A28). There is a paucity of data to allow a more robust characterization of the seasonal effects. Several months during the year have no data, and others have large standard deviations making interpretations of the seasonal changes more difficult. For example, determining whether the observed mercury is adsorbed to sediment perhaps in metallic form, or present as methylmercury, could help resolve whether a physical or biological process is likely to be involved in delivering mercury to streams. In addition, this information could be used to determine whether these different mechanisms operate at certain times of the year.

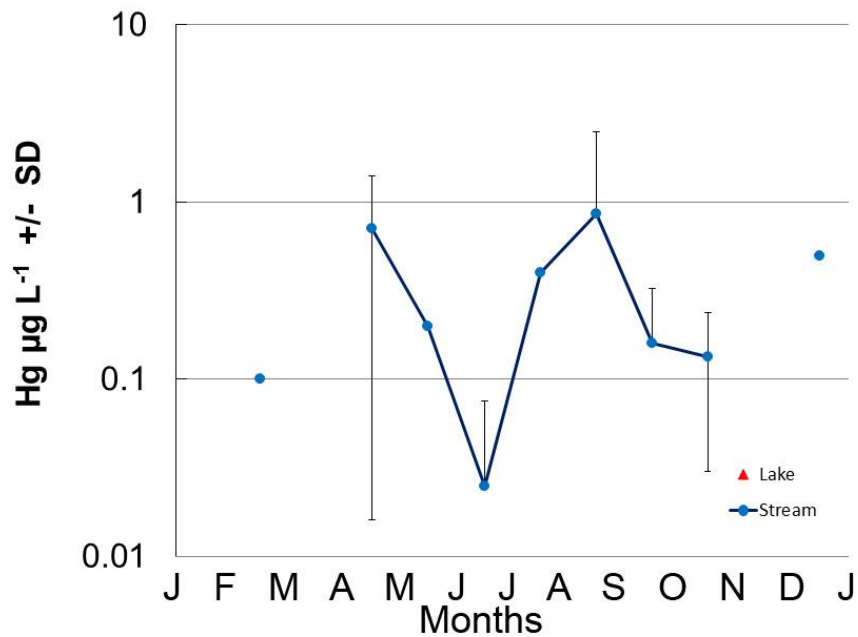


Figure A28. Seasonal variation of mean mercury, concentration (mg L^{-1}) in SEKI Lakes and Streams, 1971 to 1994. Seasonal mean Hg concentrations and standard deviations were calculated. There were no data for lakes and lake. Rivers and creeks were combined as 'Streams'. Standard deviation values less than zero are not shown.

Lead

There were three mercury record sets in the SIEN database: 1) lead, water, filtered, milligrams per liter; 2) lead, suspended sediment, recoverable, milligrams per liter; 3) lead, water, unfiltered, recoverable, milligrams per liter. We aggregated the three mercury record sets from the above with a total of 227 values, 123 flagged as below the detection limit.

The solubility of lead greatly increases as pH decreases, e.g. $10,000 \text{ mg L}^{-1}$ at pH 5.5. Lead concentrations in high elevation lakes in SEKI could be much higher than lead levels measured at lower elevation. As observed with aluminum concentrations in KNP (see *Aluminum* in 'Spatial and temporal analyses'), certain lakes may have much higher lead concentrations than other, perhaps due to acid-producing geochemical features. It is important to distinguish between a local source of lead in rock, or exogenous lead accumulated via atmospheric deposition. Under natural conditions, biota present should be better able to tolerate ambient conditions. With exogenous lead transport and deposition, it is unknown whether significant toxic effects are impacting critical species. Hardness may partially mitigate some lead effects, however, the waters of SEKI, especially the high elevation lakes, are very soft.

