Water Quality Review: Sierra Nevada 2005 Lake Monitoring

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Executive Summary

Twelve lakes in eight Class I and one Class II Wilderness Areas were sampled for acid-base water chemistry, water transparency, and zooplanktons between mid-July and mid-August 2005 as part of Project LAKES, the Sierra Nevada lake monitoring project of the Pacific Southwest Region, USDA Forest Service Air Resources Program. In addition, twenty-nine lakes in John Muir Wilderness (JM) were synoptically sampled; several of these lakes are potentially good candidates for addition in 2006 to the long-term monitoring network.

An intent of the monitoring project is to monitor lakes from all nine Class I Areas in the Sierra Nevada, southern Cascades, and northeastern California overseen by the USDA Forest Service (one Class I Area in the southern Sierra Nevada, Domeland, has no lakes). This objective will probably be reached next year when lakes from the last remaining section of one Wilderness (southern JM) will be synoptically sampled and one or more lakes selected for long-term monitoring.

Four long-term monitoring lakes have records of between 5 and 10 years in length, long enough for preliminary statistical analysis for temporal change. A statistically significant decline in sulfate was identified for Waca Lake, in Desolation Wilderness immediately west of Lake Tahoe. The change is slight, from the 4-6 μEq L^{-1} range between 1985 and 1992 to the 2-3 μEq L^{-1} range since 2000. At Key Lake in Emigrant Wilderness, ANC dropped from 8-10 μEq L^{-1} in 2000-2003 to less than 1.4 μEq L^{-1} in 2004 and 2005. No other temporal change was identified for any of the four lakes having 5 or more years of data. Because no other changes were identified, the ANC change at Key Lake is in the range of questionable ANC values, and the duration of records is still relatively short, these changes do not appear to warrant further assessment at this time.

A quality assurance review of the chemistry data identified a "rebound" in the quality of the chemical analyses from 2004. For several metrics, the 2005 results are generally on a par with the pre-2004 results. For instance, appreciably more of the samples were analyzed at a "higher quality" level for percent ion differences in 2005 than in 2004.

Ion imbalances evident in prior years persisted in 2005. This continuing imbalance suggests that one or more constituents causing the imbalance are not currently being analyzed.

Lakes in most of these Wildernesses are sensitive to potential acidification, with acid neutralizing capacity (ANC) less than 50 μEq L^{-1} for many lakes in most Wildernesses.

From synoptic data collected since 2000, concentrations for most chemicals are similar among seven of the Wildernesses (Dinkey, Kaiser, Emigrant, Mokelumne, Desolation, Thousand Lakes and Caribou). Higher, and more variable, concentrations are evident in Wildernesses with lakes in the eastern part of California (Ansel Adams, John Muir and South Warner). Baseline data for major cation and anion concentrations are provided as well as levels of conductivity, ANC and pH.

Three lakes were identified in Ansel Adams Wilderness last year having relatively high nitrate and sulfate concentrations. One of these, Dana Lake, also had high sulfate and nitrate concentrations when it was sampled again in 2005 (the other two lakes were not sampled in 2005). Two synoptically-sampled lakes in JM also had high sulfate and nitrate concentrations in 2005. These lakes differed from Dana Lake in that they also had high ANC, whereas Dana combined the relatively uncommon combination of high sulfate and nitrate with low ANC.

Although only relatively minor chemical differences were identified between shallow and deep samples collected fourteen times at "long-term" monitoring lakes since 2002, the sample size is too small to conclusively state that mid-lake sample collection in thermally stratified lakes is not providing useful information.

Recommendations

1) Complete synoptic sampling for southern Join Muir Wilderness (JM) in 2006.
Sampling of the southern section of JM will complete the synoptic sampling and allow establishment of the full network of long-term monitoring lakes by 2007.

2) Select long-term monitoring lakes in central and northern JM. The number of long-term monitoring lakes needs to be decided as well as the specific lakes.
JM has more lakes than any other Sierra Nevada Wilderness and JM is larger than any other Sierra Wilderness (e.g., 580,323 hectares vs. 230,258 hectares for Ansel Adams). These attributes suggest that JM should have a fair number of long-term monitoring lakes. Earlier analysis (Berg 2002) recommended seven long-term lakes for JM. This number still seems reasonable from a technical standpoint.

Because of the broad north-south extent of JM, and evidence of east-west chemical differences from the synoptic sampling of JM, selection of geographically-spaced lakes in JM for long-term monitoring may be advisable. Several lakes with the lowest (or very low) sampled ANC (i.e. below 20 μEq L^{-1}) in JM (Bullet, Ram, East and West Twin Buck Lakes) are clustered together in the west central portion of the Wilderness (Figure 1). Potentially one of these could be selected for long-term monitoring. Stanford Lake, with ANC = 18.8 μEq L^{-1}, is located at the far northeast and is also a candidate for long-term monitoring. Only one lake on the eastern or southern portion of JM has an ANC less than 40 μEq L^{-1}. This lake, Thunder and Lightning, plus Marshall Lake on the northwest, and Bench Lake on the southeast (ANC = 31 and 51 μEq L^{-1} respectively), are potential long-term monitoring lakes. These recommendations are based solely on lake

location and measured ANC; other factors, like accessibility and location of air pathways should be incorporated into the decision-making process for JM long-term lakes.

3) For unknown reasons samples were in transit longer in 2005 than in any previous year. Although many of the longer-than-normal transit times were for samples from JM, a relatively remove Wilderness, **reasons for the longer-than-normal transit times should be discussed and actions taken (if warranted) to attempt to reduce future transit times.**

4) **Re-emphasize in training sessions and any other communications with sampling crews the need to wear gloves and not touch any sample liquid with body parts.** Four lakes had samples originally described by the analytical laboratory as having "NaCl Contamination". After analysis of backup samples for these lakes laboratory staff removed the "contamination" label from three of the four original samples. Although the source of the salt contamination is unknown, it is typically caused by body contact with sample liquid. All efforts should be made to minimize the potential for future contamination, for instance by using the 2005 salt contamination as a discussion point in future training.

5) **Resolve the status future sampling of Smith Lake**. Smith Lake, in Desolation Wilderness, was sampled in 2005 for the first time since 2000. Will it be sampled in the future, and if so will the sampling be from mid-lake—as a long-term monitoring lake—or from its outlet?

6) **Assess the zooplankton data and decide whether to continue zooplankton sampling.** Zooplankton have been collected each year at the long-term monitoring lakes and although zooplankton taxonomy and metrics have been reported for all years except 2005, no comprehensive data analysis has been done. A comprehensive data analysis of the zooplankton database would provide input on whether continued collection of zooplankton samples is worthwhile.

7) **Analysis for dissolved organic carbon in 2006 should be considered to attempt to explain the continuing ionic imbalance.**

8) Outlet sample collection could potentially replace mid-lake sample collection. Outlet sampling would be faster and potentially less costly than mid-lake sampling. Insufficient R5 data are currently available to determine if the chemistry of outlet samples matches the chemistry of mid-lake samples. A decision to move to solely outlet sampling could be based on data from elsewhere. However, before making a decision on outlet sampling a prudent approach would be to—
   a. **Concurrently collect both outlet and mid-lake samples at all or most long-term monitoring lakes and compare the chemical concentrations.**
   b. **Because they require mid-lake sampling, analyze the zooplankton data and discuss pros and cons of continued transparency and zooplankton collection.**

1.0 Introduction

Wilderness Areas are important national resources providing relatively unaltered natural landscapes for our enjoyment. Although watershed activities in Wildernesses are highly constrained, damage to some of these fragile resources is possible through long-range transport of air pollutants (Eilers 2003). To address this concern, in 2000 the Air Resources Program of the Pacific Southwest Region of the USDA Forest Service Forest Service initiated lake monitoring in Class I Wilderness Areas of the Sierra Nevada, California Cascades and northeastern California. A monitoring goal is to provide early indication of possible impacts associated with deposition of acid-rain precursors.

This report assesses and interprets water chemistry data collected in 2005 and compares these data against information obtained in prior years. Last year's report addressed lake transparency and options for outlet instead of mid-lake water sampling. Those topics, and the status of zooplankton sampling, are not addressed in the current report.

2.0 Lake Monitoring Network

One intent of the Region 5 lake monitoring program is to follow the precedent of other FS regions by identifying a small number of lakes sensitive to atmospherically-driven acidification in each Class I Area and monitoring them over the long term. The premise is that monitoring lakes (operationally defined as water bodies greater than one hectare in area and greater than one meter in depth) particularly vulnerable to potential acidification will act as "a canary in a coal mine" and that their protection presupposes protection of less sensitive lakes.

