

Water Quality Review: Sierra Nevada 2004 Lake Monitoring

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Executive Summary

Ten lakes in seven Class I Wilderness Areas were sampled for acid-base water chemistry, water transparency, and zooplankton between mid-June and mid-July 2004 as part of the long-term lake monitoring project of the Pacific Southwest Region, USDA Forest Service Air Resources Program. Fifteen lakes in Ansel Adams and four lakes in Dinkey Lakes Wildernesses were synoptically sampled; several of these lakes are potentially good candidates for addition in 2005 to the long-term monitoring network.

Two long-term monitoring lakes have records long enough to be worth statistical analysis for temporal change. A statistically significant decline in sulfate was identified for Waca Lake, in Desolation Wilderness. The change is slight, from the 4-6 $\mu\text{Eq L}^{-1}$ range between 1985 and 1992 to the 2-3 $\mu\text{Eq L}^{-1}$ range since 2000. No other temporal change was identified for either Waca or Key Lake in Emigrant Wilderness.

A quality assurance review of the chemistry data identified a decline in the quality of the chemical analyses from 2003. For instance, appreciably fewer of the samples were analyzed at a "higher quality" level in 2004 than in 2003.

Ion imbalances evident in prior years persisted in 2004 for chemical analyses done at both the main laboratory that's been used every year as well as a second lab used in 2004. 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 $\mu\text{Eq L}^{-1}$. From synoptic data collected since 2000, mean chemical concentrations from South Warner Wilderness differ statistically from the other eight Wildernesses, although more subtle differences in other metrics exist. Baseline data for major cation and anion concentrations are provided as well as levels of conductivity, ANC and pH.

The option to save time and money by monitoring lakes only from the lake outlet is tempting. However, data from the R5 monitoring program is currently insufficient to base a decision to abandon mid-lake sampling. Studies from elsewhere suggest little chemistry differences between outlet and mid-lake sampling, although samples in some of those studies were collected after mixing of lake water occurred; several lakes in the R5 program have routinely not been mixed at the time of sample collection and consequently their chemistry may vary with depth.

Recommendations

- 1) **Lakes for long-term monitoring in Ansel Adams (and Dinkey?) Wilderness need to be selected.**
 - a. The two labs that analyzed the 2004 synoptic samples had appreciably different ANC values for one low-ANC lake that otherwise could be a good candidate for selection as a long-term monitoring lake. Lower Fernandez Lake had Rocky Mtn lab (RM) ANC = $15.8 \mu\text{Eq L}^{-1}$ and UCSB lab ANC = $9.9 \mu\text{Eq L}^{-1}$. From a review of the data there's no obvious reason to believe either the RM or UCSB value is more reliable. A conservative option is to average the two ANC values for purposes of long-term monitoring lake selection.
 - b. Selection of geographically-spaced lakes in Ansel Adams for long-term monitoring may be advisable. Unfortunately, the only two lakes at the north end of the Wilderness (Dana and Kidney) do not appear representative. Their nitrate, sulfate and calcium concentrations are among the highest recorded during synoptic sampling since 2000 at any Wilderness.
- 2) Several long-term monitoring lake samples have appreciably different concentrations between the two labs used for sample analysis in 2004, and other samples differ between two analyses conducted by the RM lab. **Resolution on the concentrations to enter into the long-term database is needed.** Specifically, the average of the ANC values for Key Lake is a conservative option, and is recommended. Calcium concentrations for three lakes from the Forest Service lab at Rocky Mountain Station (RM) were both extremely low (compared to prior years) and much lower than concentrations from the UC Santa Barbara lab (UCSB). Adoption of the UCSB calcium concentrations is suggested for the long-term database. Averaging the differences for other samples may be appropriate given that the differences are relatively minor.
- 3) Comparison of 2004 results from the UCSB and RM labs suggest that one or more constituents aren't being analyzed; there is a continuing ion bias/imbalance in all of the results. Dissolved Organic Carbon (DOC) may be a likely "missed" constituent. **Analysis for DOC in 2005 should be considered to attempt to explain the continuing ionic imbalance.**
- 4) Outlet sample collection could potentially replace mid-lake sample collection. 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 the outlet sampling alternative 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. **Analyze the zooplankton data and discuss pros and cons of continued transparency and zooplankton collection.**
 - c. **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.**

- 5) Because recorded lake depth at some long-term monitoring lakes has varied up to 4 m, the lake samples and transparency data may be being collected at different locations each year. **To help standardize sample collection location, “GPSing” the Index Location for each long-term monitoring lake should be considered.**
- 6) **Crew training should stress that sunglasses shouldn’t be worn during the Secchi disc/transparency measurement.** The two transparency measurements that were observed through sunglasses are both lower than for other years at the same lakes.
- 7) **The zooplankton data collected since the beginning of the monitoring program should be assessed by an expert.**
- 8) Some synoptically-sampled lakes in some Wildernesses (e.g., Winnemucca in S. Warner; Leopold, Big, Shallow, Fraser, S Wire, Blackhawk and Oyl Lakes in Emigrant) have lower ANC’s than the lakes chosen for long-term monitoring. **Documentation of the reason(s) for not selecting the lowest ANC lake in a Wilderness is probably needed,** to counter any future criticism that long-term monitoring lake selection may have been arbitrary or done with an undisclosed purpose.
- 9) In future synoptic sampling to identify a candidate pool of lakes for long-term monitoring, **reason(s) for not synoptically sampling lakes with the lowest predicted/modeled ANC should be incorporated into the permanent database, and consideration should be given to determining if low predicted ANC lakes in other Wildernesses were not sampled in the past.**

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.

