## §EPA

## National Surface Water Survey

## Temporal Variability in Lakewater Chemistry in the Northeastern United States: Results of Phase II of the Eastern Lake Survey



# TEMPORAL VARIABILITY IN LAKEWATER CHEMISTRY <br> IN THE NORTHEASTERN UNITED STATES: <br> RESULTS OF PHASE II OF THE EASTERN LAKE SURVEY 

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## EXECUTIVE SUMMARY

The Eastern Lake Survey - Phase II (ELS-II) was conducted in spring, summer, and fall of 1986 as part of the U.S. Environmental Protection Agency's (EPA) National Surface Water Survey (NSWS). The NSWS is a contribution to the National Acid Precipitation Assessment Program, which was charged by the U.S. Congress to provide policymakers with sound technical information regarding the effects of acidic deposition.

In Phase I of the Eastern Lake Survey (ELS-I), the acid-base status of lakes in the eastern United States was quantitatively estimated using a statistical approach whereby a single lakewater sample was collected in the fall (the fall index sample). Fall was selected as the index period in ELS-I because it is a period of reasonable length (about 6 weeks) during which lakes are relatively well mixed and samples from over 1,500 lakes could be collected. A similar well-mixed period in the spring can be very short. In addition, chemical conditions vary less in fall than in spring, which was consistent with the objective of ELS-I to assess chronic acidity rather than seasonal acidity.

The major objective of ELS-II was to assess the temporal variability in regional lakewater chemistry with respect to acidic deposition effects. ELS-II had three major goals:

1. Assess the sampling error associated with the ELS-I fall index sample.
2. Estimate the number of lakes that are not acidic (ANC $>0$ ) in the fall, but are acidic (ANC $\leq 0$ ) in other seasons.
3. Establish seasonal water chemistry characteristics among lakes and relate the fall index sample to seasonal and annual water chemistry patterns.

To accomplish these goals, water samples were collected from 145 statistically representative lakes in the spring, summer, and fall of 1986. These three seasonal samples were used to assess among-season variability, and to estimate between-year variability by comparing the fall 1986 ELS-II samples to the fall 1984 ELS-I samples. In 41 ELS-II lakes, two additional samples from independently selected locations in the deepest part of the lake were collected during the fall index period to assess variability within index periods and in site selection.

Lakes analyzed in ELS-II were chosen from those sampled in ELS-I using a variable probability sample. Thus, ELS-II data, like ELS-I data, can be used to provide unbiased estimates of the status and extent of acidic and low ANC lakes for the explicitly defined lake population from which the sample was drawn. A number of restrictions were placed on ELS-I lakes included in the ELS-II target population in order to concentrate sampling on the lakes of most interest with respect to acidic deposition effects. Specifically, lakes with the following characteristics were not sampled in ELS-II:

1. Lakes with high acid neutralizing capacity (ANC >400 $\mu \mathrm{eq} / \mathrm{L}$ ), because these lakes probably will not be chronically affected at current rates of acidic deposition.
2. Lakes severely enriched with nutrients that would either (1) internally generate enough ANC for the lake to be considered insensitive to acidic deposition, or (2) seriously distort the natural chemical composition of the lake and confound data interpretation.
3. Shallow lakes ( $<1.5 \mathrm{~m}$ deep).
4. Large lakes ( $>20 \mathrm{~km}^{2}$ ) that exhibit considerable spatial variability in water chemistry and present difficult logistic problems (e.g., Lake Champlain).
5. Lakes modified by (1) anthropogenic cultural disturbances (e.g., major wastewater treatment plant discharge) or (2) recent in-lake management practices (e.g., liming) to such an extent that the results would not be representative of other lakes in the population.

Lastly, only lakes in the northeastern United States (ELS-I Region 1) were sampled in ELS-II, in order to focus resources on a region of high interest. Thus the subregions analyzed in ELS-II include the Adirondacks, the Poconos/Catskills, northern New England, southern New England, and Maine.

The use and interpretation of any data set are restricted by the design, the quality of the data obtained, and the sampling protocols, which are presented in detail in Sections 2, 3, and 4 of this report. These aspects of the survey should be well understood before drawing conclusions both within and beyond the scope of the original objectives. For example, the ELS-II spring sample was collected after ice-out, 2 to 3 weeks after maximum lake discharge. Site intensive studies have shown that maximum lakewater ANC depressions generally occur during peak discharge. Thus, one should not conclude that the ELS-II estimates of acid-base status in the spring represent the maximum number of lakes that become acidic during spring snowmelt.

## RESULTS

## Between-Year Variability

Changes in acid neutralizing capacity (ANC) and pH between fall 1984 and fall 1986 were small, and estimates of the number of acidic and low pH lakes were very similar between the two years. For example, within the ELS-II target population, there were 307 acidic lakes (ANC $\leq 0 ; 8 \%$ ) and 471 low pH lakes ( $\mathrm{pH} \leq 5.5 ; 12 \%$ ) in fall 1984, versus 343 acidic lakes ( $9 \%$ ) and 478 low pH lakes ( $12 \%$ ) in fall 1986. The median pH change in the ELS-II lake population between fall 1984 and fall 1986 was only 0.06 pH units. Sulfate and DOC distributions were very similar in both years. Base cation and chloride concentrations tended to be higher in 1986 than in 1984, probably due to the drier conditions in 1986. Fall nitrate and extractable aluminum concentrations were very low in most lakes in both years, so that between- year differences were usually small. In lakes with elevated nitrate and extractable aluminum, neither year had consistently higher concentrations than the other. A comparison between ELS-I and

ELS-II data shows that conclusions about the acid-base status of lakes in the northeastern United States lakes would have been similar whether the assessment had been done in fall 1984 or fall 1986.

## Within-Fall Season Variability: Robustness of the Fall Index

Chemical variability within the fall index period was very small. Population estimates of the proportion of lakes with ANC or pH below reference values were not greatly affected by fall temporal and site selection variability. Overall conclusions about the acid-base status of northeastern lakes would have been the same if sampling had occurred during any of the three fall sample visits or at any of the sampling locations. All observed concentrations of $\mathrm{ANC}, \mathrm{pH}, \mathrm{sum}$ of base cations, DOC, and inorganic monomeric aluminum concentrations showed very little difference among the three fall visits. Mineral acid anion concentrations (sulfate, nitrate, and chloride) also showed little difference among the three lake visits, except at the highest observed concentrations, at which some within-season variability was evident. The median standard deviation of the three lake visits was $6 \mu \mathrm{eq} / \mathrm{L}$ for $A N C, 4 \mu \mathrm{eq} / \mathrm{L}$ for sulfate, $8 \mu \mathrm{eq} / \mathrm{L}$ for sum of base cations, and 0.05 pH units. For ANC , pH , and base cations, variability in sample preparation and analysis was the major component of within season variability. Based on data from the ELS-II Fall Variability Study, a single fall index sample is a robust estimator of conditions during the fall index period.

## Among-Season Variability

The ELS-II spring sample was collected during a period of spring ANC depression, generally within two to three weeks after icemelt; however, it almost certainly does not represent the worst case (minimum ANC) conditions. Based on intensive monitoring studies, the minimum lake outlet ANC and pH and the maximum nitrate and inorganic monomeric aluminum concentrations usually occur around peak lake discharge, while ice is still on the lake. Based on this observation, it would be expected that the minimum ANC in ELS-II lakes would be lower than the observed values of the ELS-II spring samples, which were collected 2 to 3 weeks after peak discharge. Thus, the ELS-II spring data do not indicate worst case episodic spring conditions, but rather are indicative of post-snowmelt spring seasonal conditions. The seasonal comparisons presented in the next three paragraphs need to be interpreted with these facts in mind. In the following discussion, spring refers to post-snowmelt spring seasonal conditions, not worst case spring episodic conditions.

For most chemical variables, among-season variability was greater than between-year or within-fall variability. Chemical conditions in the spring, however, were positively correlated with fall index conditions, although ANC, $\mathrm{pH}, \mathrm{DOC}$, and sum of base cation concentrations were typically lower in the spring than in the summer and fall. Summer conditions for these ions were more similar to fall conditions than spring conditions. Nitrate and inorganic monomeric aluminum concentrations were highest in
the spring relative to summer and fall, although both were found at very low concentrations in the majority of ELS-II lakes. ELS-II population estimates show that there were $24 \%$ more acidic lakes (ANC $\leq 0$ ) in the spring ( 424 lakes) than in the fall or summer ( 343 lakes). This corresponds to an increase in the percentage of acidic lakes from $9 \%$ to $11 \%$ in the ELS-II target population. Similarly, the percentage of ELS-Il lakes with ANC $\leq 50 \mu \mathrm{eq} / \mathrm{L}$ increased from $25 \%$ to $34 \%$ (fall to spring) and the percentage with ANC $\leq 100 \mu \mathrm{eq} / \mathrm{L}$ increased from $43 \%$ to $62 \%$. The number of low pH lakes was also higher in spring than in fall. The percentage of ELS-II lakes with $\mathrm{pH} \leq 5.0$ increased from $4 \%$ to $5 \%$, the percentage of lakes with $\mathrm{pH} \leq 5.5$ increased from $12 \%$ to $14 \%$, and the percentage of lakes with $\mathrm{pH} \leq 6.0$ increased from $19 \%$ to $27 \%$.

The largest spring depressions in ANC (relative to fall ANC) were observed in the highest ANC (200-400 $\mu \mathrm{eq} / \mathrm{L}$ ) ELS-II lakes. In lakes with ANC $>50 \mu \mathrm{eq} / \mathrm{L}$, spring ANC depressions (median ANC depression $=60 \mu \mathrm{eq} / \mathrm{L}$ ) were associated with decreases in base cation concentrations, probably due to dilution by spring snowmelt runoff low in ANC and base cations. In low ANC $\leq 50 \mu \mathrm{eq} / \mathrm{L}$ ) lakes, spring ANC depressions were small (median $=3 \mu \mathrm{eq} / \mathrm{L}$, median pH decrease $=0.1 \mathrm{pH}$ unit) and were associated with increases in nitrate in the Adirondacks and Poconos/Catskills. In all ELS-II regions, spring ANC depressions in low ANC lakes were also associated with increasing spring inorganic monomeric aluminum concentrations. Sulfate concentrations were very similar in the spring, summer, and fall seasonal surveys.

Acid stress to fish was assessed using an acid stress index based on lakewater pH , inorganic aluminum, and calcium concentration. The results showed that there was very little difference in the number of lakes unsuitable for fish between spring, summer, and fall in the ELS-II lake population. Thus it appears that the observed seasonal changes in pH , calcium, and aluminum were not great enough to cause a significant seasonal change in the regional estimates of lakes with acid stress, as estimated by the acid stress index. The main reason for this was that the largest ANC changes occurred in higher ANC lakes that did not have a corresponding pH decrease into the range of stressful values. The low ANC lakes that are most susceptible to acidic deposition effects did not have large changes in pH , calcium, and inorganic aluminum and thus there were only small changes in estimated biological effects.

## SECTION 1 <br> INTRODUCTION

### 1.1 OVERVIEW

The extent and magnitude of surface water acidification caused by atmospheric deposition has been one of the most important and politically controversial environmental issues of recent times. Research on individual lakes and streams suggests that pH and acid neutralizing capacity (ANC) have declined over the past half century in some European and North American surface waters (Beamish et al., 1975; Wright and Gjessing, 1976; Schofield, 1976). Atmospheric acidic deposition resulting from fossil fuel combustion has been implicated as a cause of these declines (Schindler, 1988; Sharpe et al., 1984), though alternative hypotheses have been advanced and debated (Rosenqvist, 1978; Krug and Frink, 1983). Regional paleolimnological data from the Adirondacks has shown that most lakes with ANC $<50 \mu \mathrm{eq} / \mathrm{L}$ have declined in pH since industrialization and that there are three times as many acidic lakes now as there were in preindustrial times (Sullivan et al., 1990). The timing of recent lake acidification can best be explained by the onset of acidic deposition (Sullivan, 1990).

A prerequisite for a regional-scale understanding of the effects of acidic deposition on surface waters is knowledge of the present chemical status of surface waters over broad regional areas. To accomplish this goal, the U.S. Environmental Protection Agency (EPA) began the National Surface Water Survey (NSWS) in 1983. The objective of the NSWS was to quantify the physical and chemical characteristics of lake and stream populations within acid-sensitive geographic regions of the United States. In Phase I of the NSWS, surface waters were selected in a systematic random fashion from a statistical frame to allow unbiased estimates of the status and extent of acidic and low ANC systems. Phase I of the NSWS determined that about $6 \%$ of the lakes $>4$ ha in size in the northeastern United States are acidic, and most of them have acid anion compositions dominated by sulfate from atmospheric deposition (L. Baker et al., 1990; Linthurst et al., 1985). The conclusions from Phase I of the NSWS are based on the premise that one (for lakes) or two (for streams) samples can be used as an index to characterize the present chemical status of surface waters. For lakes, a single fall epilimnetic sample was used to provide an index of lake chemical status and to identify acidic and potentially sensitive lakes (Linthurst et al., 1985). The fall index data alone, however, do not provide information on how these descriptions of lake populations might differ if temporal or spatial variability in individual lakewater chemistry had been addressed. In addition, a major criticism of the lake surveys was that a single water sample is insufficient for characterizing a lake, and therefore is insufficient for characterizing lake populations. The primary restriction of Phase I of the NSWS was that questions of the effects of temporal variability of lake chemistry could not be addressed.

Phase II of the NSWS was designed to supplement the data and results from Phase I by providing information on the temporal variability of surface water chemistry. This report presents the results of the
spring, summer, and fall 1986 lakewater chemistry surveys conducted in the northeastern United States as part of Phase II of the Eastern Lake Survey (ELS-II).

The ELS-II was designed to chemically and physically characterize a probability based subsample of Phase I lakes during the spring, summer, and fall seasons. The primary objectives of ELS-II were to:

- Assess the sampling error associated with the ELS-I fall index sample.
- Estimate the number of low ANC (potentially susceptible) lakes not acidic in the fall that are acidic in other seasons, emphasizing spring variability in water chemistry.
- Establish seasonal water chemistry characteristics among lakes and relate the fall index sample to seasonal and annual water chemistry patterns.

Ideally, it would have been desirable to study lakes in all of the ELS-I regions. Logistical and resource constraints, however, dictated that only one region could be analyzed. The Northeast Region (ELS Region 1) was chosen because the Phase I data indicated that it was the ELSII region most impacted by acidic deposition.

### 1.2 THE NATIONAL SURFACE WATER SURVEY

In response to the need for knowledge regarding the present extent of acidic or potentially susceptible aquatic resources and their associated biota, the U.S. EPA and cooperating scientists were asked in 1983 to design a program that would achieve five major goals:

1. Characterize the chemistry of surface waters (both lakes and streams) in regions of the United States presently believed to be potentially susceptible to change as a result of acid deposition.
2. Examine associations among chemical constituents and define important factors that may affect surface water chemistry.
3. Determine the biological resources within these systems.
4. Evaluate correlations among surface water chemistry and the corresponding biological resources.
5. Quantify regional trends in surface water chemistry and biological resources.

The program designed to meet these goals was designated the National Surface Water Survey (NSWS). The NSWS became an integral part of the National Acid Precipitation Assessment Program (NAPAP), an interagency research, monitoring, and assessment effort mandated by Congress in 1980.
NAPAP provides policymakers with technical information concerning the extent and severity of the effects of acid deposition on human, terrestrial, aquatic, and material resources.

The NSWS design (Figure 1-1) incorporates two parallel components, the National Lake Survey (NLS) and the National Stream Survey (NSS), in order to satisfy the five major research goals. In both components, early project phases contributed to the design and interpretation of subsequent phases. The synoptic surveys of lake and stream chemistry performed in the early phases of the NLS and NSS contribute substantially to the design and interpretation of subsequent project phases and are essential to the regional extrapolation of their results.

The NSWS design grew out of the recognition that although it is clearly not feasible to perform intensive, process-oriented studies or monitoring programs on all surface waters within the United States, it is equally inappropriate to study a few systems that later may be found to have atypical biological and chemical characteristics. Therefore, each component of the NSWS begins with Phase I, a synoptic survey designed to characterize and quantify the chemistry of lakes and streams throughout areas of the United States expected to contain the majority of low ANC waters. In the NSWS, lakes and streams were sampled on a regional basis using a statistically rigorous survey design, appropriate standardized and documented field and analytical techniques, a relatively complete set of chemical and physical measurements, and a quality assurance/quality control (QA/QC) program to explicitly define uncertainty in the resulting data. The initial survey component (Phase I) provides a snapshot of the present condition of surface waters in regions of the United States most likely to be affected by acidic deposition. The Phase I data also serves as a basis for classification of lakes and streams. Such classifications allow the regional extrapolation, with known confidence, of results from past and future intensive studies on both high-interest aquatic subpopulations and individual lakes and streams.

In the second phase of the National Lake Survey, the Eastern Lake Survey - Phase II (ELS-II), and in the Episodic Response Project (ERP), short-term (seasonal, weekly, or episodic) variability in water chemistry is quantified within and among lakes and streams of most interest with respect to acidic deposition effects. These surface waters were defined on the basis of Phase I water chemistry and associated hydrology, aquatic organisms, regional acid deposition inputs, land use, physiography, and other basin characteristics.

### 1.3 EASTERN LAKE SURVEY - PHASE II

The major component of ELS-II was the spring, summer, and fall seasonal surveys and Fall Variability Study of lakewater chemistry in the northeastern United States. ELS-II lakes were sampled once in the spring, summer, and fall at the same location on the lake where the ELS-I sample was collected. In the fall variability study, a subset of ELS-II lakes was sampled on two additional dates at two independently selected locations believed to be the deepest point in the lake. ELS-II data, in conjunction with ELS-I data can be used to assess between-year, within-season, and among-season chemical variability, as well as spatial variability due to site selection.


Figure 1-1. Organization of the National Surface Water Survey, showing the two major components, the National Lake Survey and the National Stream Survey, and their relationship to later phases of study. Dates in parentheses are years of field data collection.

In addition to the northeastern chemistry surveys, biological sampling was also conducted in lakes of the eastern Upper Midwest. Data from this study are not discussed in this report. Biological data from the Upper Midwest sampling effort is discussed in Cusimano et al. (1990) and J. Baker et al. (1990a).

### 1.4 THE ELS-II DATA REPORT

This ELS-II data report discusses only data from the seasonal surveys of lakewater chemistry in northeastern lakes. Section 2 discusses the statistical design of ELS-II and Section 3 describes the field and laboratory methodologies. Section 4 details the results of the quality assurance (QA) program. Section 5 presents the major results and analyses of the three main components of temporal variabiity studied in ELS-II: between-year variability, within-season variability, and among-season variability. Between-year variability was addressed by comparing the results from ELS-1 (fall 1984) with those measured in the ELS-II fall seasonal survey (fall 1986). Among-season variability was analyzed by comparing the spring, summer, and fall ELS-II seasonal surveys. Within-season variability was addressed in the ELS-II fall variability study, which sampled a subset of ELS-II lakes at three different times at independently selected locations on the lakes within the fall index period. The last section (6) of the report is a synthesis and discussion of the relative importance of the various components of temporal variability.

## SECTION 2 <br> ELS-II SURVEY DESIGN

### 2.1 OVERVIEW


#### Abstract

Phase II of the Eastern Lake Survey (ELS-II) was designed to assess temporal variability in regional lakewater chemistry. The ELS-II is based on a probability sample of 160 lakes from an explicitly defined subpopulation of lakes sampled in Phase I of the Eastern Lake Survey (ELS-I). As in ELS-I, ELS-II samples are weighted proportionally to the number of lakes they represent in the target population, so that conditions may be inferred for the target population as a whole, not just the sampled lakes. Only lakes from the Northeast Region (Region 1) of the ELS-I were sampled in ELS-II.


### 2.2 EASTERN LAKE SURVEY - PHASE I

As the lakes selected for ELS-II are a subset of the lakes sampled in ELS-I, a short background on the design of ELS-I is warranted. A more detailed discussion of the ELS-I design can be found in Linthurst et al. (1986) and Landers et al. (1988). There were three stratification factors in the ELS-1 design: region (Northeast, Upper Midwest, or Southeast), subregion, and ANC map class (< 100, $100-200$ or $>200 \mu \mathrm{eq} / \mathrm{L})$. A total of 33 separate strata were coded by region, subregion, and ANC map class. For example, 1A2 designates Region 1 (Northeast), subregion A (Adirondacks), and map class 2 (expected ANC class of $100-200 \mu \mathrm{eq} / \mathrm{L}$ ). Only the Northeast Region (Region 1) was sampled for chemical variability in ELS-II. Within the Northeast Region (Figure 2-1), there were five subregions:
Adirondacks (1A), Poconos/Catskills (1B), Central New England (1C), Southern New England (1D), and Maine (1E).

Strata boundaries were overlain on 1:250,000-scale USGS maps and a list was compiled of all lakes on the map in each strata. This list of lakes is known as the statistical frame population and represents the universe of lakes considered for study in the ELS-I. All population estimates computed in ELS-I, and thus those in ELS-II, refer to the map frame population and do not represent conditions in lakes outside the area of coverage or in systems not depicted on the USGS maps used. The main limitation of the map population is that lakes smaller than 4 ha are not part of the ELS population because they are not generally depicted on $1: 250,000$-scale maps. A comparison of the number of ELS-I target and nontarget lakes and the total number of lakes in the northeastern United States can be found in Johnson et al. (1989).

The sampling plan for ELS-I employed a stratified random design, with equal allocation of number of sample lakes to strata. Lakes were selected from each stratum by systematic sampling from an ordered list following a random start. In general, 50 lakes per stratum were selected for sampling. A target population of lakes was defined by excluding lakes with noninterest attributes (e.g., heavy


Figure 2-1. ELS-II sample lakes in the five subregions of the northeastern United States. Clusters were delineated on the basis of 1984 fall index ANC in ELS-I (Section 2.3.2). Cluster I had ANC $\leq 25 \mu \mathrm{eq} / \mathrm{L}$, Cluster II had ANC between 25 and $100 \mu \mathrm{eq} / \mathrm{L}$, and Cluster III had ANC between 100 and $400 \mu \mathrm{eq} / \mathrm{L}$.
anthropogenic activity, no lake present, marsh/swamp) based on larger scale map examination and field visitation. Each sampled lake was assigned a sample weight equivalent to the number of lakes it represents in the target population. In ELS-I, all the lakes in a stratum have the same weight, equivalent to $\hat{N} / n^{* * *}$, where $\hat{N}$ is the estimated total number of target lakes in the frame population in the stratum and $\mathrm{n}^{* * *}$ is the number of target lakes sampled in the stratum. For example, if 1,000 target lakes are estimated to be in a stratum and 50 target lakes were sampled, then each sample lake represents 20 lakes in the target population and has a weight of 20 . In total, there are an estimated 7,157 ELS-I target lakes in the Northeast Region out of a frame population of 10,758 lakes.

### 2.3 EASTERN LAKE SURVEY - PHASE II

ELS-II was designed to sample a subset of the ELS-I lakes to estimate the number of lakes not acidic in the fall that are acidic in other seasons and to assess the sampling error associated with the ELS-I fall index sample. In addition, ELS-II was designed to establish the seasonal characteristics among lakes thought to be in an acid-sensitive class of lakes, in order to aid in detecting trends and evaluating episodic acidification.

### 2.3.1 Defining the Population of Interest

To better characterize the population of interest, a group of lakes of low interest to the goals of ELS-II was defined. These low-interest lakes were not subsampled for inclusion in the ELS-II population and are not represented by any of the data discussed in this report. Lakes of low interest were defined as having any of the following characteristics (Thornton et al., 1986):

- ANC levels such that a lake probably would not become acidic at current rates of deposition (termed capacity protected systems). High ANC lakes were defined as those having ELS-I index chemistry > $400 \mu \mathrm{eq} / \mathrm{L}$.
- Highly enriched by nutrients that would either (1) internally generate enough ANC for a lake to be considered capacity protected, or (2) seriously distort the chemical composition of the lake and confound data interpretation. Nutrient enriched lakes were defined as those having either total phosphorous $>90 \mu \mathrm{~g} / \mathrm{L}, \mathrm{NO}_{3}{ }^{-}>50 \mu \mathrm{eq} / \mathrm{L}, \mathrm{NH}_{4}{ }^{+}>30 \mu \mathrm{eq} / \mathrm{L}$, turbidity $>7 \mathrm{NTU}$, or Secchi disk depth $<0.5 \mathrm{~m}$, based on ELS-I index chemistry.
- Shallow lakes (defined as those with ELS-I site depth $<\mathbf{1 . 5} \mathbf{m}$ ). At the time of ELS-li site selection, it was believed that shallow lakes did not contain a significant fishery resource. In hindsight, this does not appear to have been a useful exclusion. Shallow lakes do support a fishery resource.
- Lakes so large that they exhibit considerable spatial variability in water chemistry and present difficult logistic problems (e.g., Lake Champlain or the Finger Lakes of central New York). Large lakes were defined as those with surface areas $>2,000$ ha $\left(20 \mathrm{~km}^{2}\right)$.
- Modified by anthropogenic cultural disturbances to such an extent that the results would not be representative of other lakes in the population (e.g., major wastewater treatment plant discharge into the lake).
- Modified by recent in-lake management practices resulting in a serious disturbance of either the biota or the lake chemistry (e.g., rotenone treatment, removal of a dam, liming).

The first four factors were used to exclude ELS-I lakes from inclusion in the ELS-II sample. Factors 5 and 6 were evaluated after site selection on an individual lake basis to further refine the ELS-II population of interest.

### 2.3.2 Statistical Sampling Design

The ELS-II is a double, or two-phase, sampling design. The first phase was the ELS-I sampling and the second phase was the ELS-II subsampling of lakes selected from the ELS-I sampled lakes. Logistical considerations for ELS-II limited the number of lakes that could be adequately analyzed to a total of about 150. Based on ELS-I experience, statistical precision requirements for making population estimates (proportion of lakes with values below reference values) indicated that a sample size of about 50 lakes was desirable for a stratum (Linthurst et al., 1986). Thus the ELS-II design was based on a sampling of 50 lakes from each of three clusters of ELS-I lakes. Clusters were chosen by analyzing data from all 15 ELS-I strata in the Northeast (Region 1) using cluster analysis to identify meaningful subgroups, on the basis of lake chemistry or other attributes. Lakes of low interest (as defined in Section 2.3.1) were assigned to a reserved fourth cluster and not used in site selection. The results indicated that a univariate criterion based on ANC coincided closely with the results of cluster analysis using a variety of variables, including $\mathrm{pH}, \mathrm{ANC}, \mathrm{DOC}$, color, sulfate, methyl-isobutyl-ketone (MIBK) extractable aluminum, and base cations (Thornton et al., 1986). Thus, the three clusters used as stratification factors in the ELS-II design were:

$$
\begin{array}{ll}
\text { Cluster I. } & \text { ANC } \leq 25 \mu \mathrm{eq} / \mathrm{L} \\
\text { Cluster II. } 25<\text { ANC } \leq 100 \mu \mathrm{eq} / \mathrm{L} \\
\text { Cluster III. } 100<\text { ANC } \leq 400 \mu \mathrm{eq} / \mathrm{L}
\end{array}
$$

The ELS-II subsampling process employed a fixed-size systematic variable probability sample (Overton, 1987). Selection was with probability proportional to the ELS-I sample weight (inversely proportional to the ELS-I inclusion probability), with the result that the total ELS-II sample weights within the three clusters are nearly equal. The final ELS-II sample weight for lake $\mathrm{i}, \mathrm{W} 2_{\mathrm{i}}$, is equal to (equation 1 ):

$$
\begin{equation*}
\mathrm{W} 2_{\mathrm{i}}=\mathrm{W}_{\text {cond, } \mathrm{i}} * \mathrm{~W}_{1} \mathrm{i}_{\mathrm{i}} \tag{1}
\end{equation*}
$$

where $W_{\text {cond, } i}$ is the ELS-II conditional inclusion weight and $W_{i}$ is the ELS-I sample weight. $W_{\text {cond, } i}$ is calculated for each cluster in each strata from equation 2 :

$$
\begin{equation*}
W_{\text {cond }, i}=T_{w} /\left(W 1_{i} * n\right) \tag{2}
\end{equation*}
$$

where $T_{w}$ is the estimated number of mapped target lakes (the sum of the ELS-I sample weights) in the cluster and $n$ is the number of lakes to be sampled in the cluster.

In selection, clusters were treated as stratification factors. Prior to selection, the ELS-I sample lakes in each cluster were sorted by subregion (major) and site depth (minor). Sorting by these two factors increased the probability of obtaining representative spatial coverage of lakes throughout the region and varied lake types. Measured ANC was the primary basis of the clusters so that all three of these factors were thus controlled in lake selection. After a random start, ELS-II sample lakes were then chosen from the sorted list of ELS-I lakes at equal intervals (i.e., every 10th lake, or every 23rd lake, depending on the desired sample size).

Three minor difficulties arose. First, five lakes in cluster I and two lakes in cluster II had ELS-I weights $\left(W 1_{i}\right)>T_{w} / n$ and had to be sampled with $W_{\text {cond, } i}$ equal to 1 , otherwise the $W_{\text {cond, } i}$ calculated from equation 2 would be $<1$ (implying an inclusion probability $>1$ ). Thus, these seven ELS-I lakes were included with certainty in the ELS-II sample. Those samples selected with a $\mathrm{W}_{\text {cond, }}$ of 1 had an ELS-II sample weight the same as the ELS-I sample weight (see equation 1). Sampling these lakes with certainty affected the $\mathrm{W}_{\text {cond, }}$ in clusters I and II, because n and $\mathrm{T}_{\mathrm{w}}$ change. $\mathrm{T}_{\mathrm{w}}$ is decreased by the sum of the ELS-I weights sampled with certainty in each cluster and n is decreased by five lakes in cluster I and two lakes in cluster II.

A second difficulty is that it is awkward to construct an expanding sample using this scheme. That is, if the sample size were set to 50 and it was necessary to add two lakes to bring the number to 52 , and keep the same statistical properties of the resultant sample, the required procedure would be complex. It is easier to draw a larger sample, and reduce it while retaining the desired statistical properties. The lakes eliminated by the reduction are thus available for expansion, if necessary. In ELS-II, it was decided to select 60 lakes in clusters II and III to provide for 10 alternate lakes in each of these two clusters. The alternates were needed in cluster II because of post-selection exclusions (see Section 2.4.1), but were deemed unnecessary in cluster III. Therefore, 160 sample lakes represent the initial ELS-II target population: 50 from cluster I, 60 from cluster II, and 50 from cluster III.