Acid neutralizing capacity (ANC) is the single best indicator of lake sensitivity to acidification (Sullivan et al. 2001). Lakes with low ANC are sensitive to acidification. The selection process for long-term monitoring lakes (those with low ANC) is not simple and requires a combination of modeling and synoptic sampling prior to final selection of long-term monitoring lakes. Twelve long-term monitoring lakes were sampled in 2005. These lakes were selected after a one-time synoptic sampling of many lakes in each Wilderness in which ANC and other chemical constituents were evaluated. Future additions to the monitoring network will also be low-ANC lakes, and their selection will be partially based on future synoptic samplings. The monitoring program will eventually incorporate approximately 20 lakes in ten Class I Wildernesses ranging from the Sierra National Forest in the southern Sierra Nevada to the Modoc National Forest in the northeastern corner of California.   In 2005 42 lakes were sampled from nine Wildernesses as follows:

Wilderness	Number of Lakes Sampled	Long-term Monitoring Lakes
John Muir	29	0
Kaiser	1	1
Ansel Adams	2	2
Dinkey Lakes	1	1
Mokelumne	2	2
Desolation	2	1
Emigrant	2	2
Caribou	1	1
1000 Lakes	1	1
South Warner	1	1

One long-term monitoring lake, Waca in Desolation Wilderness, has been monitored ten times since 1985; monitoring of the rest of the lakes began more recently:

Lake	Wilderness	Years of Data	Years Sampled
Powell	Emigrant	5	2000, 2002-05
Key	Emigrant	6	2000-05
Karls	Emigrant	3	2000, 2003-04
Long	Kaiser	5	2000, 2002-05
Patterson	S. Warner	4	2002-05
Mokelumne 14	Mokelumne	4	2002-05
Lower Cole Creek	Mokelumne	4	2002-05
Hufford	1000 Lakes	4	2002-05
Caribou 8	Caribou	4	2002-05
Waca	Desolation	10	1985, 1991-93, 2000-05
Walton & Dana	Ansel Adams	2	2004-05

Besides the long-term monitoring lakes, since 2000 over 160 other lakes have been sampled in California Wildernesses administered by the USDA Forest Service. Lakes in JM were synoptically-sampled in 2005 to identify candidate lakes for long-term monitoring. Their locations are mapped in Figure 1. Before summer 2006 several lakes in this Wilderness will be selected for long-term monitoring, depending upon their sensitivity to acid precursors and other factors. Funding was not available in 2005 to complete the synoptic survey of all JM lakes. Presuming available funding, the southern portion of JM will be synoptically-sampled in 2006. When this sampling is complete, and final lakes selected for long-term monitoring in JM, the monitoring network will be complete.

This report addresses lake chemistry in the context of an early-warning monitoring program for acidification of Wilderness lakes. The monitoring program is not a research study, and relatively minor irregularities in the quality assurance results are not presumed to be causes for major concern.
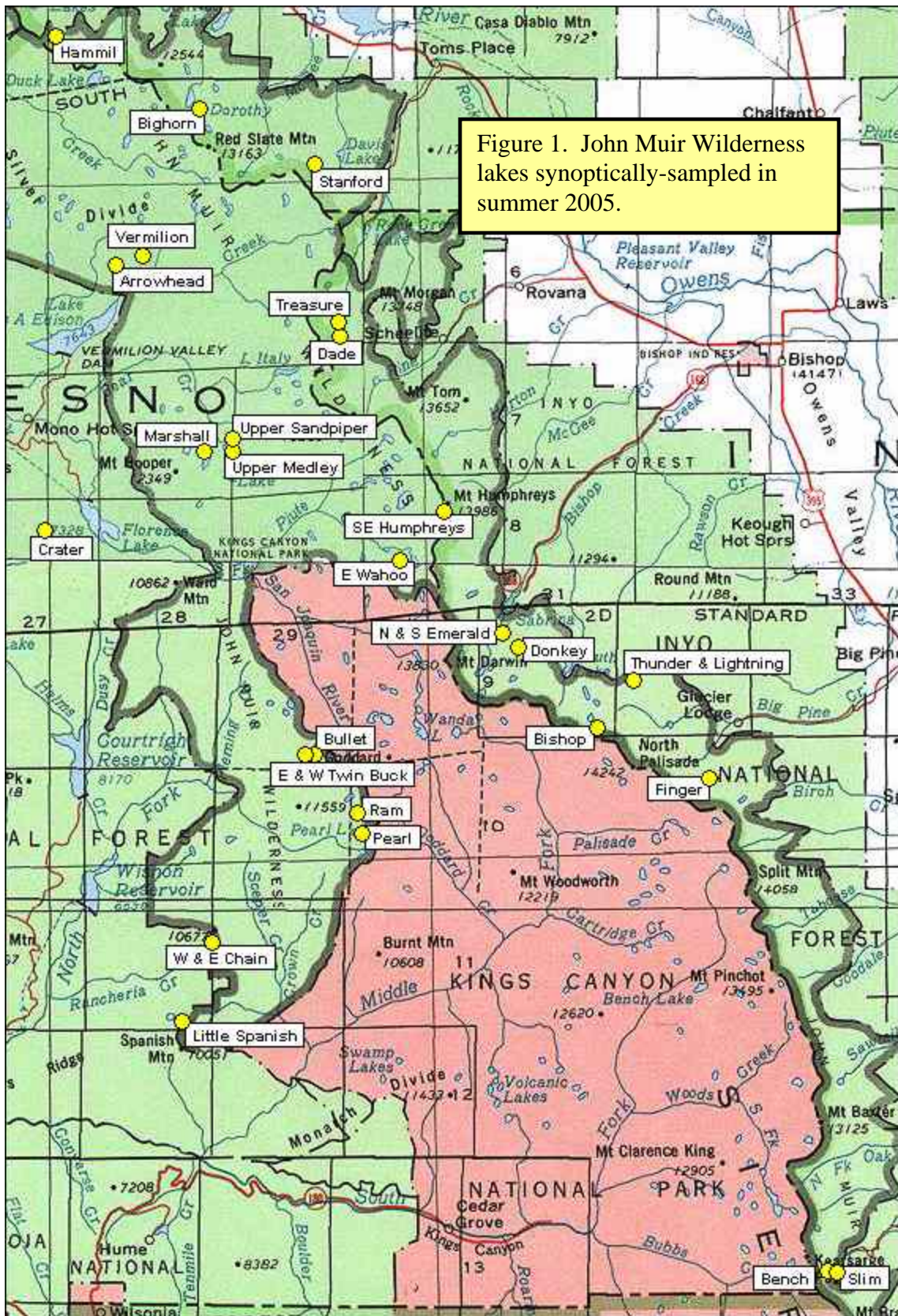
Figure 1. John Muir Wilderness lakes synoptically-sampled in summer 2005.

3.0 Objectives

This report has five primary objectives:

1) Assess the quality of laboratory analyses of lake water samples collected in 2005, specifically to identify any samples that may need re-analysis or that otherwise may require additional action (e.g., revision of sample type/label or deletion of the data).
2) Summarize the relationships between the 2005 lake chemistry and data collected in prior monitoring (e.g., trends through time).
3) Identify any differences in lake chemistries among the Wildernesses based on the combination of synoptic and long-term monitoring data.
4) Flag any lakes having unexpected chemical concentrations in JM Wilderness.
5) Quantify chemical differences between shallow and deep samples collected at thermally-stratified lakes.

This report is not comprehensive in that some components of the 2005 (and earlier) data collection are not evaluated (e.g., data from field data sheets, including water temperature information, and zooplankton data). Nor are other potentially relevant components of monitoring program comprehensively addressed (e.g., adequacy of training, dataset formalization).

4.0 Methods

To address the quality assurance objective, a variety of standardized techniques are available. This assessment focuses on commonly-used techniques described and exemplified in prior assessments for Forest Service lakes (e.g., Turk 2001, Eilers 2003, Eilers et al. 1998) and does not include all possible assessment procedures. The procedures evaluate (1) internal consistency of samples (e.g., transit time, ion balances, calculated versus measured ANC, calculated versus measured conductivity, and outlier assessment), (2) precision through analysis of duplicate samples, and (3) bias or contamination through assessment of field blanks. Each technique is described briefly below. The data were analyzed with the Excel® software package. A section in the quality assurance section of this report addresses samples originally labeled by the analytical laboratory as having "NaCl Contamination".