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 in each Class I Area sensitive to atmospherically-driven acidification and monitoring them over the long term. The premise is that monitoring lakes particularly vulnerable to potential acidification will act as “a canary in a coal mine” and 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). The selection process for long-term monitoring lakes is not simple and requires a combination of modeling and synoptic sampling prior to final

selection of long-term monitoring lakes. Ten long-term monitoring lakes were sampled in 2004. 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 2004 29 lakes were sampled from nine Wildernesses as follows:

Wilderness	Number of Lakes Sampled	Long-term Monitoring Lakes
Kaiser	1	1
Ansel Adams	15	0
Dinkey Lakes	4	0
Mokelumne	2	2
Desolation	1	1
Emigrant	3	3
Caribou	1	1
1000 Lakes	1	1
South Warner	1	1

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

Lake	Wilderness	Years Sampled
Powell	Emigrant	2000, 2002-04
Key	Emigrant	2000-04
Karls	Emigrant	2000, 2003-04
Long	Kaiser	2000, 2002-04
Patterson	S. Warner	2002-04
Mokelumne 14	Mokelumne	2002-04
Lower Cole Creek	Mokelumne	2002-04
Hufford	1000 Lakes	2002-04
Caribou 8	Caribou	2002-04
Waca	Desolation	1985, 1991-93, 2000-04

Besides the long-term monitoring lakes, since 2000 over 130 other lakes have been sampled in Sierra Nevada Wildernesses administered by the USDA Forest Service. All lakes sampled in 2004 in the Ansel Adams and Dinkey Lakes Wildernesses were synoptically-sampled to identify candidate lakes for long-term monitoring. Their locations are mapped in Figures 1 and 2. Before summer 2005 several lakes in these Wildernesses will be selected for long-term monitoring, depending upon their sensitivity to acid precursors and other factors.

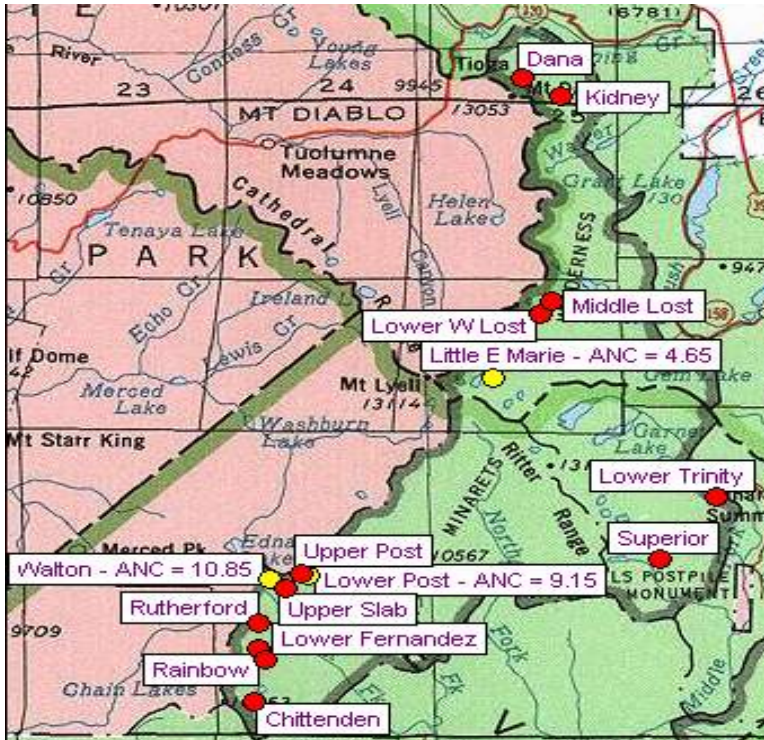


Figure 1. Lakes synoptically sampled in Ansel Adams Wilderness in summer 2004. The three lakes identified with yellow circles have the lowest observed ANC.



Figure 2. Lakes synoptically sampled in Dinkey Lakes Wilderness in summer 2004.

This report addresses lake chemistry and transparency 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.

3.0 Objectives

This report has four primary objectives:

- 1) Assess the quality of laboratory analyses of lake water samples collected in 2004, 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 2004 lake chemistry and transparency data and information 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) Investigate the possibility of replacing mid-lake chemistry sampling with outlet sampling at long-term monitoring lakes.

This report is not comprehensive in that some components of the 2004 (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 addressed (e.g., adequacy of training, dataset formalization).

4.0 Methods

To address the quality assurance objective, a variety of standardized techniques exist for the quality assessment of water sample analyses. 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 techniques 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 (2) bias or contamination through assessment of field blanks. Each technique is described briefly below. The data were analyzed with the Excel[®] software package.

Most samples were analyzed at the USDA Forest Service Rocky Mountain Station analytical laboratory in Ft. Collins, Colorado (hereafter referred to as RM), although 18 duplicates were analyzed at the University of California, Santa Barbara (hereafter referred to as UCSB), to provide comparison to the RM analyses. The UCSB lab specializes in analysis of the dilute waters found in high elevation lakes in the Sierra Nevada.

Several of the “long-term” lakes were sampled both near the surface (epilimnion) and at depth (hypolimnion) if they were thermally stratified. One lake was also sampled at its outlet, to provide comparative information between within-lake and outlet water chemistry.

The summarization objective addresses temporal change with time series plots and tests for statistical trends in chemistry at lakes with at least 5 years of data. Chemical

differences among the Wildernesses are based on data collected from synoptic surveys in 2000, 2002 and 2004. Transparency trends through time are also displayed and discussed. The transparency data are not analyzed statistically because of the short (2-3 yr) length of the dataset.

To assess outlet versus mid-lake sampling, R5 data are evaluated along with more substantial datasets from two other studies.

Recommendations for procedural changes, decision and other actions are summarized at the beginning of this report and a listing of the 2004 chemistry data is given in Appendix I. Appendix II lists all of the transparency data.

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 62% of the lakes sampled in 2004 arrived at the laboratory within 3 days of sample collection (compared to 64% in 2003). A sample from one lake in 2004 was in transit 8 days; none took 8 days in 2003 although samples from one lake in both 2003 and 2004 were in transit 7 days. Eight samples were in transit 6 days in 2004; none were in transit 6 days in 2003.

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 sample collection and receipt at the lab, the greater the chance for sample degradation. In this regard in 2004 samples from almost one-half of the lakes arrived at the lab within 2 days of collection, a much higher percentage than in 2002 and 2003.

Transit Time (days)	Number of Lakes (2004)	Number of Lakes (2003)	Number of Lakes (2002)
1	0	0	1
2	14	3	6
3	4	4	3
4	0	2	25
5	4	1	5
6	5	0	1
7	1	1	1
8	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 values for a set of samples should approximate zero. Bias is often attributed either to laboratory error or lack of testing for either 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 RM chemistry of the 2004 lake samples is biased, and has a consistent under-estimation of the anions or over-estimation of the cations, with 98% of the 2004 non-blank samples having a greater cation sum than anion sum, and an overall average of 15.91 $\mu\text{Eq L}^{-1}$ cation excess/anion deficiency per sample. This bias compares with averages in 2003, 2001 and 2000 of 9.1, 10.7 and 8.75 $\mu\text{Eq L}^{-1}$ respectively (Figure 3). A continuing cation excess/anion deficiency bias has been evident during every year of sample analysis, and by one measure, the bias is appreciably worse in 2004 than in three prior years.

