J.C. Headwaters, Inc.

Water Quality Review of Selected Lakes in the Northern Rocky Mountains

Prepared for the
Gallatin National Forest
Bozeman, Montana

by

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February 2003

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INTRODUCTION

Wilderness areas are an important national resource and provide relatively unaltered natural landscapes for our enjoyment. Although watershed activities in wilderness areas are highly constrained, it is still possible to damage some of these fragile resources through long-range transport of air pollutants (Charles 1991). To address this concern, the Forest Service has established monitoring programs of a number of lakes in wilderness areas. The objective of the lake monitoring is to provide some early indication of possible impacts associated with deposition of acid-rain precursors. Within the Gallatin National Forest, six lakes have been monitored for up to 10 years. The purpose of this report is to present the results of this monitoring activity and to evaluate if changes have occurred in the lakes over the last decade.

METHODS

A number of Excel® files were provided to JC Headwaters, Inc. by Mark Story, hydrologist with the Gallatin National Forest. The data files were concatenated into a single file for data analysis. Copies of the discrete and integrated data files are attached in the enclosed CD. The major ion chemistry data were provided in both concentrations (mg/L) and equivalents (µeq/L). I elected to work exclusively with the data in equivalents. The data were examined in both Statistix® and Grapher® software packages. Relationships between variables were expressed as linear or log-normal expressions as appropriate. Checks for changes in water chemistry variables over time were evaluated using a Runs test (cf. Sokal and Rohlf 1981) with the median as the cutoff value. The Runs test was selected because of the relatively small number of observations per lake, the irregular nature of the sampling, and the non-parametric assumptions associated with the test. He Runs test

RESULTS

A quality assurance review was conducted of the lakes samples provided in the combined data set, which included a number of other lakes in addition to the six included in the Phase 3 (long-term monitoring) program. The ion balance for the lake samples (n = 168) exhibits close agreement between anions and cations (Figure 1). There is a slight anion deficit (or cation excess) that could be attributed to lack of measurement of two minor anions, fluoride and organic anions. However, the magnitude of the anion deficit (average = 7 µeq/L) is small in these lakes and the analysis is not compromised by omission of these anions for most purposes in these high-elevation lakes.

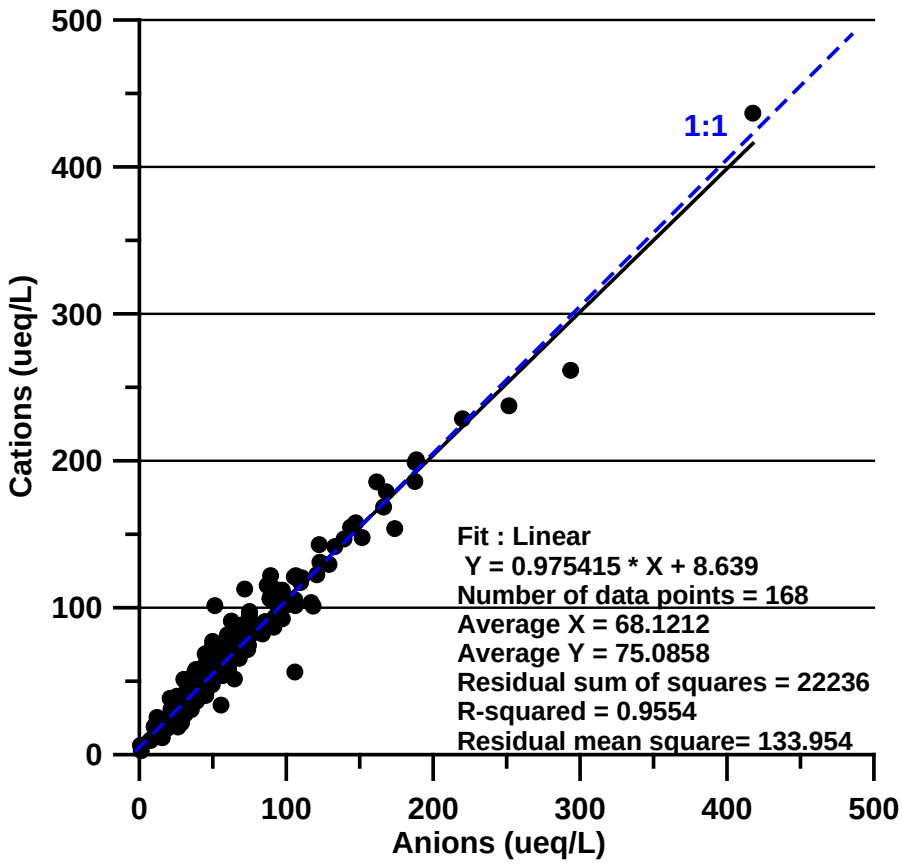


Figure 1. Cations versus anions in USFS Region 1 study lakes.

A check on the measured conductivity versus theoretical conductivity (using equivalent conductances listed in Dean [1985]) showed the samples exhibited a slight negative bias of about 10% (Figure 2). It is possible is that some of the ions measured in the analytical process were not dissolved, which could also account for a slight overestimation of theoretical conductivity. Again, this relatively small, systematic difference is not a significant concern with respect to the quality of the data.

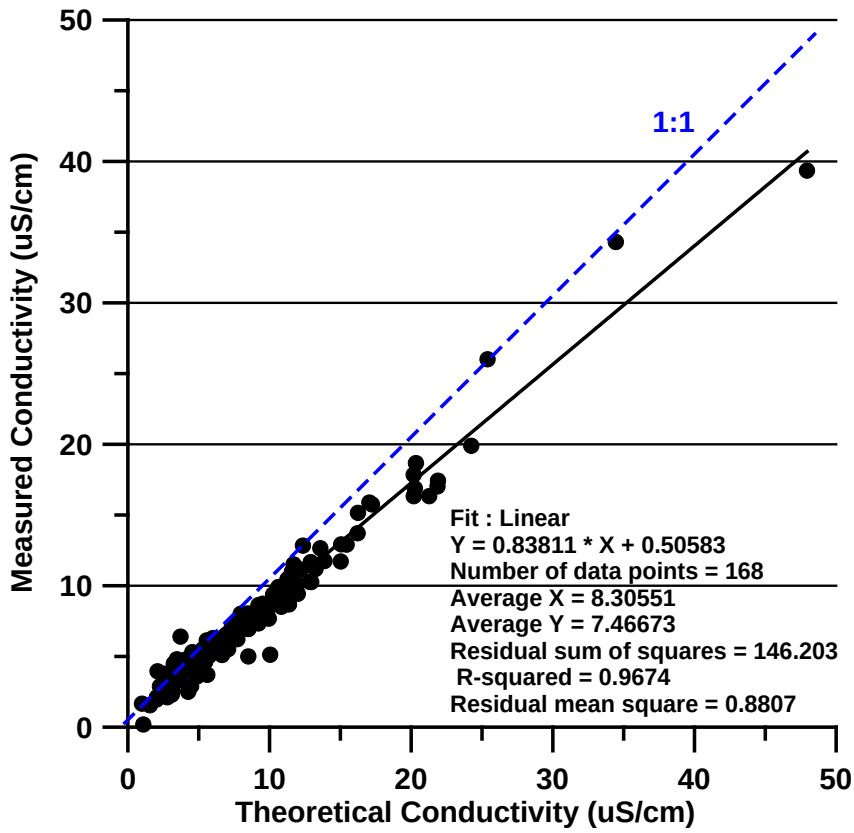


Figure 2. Measured versus theoretical conductivity in Region 1 study lakes.

Another check on the analytical uncertainty was performed by comparing the measured acid neutralizing capacity (ANC) versus alkalinity calculated as the difference between the sum of base cations (C_B = Ca + Mg + Na + K) and acid anions (C_A = SO_4 + Cl + NO_3). The results show good agreement between the two parameters with an average difference between the measured and calculated forms of about 4 µeq/L (Figure 3).