All samples were analyzed at the USDA Forest Service Rocky Mountain Station analytical laboratory in Ft. Collins, Colorado (hereafter referred to as RM).

Several of the "long-term" lakes were sampled both near the surface (epilimnion), and at depth (hypolimnion) if they were thermally stratified; otherwise the thermally un-stratified long-term lakes were sampled near the surface. All of the JM synoptic lakes were sampled at their outlets, or if an outlet wasn't found, along the shoreline. Specific sampling and monitoring protocols are detailed in Berg and Grant (2004) for the long-term lakes and in Berg and Grant (2002) for the synoptically-sampled lakes.

The summarization objective addresses temporal change with time series plots and tests for statistical trends in chemistry for lakes with at least 5 years of data. Chemical differences among the Wildernesses are based on data collected from synoptic surveys in 2000, 2002, 2004 and 2005. Lakes with unexpected chemical concentrations are identified in the outlier assessment.

Differences in the chemistry from shallow and deep locations in thermally stratified lakes were assessed by comparing these differences against duplicate sample pairs, against deep and shallow samples collected at lakes in Bridger-Teton National Forest, and statistically.

Recommendations for procedural changes, decisions needed and other actions are summarized at the beginning of this report and a listing of the 2005 chemistry data is given in Appendix I.

5.0 Results

5.1 Quality Assurance

5.1.1 Internal Consistency

     5.1.1.1 Transit Time

After collection, samples need to be kept cool to preserve their chemical integrity. Sample warming elevates the risk of biological activity in the sample that could alter the concentration of some chemical constituents. Refrigerant is included in sample mailing packages. The refrigerant has an unknown, but probably relatively short effective lifespan. All effort should be made to assure sample arrival at the analytical laboratory as soon as possible after collection. To this end a courier system is used to expedite shipping of samples from lake to laboratory. If needed, samples should be stored in a refrigerator rather than mailed over a weekend.

Samples from 26% of the lakes sampled in 2005 arrived at the laboratory within 3 days of sample collection (compared to 64% in 2003 and 62% in 2004). Samples from over 57% of the lakes in 2005 samples had transit times of 5 days or longer, with over 47% of the samples in transit 6 days or more. This contrasts to a much smaller percentage of samples taking this long in any prior year. Many of the samples taking 6 or more days in transit were from the JM, a relatively remote Wilderness. The longer transit times may be due in part to relatively long hiking times within the JM.

The critical time period is not the total transit time, but the duration that a sample is kept cool by a short-lived refrigerant (e.g., "blue ice") versus a dedicated coolant (e.g., a refrigerator). Information is not readily available on the time samples were cooled by a short-lived refrigerant so the potential for sample degradation due to inadequate cooling can't be completely assessed. Nevertheless, in general the longer the time between

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sample collection and receipt at the lab, the greater the chance for sample degradation. In this regard the longer transit times for the 2005 samples suggest that consideration be given to reviewing sample storage and transmission procedures to assure samples are kept as cold as possible after collection and that transit times are expedited.

Transit Time (days)	Number of Lakes			
	2005	2004	2003	2002
1	1	0	0	1
2	8	14	3	6
3	2	4	4	3
4	7	0	2	25
5	4	4	1	5
6	15	5	0	1
7	4	1	1	1
8	1	1	0	0

5.1.1.2 Ion Balance

A basic premise in ion balance determinations is that the sum of the negatively charged constituents (anions) should balance the sum of the positively charged constituents (cations) in each sample. Analytical procedures are not perfect so that typically the ion balance is not exact for a set of samples. Ideally, however, there should be no bias; the sum of the cation – anion concentrations for a set of samples should approximate zero. Bias is often attributed either to laboratory error or lack of testing for one or more cations or anions. Several related techniques address ion balance, either for potential problems with specific samples or as indicators of overall trends among samples.

Considered as a whole, the chemistry of the 2005 lake samples is biased (Figure 2), and has a consistent under-estimation of the anions or over-estimation of the cations. 91% of the 2005 non-blank samples have a greater cation sum than anion sum, and there is an overall average of 16.4 $\mu Eq\ L^{-1}$ cation excess/anion deficiency per sample. This bias compares with averages in 2004, 2003, 2001 and 2000 of 15.9, 9.1, 10.7 and 8.75 $\mu Eq\ L^{-1}$ respectively.   A continuing cation excess/anion deficiency bias has been evident during every year of sample analysis, and by one measure, the bias is worse in 2005 than in four prior years.   One synoptic sample, from Bighorn Lake in JM, has exceptionally high sulfate concentration (409 $\mu Eq\ L^{-1}$), over four times higher than any other 2005 sample and 100 fold higher than the median sulfate concentration for the 2005 samples. The high sulfate concentration for this sample contributes significantly to the ion imbalance; without the Bighorn Lake sample, the mean bias drops to 12.4 $\mu Eq\ L^{-1}$.

A four-quadrant plot (Figure 3) provides additional information on the cation excess-anion deficiency problem. This plot shows that the bias is best characterized as an under-estimation of anions. Cation under-estimation has also been consistent through all prior years of the project.

Although the 2005 ion balance results are relatively poor compared to previous years (i.e. without Bighorn Lake better than 2004 but poorer than other earlier years), the ion balance problem has been evident during all years of sample collection. Samples from other dilute waters commonly have a similar imbalance, but the future utility of the data may be compromised until/unless a reason for the imbalance is determined. In past years both Jim Sickman and Joe Eilers independently suggested testing for dissolved organic carbon (DOC) to help determine if relevant constituents are not being analyzed. And both of these individuals also suggested that some samples (or split samples) be analyzed at a laboratory specializing in dilute waters. Last year a sub-set of samples was analyzed by a second laboratory. The second laboratory also identified cation underestimation. If funds are available, analysis for dissolved organic carbon (DOC) should be undertaken in 2006 to help identify if lack of current testing for DOC is a cause of the ionic imbalance.

5.1.1.3. Cation and Anion Sums

The ion balance calculations in section 5.1.1.2 address the sample chemistry as a whole. For individual samples Turk (2001) identified two triggers for cation/anion sum problems—to meet "mandatory" and "higher-quality" levels:

Total Ion Strength (cations + anions) (μEq L^{-1})	% Ion Difference— Mandatory	% Ion Difference— Higher Quality Data
<50	>60	>25
50-100	>30	>15
≥100	>15	>10

Both sets of criteria are percent-based and take into account the fact that percentage values increase for the same absolute differences in concentrations as concentration levels decrease. Percent of samples meeting the two criteria are listed below for monitoring years 2002-2005:

Year	% Meeting Mandatory Criterion	% Meeting Higher Quality Criterion
2005	91	73
2004	90	20
2003	100	83
2002	100	87

In comparison to earlier years, the 2005 data are of intermediate quality in that a higher percentage of the samples in 2005 than in 2004 meet the higher quality criterion, but the 2005 percentages are lower than 2002 and 2003 for both the mandatory and higher quality criteria.

The five 2005 samples not meeting the mandatory criteria are from West Chain, Bighorn (both synoptically-sampled), Huffard, Long (hypolimnion), and Bullfrog (hypolimnion) (long-term monitoring samples).

5.1.1.4 Calculated versus Measured ANC

Another index of potential ion imbalance is the comparison of measured ANC against ANC calculated as the difference in the sum of base cations $(Ca + Mg + Na + K)$ and acid anions $(SO_4 + Cl + NO_3)$. A bias similar to the ion imbalance also exists for the 2005 ANC comparison (Figure 4). The calculated value on average is 15.8 μEq L^{-1} greater than the measured value (compared to 15.65 μEq L^{-1} greater in 2004 and 7.55 μEq L^{-1} greater in 2003), with 91% of the individual samples having greater calculated than measured ANC. The 15.8 μEq L^{-1} average is conditioned largely by one sample, from Bighorn Lake, with calculated ANC = 480 and measured ANC = 243. Without the Bighorn Lake sample the calculated value on average is 11.8 μEq L^{-1} greater than the measured value. Fifty-four percent of the non-blank 2005 samples had calculated minus measured ANCs > 10 μEq L^{-1} (compared to 80% in 2004 and 27% in 2003). Eilers et al. (1998) label samples having calculated minus measured ANCs > 5 μEq L^{-1} as "outliers". By this definition 79% of the 2005 samples would be "outliers" (compared to over 92% in 2004).

The imbalance between calculated and measured ANC is further evidence that either one or more constituents aren't being analyzed , or there are laboratory problems. By this measure the 2005 sample analysis is of higher quality than the 2004 analysis, and lower quality than the 2003 analysis.