A four-quadrant plot (Figure 4) 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.

Although the 2004 ion balance results are poorer than in previous years (i.e. 15.91 $\mu\text{Eq L}^{-1}$ imbalance in 2004 versus less than 10 $\mu\text{Eq L}^{-1}$ imbalance in all 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.

5.1.1.2.1 Interlaboratory Comparison -- A subset of the 2004 samples was analyzed at a UC Santa Barbara laboratory specializing in the dilute water samples commonly found in Sierra Nevada lakes. Samples analyzed by both labs included all samples from the long-term monitoring lakes plus several samples from the synoptically-surveyed lakes. The ion balance calculated from both labs is plotted in Figure 5. Although the bias from the UCSB analysis is less than from the RM laboratory, results from both labs are biased, suggesting that additional constituents (e.g., DOC) need to be incorporated into the lab analyses. When three labs were used several years ago all three similarly identified a bias, suggesting that the bias is not necessarily a laboratory problem. To help determine the cause of the continuing cation excess/anion deficiency bias, the next step is to test for DOC. Split samples could be sent next year to either the NADP/NTN laboratory in Illinois or the USGS lab in Denver to test for DOC.

5.1.1.3. Cation and Anion Sums

The ion balance calculations address the sample chemistry as a whole. For individual samples Turk (2001) identifies two sets of triggers for cation/anion sum problems, “mandatory” and for “higher-quality” data:

Total Ion Strength (cations + anions) ($\mu\text{Eq L}^{-1}$)	% 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. All 2003 samples met the “mandatory” criteria; in 2004 90% of the samples met this standard. In 2003 17% of the 2003 samples did not meet the “higher quality data” criteria; in 2004 over 80% of the samples did not meet the “higher quality” standard. Although several samples in both years were marginally over the criteria, the 2004 results are clearly inferior to the 2003 results. A cause for concern is that the vast majority of the 2004 samples did not meet the “higher quality” criteria.

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 ($\text{SO}_4 + \text{Cl} + \text{NO}_3$). A bias similar to the ion imbalance also exists for the ANC comparison (Figure 6). The calculated value on average is $15.65 \mu\text{Eq L}^{-1}$ greater than the measured value (compared to $7.55 \mu\text{Eq L}^{-1}$ greater in 2003), with 95% of the individual samples having greater calculated than measured ANC. Over 80% of the non-blank 2004 samples had calculated minus measured ANCs $> 10 \mu\text{Eq L}^{-1}$ (compared to over 27% in 2003). Eilers et al. (1998) labels samples having calculated minus measured ANCs > 5

$\mu\text{Eq L}^{-1}$ as “outliers”. By this definition over 92% of the 2004 samples would be “outliers”.

The imbalance between calculated and measured ANC is further evidence that either one or more constituents aren't being analyzed for, or there are laboratory problems. By this measure the 2004 sample analysis is not of particularly high quality, and the quality has dropped since 2003.

5.1.1.5 Theoretical versus Measured Conductivity

The measured versus theoretical conductivities from the 2004 lake samples show most samples (88%) to be within the $\pm 1 \mu\text{S cm}^{-1}$ criteria used by Eilers et al. (1998) to identify “outlier” values (Figure 7). The measured minus theoretical conductivity for the Dana Lk sample, however, at $3.43 \mu\text{S cm}^{-1}$, is almost three times greater than the next highest value. This suggests a possible problem with the Dana Lk sample. This sample will be discussed later in this report.

Although there is some bias—over 80% of the non-blank samples have greater measured than calculated conductivity (compared to over 75% in 2003)—the mean bias is relatively small, $0.4 \mu\text{S cm}^{-1}$. Eilers (2003) described Gallatin National Forest lake samples with slightly higher bias as not presenting “... a significant concern with respect to the quality of the data”.

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. Concentrations of calcium, sodium, magnesium and ANC are plotted in Figure 8, and concentrations of chloride, nitrate and sulfate are plotted in Figure 9. Three samples, two from Dana Lake and the third from Kidney Lake, have sulfate and calcium concentrations two to three times higher than any other samples. Independent analysis by the UCSB laboratory, of a duplicate Kidney Lake sample, confirms the high concentrations for Kidney Lake, and suggests that the high calcium and sulfate concentrations for the three samples are not necessarily erroneous. Two samples from Patterson Lake have calcium concentrations above $70 \mu\text{Eq L}^{-1}$ and ANCs above $140 \mu\text{Eq L}^{-1}$. Samples from this lake in 2003 had concentrations almost identical to the 2004 values, suggesting that the 2004 analysis of these samples is not problematic.

In summary, there is no evidence that any outliers exist in the 2004 dataset.

5.1.2 Precision -- Duplicate Samples

Seven lakes in 2004 had “duplicate” samples that were analyzed by the Ft. Collins (RM) laboratory. The duplicates were all collected from near the lake surface, between one and five minutes apart. These duplicates should be nearly identical in their constituent concentrations. A measure of variation, the percent relative standard deviation (%RSD)

of ANC was calculated for all duplicates. Per B. Gauthier (5/30/02 email to J. Peterson) the %RSD for duplicate samples should be $\leq 10\%$.

Four of the seven (57%) duplicated samples had %RSD $> 10\%$ for ANC (compared to 36% in 2003). The %RSD for one of the ANC duplicates, for Little East Marie Lake in Ansel Adams Wilderness, was over 37%. The other %RSDs $> 10\%$ were no greater than 13% (e.g., not much above the 10% triggering value).

There are several reasons to believe that the high %RSD for the Little East Marie Lake duplicates is not a major problem. Comparison of the chemical concentrations for the two Little East Marie Lake samples showed very low ANC concentrations (3.4 and 5.9 $\mu\text{Eq L}^{-1}$), the second lowest ANCs in this year's sampling. ANC determination in the $\mu\text{Eq L}^{-1}$ range below 10 is somewhat problematic and typically more variable than for ANCs $> 10 \mu\text{Eq L}^{-1}$. Also, because the ANCs are low, a relatively small absolute difference in ANC ($5.9 - 3.4 = 2.5 \mu\text{Eq L}^{-1}$) produced a relatively large %RSD. None of the non-ANC chemical concentrations vary appreciably between the two Little E. Marie Lake samples. Last, the %RSD calculation procedure is also sensitive to "sample size". Calculation of standard deviations on the basis of two values is marginal; typically at least three values are used. It is possible that the statistical equivalent of "significance" might not be met for most of the duplicate pairs with %RSD > 10 . Considering these factors in combination, there does not appear to be a problem with the two Little E. Marie Lake samples.