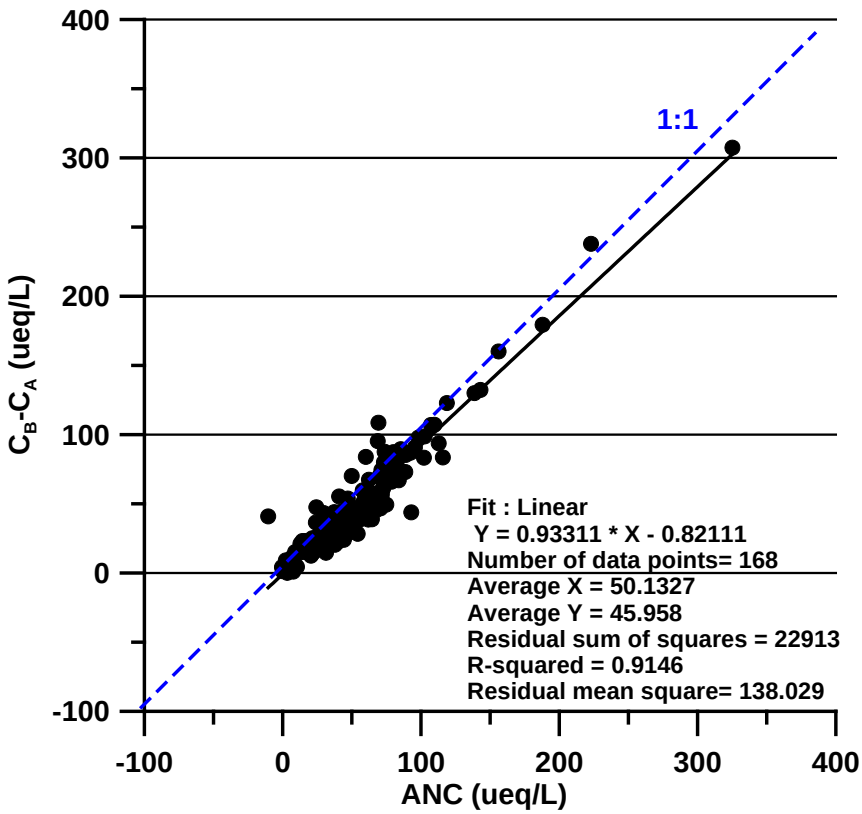


Figure 3. Calculated alkalinity ($C_B – C_A$) versus measured ANC for Region 1 study lakes.

The relationship between pH and ANC for natural lakes not impacted by either organic anions or acidic deposition forms a predictable log-normal pattern. In high-elevation lakes, the partial pressure of carbon dioxide is generally different than that found for low-elevation lakes. The pattern observed for the Region 1 lakes (Figure 4) is typical of high elevation lakes which exhibit P_{CO2} values of about $10^{-3.0}$, whereas equilibrium values at sea-level would be expected to be closer to $10^{-3.5}$.

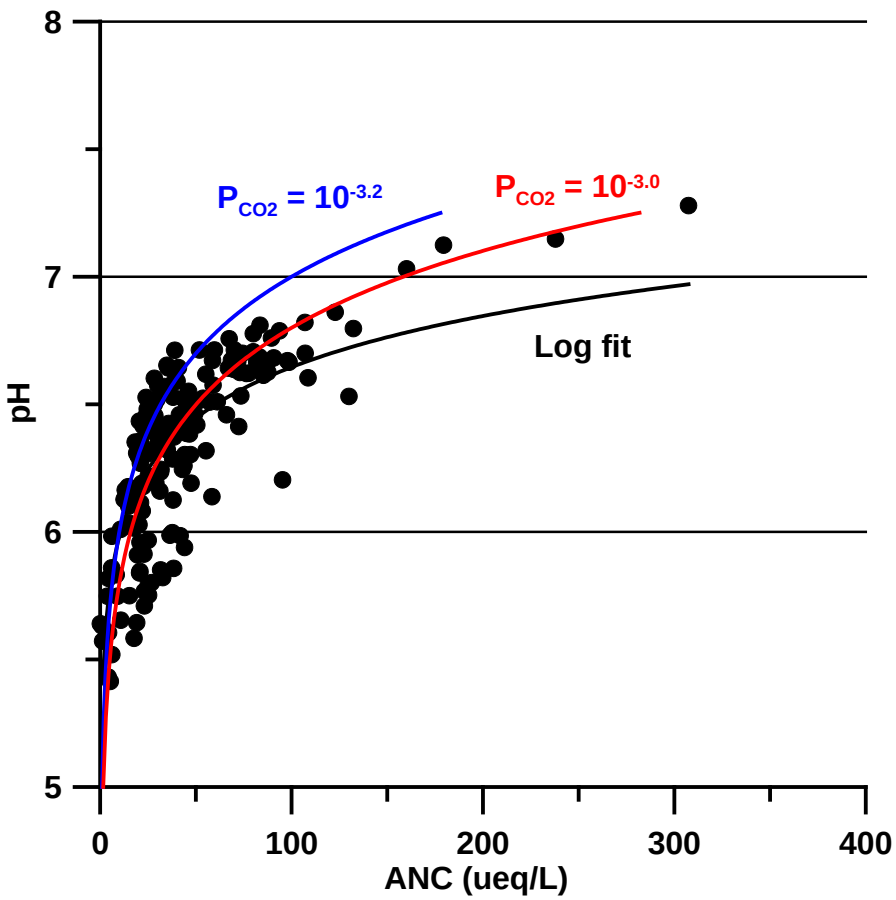
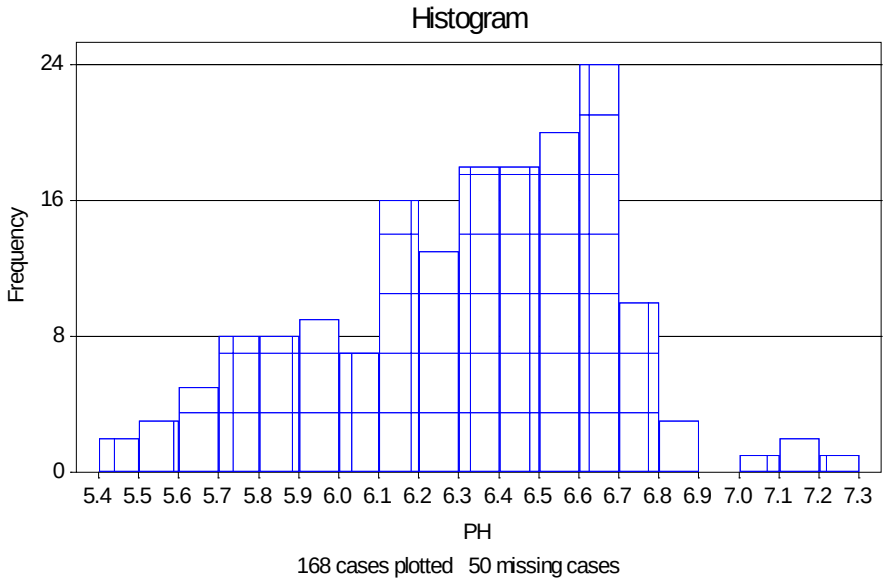


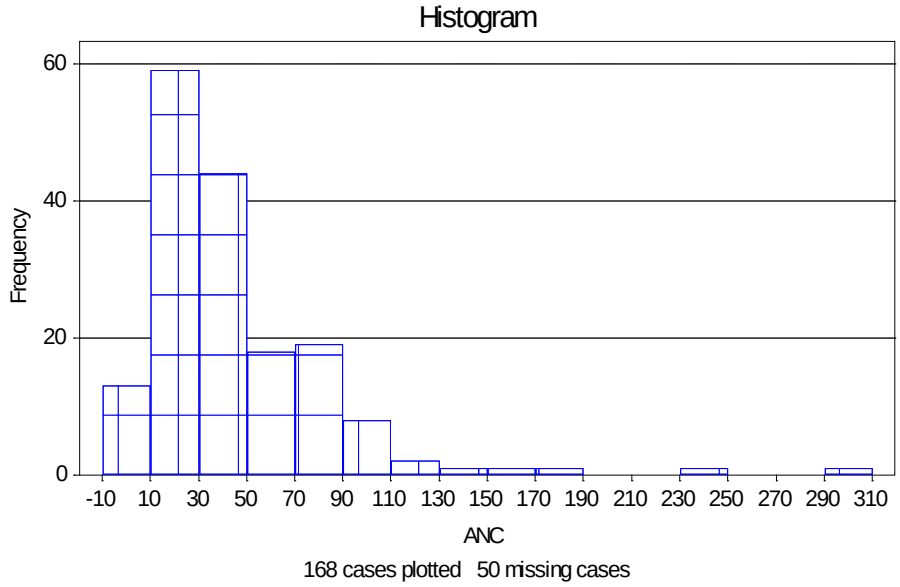
Figure 4. pH versus measured ANC in Region 1 study lakes. Three different curves are superimposed on the data for comparison.