The absolute value of the difference between measured and calculated ANC is greater than 25 μEq L^{-1} for four samples collected in 2005: Bighorn (237 μEq L^{-1} difference), Long hypolimnion (41 μEq L^{-1}), Bullfrog hypolimnion (36 μEq L^{-1}), and Lower Cole duplicate (30 μEq L^{-1}).

5.1.1.5 Theoretical versus Measured Conductivity

The measured versus theoretical conductivities from the 2004 lake samples show most samples (86%) to be within the +/- 1 μS cm^{-1} criteria used by Eilers et al. (1998) to identify "outlier" values (Figure 5). The 86% approximates earlier year percentages: 88 in all three prior years. The measured minus theoretical conductivity for the Bighorn Lk sample, however, at 6.63 μS cm^{-1}, is four times greater than the next highest value. This suggests a possible problem with the Bighorn Lk sample. This sample will be discussed later in this report.

Although there is some bias—over 89% of the non-blank samples have greater measured than calculated conductivity (compared to over 80% in 2004 and 75% in 2003)--the mean bias is relatively small, 0.6 μS cm^{-1}. Eilers (2003) described Gallatin National Forest lake samples with this approximate bias as not presenting "… a significant concern with respect to the quality of the data".

Besides the Bighorn Lake sample, seven other samples collected in 2005 exceeded Eilers et al.'s +/- 1 µS cm^{-1} criteria. These samples were from Patterson hypolimnion (1.63 µS cm^{-1} difference), Lower Cole Creek (-1.43 µS cm^{-1}), Long hypolimnion (-1.41 µS cm^{-1}), Bullfrog hypolimnion (-1.41 µS cm^{-1}), Caribou 8 (-1.28 µS cm^{-1}), S Emerald (-1.26 µS cm^{-1}), and Finger duplicate (-1.07 µS cm^{-1}).

5.1.1.6 Outliers

Outliers are extreme values that are inexplicable. Contamination by body contact with sample liquid, for instance, is typically identified by outlier values of sodium and chloride. For all 2005 samples, concentrations of calcium, sodium, magnesium and ANC are plotted in Figure 6, and concentrations of chloride, nitrate and sulfate are plotted in Figure 7.

Three samples, two from Finger Lake and the third from Dana Lake, have sulfate concentrations two to three times higher than any other samples. Because the duplicate samples from Finger Lake have approximately equal sulfate concentrations, the relatively high sulfate concentrations from this lake do not appear to be due to either a sample collection or laboratory error. Similarly, both Dana Lake samples collected in 2004 had high sulfate concentrations, implying that the high sulfate at Dana in 2005 is legitimate.

The high chloride concentration (64 µEq L^{-1}) from the Lower Cole Creek Lake sample was flagged by RM as "NaCl contamination".   Other samples were initially labeled "NaCl contamination". See the Salt Contamination section below for a discussion of these samples.

Many ANC and calcium values plotted in Figure 6 are relatively high. Strong positive correlations between ANC and calcium (and often sodium and magnesium as well) are common (Landers et al. 1987) and pairing of high ANC with high calcium is not unexpected. The Patterson Lake hypolimnion and epilimnion samples (numbers 9 and 25 in Figure 6), for instance, have relatively high ANC, calcium, sodium and magnesium concentrations. Similarly high concentrations of these constituents for this lake were recorded in prior years.

Except for the aforementioned "salt-contaminated" sample, and the Dana and Finger Lake samples, with one exception the outlier plots do not suggest problems with any individual samples. The one exception is the sample from Bighorn Lake (number 56 in Figures 6 and 7). This sample has the highest ANC, conductivity, calcium and sulfate concentrations of any sample collected in 2005, as well as a high nitrate concentration. Concentrations of these magnitudes for these constituents are uncommon for Sierra Nevada lakes, although some California lakes in the Western Lake Survey of the mid-1980s also had high calcium and sulfate concentrations (e.g., Hoover Lake in Hoover Wilderness with sulfate = 386 µEq L^{-1} and calcium = 493 µEq L^{-1}). Lakes outside of the Sierra commonly have higher concentrations. For instance, the mean calcium and ANC

concentrations of 1798 lakes surveyed in the Eastern Lake Survey were 245 and 264 µEq L^{-1} respectively (Kanciruk et al. 1986).

5.1.2 Precision -- Duplicate Samples

Nine lakes in 2005 had "duplicate" samples that were collected either from near the lake surface (three samples from long-term monitoring lakes) a few minutes apart, or at lake outlets (six synoptically-collected samples from JM), also a few minutes apart. These duplicates should be nearly identical in their constituent concentrations. A measure of chemical variation, the percent relative standard deviation (%RSD), was calculated for all duplicates for ANC, calcium, nitrate, conductivity, magnesium, sodium, chloride, potassium and sulfate concentrations. Per B. Gauthier (5/30/02 email to J. Peterson) the %RSD for duplicate samples should be $\leq 10\%$. The following table lists the percentage of the pairs of duplicate samples with %RSD greater than 10% for samples collected between 2001 and 2005:

	Percent of Duplicates with %RSD > 10%				
	2005	**2004**	**2003**	**2002**	**2001**
Number of Duplicate Pairs	9	8	14	11	12
Chemical Constituent					
ANC	44	43	23	55	8
Calcium	11	14	38	36	25
Nitrate	0	29	8	0	9
Conductivity	22	0	46	18	17
Magnesium	11	29	8	36	8
Sodium	22	14	8	9	8
Potassium	22	57	8	18	8
Chloride	56	29	23	27	17
Sulfate	22	0	23	9	25

For the %RSD metric, compared to earlier years, the 2005 duplicate samples were approximately as precise as the 2004 and 2002 duplicates and not precise as the 2003 and 2001 duplicates.

The %RSD calculation procedure is sensitive to "sample size". Calculation of standard deviations on the basis of two values is marginal; typically at least three values are used, and ideally a much larger sample size should be the basis for the %RSD calculation. The relatively high values listed in the table above may be partially due to this sample size effect.

ANC is the single best constituent for %RSD assessment because it tends to integrate the concentrations several of the other constituents. %RSD calculations were also undertaken for the other chemical constituents having a preponderance of non-0 concentrations. Over 84% of the 2005 duplicate pairs with %RSD > 10% were from three lakes, or one-third of the lakes with duplicated samples. And over one-third of the %RSDs > 10% were from one of these lakes, Lower Cole Creek. This focus on three lakes implies the

need for closer scrutiny on the chemistry of those lakes. Two of the three lakes, long-term monitoring lakes Waca and Mokelumne 14, often had low concentrations of the constituents with %RSD > 10%. When constituent concentrations are low, small differences in concentrations can produce relatively large %RSD values. This is particularly accentuated for ANC, because laboratory determination of ANCs in the μEq L^{-1} range below 10 is somewhat problematic and typically more variable than for ANCs > 10 μEq L^{-1}. As an example, the relatively small absolute difference in ANC for Waca Lake (10.9-5.8 = 5.1 μEq L^{-1}) produced a large %RSD of 43.7, at least partially because the ANC is small to begin with; a relatively small absolute difference between duplicates becomes a relatively large %RSD when the difference is divided by a small number. The 43.7 %RSD for Waca ANC was by far the largest %RSD for Waca; all other Waca %RSDs were below 15 except for chloride, at 19.

Although fewer constituents had %RSDs > 10 for Mokelumne 14 than Waca, the %RSD magnitudes were greater (i.e. 35 for ANC, 26 for conductivity, 75 for potassium and 65 for chloride). The high %RSDs were associated with relatively low absolute values of ANC and conductivity but not potassium or chloride. Lower Cole Creek Lake also had high potassium and chloride %RSDs (129 and 127 respectively), and more duplicates had high %RSD for chloride than any other constituent (5 of the 9 duplicate pairs). High chloride %RSD values suggest the possibility of contamination by perspiration, and RM lab staff identified the Lower Cole Creek Lake sample (but not the duplicate) as having "NaCl contamination." Salt contamination is discussed in more detail later in this report.