The dependence of acute lead toxicity on hardness in fresh water was assessed by comparing results in three vertebrate and one invertebrate species for which acute values were available over a range of hardness at least one half log, and highest hardness concentration at least 100 mg L^{-1} higher than the lowest (see *Lead* in 'Spatial and temporal analyses'). Rainbow trout data were originally included in the assessment of hardness, but the species was removed because the dependence of acute toxicity on hardness was much stronger than the other three species. No lifecycle studies were conducted with fish, but one was performed with a snail. There were no

observed effects related to growth or reproduction, however, survival was strongly dependent on the lead concentration. No effect on survival was observed at $12 \mu\text{g L}^{-1}$, while few snails survived at $54 \mu\text{g L}^{-1}$. Non-lethal effects such as spinal deformity in fish were also assessed. Fresh water plants appear to be unaffected at lead concentrations that produce effects in animals. Bioaccumulation studies indicate invertebrates retain lead to a greater degree than vertebrates. Bioconcentration factors were approximately 1000 and 45, respectively.

The limitations of data regarding lead in the SIEN database are readily apparent in Figure A29. It underscores the need to collect more data of higher quality to identify streams and lakes at risk, and when these risks are most severe.

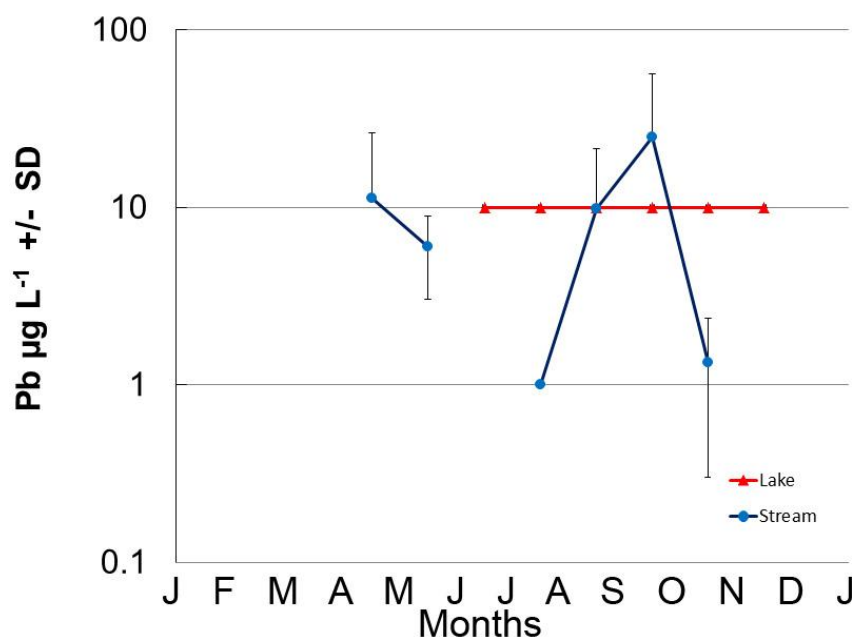


Figure A29. Seasonal variation of mean lead, concentration (mg L^{-1}) in SEKI Lakes and Streams, 1974 to 1994. Seasonal mean Pb concentrations and standard deviations were calculated. Lakes and lake outlets were combined as 'Lakes'. Rivers and creeks were combined as 'Streams'. Standard deviation values less than zero are not shown.

Aluminum

There were two aluminum record sets in the SIEN database: 1) aluminum, water, unfiltered, recoverable, micrograms per liter; 2) aluminum, water, filtered, milligrams per liter. We aggregated the two aluminum record sets from the above with a total of 353 values, 93 flagged as below the detection limit.

Aluminum solubility increases under acidic conditions. Aluminum solubility is more complicated than many other metals, because aluminum forms reversible complexes with various ions. These complexes may or may not be soluble, and solubility equilibrium is achieved slowly. Aluminum forms polymers with hydroxide ions {Parks, 1972 #157}.