A final complication was that after selection of the ELS-II sample, small revisions were made to the ELS-I weights in the 1B2, 1D2, 1D3, 1E1, and 1E2 strata because some of the ELS-I lakes chosen for sampling were not actually sampled. $W_{\text {cond, }}$ is fixed at the time of site selection and does not change, but the change in the ELS-I weight $\left(W_{1} 1_{i}\right)$ does change the final ELS-II sample weight (see equation 1 ). The resulting changes were fairly small, but the final ELS-II sample weights are not quite uniform in each cluster as they would have been if the ELS-I weights had not been revised.

### 2.4 ELS-II TARGET POPULATION

Of the estimated 7,157 target ELS-I lakes, an estimated 4,426 are represented by the 160 ELS-II lake samples (Table 2-1). The remaining 2,731 lakes were of low interest to ELS-1I for the reasons described in Section 2.3.1 and enumerated in Table 2-1. The major reasons for a low interest designation were high ANC and shallow depth. The sample lakes in the initial ELS-II target population were then examined in more detail to check for low interest attributes.

### 2.4.1 Refinement of the Target Population

As discussed in Section 2.3.1, lakes that were managed or modified by cultural disturbances were considered of low interest for ELS-II because their inclusion would interfere with an assessment of natural chemical variability. After selection, the 160 study lakes were evaluated on an individual basis for evidence of perturbance by consulting external data sources (state files, liming records, etc.). As a result of this analysis, 147 lakes were targeted for field visitation and 13 lakes were eliminated from the population of interest. Seven of the 13 excluded lakes were removed because they had been limed and were being managed, 5 were removed due to point sources of pollution, and 1 was removed because it was a bog.

After field visitation, an additional lake (1B3-025) was removed from the population of interest. This lake was managed by a private club that denied permission for access to the lake. This lake was classified as of low interest due to management. In addition, one lake (1A2-058) in cluster III that could not be sampled in the fall due to inclement weather was sampled in the spring and summer. Rather than have unequal sample sizes and thus different weights in the different seasonal data sets, it was decided that this lake would be considered a random miss in all of the seasons. Data from this lake for spring and summer were not used to make population estimates. $\mathrm{W}_{\mathrm{i}}$ and $\mathrm{W}_{\text {cond, } \mathrm{i}}$ were adjusted for the random miss by decreasing the sample size, $n$, in cluster III by 1 and recalculating the weights using equations 1 and 2 .

In sum, 145 of the 160 lakes in the initial ELS-II population were used to make population estimates. Of the 15 eliminated lakes, 14 were classified as low interest and one was a random miss. Extrapolating to the population, about $10 \%$ (an estimated 443 lakes) of the 4,426 lakes in the initial ELS-II population were excluded for low interest attributes. A complete breakdown of the ELS-I and ELS-II target populations is presented in Table 2-1. The refined ELS-II target population with which population estimates are made is based on a sample of 145 lakes representing a population of 3,993 mapped lakes. The location and cluster of the 145 ELS-II sample lakes is shown in Figure 2-1. The distribution of ELS-II lakes in the Northeast is patchy due to either a low density of lakes greater than 4 ha in some regions (e.g. Vermont), the prevalence of high ANC lakes in some areas (e.g. the St. Lawrence Lowlands), or random chance.

## Table 2-1. Estimated Population and Sample Sizes of Northeastern Lakes (Region 1) in ELS-I and ELS-II

|  | Sample Size | Population Size |
| :---: | :---: | :---: |
| ELS - Phase I |  |  |
| Map Frame Population | --- | 10,758 |
| ELS-I Target Population | 768 | 7,157 |
| ELS-II Selection Exclusions |  |  |
| High ANC Lakes (> $400 \mu \mathrm{eq} / \mathrm{L}$ ) Culturally Enriched Lakes | $\begin{array}{r} 114 \\ 24 \end{array}$ | $\begin{array}{r}1,409 \\ \hline 64\end{array}$ |
| Shallow Lakes ( $<1.5 \mathrm{~m}$ ) | 119 | 997 |
| Big Lakes (> 2000 ha) | 5 | 61 |
|  | - | - |
| Exclusions Subtotal | 262 | 2,731 |
| Potential ELS-II Lakes | 506 | 4,426 |
| ELS - Phase II |  |  |
| Initial Target Population | 160 | 4,426 |
| Post Selection Exclusions |  |  |
| Managed Lakes | 8 | 245 |
| Polluted Lakes | 5 | 139 |
| Bog Lakes | 1 | 49 |
| Random Miss | 1 | $0^{\text {a }}$ |
|  | - | - |
| Exclusions Subtotal | 15 | 433 |
| Refined Target Population ${ }^{\text {b }}$ | 145 | 3,993 |
| a Sample weights were adjusted to account for the random miss so that there was no change to the population size. |  |  |

### 2.4.2 Making ELS-II Population Estimates

Population estimates in ELS-II were made in much the same manner as those in other surveys of the NSWS (Linthurst et al., 1986; Landers et al., 1987; Kaufmann et al., 1988). Details of estimation, along with the statistical foundation of the methods, are provided elsewhere (Overton, 1987; Blick et al., 1987). The general form of estimator:

$$
\begin{equation*}
\hat{T}_{y}=\sum_{S} W z_{i} y \tag{3}
\end{equation*}
$$

where:
$\hat{\mathrm{T}}_{y}$ is the estimate of the total of any attribute, $y$, over the population.
$y \quad$ is any lake attribute of interest (e.g., number or area), known over the sample, $S$.
$\Sigma \quad$ indicates summation over the appropriate sample of target reaches, whether the full sample, a subsample, or mixed cluster sample.
$\mathrm{W} 2_{i}$ is the ELS-II sample weight assigned to the lake in making population estimates (see Appendix B).

This estimator is similar to the Horvitz-Thompson (1952) estimator for variable-probability samples, but it is not exactly the same due to the two-phase nature of the sampling (Sarndal and Swensson, 1987). By assigning different definitions to $y$, and by summing over different sets of sample units, $S$, the various attributes of the target population of lakes can be estimated from this one equation. Specifically, in the ELS-II, two attributes are identified as parameters of the resource of interest:

1. Total number of target lakes $(\hat{N}), y=1: \hat{N}=\Sigma W 2_{i}$
2. Total area of target lakes $(\hat{A}), y=A: \hat{A}=\Sigma W 2_{i} A$
where $A$ is the surface area of the lake.
Specific subpopulations are assessed by combining the samples from those subpopulations, and in general it is necessary only for the sample subset to be defined in exactly the same way as the estimated population. For example, the number of ELS-II target lakes in the Adirondack Mountains with $\mathrm{pH}<6.0$ is estimated by summing the sample weights of all Adirondack Mountain lakes with $\mathrm{pH}<6.0$ in the ELS-II sample. Similarly, the area of ELS-II target lakes in Maine with elevation $>500 \mathrm{~m}$ is calculated by summing the product of the weight and lake area for all ELS-II sample lakes in Maine with elevation > 500 m .

Estimates of the variance of estimated target population totals were calculated by using appropriate variable-probability variance estimators adapted for the two-phase nature of the sampling (Overton, 1987). The variance estimator again closely resembles the Horvitz-Thompson variance estimator, but it is not exactly the same because of the two-phase nature of the sampling. Additional complications due to the systematic nature of the sampling are addressed by Stehman and Overton (1987). The formula for estimated variance is:

$$
\begin{equation*}
\hat{V}(\hat{T} y)=\sum_{S} y^{2} W z_{i}\left(W z_{i}-1\right)+\sum_{i \in S} \sum_{\substack{j \in S \\ j \neq i}} y_{i} y_{j}\left(W z_{i} W z_{j}-W_{i j}\right) \tag{4}
\end{equation*}
$$

where $W_{i j}=A_{i j} B_{i j}$ is the inverse of the pairwise inclusion probability (see Appendix $A$ for details). The second term in equation 4 represents a pairwise comparison of every possible $i, j$ pair in the population of interest. The estimated standard error (SE) of the estimated population total is then calculated as the square root of the variance estimate, $\hat{\mathrm{V}}\left(\hat{T}_{\mathrm{y}}\right)$.

The primary outputs of these population estimates are descriptions of the various distributions of the chemical variables. Distributions of chemistry within any subset of the target population were analyzed in the same way. That is, an estimate was made of the number of lakes in the subpopulation having a value of the variable less than or equal to a particular value.

$$
\begin{equation*}
\hat{N}(x)=\sum_{X \leq X} W z_{i} \tag{5}
\end{equation*}
$$

In the NSWS, population data are often presented as a cumulative distribution function (CDF). Values of the variable of interest are sorted and distributions are generated by computing the above estimates for each value of x in the sample, and then scaling these estimates by the estimated population total. Associated confidence bounds are generated by estimating the standard errors of each of these quantities for all values of x , from which are determined the confidence bounds on the quantities estimated; these are similarly scaled by dividing by the estimated total quantities. For example:

$$
\begin{equation*}
F(x)=\hat{N}(x) / \hat{N} \tag{6}
\end{equation*}
$$

Thus $F(x)$ represents the estimated proportion of the population having a value less than or equal to $x$. Similar distributions can be calculated for any other lake attribute of interest. In Appendix A, chemical variable CDFs are given for both lake number $(F(x))$ and lake surface area $(G(x))$, where $G(x)$ represents the proportion of the total population lake area having values less than or equal to $\times$ (based on $\hat{A}$ ).

Other population statistics of interest can be generated from the distributions. Each distribution has identified quantiles, for example the median and the two quartiles, $Q_{1}$, and $Q_{3}$. The median of any variable is the value of $x$ such that $F(x)=0.5$. The first quartile of any variable, $Q_{1}$, is the value of $x$ such that $F(x)=0.25$. These statistics can be defined for all distributions. Additionally, from the frequency distribution, $\mathrm{F}(\mathrm{x})$, the mean and standard deviation of the variable x on the population is estimated.

$$
\begin{align*}
& \operatorname{Mean}(x)=\Sigma W 2_{i} x / \Sigma W 2_{i}  \tag{7}\\
& S D(x)=\left(\Sigma W 2_{i} x^{2} / \Sigma W 2_{i}-\left[\Sigma W 2_{i} x / \Sigma W 2_{i}\right]^{2}\right)^{0.5} \tag{8}
\end{align*}
$$

### 2.4.3 Comparison to DDRP Population

Northeastern lakes studied in the EPA's Direct/Delayed Response Project (DDRP) were selected concurrently and with the same statistical design as ELS-II (Church et al., 1989). The DDRP, however, had additional site restrictions (e.g., watershed areas had to be < 3,000 ha) so that there is not a complete overlap between the DDRP and ELS-II sites. In addition, some of the lakes that were dropped from ELS-II after site selection, during the target population refinement (Section 2.4.1), were analyzed in the DDRP. Overall, both surveys sampled 145 target lakes but the DDRP had an estimated target population of 3,668 lakes, whereas ELS-II had an estimated target population of 3,993 lakes. There were 118 sample lakes representing an estimated 3,078 lakes in the target population common to both surveys ( $77 \%$ of the DDRP population was in the refined ELS-II population).

## SECTION 3

## METHODS

### 3.1 OVERVIEW

This section discusses the methods employed in Phase II of the Eastern Lake Survey (ELS-II) for sample collection, handling, and analysis. It also describes the quality assurance and quality control (QA/QC) protocols that were implemented, including the procedures for data management (verification, validation, and construction of the final data bases used for analysis).

Much of the ELS-II methodology was shared with other components of the National Surface Water Survey (NSWS): Phase I of the Eastern (Linthurst et al., 1986) and Western (Landers et al., 1987) Lake Surveys and the National Stream Survey (Kaufmann et al., 1988). The QA/QC sample collection design, data management protocol, and processing laboratory activity for ELS-II were similar to the procedures implemented in the other surface water surveys.

The chemical and physical characteristics of lake water that were analyzed for all ELS-II samples are listed in Table 3-1. A description of each parameter is given in the ELS-II analytical methods manual (Kerfoot et al., 1988). Once collected, water samples were transported via express courier to a central processing laboratory where they were preserved and split into aliquots within 36 hours after sample collection. In addition to preparing the samples for shipment to the contract analytical laboratory, the processing laboratory measured pH , dissolved inorganic carbon (DIC), color, turbidity, specific conductance, and certain aluminum species. At the analytical laboratory, 24 major chemical variables were measured (Table 3-1). Data from the analytical laboratory were entered into a data base, which then underwent a series of QA checks.

### 3.2 FIELD SAMPLING PLAN

A total of 147 statistically selected lakes were targeted for field visitation during ELS-11 (as described in Section 2; however, only 145 lakes are in the refined target population) during the spring, summer, and fall of 1986. In addition to these seasonal surveys, a variability survey was conducted during the Fall Seasonal Survey. The Fall Variability Survey was designed to sample a subset of 50 of the ELS-II lakes at three different times at independently selected locations believed to be the deepest points in the lakes during the fall index period.

In situ measurements of pH, specific conductance, temperature, and dissolved oxygen (Table 3-1) were made at 1.5 m below the surface and 1.5 m above the bottom in all lakes. If the lake was stratified (temperature difference $>4^{\circ} \mathrm{C}$ ), depth profiles of the in situ measurements were made. Water samples for laboratory analyses were collected from the epilimnion at 1.5 m below the surface in lakes more than

Table 3-1. Chemical and Physical Variables Measured in ELS-II and Methods Employed

| Parameters | Instrument or analytical methods | Reference laboratory methods ${ }^{2}$ |
| :---: | :---: | :---: |
| FIELD SITE |  |  |
| pH , in situ | Potentiometer Hydrolab (Surveyor II) | Merritt and Sheppe (1988) |
| Specific conductance and temperature, in situ | Conductivity cell and Thermistor Hydrolab (Surveyor II) | Merritt and Sheppe (1988) |
| Dissolved oxygen, in situ | Oxygen probe Hydrolab (Surveyor II) | Merritt and Sheppe (1988) |
| Secchi Disk Transparency | Secchi disk | Merritt and Sheppe (1988) |
| PROCESSING LABORATORY |  |  |
| Aluminum |  |  |
| Total monomeric | Colorimetry (pyrocatechol violet, automated flow injection analyzer) | Arent et al. (1988) |
| Nonexchangeable monomeric | Colorimetry as with total monomeric (after passing through strong cation-exchange column) | Arent et al. (1988) |
| Specific conductance | YSI conductivity meter (Model 32); YSI cell (YSI 3417) | EPA 120.1 |
| pH , closed system | pH meter (Orion Model 611); glass combination electrode (Orion Model 8104) | EPA 150.1 |
| Dissolved inorganic carbon, closed system | Infrared spectrophotometry (Dohrmann DC-80 carbon analyzer) | EPA 415.2 (modified) |
| True color | Comparator (Hach Model CO-1) | EPA 110.2 (modified) |
| Turbidity | Nephelometer (Monitek Model 21) | EPA 180.1 |

[^0](Continued)

Table 3-1. Chemical and Physical Variables Measured in ELS-II and Methods Employed (Continued)

| Parameters | Instrument or analytical methods | Reference laboratory methods ${ }^{\text {a }}$ |
| :---: | :---: | :---: |
| CONTRACT ANALYTICAL LABORATORY |  |  |
| Acid neutralizing capacity (ANC) | Acidimetric titration, modified Gran analysis | Hillman et al. (1987); Kramer (1984) |
| Aluminum |  |  |
| Extractable | Atomic absorption spectroscopy (furnace) on methyl-isobutylketone extract | Hillman et al. (1987); EPA 202.2 |
| Total | Atomic absorption spectroscopy (furnace) | EPA 202.2 |
| Ammonium | Colorimetry (phenate, automated) | EPA 350.1 |
| Base neutralizing capacity (BNC) | Alkalimetric titration, modified Gran analysis | Hillman et al. (1987); Kramer (1984) |
| Calcium | Atomic absorption spectroscopy (flame) | EPA 215.1 |
| Chloride | Ion chromatography | ASTM (1984); O'Dell et al. (1984) |
| Dissolved inorganic carbon (DIC) |  |  |
| Initial | Infrared spectrophotometry | EPA 415.2 (modified) |
| Air equilibrated | Infrared spectrophotometry, after bubbling with 300 ppm $\mathrm{CO}_{2}$ air for 20 minutes | EFA 415.2 (modified) |
| Dissolved organic carbon (DOC) | Infrared spectrophotometry, after acidification and sparging to remove DIC | EPA 415.2 |
| Fluoride, total dissolved | Ion-specific electrode | EPA 340.2 (modified) |
| Iron | Atomic absorption spectroscopy (flame) | EPA 236.1 |

[^1]Table 3-1. Chemical and Physical Variables Measured in ELS-II and Methods Employed (Continued)

| Instrument or |  |  |
| :--- | :--- | :--- |
| Parameters | Inslytical methods | Reference <br> laboratory <br> methods $^{2}$ |
| Magnesium | Atomic absorption spectroscopy <br> (flame) | EPA 242.1 |

[^2]EPA methods are taken from U.S. EPA (1983); USGS methods are from Skougstad et al. (1979).

3 m deep. In lakes < 3 m deep, epilimnetic samples were collected at 0.5 m below the surface. ELS-II field operations are discussed in detail by Merritt and Sheppe (1988).

### 3.2.1 Spring Seasonal Survey

ELS-II lakes in the Northeast were sampled once in the spring of 1986 in the epilimnion at the same location in the lake as the fall index sample in ELS-I (Figure 3-1). Lakes were sampled as soon after iceout as was practical. Water samples were collected from 146 lakes between March 25 and May 3, 1986. The relationship between the ELS-II sampling window and lake outlet discharge in ELS-II subregions is discussed in Section 6.3.3.

### 3.2.2 Summer Seasonal Survey

ELS-II Lakes were sampled once in the epilimnion in the summer of 1986 at the same location in the lake as the fall index sample in ELS-I (Figure 3-2). Water samples were collected from 147 lakes. In addition to the epilimnetic sample, a hypolimnetic sample was collected in 123 of these lakes. Hypolimnetic samples were drawn from the middle of the hypolimnion in stratified lakes, and at 1.5 m from the bottom in nonstratified lakes and in lakes < 5 m deep. Hypolimnetic samples were not collected from lakes < 3 m deep. Summer seasonal survey samples were collected between July 23 and August 11, 1986. A number of special studies were also conducted during the summer seasonal survey (e.g., zooplankton analyses, chlorophyll-a; see Figure 3-2). Data from these studies, as well as the hypolimnetic data, are not discussed in this report. Details of the zooplankton study can be found in Tessier and Horwitz (1988, 1990).

### 3.2.3 Fall Survey and Variability Study

A variability study was conducted in fall 1986 along with the regular seasonal survey to assess the within-season and within-lake spatial variability in index chemistry (Figure 3-3). In addition to the fall seasonal survey visits at the ELS-I sample locations, a subset of 50 ELS-II lakes, in two sets of 25 , was selected for sampling at two additional times during the fall index period at two independently selected locations in each lake. The Fall Variability Study sampling locations were chosen at the time of sample visits (by independent field crews) by locating a spot that appeared to be the deepest part of a lake, according to lake shape, surrounding topography, and depth measurements, in the same manner as the original ELS-I sites were chosen. A set of 25 fall variability lakes was randomly selected from all the ELS-II lakes in each of two geographic regions of the northeastern United States: the Adirondacks, and southeastern New England (Connecticut, Rhode Island, Massachusetts, and southern New Hampshire).


Figure 3-1. Sampling strategies for the Spring Seasonal Survey, ELS-II (from Merritt and Sheppe, 1988).


Figure 3-2. Sampling strategies for the Summer Seasonal Survey, ELS-II (from Merritt and Sheppe, 1988).

## FALL SEASONAL



Figure 3-3. Sampling strategies for the Fall Seasonal Survey, ELS-II (from Merritt and Sheppe, 1988).

Due to inclement weather and logistic constraints, only 41 of the 50 selected lakes (17 in the Adirondacks and 24 in central and southeastern New England) were sampled three times in the fall.

The ELS-II lakes not included in the Fall Variability Study were sampled only once in the fall at the same location as the ELS-I sample. In total, water samples were collected from 152 lakes, 7 of which were special interest sites (lakes that are not part of the statistical sample but are of interest in comparing ELS-II results with those of other researchers). Only epilimnetic water samples were collected. All fall seasonal and variability study samples were collected between October 8 and November 14, 1986. In the fall variability study, there were typically (median) 10 days between the first and third sample visits (interquartile range $=7-15$ days) .

### 3.3 FIELD METHODS

### 3.3.1 Site Location

Samplers identified the study lakes by comparing their features with those depicted on 1:24,000scale USGS maps. Helicopter crews verified the location of each lake by comparing lake latitude and longitude obtained via a LORAN-C guidance system with those established during ELS-I, also using LORAN-C. In the spring, summer, and fall Seasonal Surveys, samples were collected from the same general location on a lake as those in ELS-I by using ELS-I data sheets showing the lake outline, sample location, and sample depth (Merritt and Sheppe, 1988). Lakes were accessed by either helicopter or boat. A comparability study of the two access methods conducted during the Western Lake Survey demonstrated that there were no significant differences that would affect data interpretation (Landers et al., 1987).

### 3.3.2 Sample Collection

Water samples were collected from the lake using a 6.2-L Van Dorn bottle fitted with a nylon Leurlok valve. Before any container was filled, it was rinsed three times with sample water from the Van Dorn. Four gas-tight $60-\mathrm{mL}$ polypropylene syringe samples were filled from the Van Dorn without exposing the samples to the atmosphere, in order to minimize changes (e.g., degassing) in the water sample prior to analysis. These syringes were analyzed in the processing laboratory for pH , dissolved inorganic carbon (DIC), and total monomeric and nonexchangeable aluminum (Table 3-1). Next, a 4-L cubitainer was filled with water from the Van Dorn bottle. Thus, a routine sample consisted of four syringes and one cubitainer.

Two types of QC samples were collected in the field, blanks and replicates. Blanks were collected by rinsing and filling the Van Dorn bottle with deionized water and then filling the syringes and cubitainer. For replicates, another set of four syringes and one cubitainer were filled with lake water
from the Van Dorn bottle. At least one field blank was collected per day for each laboratory batch. A replicate water sample was collected from at least one lake per day. In the summer, triplicate samples were also collected to assess analytical laboratory bias.

### 3.3.3 In Situ Measurements

After confirming the sampling location on the lake, in situ chemical measurements were made (Table 3-1). In situ chemistry measurements included pH , specific conductance, dissolved oxygen, Secchi depth, and temperature. All field pH , specific conductance, temperature, and dissolved oxygen determinations were made using Hydrolabs (Surveyor II). The Hydrolab pH probes were calibrated each morning using commercially available high ionic strength buffer solutions ( pH 4.0 and 7.0). A low ionic strength quality control check sample (QCCS) was used to check the calibration of the meter before leaving for the field and again before and after in situ measurements. Measurement and calibration techniques for all in situ measurements are described in detail in Merritt and Sheppe (1988)

### 3.4 SAMPLE HANDLING

Water samples were transported from the sample site in coolers containing frozen chemical refrigerant packs that maintained a temperature of approximately $4^{\circ} \mathrm{C}$ until the samples arrived at the processing laboratory. Samples were shipped by overnight courier to ensure their arrival at the processing laboratory in Las Vegas, Nevada, on the morning after collection. Upon arrival at the processing laboratory, samples were organized into a batch for processing. A sample batch consisted of a group of routine lake samples and related QC samples. In almost all cases, processing laboratory analyses were completed and samples were preserved and split into aliquots within 36 hours after sampling.

Within each batch, each sample was assigned a unique identification number to distinguish it from all other samples in the survey. After the batch of samples was preserved and split into aliquots, it was shipped by overnight courier to a contracted analytical laboratory for chemical analysis (Table 3-1).

### 3.5 PROCESSING LABORATORY TECHNIQUES

The processing laboratory provided a controlled environment for processing and preserving water samples and performing certain chemical measurements that needed to be completed as soon as possible after sample collection. Figure 3-4 illustrates the processing laboratory activities. Chemical parameters that tend to become unstable over time (i.e., pH , DIC, and the aluminum species) were measured in the processing laboratory.


Figure 3-4. Processing laboratory activities, ELS-II.

Each 4-L cubitainer sample was split into seven aliquots and prepared for shipping to analytical laboratories for additional analyses. Subsamples were also taken from each Cubitainer for measuring turbidity, specific conductance, and true color (Table 3-1). Field crews capped the syringe samples with air-tight teflon valves to prevent air equilibration from occurring before analysis. The syringe samples were used to measure $\mathrm{pH}, \mathrm{DIC}$, and total and nonexchangeable monomeric aluminum species and to prepare the total extractable aluminum aliquot (Table 3-1). Processing laboratory measurements of these variables were essential for providing quality data within holding time requirements. Processing laboratory analytical methods are described in Arent et al. (1988) and Hillman et al. (1987).

Figure 3-4 depicts the seven aliquots prepared from each Cubitainer. The aliquots were stabilized by filtration ( $0.45-\mu \mathrm{m}$ filter), acid preservation, or refrigeration, or some combination of these procedures. All aliquots were stored and shipped at $4^{\circ} \mathrm{C}$ to reduce biological activity and, for total extractable aluminum aliquots, to reduce volatilization of solvent. Arent et al. (1988) give a detailed discussion of processing laboratory activities for ELS-II.

### 3.6 ANALYTICAL LABORATORY SUPPORT

Standard EPA contract laboratory procurement procedures were used to secure the services of two analytical laboratories (Mitchell-Hall et al., 1989). Laboratory 1 analyzed the spring samples and laboratory 2 analyzed the fall samples. Both laboratories were involved in the analysis of summer samples. Table 3-1 lists the analytical instruments and methods used by the analytical laboratories. A detailed description of each analytical method is given in the ELS-II analytical methods manual (Kerfoot et al., 1988). The maximum allowable holding time for each analyte before analysis is given in Table 3-2.

### 3.7 DATA BASE DEVELOPMENT

ELS-II data management and analysis were patterned after procedures developed for the ELS-I (Kanciruk et al., 1986). The ELS-II data base used in this report has been subjected to four levels of QA evaluation to ensure that the data collected during ELS-II is representative of the physical and chemical characteristics of the lakes at the time of sampling. The completion of each level of QA produced a new working data set of increased refinement. These working data bases are defined as: raw (Data Set 1), verified (Data Set 2), validated (Data Set 3), and enhanced (Data Set 4). The final product of this refinement process, the enhanced data set (Data Set 4), incorporates data substitution and replacement of missing values. This is the data set that is used for calculating ELS-II population estimates. Figure 3-5 summarizes the development of these working data bases. A detailed discussion of the data base creation and contents is included in the ELS-II Data Base Dictionary (Jimenez et al., in press).

After the completion of the ELS-II survey, all lakes successfully sampled were targeted for morphometric analysis. The bathymetric mapping was successfully completed for 129 lakes in the summer of

Table 3-2. Maximum Holding Times Specified for ELS-II Samples ${ }^{\text {a }}$

|  | Variable | Holding Time |
| :---: | :---: | :---: |
|  | $\mathrm{NO}_{3}^{-b} ;$ MIBK-extractable aluminum | 7 days |
|  | ANC; BNC; specific conductance; DIC; DOC; $\mathrm{pH}^{\text {c }}$ | 14 days |
|  | $\mathrm{P} ; \mathrm{NH}_{4}^{+} ; \mathrm{Cl}^{-} \mathrm{SO}_{4}{ }^{2-} \mathrm{F}^{-} \mathrm{SiO}_{2}$ | 28 days |
|  | $\mathrm{Ca} ; \mathrm{Fe} ; \mathrm{K} ; \mathrm{Mg} ; \mathrm{Mn} ; \mathrm{Na}$; total aluminum | 28 days ${ }^{\text {d }}$ |
| Sample preservation methodology is summarized in Figure 3-4. |  |  |
| $b$ | Although the EPA (U.S. EPA, 1983) recommends that nitrate in unpreserved samples (unacidified) be determined within 48 hours of collection, evidence exists (Peden, 1981; APHA, 1985) that nitrate is stable for 2 to 4 weeks, if the sample is stored in the dark at 4 C . |  |
|  | Although the EPA (U.S. EPA, 1983) recommends that pH be measured immediately after sample collection, evidence exists (McQuaker et al., 1983) that it is stable for as long as 15 days, if the sample is stored at 4 C and sealed from the atmosphere. The pH was also measured in a sealed sample at the processing laboratory within $24-36$ hours of sample coilection. |  |
| d | Although the EPA (U.S. EPA, 1983) recommends a 6 -month holding time for these metals, this study required that all the metals be determined within 28 days, which ensured that significant changes would not occur and that data would be obtained in a timely manner. |  |



Figure 3-5. ELS-II data base development.

1987 using small craft equipped with a recording depth sounding instrument. Data from each lake were then analyzed using a computer program developed by the Adirondack Lake Survey Corporation that calculated the lake volume and residence time, and created a bathymetric map (J. Baker et al., 1990b). These data are contained in the validated and enhanced ELS-II data bases.

### 3.7.1 Raw Data Set (Data Set 1)

The collective data from all components of the sampling and analysis made up the raw data set. Field, processing laboratory, and analytical laboratory personnel sent the original data forms to the QA staff at the Environmental Monitoring Systems Laboratory (EMSL) in Las Vegas for review, in order to ensure that data were correct and consistent. Completed forms were then forwarded to Systems Applications, Inc. (SAI), where the data were entered into the data base. To ensure accurate data transfer from the data forms to computer files, the information was double-entered into computer files and subjected to automated checking procedures. The raw data set was used to screen the data for problems, perform exploratory analysis, and evaluate the need for any adjustments in the data analysis plan.

### 3.7.2 Verified Data Set (Data Set 2)

The objectives of the data verification process were to identify, correct, and flag raw data of questionable or unacceptable quality and to identify data that might need to be corrected during or after data validation. These objectives were met by reviewing the QC data measured and recorded at the sampling site, at the processing laboratory, and at the analytical laboratories. The verification process was automated as much as possible through applicable computer programs.