The mean absolute differences between the duplicates (the precision) for major chemical constituents are compared below for years 2003 through 2005:]

Constituent	Unit	Mean Absolute Difference		
		2005	2004	2003
ANC	μEq L^{-1}	3.62	2.35	3.18
Conductivity	μS cm^{-1}	1.36	0.49	0.22
Calcium	μEq L^{-1}	1.08	1.34	1.91
Magnesium	μEq L^{-1}	0.29	0.80	0.72
Sodium	μEq L^{-1}	1.12	2.70	0.72
Potassium	μEq L^{-1}	8.81	1.91	0.34
Chloride	μEq L^{-1}	7.94	0.16	0.62
Sulfate	μEq L^{-1}	0.20	0.33	0.24
Nitrate	μEq L^{-1}	0.03	0.25	0.09

The 2005 results are generally comparable with the two earlier years for all constituents except potassium and chloride. The high differences for these constituents are potentially due to contamination by perspiration. In a study of lake waters on the Mt. Baker-Snoqualmie National Forest in Washington, Eilers et al. (1998) characterized samples with mean absolute differences $\leq$ 1.0 μEq L^{-1} as dilute waters. Except again for potassium and chloride, the 2005 Sierran samples generally match this criterion for dilute lake water.

5.1.3 Bias -- Field Blanks

To help assure that water collection bottles are not contaminating samples, "field blanks" have water—typically de-ionized with very low or undetectable constituent concentrations—that is stored in the bottles for time periods comparable to the amount of time sample water remains in a bottle prior to analysis. Field blanks are typically sent out by the laboratory with the other bottles and taken to the field along with the actual sample bottles. Common contaminants in the field blanks are sodium and chloride, from perspiration, or elevated acidity as a residue from prior cleaning of the bottle. PSW Station's Riverside chemistry laboratory QA/QC protocol states that "[T]he value of a blank reading should be less than ± 0.05 mg/l from zero" and Eilers et al. (1998) used 1.0 $\mu Eq\ L^{-1}$ for individual ions as a trigger value for blank contamination.

Nine field blanks were incorporated into the 2005 sample collection. Twenty-seven of 81 constituent analyses (9 constituents for each blank) had detectable results. Four of the 27 detections were ≥ 0.05 mg/l, PSW Riverside's threshold value. None of these detections had concentrations above 0.066 mg/l, only slightly above the threshold value. Ten of the 27 detection were $\geq 1.0\ \mu Eq\ L^{-1}$, Eilers et al.'s (1998) criterion for individual ions.   The highest concentration was 3.29 $\mu Eq\ L^{-1}$, and the three highest concentrations were for calcium. None of the detected concentrations were particularly high and the detections appear to be randomly distributed among the nine field blanks (in other words, no single sample or samples had a preponderance of detections). Although there may be an issue with determination of calcium concentrations, there does not appear to be overwhelming evidence for a calcium problem. Potentially a problem with determination of calcium concentrations could relate to the ion imbalance that has persisted through all years of the monitoring program.

 In summary, the field blank assessment does not appear to identify a systematic problem with sample collection. Nor does it identify any individual problematic samples or individual constituents.

5.1.4   Salt-contaminated Samples

Four samples, all from long-term monitoring lakes (Bullfrog-hypolimnion, Long-hypolimniom, Powell-hypolimnion and Lower Cole Creek-epilimnion), were initially labeled by RM staff as having "NaCl contamination". One of the four "contaminated" samples was a duplicate. The sample paired to the duplicate was not contaminated.

Salt contamination is typically caused by perspiration mixing with sample liquid. These were the first salt-contaminated samples identified by RM since the LAKES project began. Because salt contamination implies improper handling of the samples—sample liquid should not be touched—there are ramifications to sampling handling, and therefore crew training, that need resolution.

LAKES project protocols call for at least two samples to be collected concurrently at each lake. One of the two is sent to RM with the other kept in refrigerated storage on-Forest as a backup. The backups for the three "contaminated" samples were analyzed by RM in November 2005. After review of the concentrations of the backup samples, and further consideration, RM staff decided to remove the "NaCl contamination" comment for the original Powell, Long and Bullfrog samples—but retain it for the Lower Cole Creek sample. The final RM dataset includes these changes plus results for the three backup samples. It is recommended that the salt-contaminated Lower Cole Creek Lake sample be retained in the dataset but not used in any analyses.

5.1.4.1 Training and Sampling Handling

The source(s) of the contamination of the Lower Cole Creek Lake sample cannot conclusively be determined. It nevertheless seems prudent to notify all sampling crews that a 2005 sample was contaminated by perspiration, and reiterate to them the need for careful handling of samples to minimize the likelihood of contamination.

5.1.4.2 Interpretation of Results of Paired Samples

For some constituents, concentrations for the Long, Powell and Bullfrog original and backup paired samples differ appreciably among the pairs and with respect to samples collected in the past at these lakes:

Lake and Sample Type	Concentration (μEq L^{-1}, except for μScm^{-1} for conductivity)						
	ANC	Cond.	SO4	NO3	Ca	Cl	Na
Long "Contaminated"	34.8	8.3	3.6	1.2	39.0	2.8	28.8
Long Backup	53.7	8.1	3.1	1.2	32.5	2.6	25.4
Long 2003-04 Mean	46.7	6.3	2.8	0.2	25.2	2.8	25.6
Powell "Contaminated"	47.5	7.3	1.1	0	26.7	3.9	20.1
Powell Backup	41.3	7.0	1.3	0	23.8	3.8	17.7
Powell 2002-04 Mean	38.7	6.1	2.4	0	21.1	5.6	21.8
Bullfrog "Contaminated"	7.0	5.5	1.9	0	17.5	5.8	22.7
Bullfrog Backup*	21.6	5.0	1.6	0	11.1	4.8	19.1

* 2005 is the second year for sampling of Bullfrog Lake. In 2004 Bullfrog was sampled from the lake's outlet. Outlet and hypolimnion samples would not be expected to be comparable so pre-2005 Bullfrog data aren't listed.

A possible reason for the differing concentrations is degradation of the backup samples during storage. The storage duration was not unusually long and this cause for the differences is relatively unlikely. The differences between the 2005 and prior year samples could be due to change through time or simple between-year variation. The ANC differences between the "contaminated" and backup samples are relatively large, particularly for Bullfrog and Long Lakes. The bottom line recommendation is to simply

retain all the data, from all pairs, in the dataset and document the circumstances surrounding the need for the backup samples.

5.1.4   Summary of Quality Control Findings

The ion imbalance identified in earlier years persisted in 2005. Analysis of a subset of the samples by a second laboratory in earlier years suggested that the cause for the imbalance is not necessarily a laboratory problem but is probably lack of analysis of one or more constituents that cause the current imbalance. Dissolved organic carbon is a candidate constituent that should be tested to help resolve the cause of the imbalance.

Two irregularities for individuals samples are the outlier status of the Bighorn Lake sample and the salt contamination of one sample.

The Bighorn Lake sample clearly has concentrations for several constituents that are atypical for samples previously collected in the LAKES program. However, as mentioned above, some Sierran lakes have similarly high concentrations, and lakes in the eastern US routinely have concentrations in the ranges of those from Bighorn Lake. Although the Bighorn Lake sample strongly influences statistical analysis of the JM sample set, on balance there does not appear to be a compelling reason to delete this sample from the dataset.

It is recommended that the salt-contaminated Lower Cole Creek Lake sample be retained in the dataset but not used in any analyses. An alternative would be to delete this sample from the dataset.