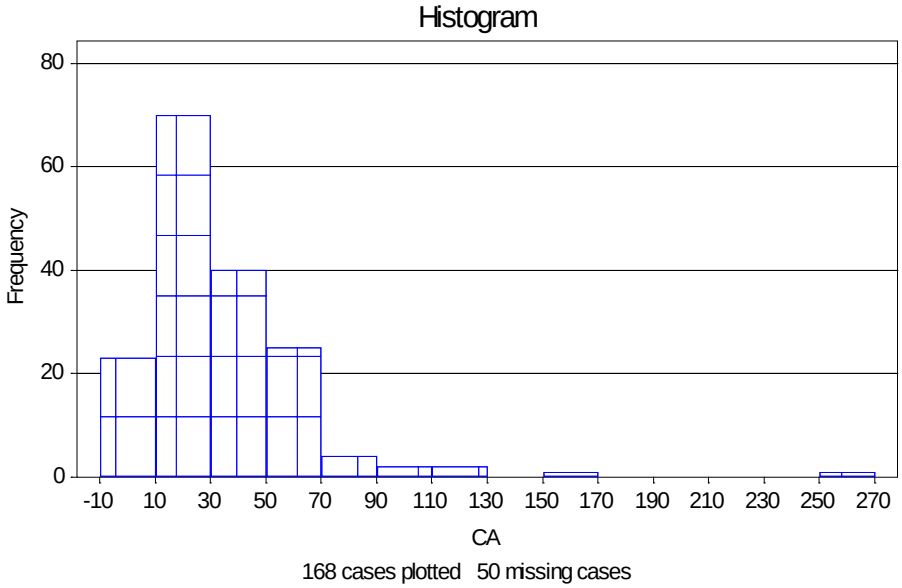
Histograms for the water chemistry variables were plotted to display the nature of the study lake data (includes all lakes, not just the six Phase 3 lakes). The results in Figure 5a-k, show that most of the distributions approximate a log-normal distribution. There are several suspicious samples for Upper Libby Lake collected from 1997-1999. At least one and possibly more of these samples appear to be blanks with virtually no measurable base cations. For example, the sample collected in 1999 shows a measured conductivity of 0.19 µS/cm which is less than distilled/deionized water in equilibrium with the atmosphere. In this case, the H^+ alone would be sufficient to result in a conductivity over 1.5 µS/cm. I recommend that some of these values be rechecked against the laboratory sheets.

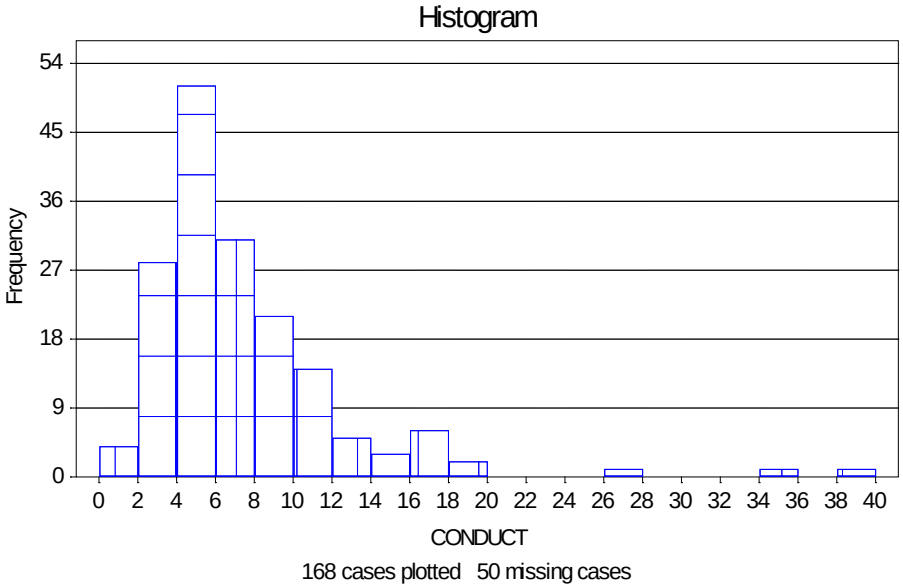
This review of the data quality of the Region 1 study lakes indicates that the vast majority of the data appear to be internally consistent and more than adequate for the intended purposes.

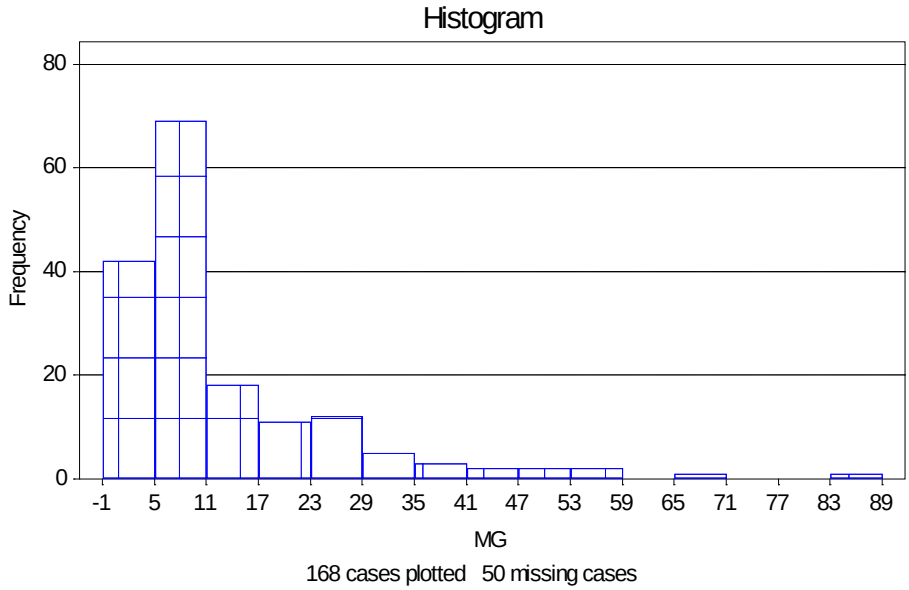
Figure 5. Histograms of water chemistry parameters for (a) pH, (b) ANC, (c) conductivity, (d) calcium, (e) magnesium, (f) sodium, (g) potassium, (h) ammonium, (i) chloride, (j) nitrate, and (k) sulfate. All units are in µeq/L except for pH and conductivity (µS/cm).

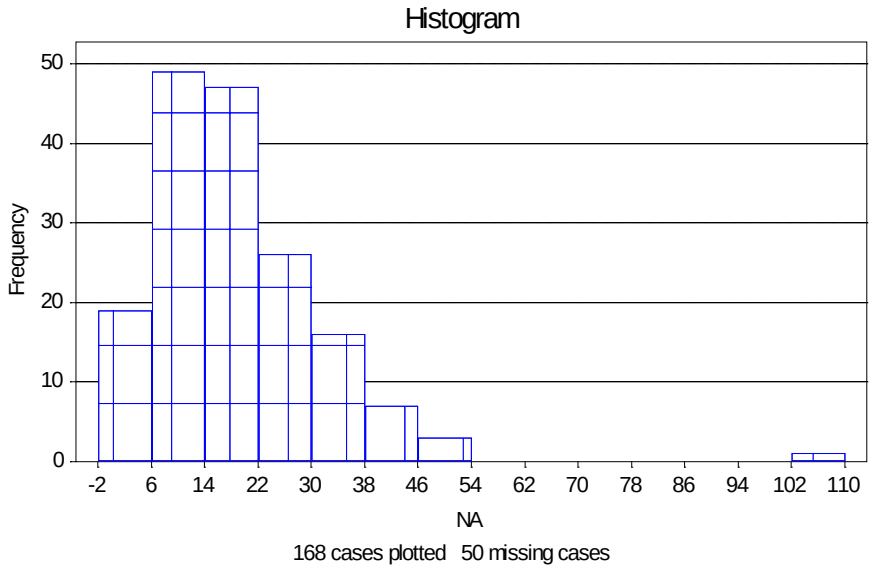


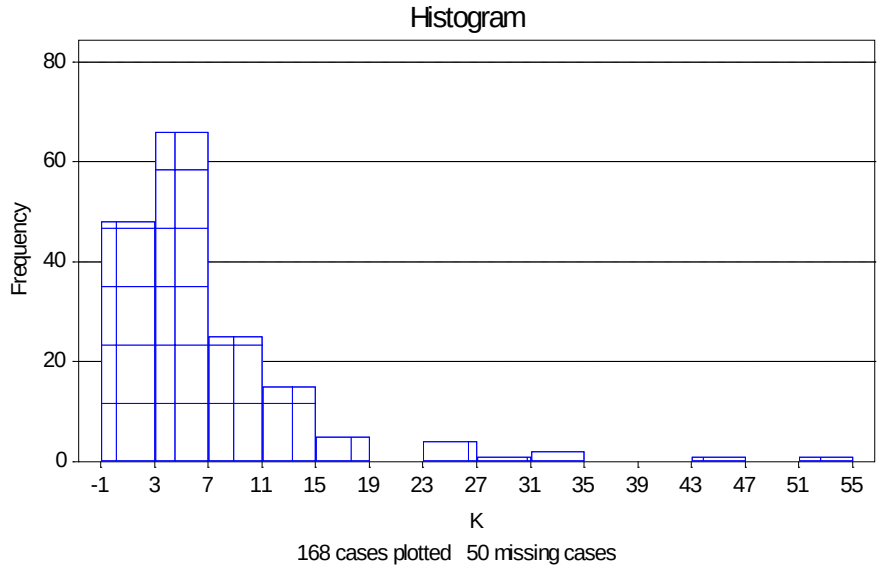

Histogram
Frequency
60
40
20
0
-10 10 30 50 70 90 110 130 150 170 190 210 230 250 270 290 310
ANC
168 cases plotted 50 missing cases