Verification began with receipt of the data forms from the field and processing laboratory. An auditor reviewed the forms for completeness, agreement between field and laboratory forms, and proper assignment of sample identification codes and data qualifier tags. Data anomalies were reported to the field base site and processing laboratory coordinators for corrective action. Data reporting errors were usually corrected on the data forms before the data were entered into the raw data set. During verification, each sample was evaluated individually and by analytical batch. Individual values that were identified as exceptions (as a result of cation/anion balances, specific conductance balance, or protolyte analysis) or that did not meet the acceptance criteria, were flagged in the data base. Suspect values were also identified by examining QC data (blank, duplicate, and audit samples) measured and recorded at the processing and analytical laboratories. In addition, data qualifier flags were added when QC samples did not meet acceptance criteria, or when sample analysis holding time requirements or instrument detection limits were not met. The output from these checks, along with original data and field notebooks, was used to evaluate the quality of the analytical results. Based on the evaluation of the
analytical results reported for QC samples, analytical laboratories were directed to confirm reported values or to reanalyze selected samples. If a value was identified as an exception to expected results, a flag was placed in the data base.

During the ELS-II data verification and validation activities, concern arose regarding several data quality issues. This concern, focusing primarily on spring data from the chloride, nitrate, sulfate, and ANC analyses, prompted a special data assessment, which took place after the completion of the official verified data base. This special assessment included an extensive examination of the raw data from both analytical laboratories for many parameters and resulted in the creation of a modified verified data set. The validated and enhanced data sets were then constructed from this modified verified data set. A complete description and listing of all changes made between the original verified data set and the modified verified data set are given in the ELS-II QA Report (Mitchell-Hall et al., 1989).

In the special data assessment, analytical data were reevaluated for fall sodium, spring anions ( Cl , $\mathrm{SO}_{4}{ }^{2-}, \mathrm{NO}_{3}{ }^{-}$), and two batches of spring ANC values. In addition to these changes, the data base was also updated to reflect sample switches and transcription errors, and missing values that had been inadvertently reported as zero were set back to missing values.

At laboratory 2, fall sodium was measured by both atomic absorption spectroscopy (AAS) and inductively coupled plasma emission spectroscopy (ICPES). The original verified data were based exclusively on the AAS data. Examination of the precision of the two methods for fall sodium audit samples showed that ICPES was much more precise than AAS in all but three batches of samples in the fall data. Thus, ICPES sodium data were substituted for AAS sodium data in the fall modified verified data base for all samples not in one of the three batches that showed better AAS audit precision (see Mitchell-Hall et al., 1989, p. 39 for more detail).

Problems with the spring chloride, nitrate, and sulfate data were recognized early in the data validation process. Several types of errors contributed to the problems with these anion data, including (1) dilution errors (sample values outside the range of calibration standards), (2) QC check solution vaiues exceeding contract-required detection limits, and (3) reporting errors. As a result, spring anion aliquots were analyzed twice and in some cases three times for sulfate, nitrate, and chloride. Analysis 1 was the original analysis in March and April of 1986. Analysis 2, a reanalysis, occurred in May and June of 1986. Finally, several samples ( $19 \%$ of the chloride data, and $11 \%$ of the sulfate and nitrate data) were selected for a third analysis, a year later, in May 1987.

Much of the effort of the special data assessment centered on deciding which analysis results to use in the modified data base for each batch of samples. Accuracy estimates (from audit samples) and precision estimates (from duplicate samples) were calculated for each of the spring sample batches for sulfate, nitrate, and chloride (see Section 4 for details on accuracy and precision estimates). In each of the sample batches, data from the analysis with the best accuracy and precision were used in the modified verified data base. For sulfate, among the 28 batches analyzed in the spring ELS-II survey, data from 11 of the batches were based on analysis 1 , data from 16 batches were based on analysis 2 , and
data from 1 batch was based on analysis 3. For nitrate, data from 12 batches were based on analysis 1 and data from 16 batches were based on analysis 2. For chloride, data from 8 batches were based on analysis 1, data from 17 batches were based on analysis 2, and data from 3 batches were based on analysis 3. Details of the three analyses, the analysis selection process, and within-batch accuracy and precision estimates are presented in Mitchell-Hall et al. (1989). The resulting overall estimates for spring precision and accuracy are discussed in Section 4.

In the original verified spring data base, 2 batches of samples (out of 28 ) had ANC values much higher than the carbonate alkalinity values calculated from both processing and analytical laboratory pH and DIC measurements. A detailed investigation indicated that the actual concentration of the acid titrant reported by the laboratory and used in calculating ANC in these two batches was less than onehalf the value that the laboratory reported. The ANC values for these batches were recalculated for the modified verified data base using a calculated concentration of the acid titrant and the data from the autotitrator (see Mitchell-Hall et al., 1989, pp. 35-38).

Other than the changes just described for fall sodium, spring anions, and the two batches of spring ANC samples, the number of changes made to the data base during the special data assessment was relatively small. For the variables analyzed in Sections 5 and 6, changes were made to routine/ duplicate lakewater data for two sodium values and one calcium value in the spring. In the summer, three DOC, seven nitrate, and five sulfate values were changed. Other than fixing one sample switch, none of the fall data presented in Sections 5 and 6 were changed by the special data assessment.

### 3.7.3 Validated Data Set (Data Set 3)

The purpose of the verification procedures was to evaluate data at the sample and batch level. Validation, on the other hand, was intended to compare samples across the population of lakes and across variables. The two main components of the validation process were (1) identification of outliers from regional distributions of chemistry and (2) evaluation of possible systematic errors in the measurement process. During validation, missing values and values with known errors, based on relationships with other variables, were identified and assigned validation flags. Values with validation flags were deleted in the creation of the enhanced data set. Only the major variables (shown in Table 3-3), whose cumulative distribution functions (CDF) are presented in Appendix A, were validated in ELS-II.

The creation of the seasonal validated data sets from the modified verified data sets involved (1) changing units from $\mathrm{mg} / \mathrm{L}$ to $\mu \mathrm{eq} / \mathrm{L}$ where appropriate, (2) creating two new variables, mean Secchi depth, and labile (inorganic) monomeric aluminum calculated as the difference between total monomeric aluminum and organic monomeric aluminum, (3) adding Adirondack Lake Survey Corporation physical data, (4) adding cluster and phase II weights, (5) rounding, and (6) concatenating the validation flags to the verification flags.

Table 3-3. Variables Validated in ELS-II

| Base neutralizing capacity | Monomeric (PCV) aluminum | Organic monomeric (PCV) aluminum |
| :--- | :--- | :--- |
| MIBK-extractable aluminum | Acid neutralizing capacity | Calcium |
| Chloride | Color | Specific conductance |
| Closed headspace DIC | Dissolved organic carbon | Iron |
| Total fluoride | Potassium | Magnesium |
| Manganese | Sodium | Ammonium |
| Nitrate | Air-equilibrated pH | Closed headspace pH |
| Total phosphorous | Sulfate | Silica |

### 3.7.4 Enhanced Data Set (Data Set 4)

The enhanced (final) data set for each seasonal chemistry survey was constructed from the validated data set by (1) deleting all values with a validation flag, (2) averaging all duplicate values (from field duplicate samples), (3) changing negative values (except for ANC and BNC) to zero, and (4) replacing all missing values with values calculated from regression models, so that population estimates could be made.

Calculation of population estimates and their confidence bounds is difficult if there are missing values in the data, thus missing values and deleted validation outliers were replaced in the enhanced data set if they were necessary for making population estimates (epilimnion samples from target lakes). When necessary, substitutions were determined, using a linear regression model, by calculating a predicted value based on observed relationships with other chemical variables. Of the more than 10,000 major chemical values in the ELS-II data base, 12 values were replaced in the spring data, 14 values in the summer data, and 4 in the fall data.

## SECTION 4 <br> DATA QUALITY ASSESSMENT

### 4.1 INTRODUCTION

Objectives of Phase II of the Eastern Lake Survey (ELS-II) were that the data be of high quality, have low and quantifiable analytical error, have known precision, and be representative of the state-of-the-art analysis attainable in high-volume contract analytical laboratories. The quality assurance and quality control (QA/QC) program of ELS-II was designed to maximize the utility of the collected data and to minimize the likelihood of erroneous chemical data. Data quality objectives (DQOs) were established and used as guidelines in maintaining data integrity during the sampling, analysis, and data collection and recording (Mitchell-Hall et al., 1989).

This section describes the analytical approach, results, and conclusions for each of the five aspects of data quality (completeness, comparability, representativeness, accuracy, and precision), plus detectability, applicable to ELS-II data. Detectability was analyzed because the low ionic strength of many of the ELS-II samples necessitated an evaluation of the background levels of analytes.

Representativeness, completeness, and comparability were considered important data quality goals in the development of the statistical sampling design of the ELS-II and the QA plan. As explained in Section 2, they were affected by uncontrollable events that influenced the number of samples actually collected and analyzed by the proper protocols during the course of the survey. Detectability, accuracy, laboratory bias, and precision were quantitatively assessed by using the analytical results from QC samples.

Analysis of the QC samples (blanks, natural audit samples, and field duplicates) provided two kinds of information for the assessment of data quality. Sampling and laboratory performance could be gauged against the DQOs established for precision, accuracy, and detectability. In addition, unforeseen effects of the collection and measurement process on analytical results could be quantified and their impact on data interpretation discerned. For example, the addition of background levels of an analyte during sample collection and subsequent handling can hinder the comparison and interpretation of data from lakes having naturally low levels of that analyte. Interlaboratory bias also can confound statistical comparisons of data, because true differences may not be distinguishable from differences resulting from systematic measurement errors at the different laboratories.

### 4.2 COMPLETENESS, COMPARABILITY, AND REPRESENTATIVENESS

Of the 147 lakes initially selected for field sampling, 145 ( $99 \%$ ) were actually visited in the field in all three seasons. One lake was not sampled in the fall due to inclement weather and the other lake was not sampled in the spring and fall because of access permission difficulties (see Section 2.4.1). Sample
weights were adjusted for these missing samples as described in Section 2 so that the ELS-II project objectives were not affected by the missing lake data. Of the 742 lakewater samples collected during ELS-II, 732 were analyzed for all planned chemical variables. Only 10 missing values were replaced during the creation of the enhanced data set.

All the ELS-II field crews and laboratory personnel used standardized protocols (Arent et al., 1988; Merritt and Sheppe, 1988; Kerfoot et al., 1988), which maximized internal comparability. Similarly, the use of these standard methods, combined with the quantitative results of QC sample analysis (MitcheilHall et al., 1989), allowed comparison with data from other studies, such as the ELS-I (Linthurst et al., 1986), WLS (Landers et al., 1987), and NSS (Kaufmann et al., 1988), and facilitated detailed process oriented studies on ELS-II special interest sites.

Representativeness can be viewed in a hierarchical manner from specific analyses to the general representativeness of the group of sample lakes. At the lowest level, representativeness refers to how well our chemical and physical analyses reflect the physical and chemical conditions at the sampling location in the lake. This aspect of data quality is discussed in Section 4.3 (detectability, accuracy, and precision).

At a higher level, the concept of representativeness refers to how well a water sample characterizes a specific lake. Representativeness in this context is influenced by the location of the sampling site, the specific location (or microhabitat) from which the sample was collected, and the local conditions at the time of collection. One goal of ELS-II is to assess the representativeness of the ELS-I fall index sample by taking multiple lake samples during the Fall Variability Study. At the population level, representativeness refers to whether the ELS-II sample lakes were representative of the target population as a whole. The probability sampling design employed by ELS-II makes it extremely unlikely that substantial bias might result from seriously undersampling any particular geographic area or class of lakes defined as part of the target population. Recall that in the ELS-II, specific populations of lakes were deliberately not sampled (high ANC or shallow lakes; see Section 2.3.1).

### 4.3 DETECTABILITY, ACCURACY, PRECISION, AND LABORATORY BIAS

Indices of detectability, accuracy, and precision can be calculated at both the method level and the system level. Indices of analytical error are calculated from laboratory blank, audit, and duplicate samples and refer to the quality of the analytical methodology. On the other hand, indices of sampling error are determined from blank, audit and duplicate samples processed in the field, and they apply to detectability, accuracy, and precision of the whole sampling process (sample collection, handling, processing, and shipping, as well as analytical methodology). This section discusses only the sampling error indices, because they are more inclusive of the total variability involved in collecting the data. Also, the discussion is restricted to the 12 major variables on which this report concentrates (ANC, $\mathrm{pH}, \mathrm{SO}_{4}{ }^{2-}$, $\mathrm{NO}_{3}{ }^{-}, \mathrm{Cl}$, base cations, DOC, and aluminum). A more complete description of the ELS-II QA process,

QA data, and information on all ELS-II variables can be found in Mitchell-Hall et al. (1989). This section first explains how the indices were determined and concludes with a variable-by-variable assessment of detectablilty, accuracy, precision, and laboratory bias.

### 4.3.1 Detectability

Background levels of analyte added during the analysis, collection, or handling of samples were estimated by computing a system decision limit (SDL). The SDL represents the lowest measured sample value that can be distinguished from a blank sample or from background noise. In ELS-II, the SDL was based on the mean and standard deviation of field blanks. Field blanks were reagent-grade deionized water put into Cubitainers and syringes in the field and treated as samples throughout shipping, processing, and analysis. SDLs were calculated as:

$$
\begin{equation*}
\text { SDL }=\text { Mean }_{\text {blanks }}+1.65\left(\text { standard deviation }_{\text {bianks }}\right) \tag{9}
\end{equation*}
$$

Thus, the SDL corresponds to the 95th percentile of the blank measurements (assumes a normal distribution) and there is a 0.05 probability of concluding that an analyte is present when in fact it is not. SDLs for the major ELS-II chemical variables are listed in Table 4-1.

System decision limits are important in the interpretation of ELS-II chemical distributions. Population estimates of lake resources with concentrations at or below the SDL should be interpreted with caution. There can be little confidence that values reported at these very low analyte levels are significantly different from zero. It is likely that variations in the distributions of observed values less than the SDL are artifacts of sample collection, handling, and analysis. For the same reason, groups of lakes characterized by analyte levels below the SDL should not be compared.

### 4.3.2 Accuracy

Accuracy is defined as the closeness of a measurement to a true or known value. Typically, the EPA has evaluated accuracy by calculating a percent difference from a known value. Although this approach to data quality has proven effective for studies of a single analyte over a limited range of concentrations, it is not as effective when evaluating multianalyte survey data with a wide range of concentration. In ELS-II, the approach for assessing accuracy was different than in previous NSWS surveys (Mitchell-Hall et al., 1989). Accuracy was assessed by comparing the distribution of field natural audit samples to a target value. The target value was the median of all of the available natural audit sample data (including ELS-II, National Stream Survey, and Spring Variability Pilot Study data). Two natural audit samples were analyzed repeatedly in the ELS-II: lake water from Big Moose Lake (an acidic lake;

Table 4-1. System Decision Limits (Mean + 1.65 Standard Deviation of Field Blanks) for Major ELS-II Analytes

| Variable | Seasonal Survey ${ }^{\text {a }}$ |  |  |
| :---: | :---: | :---: | :---: |
|  | Spring | Summer | Fall |
| $\mathrm{Al}_{\text {MIBK }}{ }^{\text {b }}(\mu \mathrm{g} / \mathrm{L})$ | 1 | 12 | 8 |
| $\mathrm{Al}_{\mathrm{m}}{ }^{\text {c }}(\mu \mathrm{g} / \mathrm{L})$ | 16 | 16 | 17 |
| $\mathrm{Ca}^{2+}(\mu \mathrm{eq} / \mathrm{L})$ | 1.2 | 1.4 | 0.7 |
| $\mathrm{Cl}^{-}(\mu \mathrm{eq} / \mathrm{L})$ | 8.0 | 2.2 | 0.8 |
| DOC (mg/L) | 0.6 | 0.4 | 0.3 |
| $\mathrm{K}^{+}(\mu \mathrm{eq} / \mathrm{L})$ | 0.5 | 0.2 | 0.2 |
| $\mathrm{Mg}^{2+}$ ( $\mu \mathrm{eq} / \mathrm{L}$ ) | 0.6 | 1.1 | 0.2 |
| $\mathrm{Na}^{+}(\mu \mathrm{eq} / \mathrm{L})$ | 3.1 | 0.4 | 2.8 |
| $\mathrm{NO}_{3}{ }^{-}(\mu \mathrm{eq} / \mathrm{L})$ | 0.5 | 0.9 | 0.5 |
| $\mathrm{SO}_{4}{ }^{2-}(\mu \mathrm{eq} / \mathrm{L})$ | 1.4 | 1.0 | 0.8 |

a 29 blank samples were analyzed in spring, 17 in summer, and 26 in fall.
${ }^{\mathrm{b}} \mathrm{Al}_{\text {MIBK }}=$ MIBK extractable aluminum.
${ }^{c} \mathrm{Al}_{\mathrm{m}}=\mathrm{PCV}$ reactive (total monomeric) aluminum.

ANC $=-3 \mu \mathrm{eq} / \mathrm{L}$ ) and lake water from Seventh Lake (a circumneutral lake; ANC $=155 \mu \mathrm{eq} / \mathrm{L}$ ). Field natural audit samples were prepared at a support laboratory and processed in the processing laboratory as routine samples. Natural audit samples were taken from the same large containers of lake water throughout all the ELS-II seasonal surveys. Target values and the mean $\pm$ standard deviation of natural audit sample data in each season are given in Table 4-2 for the major ELS-II chemical variables.

### 4.3.3 Precision

Analysis of field duplicate pairs provided an estimate of overall sample precision within a batch, including the effects of sample collection, processing, and analysis. Repeated measurements of natural audit samples provided estimates of among-batch precision within a laboratory, and when pooled across the two laboratories, as they were in summer, this included the effects of interlaboratory bias. A batch refers to a batch of samples grouped together at the processing laboratory and kept together throughout the analytical process with the same batch identifier.

For each variable, within-batch precision was estimated as a pooled standard deviation based on the means and variances of the duplicate sample pairs. The individual variances of each sample pair were summed to calculate a pooled variance, and a pooled standard deviation was calculated as the square root of the pooled variance after dividing by the sample size. The percent relative standard deviation (\%RSD) was then calculated as:

$$
\% \text { RSD }=\frac{\text { pooled standard deviation }}{\text { grand mean of duplicate samples }} * 100
$$

where the grand mean equals the average of all of the sample pair means. Grand means and \%RSD for within-batch precision are given in Table 4-3 for the major ELS-II chemical variables. Because of the dilute nature of the waters sampled during the ELS-II, the single \%RSD estimate of precision for the entire range of analyte values should be interpreted with caution. If many of the sample pairs have very low concentrations, the \%RSD can be high, even though the actual variability may be small. For example, the \%RSD for nitrate in the summer seasonal survey was $28 \%$ (Table 4-3). The grand mean, however, was $1 \mu \mathrm{eq} / \mathrm{L}$, so the pooled standard deviation was only $0.28 \mu \mathrm{eq} / \mathrm{L}$. Therefore, it is important to consider the grand mean as well as the \%RSD when interpreting these data.

The \%RSD for among-batch precision in Table 4-4 was calculated from the data in Table 4-2 by dividing the standard deviation of the repeated analyses of the natural audit samples by the mean value. \%RSD for within-batch (from Table 4-3) and among-batch data precision are compared in Table 4-4. Summer data for the among-batch \%RSDs (natural audit samples) were pooled from data from both analytical laboratories and thus also include the effects of interlaboratory bias.

Table 4-2. Mean $\pm$ One Standard Deviation of Seventh Lake (SL) and Big Moose Lake (BML) Field Natural Audits for Major ELS-II Analytes ${ }^{\text {a }}$

| Variable | Audit | Target ${ }^{\text {b }}$ Value | Seasonal Survey |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  | Spring | Summer | Fall |
| $\mathrm{Al}_{\text {MIBK }}$ | SL | 16.3 | $20.5 \pm 7.4$ | $8.9 \pm 9.2$ | $13.2 \pm 4.3$ |
|  | BML | 166 | $142 \pm 30$ | $147 \pm 54$ | $137 \pm 17$ |
| $A l_{m}$ | SL | 21.2 | $22.5 \pm 5.0$ | $20.9 \pm 5.8$ | $24.6 \pm 3.4$ |
|  | BML | 193 | $200 \pm 13$ | $178 \pm 20$ | $196 \pm 8.1$ |
| ANC | SL | 155 | $150 \pm 18$ | $160 \pm 21$ | $159 \pm 9$ |
|  | BML | -3 | $-4 \pm 4$ | $-3 \pm 4$ | $-2 \pm 2$ |
| $\mathrm{Ca}^{2+}$ | SL | 252 | $245 \pm 5.8$ | $249 \pm 5.7$ | $258 \pm 4.7$ |
|  | BML | 95.9 | $96.2 \pm 2.0$ | $95.4 \pm 1.8$ | $98.2 \pm 2.0$ |
| $\mathrm{Cl}^{-}$ | SL | 82.9 | $89.6 \pm 31.1$ | $75.5 \pm 8.3$ | $82.2 \pm 5.1$ |
|  | BML | 11.6 | $11.5 \pm 2.2$ | $11.1 \pm 1.0$ | $11.6 \pm 0.2$ |
| DOC | SL | 3.6 | $3.5 \pm 0.3$ | $3.7 \pm 0.1$ | $3.5 \pm 0.1$ |
|  | BML | 3.6 | $3.5 \pm 0.2$ | $3.5 \pm 0.2$ | $3.4 \pm 0.2$ |
| $\mathrm{K}^{+}$ | SL | 12.5 | $12.6 \pm 0.4$ | $12.7 \pm 0.5$ | $11.9 \pm 1.5$ |
|  | BML | 10.5 | $10.4 \pm 0.4$ | $10.6 \pm 0.4$ | $9.7 \pm 1.1$ |
| $\mathrm{Mg}^{2+}$ | SL | 67.8 | $67.8 \pm 1.3$ | $66.5 \pm 1.9$ | $67.8 \pm 1.0$ |
|  | BML | 26.8 | $26.8 \pm 0.8$ | $26.2 \pm 0.7$ | $27.3 \pm 1.1$ |
| $\mathrm{Na}^{+}$ | SL | 94.7 | $93.0 \pm 3.6$ | $96.7 \pm 10.4$ | $95.8 \pm 2.9$ |
|  | BML | 26.4 | $26.4 \pm 1.7$ | $26.1 \pm 1.0$ | $27.1 \pm 1.8$ |
| $\mathrm{NO}_{3}{ }^{-}$ | SL | 20.5 | $20.3 \pm 1.7$ | $20.8 \pm 0.6$ | $20.0 \pm 1.2$ |
|  | BML | 19.7 | $17.5 \pm 2.2$ | $19.6 \pm 0.5$ | $19.4 \pm 0.5$ |
| pH | SL | 6.9 | $6.9 \pm 0.03$ | $6.7 \pm 0.09$ | $6.9 \pm 0.04$ |
|  | BML | 5.1 | $5.2 \pm 0.04$ | $5.1 \pm 0.06$ | $5.1 \pm 0.03$ |
| $\mathrm{SO}_{4}{ }^{2-}$ | SL | 143 | $142 \pm 6.7$ | $143 \pm 9.7$ | $141 \pm 19$ |
|  | BML | 132 | $127 \pm 12$ | $135 \pm 10$ | $132 \pm 4.7$ |

[^3]Table 4-3. Grand Mean $\left(\bar{X}_{\mathrm{G}}\right)$ and Percent Relative Standard Deviation (\% RSD) of Field Duplicate Pairs for Major ELS-II Analytes ${ }^{\text {a }}$

| Variable | Spring $\mathrm{n}=26$ |  | Summer $\mathrm{n}=17$ |  | Fall $\mathrm{n}=29$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $\overline{\bar{x}}_{G}$ | \% RSD | $\overline{\bar{x}}_{G}$ | \%RSD | $\overline{\bar{X}}_{G}$ | \%RSD |
| $\mathrm{Al}_{\text {MIBK }}$ | 43 | 56 | 13 | 71 | 34 | 11 |
| $A l_{m}$ | 65 | 4.5 | 41 | 6.6 | 63 | 4.5 |
| ANC | 52 | 8.8 | 132 | 4.7 | 94 | 5.4 |
| $\mathrm{Ca}^{2+}$ | 121 | 2.0 | 173 | 1.8 | 149 | 1.1 |
| Cl | 159 | 20 | 137 | 25 | 115 | 4.4 |
| DOC | 3.4 | 11 | 4.2 | 9.6 | 4.6 | 6.2 |
| $\mathrm{K}^{+}$ | 11.4 | 5.4 | 11.0 | 2.8 | 10.7 | 12 |
| $\mathrm{Mg}^{2+}$ | 57.8 | 1.7 | 75.1 | 3.5 | 52.1 | 1.1 |
| $\mathrm{Na}^{+}$ | 149 | 2.8 | 138 | 4.5 | 134 | 1.2 |
| $\mathrm{NO}_{3}{ }^{-}$ | 7.2 | 6.7 | 1.0 | 28 | 2.5 | 11.6 |
| $\mathrm{pH}{ }^{\text {b }}$ | $5.9 \pm 0.03$ |  | $6.3 \pm 0.1$ |  | $6.0 \pm 0.02$ |  |
| $\mathrm{SO}_{4}{ }^{\text {-- }}$ | 123 | 3.0 | 117 | 2.0 | 108 | 2.4 |

[^4]Table 4-4. Within-Batch and Among-Batch Precision ${ }^{\text {a }}$ (\% RSD) for Major ELS-II Analytes

| Variable | Spring |  |  | Summer |  |  | Fall |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Within Batch | Among Batch |  | Within Batch | Among Batch |  | Within Batch | Among Batch |  |
|  |  | SL | BML |  | SL | BML |  | SL | BML |
| $\mathrm{Al}_{\text {M1BK }}$ | 56 | 36 | 21 | 71 | 103 | 12 | 11 | 33 | 12 |
| $\mathrm{Al}_{\mathrm{m}}$ | 4.5 | 22 | 6.5 | 6.6 | 28 | 11 | 4.5 | 14 | 4.1 |
| ANC | 8.8 | 12 | 100 | 4.7 | 13 | 133 | 5.4 | 5.6 | 100 |
| $\mathrm{Ca}^{2+}$ | 2.0 | 2.4 | 2.1 | 1.8 | 2.3 | 1.8 | 1.1 | 1.8 | 2.0 |
| $\mathrm{Cl}^{-}$ | 20 | 35 | 19 | 25 | 11 | 9 | 4.4 | 6.2 | 1.7 |
| DOC | 11 | 8.6 | 5.7 | 9.6 | 2.7 | 5.7 | 6.2 | 2.9 | 5.9 |
| $\mathrm{K}^{+}$ | 5.4 | 3.2 | 3.8 | 2.8 | 3.9 | 3.8 | 12 | 13 | 11 |
| $\mathrm{Mg}^{2+}$ | 1.7 | 1.9 | 3.0 | 3.5 | 2.9 | 2.7 | 1.1 | 1.4 | 4.0 |
| $\mathrm{Na}^{+}$ | 2.8 | 3.9 | 6.4 | 4.5 | 11 | 3.8 | 1.2 | 3.0 | 6.6 |
| $\mathrm{NO}_{3}{ }^{-}$ | 6.7 | 8.4 | 13 | 28 | 2.9 | 2.6 | 12 | 6.1 | 2.6 |
| $\mathrm{pH}^{\text {b }}$ | 0.03 | 0.03 | 0.04 | 0.10 | 0.09 | 0.06 | 0.02 | 0.04 | 0.03 |
| $\mathrm{SO}_{4}{ }^{2-}$ | 3.0 | 4.7 | 9.4 | 2.0 | 6.8 | 7.4 | 2.4 | 13 | 3.6 |

[^5]
### 4.3.4 Laboratory Bias

In the ELS-II, two analytical laboratories were used to analyze the data. All the spring data were analyzed by laboratory 1 and all the fall data were analyzed by laboratory 2. In the summer, both laboratories were involved in sample analysis. Thus, if significant analytical bias exists between the laboratories, apparent seasonal differences between samples could simply be the result of interiaboratory bias rather than actual differences. Laboratory bias can be evaluated three different ways. One way is to compare split samples that were analyzed by both laboratories during the summer seasonal survey. Split differences are summarized in Table 4-5, and plots of laboratory 1 values versus laboratory 2 values are shown in Figures 4-1 and 4-2 for select variables. Secondly, laboratory bias may also be examined by comparing mean natural audit sample values in the spring (all laboratory 1) with those in the fall (all laboratory 2) (Table 4-2). A third way to assess laboratory bias is to compare the among-batch precision estimates made in the summer with those made in the fall and spring. Spring and fall \%RSD values reflect only the precision of the one laboratory that did the analyses in that season. The summer data are pooled across laboratories and laboratory bias is incorporated into the \%RSD. If the two laboratories are measuring substantially different values in the summer data for the audit sample material, then this would be reflected in an elevated \%RSD relative to spring and fall \%RSDs.

### 4.3.5 Variable by Variable Summaries

### 4.3.5.1 ANC and $\mathbf{p H}$

For obvious reasons, detectability was not assessed for ANC (it can be negative) and pH . In this section, pH refers to the closed-headspace (syringe sample) pH measured at the processing laboratory. Closed-headspace pH is also the pH variable used in this report to make population estimates of lakewater pH conditions. In terms of accuracy, mean ANC values of the natural audit samples were within 5 $\mu \mathrm{eq} / \mathrm{L}$ of the target value in each of the seasonal surveys for the high ANC (Seventh Lake) audit sample. In the acidic audit sample (Big Moose Lake), mean values were within $1 \mu \mathrm{eq} / \mathrm{L}$ of the target value (Table $4-2)$. Mean audit sample values for pH were within 0.1 pH unit of target values, except for the summer Seventh Lake audit sample, which was within 0.2 pH unit.

Duplicate sample precision (\%RSD) for ANC ranged from $4 \%$ to $7 \%$ in the three seasonal surveys (Table 4-3). Precision for the higher ANC natural audit sample ranged from $5 \%$ to $13 \%$. Precision for the acidic audit sample was about $100 \%$, because the mean values were only -2 to $-4 \mu \mathrm{eq} / \mathrm{L}$. Pooled standard deviations in the acidic audit samples, however, were very low ( $2-4 \mu \mathrm{eq} / \mathrm{L}$; Table 4-2). Pooled standard deviations for both audit samples and duplicate samples were $<0.1 \mathrm{pH}$ unit for closed-system (processing laboratory) pH . Precision for pH was not expressed as \%RSD because of its logarithmic nature.