5.2 Time Trends for Long-term Monitoring Lakes

Four lakes have been monitored at least five times (see table on page 5), with one of these, Waca Lake in Desolation Wilderness, sampled ten times since 1985. A monitoring duration of 5 or 6 years is minimal for preliminary assessment of temporal change, and the literature suggests that typically a much longer time period is needed before temporal trends can be statistically verified. To offer a preliminary assessment of temporal change, plots of the chemistry of the four lakes are presented in Figure 8, and the results of a simplified trend analysis are presented.
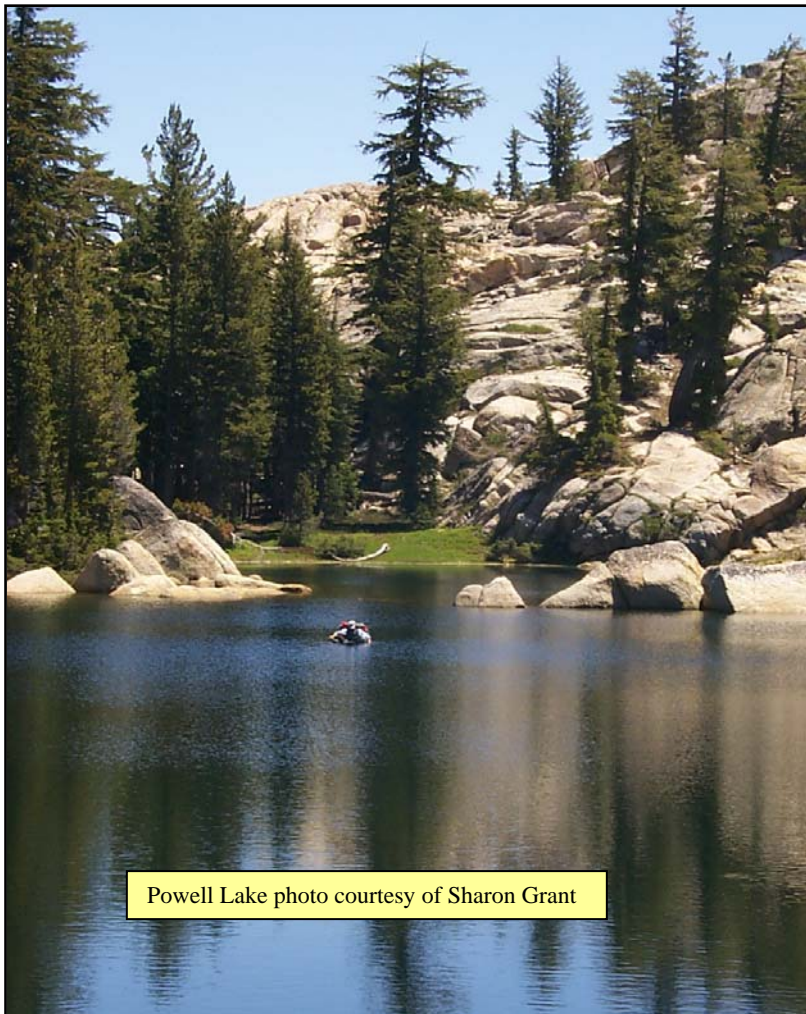
Powell Lake photo courtesy of Sharon Grant

The magnitudes of the concentrations changes between years are typically small, on the order of one to a few µEq L^{-1}. During development of the monitoring component of the Sierra Nevada Framework extensive research identified that annual ANC, sulfate and nitrate changes less than 30% would not be cause for alarm (personal communications, Al Leydecker and Jim Sickman 2000). The percent changes in Figure 8 are typically less than 30%, even for the very low concentrations levels for which very low absolute differences would be relatively large percentage differences.

5.2.1 Waca Lake

Waca Lake has a record of sufficient duration to assess change through time (Figures 8a and 8b). To statistically determine temporal change, simple linear regression, of year of data collection versus constituent concentration, was undertaken for each chemical constituent. In this context, a regression slope that is statistically different (at the 5% level) from 0 implies a statistically significant temporal change.

Similar to a trend first identified in 2004, the regression slope for sulfate differs significantly from 0 at the 5% level, and the +/- 95% band on the slopes is negative. This analysis identifies a downward trend through time; sulfate concentrations in the 4-6+ µEq L^{-1} range between 1985 and 1993 have more recently dropped to the 2-3+ range. The trend for both 2004 and 2005 is a 0.15 µEq L^{-1} decrease per year since 1985. Evidence from recent atmospheric deposition measurements in the Sierra Nevada also shows a downtrend in sulfate through time. The regression slopes for ANC and nitrate, two other important indicators of potential acidification, are not significantly different from 0 (at

the 5% level) and the +/- 95% band on the slopes contain 0, indicating non-significance for ANC and nitrate. Statistics from the regression analyses for these constituents are below:

Constituent	Adjusted R^2	Regression slope	F-value*
ANC	0.20	-0.30	0.11
Sulfate	0.44	-.15	0.02
Nitrate	0.49	-0.03	0.22
Calcium	0.08	-0.20	0.22

*: Values $\leq$ 0.05 imply statistical significance at the 0.05 level.

Theoretically, increases in sulfate and nitrate, and a decrease in ANC over time, could be a precursor to acidification, although alternative explanations for changing levels of these constituents are possible. The regression slopes for sulfate and nitrate are negative, suggesting decreases in those constituents over time, rather than increases than might imply acidification. The negative slope for ANC could be evidence for acidification if the slope were significant.

The 30% change criterion, mentioned above as an indicator of potential concern, is met for ANC and marginally for sulfate. These higher percent changes are not believed to foretell acidification because (1) sulfate is decreasing over time, rather than increasing as would be expected as a precursor for acidification, and (2) a single low ANC concentration, from 2001, causes the 30% criterion to be triggered. The low concentration is followed in 2002 through 2005 with ANC levels similar to prior years. ANC concentrations in the 1-2 μEq L^{-1} range (as in 2001) are at the edge of the resolution band for typical laboratory analysis; values in this range are less reproducible than higher values.

5.2.2 Key Lake

At Key Lake in the Emigrant Wilderness, ANC dropped from the 8-10 μEq L^{-1} range between 2000 and 2003 to less than 1.4 μEq L^{-1} in 2004 and 2005, causing a significant change in ANC at Key Lake for the six survey years from 2000 to 2005. There were no statistically significant changes for either sulfate or nitrate—two other potential precursors of acidification—at Key Lake. Data from future years are needed before interpreting further the ANC changes. Statistics from the regression analyses are:

Constituent	Adjusted R^2	Regression slope	F-value*
ANC	0.62	-1.87	0.04
Sulfate	-0.07	-0.17	0.45
Nitrate	-0.23	0.05	0.80
Calcium	-0.25	-0.01	0.98

*: Values $\leq$ 0.05 imply statistical significance at the 0.05 level.

Some of the year-to-year ANC, sulfate and nitrate differences meet the 30% triggering value. However, except for ANC, the absolute value of the yearly differences are small, typically less than 2 μEq L^{-1}, and probably not realistically significant.

None of the constituent concentrations plotted in Figure 8d show an obvious trend through time; increases are typically followed by decreases (or vice versa), and none of the trends are statistically significant.

5.2.3 Long Lake

At Long Lake in Kaiser Wilderness ANC is higher than at the other three lakes addressed in this section, and ranged from the low to high 30 μEq L^{-1} between 2000 and 2005 (Figure 8e). Calcium and sodium concentrations have also been slightly higher at Long than the other three lakes. No trends through time are identified for this lake, and any incipient increases through time—for instance for sodium and potassium between 2000 and 2004—were negated by downturns in 2005 (Figure 8f). Except for ANC, year-to-year changes for the other constituents have typically been 1 to 2 μEq L^{-1} and none of the annual ANC, sulfate or nitrate concentration changes meet the 30% criterion.

Constituent	Adjusted R^2	Regression slope	F-value*
ANC	-0.28	0.38	0.74
Sulfate	-0.07	0.14	0.45
Nitrate	0.26	0.25	0.22
Calcium	0.16	0.70	0.28

*: Values $\leq$ 0.05 imply statistical significance at the 0.05 level.

5.2.4 Powell

At Powell Lake in Emigrant Wilderness no statistically significant trends through time were identified for any chemical constituent. Similar to Long Lake, at Powell there has been very little variation through time in conductivity, magnesium, potassium, ammonium and sulfate (Figures 8g and h). Like the other three lakes nitrate concentrations have been very low, and at Powell were below the detection limit for all five surveys between 2000 and 2005. None of the annual ANC, sulfate or nitrate concentration changes at Powell Lake meet the 30% criterion.

Constituent	Adjusted R^2	Regression slope	F-value*
ANC	-0.33	0.71	0.18
Sulfate	-0.33	-0.01	0.90
Nitrate	NA**	NA	NA
Calcium	-0.09	0.18	0.48

*: Values $\leq$ 0.05 imply statistical significance at the 0.05 level.
**: NA = Not applicable. All nitrate values were 0 and a regression equation could not be calculated.

5.3 Lake Chemistry Differences Among Class I Areas

Chemistry information is available from synoptic surveys of lakes from ten Class I Wildernesses. Because the data were collected for different reasons, the results are not strictly comparable among Wildernesses. For instance, Wildernesses with a relatively small number of lakes (South Warner, Kaiser and 1000 Lakes) were censused—all lakes in these Wildernesses were sampled. In Wildernesses with more lakes, lakes were selected for low ANC (JM, Ansel Adams, Mokelumne and Caribou) or to be more representative of lakes in the Wilderness (e.g., Emigrant where lakes on both granitic and volcanic terrain were purposively sampled). One ramification of these different lake selection criteria is that JM, Ansel Adams (AA), Mokelume and Caribou Wildernesses would be expected to have lower ANCs than the others because the lakes sampled in these Wildernesses were modeled to have low ANC. Also the chemical variability would be expected to be greater in the censused Wildernesses and Emigrant where a broader spectrum of lake chemistries were presumably sampled. Last, sample size differences could influence the results; 13 times more lakes were sampled in Emigrant than in Dinkey (Figure 9a). The results described below for JM are incomplete in that the southern portion of that Wilderness has not yet been sampled.