The other samples with %RSD $> 10\%$ are similar to the Little E. Marie Lake duplicates in that their ANCs are relatively low (in the teens or $< 10 \mu\text{Eq L}^{-1}$), and their non-ANC chemical concentrations are generally similar between the duplicates from each lake. Consequently, although ideally their %RSDs would be lower; none of the samples appear to need re-analysis for ANC.

ANC was selected as 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. Most of these comparisons showed that the %RSD was either $< 10\%$ or slightly above 10%, suggesting no problems. The %RSD comparison for the two Walton Lake duplicates, however, suggested a problem: the sodium and potassium concentrations for the two duplicate samples differed drastically (e.g., 17.7 $\mu\text{Eq L}^{-1}$ for sodium and 9.4 $\mu\text{Eq L}^{-1}$ for potassium). Reanalysis of these duplicates by the RM lab reduced the differences to 0.9 and 0.2 $\mu\text{Eq L}^{-1}$ respectively. I recommend replacing the initial concentrations for the duplicate sample (SI17) with the revised concentrations.

The mean absolute differences between the duplicates (the precision) for constituents with predominantly non-0 concentrations are all relatively low, although they were generally higher in 2004 than in 2003:

Constituent	Unit	Mean Absolute Difference	
		2004	2003
ANC	$\mu\text{Eq L}^{-1}$	2.35	1.77
Conductivity	$\mu\text{S cm}^{-1}$	0.37	0.04
Calcium	$\mu\text{Eq L}^{-1}$	0.67	0.45
Magnesium	$\mu\text{Eq L}^{-1}$	0.54	0.01
Sodium	$\mu\text{Eq L}^{-1}$	2.51	0.70
Potassium	$\mu\text{Eq L}^{-1}$	1.24	0.01
Chloride	$\mu\text{Eq L}^{-1}$	0.05	0.54
Sulfate	$\mu\text{Eq L}^{-1}$	0.21	0.13
Nitrate	$\mu\text{Eq L}^{-1}$	0.11	NA

Except for sodium and potassium, these mean absolute differences compare favorably with the $1.0 \mu\text{Eq L}^{-1}$ criterion used by Eilers et al. (1998) for dilute lake water on the Mt. Baker-Snoqualmie National Forest in Washington. Without the Walton Lake samples, the sodium and potassium mean absolute differences would be 0.03 and $0.11 \mu\text{Eq L}^{-1}$, well below the Eilers et al. (1998) criterion.

On balance, except for the Walton Lake samples, the duplicates assessment does not identify major irregularities. Unfortunately, the value of this QA/QC metric also was poorer in 2004 than 2003.

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 chemical laboratory QA/QC protocol states that “[T]he value of a blank reading should be less than $\pm 0.05 \text{ mg/l}$ from zero” and Eilers et al. (1998) used a $1.0 \mu\text{Eq L}^{-1}$ criterion for individual ions.

Six field blanks were incorporated into the 2004 sample collection. Eighteen of 60 constituent analyses (done for the six blanks) had detectable results. Thirteen of the 18 detections were $\leq 0.05 \text{ mg/l}$, PSW Riverside’s threshold value. Two of the 18 detections had relatively high concentrations (0.67 and 0.14 mg/l for calcium and sulfate respectively). Both of these detections were from one sample, from Dana Lake in the Ansel Adams Wilderness. This sample also had out-of-the-ordinary ANC, pH and conductivity values, suggesting that it is a problematic sample. Coincidentally, the two duplicate non-blank samples from Dana Lake had high sulfate and calcium concentrations and one of those two duplicates had an inordinately high value of

theoretical minus measured conductivity. Re-analysis by the RM lab of the three Dana Lake samples showed no difference from the original values. RM lab manager Louise O'Deen could not explain the odd concentrations for the field blank, although she speculated that impure de-ionized lab water may have been a cause. Her suggestion is to delete this sample from the database.

The field blank assessment does not appear to identify a systematic problem with sample collection. In future years, if the same crew that collected the Dana Lake samples will be part of the sample collection effort, consideration should be given to emphasize in their training that contamination can occur; this should help minimize the risk of sample contamination by the crew members.

5.2 Chemistry of Long-term Monitoring Lakes

From the standpoint of a long-term monitoring program, the chemistry of the long-term monitoring lakes is more important than the chemistry of the synoptically-sampled lakes. Temporal trends and other comparisons require high quality data. Consequently, any concentration differences between the two laboratories used for analysis of the 2004 long-term lake samples need resolution.

Calcium concentration differences were large between the two labs for four of the 10 long-term monitoring lakes. For three of these lakes the RM calcium values in 2004 were much lower than in any prior year. Specifically, at Waca lake during eight prior sample collections calcium ranged from 8 to 12 $\mu\text{Eq L}^{-1}$; in 2004 the RM value was 0.6 $\mu\text{Eq L}^{-1}$. Similarly, calcium ranged from 6 to 12 $\mu\text{Eq L}^{-1}$ at Mokelumne 14 in 2002 and 2003; in 2004 the RM value was 0.6 $\mu\text{Eq L}^{-1}$. Last, Lower Cole calcium was 20.55 $\mu\text{Eq L}^{-1}$ in 2003 and 20.4 $\mu\text{Eq L}^{-1}$ in 2002; in 2004 the RM Ca concentration was 1.05 $\mu\text{Eq L}^{-1}$. The 2004 UCSB calcium concentrations for these three lakes were 8.9, 9.6 and 21.3 $\mu\text{Eq L}^{-1}$ for Waca, Mokelumne 14 and Lower Cole respectively. The UCSB calcium concentrations for these three lakes were all within the range of concentrations for a pre-2004 samples. Because the RM calcium concentrations for all three lakes are extraordinarily low in comparison with prior years, I recommend substitution of the UCSB calcium concentrations for these lakes into the long-term database. Such a substitution needs to be confirmed by the Regional Air Specialist.