Table 4-5. Differences between Summer Split Samples Analyzed at the Two Analytical Laboratories

|  | All data, $\mathrm{n}=25$ <br> Lab 1-Lab 2 <br> Median |  |  |  | $\mathrm{Q}_{3}$ |
| :--- | :---: | :---: | :---: | :---: | :---: |


|  | ANC $\leq 50 \mu e q / L, n=11$ <br> Lab 1-Lab 2 <br> Median |  |  |  |  |
| :--- | :---: | :---: | :---: | :---: | :---: |
| Variable | Minimum | $Q_{1}$ | $Q_{3}$ | Maximum |  |
| ANC | -11 | -3 | 0 | 3 | 10 |
| $\mathrm{SO}_{4}{ }^{2-}$ | -33 | -28 | -13 | 1 | 8 |
| $\mathrm{NO}_{3}{ }^{-}$ | -0.9 | 0.1 | 0.5 | 0.8 | 1.5 |
| $\mathrm{C}_{\mathrm{B}}{ }^{\text {a }}$ | -11 | -6 | -2 | 6 | 18 |
| DOC | -0.9 | -0.2 | 0.1 | 0.3 | 0.4 |

[^6]

Figure 4-1. Comparison of laboratory 1 and laboratory 2 values for replicate samples analyzed during the summer seasonal survey: (a) ANC, (b) sultate, (c) nitrate, (d) DOC, and (e) chloride. Taken from Mitchell-Hall et al. (1989), Appendix E.


Figure 4-2. Comparison of laboratory 1 and laboratory 2 values for replicate samples analyzed during the summer seasonal survey: (a) sodium, (b) potassium, (c) calcium, and (d) magnesium. Taken from Mitchell-Hall et al. (1989), Appendix F.

There was no evidence of laboratory bias for ANC in the acidic audit sample or in low ANC $\leqslant 50$ $\mu \mathrm{eq} / \mathrm{L}$ ) summer replicate (split) samples (Figure 4-1; Table 4-5). At higher ANC levels, there was some indication of laboratory bias in the summer split samples. Overall, the interquartile range for the difference between laboratory split samples was $19 \mu \mathrm{eq} / \mathrm{L}$ (laboratory 2 ANC values were usually higher than laboratory 1 values). Also, there was a $9 \mu \mathrm{eq} / \mathrm{L}$ difference between the Seventh Lake audit sample mean concentrations for fall and spring. The pH values used to make population estimates in this report are those measured at the processing laboratory. As there was only one processing laboratory, laboratory bias is not an issue for the pH measurements presented in this report.

### 4.3.5.2 Sulfate

The system decision limit for sulfate was $<1.5 \mu \mathrm{eq} / \mathrm{L}$ for all the seasonal surveys, and thus background contamination or detectability should cause no problems for sulfate data interpretation in ELS-II (Table 4-1). Seasonal mean sulfate audit sample values were always within $4 \%$ of the target value (Table 4-2). Sample duplicate (within-batch) precision was < 3\% (\%RSD) in all the seasonal surveys. Among-batch precision was $<10 \%$ in all the audit sample data except for the fall Seventh Lake data, which had a \%RSD of $13 \%$ (Table 4-4). The relatively high variability in this seasonal audit sample appears to be due to two outliers rather than to systematic imprecision. Laboratory bias does not appear to be a problem for sulfate, based on laboratory split samples (Figure 4-1) and a comparison of seasonal audit sample means.

### 4.3.5.3 Nitrate

The system decision limit for nitrate ranged from 0.5 to $0.9 \mu \mathrm{eq} / \mathrm{L}$ in the three seasonal surveys (Table 4-1). Because many of the ELS-II samples have low nitrate, these numbers should be kept in mind when interpreting the data. Seasonal mean nitrate audit sample values were usually within $3 \%$ of the target value, except for one seasonal audit sample that was within $10 \%$ of the target value (Table $4-2)$. Nitrate concentrations were relatively high ( $20 \mu \mathrm{eq} / \mathrm{L}$ ) in the audit samples and among-batch precision ranged from $2 \%$ to $13 \%$. Sample duplicate precision had fairly high \%RSD ( $7 \%$ to $28 \%$ ), but this was mainly due to the low nitrate concentrations in most of the sample pairs (grand means ranged from 1 to $7 \mu \mathrm{eq} / \mathrm{L}$ ). Pooled standard deviations in the sample pairs ranged from 0.3 to $0.5 \mu \mathrm{eq} / \mathrm{L}$ (Table $4-3$ ). There was poor correlation between the summer laboratory split samples (Figure 4-1), probably due to the low nitrate concentrations in the split samples and not to laboratory bias. Most of the split samples had concentrations below the SDL for nitrate ( $0.9 \mu \mathrm{eq} / \mathrm{L}$ ) and thus were not significantly different from deionized water blank samples. A seasonal comparison of the audit samples shows only smail ( $<2 \mu \mathrm{eq} / \mathrm{L}$ ) differences between means and \%RSDs (Table 4-4). There are, however, two data points on the laboratory split plots (Figure 4-1b) that show relatively high nitrate in laboratory 1 measurements ( $9 \mu \mathrm{eq} / \mathrm{L}$ ), but almost no nitrate ( $<1 \mu \mathrm{eq} / \mathrm{L}$ ) in laboratory 2 measurements.

### 4.3.5.4 Chloride

There were data quality problems with chloride in analyses performed at laboratory 1. Precision and detectability at laboratory 1 greatly exceeded the DQOs. We recommend not using any of the chloride values from laboratory 1 and they have not been used in this report. Thus ELS-II population estimates were not made for summer or spring chloride distributions. These data quality problems can be seen for spring chloride detectability ( $S D L=8 \mu \mathrm{eq} / \mathrm{L}$ ), and precision (withinbatch $\%$ RSD $=20 \%$; among-batch $\%$ RSD $=19-35 \%$ ). Data quality does not appear as poor in the summer because only about half the data were analyzed at laboratory 1 . When the summer data are separated by laboratory, laboratory 1 data are still poor, whereas laboratory 2 summer chloride data are comparable to the fall results (Mitchell-Hall et al., 1989). There do not appear to be any chioride data quality problems in the laboratory 2 fall and summer data (SDL $<1 \mu \mathrm{eq} / \mathrm{L} ; \% \mathrm{RSD}=2-6 \%$ ).

### 4.3.5.5 Dissolved Organic Carbon

The SDL for DOC ranged from 0.3 to $0.6 \mathrm{mg} / \mathrm{L}$ over the three seasonal surveys. Seasonal mean audit sample DOC concentrations were within $0.2 \mathrm{mg} / \mathrm{L}$ of the target values (Table 4-2). Duplicate sample precision ranges from 6 to $11 \%$ RSD and audit sample precision ranged from 3 to $9 \%$ RSD. In terms of laboratory bias, the summer split samples showed close agreement for DOC values $<5 \mathrm{mg} / \mathrm{L}$, but there was some scatter (but no bias) at higher DOC (Figure 4-1). Summer split sample differences between the two laboratories were typically (interquartile range) $<0.4 \mathrm{mg} / \mathrm{L}$. Very similar seasonal audit sample means (within $0.2 \mathrm{mg} / \mathrm{L}$ ) also indicate a lack of laboratory bias for DOC $<5 \mathrm{mg} / \mathrm{L}$.

## 4.3-5.6 Base Cations

The base cations $\left(\mathrm{Na}^{+}, \mathrm{K}^{+}, \mathrm{Mg}^{2+}\right.$, and $\mathrm{Ca}^{2+}$ ) all had SDLs $<1.5 \mu \mathrm{eq} / \mathrm{L}$, except for sodium in the spring ( $3 \mu \mathrm{eq} / \mathrm{L}$ ). Base cation seasonal audit sample mean concentrations were usually within $3 \%$ and always within $8 \%$ of the target values (Table 4-2). Base cation sample duplicate (within-batch) precision and natural audit sample (among-batch) precision almost always had \%RSDs < $5 \%$ Only $\mathrm{K}^{+}$in the fall (11-13\%) and the Seventh Lake $\mathrm{Na}^{+}$audit sample in the summer (11\%) had a \%RSD > $10 \%$ (Table 4-4). The imprecision in the summer $\mathrm{Na}^{+}$data, however, is due to a single outlying value rather than to a general scatter in the data. Summer split samples show very good agreement between the two laboratories for all the base cations (Figure 4-2). Seasonal mean audit sample concentrations were within $3 \mu \mathrm{eq} / \mathrm{L}$ of each other for all base cations except the Seventh Lake calcium audit sample, which had a fall/spring (laboratory \#1/laboratory \#2) difference of $13 \mu \mathrm{eq} / \mathrm{L}^{(t a r g e t ~} \mathrm{Ca}^{2+}=252 \mu \mathrm{eq} / \mathrm{L}$ ). Sum of base cation differences in the summer split samples between the two laboratories were typically < 11 $\mu \mathrm{eq} / \mathrm{L}[6 \mu \mathrm{eq} / \mathrm{L}$ in low ANC $(\leqslant 50 \mu \mathrm{eq} / \mathrm{L})$ systems].

### 4.3.5.7 Aluminum

MIBK-extractable aluminum ( $\mathrm{AI}_{\text {MIBK }}$ ) was measured in ELS-I, therefore it was also measured in ELS-II for comparison purposes. PCV-reactive aluminum ( $\mathrm{Al}_{\mathrm{m}}$ ), another measure of total monomeric aluminum, was also measured in ELS-II and is used to calculate inorganic monomeric aluminum by subtracting of organic monomeric aluminum (measured by PCV colorimetry after passing the sample through a strong cation exchange column). The SDL of both aluminum species was usually between 10 and $20 \mu \mathrm{~g} / \mathrm{L}$ (Table 4-1), which should be kept in mind when interpreting the aluminum data because many ELS-II samples have very low aluminum concentrations. It is uncertain whether samples with aluminum below the SDL really contain any aluminum at all.

In interpreting accuracy, precision, and laboratory bias for the aluminum variables, it is important to remember that many duplicate sample pairs and the Seventh Lake natural audit sample were very close to or below the SDL and would be expected to be somewhat imprecise because the magnitude of the signal is not much greater than the noise. Thus the Seventh Lake audit samples ( $\mathrm{Al}_{\mathrm{m}}=21 \mu \mathrm{~g} / \mathrm{L}$, $A I_{\text {MIBK }}=16 \mu \mathrm{~g} / \mathrm{L}$ ) had \%RSDs ranging from $14 \%$ to $103 \%$ for the aluminum variables. In the Big Moose Lake audit sample ( $\mathrm{Al} \mathrm{I}_{\mathrm{m}}=193 \mu \mathrm{~g} / \mathrm{L} ; \mathrm{Al}_{\mathrm{M} B \mathrm{BK}}=166 \mu \mathrm{~g} / \mathrm{L}$ ), $\mathrm{Al}_{\mathrm{m}}$ was more precise $(\% \mathrm{RSD}=4-11 \%$ ) than $\mathrm{Al}_{\text {MIBK }}(12-21 \%)$. A similar pattern of precision was seen in the field duplicate sample pairs (Table 4-3). For $\mathrm{Al}_{\mathrm{m}}$, Big Moose Lake mean audit samples were within $8 \%$ of the target value in all seasons, whereas $\mathrm{Al}_{\text {MIBK }}$ means were from $11 \%$ to $17 \%$ lower than the target value. Overall, $\mathrm{Al}_{\mathrm{m}}$ data seem to be of better quality than $\mathrm{Al}_{\text {MIBK }}$ data. In this report, only the $\mathrm{Al}_{\text {MIBK }}$ data are used to make between-year comparisons (fall 1984/1986), because Al $_{\mathrm{m}}$ was not measured in the ELS-I fall 1984 survey.

### 4.5 CONCLUSIONS

In a final assessment, data quality can be considered good if it meets the initially established data quality objectives (DQO). A detailed discussion of the ELS-II QA data in comparison to the ELS-II DQOs is given in the ELS-II QA report (Mitchell-Hall et al., 1989). In brief, Mitchell-Hall et al. found that data quality for a majority of analytes was within or very close to the DQOs. In terms of the 12 analytes focused on in this report, only chloride and $\mathrm{Al}_{\text {MIBK }}$ were problem variables. Rather than concentrating on DQOs, we have tried in this section to present the QA data in relation to the degree of precision, bias, and background contamination, in order to aid in data interpretation. In short, how do the observed data precision, detectability, and laboratory bias affect the conclusions that can be drawn from the data? Our overall conclusions are:

1. For $\mathrm{ANC}, \mathrm{pH}, \mathrm{PCV}$-aluminum, base cations, and DOC , the data are of sufficient quality to make reliable population estimates of seasonal lakewater chemistry.
2. Based on the sample QA data, sulfate and nitrate data appear to be of sufficient quality to make reliable population estimates. The quality of sulfate and nitrate data from laboratory 1 (spring and
half of summer), however, has an element of uncertainty due to the two reanalyses and best batch selection processes that occurred during the special data assessment.
3. Chloride data quality from laboratory 1 were suspect and we believe that the data cannot be used to make population estimates of temporal variability. Thus, spring and summer population estimates were not made for chioride chemistry. No problems were found in chloride data from laboratory 2 (all fall data) that would confound data interpretation. Thus, chloride population estimates were made for the fall seasonal data and variability survey.
4. The poor quality of the laboratory 1 chloride data renders the typical QA procedures for betweenvariable assessments (charge balance, calculated versus measured conductivity) meaningless. Chloride is present in significant concentrations relative to the total anion charge in most lakes, so that there were poor charge balances and conductivity checks in much of the laboratory 1 data. Charge balance and conductivity checks for laboratory 2 data, however, were good (see MitchellHall et al., 1989).
5. Due to the low lakewater concentrations of nitrate and aluminum, the system decision limit (SDL) must be considered when interpreting these data. The SDL for aluminum variables was typically between 10 and $20 \mu \mathrm{~g} / \mathrm{L}$; for nitrate, the SDL was between 0.5 and $1 \mu \mathrm{eq} / \mathrm{L}$. Lakewater concentrations below these SDLs are not significantly different from field blank concentrations at a $95 \%$ confidence level.
6. MIBK-extractable aluminum is less precise and accurate than the other major ELS-II variables analyzed in this section (\%RSD 10-20\%).
7. Any assessment of temporal variability must take into account the variability inherent in sampling and measuring the system. Temporal changes must be interpreted in light of the sampling variabilities reported in this section.

## SECTION 5

## RESULTS - TEMPORAL VARIABILITY IN THE NORTHEAST

### 5.1 OVERVIEW

This section presents the effects of temporal variability on lakewater chemistry in the northeastern United States. Temporal variability was examined in terms of population estimates of the distribution of chemical variables across the target lake population and the magnitude of observed chemical changes. This section focuses on those variables of primary interest in acidic deposition research: ANC, pH , sulfate, nitrate, base cations, DOC, and aluminum. Information on other variables is presented in Appendix A.

### 5.1.1 Components of Temporal Variability

Three components of temporal variability were examined in Phase II of the Eastern Lake Survey (ELS-II): between-year, within-season, and among-season temporal variability. Between-year variability was examined by comparing the fall seasonal survey data collected in 1986 during the ELS-ll with fall data from the same lakes collected in 1984 during ELS-I. Within-season variability was assessed using data from the Fall Variability Study. In the Fall Variability Study, lakes were sampled three times during the fall index period at three independently selected locations on the lake (selected using a consistent protocol). Among-season variability was determined by comparing the results of the ELS-II spring, summer, and fall seasonal surveys undertaken in 1986.

### 5.1.2 Cumulative Distribution Functions

One of the most useful ways to present results from ELS-II, as was the case in other components of the National Surface Water Survey (NSWS), is the cumulative distribution function (CDF). CDFs show the distribution of the study variable in the target population and are used extensively in this report. Appendix A presents CDFs for many of the ELS-II variables in each of the seasonal surveys. Overlapping CDFs are used in this section of the report to show the effects of the different temporal components on the variables in question.

A CDF (illustrated in Figure 5-1) is a frequency distribution, interpreted as the proportion of ELS-II target lakes having values of the attribute $X$ less than or equal to the value $x$. The cumulative proportion, $F(x)$, is calculated as described in Section 2.4.2 (equation 6). To read the example CDF (Figure 5-1), pick a value, $x$, for the variable of interest along the horizontal axis (ANC in this example) and read the $y$-axis value of the curve, $F(x)$, at this value. $F(x)$ is the estimated cumulative proportion of lakes in the


Figure 5-1. Hypothetical example of the type of cumulative distribution function plot used in the ELS-II report.
population with an ANC equal to or less than the selected value $x$. By overlaying $F(x)$ lines from different populations on the same CDF, it is easy to make population comparisons across the distribution. In this section we use overlying CDFs to compare variable distributions in different seasons, years, and sample visits within season.

In addition to CDFs, we also present scatter plots of the 1984/1986 and spring/fall data. Scatter plots are useful in that they show how each individual lake varied between times, rather than how the population changed, as is the case in the CDFs. The scatter plots, however, do not reflect the sample weights and may give a misleading indication of how the population as a whole was changing. A statistical analysis of 1984/1986 and spring/tall population differences using chi-square analyses is presented in Appendix $C$.

### 5.1.3 Characteristics of the ELS-II Target Population

In the ELS-II, 145 sample lakes represented 3,993 lakes in the target population with a total lake area of $3,549 \mathrm{~km}^{2}$. Lakes were sampled from five subregions, divided for the purposes of this report into three regions: Adirondacks subregion, Poconos/Catskills subregion, and New England subregions (Table 5-1). The majority of ELS-II lakes were in New York and Maine. EL.S-II lakes are not uniformly distributed across the Northeast (see Figure 2-1) because of the selection factors (Section 2.2) used in defining the interest attributes for ELS-II. The median ELS-II lake was 6.5 m deep at an elevation of 275 m and had a surface area of 24 ha (Table 5-2). Most ELS-II lakes were drainage lakes (72\%) or reservoirs (15\%). The remaining $13 \%$ were seepage or closed lakes. In the fall, most lakes ( $85 \%$ ) were well mixed (top-bottom temperature difference $<1^{\circ} \mathrm{C}$ ), whereas in summer, most lakes ( $66 \%$ ) were strongly stratified ( $>4^{\circ} \mathrm{C}$ change). Spring stratification conditions were intermediate between fall and summer (Table 5-2).

### 5.1.4 Aluminum Measurements

In the ELS-II, inorganic monomeric aluminum ( $\mathrm{Al}_{\mathrm{im}}$ ) was determined as the difference between total pyrocatechol violet (PCV) reactive aluminum and nonexchangeable (organic) PCV reactive aluminum. $\mathrm{Al}_{\mathrm{im}}$ is thought to be the form of aluminum most toxic to aquatic organisms (Baker and Schofield, 1982; J. Baker et al., 1990a; Driscoll et al., 1980) and is thus of most interest in terms of acidic deposition effects. Al $_{\mathrm{im}}$, however, was not measured in ELS-I, preventing fall $1984 /$ fall 1986 comparisons. Methyl-isobutyl-ketone (MIBK) extractable aluminum ( $A I_{\text {MiBK }}$ ), an alternate estimate of total monomeric aluminum, was measured in both ELS-I and ELS-II. Thus, we are able to make year-to-year comparisons for aluminum with $\mathrm{Al}_{\text {MiBK. }}$. For all other temporal comparisons, we use $\mathrm{Al}_{\mathrm{im}}$ because it is of more direct biological interest.

Table 5-1. Breakdown of the ELS-11 Target Population ${ }^{\text {a }}$

| Area | n | $\hat{\mathrm{N}}$ | $\hat{\mathrm{A}}\left(\mathrm{km}^{2}\right)$ |
| :--- | ---: | ---: | ---: |
| SUBREGION |  |  |  |
| Adirondacks (1A) | 36 | 754 | 1,004 |
| Poconos/Catskills (1B) | 18 | 608 | 134 |
| New England Subregions | 91 | 2,631 | 2,411 |
| $\quad$ Central (1C) | 32 | 931 | 802 |
| $\quad$ Southern (1D) | 25 | 659 | 297 |
| $\quad$ Maine (1E) | 34 | 1,040 |  |
|  |  |  |  |
| TOTAL ELS- II | 145 | 3,549 |  |
|  |  |  |  |
| STATE | 4 | 144 | 45 |
| Connecticut | 21 | 459 | 223 |
| Massachusetts | 45 | 1,475 | 1,454 |
| Maine | 16 | 406 | 640 |
| New Hampshire | 41 | 901 | 1,024 |
| New York | 14 | 477 | 101 |
| Pennsylvania | 4 | 131 | 64 |
| Rhode Island |  |  |  |

[^7]Table 5-2. Physical Characteristics of the ELS-II Target Population

| Variable | Minimum | $\mathrm{Q}_{1}{ }^{\text {a }}$ | Median | $Q_{3}{ }^{\text {a }}$ | Maximum |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Lake Depth (m) | 1.2 | 4.0 | 6.5 | 10.5 | 30.5 |
| Elevation (m) | 2 | 116 | 275 | 459 | 791 |
| Lake Area (ha) | 4 | 10 | 24 | 92 | 1,619 |
| Watershed Area (ha) | 13 | 145 | 425 | 1,417 | 81,420 |
| Watershed: Lake Area | 2 | 7 | 15 | 32 | 2932 |
| Residence Time (yr) ${ }^{\text {b }}$ | 0.001 | 0.13 | 0.30 | 0.84 | 10.0 |
| Temperature Stratification | Percent of Lakes |  |  |  |  |
| (Top-Bottom) | Spring |  | Summer |  | Fall |
| $<1^{\circ} \mathrm{C}$ | 47 |  | 18 |  | 85 |
| $1-2^{\circ} \mathrm{C}$ | 7 |  | 9 |  | 4 |
| $2-4^{\circ} \mathrm{C}$ | 23 |  | 7 |  | 7 |
| $>4^{\circ} \mathrm{C}$ | 23 |  | 66 |  | 4 |

\% Drainage Lakes ${ }^{c}$ ..... 72
\% Seepage Lakes ${ }^{\text {c }}$ ..... 9
\% Closed Lakes ${ }^{\text {c }}$ ..... 4
\% Reservoirs ..... 15
a $Q_{1}=25$ th percentile, $Q_{3}=75$ th percentile.
b
Residence time (RT) calculated as: $R T=A_{\text {ake }} Z /\left[R\left(A_{\text {ws }}-A_{\text {ake }}\right)+P\left(A_{\text {ake }}\right)\right]$, where $A_{\text {ake }}=$ lake area, $A_{\text {ws }}=$ watershed area, $Z=$ site depth, $R=$ runoff, and $P=$ precipitation.
c Drainage lakes have mapped outlets, seepage lakes have no mapped inlets or outlets, and closed lakes have inlets but no mapped outlets.

### 5.2 BETWEEN-YEAR VARIABILITY (FALL 1986 VS. FALL 1984)

As only two different years were sampled in both phases of the ELS, it is not our intent to make a rigorous statement about interannual variability. However, the comparison of ELS-I (fall 1984 sample) and ELS-II (fall 1986 sample) data does provide useful information about annual difference in our ability to estimate attributes of regional lake populations. In this subsection, only ELS-II data collected from the ELS-I fall index site as defined on the original data sheet are presented. Data collected during the two subsequent lake visits of the fall variability study were not used to assess between-year variability. Thus, the fall 1984 and 1986 chemistry data analyzed in this subsection were collected from the same general lake location.

In terms of hydrology, 1984 was a "wet water year" in the northeastern United States. Runoff for the year was above average to excessive throughout the Northeast (upper 25th percentile compared to long-term records; Blackey et al., 1985; Firda et al., 1985; Gadoury et al., 1985; Haskell et al., 1985). In general, these excesses were due to large precipitation inputs in the summer of 1984, which caused some flooding and filled reservoirs to capacity. Runoff tended to return to more normal levels during the fall of 1984. In contrast, runoff throughout the 1986 water year was average to above average (Firda et al., 1987). Water levels in lakes in the Adirondacks and Poconos/Catskills were at or slightly above long-term averages and fall 1986 runoff in eastern New York was about 100-110\% of 30-year averages (Firda et al., 1988).

### 5.2.1 Population Estimates of Acidic and Low ANC Lakes

The percentage of acidic (ANC $\leq 0 \mu \mathrm{eq} / \mathrm{L}$ ) ELS-I lakes in fall 1984 ( $6.2 \%$ ) was almost the same as that calculated for the fall of 1984 using only the ELS-II (7.7\%) subset of sample lakes (Table 5-3). ELS-II and ELS-I percentages are similar, despite the exclusion of high ANC ( $>400 \mu \mathrm{eq} / \mathrm{L}$ ) lakes in ELS-II, because a number of acidic and low ANC lakes were excluded from ELS-II because they were shallow or historically had been limed. As can be seen in Table 5-3, an estimated 134 of the estimated 441 acidic ELS-I lakes were excluded from the ELS-II target population. All these acidic lakes were excluded because they were too shallow (site depths $<\mathbf{1 . 5} \mathrm{m}$ ).

There were roughly $10 \%$ more acidic ELS-II lakes in the fall of 1986 than in fall 1984 (Table 5-3). On the other hand, there were about $10 \%$ fewer lakes with ANC < 50,100 , and $200 \mu \mathrm{eq} / \mathrm{L}$ in fall 1986. Overall, these between-year differences correspond to small changes in the percentage of the target population with ANC below reference values. The reference values for pH and ANC used in Table 5-3 are those that are commonly used in acidic deposition research. Lakes with ANC < 0 have lost the capacity to neutralize incoming acids and lakes with ANC $\leq 50 \mu \mathrm{eq} / \mathrm{L}$ have been defined as extremely sensitive to acidic deposition (Schindler, 1988).

Table 5-3. Population Estimates of the Number ( $\hat{\mathbf{N}}$ ) and Percentage of Lakes with ANC and pH below Reference Values in the Fall of 1984 (ELS-I) and 1986 (ELS-II) in the Northeastern United States

| Reference <br> Values ${ }^{\text {a }}$ | ELS-I Lakes <br> Fall $1984^{\text {b }}$ |  | ELS-II Lakes |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  | Fall $1984^{\text {c }}$ |  | Fall $1986{ }^{\text {d }}$ |  |
|  | $\hat{\mathrm{N}}$ | \% | $\hat{N}$ | \% | $\hat{N}$ | \% |
| ANC $\leq 0 \mu \mathrm{eq} / \mathrm{L}$ | 441 | 6.2 | 307 | 7.7 | 343 | 8.6 |
| ANC $\leq 50$ | 1,556 | 21.7 | 1,089 | 27.3 | 1,000 | 25.1 |
| ANC $\leq 100$ | 2,632 | 36.8 | 1,873 | 46.9 | 1,711 | 42.8 |
| ANC $\leq 200$ | 4,324 | 60.4 | 3,005 | 75.3 | 2,760 | 69.1 |
| $\mathrm{pH} \leq 5.0$ | 240 | 3.4 | 155 | 3.9 | 167 | 4.2 |
| $\mathrm{pH} \leq 5.5$ | 613 | 8.6 | 471 | 11.8 | 478 | 12.0 |
| $\mathrm{pH} \leq 6.0$ | 916 | 12.8 | 660 | 16.5 | 777 | 19.5 |
| $\mathrm{pH} \leq 6.5$ | 1,868 | 26.1 | 1,346 | 33.7 | 1,324 | 33.2 |
| Sample size | 768 |  | 145 |  | 145 |  |
| Population size | 7,157 |  | 3,993 |  | 3,993 |  |

[^8]ELS-II population estimates of the number of lakes with pH below reference values were also very similar in fall 1984 arid fall 1986 (Table 5-3). Percentage estimates were within $1 \%$ of each other for lakes with $\mathrm{pH} \leq 5.0,5.5$, and 6.5 . Based on ELS-II data, conclusions about the acid-base status of lakes in the northeastern United States would have been similar whether the surveys had been implemented in fall 1984 or fall 1986.

### 5.2.2 Chemical Changes

### 5.2.2.1 ANC/pH

Overall, CDFs for ANC (Figure 5-2) and pH (Figure 5-3) show similar distributions for fall 1984 and fall 1986. ANC values were very similar between the two years at low ANC (< $50 \mu \mathrm{eq} / \mathrm{L}$ ). At higher ANC values, 1986 ANC tended to be slightly higher than 1984 ANC (Figure 5-2). The median change in ANC between the two years was a gain of $15 \mu \mathrm{eq} / \mathrm{L}$ from 1984 to 1986 (Table 5-4). One-fourth of the lakes increased by more than $33 \mu \mathrm{eq} / \mathrm{L}$ from fall 1984 to fall 1986. All of these lakes, however, had ANC over $50 \mu \mathrm{eq} / \mathrm{L}$. In low ANC systems ( $\leqslant 50 \mu \mathrm{eq} / \mathrm{L}$ ), the median 1984/1986 ANC change was only 2 $\mu \mathrm{eq} / \mathrm{L}$, and over half the low ANC lakes changed by less than $6 \mu \mathrm{eq} / \mathrm{L}$. Between-year differences in pH were low, with 1984 pH levels tending to be slightly higher than 1986 pH levels (Figure 5-3). The median pH change in ELS-II lakes was 0.06 pH units, with an interquartile range of 0.18 pH units (Table 5-4). Note that the pooled standard deviation of duplicate lake samples was $5.1 \mu \mathrm{eq} / \mathrm{L}$ for ANC and 0.02 pH units in fall 1986 (Table 4-3). Differences smaller than these should be interpreted with caution.

### 5.2.2.2 Inorganic Acid Anions

Distribution of sulfate concentration in ELS-II lakes were nearly identical in 1984 and 1986 (Figure $5-4$ ). Fall 1984/Fall 1986 scatter plots, however, show some large deviations from the $1: 1$ line at sulfate concentrations $>200 \mu \mathrm{eq} / \mathrm{L}$. At these relatively high concentrations, these lakes are dominated by internal watershed sources of sulfate rather than deposition sulfate sources (L. Baker et al., 1990). Compared to deposition, which is a relatively stable sulfate source, fluxes of watershed-derived sulfate are more variable because they are more dependent on flowpaths, weathering rates, and other biogeochemical processes. Thus, lakes with watershed sources of sulfate are likely to experience greater variability over time than lakes whose sulfate is derived primarily from deposition. Overall, in most lakes the year-to-year changes in sulfate concentration were small. The median change was a decrease of 3 $\mu \mathrm{eq} / \mathrm{L}$ from fall 1984 to fall 1986, and over half of both the low and high ANC lakes changed by less than $10 \mu \mathrm{eq} / \mathrm{L}$. Sulfate duplicate sample precision (pooled SD) in fall 1986 was $2.6 \mu \mathrm{eq} / \mathrm{L}$.