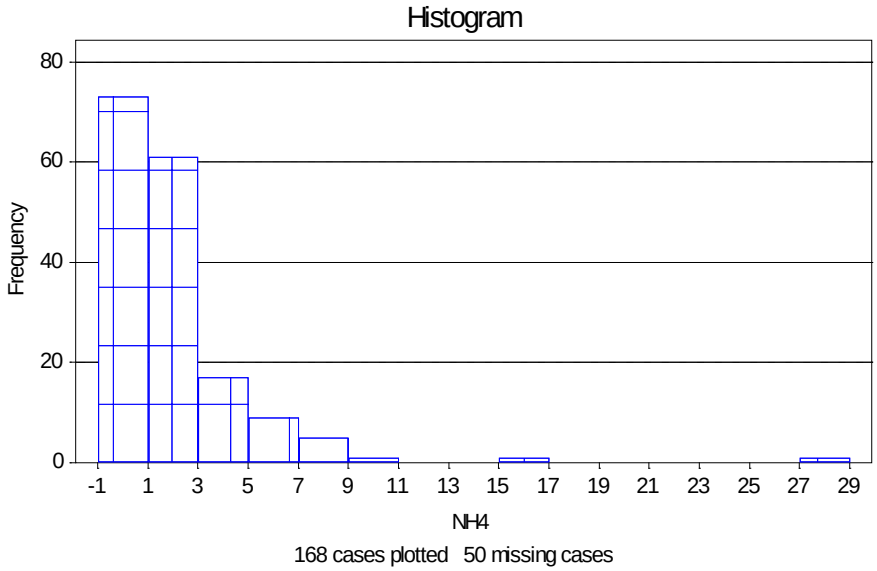

Histogram
Frequency
80
60
40
20
0
-10 10 30 50 70 90 110 130 150 170 190 210 230 250 270
CA
168 cases plotted 50 missing cases

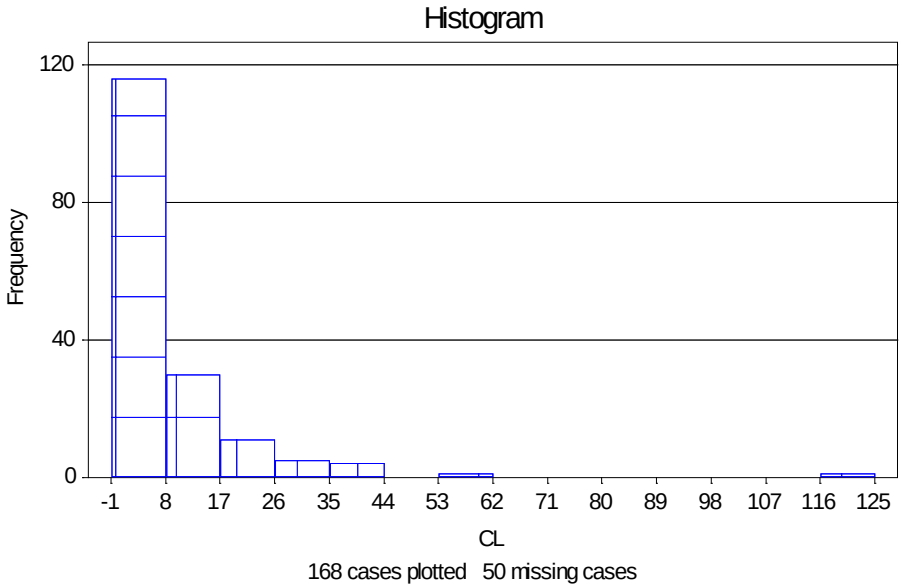

Histogram
Frequency
54
45
36
27
18
9
0
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34 36 38 40
CONDUCT
168 cases plotted 50 missing cases

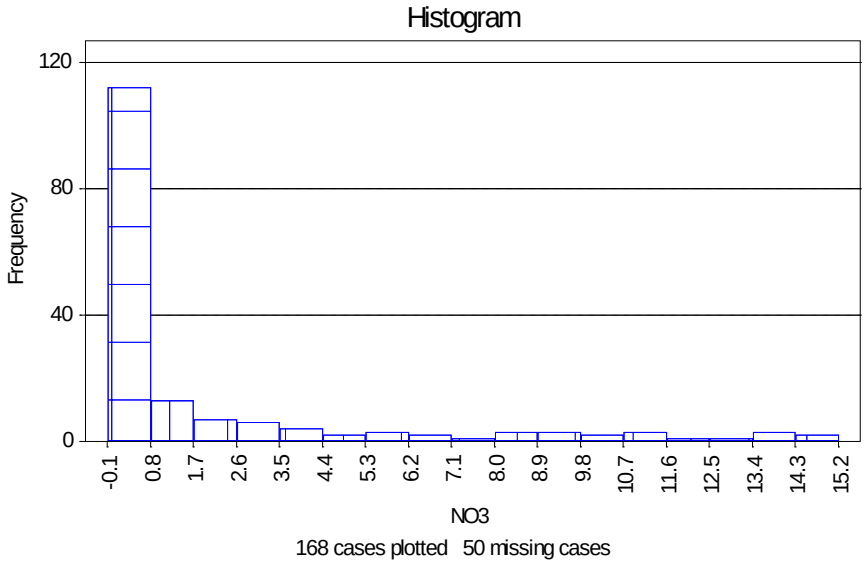

Histogram
Frequency
80
60
40
20
0
-1 5 11 17 23 29 35 41 47 53 59 65 71 77 83 89
MG
168 cases plotted 50 missing cases

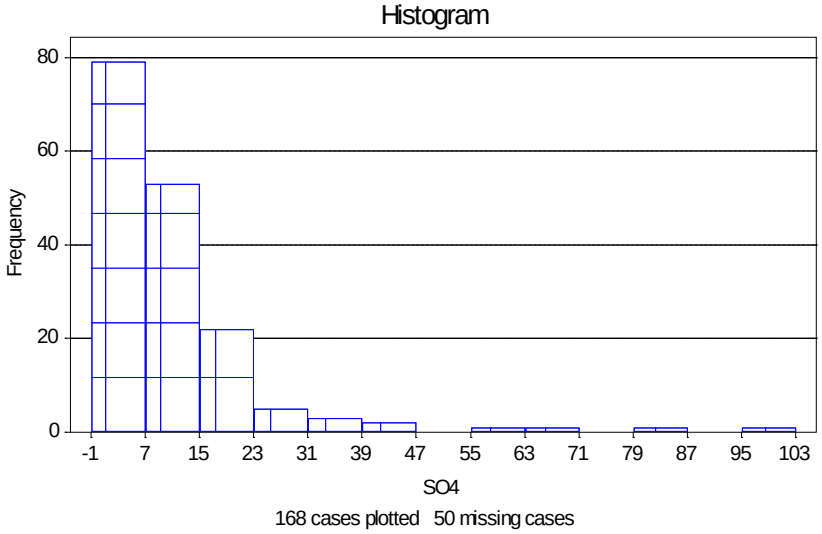

Histogram
Frequency
50
40
30
20
10
0
-2 6 14 22 30 38 46 54 62 70 78 86 94 102 110
NA
168 cases plotted 50 missing cases


Histogram
Frequency
80
60
40
20
0
-1 3 7 11 15 19 23 27 31 35 39 43 47 51 55
K
168 cases plotted 50 missing cases


Histogram
Frequency
80
60
40
20
0
-1 1 3 5 7 9 11 13 15 17 19 21 23 25 27 29
NH4
168 cases plotted 50 missing cases