ANC differences between the two labs for Key Lake, a long-term monitoring lake, need to be resolved. Prior to 2004, the RM ANC for Key Lake varied between 8 and 10 $\mu\text{Eq L}^{-1}$. In 2004, the RM Key Lake ANC was 0.3 $\mu\text{Eq L}^{-1}$ and the UCSB ANC was 4.4 $\mu\text{Eq L}^{-1}$. Although the UCSB 4.4 $\mu\text{Eq L}^{-1}$ is closer to the long-term mean ANC for Key Lake, there's no other obvious reason to presume that the UCSB ANC is more correct than the RM ANC. One option could be to average the RM and UCSB ANCs for Key lake as the value for the long-term database. This option is relatively conservative.

5.3 Time Trends

ANC and selected acid and base constituents are plotted through time for one lake in each Wilderness (Figure 10). Because only two lakes have records longer than 4 years, no other constituents are addressed nor are all lakes in each Wilderness assessed. Three years is too short a time period for extensive analysis, and 4 years is marginally adequate to begin to discuss long-term trends. The literature suggests that typically a much longer time period is needed before temporal trends can be statistically verified. Waca Lake (pictured below) and Key Lake have 5+ year records; the full suite of constituents for these two lakes is plotted through time in Figure 11.



Although the 3 or 4-year time period is too short for extensive time series analysis, for the lakes with records of this duration (Karls and Powell in Emigrant, Long in Kaiser, Patterson in S Warner, Mokelumne and Lower Cole Ck in Mokelumne, Hufford in 1000 Lakes, and Caribou 8 in Caribou) most of the differences in concentrations among years are low, and often within the range of the differences in duplicates for a single year. For instance, the 2002 Powell Lake ANC duplicates had concentrations = 22.9 and 19.9 $\mu\text{Eq L}^{-1}$, a difference of 3 $\mu\text{Eq L}^{-1}$. The mean Powell Lake ANCs are 18.6 (2000), 21.4 (2002), 18.45 (2003) and 21.7 (2004) $\mu\text{Eq L}^{-1}$. These means differ by 3.1 $\mu\text{Eq L}^{-1}$, implying that the inter-year differences approximate the difference between duplicates collected in a given year. Therefore the inter-year differences, rather than being “real”, could be due largely to variability in the sample collection process, natural processes or laboratory analysis.

Irrespective of the duplicate values, the magnitudes of the changes between years are typically small, on the order of one to a few $\mu\text{Eq L}^{-1}$. During development of the monitoring component of the Sierra Nevada Framework extensive research identified 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 10 are typically less than 30%, even for the very low concentrations levels for which very low absolute differences would be relatively large percentage differences.

The direction of any trend through time is important. For instance, improved buffering of incoming acids could be signaled by an increase in ANC and cations (e.g., calcium). An increase over time in sulfate and/or nitrate could suggest increasing acidic inputs. The occurrence of direction changes through in time Figure 10 is approximately equal; an equal number of lakes have increases as decreases, suggesting that overall there is little change and further implying that for the lakes depicted conditions are not deteriorating.

5.3.1 Waca Lake

Waca Lake has a record of sufficient duration to assess change through time (Figure 11). 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 from 0 implies a statistically significant temporal change.

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

Constituent	Adjusted R ²	Regression slope	Significance
ANC	0.20	-0.33	0.13
Sulfate	0.41	-.15	0.039
Nitrate	0.03	-0.03	0.31

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 that might imply acidification. The negative slope for ANC would 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 broken. The low concentration is followed in 2002 and 2003 with ANC levels similar to prior years. ANC concentrations in the 1-2 $\mu\text{Eq L}^{-1}$ 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.

5.3.2 Key Lake

None of the regression slopes of year versus concentrations differ significantly from 0 at the 5% level for Key Lake ANC, sulfate and nitrate, and the +/- 95% band on the slopes all contain 0. Statistics from the regression analyses are:

Constituent	Adjusted R ²	Regression slope	Significance
ANC	0.39	-1.79	0.15
Sulfate	-0.33	-0.02	0.96
Nitrate	-.17	0.17	0.56

From Figure 11d, sodium and magnesium had greater concentrations in 2004 than in 2000, and the sodium concentration increase through time is probably statistically significant. Increasing sodium and magnesium over time could act to reduce the potential for acidification by countering any sulfate and nitrate increases by adding buffering material.

5.4 Lake Chemistry Differences Among Class I Areas

Chemistry information is available from synoptic surveys of lakes from nine 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 (e.g., S. 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 (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 Ansel Adams, Mokelumne and Caribou Wildernesses would be expected to have lower ANCs than the others because the lakes sampled in these Wildernesses were pre-selected 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 12a).

Mean and standard deviation plots for ANC and calcium suggest that eight of the nine Wildernesses, with S. Warner the exception, have approximately the same chemistry for these constituents (Figure 12a and b). ANC is displayed as the single best gauge of sensitivity to acidification. Calcium is representative of alkaline inputs and sulfate represents acidic inputs that typically have an atmospheric source. In the figures overlapping standard deviation (SD) values (the small diamonds) imply lack of a statistically significant difference at the 5% level (e.g., although the 1 SD band around the Desolation mean ANC is narrow, it still overlaps the 1 SD band for most other

Wildernesses except maybe Caribou's and definitely S. Warner's). Seven of the nine Wildernesses have approximately equal sulfate concentrations, with again S Warner as one exception. The high mean sulfate concentration for Ansel Adams is primarily due to the high sulfate at Dana and Kidney Lakes (discussed above). Removing Dana and Kidney from the sulfate calculation gives mean and SD sulfate concentrations for Ansel Adams equaling 5.25 and 3.1 $\mu\text{Eq L}^{-1}$ respectively. Without the Dana and Kidney Lake samples, the 1 SD band for sulfate at Ansel Adams overlaps the 1 SD bands from the non-S Warner Wildernesses. The means for all three constituents are higher in S. Warner, and the S. Warner mean ANC is statistically higher than the mean ANCs from the other Wildernesses (at the 5% level per Excel's Single Factor Analysis of Variance procedure) (statistical tests were not conducted for other constituents).