More lakes had nitrate concentrations $>1 \mu \mathrm{eq} / \mathrm{L}$ in fall 1986 than fall 1984 (Figure 5-5). In both years, however, most lakes had low nitrate concentrations and thus between-year nitrate changes were small (majority $<2 \mu \mathrm{eq} / \mathrm{L}$; Table 5-4). The largest observed nitrate changes were a $13 \mu \mathrm{eq} / \mathrm{L}$ increase and a $7 \mu \mathrm{eq} /$ L decrease from 1984 to 1986 . The main difference between the two years was an


Figure 5-2. Population distribution and comparison of fall 1986 ANC with fall 1984 ANC in ELS-II lakes.


Figure 5-3. Population distribution and comparison of fall 1986 pH with fall 1984 pH in ELS-II lakes.

Table 5-4. Population Characteristics of Between-Year Chemical Changes (Fall 1984 - Fall 1986) in ELS-II Lakes ${ }^{\text {a }}$

|  | Fall $1984^{\mathrm{b}}-$ Fall 1986 |  |  |  |  |
| :--- | :---: | :---: | :---: | :---: | :---: |
| Variable | Minimum | $\mathrm{Q}_{1}{ }^{\mathrm{C}}$ | Median | $\mathrm{Q}_{3}{ }^{\mathrm{b}}$ | Maximum |
|  |  |  |  |  |  |
| All ELS-II $(\hat{\mathbf{N}}=\mathbf{3 , 9 9 3})$ |  | -33 | -15 | -2 | 39 |
| ANC | -112 | -0.03 | 0.06 | 0.15 | 1.2 |
| pH | -0.37 | -4 | 3 | 10 | 44 |
| $\mathrm{SO}_{4}{ }^{2-}$ | -101 | -2 | -0.4 | -0.1 | 7 |
| $\mathrm{NO}_{3}{ }^{-}$ | -13 | -18 | -3 | 0.2 | 139 |
| $\mathrm{Cl}^{-}$ | -201 | -74 | -38 | -16 | 69 |
| Base cations $^{\text {DOC }}$ | -338 | -0.6 | -0.1 | 0.3 | 2.7 |
| $\mathrm{Al}_{\text {MIBK }}$ | -4.6 | -6 | -2 | 3 | 79 |

Fall 1986 ANC $\leq 50 \mu \mathrm{eq} / \mathrm{L}(\hat{\mathbf{N}}=1,000)$

| $\mathrm{ANC}(\mu \mathrm{eq} / \mathrm{L})$ | -16 | -6 | -2 | 4 | 39 |
| :--- | :---: | :--- | :---: | :--- | :---: |
| pH | -0.37 | -0.10 | 0.04 | 0.14 | 1.2 |
| $\mathrm{SO}_{4}{ }^{2-}$ | -101 | -8 | 2 | 9 | 44 |
| $\mathrm{NO}_{3}{ }^{-}$ | -10 | -1 | 0 | 0 | 7 |
| $\mathrm{Cl}^{-}$ | -156 | -5 | 0 | 1 | 139 |
| Base Cations | -321 | -38 | -18 | -9 | 34 |
| DOC | -4.2 | -0.4 | 0 | 0.4 | 2.7 |
| Al $_{\text {MIBK }}$ | -166 | -20 | -7 | 2 | 79 |

[^9]

Figure 5-4. Population distribution and comparison of fall 1986 sulfate with fall 1984 sulfate in ELS-II lakes.


Figure 5-5. Population distribution and comparison of fall 1986 nitrate with fall 1984 nitrate in ELS-ll lakes.
increase in the number of lakes with nitrate between 1 and $5 \mu \mathrm{eq} / \mathrm{L}$ from fall 1984 to fall 1986. According to chi-square analysis, nitrate concentrations in the fall 1986 population were different than those in the fall 1984 population in all three ELS-II sample clusters (see Appendix C, Table C-1).

Similar chloride distributions were observed for lakes with low chloride values ( $<100 \mu \mathrm{eq} / \mathrm{L}$ ) in fall 1984 and 1986 (Figure 5-6). In lakes with higher chloride concentrations, 1986 values were slightly higher than 1984 values. As with sulfate, the biggest year-to-year changes were observed in systems with the highest concentrations. These high chloride lakes receive either extensive inputs of marine salts or internal watershed inputs of chloride (e.g., road salt). The majority of low ANC lakes showed only small changes ( $<5 \mu \mathrm{eq} / \mathrm{L}$ ) in chloride (Table 5-4).

### 5.2.2.3 Sum of Base Cations

Sum of base cation concentrations in the fall of 1986 were consistently higher than those observed in the fall of 1984 (Figure 5-7). The median base cation increase was $38 \mu \mathrm{eq} / \mathrm{L}(18 \mu \mathrm{eq} / \mathrm{L}$ in low ANC lakes; Table 5-4). Three-fourths of the ELS-II lakes had base cation increases of more than $16 \mu \mathrm{eq} / \mathrm{L}$ between fall index periods in 1984 and 1986. These differences are most likely attributable to the different hydrological conditions in the two years. 1984 was a "wetter" year, resulting in more dilute conditions and thus lower base cations. According to chi-square analysis, the fall 1986 population had significantly different ( $\mathrm{p}<0.01$ ) base cation concentrations than the fall 1984 population (see Appendix C, Table C-1).

### 5.2.2.4 DOC/Aluminum

DOC distributions for fall 1984 and fall 1986 were nearly identical (Figure 5-8). Fall 1984/Fall 1986 scatter plots show no tendency for higher DOC in either year, and the scatter in the relationship was fairly consistent across all DOC levels. Overall, the median change in DOC ( $0.1 \mathrm{mg} / \mathrm{L}$ ) was very small and was within the precision of the sampling process. The majority of lakes changed by less than 0.6 $\mathrm{mg} / \mathrm{L}$ (Table 5-4).

MIBK-extractable aluminum ( $\mathrm{Al}_{\text {MIBK }}$ ) is an estimate of total monomeric aluminum and was the only aluminum species measured in ELS-I. Al ${ }_{\text {MIBK }}$ population distributions were about the same in fall 1984 as in fall 1986 (Figure 5-9). As with nitrate, most of the lakes had low $\mathrm{Al}_{\text {MIBK }}$ concentrations and thus had small year to year changes (median $=2 \mu \mathrm{~g} / \mathrm{L}$; Table 5-4). The majority of low ANC lakes also had small changes in $\mathrm{Al}_{\text {MIBK }}(<20 \mu \mathrm{~g} / \mathrm{L})$.

### 5.2.3 Conclusions: Between-Year Variability

Fall 1984/Fall 1986 changes in ANC and pH were small and estimates of the number of lakes with ANC and pH below reference values commonly used in acidic deposition research were very similar between the two years. Based on ELS-II data, major conclusions about the acid-base status of lakes in the northeastern United States would have been very similar, whether the surveys had occurred in fall


Figure 5-6. Population distribution and comparison of fall 1986 chloride with fall 1984 chloride in ELS-II lakes.


Figure 5-7. Population distribution and comparison of fall 1986 sum of base cations with fall 1984 sum of base cations in ELS-II lakes.


Figure 5-8. Population distribution and comparison of fall 1986 DOC with fall 1984 DOC in ELS-II lakes.


Figure 5-9. Population distribution and comparison of fall 1986 MIBK-extractable aluminum with fall 1984 MIBK-extractable aluminum in ELS-II lakes.

1984 or fall 1986. Sulfate and DOC distributions were very similar in both years. Base cation and chloride concentrations tended to be higher in 1986 than in 1984, probably because of the dryer conditions in 1986. Nitrate and $\mathrm{Al}_{\text {MIBK }}$ concentrations were very low in most lakes in both years, so that between-year differences were usually small. In lakes with elevated nitrate and $A I_{\text {MIBK }}$, neither year appeared to have higher concentrations than the other.

### 5.3 WITHIN-SEASON VARIABILITY (FALL 1986)

A subset of 41 lakes was sampled three times at three independently selected locations on each lake during the fall index period of 1986. One visit was made at the mapped ELS-I index site, whereas the other two visits were made, following the established protocol, to the "deepest spot on the lake" in the judgement of independent field crews. The average time between the first and third sample visits was 12 days $(S O=7)$. Thus the fall variability study has a spatial component as well as the withinseason temporal component. These 41 fall variability lakes represent 1,012 lakes with a surface area of $551 \mathrm{~km}^{2}$ in the ELS-II target population. As in the entire ELS-II population, the vast majority of the fall variability lakes were drainage lakes (59\%) or reservoirs ( $21 \%$ ). Of these 41 lakes, 17 were in the Adirondack Mountains, and 24 were in the coastal areas of southern New England (within 61 km of the ocean). In examining within-season variability, no spatial (regional) patterns were observed in the data, so we will not report separate results for the two groups of fall variability lakes. In this section, Fall Variability Study data are presented in two ways: (1) by CDFs showing the population distributions during visits 1,2 , and 3 , and (2) by scatterplots showing the relationships between all possible study pairs (visit $1 /$ visit 2 , visit $2 /$ visit 3 , visit $1 / v i s i t 3$ ).

### 5.3.1 Chemical Differences

### 5.3.1.1 ANC/pH

Distribution of ANC and pH were very similar among samples from the three lake visits (Figures 5-10 and 5-11). Visit 2 was the visit to the mapped 1984 ELS-I fall index site. Median ANC and pH values were within $2 \mu \mathrm{eq} / \mathrm{L}$ and 0.05 pH units of each other among the three lake visits. The median standard deviation of the 41 sets of lake triplicate (three visits) samples was $6 \mu \mathrm{eq} / \mathrm{L}$ for ANC and 0.05 units for pH (Table 5-5). Over three-fourths of the fall variability lake population had triplicate standard deviations $<12 \mu \mathrm{eq} / \mathrm{L}$ and 0.07 pH units. From the CDFs of ANC and pH , and from the scatterplots of all possible visit pairs, it is apparent that population estimates of the proportion of lakes with ANC or pH below reference values were not greatly affected by fall temporal and site selection variability. Overall conclusions about the acid-base status of northeastern lakes would have been the same if sampling had occurred only during visit 1,2 , or 3 . Therefore, the fall index sample appears to be quite stable for ANC and pH .


Figure 5-10. Population distribution of the three sample visits in the ELS-II Fall Variability Study: (a) ANC, and (b) pH.

Fall Variability Study Pairs


Figure 5-11. Scatterplot of all possible Fall Variability Study pairs (visit $\mathbf{1 / v i s i t} 2$, visit $2 /$ visit 3, and visit $1 /$ visit 3 ) for (a) ANC, and (b) pH .

Table 5-5. Population Distribution of the Standard Deviation of the Three Lake Samples Collected during the Fall Index Period in the ELS-II Fall Variability Study ${ }^{\text {a }}$

| Variable | Grand ${ }^{\text {b }}$ <br> Mean | Triplicate Standard Deviation ${ }^{\text {c }}$ |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | $\overline{\text { Minimum }}$ | $\mathrm{Q}_{1}$ | Median | $\mathrm{Q}_{3}$ | Maximum |
| ANC | 61 | 0.3 | 2.1 | 6.1 | 12 | 19 |
| pH | 5.9 | 0.01 | 0.03 | 0.05 | 0.07 | 0.11 |
| $\mathrm{SO}_{4}{ }^{\text {- }}$ | 124 | 0.5 | 2.8 | 4.1 | 8.6 | 57 |
| $\mathrm{NO}_{3}{ }^{-}$ | 4 | 0.02 | 0.1 | 0.3 | 0.6 | 4.8 |
| $\mathrm{Cl}^{-}$ | 161 | 0.1 | 0.8 | 4.9 | 18 | 96 |
| Base Cations | 374 | 1.5 | 4.4 | 7.7 | 18 | 35 |
| DOC | 3.8 | 0.01 | 0.09 | 0.17 | 0.24 | 0.46 |
| $\mathrm{Al}_{\text {im }}$ | 42 | 0.50 | 1.7 | 3.3 | 7.8 | 13 |

[^10]
### 5.3.1.2 Inorganic Acid Anions

Sulfate changes were minimal among the three lake visits of the fall variability study (Figures 5-12 and 5-13). Median and quartile values were within $10 \mu \mathrm{eq} / \mathrm{L}$ of each other among the three lake visits. Maximum sulfate values showed the greatest among-visit difference ( $328-438 \mu \mathrm{eq} / \mathrm{L}$ ), probably due to varying inputs of watershed sulfate. Over three-fourths of the fall variability lake population are estimated to have fall variability (standard deviation of the three lake samples) less than $9 \mu \mathrm{eq} / \mathrm{L}$.

Nitrate distributions were fairly similar among the three lake visits with most ( $>60 \%$ ) lakes having very low nitrate ( $<3 \mu \mathrm{eq} / \mathrm{L}$ ) concentrations (Figures 5-12 and 5-13). The 75 th percentile for nitrate varied from 8.8 to $10.0 \mu \mathrm{eq} / \mathrm{L}$ and maximum nitrate varied from 19 to $27 \mu \mathrm{eq} / \mathrm{L}$ among the three visits. Most (>75\%) of the fall variability lakes had triplicate nitrate standard deviations $<1 \mu \mathrm{eq} / \mathrm{L}$ and all of them had standard deviations $<5 \mu \mathrm{eq} / \mathrm{L}$ (Table 5-5).

Median chloride concentrations were almost identical (138-140 $\mu \mathrm{eq} / \mathrm{L}$ ) among the three lake visits (Figure 5-13). As with the other acid anions, the maximum variability among the three lake visits was observed at the high end of the distribution (Figure 5-13). Overall, the median chloride triplicate standard deviation in the fall variability lakes was $5 \mu \mathrm{eq} / \mathrm{L}$ and over $75 \%$ of the population had standard deviations below $18 \mu \mathrm{eq} / \mathrm{L}$ (Table 5-5).

### 5.3.1.3 Sum of Base Cations

CDFs of the three lake visits during the Fall Variability Study almost completely overlap for the sum of base cations (Figure 5-14). Population minimums, quartiles, medians, and maximums are nearly identical among the three visits. The median triplicate standard deviation for the sum of base cations was $7.7 \mu \mathrm{q} / \mathrm{L}$ (maximum $=35 \mu \mathrm{eq} / \mathrm{L}$ ) for the fall variability lake population (Table 5-5) scatterplot. The fall index appears to be extremely stable for base cations.

### 5.3.1.4 DOC/Aluminum

DOC values are very similar among all the possible pairs among the three lake visits in the Fall Variability Study (Figure 5-15). CDFs for DOC showed almost no differences among the three lake visits (data not shown). The largest triplicate DOC standard deviation in any of the lakes was $0.46 \mathrm{mg} / \mathrm{L}$ (Table 5-5). The median standard deviation was only $0.17 \mathrm{mg} / \mathrm{L}$. The fall index appears to be extremely stable for DOC.

Inorganic monomeric aluminum ( $\mathrm{Al}_{\mathrm{im}}$ ) concentrations were low in most fall variability lakes (Figure 5-14). The SDL for $\mathrm{Al}_{\mathrm{im}}$ was $17 \mu \mathrm{~g} / \mathrm{L}$ and values below this value are not significantly different than field blanks. All the median $\mathrm{Al}_{\mathrm{im}}$ values for the three lake visits are below the SDL. At all concentrations, variability among the three lake visits was small (Figure 5-15). Triplicate visit standard deviation for $\mathrm{Al}_{\mathrm{im}}$ ranged from 0.5 to $13 \mu \mathrm{~g} / \mathrm{L}$ in the fall variability lakes. The fall index appears to be extremely stable for $A l_{i m}$.


Figure 5-12. Population distribution of the three sample visits in the ELS-II Fall Variability Study: (a) sulfate, and (b) nitrate.

Fall Variability Study Pairs


Figure 5-13. Scatterplot of all possible Fall Variability Study pairs (visit 1/visit 2, visit 2/visit 3, and visit $1 / v i s i t$ 3) for (a) sulfate, (b) nitrate, and (c) chloride.


Figure 5-14. Population distribution of the three sample visits in the ELS-II Fall Variability Study: (a) sum of base cations, and (b) inorganic monomeric aluminum.

Fall Variability Study Pairs


Figure 5-15. Scatterplot of all possible Fall Variability Study pairs (visit 1/visit 2, visit 2/visit 3, and visit $1 /$ visit 3) for (a) sum of base cations, (b) DOC, and (c) inorganic monomeric aluminum.

### 5.3.2 Conclusions: Robustness of the Fall Index

Based on data from the ELS-II Fall Variability Study, a single fall index sample is a robust estimator of conditions during the fall index period (after fall turnover). Overall, variability among the three lake visits was very small. Population estimates of the proportion of lakes with ANC or pH below reference values were not greatly affected by fall temporal and site selection variability. Overall conclusions about the acid-base status of northeastern lakes would have been the same if sampling had occurred only during visit 1,2 , or 3 . $\mathrm{ANC}, \mathrm{pH}$, sum of base cations, DOC , and $\mathrm{Al}_{\mathrm{im}}$ showed almost identical distributions among the three lake visits over all observed concentrations. Acid anions (sulfate, nitrate, and chloride) showed very little differences among the three lake visits except at the highest observed concentrations where some larger within-season differences were evident. Sample processing and analytical variability are components of within-season variability. Section 6.1 provides a comparison of the magnitude of analytical and temporal variability.

### 5.4 AMONG SEASON VARIABILITY (SPRING, SUMMER, AND FALL 1986)

Among-season variability is assessed by comparing the results of the 1986 ELS-11 spring, summer, and fall seasonal surveys. All of these seasonal samples were collected from the same general location in the lakes as the 1984 ELS-I sample. Fall samples were collected after turnover (October to midNovember) when conditions were isothermal (Table 5-2) and chemical variability low (Section 5.3). Summer samples were collected from mid-July to mid-August, when most lakes were stratified (Table $5-2$ ). Only epilimnetic sample data are discussed in this section. Spring data were collected in April as soon after ice-out as possible. However, since peak lake discharge usually precedes ice-out, the ELS-II spring sample does not represent peak flow conditions when episodic acidification effects would be most severe. A detailed discussion of the ELS-II spring sample in relation to lake discharge is given in Section 6.3.3. In summary, the ELS-II fall sample represents epilimnetic conditions in the profundal zone after fall turnover. The ELS-II spring sample represents post-snowmelt (2-3 weeks), non-episodic spring conditions.

### 5.4.1 Population Estimates of Acidic and Low ANC Lakes

One of the major objectives of ELS-II was to estimate the number of systems that would be acidic or have low ANC in seasons other than the fall index period sampled in ELS-I. ELS-II population estimates show that there were $24 \%$ more acidic lakes (ANC $\leq 0$ ) in the spring (an estimated 424 lakes) than in the fall (an estimated 343 lakes; Table $5-6$ ). This corresponds to an increase in the percentage of acidic ELS-II lakes from $9 \%$ to $11 \%$. It should be noted that the number of acidic lakes in the spring is

Table 5-6. Population Estimates ( $\hat{N} \pm$ Standard Error) of the Number of ELS-II Lakes with ANC ( $\mu \mathrm{eq} / \mathrm{L}$ ) below Reference Values in the Three Seasonal Surveys ${ }^{\text {a }}$

| Reference <br> Value | Region | Spring <br> 1986 | Summer | Fall |
| :--- | :--- | :--- | :--- | :--- |
|  |  |  | 1986 | 1986 |
| ANC $\leq 0$ | Adirondacks | $184 \pm 42$ | $160 \pm 39$ | $135 \pm 37$ |
|  | Poconos/Catskills | $67 \pm 39$ | $67 \pm 39$ | $67 \pm 39$ |
|  | New England | $173 \pm 45$ | $117 \pm 37$ | $142 \pm 40$ |
|  | All ELS-II | $424 \pm 69$ | $343 \pm 64$ | $343 \pm 64$ |
|  |  |  |  |  |
|  | Adirondacks | $440 \pm 82$ | $346 \pm 62$ | $346 \pm 62$ |
|  | Poconos/Catskills | $185 \pm 61$ | $185 \pm 61$ | $141 \pm 54$ |
|  | New England | $713 \pm 98$ | $558 \pm 88$ | $514 \pm 85$ |
|  | All ELS-II | $1,338 \pm 128$ | $1,089 \pm 113$ | $1,000 \pm 109$ |
|  |  |  |  |  |
|  | Adirondacks | $555 \pm 99$ | $456 \pm 74$ | $456 \pm 74$ |
|  | Poconos/Catskills | $311 \pm 94$ | $212 \pm 66$ | $185 \pm 61$ |
|  | New England | $1,598 \pm 169$ | $1,115 \pm 117$ | $1,070 \pm 117$ |
|  | All ELS-II | $2,465 \pm 192$ | $1,783 \pm 130$ | $1,711 \pm 129$ |

[^11]less than the upper $95 \%$ confidence limit of the number of acidic ELS-II lakes in the fall $(343+1.65 * 64$ $=449$ lakes; Table 5-6). There were also increases in the numbers of low ANC lakes in the spring relative to fall; the percentage of ELS-II lakes with ANC $\leq 50 \mu \mathrm{eq} / \mathrm{L}$ increased from $25 \%$ to $34 \%$ (fall to spring) and the percentage with $\mathrm{ANC} \leq 100 \mu \mathrm{eq} / \mathrm{L}$ increased from $43 \%$ to $62 \%$. Summer conditions were usually more similar to fall conditions than to spring conditions. Broken down by region, the Adirondacks showed the greatest relative fall-to-spring increase in the number of acidic lakes, but the smallest relative increase in the number of lakes with ANC $<50$ or $100 \mu \mathrm{eq} / \mathrm{L}$ (Table 5-6).

There was a $13 \%$ increase in the number of lakes with $\mathrm{pH} \leq 5.0$ in the spring relative to fall and there were slightly more lakes with $\mathrm{pH} \leq 5.0$ in the summer than in the spring (Table 5-7). The largest numbers of lakes with $\mathrm{pH} \leq 5.5$ and $\mathrm{pH} \leq 6.0$ were observed in the spring in all regions. The lowest number of lakes with $\mathrm{pH} \leq 5.5$ was observed in the summer, whereas the lowest number of lakes with $\mathrm{pH} \leq 6.0$ was observed in the fall. In a fall/spring comparison, the percentage of ELS-II lakes with: (1) $\mathrm{pH} \leq 5.0$ increased from $4 \%$ to $5 \%$, (2) $\mathrm{pH} \leq 5.5$ increased from $12 \%$ to $14 \%$, and (3) $\mathrm{pH} \leq 6.0$ increased from $19 \%$ to $27 \%$ (Table 5-7). Similarly small increases in the percentages of acidic and low pH lakes in the spring relative to fall were also observed in the 1,715 lakes sampled in Massachusetts during Phase II of the Acid Rain Monitoring Project (ARM). For ARM lakes $>4$ ha, $9 \%$ were acidic and $27 \%$ had pH $\leq 6.0$ in the spring (April) versus $6 \%$ and $23 \%$, respectively, in the fall (Ruby et al., 1988). For smaller lakes, spring/fall percentage differences were even smaller.

### 5.4.2 Seasonal Chemical Differences

Seasonal differences are presented by overlaying distributions of the study variable in different seasons on one plot. Also, seasonal minimums, quartiles, medians, and maximums are presented for each season using floating bar diagrams. In more detailed analyses, we have concentrated on presenting spring/fall differences because spring samples had the lowest ANC in the ELS-II survey, and we wished to compare those values to the index period measured in ELS-I. In examining seasonal chemical differences, there were different patterns of seasonal change in low and high ANC lakes. Thus, we have presented spring/fall comparisons for lakes greater than and less than $50 \mu \mathrm{eq} / \mathrm{L}$ as well as for all lakes (Table 5-8). An ANC cutoff of $50 \mu \mathrm{eq} / \mathrm{L}$ was chosen to define those lakes of most interest with respect to acidic deposition effects. Paleolimnological data in the Adirondacks have shown that most ELS lakes with current ANC $<50 \mu \mathrm{eq} / \mathrm{L}$ have acidified since pre-industrial times, whereas those with ANC>50 $\mu \mathrm{eq} / \mathrm{L}$ have increased in ANC (Sullivan et al., 1990). Also, an ANC level of $50 \mu \mathrm{eq} / \mathrm{L}$ has been commonly used to define "extremely sensitive" systems (Schindler, 1988). There were also regional differences in spring/fall changes in low ANC lakes, so regional estimates are also presented (Table 5-9). All among-season differences should be interpreted in light of the laboratory bias (Table 4-5) and precision estimates presented in Section 4.

Table 5-7. Population Estimates ( $\hat{\mathbf{N}} \pm$ Standard Error) of the Number of ELS-II Lakes with pH below Reference Values in the Three Seasonal Surveys ${ }^{\text {a }}$

| Reference <br> Value | Region | Spring | Summer | Fall |
| :--- | :--- | :--- | :--- | :--- |
|  |  | 1986 | 1986 | 1986 |
| pH $\leq 5.0$ | Adirondacks | $111 \pm 33$ | $123 \pm 35$ | $98 \pm 32$ |
|  | Poconos/Catskills | $12 \pm 12$ | $12 \pm 12$ | $12 \pm 12$ |
|  | New England | $69 \pm 30$ | $69 \pm 30$ | $56 \pm 28$ |
|  | All ELS-II | $191 \pm 45$ | $204 \pm 46$ | $167 \pm 43$ |
|  |  |  |  |  |
|  | Adirondacks | $233 \pm 45$ | $197 \pm 43$ | $197 \pm 43$ |
|  | Poconos/Catskills | $79 \pm 41$ | $67 \pm 39$ | $94 \pm 47$ |
|  | New England | $264 \pm 60$ | $173 \pm 45$ | $188 \pm 47$ |
|  | All ELS-II | $576 \pm 81$ | $436 \pm 70$ | $478 \pm 75$ |
|  |  |  |  |  |
|  | Adirondacks | $368 \pm 64$ | $302 \pm 55$ | $302 \pm 55$ |
|  | Poconos/Catskills | $185 \pm 61$ | $151 \pm 67$ | $106 \pm 48$ |
|  | New England | $511 \pm 85$ | $379 \pm 72$ | $369 \pm 70$ |

[^12]Table 5-8. Population Characteristics of Between-Season Chemical Changes (Spring 1986-Fall 1986) in ELS-II Lakes ${ }^{\text {a }}$

| Variable | Spring 1986-Fall 1986 |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | Minimum | $Q_{1}{ }^{\text {b }}$ | Median | $\mathrm{Q}_{3}{ }^{\text {b }}$ | Maximum |
| All ELS-II |  |  |  |  |  |
| ANC | -177 | -84 | -44 | -10 | 21 |
| pH | -0.97 | -0.34 | -0.18 | -0.02 | 0.7 |
| $\mathrm{SO}_{4}{ }^{2-}$ | -70 | -6 | 3 | 16 | 97 |
| $\mathrm{NO}_{3}{ }^{-}$ | -6 | -0.1 | 2 | 6 | 33 |
| Base cations | -335 | -85 | -49 | -16 | 32 |
| DOC | -7.0 | -1.5 | -0.5 | 0.1 | 5.0 |
| $\mathrm{Al}_{\text {im }}$ | -101 | -10 | -7 | -2 | 217 |
| Fall ANC $\leq 50 \mu \mathrm{eq} / \mathrm{L}^{\text {c }}$ |  |  |  |  |  |
| ANC | -31 | -10 | -3 | 4 | 21 |
| pH | -0.76 | -0.28 | -0.11 | 0.07 | 0.70 |
| $\mathrm{SO}_{4}{ }^{2-}$ | -70 | -9 | -2 | 6 | 42 |
| $\mathrm{NO}_{3}{ }^{-}$ | -2 | 1 | 2 | 9 | 33 |
| Base cations | -335 | -22 | -6 | 2 | 32 |
| DOC | -7.0 | -0.8 | -0.4 | 0.2 | 5.0 |
| $\mathrm{AL}_{\text {im }}$ | -101 | -9 | -1 | 42 | 217 |
| Fall ANC $>\mathbf{5 0} \mu \mathrm{eq} / \mathrm{L}^{\text {c }}$ |  |  |  |  |  |
| ANC | -177 | -97 | -60 | -35 | 11 |
| pH | -0.97 | -0.39 | -0.19 | -0.06 | 0.31 |
| $\mathrm{SO}_{4}{ }^{2-}$ | -65 | -5 | 3 | 20 | 97 |
| $\mathrm{NO}_{3}{ }^{-}$ | -6 | 0 | 2 | 5 | 14 |
| Base cations | -279 | -112 | -69 | -35 | 8 |
| DOC | -5.8 | -1.7 | -0.6 | 0.1 | 3.3 |
| $\mathrm{Al}_{\text {im }}$ | -24 | -10 | -8 | -4 | 29 |
| ${ }^{\text {a }}$ All units are in $\mu \mathrm{eq} / \mathrm{L}$ except for $\mathrm{pH}, \mathrm{DOC}(\mathrm{mg} / \mathrm{L})$, and aluminum ( $\mu \mathrm{g} / \mathrm{L}$ ). |  |  |  |  |  |
| ${ }^{\text {b }} Q_{1}=25$ th percentile, $Q_{3}=75$ th percentile. |  |  |  |  |  |
| There were an | 000 ELS-II lak | th fall ANC | /L and 2, | with fal | q/L. |

Table 5-9. Regional Population Characteristics of Between-Season Chemical Changes (Spring 1986 - Fall 1986) in Lakes with Fall 1986 ANC $\leq 50 \mu \mathrm{eq} / \mathrm{L}^{\text {a }}$

| Variable | Fall ANC $\leq 50 \mu \mathrm{eq} / \mathrm{L}$ Spring 1986 - Fall 1986 |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | Minimum | $Q_{1}{ }^{\text {b }}$ | Median | $Q_{3}{ }^{\text {b }}$ | Maximum |
| Adirondacks ${ }^{\text {c }}$ |  |  |  |  |  |
| ANC | -28 | -10 | -7 | 0 | 15 |
| pH | -0.50 | -0.24 | -0.08 | 0.04 | 0.27 |
| $\mathrm{SO}_{4}{ }^{2-}$ | -25 | -14 | -6 | 1 | 9 |
| $\mathrm{NO}_{3}{ }^{-}$ | 1 | 6 | 13 | 19 | 33 |
| Base cations | -16 | -5 | 1 | 7 | 25 |
| DOC | -2.6 | -1.4 | -0.7 | -0.3 | 5.0 |
| $\mathrm{Al}_{\text {im }}$ | -101 | -5 | 36 | 71 | 217 |

Poconos/Catskills ${ }^{\text {c }}$

| ANC | -31 | -5 | -4 | -1 | 19 |
| :--- | :---: | :---: | :--- | :---: | :---: |
| pH | -0.58 | -0.33 | -0.26 | -0.12 | 0.7 |
| $\mathrm{SO}_{4}{ }^{2-}$ | -71 | -27 | -6 | 9 | 39 |
| $\mathrm{NO}_{3}{ }^{-}$ | -1 | 0 | 1 | 6 | 24 |
| Base cations | -83 | -7 | -6 | 5 | 32 |
| DOC | -1.2 | -1.0 | -0.4 | 0.1 | 0.2 |
| $\mathrm{Al}_{\mathrm{im}}$ | -29 | -6 | 15 | 74 | 202 |

New England Subregions ${ }^{\text {c }}$

| ANC | -23 | -12 | -1 | 10 | 21 |
| :--- | :---: | :---: | :---: | :---: | :---: |
| pH | -0.76 | -0.30 | -0.05 | 0.08 | 0.33 |
| $\mathrm{SO}_{4}{ }^{2-}$ | -42 | -5 | 3 | 12 | 42 |
| $\mathrm{NO}_{3}{ }^{-}$ | -2 | 0 | 1 | 2 | 10 |
| Base cations $_{\text {DOC }}$ | -335 | -34 | -19 | -6 | 19 |
| $\mathrm{Al}_{\text {im }}$ | -7.0 | -0.6 | -0.1 | 0.4 | 1.3 |
|  | -24 | -12 | -8 | 19 | 48 |

[^13]
### 5.4.2.1 ANC/pH

Seasonal distributions of ANC show that ANC was lowest in spring, highest in fall, and intermediate in summer (Figure 5-16). ANC differences were most pronounced at higher ANC (> 50-100 $\mu \mathrm{eq} / \mathrm{L}$ ). The typical ELS-II lake (median) had ANC $44 \mu \mathrm{eq} / \mathrm{L}$ lower in spring than fall (Table 5-8). In lakes with ANC $\leq 50 \mu \mathrm{eq} / \mathrm{L}$, the median spring minus fall ANC change was only $-3 \mu \mathrm{eq} / \mathrm{L}$, and over half the lake population changed by $<10 \mu \mathrm{eq} / \mathrm{L}$. On the other hand, high ANC lakes decreased by a median $60 \mu \mathrm{eq} / \mathrm{L}$ between spring and fall. Three-fourths of the high ANC lakes had a spring ANC depression > $35 \mu \mathrm{eq} / \mathrm{L}$. Chi-square analysis indicates that the spring population had a significantly different ANC distribution than the fall population in all ELS-II sample clusters (see Appendix C, Table $\mathrm{C}-2$ ).