Histogram
Frequency
120
80
40
0
-1 8 17 26 35 44 53 62 71 80 89 98 107 116 125
CL
168 cases plotted 50 missing cases


Histogram
Frequency
120
80
40
0
-0.1 0.8 1.7 2.6 3.5 4.4 5.3 6.2 7.1 8.0 8.9 9.8 10.7 11.6 12.5 13.4 14.3 15.2
NO3
168 cases plotted 50 missing cases



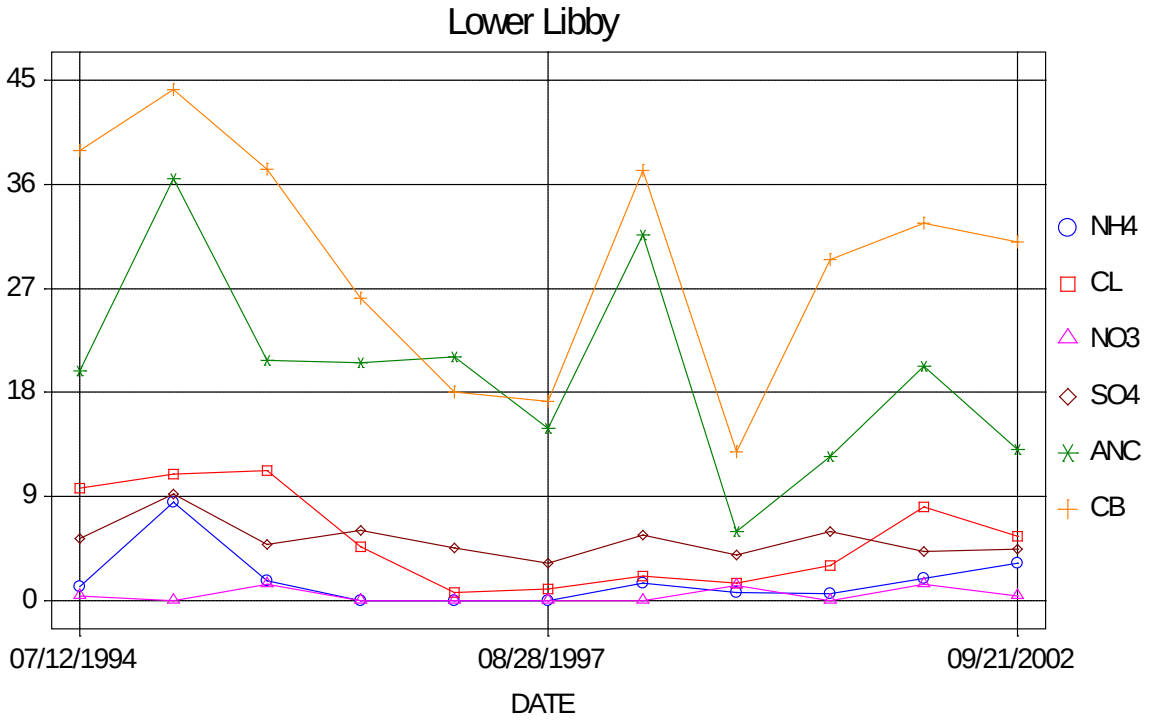
Temporal patterns in the time series data of the six Phase 3 study lakes were examined by plotting key variables for each of the six lakes separately (Figure 6 a-f) and for pH for all lakes grouped together (Figure 7). Statistical evaluation of randomness in the study lakes were conducted for all measured variables (with the exception of silica for which there were insufficient analyses per lake) and are summarized in Table 1.

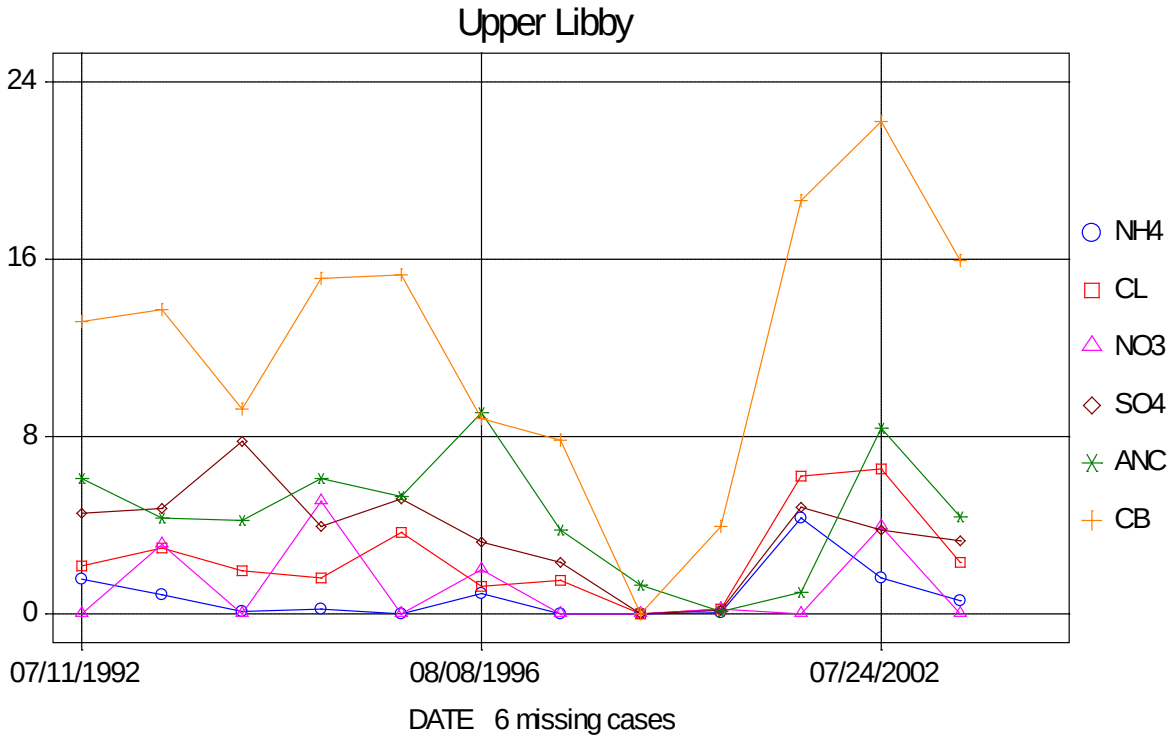
Table 1. P values for Runs test (two-tailed, median as cutoff value). Significant (P = 0.05) patterns are highlighted in yellow and marginally significant (P = 0.10) are highlighted in blue.

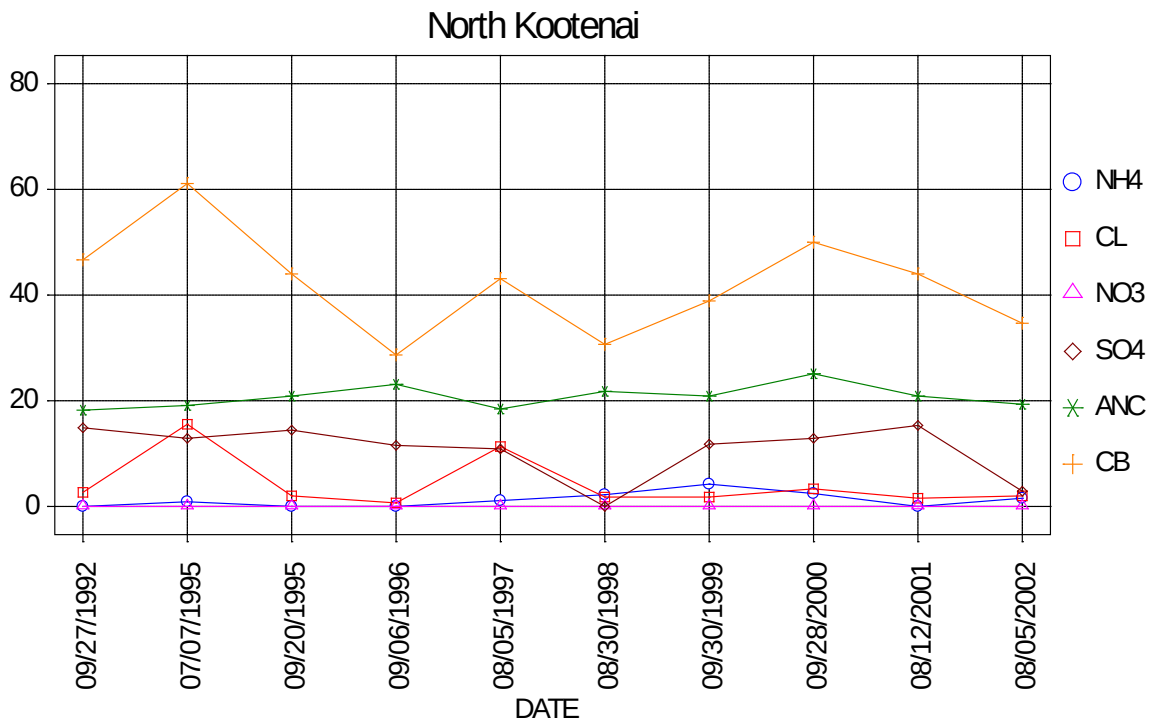
	Lower Libby[a]	Upper Libby	North Kootenai	Shasta	Stepping Stone	Twin Island
pH	0.714	0.784	0.333	0.229	0.714	1.000
Conductivity	0.016	0.784	1.000	0.743	0.333	1.000
Ca	0.714	0.351	1.000	1.000	0.333	0.229
Mg	0.714	0.784	1.000	1.000	0.333	0.229
Na	0.079	0.784	1.000	0.743	0.333	1.000
K	1.000	0.351	0.714	0.743	0.714	1.000
NH_4	0.714	0.351	0.333	0.743	0.333	0.743
Cl	0.079	0.351	0.714	0.743	0.333	0.057
NO_3	--[b]	--	--	--	--	--
SO_4	1.000	0.134	0.333	0.229	0.333	0.229
ANC	0.714	0.351	0.714	0.743	0.079	1.000
C_B	0.714	0.784	0.333	0.229	1.000	0.229
C_A	0.079	0.351	1.000	1.000	0.333	1.000
Alkalinity	0.714	0.351	0.714	0.229	1.000	0.229
Cations	0.714	0.784	1.000	0.229	1.000	0.229
Anions	1.000	0.351	0.714	1.000	0.714	1.000