The lack of substantial differences between the southern and northern Sierra Wildernesses (except S. Warner) is somewhat surprising, although statistical artifacts of the datasets may mask more substantive differences, and the reasons given in the first paragraph of this section may mask differences among the Wildernesses. Geologic and atmospheric influences on lake chemistry would appear to drive ANCs lower in the southern Sierra so that lakes in the granite-dominated southern Sierra were anticipated to have lower ANC than lakes further north. The mean ANCs for Kaiser (southern), Caribou (northern) and 1000 Lakes (northern) Wildernesses, for instance, are similar, at 66, 61 and 74 $\mu\text{Eq L}^{-1}$ respectively. The elevated constituent levels at S. Warner make sense in that this Wilderness may receive alkaline atmospheric inputs from the adjacent Great Basin.

Rather than relying on mean differences among Wildernesses as the sole differentiating criteria, lake ANC distributions by Wilderness are compared in Figure 13. Substantially over one-half of the lakes sampled in the central Sierra—Emigrant, Mokelumne and Desolation Wildernesses had ANCs less than 50 $\mu\text{Eq L}^{-1}$, a value identified by Sullivan (2001) as the ANC level probably protecting Sierra Nevada lakes from foreseeable episodic acidification. These Wildernesses, and Ansel Adams, may therefore be more at risk than Kaiser Wilderness further south and the more northern Wildernesses.

5.5 Lake Transparency and Depth

5.5.1 Lake Transparency

Build-up of nutrients, sediment and other materials reduce water clarity and promote a proliferation of plant life, often algae, which reduces the dissolved oxygen content and often causes the extinction of other organisms (i.e. eutrophication). Lake clarity is an indirect index of the trophic state of a lake and is a good indicator of potential eutrophication. Most high-elevation Wilderness lakes are presumed to have good clarity and not to be eutrophied. Probably the most easily explainable component of water quality change is a reduction over time in water transparency, as measured by a Secchi disk. The disk is lowered into the water and the depth of disk disappearance is the basic measurement. Measurements are subject to individual eyesight problems, glare on the

water, waves, and potentially other factors, so ideally the measurement should be made without sunglasses, to reduce one source of variability in observed disk depth.

Transparency measurements at Lake Tahoe go back to the 1960s. This record is the longest transparency record for Sierra Nevada lakes, and although they probably exist, no transparency records of other Sierra Nevada high-elevation lakes were identified during a web search. At Lake Tahoe, mean year-to-year transparency differences of up to 3 m are evident, along with within-year standard deviations in transparency typically ranging from 2 to 4 m (Elliott-Fisk et al. 1997). Although Lake Tahoe is not the best analogue for the much smaller and shallower lakes monitoring in the R5 program, it provides the best available information on year-to-year variability.

Although atmospheric deposition is identified as a major contributor to reduced clarity in Lake Tahoe, some temporal changes in clarity may be driven by differences in annual precipitation as it drives pollutant loading, for instance as exemplified by improved clarity in Lake Tahoe in some recent years

(http://www.waterboards.ca.gov/lahontan/TMDL/Tahoe/Spring_2004_TMDL_Newsletter.pdf accessed 12/29/04).

Transparency data have been collected in the Wilderness lakes since 2002 (3 years) for four lakes and since 2003 (2 years) for six lakes. These time periods are too short to allow determination of trends through time (for instance, a monitoring program for Lake Superior describes a 5-yr Secchi disk dataset as being of “marginal usefulness” for trend determination, with a 10-15 yr dataset constituting “a valuable dataset” (<http://www.epa.gov/glnpo/lakesuperior/epo1998.pdf> accessed 12/29/04). Similarly, a study of transparency of Minnesota lakes identified 8-10 yrs as needed to detect a 10% change in transparency (<http://www.pca.state.mn.us/water/pubs/lar-fleming.pdf> accessed 12/29/04).

Although our transparency dataset is too short for determination of time trends, some preliminary results can be seen (Figure 14):

- Transparencies ranged from 1.5 to 9.5 m between 2002 and 2004.
- In four of the 10 lakes monitored, the lake bottom was observed, thereby “limiting” the Secchi disk depth. The transparency depths for these four lakes are potentially unrealistically low because they are bounded by shallow lake depth.
- In most of the lakes transparency change from year to year was very small, less than one-half m.
- The transparency of Patterson Lake in S Warner Wilderness, at < 1.75 m, was the lowest of the 10 lakes. Coincidentally, this is the deepest long-term lake currently being monitored (@ 34 m depth). This lake's chemistry has also historically diverted from the other lakes. For instance, its ANC was 143 $\mu\text{Eq L}^{-1}$ this year, over 3 fold above the long-term monitoring lake with the next highest ANC. Given the relatively low transparency in combination with relatively high concentrations for several constituents, this lake may be atypical in several characteristics compared to lakes in Wildernesses further south.

5.5.2. Lake Depth

Lake depth, as documented in the “Index Location Depth” on the field form, is generally consistent among years at each long-term monitoring lake. However, there are some differences that suggest the possible need for assurance that the same index location is used each year. For instance, the index location depths over the years vary by up to four m at Long Lk, over 3 m at Powell Lk, and 1.4 m at Waca Lk. These differences imply that samples were collected and transparency measurements were made at different locations throughout the years. These differences can potentially influence both the chemistry and transparency results.

The protocol for determining Index Location does not appear to include use of GPS technology to help pinpoint the Index location. Consideration should be given to “GPSing” the Index Location of all long-term lakes to help standardize sample and transparency data collection in the future.

5.6 Outlet versus Mid-lake Chemistry Sampling

The current R5 lake monitoring protocol collects mid-lake water samples. An alternative is to solely collect samples from the lake outlet. There are pros and cons for both approaches. Mid-lake sampling assures a reasonable estimate of water chemistry from the entire depth of each lake. The chemistry of thermally stratified lakes may differ chemically between the two strata. This difference cannot be determined from outlet or shoreline sample collection and must instead be determined from mid-lake sampling. Mid-lake water transparency and zooplankton are also monitored, largely to round out the suite of monitoring attributes and not be reliant solely on water chemistry. On the other hand, outlet sampling represents the average or “mixed” lake chemistry, which may be an adequate index of chemistry for land managers. Nitrogen export from a lake, as an indication of nitrogen saturation of the system, is also most easily determined from outlet sampling.

Currently we’re following a monitoring “rule of thumb” to address chemical, physical and biological attributes (not solely chemical). Transparency information could not be collected from the lake outlet and although zooplankton could be collected from the shoreline, a different sampling methodology would be required that may not be comparable with the zooplankton information collected thusfar.