Mean and standard deviation plots for ANC, calcium, nitrate and sulfate are shown in Figure 9a-d. ANC is displayed as the single best gauge of sensitivity to acidification. Calcium is representative of alkaline inputs. The atmosphere is the primary source of nitrate in wildlands and sulfate represents acidic inputs that can have an atmospheric source.

In the figures standard deviation (SD) values (the small diamonds) that overlap horizontally imply lack of a statistically significant difference at the 5% level. For instance, the lower ANC 1 SD value for S. Warner Wilderness—at approximately 163 μEq L^{-1} – is greater than any other 1 SD value, with the upper 1 SD value for JM Wilderness, at 132 μEq L^{-1}, the most comparable 1 SD value. On the basis of this visual comparison of 1 SD bands, ANC is greater in S Warner than any other Wilderness, and because the +/- 1SD values of the other Wildernesses overlap, the ANCs of the other Wildernesses are not statistically different at the 5% level. Also using this visual comparison technique—

- Calcium at S Warner is greater than the other Wildernesses except JM and possibly Emigrant.
- Sulfate and nitrate concentrations among the Wildernesses do not differ significantly because the +/- 1 SD bands overlap.

Rather than relying on mean differences among Wildernesses as the sole differentiating criteria, ANC and nitrate distributions by Wilderness are compared in Figures 10 and 11. These graphs relate the percentage of samples in each Wilderness with concentrations less than any specified ANC or nitrate concentration. For instance, 70% of the JM samples had nitrate concentrations less than about 6 μEq L^{-1}, but for the same 70%

"benchmark" all other Wildernesses had much lower nitrate concentration, and for several Wildernesses over 70% of their samples had undetectable (0) nitrates.

From Figure 10, South Warner Wilderness is clearly distinctive from all other Wildernesses in having much higher ANC values. Furthermore, at least one-half of the lakes sampled in all other Wildernesses had ANCs less than 50 μEq L^{-1}, a value identified by Sullivan (2001) as the ANC level probably protecting Sierra Nevada lakes from foreseeable episodic acidification. These Wildernesses are therefore at greater risk than South Warner in terms of potential acidification. Among the non-South Warner Wildernesses, Dinkey, Desolation and Ansel Adams have either all or a preponderance of their samples lakes with ANC < 50 μEq L^{-1}, suggesting these Wildernesses may be particularly sensitive to acidification. Emigrant and JM have several high-ANC lakes probably because lakes in volcanic terrain were sampled in Emigrant, and lakes influenced by atmospheric influxes of dust from east of the Sierra were sampled in JM.

5.3.1 Elevated Nitrate and Sulfate Concentrations East of the Sierran Crest

From Figures 9d and 11, appreciably more of the lakes sampled in AA and JM Wildernesses had relatively high nitrate than in the other Wildernesses.   Sulfate concentrations for the AA and JM samples are also generally higher than for the other Wildernesses (Figure 9c). Because the variability in concentrations for these two constituents is very large, statistically the AA and JM samples do not differ from the samples from the other Wildernesses. Nevertheless the generally higher nitrate and sulfate in AA and JM warrant discussion. Except for S Warner, samples from the other Wildernesses have low concentrations of most constituents.   Candidate explanations for the generally greater nitrate and sulfate in AA and JM are:
- Nitrate and sulfate concentrations have changed recently across the Sierra Nevada and this change is seen only in the two most recently sampled Wildernesses, AA and JM.
- The modeling has been less effective in AA and JM in identifying dilute lakes so that the lakes sampled in these two Wildernesses have higher concentrations than in the lakes sampled earlier in the monitoring program.
- Lakes have higher nitrate and sulfate concentrations in AA and JM than other Wildernesses in the Sierra Nevada and southern Cascades.
- A small number of unrepresentative lakes in AA and JM force higher mean and standard deviations for nitrate and sulfate.

With the information currently available, it's not possible to conclusively determine the cause for the higher nitrate and sulfate in JM and AA. However, the second explanation is not supported by the ANC data in that the mean ANC for AA and JM is similar to the mean ANC of most other Wildernesses (Figure 9a). Lakes on the eastern side of both AA and JM have higher sulfate and nitrate concentrations than lakes west of the Sierran crest. S Warner, a Wilderness with relatively high mean nitrate and sulfate concentrations, is also located in eastern California. Potentially atmospheric pathways with sources in the alkaline Grate Basin are influencing these eastern lakes, and are therefore the cause of the higher means and standard deviations for nitrate and sulfate in these three Wildernesses.

Taken together, figures 9-11 suggest that ANC, calcium, sulfate and nitrate concentrations are generally similar for Wildernesses on the western sides of the Southern Cascades and Sierra Nevada. The chemistries of lakes in these Wildernesses are dissimilar from lakes potentially receiving atmospheric deposition from the east—all of S Warner, and some lakes in AA and JM. The variability in concentrations at JM, and to a lesser extent in S Warner and AA lakes, is greater than in the "west-side only" Wildernesses. This may also be influenced by the east-west nature of the distribution of lakes in JM and Ansel Adams. Higher nitrate and sulfate exist east of the Sierran crest in the JM and Ansel Adams lakes. Combining relatively high concentrations for east-side lakes with relatively low concentrations for west-side lakes produces high variability overall. In this regard it will be interesting to quantify lake chemistry for Hoover Wilderness in that Hoover is located entirely east of the Sierran crest.

5.4 Chemistry of Thermally-stratified Lakes

In the R5 monitoring program, lakes are sampled in early summer, soon after maximum snowmelt, to help assure that the lowest ANC of the year is quantified. Some Sierran lakes are thermally stratified at this period of the year. Thermal stratification infers stability of water masses in a lake and the probability of differing water chemistries in the different thermal strata. Thermal stratification is generally expressed as three temperature zones, an upper, warmer portion of the lake (epilimnion), a transitional zone (metalimnion) and the deeper, colder hypolimnion. The metalimnion is usually relatively thin and sampling in stratified lakes focuses on the epilimnion and hypolimnion.

The chemistry of the eplimnion and hypolimnion often differ. As a generality, the hypolimnion can be oxygen-deficient, after plant decomposition processes deplete the available dissolved oxygen and oxygen isn't replenished by mixing of lake waters. Low oxygen levels may restrict where fish can go in a lake and limit the types and numbers of fish in the hypolimnion. Coldwater fish typical of high-elevation Sierran lakes require 6-7 mgL^{-1} of dissolved oxygen to survive, and will migrate to areas of higher dissolved oxygen (the shallower epilimnion) if dissolved oxygen concentrations aren't adequate in the deeper regions of a lake. Phosphorus and nitrogen differences can exist between the shallow and deep zones, although generalities about these differences are not simply made because different scenarios are possible, and often depend upon the trophic status of the lake.

An objective of the monitoring program is to quantify major parameters of lake chemistry during periods of anticipated low ANC. A presumption during development of the monitoring program was that thermal stratification would require sampling of both the eplimnion and hypolimnion, to quantify the chemistry of the entire lake; sampling of the shallow zone alone would not represent the chemistry of the entire lake. This presumption is addressed in this section, by—
- Assessing the occurrence of stratified lakes sampled to date on the reasoning that if few or no lakes were stratified when sampled, there is no need to sample the deep zone and potentially sampling could be simplified to outlet sampling only.

- Comparing differences in shallow and deep chemistries to the differences between duplicate samples, against thermally stratified lakes elsewhere, and statistically to identify any significant differences.

5.4.1. Occurrence of Thermal Stratification

Between 2002 and 2005, 39% of the 36 lakes assessed for thermal stratification were stratified. Several lakes (e.g., Patterson, Powell and Long) were stratified during each sampling. Waca Lake, in Desolation Wilderness, was stratified in 2002 and 2003, but not in more recent years. These four lakes are much deeper (averaging almost 10 m deeper at the sampling location) than the other long-term monitoring lakes. Because almost 40% of the "long-term" lakes were stratified, comparison of the shallow and deep chemistries was undertaken.

5.4.2. Comparison Against Duplicate Samples

Duplicate samples collected a few minutes apart should have nearly identical chemical concentrations. Any differences between the duplicates should quantify the precision of the sampling and laboratory testing activities, and a measure of differences between duplicates can be considered a conservative measure for comparison to differences between shallow and deep samples.