As with ANC, pH was generally lowest in the spring, highest in the fall, and intermediate in the summer (Figure 5-17). The largest seasonal differences in pH were observed in higher pH lakes. Note that the maximum observed pH (9.08) occurred in the summer, probably due to high rates of photosynthesis. The 75th percentile in summer, however, was lower than that measured in the fall (Figure 5-18). In the ELS-II target population, the median pH decrease from fall to spring was 0.18 (Table 5-8). Fall/spring pH changes were similar in both high and low ANC lakes. No lake changed by more than 1 pH unit, and most lakes changed by $<0.5 \mathrm{pH}$ units. Fall/spring changes in ANC and pH in low ANC systems were fairly similar between regions (Table 5-9).

### 5.4.2.2 Inorganic Acid Anions

Seasonal distributions of sulfate concentration were similar in spring, summer, and fall (Figures 5-19 and 5-20). Fall/spring changes in sulfate concentration were small in both high and low ANC lakes (median $=3 \mu \mathrm{eq} / \mathrm{L}$; interquartile range $=-6$ to $16 \mu \mathrm{eq} / \mathrm{L}$; Table 5-8).

Seasonal distributions of nitrate concentration show the lowest concentrations in the summer and the highest concentrations in the spring (Figure 5-21). Fall values are intermediate between spring and summer values. Over $75 \%$ of the ELS-II lakes have nitrate concentrations $<1 \mu \mathrm{eq} / \mathrm{L}$ in the summer. In contrast, the 75th percentile for nitrate in the spring is $7.7 \mu \mathrm{eq} / \mathrm{L}$ (Figure 5-20). Thus biological activity in the summer is very effective at removing nitrate in almost all the ELS-II lakes. Reduced biological activity as temperatures decrease in the fall is probably responsible for the observed nitrate increase between summer and fall. It should be noted, however, that the 25th percentile for nitrate is below the SDL for nitrate ( $0.5-0.9 \mu \mathrm{eq} / \mathrm{L}$ ) in all seasons. Due to the low spring nitrate concentrations in most ELS-II lakes, fall/spring nitrate changes were typically small (interquartile range $=0-6 \mu \mathrm{eq} / \mathrm{L}$ ). The largest observed spring increase in nitrate concentrations was $32 \mu \mathrm{eq} / \mathrm{L}$.

Kelly et al. (1990) have proposed that a summer surface nitrate concentration of $1 \mu \mathrm{eq} / \mathrm{L}$ be used as an indicator of lakes that have exceeded their algal nitrogen requirements. Lakes with summer nitrate concentrations > $1 \mu \mathrm{eq} / \mathrm{L}$ would thus be susceptible to lake acidification if nitrate loadings were to increase. Based on ELS-II summer surface nitrate data (Figure 5-21), 25\% of the ELS-II target lake population had nitrate concentrations $>1 \mu \mathrm{eq} / \mathrm{L}$. Just over $8 \%$ of the ELS-II lake population had summer nitrate concentrations $>5 \mu \mathrm{eq} / \mathrm{L}$. These higher nitrate lakes lakes were located primarily in the


Figure 5-16. ANC population distribution for the spring, summer, and fall seasonal surveys and comparison of spring 1986 and fall 1986 ANC in ELS-II lakes.


Figure 5-17. pH population distribution for the spring, summer, and fall seasonal surveys and comparison of spring 1986 and fall 1986 pH in ELS-II lakes.


SPRING 1986

SUMMER 1986

FALL 1986

Figure 5-18. Population minimum, 25th percentile, median, 75th percentile, and maximum values in each of the three ELS-II seasonal surveys for (a) ANC, and (b) pH .


Figure 5-19. Sulfate population distribution for the spring, summer, and fall seasonal surveys and comparison of spring 1986 and fall 1986 sulfate in ELS-II lakes.



Figure 5-20. Population minimum, 25th percentile, median, 75th percentile, and maximum values in each of the three ELS-II seasonal surveys for (a) sulfate, and (b) nitrate.


Figure 5-21. Nitrate population distribution for the spring, summer, and fall seasonal surveys and comparison of spring 1986 and fall 1986 nitrate in ELS-II lakes.

Adirondacks and are of high interest with respect to possible future increases in nitrate due to nitrate breakthrough.

### 5.4.2.3 Sum of Base Cations

Sum of base cations was generally lowest in the spring and highest in the fall (Figure 5-22). At low base cation concentrations ( $<200 \mu \mathrm{eq} / \mathrm{L}$ ), spring and fall concentrations were similar, whereas at higher concentrations, spring values were almost all lower than fall values (Figure 5-22). As base cation concentrations are closely related to ANC, these changes are clearly evident in the comparison of low and high ANC lakes (Table 5-8). Median spring/fall change in base cations decreased by only $6 \mu \mathrm{eq} / \mathrm{L}$ in low ANC ( $\leq 50 \mu \mathrm{eq} / \mathrm{L}$ ) lakes compared to a $69 \mu \mathrm{eq} / \mathrm{L}$ decrease in high ANC lakes.

### 5.4.2.4 DOC/Aluminum

Fall and summer distributions of DOC are very similar but spring distributions are noticeably lower (Figures $5-23$ and 5-24). Lower spring concentrations are probably attributable to dilution during spring runoff and decreased decomposition during the colder winter months. The median DOC increase from spring to fall was $0.5 \mathrm{mg} / \mathrm{L}$ (interquartile range $=-0.1$ to $1.5 \mathrm{mg} / \mathrm{L}$ ) and was about the same in both high and low ANC lakes (Table 5-8).

Before discussing inorganic monomeric aluminum ( $\mathrm{Al}_{\mathrm{im}}$ ), it should be emphasized that the $\mathrm{Al}_{\mathrm{im}}$ SDL is about $20 \mu \mathrm{~g} / \mathrm{L}$ and values below this may not actually contain any $\mathrm{Al}_{\mathrm{im}}$. About $80 \%$ of the lakes in all seasons had $\mathrm{Al}_{\mathrm{im}}<20 \mu \mathrm{~g} / \mathrm{L}$ (Figure 5-25). Due to the large number of lakes with $\mathrm{Al}_{\mathrm{im}}$ below the SDL, medians and quartiles of spring/fall $\mathrm{Al}_{\mathrm{im}}$ changes are negligible (Table 5-8). There was, however, a consistent pattern of higher spring than fall $\mathrm{Al}_{\mathrm{im}}$ concentrations in lakes with $\mathrm{Al}_{\mathrm{im}}$ concentrations $>50$ $\mu \mathrm{g} / \mathrm{L}$ (Figure 5-25). Due to the strong control of pH on aluminum solubility, all the lakes with elevated $\mathrm{Al}_{\mathrm{im}}$ ( $>50 \mu \mathrm{~g} / \mathrm{L}$ ) had $\mathrm{pH}<6.0$. Thus lakes with ANC $>50 \mu \mathrm{eq} / \mathrm{L}$ (all had $\mathrm{pH}>6.0$ ) had very low $\mathrm{Al}_{\mathrm{im}}$ concentrations and showed no significant seasonal changes (Table $5-8$ ). In lakes with ANC $\leq 50 \mu \mathrm{eq} / \mathrm{L}$, the upper quartile showed significantly higher $\mathrm{Al}_{\mathrm{i}}$ in the spring than in the fall ( $42-217 \mu \mathrm{~g} / \mathrm{L}$ ). The majority of low ANC lakes, however, had little change in $\mathrm{Al}_{\mathrm{im}}$ (Table 5-8). In low ANC lakes, spring/fall changes in $\mathrm{Al}_{\mathrm{im}}$ concentrations were most noticeable in the Adirondacks and Poconos/Catskills (Table 5-9). Fewer low ANC lakes in New England showed significant fall to spring $\mathrm{Al}_{\mathrm{im}}$ increases (75th percentile $=19 \mu \mathrm{~g} / \mathrm{L}$; maximum $=48 \mu \mathrm{~g} / \mathrm{L})$. In contrast, the 75 th percentiles for spring Al $\mathrm{im}_{\text {im }}$ increases in the Adirondacks and Poconos/Catskills low ANC lakes were 74 and $71 \mu \mathrm{~g} / \mathrm{L}$, respectively (maximum increases were 217 and $202 \mu \mathrm{~g} / \mathrm{L}$ ).
$\mathrm{Al}_{\mathrm{im}}$ concentrations of $50-200 \mu \mathrm{~g} / \mathrm{L}$ have often been used as rough indicators of stressful levels of aluminum on some aquatic organisms (L. Baker et al., 1990), although the toxic effects of aluminum vary greatly among species and are dependent on the concentrations of other ions (especially $\mathrm{H}^{+}$and $\mathrm{Ca}^{2+}$; J. Baker et al., 1990a). Percentages of ELS-II lakes with $\mathrm{Al}_{\mathrm{im}}$ concentrations above the indicator values were always highest or the same in the spring compared to fall and summer (Table 5-10). The


Figure 5-22. Sum of base cation population distribution for the spring, summer, and fall seasonal surveys and comparison of spring 1986 and fall 1986 sum of base cations in ELS-II lakes.


Figure 5-23. DOC population distribution for the spring, summer, and fall seasonal surveys and comparison of spring 1986 and fall 1986 DOC in ELS-II lakes.


Figure 5-24. Population minimum, 25th percentile, median, 75th percentile, and maximum values in each of the three ELS-II seasonal surveys for (a) sum of base cations, (b) DOC, and (c) inorganic monomeric aluminum.


Figure 5-25. Inorganic monomeric aluminum population distribution for the spring, summer, and fall seasonal surveys and comparison of spring 1986 and fall 1986 inorganic monomeric aluminum in ELS-II lakes.

Table 5-10. Percentage of ELS-II Lakes with Inorganic Monomeric Aluminum ( $\mathrm{Al}_{\mathrm{im}}$ ) Concentrations above Reference Values

| Reference Value | Region | \% of ELS-II Lakes |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  | Spring | Summer | Fall |
| $\mathrm{Al}_{\text {im }}>50 \mu \mathrm{~g} / \mathrm{L}$ | Adirondacks | 32 | 29 | 24 |
|  | Poconos/Catskills | 13 | 7 | 7 |
|  | New England | 5 | 4 | 4 |
|  | All ELS-II | 11 | 9 | 8 |
| $\mathrm{Al}_{\mathrm{im}}>100 \mu \mathrm{~g} / \mathrm{L}$ | Adirondacks | 24 | 16 | 15 |
|  | Poconos/Catskills | 7 | 2 | 2 |
|  | New England | 2 | 1 | 2 |
|  | All ELS-II | 7 | 4 | 4 |
| $\mathrm{Al}_{\mathrm{im}}>200 \mu \mathrm{~g} / \mathrm{L}$ | Adirondacks | 13 | 8 | 10 |
|  | Poconos/Catskills | 2 | 2 | 2 |
|  | New England | 1 | 0 | 0 |
|  | All ELS-II | 3 | 2 | 2 |

Adirondacks have the highest percentage of lakes with elevated $\mathrm{Al}_{\mathrm{im}}$ concentrations ( $32 \%>50 \mu \mathrm{~g} / \mathrm{L}$ and $13 \%>200 \mu \mathrm{~g} / \mathrm{L}$ in the spring). Fewer lakes in New England had elevated $\mathrm{Al}_{\mathrm{im}}(5 \%>50 \mu \mathrm{~g} / \mathrm{L})$ and there was almost no change in the percentage of high $\mathrm{Al}_{\mathrm{im}}$ systems among the spring, summer, and fall seasonal surveys (Table 5-10). These similar percentages reflect the small $\mathrm{Al}_{\mathrm{im}}$ changes between spring and fall in New England (Table 5-9). Seasonal changes in the percentage of high $\mathrm{Al}_{\mathrm{im}}$ lakes were much more pronounced in the Adirondacks and the Poconos/Catskills.

### 5.4.3 Conclusions: Among Season Variability

ANC, $\mathrm{pH}, \mathrm{DOC}$, and sum of base cations were lower in the spring than in the summer or fall. Summer concentrations for these ions were more similar to concentrations in the fall than in spring. Nitrate and inorganic monomeric aluminum concentrations were highest in the spring relative to summer and fall, although they were found in very low concentrations in all seasons in the majority of ELS-II lakes. ELS-II population estimates show that there were $24 \%$ more acidic lakes (ANC $\leq 0$ ) in the spring than in the fall. This corresponds to an increase in the percentage of acidic ELS-II lakes from 9\% to 11\%. Similarly, the percentage of ELS-II lakes with ANC $\leq 50 \mu \mathrm{eq} / \mathrm{L}$ increased from $25 \%$ to $34 \%$ (fall to spring) and the percentage with $\mathrm{ANC} \leq 100 \mu \mathrm{eq} / \mathrm{L}$ increased from $43 \%$ to $62 \%$. The number of low pH lakes was also higher in the spring than the fall. The percentage of ELS-II lakes with $\mathrm{pH} \leq 5.0$ increased from $4 \%$ to $5 \%$, those with $\mathrm{pH} \leq 5.5$ increased from $12 \%$ to $14 \%$, and lakes with $\mathrm{pH} \leq 6.0$ increased from $19 \%$ to $27 \%$. The greatest spring depressions in ANC (relative to fall) were observed in ELS-II lakes with the highest ANC ( $200-400 \mu \mathrm{eq} / \mathrm{L}$ ). In lakes with ANC $>50 \mu \mathrm{eq} / \mathrm{L}$, the median ANC depression was 60 $\mu \mathrm{eq} / \mathrm{L}$ and was associated with decreases in base cation concentrations, probably due to dilution by low ANC, low base cation spring snowmelt runoff. In low ANC ( $\leqslant 50 \mu \mathrm{eq} / \mathrm{L}$ ) lakes, spring ANC depressions were small (median $=3 \mu \mathrm{eq} / \mathrm{L}$; median pH decrease $=0.1 \mathrm{pH}$ unit) and were associated with increases in nitrate and inorganic monomeric aluminum. Sulfate concentrations were very similar in the spring, summer, and fall seasonal surveys.

## SECTION 6

## SYNTHESIS AND DISCUSSION

### 6.1 ASSESSMENT OF ELS-II VARIABILITY

### 6.1.1 Components of Variability

Data from ELS-II provides an excellent opportunity to assess the relative importance of different factors on the observed variability of lakewater chemistry on a regional scale. Lakewater chemistry varies along a number of different annual, seasonal, daily, and hourly time scales. Spatial variability is also an important source of lakewater chemical variability. Spatial variability includes both differences in lakewater chemistry within an individual basin and differences among lakes in a region. Variability is also introduced by the methods used to collect, transport, and store water samples, and by the analytical techniques used to measure the variables of interest. The variability in ELS-II data was examined to determine the influence of these temporal, spatial, and analytical components.

### 6.1.2 Pooling Variance Estimates

Five components of variability were assessed for the ELS-II data: analytical, within-season temporal, among-season temporal, between-year temporal, and among-lake spatial. Within-lake spatial variability is marginally accounted for in the within-season temporal component in the ELS-II data, because the multiple within-season observations in the Fall Variability Study were collected from independently selected locations on the study lakes. As the objective was to collect samples from epilimnetic locations in the deepest part of the lake, this assessment does not address the questions of littoral versus profundal variability and depth variability.

Temporal variability components were assessed by calculating a standard deviation and sum of squares error (SSE) for each study lake with multiple observations for the temporal component of interest. For example, the among-season component was analyzed by calculating the mean, standard deviation, and SSE of the three seasonal measurements (spring, summer, and fall seasonal surveys) for each of the 145 ELS-II study lakes:

$$
\begin{equation*}
\text { SSE }=\sum_{i=1}^{n}\left(X_{i}-X_{\text {mean }}\right)^{2} \tag{11}
\end{equation*}
$$

where $X_{i}$ is the observation, $X_{\text {mean }}$ is the mean of the multiple observations, and $n$ equals the number of observations in each study lake for the temporal component of interest. For the among-season and within-fall-season components, there were three observations at each lake: three visits in the Fall

Variability Study and three separate seasonal visits ( $\mathrm{n}=3$ ). There were only two observations ( $\mathrm{n}=2$ ) for between-year variability (fall 1984/fall 1986). Note that within-fall variability could only be assessed for the 41 lakes in the Fall Variability Study that had multiple within-season observations. A pooled standard deviation ( $\mathrm{SD}_{\text {pool }}$ ) was calculated for each temporal component by dividing the total SSE in the population by the total degrees of freedom:

$$
\begin{equation*}
S D_{\text {pool }}=\underset{S}{\left[\Sigma S S E / \sum_{S}(n-1)\right]^{0.5}} \tag{12}
\end{equation*}
$$

where $\Sigma$ over S indicates the summation of all the lakes in the population of interest.
In the rest of this section, we refer to among-lake variability as spatial variability. Spatial variability was simply calculated as the standard deviation of the lake chemistry at the ELS-I index site in fall 1986 in all lakes in the study population. The fall 1986 data were chosen, as opposed to spring or summer data, because fall data are common to all the components of temporal variability. Analytical variability was assessed in the same manner as temporal variability using sample duplicates. $A n S D_{\text {pool }}$ was calculated for each variable using equations 11 and 12 and the 84 duplicate sample pairs $(\mathrm{n}=2)$ collected throughout ELS-II.

### 6.1.3 Relative Importance of Variability Components

The $\mathrm{SD}_{\text {pool }}$ is a single value that can be used to compare the magnitude of variability of the different components. It is also possible to plot CDFs of the individual lake standard deviations for the different temporal components to study the distribution of lake temporal variability across the ELS-II target population. We have constructed two CDFs for each study variable: one for all 145 lakes in the ELS-II target population in which among-season and between-year variability is compared, and one for the 41 Fall Variability Study lakes in which within-season, among-season, and between-year variability can be compared. $\mathrm{SD}_{\text {pool }}$ values are also presented for all data and the Fall Variability Study lake subset. Only one estimate of the $\mathrm{SD}_{\text {pool }}$ for analytical variability, based on all available ELS-II sample duplicates, was calculated and it is presented for both groups. Sample duplicates were not collected from all lakes. The analytical $S D_{\text {pool }}$ is based on 84 duplicate pairs from 60 different lakes.

As measured in ELS-II, the different components of variability are not independent. Analytical variability is nested within all the other variability components. Similarly, within-season variability is a part of among-season and between-year variability because ELS-II samples were collected throughout the seasonal index period. The $S D_{\text {pool }}$ values for the different components of variability in ELS-II are presented in Table 6-1. To assess pooled variance, in order to make estimates of the percent of variance accounted for by the different components, the $S_{\text {pool }}$ values in Table 6-1 can be squared.

Table 6-1. Pooled Standard Deviation of Multiple Observations in ELS-II for Duplicate Samples (Analytical), between Lakes (Spatial), within Season (Fall 1986), among Season (Spring, Winter, Fall 1986), and between Year (Fall 1984/Fall 1986) ${ }^{\text {a }}$

| Variable | Pooled Standard Deviation |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | Analytical ${ }^{\text {b }}$ | Within | Among | Between | Spatial ${ }^{\text {c }}$ |
| ALL DATA ( $\mathrm{n}=145$ ) |  |  |  |  |  |
| ANC | 8.3 | - | 28.0 | 18.8 | 96 |
| pH | 0.10 | - | 0.25 | 0.14 | 0.77 |
| $\mathrm{SO}_{4}{ }^{2-}$ | 2.9 | - | 13.4 | 12.8 | 47 |
| $\mathrm{NO}_{3}{ }^{-}$ | 0.36 | - | 5.1 | 1.9 | 4.4 |
| Base cations | 12.4 | - | 38.6 | 57.6 | 225 |
| DOC | 0.10 | - | 1.1 | 0.75 | 2.6 |

FALL VARIABILITY LAKES $(\mathrm{n}=41)$

| ANC | 8.3 | 7.5 | 22.8 | 16.0 | 87.3 |
| :--- | :---: | :---: | :---: | :---: | :---: |
| pH | 0.10 | 0.06 | 0.19 | 0.13 | 0.76 |
| $\mathrm{SO}_{4}{ }^{2-}$ | 2.9 | 11.2 | 13.8 | 15.1 | 52.6 |
| $\mathrm{NO}_{3}{ }^{-}$ | 0.36 | 0.95 | 5.3 | 2.3 | 5.3 |
| Base cations | 12.4 | 12.2 | 41.2 | 71.7 | 267.6 |
| DOC | 0.10 | 0.20 | 1.1 | 0.58 | 2.5 |

[^14]
### 6.1.3.1 ANC and pH

For ANC and pH , within-season $\mathrm{SD}_{\text {pool }}$ values and analytical $\mathrm{SD}_{\text {pool }}$ values were very similar, indicating that the major component of within-season variability is due to analytical variability (Table 6-1). ANC and pH spatial variability among lakes is much greater than any of the temporal or analytical components ( SD $_{\text {pool }}{ }^{3-10}$ times higher). Between-year $\mathrm{SD}_{\text {pool }}$ values for ANC and pH were about twice those of within-season values, whereas among-season $\mathrm{SD}_{\text {pool }}$ values were about three times withinseason values (Table 6-1). For both ANC and pH , among-season variability was consistently higher than between-year variability, which was almost always higher than within-season variability (Figures 6-1a,b).

### 6.1.3.2 Sulfate and Nitrate

Sulfate spatial variability among lakes was much greater than temporal or analytical variability (Table 6-1), indicating that regional sulfate deposition differences or watershed sulfate source differences exert a much greater control on lakewater sulfate concentrations than temporal changes within a lake. Within-season, among-season, and between-year sulfate changes were fairly similar in both the Fall Variability Study lakes and all ELS-II lakes (Figure 6-2a), although among-season variability was usually the largest. Over $80 \%$ of the ELS-II lake population had temporal standard deviations in sulfate concentration $<20 \mu \mathrm{eq} / \mathrm{L}$. As within-season changes are nested within among-season and betweenyear changes, these data indicate that short-term (day-to-day or week-to-week) changes are an important component of longer term sulfate temporal variability. The within-season $\mathrm{SD}_{\text {pool }}$ for sulfate was about four times the analytical $\mathrm{SD}_{\text {pooi, }}$, so analytical variability accounts for only a minor portion of the sulfate temporal variability.

Among-season $\mathrm{SD}_{\text {pool }}$ values for nitrate were the same or greater than fall spatial variability (Table $6-1$ ). Thus, the seasonal changes in nitrate concentration within a lake are about the same as the differences in fall nitrate concentration among the ELS-II lakes in the northeastern United States. Spring spatial variability $\left(\mathrm{SD}_{\text {pool }}=10 \mu \mathrm{eq} / \mathrm{L}\right)$, however, was twice as high as fall spatial variability. Among-
 higher than within-season $\mathrm{SD}_{\text {pool }}$ values, and 10 times higher than analytical $\mathrm{SD}_{\text {pool }}$ values. Therefore, population estimates of the regional distribution of nitrate are very dependent on the season in which they are measured. Nitrate temporal standard deviations, however, were very low ( $75 \%<5 \mu \mathrm{eq} / \mathrm{L}$ ) due to the low nitrate concentrations in most lakes (Figure 6-2b).

### 6.1.3.3 Sum of Base Cations

The spatial $S D_{\text {pool }}$ for sum of base cations is four times that of the largest temporal component (Table 6-1), indicating that differences in watershed base cation mobilization among lakes accounts for far more regional variability than temporal changes within lakes. In terms of temporal variability, between-year $\mathrm{SD}_{\text {pool }}$ values are the same or slightly higher than among-season $\mathrm{SD}_{\text {pool }}$ values (Figure 6-3a). Thus, year-to-year changes in hydrologic conditions appear to be equally as important in


Figure 6-1. Population distribution of the temporal standard deviation in the 41 Fall Variability Study lakes for (a) ANC, and (b) pH.


Figure 6-2. Population distribution of the temporal standard deviation in the 41 Fall Variability Study lakes for (a) sulfate, and (b) nitrate.


Figure 6-3. Population distribution of the temporal standard deviation in the 41 Fall Variability Study lakes for (a) sum of base cations, and (b) DOC.
controlling base cation concentrations as seasonal changes, at least between the 1984 and 1986 years. Whether between-year regional lakewater base cation changes would be as high for two years that were more hydrologically similar than 1984 and 1986 is unknown. Within-season SD $_{\text {pool }}$ values were about
 For base cations, analytical variability is thus the major component of within-season variability. Base cations were very stable during the fall index period compared to annual and seasonal variability.

### 6.1.3.4 DOC

Within-season DOC SD $_{\text {pool }}$ values were twice as high as analytical $\mathrm{SD}_{\text {poot }}$ values (Table 6-1). Among-season variability was consistently higher than between-year variability, which was higher or the same as within-season variability (Figure 6-3b). Overall, among-lake spatial variability was higher than any of the temporal variability components.

### 6.1.4 Conclusions and Comparison to Long Term Monitoring Data

With the exception of nitrate, among-lake spatial variability is much larger than temporal or analytical variability. Thus the regional factors explaining differences among lakes are more important than within-lake temporal variability in explaining the distribution of $\mathrm{ANC}, \mathrm{pH}$, sulfate, DOC , and base cations in the ELS-II population. In terms of temporal variability, for ANC, $\mathrm{pH}, \mathrm{DOC}$ and nitrate:

$$
\text { among-season variability }>\text { between-year variability } \gg \text { within-season variability. }
$$

For base cations:
between-year variability $>$ among-season variability $\gg$ within-season variability.

For sulfate, the three components of temporal variability were about equal. Analytical variability was the major component of within-season variability for $\mathrm{ANC}, \mathrm{pH}$ and base cations.
L. Baker et al. (1990) analyzed data from EPA's Long Term Monitoring (LTM) Project (Newell et al., 1987) to assess among-year and among-season variability in lakewater chemistry. Based on 15 lakes in the Adirondacks, and 5 lakes in Maine, they found that year-to-year changes in fall index values between 1982 and 1988 fell within a consistent range. No one year stood out as being atypical. Comparisons of spring and fall chemistry in the LTM data showed strong correlations. Spring ANC and pH were typically lower than or the same as fall values and spring values could often be predicted with moderate success from fall values. These predictive relationships, however, were not consistent among different years in the 1982-1988 study period (Newell, 1987). Overall, in all the LTM data from lakes in Maine, Vermont, the Adirondacks, and the Upper Midwest, among-lake variability exceeded annual and seasonal temporal
variability (Newell et al., 1987). As in ElS-II, spatial variability accounts for more variability in regional lakewater chemistry than temporal variability. Thus, Newell et al. (1987) have suggested that sampling more lakes in a region would allow for a more accurate characterization of regional trends than would sampling a similar number of lakes more intensively: an important consideration for future regional monitoring efforts that is supported by the analyses reported here.

### 6.2 ROBUSTNESS OF THE ELS-I FALL INDEX SAMPLE

### 6.2.1 Fall Index Variability

One of the major goals of ELS-II was to assess the sampling error associated with the ELS-I fall index sample. The success of ELS-I was based on the premise that a single fall epilimnion sample adequately characterizes the acid-base status of a study lake and that these data could then be used to estimate regional chronic lake acidity. All the within-season data collected in ELS-II support the adequacy of the fall index concept. Overall, variability among the three lake visits at independently selected sites in the Fall Variability Study was very small and was about equal to analytical variability for ANC, pH , and base cations. Population estimates of the proportion of lakes with ANC or pH below reference values were not greatly affected by fall temporal or within-lake site selection variability. Conclusions about the acid-base status of northeastern lakes would have been the same if sampling had occurred at any of the three sample visits or sampling locations. Thus, in terms of variables of interest for acidic deposition effects, mid-lake epilimnetic conditions during the fall index period are well represented by a single sample. Collection of additional samples during the fall index period would have yielded little additional information on the acid-base status of lakes.