For water within the standard pH range, early studies indicated aluminum toxicity increased with pH, perhaps due to increased solubility. Further studies indicated only inorganic forms of

aluminum were toxic and only aluminum passing through a 0.45 μm filter was toxic. It was finally determined that the most toxic forms of aluminum were AlOH^{2+} and $\text{Al}(\text{OH})_2^+$, with maximum toxicity for a green alga between pH 5.8 and 6.2. Acid leaching of aluminum from rock increases total aluminum. Cory, et al., note aluminum solubility is not certain in complex chemical systems such as lakes and streams {Cory, 2006 #158}. For example, silicates may interfere with aluminum hydroxide precipitation. Under natural conditions, it is also expected that the aluminum concentration is elevated due to the formation of soluble complexes with organic acids.

There is an apparent peak in lake Al concentration occurring during snow melt at higher elevation (Figure A30). Larger error bars indicate wide variations between locations or years. There were more data points for late spring (range 12 to 33 per month) and summer than were available winter (range 2 to 7 per month). Data quality for streams is clearly limited.

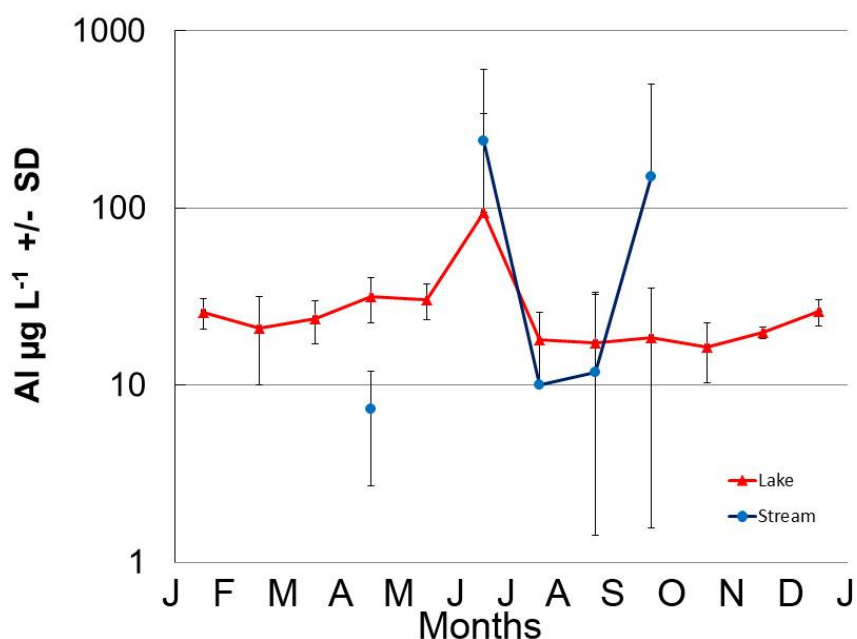


Figure A30. Seasonal variation of mean aluminum, concentration ($\mu\text{g L}^{-1}$) in SEKI Lakes and Streams, 1974 to 2004. Seasonal mean Al concentrations and standard deviations were calculated. Lakes and lake outlets were combined as 'Lakes'. Rivers and creeks were combined as 'Streams'. Standard deviation values less than zero are not shown.

Copper

There were three copper record sets in the SIEN database: 1) copper, water, filtered, micrograms per liter; 2) copper, suspended sediment, recoverable, micrograms per liter; 3) lead, water, unfiltered, recoverable, micrograms per liter. We aggregated the two aluminum record sets from the above with a total of 241 values, 153 flagged as below the detection limit.

The US EPA recommended Biotic Ligand Model (BLM) takes into consideration not only hardness, but also pH and the dissolved organic carbon (DOC) concentration. In the BLM, free copper binds receptors on the surface of an organism. The toxic action may take place inside the organism, but the occupancy of receptors on the surface determines the lethal effect. The BLM

includes DOC acting as an inhibitor through binding free copper and blocking interactions with surface receptors. US EPA considers the BLM appropriate for determining the freshwater CMC, but recommends use of the older hardness equation to determine the CCC. The BLM tables provide a range of CMC ($\mu\text{g L}^{-1}$) depending on pH and DOC at 80 mg L^{-1} hardness between 1.9 and 72.5, having apparently first-order dependence on the DOC concentration.