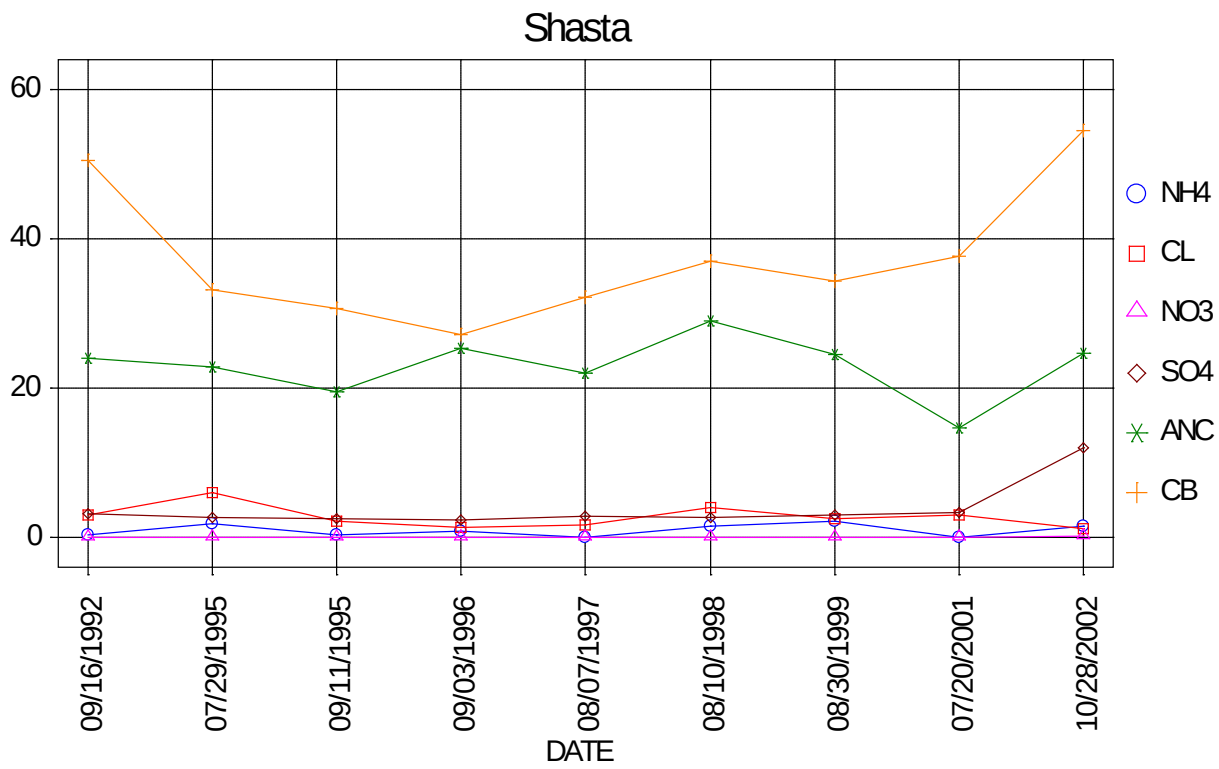
[a]Values shown are for the unedited data. Removing the observation with a conductivity of 0.19 uS/cm for Upper Libby Lake causes all results to be not significant.
[b]Insufficient number of observations greater than zero to complete test

Figure 6. Temporal trends in selected variables (NH_4, Cl, NO_3, SO_4, ANC and C_B) for (a) Lower Libby lake, (b) Upper Libby Lake, (c) North Kootenai Lake, (d) Shasta Lake, (e) Stepping Stone Lake, and (f) Twin Island Lake for 1992-2002.






North Kootenai
80
60
40
20
0
NH4
CL
NO3
SO4
ANC
CB
09/27/1992
07/07/1995
09/20/1995
09/06/1996
08/05/1997
08/30/1998
09/30/1999
09/28/2000
08/12/2001
08/05/2002
DATE


Shasta
60
40
20
0
NH4
CL
NO3
SO4
ANC
CB
09/16/1992
07/29/1995
09/11/1995
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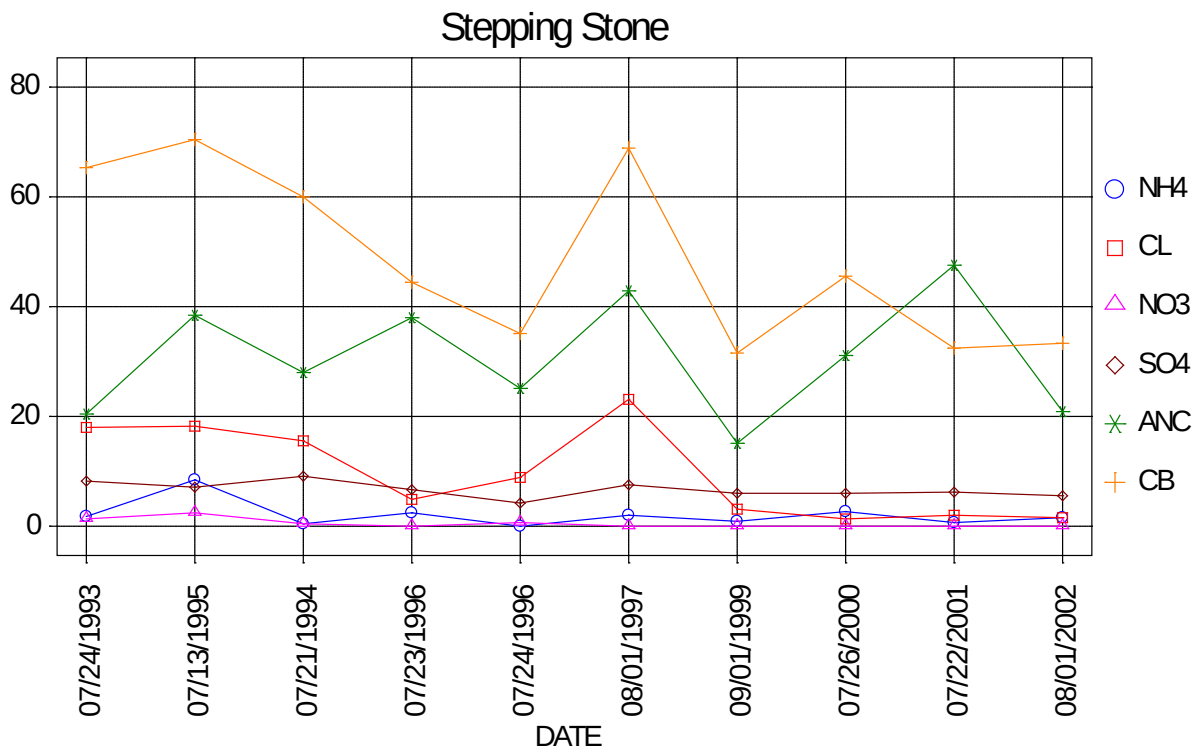
08/10/1998
08/30/1999
07/20/2001
10/28/2002
DATE