The mean of the absolute value of differences for both duplicates and between epilimnion and hypolimnion samples are listed below for ANC, calcium and sulfate (all μEq L^{-1}):

Duplicates			Epilimnion-hypolimnion		
ANC	Ca$^+$	SO4$^+$	ANC	Ca$^+$	SO4$^+$
2.8	1.7	0.2	12.1	6.2	0.5

These statistics are based on 54 pairs of duplicate samples collected from outlet and mid-lake locations between 2000 and 2005, and on 14 pairs of epilimnion-hypolimnion paired samplings. Because the means for the duplicates are substantially lower than the means for the shallow-deep samples, either there's potentially a real difference between shallow and deep concentrations or some other factor(s) is adding variation to the chemical concentrations of the deep and shallow samples (one factor in the mean ANC difference for the shallow-deep comparison is the large 2005 difference in ANC between the Patterson Lake samples, 48 μEq L^{-1}). This comparison based on precision of the duplicate samples is very conservative, and it's not surprising that as a group the epliminion-hypolimnion differences are greater than for the duplicate pairs. Also inferential statistical testing wasn't undertaken to formally assess these differences. The ANC epliminion and hypolimnion concentrations are shown in Figure 12. Fifty percent of the ANC concentrations are higher in the epilimnion; 71% are higher for calcium, and 43% are higher for sulfate.

5.4.3. Comparison to Lakes in Bridger-Teton National Forest

Several lakes in Bridger-Teton NF (BT) have been sampled periodically since the mid-1980s. Three of five lakes with available data were arbitrarily selected and the absolute differences in their epilimnion and hypolimnion ANC and sulfate concentrations were calculated (calcium data aren't available). For lakes sampled July or earlier on the BT, the mean absolute differences in ANC and sulfate were 7.0 and 1.2 μEq L^{-1} respectively. Fifty-five percent of the BT ANC concentrations are higher in the epilimnion and 72% are higher for sulfate. These comparisons aren't particularly noteworthy other than to suggest that the Sierra and BT samples are generally comparable.

5.4.4. Statistical Testing

Using the Student's t test (paired two sample for means, two-tailed text, Excel software) no statistically significant differences between means of the 14 pairs of epilimnion and hypolimnion samples collected in Sierran lakes since 2002 were found for ANC, calcium or sulfate. By this testing, there's no evidence to suggest that concentrations of ANC, calcium or sulfate were greater in either the epilimnion vs. the hypolimnion, or vice versa. The sample size is relatively small and the existence of "outlier" values, such as the large ANC difference at Patterson Lake ANC in 2005, adds variance that overwhelms relatively minor differences otherwise.

In summary, an appreciable percentage of the lakes are thermally stratified, suggesting the possibility of differing water chemistries above and below the thermocline. Although except for ANC, only relatively minor chemical differences were identified between the shallow and deep samples, the sample size is too small to conclusively state that mid-lake sample collection in thermally stratified lakes is not providing useful information.

6.0 Candidate Long-term Monitoring Lakes for John Muir Wilderness

Prior discussions call for establishment of seven long-term monitoring lakes in JM. Because the southern portion of JM was not synoptically sampled in 2005, fewer than seven lakes should probably be identified this year for long term monitoring in JM.

Twenty-nine lakes were sampled synoptically in 2005 as the candidate pool for selection of the long-term monitoring lakes. One-half of these lakes had ANC $\geq$ 50 μEq L^{-1}, and the ANC of many of these "high ANC" lakes was not well predicted through the modeling exercise.

Because of the long north-south extent of JM, the positioning of JM on both sides of the Sierran crest, and the likelihood of a variety of atmospheric pathways relevant to JM, a reasonable objective is to spread the long-term monitoring lakes both north-south and east-west across the Wilderness. The following discussion presumes this objective and does not address other issues. For instance, lakes meeting the north-south/east-west objective may not be readily accessible.

Four of the five lakes with the lowest ANC are grouped at the west-central section of JM, immediately east of Courtright and Wishon Reservoirs. From a purely "low-ANC"

perspective one of these lakes (e.g., Bullet at 15 μEq L^{-1} ANC), Stanford, Treasure or Dade on the northeast, Marshall on the northwest, Thunder and Lightning on the east-central, and Bench on the southeast give a broad spatial coverage and keep ANC below 36 μEq L^{-1} (except for Bench at 51μEq L^{-1}). The chemical concentrations for the synoptic samples from these lakes are within the expected range, except for moderately high nitrate at Stanford Lake and moderately high sulfate at Thunder and Lightning Lake. If five or six of these lakes are designated for long-term monitoring, another one or two lakes from the southern quarter of JM could be selected for long-term monitoring after synoptic sampling in 2006.

7.0 **Other Issues**

7.1 Topics from Previous Years

Three aspects of the monitoring program that have been previously discussed are the option to sample at lake outlets or along the shoreline, concerns with the ongoing ion imbalance and analysis of the zooplankton samples. There has been no change since the 2004 report on any of these issues and the recommendations from 2004 remain current:
- Consider analyzing a sub-set of the 2006 samples for dissolved organic carbon. DOC sampling requires separate bottles and cannot be done at the RM lab. Therefore more coordination would be needed prior to sample collection than otherwise.
- Concurrently collect both outlet and mid-lake samples at all or most long-term monitoring lakes and compare the chemical concentrations, and analyze the differences (if any) between epilimnion (shallow) and hypolimnion (deep) chemical concentrations to determine the usefulness of the hypolimnion data and potential risks involved with not collecting hypolimnion data in the future.
- Analyze the zooplankton data and discuss pros and cons of continued transparency and zooplankton collection in terms of potentially replacing mid-lake sample collection with outlet sample collection.

7.2 Status of Smith Lake

Smith Lake, in Desolation Wilderness, was sampled in 2005 from a mid-lake location. Both epilimnion and hypolimnion samples were collected. Smith Lake was also monitored in 1991, 1992, 2000, and possibly earlier, presumably from the lake outlet. Smith is a readily-accessible (2.8-mile hike), low-ANC lake (9.7 μEq L^{-1} in 2005) located near the western boundary of the Wilderness, about 2.5 miles from Waca Lake, a long-term monitoring lake with 10 years of data. Was sampling of Smith in 2005 a "one-time" activity, or will Smith be sampled in the future? If its sampled in the future would it become a long-term monitoring lake—with mid-lake sampling--or be sampled from the outlet for chemistry only?

If a second long-term monitoring lake is desired for Desolation Wilderness, consideration should be given to selecting Lost Lake. Lost Lake was monitored intensively by UCSB staff for several years in the early 1990s. Their research included assessment of soil and geology in the Lost Lake catchment as well as quantification of lake outlet flows and

chemistry determinations at monthly intervals (including winter sampling). The wealth of information available for this lake makes it worthy of consideration as a long-term monitoring lake. Monitoring of Lost Lake could also stimulate collaboration with UCSB.

8.0 Conclusions

The overall quality of the 2005 laboratory analysis improved with respect to 2004. Application of commonly-used quality assurance techniques identified no issues other than continuation of a long-standing imbalance between cations and anions and the identification of one lake with outlier chemical concentrations. Recommendations are given to address the ionic imbalance at the beginning of this report.

Except for four lakes, the duration of the monitoring is insufficient to quantify any temporal trends in the acid-base chemistry of the lakes. Statistically significant changes in lake chemistry were identified for one constituent in each of two lakes. Sulfate concentration decreased between 1985 and 2005 at Waca in Desolation Wilderness. At Key Lake in the Emigrant Wilderness, ANC dropped from the 8-10 μEq L^{-1} range between 2000 and 2003 to less than 1.4 μEq L^{-1} in 2004 and 2005. These differences are minor and the ANC change in particular may be an artifact of analytical procedures in that determination of near-0 ANC is problematical.

Lakes in Class I Areas located to the west of the crest of the Sierra Nevada generally have similar chemistries. South Warner Wilderness and parts of Ansel Adams and John Muir Wildernesses are more directly exposed to atmospheric deposition originating in the drier, more alkaline Great Basin terrain east of the Sierra crest. Nitrate and sulfate concentrations at Ansel Adams and Johm Muir in particular are higher and more variable than at Wildernesses located exclusively on western slope of the Sierra Nevada.

There is a potential to revise the monitoring protocol to sample only from lake outlets. This seems premature at this time and additional paired outlet and epilimnion samples should be collected to help address this alternative. Also the zooplankton data collected to date should be analyzed before a decision is made to abandon mid-lake sampling.

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