The seasonal variation of copper indicates an apparent minimum concentration in streams consistent with peak snowmelt runoff (Figure A31). Lake data for copper are of limited value. More data are needed to characterize the level or risk and when during the year risk is highest.

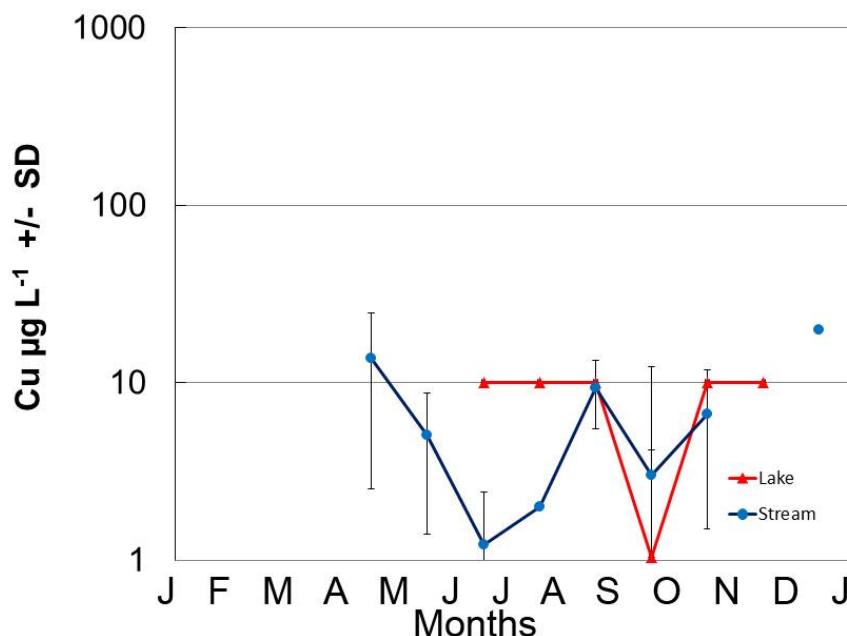


Figure A31. Seasonal variation of mean copper, concentration ($\mu\text{g L}^{-1}$) in SEKI Lakes and Streams, 1974 to 2004. Seasonal mean Cu concentrations and standard deviations were calculated. Lakes and lake outlets were combined as 'Lakes'. Rivers and creeks were combined as 'Streams'. Standard deviation values less than zero are not shown.

Sediment cores

Sediment core data for SEKI were extracted from WACAP database records. In SEKI, core samples were taken from only two lakes, Emerald Lake and Pear Lake. Flags were available to indicate a replicate or an error. Sample errors and duplicate records were removed. Replicates not replacing failed samples were removed.

Figure A32 shows metal levels detected at different dated layers in sediment cores from the two lakes. Most of these metals can be toxic and some are priority pollutants. A subset of the metals display an apparent broad peak in levels from 1960 to 2000. These are Pb, Cd, and Hg. This broad peak is clearly visible only in Pear Lake records (Figure A32-B). The lack of signal Emerald Lake is likely due to disturbance of the sediments due to avalanche. It is noteworthy that these metals are those commonly transported through the atmosphere and deposited in SEKI. The decrease observed from 1975 to the present may represent the beneficial effects of the Clean Air Act of 1970.