Time and money could potentially be saved if long-term monitoring was solely done by collecting water samples at the lake outlet or along the shoreline. At least two factors enter into any decision to change to outlet sampling: (1) representativeness of the chemistry of the outlet samples, and (2) the trade-off in losing the ability to collect transparency and zooplankton information for savings in time and money. This section addresses the first factor only, representativeness of the water chemistry. Outlet and epilimnion water chemistries are compared, but hypolimnion data are not addressed. To comprehensively assess the outlet sampling option, the utility of the hypolimnion data we’ve collected thusfar needs to be assessed.

5.6.1 Approach

Two direct pairings of outlet and mid-lake samples have been collected thusfar in the R5 program. Powell Lake and Key Lake, both in Emigrant Wilderness were sampled in 2004 and 2002 respectively, concurrently at both outlet and mid-lake locations. Similarity in the sample chemistry from these two locations supports the outlet-only option, but the number of outlet/mid-lake pairs from the R5 monitoring program is too small for statistical comparison. To use R5 data as the basis for replacing the current practice of mid-lake sampling with outlet sampling more paired sample collections would be needed. Data from the Key and Powell Lake samplings are tabulated below, followed by information from two studies that more extensively compare outlet and mid-lake sample chemistries.

5.6.2. Region 5 Outlet/Mid-lake Chemistry

The ANC and selected ion concentrations of the 2002 and 2004 outlet/mid-lake samples from Key and Powell Lakes follow:

Lake, Sample Location & Year	ANC ($\mu\text{Eq L}^{-1}$)	Ca ($\mu\text{Eq L}^{-1}$)	SO ₄ ($\mu\text{Eq L}^{-1}$)	H ($\mu\text{Eq L}^{-1}$)	Na ($\mu\text{Eq L}^{-1}$)
Key, outlet1, 2002*	13.7	5.7	2.9	1.3	7.0
Key, outlet2, 2002	9.9	0.4	2.8	1.3	6.6
Key, epilimnion1, 2002	10.8	6.6	3.0	1.4	7.2
Key, epilimnion2, 2002	8.5	6.0	3.1	1.3	6.8
Powell, outlet, 2004	17.0	11.7	2.4	0.7	15.6
Powell, epilimnion, 2004	21.7	12.1	2.3	0.5	17.0

* Duplicate samples were collected at Key Lake at both the outlet and epilimnion locations in 2002. The “1” and “2” identify each duplicate.

Realizing that a sample size of two is too small to identify substantial differences between outlet and epilimnion sampling locations, the sulfate, hydrogen and sodium concentrations from the 2004 samples are similar, and are within the mean absolute difference of the duplicate samples collected in 2004 (see section 5.1.2 above). This suggests that the outlet-epilimnion differences are within the range of variation associated with laboratory and sample collection procedures, and natural variation among samples collected concurrently from the same location—in other words, there’s no apparent difference for these constituents between outlet and epilimnion samples. Although the 2004 ANC and calcium concentration differences between outlet and epilimnion are greater than the mean absolute difference for the duplicates, these differences are still small and do not suggest that a substantial difference in chemistry exists between the two sampling locations.

The range in concentration differences between the two duplicates for the Key Lake outlet and epilimnion samples is often greater than the concentration differences between

the two sampling locations. For instance, outlet ANC varied between 13.7 and 9.9 $\mu\text{Eq L}^{-1}$, and the epilimnion concentration for both duplicates was within this range. Also, the ranges often overlapped (e.g., the 6.8-7.2 $\mu\text{Eq L}^{-1}$ range for epilimnion Na overlaps the 7.0-6.6 $\mu\text{Eq L}^{-1}$ range for outlet Na). Both of these results suggest that differences between outlet and epilimnion sample concentrations are minimal.

5.6.3. Clow et al. (2002) Outlet/Epilimnion Comparison

Clow et al. (2002) hypothesized that outlet lake chemistry should approximate epilimnion lake chemistry because most of the national park lakes they sampled in 1999 were small, shallow and frequently mixed by wind and streamflow. Samples were concurrently collected at mid-lake and outlet locations from 14 lakes in western parks (Grand Teton, Yellowstone, Rocky Mountain, Yosemite and Sequoia-Kings Canyon) to test this hypothesis. Two of these lakes were in Sequoia-Kings Canyon National Park and one was in Yosemite. The samples were collected in late autumn after most lakes had turned over. Epilimnion and outlet chemistries did not differ significantly ($p = 0.05$) for all solutes (major ions, alkalinity, conductivity, pH, dissolved organic carbon, total mercury, methylmercury). The outlet and epilimnion paired samples are shown in Figure 15.

5.6.3. Bridger-Teton NF Epilimnion/Hypolimnion Comparison (Svalberg 2004)

Data from four lakes in the Bridger-Teton NF were obtained from Terry Svalberg (Svalberg 2004). These lakes were sampled from 1984 through 1994 one to three times each year. ANC values from the “early” sample collection each year are plotted in Figure 16. The “early” collection parallels the June-July target date for sample collection in the R5 monitoring. Forty percent of the Bridger-Teton samples had outlet ANC higher than epilimnion ANC. This percentage is probably not statistically significant. Also both outlet-epilimnion and epilimnion-outlet ANC differences were large in some sample pairings (in other words the outlet concentrations were not always appreciably larger than the epilimnion concentrations, or vice versa), suggesting that neither outlet nor epilimnion locations had consistently greater or lesser ANC concentrations.

Visually the outlet-epilimnion ANC concentration differences from the Bridger-Teton lakes appear to be greater than those from the national park lakes. Summary statistics (below) support this conclusion with the caveat that the outlet/epilimnion difference for one high-ANC national park lake (outlet ANC = 1242 and epilimnion ANC = 1317 $\mu\text{Eq L}^{-1}$) skews the national park mean values.

	National Parks*	Bridger-Teton NF
Absolute ANC difference (epilimnion – outlet) ($\mu\text{Eq L}^{-1}$)		
Mean	7.3	6.6
Median	0.9	4
% Absolute ANC Difference (epilimnion – outlet) ($\mu\text{Eq L}^{-1}$)		

Mean	2.5	8.1
Median	1.2	5.1

* Without one high-ANC lake, the national park statistics would be 2.1, 0.7, 2.3 and 0.9 respectively.