### 6.2.2 Predicting Spring Conditions from Fall Index Data

A second aspect of the robustness of the fall index sample is how well it relates to conditions in the other seasons of the year. In particular, we are interested in how well the fall index period relates to spring conditions when ANC and pH are lowest. The large-scale regional survey effort in ELS-I was not conducted in the spring because of the difficulty in sampling a large number of lakes in four regions of the country during a narrow spring window that was difficult to predict. Fall was selected as the index period in ELS-I because it was a well-mixed period of reasonable duration (about 6 weeks) during which samples from more than 1,600 lakes could be collected. In addition, chemical conditions are less varying in fall than in spring, which fit the objective of ELS-I, which was to assess chronic acidity rather than episodic acidity. By utilizing the spring/fall relationship in ELS-II lakes, however, we can estimate what spring conditions would have been like in ELS-I.

Spring chemistry in ELS-Il lakes was strongly correlated with fall chemistry (Table 6-2; also see Figures $5-16,5-17,5-19,5-21,5-22,5-23$, and $5-25)$. Due to the fact that spring/fall chemical differences varied in the different ANC classes or clusters, spring/fall regressions were performed separately within the three ANC clusters used in the ELS-II site selection (see Section 2.3.2). In the lowest ANC sample cluster ( $\leq 25 \mu \mathrm{eq} / \mathrm{L}$ ), fall chemistry accounted for more than $60 \%$ of the variance in spring chemistry ( $r^{2}$ $>0.6$ ) for all of the studied variables (Table 6-2). The root mean square error (RMSE) or average residual for predicting spring ANC and pH from fall values was $11 \mu \mathrm{eq} / \mathrm{L}$ and 0.2 pH units, respectively. Similar $r^{2}$ values were seen in the two higher ANC clusters, with the exception of $\mathrm{Al}_{\mathrm{im}}$ (Table 6-2). Al $\mathrm{Al}_{\mathrm{im}}$ concentrations were almost always below the system decision limit (not different from blank values) in the higher ANC clusters (due to high pH ) and thus there was poor fall/spring predictive ability. For other variables $\left(\mathrm{SO}_{4}{ }^{2-}, \mathrm{NO}_{3}{ }^{-}\right.$, base cations, DOC$)$, there was a strong relationship between the measured fall and spring chemistry. A strong relationship ( $r^{2}=0.82$ ) between spring 1986 minimum lake outlet ANC and ELS-I fall index ANC has also been noted by Eshleman (1988), using the data of Driscoll (1986), in nine Adirondack lakes.

We can make a rough estimate of the acid-base status of the northeastern United States ELS-I target population in the spring by using the regression equations in Table 6-2 for the appropriate ANC clusters in the ELS-I data. For this exercise, we assume that lakes with ANC $>400$ (above the ELS-II cutoff) have $\mathrm{ANC}>50$ and $\mathrm{pH}>6$ in the spring. Recognize that this estimate makes the assumption that the spring/fall relationship in ELS-II (1986) is the same as the spring/fall relationship in ELS-I (1984). As noted earlier, Newell (1987) found that the spring/fall relationship in the LTM data was not always the same in different years or in different regions. The conclusions from LTM data, however, are based on individual lakes. Changes in regional lake populations are likely to be different and possibly more stable among years.

In fall 1984, 6.2\% (441 lakes) of the ELS-I lakes in the Northeast were acidic, and $21.7 \%$ had ANC $\leq 50 \mu \mathrm{eq} / \mathrm{L}$ (see Table 5-3). Using the fall/spring regressions, we would estimate that $8.1 \%$ ( 577 lakes) of the ELS-I lakes would have been acidic in the spring and $28.0 \%$ would have had ANC $\leq 50 \mu \mathrm{eq} / \mathrm{L}$. Similarly, in terms of $\mathrm{pH}, 3.4 \%$ of the ELS-I lakes in the Northeast had $\mathrm{pH} \leq 5.0$ and $8.6 \%$ had $\mathrm{pH} \leq 5.5$ in fall 1984 (see Table 5-3). Regression estimates for spring conditions in the northeastern ELS-I lakes show only small increases in the percentage of low pH lakes ( $3.6 \%$ with $\mathrm{pH} \leq 5.0$, and $8.8 \%$ with pH $\leq 5.5$ in spring). Estimates of the percentage of ELS-I lakes with $\mathrm{pH} \leq 6.0$ in the spring ( $17.1 \%$ ), however, are substantially larger than the measured fall percentage (12.8\%). Although conditions are more acidic in the spring, spring conditions are strongly related to fall index conditions. Overall, ELS-II results support the conclusion that the ELS fall index sample is a robust estimator of the acid-base status of lakes, at least in the northeastern United States.

Table 6-2. Regression Statistics for the Relationship between Spring Chemistry (Dependent Variable) and Fall Chemistry (Independent Variable) in 1986 ELS-II Data ${ }^{a}$

| Variable | $r^{2}$ | slope | y-intercept | RMSE $^{\text {b }}$ |
| :--- | :---: | :---: | :---: | :---: |
| Cluster I (ANC $\leq 25 \mu \mathrm{eq} / \mathrm{L})$ |  |  |  |  |
| ANC | 0.65 | 0.974 | -3.74 | 11.1 |
| pH | 0.77 | 0.834 | 0.815 | 0.21 |
| $\mathrm{SO}_{4}{ }^{2 .}$ | 0.72 | 0.744 | 28.3 | 16.6 |
| $\mathrm{NO}_{3}{ }^{-}$ | 0.74 | 2.14 | 3.19 | 6.7 |
| $\mathrm{C}_{\mathrm{B}}$ | 0.95 | 0.810 | 32.2 | 36.1 |
| DOC | 0.63 | 0.522 | 1.07 | 1.0 |
| $\mathrm{Al}_{\text {im }}$ | 0.82 | 1.20 | 15.6 | 56.3 |


| Cluster II $(\mathbf{2 5}<\mathbf{A N C} \leq \mathbf{1 0 0} \boldsymbol{\mu e q} / \mathrm{L})$ |  |  |  |  |
| :--- | ---: | :---: | :---: | :---: |
| ANC | 0.43 | 0.512 | 12.7 | 18.1 |
| pH | 0.53 | 0.795 | 1.02 | 0.25 |
| $\mathrm{SO}_{4}{ }^{2-}$ | 0.83 | 0.898 | 15.6 | 20.8 |
| $\mathrm{NO}_{3}{ }^{-}$ | 0.42 | 0.814 | 2.13 | 3.6 |
| $\mathrm{C}_{\mathrm{B}}$ | 0.95 | 0.883 | -3.72 | 33.7 |
| DOC | 0.70 | 0.500 | 1.22 | 1.01 |
| $\mathrm{Al}_{\text {im }}$ | 0.26 | 0.993 | -3.70 | 12.0 |

Cluster III ( $100<$ ANC $\leq 400 \mu \mathrm{eq} / \mathrm{L}$ )

| ANC | 0.88 | 0.766 | -21.9 | 29.0 |
| :--- | :--- | :--- | :---: | ---: |
| pH | 0.43 | 0.739 | 1.63 | 0.21 |
| $\mathrm{SO}_{4}{ }^{2-}$ | 0.81 | 0.893 | 19.2 | 22.2 |
| $\mathrm{NO}_{3}{ }^{-}$ | 0.60 | 1.29 | 2.46 | 4.2 |
| $\mathrm{C}_{\mathrm{B}}$ | 0.94 | 0.863 | -14.2 | 50.0 |
| DOC | 0.36 | 0.548 | 1.33 | 1.2 |
| $\mathrm{Al}_{\mathrm{im}}$ | 0.12 | 0.647 | -3.08 | 7.6 |

[^15]
### 6.3 SPRING CONDITIONS

Although the fall index period was a very stable period in which to assess the acid-base status of lakes, it is not necessarily the season of lowest ANC and pH. In regions that accumulate snowpacks, lakewater ANC and pH typically decline during spring snowmelt (Galloway et al., 1980; Jeffries et al., 1979). Based on the ELS-II seasonal surveys (Section 5.4), ANC and pH were lower in the spring than in the summer or fall in lakes in the northeastern United States. Thus, spring is of high interest from a perspective of acidic deposition effects. Of specific interest is the question of whether conditions in the spring were more toxic to biota than fall conditions. Also, the factors related to the fall/spring changes in ANC and pH are important in understanding the processes responsible for the observed spring ANC depressions. Lastly, it is also important to place the ELS-II spring sample in context with spring snowmelt hydrology. As is shown in Section 6.3.3, the ELS-II samples were generally collected 2 to 3 wkks after peak snowmelt discharges. Thus, the ELLS-II spring data do not indicate worst case episodic spring conditions, but rather post-snowmelt spring seasonal (baseflow) conditions. The seasonal comparisons made in this report need to be interpreted with these facts in mind. In this section, therefore, spring refers to post-snowmelt spring baseflow conditions, not worst case spring episodic conditions.

### 6.3.1 Seasonal Biotic Toxicity

The effects of acidity on aquatic organisms are determined by a number of different water quality variables, the most important of which are pH , calcium, and inorganic monomeric aluminum ( $\mathrm{Al}_{\mathrm{im}}$ ) ( J . Baker et al., 1990a). Declining pH caused by acidic deposition can mobilize $\mathrm{Al}_{\mathrm{im}}$ to surface waters resulting in both low pH and high $\mathrm{Al}_{\mathrm{im}}$ concentrations that are toxic to biota. The toxic effects of pH and $\mathrm{Al}_{\mathrm{im}}$, however, can be ameliorated to some extent by high $\mathrm{Ca}^{2+}$ concentrations. Toxicity is very species dependent and chemical conditions that are extremely harmful to one species may have little or no effect on another species. J. Baker et al. (1990a) have used an acid-stress index (ASI) to estimate acid stress to fish. The ASIs, which take into account the combined effects of $\mathrm{pH}, \mathrm{Al}_{\mathrm{im}}$, and calcium, were developed from laboratory bioassay data of fish mortality. The ASI is based on a logistic regression equation and represents expected percent mortality. ASIs were developed for three fish species that vary in their sensitivity to acidic conditions: brook trout (acid-tolerant), smallmouth bass (intermediate), and rainbow trout (acid-sensitive). Full details of model development and equations are given in J . Baker et al. (1990a).

Sensitive, intermediate, and tolerant ASIs were calculated for the ELS-ll lakes in each season from observed $\mathrm{pH}, \mathrm{Ca}^{2+}$, and $\mathrm{Al}_{\mathrm{im}}$ concentrations. The results showed that there was very little difference in the number of lakes unsuitable for fish between spring, summer, and fall in the ELS-II lake population (Table 6-3). Thus, it appears as if the observed spring/fall changes in pH , calcium and aluminum were

Table 6-3. Percentage of Lakes with Chemical Conditions Exceeding Acid Stress Index Values in the ELS-II Target Lake Population

|  |  |  |  |
| :---: | :---: | :---: | :---: |
| Acid Stress Index (ASI) Value $^{\text {a }}$ | Spring | Summer | Fall |
| Acid-Sensitive Species |  |  |  |
| ASI $>10$ | 72 | 80 | 73 |
| ASI $>30$ | 36 | 37 | 32 |
| ASI $>50$ | 23 | 22 | 21 |
| ASI $>80$ | 17 | 15 | 15 |

## Intermediate Species

| ASI $>10$ | 18 | 18 | 16 |
| :--- | :---: | :---: | :---: |
| ASI $>30$ | 14 | 13 | 13 |
| ASI $>50$ | 13 | 11 | 8.8 |
| ASI $>80$ | 11 | 8.4 | 7.2 |

## Acid-Tolerant Species

| ASI $>10$ | 3.7 | 4.5 | 3.4 |
| :--- | :--- | :--- | :--- |
| ASI $>30$ | 1.2 | 0.9 | 0.9 |
| ASI $>50$ | 0.3 | 0 | 0.3 |
| ASI $>80$ | 0 | 0 | 0 |

a The acid stress index (ASI) is a model estimate of percent fish mortality based on laboratory bioassays of the combined effects of calcium, pH , and inorganic monomeric aluminum (J. Baker et al., 1990a). The ASI in ELS-II lakes was calculated from the observed seasonal concentrations of $\mathrm{pH}, \mathrm{Ca}^{2+}$, and $\mathrm{Al}_{\mathrm{m}}$.

The fall index ASI values were related to observed fish presence in lakes in order to make the following generalizations: lakes with a tolerant ASI > 30 were unsuitable for all fish species, lakes with a tolerant ASI > 10 were unsuitable for brook trout, lakes with an intermediate ASt > 80 were unsuitable for other sport fish, such as smallmouth bass and lake trout, and lakes with a sensitive $\mathrm{ASI}>80$ were unsuitable for acid-sensitive species such as minnows.
not great enough to cause a significant regional change in biological effects as measured by the ASI. The main reason for the lack of a seasonal change was that the largest ANC changes occurred in higher ANC lakes that did not have a corresponding pH decrease or $\mathrm{Al}_{\mathrm{im}}$ increase into the range of stressful values. The low ANC lakes that are most susceptible to acidic deposition effects did not have large changes in $\mathrm{pH}, \mathrm{Ca}^{2+}$, and $\mathrm{Al}_{\mathrm{im}}$; thus, there were only small changes in estimated biological effects. The ASI values listed in Table 6-3 are due to the observed chemical conditions in the lake and are not necessarily the result of acidic deposition. Other causes of the acidic conditions in ELS-II lakes (e.g., organic acidity) would be expected to cause stressful conditions for some fish species. Regardless, fall index chemistry appears to be a stable estimator of biological effects. The relationship between ELS-II spring conditions and worst-case conditions is discussed in Section 6.3.3.

### 6.3.2 Factors Related to Fall/Spring ANC Changes

Of particular interest in terms of acidic deposition effects are the factors related to the observed spring depressions in ANC. An attempt was made to correlate physical variables with the observed fall/spring change in ANC. However, in the entire ELS-II data set, there was no significant relationship $\left(r^{2}<0.05 ; p>0.01\right)$ between ANC change and elevation, lake area, watershed area, residence time, lake depth, or lake volume. When examined within specific regions or within high and low ANC lake groups, there were some significant correlations with elevation and residence time. In higher ANC (> 50 $\mu \mathrm{eq} / \mathrm{L}$ ) ELS-II lakes, residence time was positively related ( $r^{2}=0.13 ; p=.002$ ) to the general increase in ANC from spring to fall in 1986. In other words, lakes with shorter residence times experienced larger spring ANC depressions. This makes intuitive sense because lakes with faster flow-through times would be the ones most susceptible to the dilution effects of low ANC runoff or inputs of acid anions. Among low ANC lakes (fall ANC $\leq 50 \mu \mathrm{eq} / \mathrm{L}$ ), elevation was negatively related ( $r^{2}=0.16 ; p=0.001$ ) to the spring minus fall difference in ANC in ELS-II lakes. This correlation was significant only in the Adirondacks $\left(r^{2}=0.55 ; p=.004\right)$ and Poconos/Catskills $\left(r^{2}=0.74 ; p=0.05\right)$ regions and not in New England ( $r^{2}=0.19 ; p=0.3$ ). Thus, low ANC lakes in New York and Pennsylvania tended to have larger spring ANC depressions at higher elevations. Measured physical variables, however, only explain a minor percentage (low $\mathrm{r}^{2}$ ) of the variance in fall/spring changes in ANC. Other factors are likely to be more important.

Fall/spring changes in ANC were similar in different hydrologic lake types (e.g., drainage, seepage lakes). For example, in lakes with fall ANC $>50 \mu \mathrm{eq} / \mathrm{L}$, the median spring minus fall ANC change in drainage lakes (including reservoirs) was $-60 \mu \mathrm{eq} / \mathrm{L}$ (interquartile range $=-41$ to $-98 \mu \mathrm{eq} / \mathrm{L}$ ). The corresponding median change in seepage lakes (including closed lakes) was $-69 \mu \mathrm{eq} / \mathrm{L}$ (interquartile range $=-9$ to $-88 \mu \mathrm{eq} / \mathrm{L}$ ). A similar pattern was also seen in lakes with fall ANC $\leq 50 \mu \mathrm{eq} / \mathrm{L}$.

Correlations between fall/spring ANC change and changes in other chemical variables were also examined. As can be seen in Figure 6-4, there was a strong relationship between fall/spring ANC


Figure 6-4. Relationship between ANC change (spring 1986 minus fall 1986) and fall 1986 index ANC in ELS-II lakes.
change and fall index ANC. Maximum fall/spring ANC changes were observed in the ELS-II lakes with the highest fall ANC valuess ( $200-450 \mu \mathrm{eq} / \mathrm{L}$ ). The largest spring ANC depression ( $-177 \mu \mathrm{eq} / \mathrm{L}$ ) occurred in a lake with a fall ANC of $326 \mu \mathrm{eq} / \mathrm{L}$. This is in contrast to the results reported by Schaefer et al. (1990) who found the biggest ANC depressions in Adirondack lakes with intermediate baseline ANC values ( $50-100 \mu \mathrm{eq} / \mathrm{L}$ ). However, they had only one lake with baseline ANC over $150 \mu \mathrm{eq} / \mathrm{L}$ with which to judge ANC changes in higher ANC lakes. In the rest of this section, lakes with ANC above and below $50 \mu \mathrm{eq} / \mathrm{L}$ are analyzed separately because they exhibited different geochemical changes associated with spring ANC depressions.

In higher ANC (> $50 \mu \mathrm{eq} / \mathrm{L}$ ) ELS-II lakes, the only significant chemical change associated with fail/spring ANC changes were changes in base cation concentrations (Figure 6-5; $r^{2}=0.36$ ). Spring depressions in ANC fall around the $1: 1$ line coincident with spring depressions in base cations. Spring/fall changes in sulfate, nitrate, DOC, and aluminum were not related to ANC change ( $r^{2}<0.05 ; \mathrm{p}$ $>0.05$ ). The spring/fall changes are also evident in Table 5-8, which shows that in lakes with fall ANC $>50 \mu \mathrm{eq} / \mathrm{L}$, median and quartile estimates of spring decreases in ANC are quite similar to decreases in base cations (median ANC change $=-60 \mu \mathrm{eq} / \mathrm{L}$; median base cation change $=-69 \mu \mathrm{eq} / \mathrm{L}$ ). This phenomenon is most likely the result of the dilution of lake water and/or runoff by low ANC, low base cation snowmelt in the spring. In higher ANC systems, episodic ANC losses during storm events have often been attributed primarily to base cation dilution (Wigington et al., 1990). Similarly, Molot et al., (1989) reported that the major contributor to spring snowmelt alkalinity depressions in Ontario streams was base cation dilution. A base cation dilution mechanism also helps explain the small fall/spring ANC changes observed in low ANC lakes. Fall "baseline" conditions in low ANC lakes more closely approximate spring snowmelt runoff and thus would not experience nearly as much dilution as higher ANC lakes. Thus, low ANC lakes would require inputs of $\mathrm{H}^{+}$acid anions to cause an ANC depression.

In low ANC $(\leqslant 50 \mu \mathrm{eq} / \mathrm{L})$ ELS-Il lakes, spring increases in both nitrate $\left(r^{2}=0.19\right)$ and $\mathrm{Al}_{\mathrm{im}}\left(\mathrm{r}^{2}=\right.$ $0.22)$ were positively correlated with spring ANC depressions. Spring depressions in ANC in low ANC lakes were not significantly correlated with either sulfate or base cation changes ( $r^{2}<0.1 ; p>0.05$ ). Relationships between seasonal ANC change and changes in other ions were different among the different regions. The spring decrease in ANC was significantly related to nitrate increases in the Adirondacks ( $r^{2}=0.22$ ) but was not related to nitrate increases in New England (Figure 6-6). Most of these low ANC Adirondack lakes had spring nitrate concentration increases greater than spring ANC depressions (Figure 6-6; Table 6-4). The same pattern of nitrate increase associated with ANC loss during snowmelt has been reported by Schaefer et al. (1990) for the RILWAS lakes in the Adirondacks. In the Poconos/ Catskills there were only seven low ANC ELS-ll sample lakes, so correlation relationships are not very useful. In one of the low ANC Pocono Mountain Lakes, however, a $31 \mu \mathrm{eq} / \mathrm{L}$ decrease in ANC was nearly balanced by a $24 \mu \mathrm{eq} / \mathrm{L}$ increase in nitrate (Table 6-4). Overall, increasing nitrate concentrations are associated with spring ANC depressions in low ANC Adirondacks and Poconos lakes but not New England lakes.

Fall ANC > 50 ueq/L


Figure 6-5. Relationship between ANC change (spring 1986 minus fall 1986) and sum of base cation concentration change (spring 1986 minus fall 1986) in ELS-II lakes with fall 1986 index ANC > $50 \mu \mathrm{eq} / \mathrm{L}$. Solid line is the $-1: 1$ line.

$$
\text { Fall ANC } \leqq 50 \quad \mathrm{ueq} / \mathrm{L}
$$



Figure 6-6. Relationship between ANC change (spring 1986 minus fall 1986) and nitrate concentration change (spring 1986 minus fall 1986) in ELS-II lakes with fall 1986 index ANC $\leq 50 \mu \mathrm{eq} / \mathrm{L}$. Solid line is the $-1: 1$ lines.

Table 6-4. Spring Minus Fall Changes ( $\Delta$ ) in Major Anions and Cations in Low ANC ELS-II Lakes with Spring ANC Depressions ( $\triangle$ ANC) $>10 \mu \mathrm{eq} / \mathrm{L}^{\text {a }}$

| Lake ID | $\triangle \mathrm{ANC}$ | $\Delta \mathrm{NO}_{3}{ }^{-}$ | $\triangle \mathrm{Al}^{\mathrm{n+}}$ | $\triangle \mathrm{C}_{\mathrm{b}}$ | $\triangle \mathrm{SO}_{4}{ }^{2-} \quad \Delta \operatorname{Org} \mathrm{A}^{-} \quad \Delta \mathrm{H}^{+}$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |

## Adirondacks

| 1A2-004 | -27.6 | 19.7 | 6.8 | -4.4 | -18.3 | 2.8 | -3.3 |
| :--- | ---: | ---: | ---: | ---: | ---: | ---: | ---: |
| 1A1-061 | -23.1 | 13.6 | -10.3 | 3.0 | -24.8 | -16.2 | -2.6 |
| 1A1-003 | -15.7 | 33.0 | 16.7 | 9.2 | -6.1 | 0.9 | 2.2 |
| 1A1-057 | -12.8 | 13.4 | 19.4 | 9.4 | 2.7 | -15.4 | 5.3 |
| 1A1-017 | -11.6 | 26.5 | 8.6 | -5.2 | -4.9 | -7.3 | 2.3 |
| 1A1-012 | -10.8 | 15.2 | 5.8 | 4.9 | -8.1 | 0.1 | 2.7 |

## Poconos/Catskills

| $1 \mathrm{~B} 1-010$ | -30.6 | 23.9 | 18.7 | -4.0 | -13.1 | 0.05 | 4.9 |
| :--- | ---: | ---: | ---: | ---: | ---: | ---: | :--- |
| 1B2-028 | -11.3 | 1.3 | 1.2 | -20.9 | -27.5 | -2.3 | 1.3 |

## New England

| 1C2-057 | -23.4 | 0.9 | 2.1 | -17.7 | 36.7 | -6.7 | 2.8 |
| :--- | ---: | ---: | ---: | :---: | ---: | :---: | :--- |
| 1D3-002 | -21.2 | 10.0 | 2.1 | -335 | 6.8 | 1.4 | 2.8 |
| 1E1-106 | -18.6 | -1.1 | 3.1 | -12.1 | -3.9 | 6.1 | 3.9 |
| 1C1-086 | -16.4 | 1.9 | -0.1 | -37.4 | 3.1 | -5.3 | 0.7 |
| 1E1-054 | -13.4 | 1.1 | -0.2 | -12.8 | -7.6 | 5.5 | 0.2 |
| 1D3-029 | -13.1 | 1.5 | 3.4 | -23.2 | 12.5 | 4.4 | 0.5 |
| 1C2-037 | -12.3 | 0.8 | -0.4 | -32.3 | 13.9 | 4.1 | 1.4 |

[^16]Spring increases in $\mathrm{Al}_{\text {in }}$ are also associated with spring ANC depressions (Figure 6-7) in the Poconos/Catskills, New England ( $r^{2}=0.33$ ), and the Adirondacks ( $r^{2}=0.32$ after removing one outlier). Spring aluminum increases in New England, however, are quite small ( $<3 \mu \mathrm{eq} / \mathrm{L}$ ) relative to the ANC decreases ( $<25 \mu \mathrm{eq} / \mathrm{L}$; Figure 6-7). In the Adirondacks and the Poconos, some of the $\mathrm{Al}_{\mathrm{im}}$ increases are about the same as the ANC decreases ( $5-20 \mu \mathrm{eq} / \mathrm{L}$ ). Spring $\mathrm{H}^{+}$increases were quite small ( $<5$ $\mu \mathrm{eq} / \mathrm{L}$ ) in all low ANC ELS-Il lakes. Thus, large spring ANC depressions ( $>10 \mu \mathrm{eq} / \mathrm{L}$ ) related to acid cation increases $\left(\mathrm{Al}^{n+}, \mathrm{H}^{+}\right)$are associated mainly with aluminum increases and not $\mathrm{H}^{+}$increases (Table 6-4). Aluminum is an effective pH buffer in acidic waters (Driscoll and Bisogni, 1984). The increase in $\mathrm{Al}_{\mathrm{im}}$ in ELS-II lakes, however, does not appear to be associated with decreases in pH (Figure 6-8). For example, the three largest individual spring $\mathrm{Al}_{\mathrm{im}}$ increases in ELS-II lakes all had spring pH depressions smaller than 0.2 pH units. Also, three lakes in which spring pH was higher than fall pH had spring $\mathrm{Al}_{\mathrm{im}}$ increases over $50 \mu \mathrm{~g} / \mathrm{L}$. It should be noted, however, that small changes in pH at low pH levels can mobilize significant amounts of aluminum.

In low ANC lakes in New England, spring/fall ANC changes were also correlated with base cation $\left(r^{2}=0.13\right)$ and DOC ( $r^{2}=0.26$ ) changes. The significant relationship with DOC was due to four lakes that had spring ANC increases ( $10-20 \mu \mathrm{eq} / \mathrm{L}$ ) associated with large DOC ( $4-7 \mathrm{mg} / \mathrm{L}$ ) decreases. It is possible that strong organic acids were diluted in these lakes during snowmelt, resulting in increased ANC. All four of these lakes are high DOC systems (fall index DOC $=7-15 \mathrm{mg} / \mathrm{L}$ ) dominated by organic anions. Although base cation concentration changes were only weakly related to ANC changes in low ANC New England lakes, the lakes in New England with spring ANC depressions greater than $10 \mu \mathrm{eq} / \mathrm{L}$ all had base cation depressions about the same or greater than the ANC depression (Table 6-4). Thus the main factor responsible for the larger ANC depressions in low ANC New England ELS-II lakes appears to be base cation dilution. It should be reiterated, however, that the observed spring depressions in ANC were fairly small in all ELS-II low ANC lakes. Only $25 \%$ of the low ANC ELS-II lakes decreased by more than $10 \mu \mathrm{eq} / \mathrm{L}$ and the maximum depression was $31 \mu \mathrm{eq} / \mathrm{L}$.

### 6.3.3 Worst Case Spring Conditions

Conditions during the fall index period (atter turnover) have been shown to be extremely stable (Section 5.3). Spring conditions, however, are much more variable. A number of studies have shown a significant amount of episodic acidification (ANC/pH decreases, $\mathrm{Al}_{\mathrm{im}} / \mathrm{NO}_{3}{ }^{-}$increases) associated with snowmelt episodes in the Adirondacks (Galloway et al., 1987; Schaefer et al., 1990; Schafran and Driscoll, 1987). A major factor behind this phenomenon is that during snowmelt, runoff occurs more rapidly through shallow flowpaths where acid neutralization is incomplete (Driscoll et al., 1987; Peters and Driscoll, 1987). The peak runoff typically occurs while ice cover is still present on the lakes, whereas the ELS-II spring index sample was scheduled (for logistics and safety reasons) to be taken within two weeks of ice-out. During baseflow conditions, acidic inputs flow through deeper flowpaths where they have longer contact times and contact with more material rich in base cations. Schaefer et


Figure 6-7. Relationship between ANC change (spring 1986 minus fall 1986) and inorganic monomeric aluminum concentration change (spring 1986 minus fall 1986) in ELS-II lakes with fall 1986 index ANC $\leq 50 \mu \mathrm{eq} / \mathrm{L}$. Inorganic aluminum was converted from $\mu \mathrm{M}$ to $\mu \mathrm{eq} / \mathrm{L}$ based on an aluminum charge calculated from an empirical equation derived from equilibrium model speciation and National Stream Survey data ( $\mathrm{Al}_{\mathrm{im}}$ charge $=7.06-\mathrm{pH}$; also see Figure 1 in Sullivan et al., 1989). Solid line is the $-1: 1$ line.


Figure 6-8. Relationship between pH change (spring 1986 minus fall 1986) and inorganic monomeric aluminum concentration change (spring 1986 minus fall 1986) in ELS-II lakes with fall 1986 index ANC $\leq 50 \mu \mathrm{eq} / \mathrm{L}$.
al. (1990) reported that lake outlet ANC depressions tended to persist for 4-8 weeks after peak outlet discharge during spring snowmelt in 1986 and 1987 in the Adirondacks. Acidic conditions, however, were most severe about the time of peak snowmelt discharge. ANC then increases as the system returns to baseflow.

Example hydrographs for conditions in the spring of 1986, along with the associated ELS-II sample windows, are shown for the Adirondacks (Figure 6-9), Pennsylvania (Figure 6-10), and Maine (Figure 6-11). As can be seen in these figures, the ELS-II spring sample was conducted $2-3$ weeks after peak discharge in each of these three areas. For example, peak discharge occurred on April 1, 1986, in Woods Lake Outlet in the Adirondacks. ELS-ll spring samples in the Adirondacks were collected between April 16 and 25, 1986, just before the time when the lake outlet hydrograph returned to baseflow levels at the end of April (Figure 6-9).