Stepping Stone
80
60
40
20
0
NH4
CL
NO3
SO4
ANC
CB
07/24/1993
07/13/1995
07/21/1994
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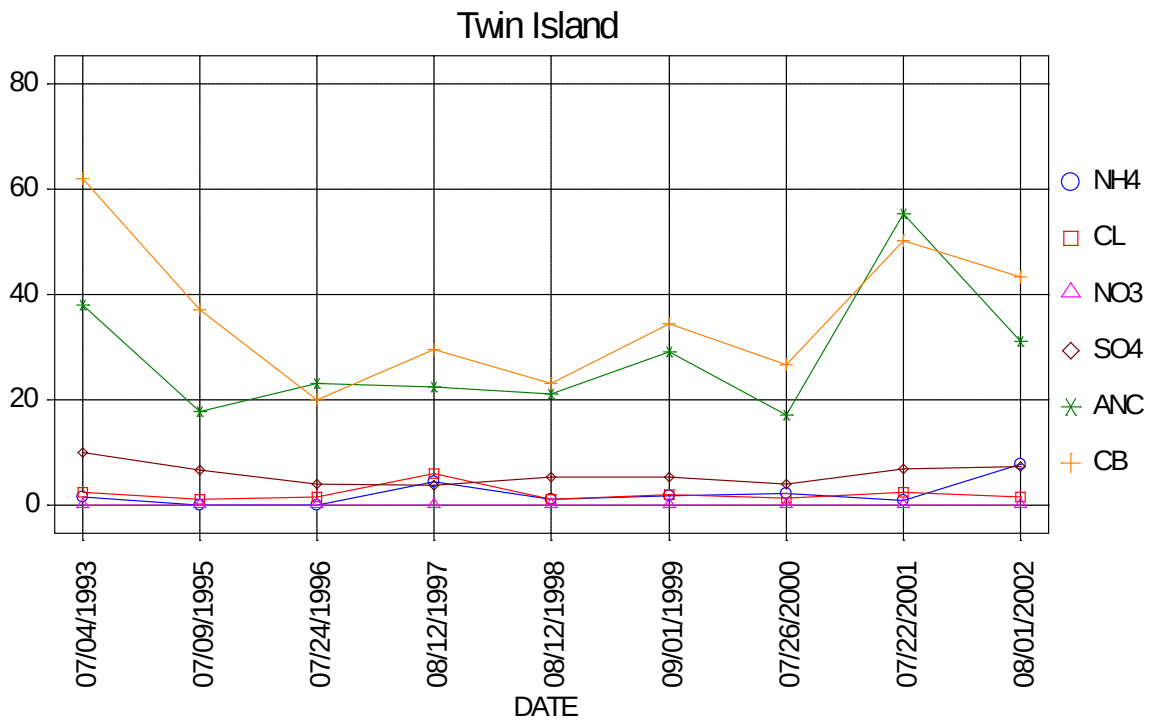
07/22/2001
08/01/2002
DATE


Twin Island
80
60
40
20
0
NH4
CL
NO3
SO4
ANC
CB
07/04/1993
07/09/1995
07/24/1996
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07/22/2001
08/01/2002
DATE

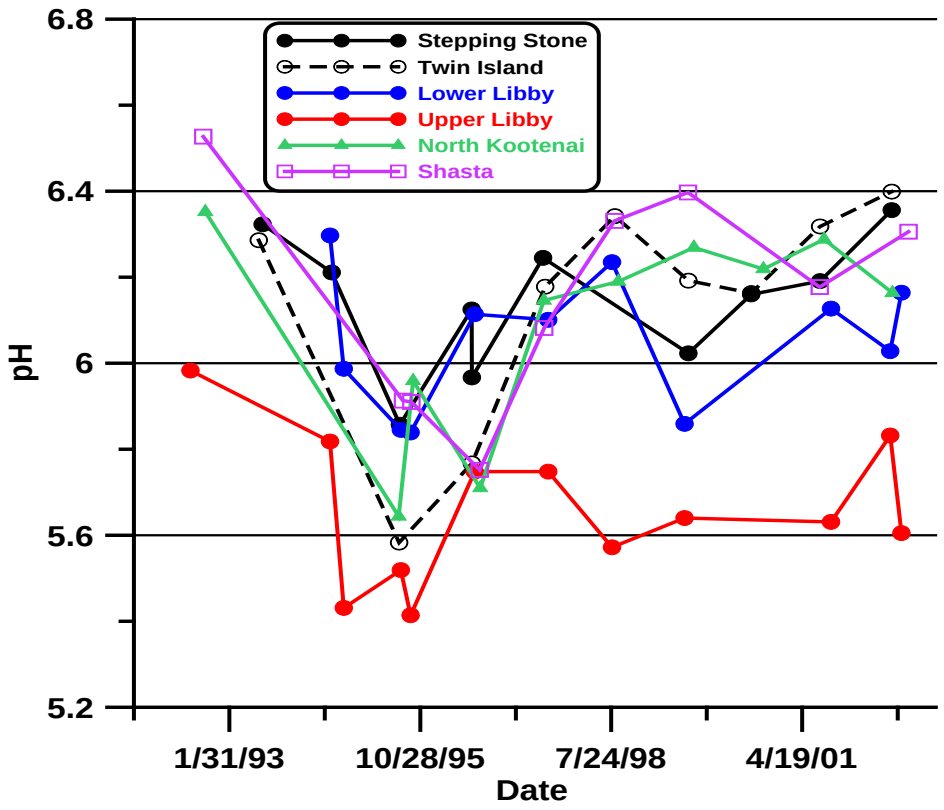

Figure 7. Time series plot of pH for the six Phase 3 study lakes shown together.

Distributions of the variables were also examined as boxplots, show in Figure 8 for several relevant parameters. All six study lakes are dilute systems with low conductivity. The two lakes with the most interesting chemical features are Upper Libby which has ANC values ~ 5 µeq/L and North Kootenai which has sulfate concentrations > 12 µeq/L. Although the ANC in Upper Libby is low, the pH is generally within the expected range for a system in equilibrium with atmospheric carbon dioxide. However, this lake warrants close scrutiny because the sulfate concentrations are similar to the ANC values and relatively small atmospheric contributions of acid anions will cause this lake to become acidic. North Kootenai Lake has the highest sulfate concentrations among the study lakes, although the base cation concentrations are similar to most of the other lakes. It is very possible that the elevated (relative to this group) sulfate concentrations in North Kootenai are the product of weathering of minerals such as FeS, a feature that could be further examined through use of isotopic techniques.