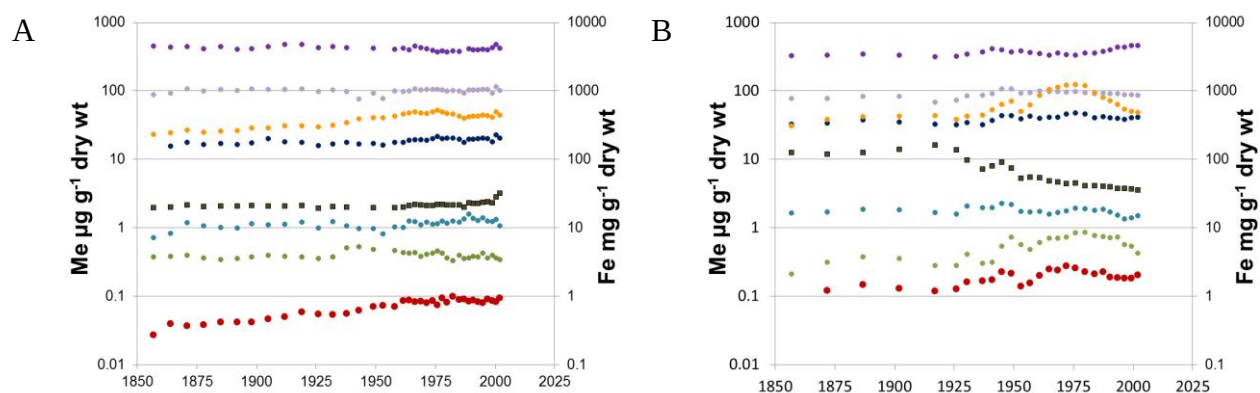


Figure A32. Metal levels measured in dated layers of sediment cores taken from Emerald Lake (A) and Pear Lake (B). With the exception of Fe, metals are distinguished as follows in order from the top: Mn is purple, Zn is violet, Pb is yellow, Cu is navy, Ni is teal, Cd is green, and Hg is red, all circles with levels indicated by the left side scale. Fe is represented by black squares with levels indicated by the right side scale.

A comparison of the sediment levels from WACAP and the water levels from SIEN suggest a possible method of estimating water levels or sediment levels when only one value is known (Figure A33).

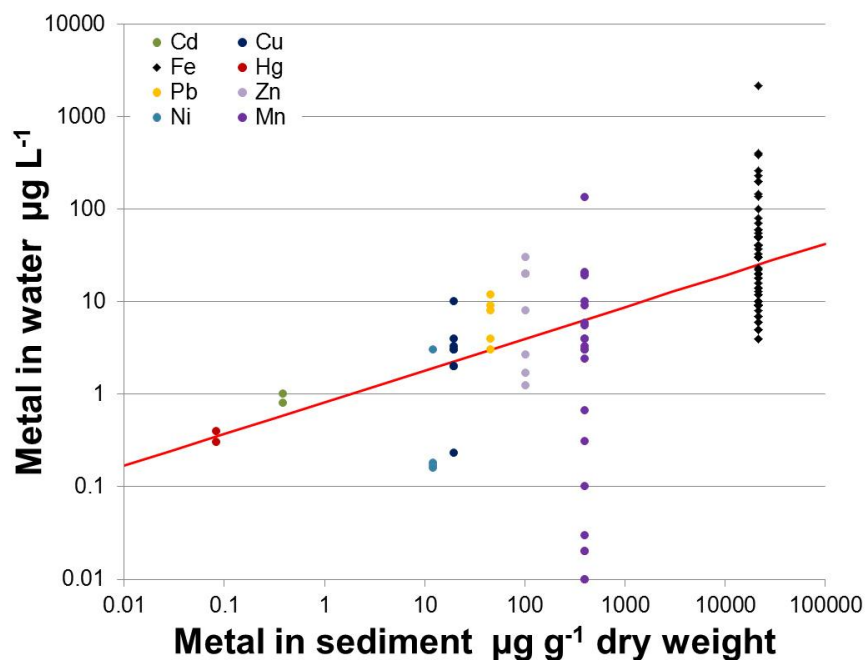


Figure A33. Toxic metal concentration median values found in SEKI surface water compared to metal concentrations in Emerald Lake sediments. Different metals are represented using different colors. Linear least squares fit of the log-log plot resulted in $R^2 = 0.48$. In the case of Mn, only the median values with more than one valid measurement per site (four points just below the red fit line (N of 4, 91, 5, 5) were used for fitting the data.

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