In conclusion, neither the Clow nor Svalberg datasets conclusively suggest differences between outlet and epilimnion ANC concentrations, and the Clow analysis specifically identifies no statistically significant concentration differences. The Clow study, however, collected samples in late autumn after lakes had mixed. The R5 monitoring occurs in June and July to assure minimum annual lake ANC. In this sense the Clow and R5 methodologies differ and strict comparison between them is problematic.

Data from the R5 program are insufficient to base a decision on the propriety of moving to an outlet-only monitoring regime. To be conservative, before any decision is contemplated to abandon mid-lake sample collection—

- More concurrently collected outlet and epilimnion samples from long-term monitoring lakes are needed
- The utility of the zooplankton data collected thusfar should be assessed
- Differences in epilimnion and hypolimnion chemistry should be assessed

6.0 Candidate Ansel Adams Long-term Monitoring Lakes

Prior decisions call for establishment of three long-term monitoring lakes for the Ansel Adams Wilderness. Fifteen lakes were chosen sampled synoptically in 2004 as the candidate pool for selection of the long-term monitoring lakes. The 15 lakes had low ANC as predicted from modeling. Several lakes with low predicted ANC were not sampled as follows (A. Gallegos, personal communication, January 2005):

- Blue Lake: unsafe and difficult access
- Rush Creek Lake: string of pools along a stream; insufficient size
- Mt. Gibbs Lake: unsafe access

Using solely the RM laboratory data, the three lakes with the lowest ANC from the synoptic survey of the Ansel Adams Wilderness are Little East Marie (ANC mean of 2 samples = 4.65 $\mu\text{Eq L}^{-1}$), Lower Post (ANC mean of 2 samples = 9.15 $\mu\text{Eq L}^{-1}$), and Walton (ANC mean of 2 samples = 10.85 $\mu\text{Eq L}^{-1}$). From strictly an acid-sensitivity/ANC standpoint these would be the best candidate long-term lakes; their ANCs are all very low. Other candidate lakes with ANC < 20 $\mu\text{Eq L}^{-1}$ are Lower Fernandez (15.8 from RM, 9.9 from UCSB), Rutherford (14.1), Upper Slab (14.3), Upper Post (15.2), Rainbow (16.1), Dana (16.65 mean of duplicates), Middle Lost (17.95 mean of duplicates) and Chittenden (18.3).

Differences in ANC for the five synoptically-sampled lake samples analyzed by the two labs could complicate the selection of long-term monitoring lakes for Ansel Adams Wilderness. Lower Fernandez Lake had ANCs of 15.8 and 9.9 $\mu\text{Eq L}^{-1}$ respectively for the RM and UCSB labs. These ANCs were among the lowest for any synoptically-

sampled lake in Ansel Adams (the other four synoptically-sampled lakes analyzed by USCB had higher ANC and would not therefore be likely candidates for selection as long-term monitoring lakes). Although Lower Fernandez Lake has a relatively low ANC (from either lab), it does not otherwise stand out as a better or worse candidate for long-term monitoring than other low-ANC lakes.

Other factors, such as accessibility and spatial representativeness, may warrant consideration of other lakes for long-term monitoring. Walton and Lower Post Lakes are located near each other, relatively close to the southern boundary of the Wilderness. Little East Marie Lake is located approximately one-half way up the Wilderness, just east of Mt. Lyell in Yosemite National Park. It may be advisable to include a long-term monitoring lake in the northern portion of the Wilderness. Only two lakes, Dana and Kidney, are appreciably north of Little East Marie Lake (Figure 1). Given its nearness to the Tioga Pass road, Dana Lake is probably more readily accessible than many other lakes in Ansel Adams Wilderness. The mean ANC of the two Dana Lake samples is $16.65 \mu\text{Eq L}^{-1}$. Five lakes (not counting Little E Marie, Lower Post and Walton) have lower ANCs than Dana Lake, and six lakes have higher ANCs.

Selecting Dana Lake, primarily for its easy access, is not advisable. Although its $16.65 \mu\text{Eq L}^{-1}$ ANC is only a few $\mu\text{Eq L}^{-1}$ higher than other candidate lakes, and the ease of access may well be worth the relatively minor elevation in ANC for Dana Lake, the calcium and sulfate concentrations at Dana and Kidney Lakes are not representative of other lakes in any Wilderness except South Warner. For instance, the calcium concentration at Dana Lake ($\sim 121 \mu\text{Eq L}^{-1}$) is higher than any synoptically-sampled lake except a few lakes in Emigrant Wilderness that were selected for their volcanic geology—not selected for low ANC. The high calcium concentration at Dana is almost twice as high as any other non-volcanic/non-S Warner lake sampled since 2000. The sulfate concentration at Dana is even more extreme, at $123 \mu\text{Eq L}^{-1}$, in comparison to a median sulfate concentration of $3 \mu\text{Eq L}^{-1}$ for the other Ansel Adams lakes. Uncommon local geologic conditions may be the cause of the atypical chemistry of Dana and Kidney Lakes. Whatever the cause, these lakes do not appear to be representative chemically of other Ansel Adams lakes.

There may be other reasons not to select the three lowest-ANC lakes as the long-term monitoring lakes in Ansel Adams Wilderness. The R5 Wilderness Lakes team needs to pool its knowledge and assess the options for long-term lake selection. If a lake(s) other than the three lakes with the lowest ANC is selected for long term monitoring, documentation of the reason for not selecting the lowest ANC lake in a Wilderness is needed, to counter any future criticism that long-term monitoring lake selection may have been arbitrary or done with an undisclosed purpose.

7.0 Conclusions

Although the overall quality of the laboratory analyses appears to have declined compared to earlier years, re-analysis of a few problematic samples cleared up relatively minor inconsistencies for specific samples. Application of commonly-used quality

assurance techniques identified no issues other than continuation of a long-standing imbalance between cations and anions. Recommendations are given to address this imbalance at the beginning of this report.

Except for two lakes, the duration of the monitoring is insufficient to quantify any temporal trends in the acid-base chemistry of the lakes. A statistically significant decrease in sulfate concentration between 1985 and 2004 was identified for one lake, Waca in Desolation Wilderness. No other changes through time were identified at the two lakes with five or more year's data. Presuming samples are collected from the same 10 lakes in the summer of 2005, several more lakes will have been sampled annually since 2000, and their record length should be adequately long to allow for trend analysis.

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 thusfar should be analyzed before a decision is made to abandon mid-lake sampling.

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