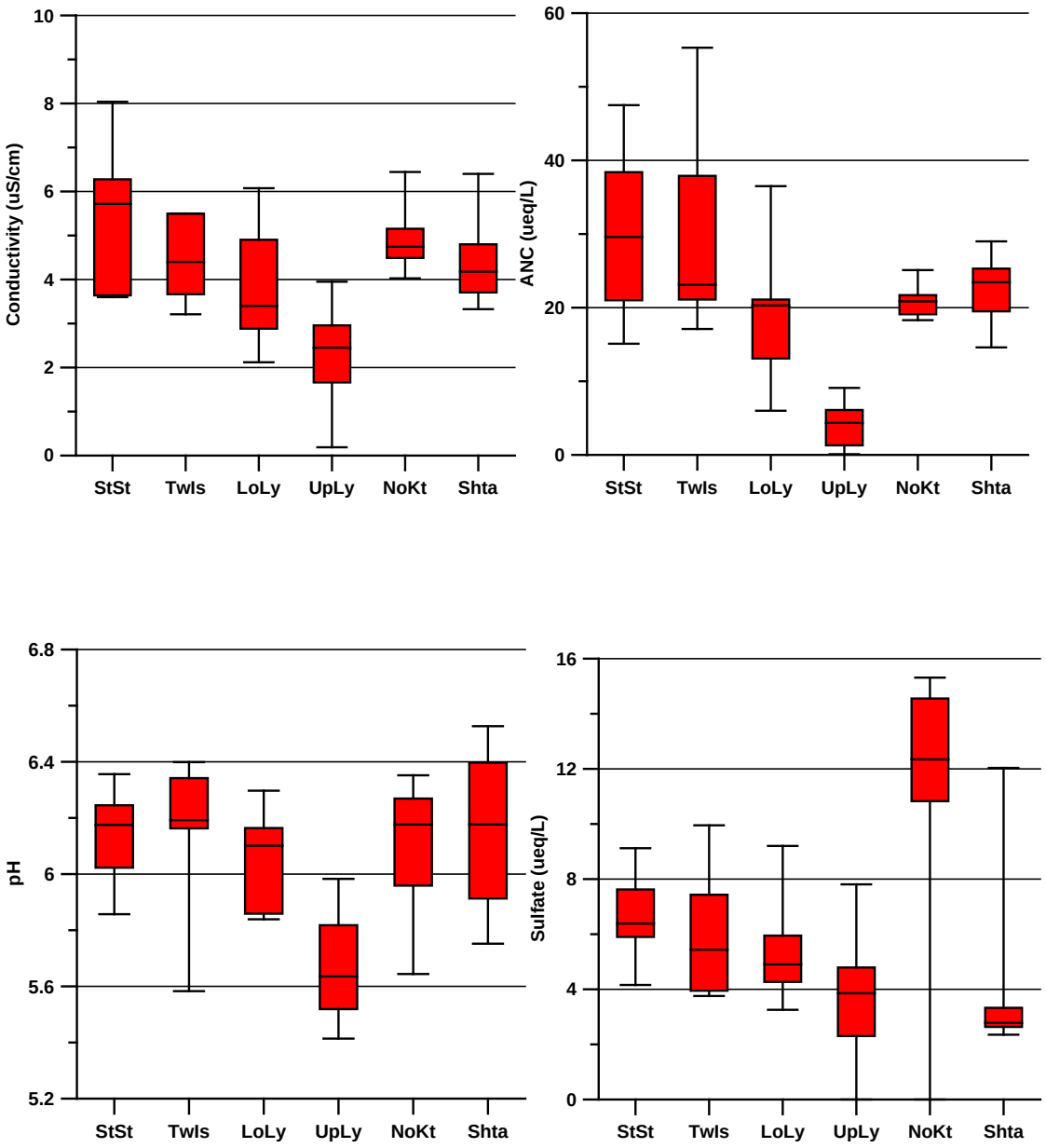

Figure 8. Boxplots of (a) conductivity , (b) ANC, (c) pH, and (d) sulfate for all samples from the six Phase 3 study lakes.

DISCUSSION

The analysis of the six study lakes shows that there are few statistically significant patterns in water chemistry. The Runs test results indicate that the patterns in the water chemistry within each of the lakes are random. The only statistically significant change was a decline in Lower Libby conductivity associated with decreases in Na and Cl. However, when the one observation with a reported conductivity of 0.19 uS/cm is removed, none of the variables show any significant variation. It is possible for the lakes to exhibit a random pattern, yet still be experiencing change. However, when we examine both the relative proportions and absolute concentrations of both ammonia and nitrate in the study lakes, there is no basis at this point to indicate any degree of nitrogen saturation.

Nitrogen saturation is expressed as excess nitrogen not used by the terrestrial or aquatic systems. In the case of the six study lakes, brief excursions of measurable inorganic nitrogen were followed by repeated observations of little or no measurable nitrogen. This type of pattern is more indicative of samplings acquired at different periods of the snowmelt process in which a lake sample collected during the active phase of snowmelt will often experience brief periods of what appears to be significant quantities of nitrogen. Some of these study lakes, especially Upper Libby Lake, are very small and the lakes can experience complete replacement of the lake volume in a brief period. In this case, measured nitrate in the water may just be a direct consequence of the snowmelt. Nitrogen saturation, however, is not just the presence of nitrogen in the lake, but is rather the chronic retention of inorganic nitrogen in a system that can no longer assimilate the nitrate or ammonia. If inorganic nitrogen were measured in these systems at mid-summer on repeated occasions, it would more clearly indicate that the inputs of nitrogen have exceeded the capability of the lake to assimilate it. So far, this does not appear to be the case.

The six lakes exhibit a variety of patterns which raises the question why the lakes are not better synchronized. pH does show some synchronization with minimum values generally observed in 1995 (Figure 7). Examination of the dates of sample collection of the six Phase 3 lakes provides an indication for the observed patterns and relative lack of synchronization (Figure 8). With the possible exceptions of 1997 and 1998, the sample collection period for the various study lakes has varied widely within years. This great disparity in sample collection dates provides for a wide range of climatic conditions to affect the lakes within any given year. In particular, lakes such as this are generally very responsive to snowmelt inputs and thus by sampling one lake during snowmelt and another lake in fall it will tend to obfuscate any potential patterns associated with atmospheric inputs and changes associated with snowmelt chemistry.

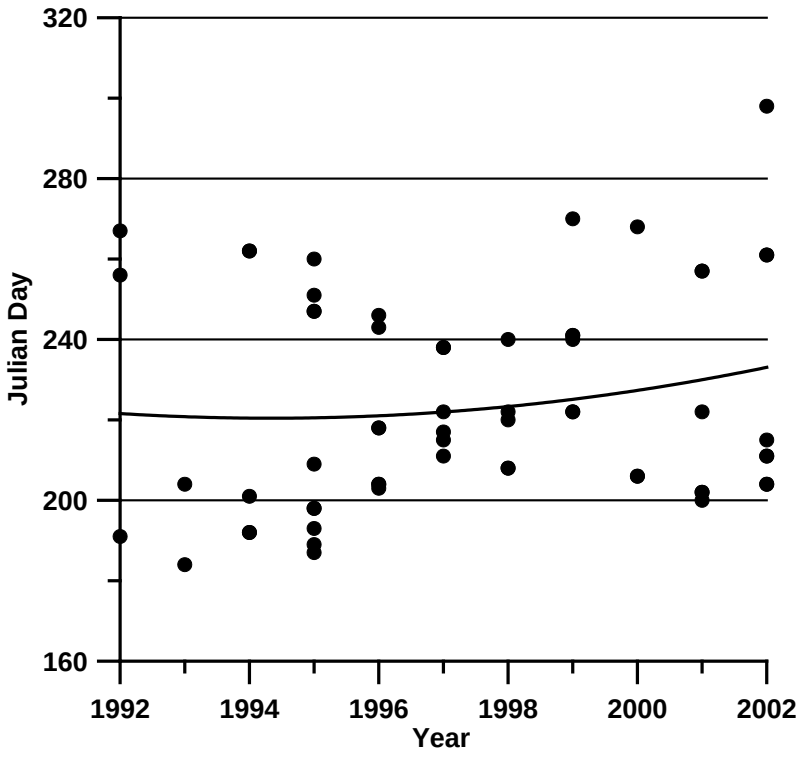

Figure 8. Julian day of lake sample collection from 1992 to 2002 for the six Phase 3 study lakes. The curve is a best-fit polynomial for the observed data.

Acid anion concentrations are relatively low in the study lakes and in the absence of any significant anion deficit (that would suggest acidification) there is no indication that the lakes are experiencing substantial inputs of acidic deposition. Most of the variations in lake chemistry would appear to represent different stages of dilution that would be expected from snowmelt and major precipitation events. The variations in lake chemistry reflect different positions within the annual hydrologic cycle of snowmelt and runoff from summer precipitation events superimposed on longer cycles of climate fluctuations.

The monitoring program as conducted to date provides very good documentation of the general current chemical status of the lakes. The lakes are dilute systems with no evidence of major impacts from atmospheric inputs. However, to optimize the monitoring design specifically for early detection of response to atmospheric nitrogen inputs, this might be a reasonable time to consider an alternative strategy. By reducing the number of study lakes to either those that are most sensitive (Upper Libby Lake) or closest to emission sources, one could allocate more resources to

repeated samplings of a lake during the year. This would make it possible to better understand the inter- and intra- year variability which are critical factors in separating effects from variation. In addition, it would also be of value to expand the list of chemical analytes to include fluoride, organic carbon, phosphorus (low-level), and total Kjeldahl nitrogen (or total nitrogen) to allow for a more complete understanding of the acid-base chemistry and the nitrogen components. Another factor that would be helpful in interpreting lake chemistry changes associated with nitrogen would be collection and analysis of phytoplankton samples. This would provide an understanding for how the lake might be responding to changes in nitrogen inputs. Under ideal study conditions, the monitoring would also collect detailed (hourly or greater) data on meteorology (solar radiation, air temperature, precipitation) and hydrology (inflows, outflows, lake volume).

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Sokal, R.R. and F.J. Rohlf. 1981. Biometry: the Principles and Practice of Statistics in Biological Research. W.H. Freeman and Company. San Francisco. 859 pp.