ELS-II spring data definitely indicate a spring ANC depression relative to a fall baseline, yet it is doubtful, and certainly not expected, that the spring ELS-II data correspond to the minimum lakewater ANC. The data of Schaefer et al. (1990) on Adirondack lake outlet chemistry during snowmelt indicate that the minimum ANC occurred at or right after peak discharge. In addition, minimum spring lake outlet ANC predicted from fall 1984 ELS-I ANC index values using the regression equation of Eshieman (1988) was typically (median) $32 \mu \mathrm{eq} / \mathrm{L}$ lower than the observed spring lakewater ANC in ELS-II Adirondack lakes. The ANC in Long-Term Monitoring Program lake outlets in the Adirondacks were on average 22 $\mu \mathrm{eq} / \mathrm{L}$ lower during spring peak flow than in late April when the ELS-ll was conducted (Driscoll, pers. comm.). Also, maximum nitrate increases during spring snowmelt episodes in the Adirondacks range from 5 to $80 \mu \mathrm{eq} / \mathrm{L}$ (Wigington, 1990) as opposed to the $2-33 \mu \mathrm{eq} / \mathrm{L}$ increases observed in the ELS-II Adirondack lakes (Figure 6-6). Based on these observations, it seems safe to conclude that the minimum ANC in ELS-II lakes would be lower than the observed ELS-II spring index values that were collected during a period of decreasing lake outflow 2-3 weeks after peak snowmelt runoff.

In addition to temporal changes in chemistry during spring snowmelt, spatial variability is also important. When colder and lighter $\left(0-4^{\circ} \mathrm{C}\right)$ acidic snowmelt enters a lake, it usually flows across the lake surface under the ice directly to the lake outlet without mixing with the denser $4^{\circ} \mathrm{C}$ water already in the lake. Thus, the bottom portion of the lake may be relatively unchanged by the acidic snowmelt inputs, whereas the surface water undergoes a severe ANC depression. This phenomenon has been observed in Cone Pond, New Hampshire (Baird et al., 1985), and in both pelagic and near-shore regions of Woods Lake in the Adirondacks (Gubala et al., in review). Gubala et al. also found that small amounts of groundwater in-seepage rich in base cations helped maintain baseline ANC conditions in the bottom water of the shallow near-shore area. However, the maintenance of a circumneutral bottom water refuge does not necessarily mean that there are no adverse biological effects in the lake from snownelt. Fish fry (e.g., brook trout) that must migrate from the benthos to the surface water to fill their air bladders after hatching in the spring may be greatly impacted by the acidic, high $\mathrm{Al}_{\mathrm{im}}$ concentrations

## Woods Lake Outlet, New York

## Spring 1986



Figure 6-9. Hydrograph of mean daily discharge during spring 1986 (March 1 to June 1) in Woods Lake Outlet, New York (Adirondacks subregion). The spring ELS-II seasonal sampling window in the Adirondacks is shown in brackets at top. Data from USGS Hydrodata.

## Towanda Creek, Pennsylvania

 Spring 1986

Date

Figure 6-10. Hydrograph of mean daily discharge during spring 1986 (March 1 to June 1) in Towanda Creek, Pennsylvania (Poconos/Catskills subregion). The spring ELS-II seasonal sampling window in Pennsylvania is shown in brackets at top. Data from USGS Hydrodata.

## Swift River, Maine

## Spring 1986



Figure 6-11. Hydrograph of mean daily discharge during spring 1986 (March 1 to June 1) in Swift River, Maine. The spring ELS-II seasonal sampling window in Maine is shown in brackets at top. Data from USGS Hydrodata.
they experience in the surface water. Thus, assessing worst case acidic conditions during spring snowmelt is not a simple task and is complicated by both spatial and temporal variability in the chemical environment. The ELS-II spring index sample is indicative of post-snowmelt spring conditions in the surface water. It should not be construed to represent worst case spring episodic conditions.

It would have been almost impossible to implement a regional synoptic survey of lakes at the time of peak runoff. For one, the large number of lakes to be sampled necessitates a long sampling window. Another problem is that identifying the peak discharge time is easy in hindsight, but identifying it in the field over a large heterogeneous region is virtually an impossible task. Finally, lake sampling during snowmelt is difficult and potentially dangerous. Sampling from the middle of the lake is unsafe until after ice-out, which is generally after the period of maximum discharge (Driscoll et al., in press). Thus the ELS-II spring sample was probably the most reasonable index of lakewater chemistry that could be made for a synoptic survey in the spring. Again, it should be emphasized that it does not represent worst case episodic spring conditions. Minimum ANC values in the spring are almost assuredly lower than the ELS-II spring index values and occur earlier.

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## APPENDIX A

## POPULATION ESTIMATES OF SELECTED PHYSICAL AND CHEMICAL VARIABLES IN THE SPRING, SUMMER, AND FALL ELS-II SEASONAL SURVEYS

This appendix presents the cumulative distribution functions (CDF) for the major ELS-II variables measured in the spring, summer, and fall seasonal surveys (Table A-1). CDFs are described in Section 5.1.2 and procedures for making these types of population estimates are presented in Section 2.4.2. To read these figures, pick a value, $x$, of the attribute $X$, along the horizontal axis, and read the $y$-axis value of the two curves, $F(x)$ (solid line) and $F_{u}(x)$ (dotted line) at this value. $F(x)$ is the estimated proportion of the number of lakes in the population with a value of the attribute equal to or less than $x$. $F_{u}(x)$ is the upper confidence bound on this proportion, to be read as: one is $95 \%$ confident that the true proportion is less than this bound. Some distributions plot the declining function, 1-F(x). For these, read the distribution as the estimated proportion of reaches having a value of the attribute equal to or greater than X . Confidence bounds are as before: an upper confidence bound on the true proportion.

A lower one-sided confidence bound on $F(x)$ can be generated, if needed, by measuring the distance between the two curves, and projecting the identical distance below $F(x)$. This curve is not presented because it could be confused with two-sided confidence bounds, which are of different width. The bound provided is the one usually considered appropriate for expressing the status of the resource.

By generating distribution functions for other characteristics, such as lake surface area, other types of distributions can be obtained. In this appendix, $G(x)$ represents the proportion of lake surface area (in hectares) associated with lakes having values of the attribute $X \leq$ some value $x$. In all cases, these distributions and the represented confidence bounds are dimensionless, and a shift from hectares to square miles has no effect on $\mathrm{G}(\mathrm{x})$ or $\mathrm{G}_{\mathrm{u}}(\mathrm{x})$. Any other distribution, such as lake watershed area or shoreline length can be analyzed in exactly the same way, requiring only an appropriate take attribute that sums to the population attribute.

Other population statistics of interest can be generated from the distributions. For each distribution, the quantiles, median, and four quintiles, $\mathrm{Q}_{1}, \mathrm{Q}_{2} \ldots, \mathrm{Q}_{4}$ (20th percentile, ... 80th percentile) are identified. The median of the population is the value of $x$ such that $F(x)=1 / 2$. The $Q_{i}$ (quintile) of the population is the value of $x$ such that $F(x)=i / 5$. These statistics are defined for all distributions. Additionally, the mean and standard deviation of the variable $x$ for the population is estimated as in Section 2.4, equations 7 and 8 .

## Making ELS-II Variance Estimates

The formula for estimated variance of the estimated population totals $\left(\hat{\boldsymbol{T}}_{y}\right)$ is:

$$
\begin{equation*}
\hat{V}\left(\hat{T}_{y}\right)=\sum_{S} y^{2} W z_{i}\left(W z_{i}-1\right)+\sum_{i \in S} \sum_{\substack{j \in S \\ j \neq i}} y_{i} y_{j}\left(W z_{i} W z_{i}-W_{i j}\right) \tag{A-1}
\end{equation*}
$$

Table A-1. Listing of Variable Names and Descriptions for CDFs Presented in Appendix A.

| Variable Name | Description |
| :--- | :--- |
| ACCO11 | Base Neutralizing Capacity |
| ALD02 | Total PCV reactive (monomeric) aluminum |
| ALO_02 | Nonexchangeable (organic) PCV reactive aluminum |
| ALDI98 | Inorganic monomeric aluminum (ALD02 - ALO_02) |
| ALEX11 | MIBK-extractable aluminum |
| ALKA11 | Acid neutralizing capacity |
| CA98 | Calcium |
| CL98 | Chloride |
| COLOR02 | Color |
| COND11 | Specific conductance - analytical laboratory |
| DIC02 | Closed headspace dissolved inorganic carbon - processing laboratory |
| DOC11 | Dissolved organic carbon |
| FE11 | Iron |
| FTL98 | Total Fluoride |
| K98 | Potassium |
| MG98 | Magnesium |
| MN11 | Manganese |
| NA98 | Sodium |
| NH498 | Ammonium |
| NO398 | Nitrate |
| PH02 | Closed headspace pH - processing laboratory |
| PTL11 | Total phosphorous |
| SECME98 | Secchi depth |
| SIO211 | Silica |
| SO498 | Sulfate |
| SOBC98 | Sum of base cations (CA98 + MG98 + K98 + NA98) |
| a Chloride CDFs are not presented for spring and summer seasonal surveys because of data quality concerns (see Section |  |
| $4)$. |  |

where $W_{i j}=A_{i j} B_{i j}$ is calculated from the following equations.

- If lakes $i$ and $j$ are from the same ELS-I strata then: $A_{i j}=W 1_{m, i}\left(N^{\star}-1\right) /\left(N^{\star} / W 1_{m, i}-1\right)$.
- If lakes $i$ and $j$ are from different ELS-I strata then: $A_{i j}=W 1_{m, i} W^{W}{ }_{m, j}$
- If the conditional ELS-II weight ( $W_{\text {cond }}$ ) of lake $i$ equals 1 then: $B_{i j}=W_{\text {cond }, j}$
- If the conditional ELS-II weight ( $W_{\text {cond }}$ ) of lake $j$ equals 1 then: $B_{i j}=W_{\text {cond, } i}$.
- If lakes i and j are from different ELS -II clusters then, $\mathrm{B}_{\mathrm{ij}}=\mathrm{W}_{\text {cond }, \mathrm{i}} \mathrm{W}_{\text {cond }, \mathrm{j}}$.

Otherwise, if lakes $i$ and $j$ are from the same ELS-II cluster then:

$$
B_{i j}=\left(N^{\prime}\left(N^{\prime}-a\right)\right) /\left(n^{\prime}\left(n^{\prime}-1\right) W 1_{o, i} W 1_{o, j}\right) ; \text { where } N^{\prime}=n W_{\text {cond }, i} W_{\text {cond }, \mathrm{j}} \text { and } \mathrm{a}=\left(W_{o} 1_{\mathrm{o}, \mathrm{i}}+W 1_{\mathrm{o}, \mathrm{j}}\right) / 2 \text {. }
$$

Variables are defined as:

- $\quad W 1_{0}=$ original ELS-I sample weight at the time of ELS-II site selection.
- $\quad \mathrm{W} 1_{\mathrm{m}}=$ modified ELS-I sample weight reflecting minor adjustments made after ELS-II site selection.
- $W_{\text {cond }}=$ ELS-II conditional weight (see Section 2, equation 2).
- $n^{\prime}=$ the cluster sample size of the initial ELS-II target population after subtracting lakes entered with certainty ( $W_{\text {cond }}=1$ ). Cluster I $n^{\prime}$ equals 45 , cluster II $n^{\prime}$ equals 58 , and cluster III $n^{\prime}$ equals 49 .

The standard error (SE) of the estimated population total is then calculated as the square root of the variance estimate, $\hat{V}\left(\hat{T}_{y}\right)$. One-sided upper $95 \%$ confidence bounds $\left(\hat{T}_{u}\right)$ are then calculated as $\hat{T}_{u}=\hat{T}_{y}$ $+1.645\left(\operatorname{SE}\left(\hat{T}_{y}\right)\right)$.

For example, there were 20 sample lakes in the ELS-II with fall DOC $<2 \mathrm{mg} / \mathrm{L}$. These represent a population of 298 lakes (calculated by summing the sample weights) or $7.5 \%$ of the target population $(F(x)=298 / 3,993=0.075)$. By using equation A-1, the estimated variance of the subpopulation was 4,173 with a standard error of 64.6 . The $95 \%$ upper confidence level is $404(298+1.645 * 64.6)$. In other words, we would say that there are 298 ( $\pm 64.6$ ) ELS-II target lakes in the northeastern United States that had fall 1986 DOC < $2 \mathrm{mg} / \mathrm{L}$; we are $95 \%$ sure that there are no more than 404 lakes with DOC $<2 \mathrm{mg} / \mathrm{L}$.



Min: $5.40 \quad Q_{1}: 37.10 \quad Q_{2}: 48.10 \quad Q_{3}: 58.80 \quad Q_{4}: 62.60 \quad \operatorname{Max}: 174.7$

| Median: | 48.30 |
| :--- | :--- |
| Mean: | 53.12 |
| Std. Dev. $:$ | 15.84 |

* Confidence bounds ore for number and area of lakes, but have been scaled.

POPULATION DESCRIPTION PHASE II LAKE SURVEY, SUMMER 1986



[^17]POPULATION DESCRIPTION PHASE II LAKE SURVEY, FALL 1986
VARIABLE: ACCO11 ( $\mu \mathrm{eq} / 1$ ) 09 MAY 1990

| Population Size (N): 3993 | SE(N): 191.6 |
| :--- | :--- | :--- |
| Lake Arec (A): 354924 | SE(A): 68995 |$\quad$ Sample Size: 145 | REGION 1 |
| :--- |
| CLUSTERS |
| $1,2, \& 3$ |


Min: $3.00 \quad Q_{1}: 29.40 \quad Q_{2}: 34.60 \quad Q_{3}: 41.30 \quad Q_{4}: 52.80 \quad \operatorname{Max}: 222.2$

Median: $\quad 38.90$
Mean: 43.81
Std. Dev.: 22.48


* Confidence bounds are for number and area of lakes, but have been scaled

POPULATION DESCRIPTION PHASE II LAKE SURVEY, SPRING 1986
VARIABLE: ALDO2 ( $\mu \mathrm{g} / \mathrm{I}$ ) 10 MAY 1990


Min: $6.10 \quad Q_{1}: 16.10 \quad Q_{2}: 24.30 \quad Q_{3}: 33.90 \quad Q_{4}: 62.50 \quad \operatorname{Max}: 517.2$
Median: $\quad 28.70$
Mean: $\quad 52.50$
Std. Dev.: 76.03

POPULATION DESCRIPTION PHASE II LAKE SURVEY, SUMMER 1986
VARIABLE: $\operatorname{ALDO2}(\mu \mathrm{g} / \mathrm{I}) \quad 10 \mathrm{MAY} 1990$
Population Size (N): 3993 SE(N): 191.6
Lake Area (A): 354924 SE(A): 68997
Sample Size: 145
REGION 1 CLUSTERS 1.2, \& 3

Min: $3.10 \quad Q_{1}: 11.30 \quad Q_{2}: 16.40 \quad Q_{3}: 23.80 \quad Q_{4}: 32.40 \quad$ Max: 328.5
Median:
18.80
Mean:
31.68
Std. Dev.:
43.75


$$
\text { Min: } 3.10 \quad Q_{1}: 12.60 \quad Q_{2}: 17.80 \quad Q_{3}: 20.00 \quad Q_{4}: 24.80 \quad \operatorname{Max}: 328.5
$$

## Median: <br> 18.80

Mean: 22.71
Std. Dev.: 21.43

* Confidence bounds are for number and area of lakes, but have been scaled.

POPULATION DESCRIPTION PHASE II LAKE SURVEY, FALL 1986


Min: $8.60 \quad Q_{1}: 16.50 \quad Q_{2}: 21.60 \quad Q_{3}: 24.50 \quad Q_{4}: 35.40 \quad$ Max: 626.5

## Median: <br> 22.30

Mean: 27.44
PHASE $\|$ DATA ANALYSIS

[^18]


Mean: $\quad 32.93$

* Confidence bounds are for number and area of lakes, but have been scaled.


POPULATION DESCRIPTION PHASE II LAKE SURVEY, FALL 1986
VARIABLE: ALO_O2 ( $\mu \mathrm{g} / 1) \quad 09$ MAY 1990

Population Size (N): 3993 SE(N): 191.6 Sample Size: 145 CLUSTERS
Lake Area (A). 354924 SE(A): 68996
1,2, \& 3



## Median: <br> 14.50

Mean: $\quad 13.70$
Std. Dev.: 8.88
FOPULATION DESCRIPTION PHASE II LAKE SURVEY, SPRING 1986
VARIABLE: ALDI98 ( $\mu \mathrm{g} / \mathrm{l}$ ) 10 MAY 1990



```
Median: 0.00
Mean: 12.19
Std. Dev.: 34.38
```

* Confidence bounds are for number and area of lokes, but have been scaled



[^19]POPULATION DESCRIPTION PHASE II LAKE SURVEY, FALL 1986
VARIABLE: ALDI98 ( $\mu \mathrm{g} / \mathrm{I}$ )
09 MAY 1990

| Population Size (N): 3993 | SE(N): 191.6 |
| :--- | :--- | :--- |
| Lake Area (A): 354924 | SE(A): 68996 |$\quad$ Sample Size: \(145\left[\begin{array}{l}REGION 1 <br>

CLUSTERS <br>
1,2, \& 3\end{array}\right]\)



- Confidence bounds are for number and area of lakes, but have been scoled.

POPULATION DESCRIPTION PHASE II LAKE SURVEY, SPRING 1986
VARIABLE: ALEX11 ( $\mu \mathrm{g} / \mathrm{I}) \quad 09$ MAY 1990


Min: $0.00 \quad Q_{1}: 0.00 \quad Q_{2}: 4.60 \quad Q_{3}: 13.90 \quad Q_{4}: 42.10 \quad$ Max: 435.2

> POPULATION DESCRIPTION PHASE II LAKE SURVEY, SUMMER 1986
> VARIABLE: ALEX11 $(\mu \mathrm{g} / 1) \quad 09$ MAY 1990
> Mean:
> 20.81

* Confidence bounds are for number and area of lakes, but have been scaled.
POPULATION DESCRIPTION PHASE II LAKE SURVEY, FALL 1986
VARIABLE: ALEX11 ( $\mu \mathrm{g} / \mathrm{I}$ ) O9 MAY 1990
Population Size (N): 3993 SE $(N)$ : $191.6 \quad$ Somple Size: 145
Lake Areo (A): 354924 SE(A): 68996
REGION 1
1.2 , \& 3

Min: $0.00 \quad Q_{1}: 4.40 \quad Q_{2}: 6.30 \quad Q_{3}: 9.80 \quad Q_{4}: 24.10 \quad \operatorname{Max}: 467.2$
Median: $\quad 7.40$
Mean: 22.64
Std. Dev.: 48.17


| Min: 0.00 | $Q_{1}:$ | 2.90 | $Q_{2}:$ | 4.50 | $Q_{3}: 8.30$ | $Q_{4}: 18.30$ | Max: 467.2 |
| :--- | ---: | ---: | ---: | ---: | ---: | ---: | ---: |
|  | 6.30 |  |  |  |  |  |  |
| Median: |  | 12.04 |  |  |  |  |  |
| Mean: |  |  |  |  |  |  |  |
| Std. Dev.: | 21.63 |  |  |  |  |  |  |

[^20]POPULATION DESCRIPTION PHASE II LAKE SURVEY. SPRING 1986
VARIABIE: ALKA11 ( $\mu \mathrm{eq} / 1$ )

Sample Size: 145 \begin{tabular}{l}
O9 MAY 1990 <br>

| REGION 1 |
| :--- |
| CLUSTERS |
| $1,2, \& 3$ |

\end{tabular}



Min: - $-63.1 \quad Q_{1}: 20.10 \quad Q_{2}: 60.80 \quad Q_{3}: 99.20 \quad Q_{4}: 168.1 \quad$ Max: 338.3
Median: $\quad 79.10$
Mean: 100.78
Std. Dev.: 92.38


[^21]POPULATION DESCRIPTION PHASE II LAKE SURVEY, SUMMER 1986

| VARIABLE: ALKA11 ( $\mu \mathrm{eq} / 1$ ) |  |  | 09 MAY 1990 |
| :---: | :---: | :---: | :---: |
|  |  |  | REGION 1 |
| Population Size (N): 3993 | SE(N): 191.6 | Sample Size: 145 | CLUSTERS |
| Lake Area (A) : 354924 | SE(A): 68996 |  | 1,2, \& 3 |



Min: $-48.6 \quad Q_{1}: 52.55 \quad Q_{2}: 94.70 \quad Q_{3}: 146.1 \quad Q_{4}: 286.7 \quad$ Max: 454.8

| Median: | 109.80 |
| :--- | :--- |
| Mean: | 151.49 |
| Std. Dev. | 108.54 |

* Confidence bounds are for number and area of lakes, but have been scaled.

POPULATION DESCRIPTION PHASE \|I LAKE SURVEY, FALL 1986
VARIABLE: ALKA11 ( $\mu \mathrm{eq} / \mathrm{I}) \quad 09$ MAY 1990



[^22]* Confidence bounds are for number and area of lakes, but have been scaled.

POPULATION DESCRIPTION PHASE II LAKE SURVEY. SPRING 1986
VARIABLE: CA98 ( $\mu \mathrm{eq} / 1) \quad 09$ MAY 1990

Population Size (N): 3993 SE(N): 191.6
Sample Size: 145
Lake Area (A): 354924 SE(A): 68995
REGION 1 CLUSTERS
1.2, \& 3


Min: $27.44 \quad Q_{1}: 88.27 \quad Q_{2}: 125.2 \quad Q_{3}: 150.4 \quad Q_{4}: 246.8 \quad \operatorname{Max}: 441.9$

## Median: <br> 139.17

Mean: 162.45
Std. Dev.: 89.61


Min: $27.44 \quad Q_{1}: 96.16 \quad Q_{2}: 134.4 \quad Q_{3}: 168.5 \quad Q_{4}: 275.2 \quad$ Max: 441.9

$$
\begin{array}{lr}
\text { Median: } & 140.62 \\
\text { Mean: } & 179.88 \\
\text { Std. Dev. : } & 90.52
\end{array}
$$

* Confidence bounds ore for number and area of lakes, but have been scaled.

POPULATION DESCRIPTION PHASE II LAKE SURVEY, SUMMER 1986
VARIABLE: CA98 ( $\mu \mathrm{eq} / 1$ ) 09 MAY 1990



Min: $23.40 \quad Q_{1}: 109.2 \quad Q_{2}: 144.6 \quad Q_{3}: 182.5 \quad Q_{4}: 309.7 \quad$ Max: 431.6

## Median: <br> 162.92

Mean: 197.51
Std. Dev.: 102.12

* Confidence bounds are for number and area of lakes, but have been scaled.



| Min: 29.89 | $Q_{1}: 118.4$ | $Q_{2}: 151.4$ | $Q_{3}: 208.6$ | $Q_{4}: 337.0$ | Max: 480.2 |
| :--- | ---: | :--- | :--- | :--- | :--- | :--- |
|  |  |  |  |  |  |
| Median: | 182.88 |  |  |  |  |
| Mean: | 212.58 |  |  |  |  |
| Std. Dev.: | 109.85 |  |  |  |  |

FOPULATION DESCRIPTION PHASE II LAKE SURVEY, FAIL 1986


Min: $5.61 \quad Q_{1}: 12.58 \quad Q_{2}: 33.85 \quad Q_{3}: 93.32 \quad Q_{4}: 134.4 \quad \operatorname{Max}: 667.9$
Median: 59.13
Mean: 106.91

Std. Dev.: 129.61
POPULATION DESCRIPTION PHASE II LAKE SURVEY, SPRING 1986
VARIABLE: COLORO2 (PCU) ..... 10 MAY 1990
Population Size (N): 3993 SE(N): 191.6 Sample Size ..... 145Lake Area (A): 354924 SE(A): 68996REGION 1CLUSTERS1,2 , \& 3

Min: $0.00 \quad Q_{1}: 10.00 \quad Q_{2}: 20.00 \quad Q_{3}: 25.00 \quad Q_{4}: 30.00 \quad \operatorname{Max}: 95.00$
Median: ..... 20.00
Mean: ..... 23.64
Std. Dev.: ..... 13.98

Min: $0.00 Q_{1}: 15.00$ 20.00 $Q_{3}: 25.00 \quad Q_{4}: 30.00$ Max: 95.00
Median: ..... 25.00
Mean: ..... 22.78
Std. Dev.: ..... 11.30

* Confidence bounds are for number and area of lakes, but have been scaled.

POPULATION DESCRIPTION PHASE II LAKE SURVE, WMMER IGB6



* Confidence bounds are for number and area of lakes, but have been scaled.

VARIABLE: COLOROZ (PCU) O9 MAY 1990

| Population Size (N): 3993 | SE(N): 191.5 |
| :--- | :--- | :--- |
| Lake Area $(A): 354924$ | $S E(A): 68996$ |$\quad$ Sample Size: \(145\left[\begin{array}{l}REGION 1 <br>

CLUSTERS <br>
1,2, \& 83 <br>
\hline\end{array}\right.\)



* Confidence bounds are for number and area of lakes, but have been scaled.

POPULATION DESCRIPTION PHASE II LAKE SURVEY, SPRING 1986



Min: $12.40 \quad Q_{1}: 28.50 \quad Q_{2}: 30.40 \quad Q_{3}: 40.00 \quad Q_{4}: 59.30 \quad$ Max: 126.2

* Confidence bounds are for number and area of lakes, but have been scaled.

POPULATION DESCRIPTION PHASE II LAKE SURVEY, SUMMER 1986
VARIABLE: COND11 ( $\mu \mathrm{S} / \mathrm{cm}$ ) 10 MAY 1990


Min: $11.20 \quad Q_{1}: 29.40 \quad Q_{2}: 32.60 \quad Q_{3}: 43.30 \quad Q_{4}: 63.60 \quad$ Max: 125.6

* Confidence bounds are for number and area of lakes, but have been scaled.


$\operatorname{Min}: 11.40 \quad Q_{1}: 30.40 \quad Q_{2}: 33.50 \quad Q_{3}: 44.10 \quad Q_{4}: 65.70 \quad$ Max: 138.8
Median: 41.30
Mean: 44.25
Std. Dev.: 20.88
* Confidence bounds are for number and area of lakes, but nove been scaled.

POPULATION DESCRIPTION PHASE II LAKE SURVEY, SPRING 1986


Min: $0.02 \quad Q_{1}: 1.07 \quad Q_{2}: 1.66 \quad Q_{3}: 2.15 \quad Q_{4}: 3.84 \quad \operatorname{Max}: 4.60$

| Median: | 1.92 |
| :--- | :--- |
| Mean: | 2.16 |
| Std. Dev. $:$ | 1.16 |

* Confidence bounds are for number and area of lakes, but have been scaled

FIPUULATION DESCRIPTION PHASE II LAKE SURVEY, SUMMER 1986
VARIABLE: $\operatorname{DICO} 2(\mathrm{mg} / \mathrm{I})$

Somple Size: 145 \begin{tabular}{l}
10 MA: 19'月. <br>

| REGION 1 |
| :--- |
| CLISIIFS |
| $1,2, \& 3$ | <br>

\hline
\end{tabular}

Population Size (N): 3993 SE(N). 191.6
Somple Size: 145
CLUSTIFS
Lake Area (A): 354924 SE(A): 68996
1,2, \&



* Confidence bounds are for number and areo of lakes, but have been scaled

FOFULAIOH DESCRIPTION PHASE II LAKE SURVEY, FALL 1986


Min: $0.23 \quad Q_{1}: 1.04 \quad Q_{2}: 1.49 \quad Q_{3}: 2.07 \quad Q_{4}: 3.42 \quad \operatorname{Max}: \quad 6.18$

| Median: | 1.78 |
| :--- | :--- |
| Mean: | 2.14 |
| Std. Dev. $:$ | 1.28 |

* Confidence bounds are for number and area of lakes, but have been scaled.

HUFULATION DESCRIFTION PHASE II LAKE SURVEY, SFRING $198 G$
VARIABLE: DOC11 (mg/i) O9 MAY 19516,


Min: $0.20 \quad Q_{1}: 2.62 \quad Q_{2}: 3.13 \quad Q_{3}: 4.02 \quad Q_{4}: 5.93$ Max: 10.92

Median: 3.45
Mean: 3.84
Std. Dev.: 1.51
, Confidence bounds are for number and area of lakes, but have heen srath


Min: $0.30 \quad Q_{1}: 2.76 \quad Q_{2}: 3.49 \quad Q_{3}: 4.66 \quad Q_{4}: 7.03 \quad \operatorname{Max}: 11.92$

| Median: | 3.74 |
| :--- | :--- |
| Mean: | 4.37 |

Std. Dev.:
1.97

* Confidence bounds are for number and area of lakes, but have been scaled.

FOPULATION DESCRIPTION PHASE IH LAKE SURVEY, FALL 1986
VARIABLE: DOC1 1 ( $\mathrm{mg} / \mathrm{I}$ ) 09 MAY 1990

| Population Size (N): 3993 |  |
| :--- | :--- |
| Lake Area (A): 354924 | SE(N):191.6 |
| SE(A): 68996 |  |$\quad$ Sample Size. \(145\left[\begin{array}{l}REGION 1 <br>

CLUSTERS <br>
1,2, \& 3\end{array}\right]\)



| Median: | 3.68 |
| :--- | :--- |
| Mean: | 4.44 |

Std. Dev.: 2.16

Median: $\quad 3.68$

## POPULATION DESCRIPTION PHASE II LAKE SURVEY, SPRING 1986




[^23]POPULATION DESCRIPTION PHASE II LAKE SURVEY, SUMMER 1986
VARIABLE: FE1 1 ( $\mu \mathrm{g} / \mathrm{I})$ ..... 10 MAY 1990
Popuiation Size (N): 3993 SE(N): 191.6 Sample Size: ..... 145

REGION 1
CLUSTERS
$1.2, \& 3$
1.2, \& 3


$$
\text { Min: } 0.00 \quad Q_{1}: 9.00 \quad Q_{2}: 18.00 \quad Q_{3}: 33.00 \quad Q_{4}: 45.00 \quad \text { Max: } 895.0
$$

Median: ..... 25.00

Median:

Median:
34.00

Mean:
62.21

Std. Dev.: 101.25
34.69
Std. Dev.: 51.42

POPULATION DESCRIPTION PHASE I LAKE SURVEY, FALL 1986



Min: $0.00 \quad Q_{1}: 14.00 \quad Q_{2}: 43.00 \quad Q_{3}: 58.00 \quad Q_{4}: 84.00 \quad \operatorname{Max}: 556.0$

| Median: | 43.00 |
| :--- | :--- |
| Mean: | 62.23 |
| Std. Dev.: | 69.42 |

Std. Dev.: 69.42

FOPULATION DESCRIPTION PHASE \| LAKE SURVEY, SPRING 1 IJRG.
VARIABLE: FTL98 ( $\mu \mathrm{eq} / \mathrm{I})$
Sample Size: $145\left[\begin{array}{l}10 \text { MAY } 1990 \\ \text { RESION } \\ \text { CISTERS } \\ 1,2, \& 3\end{array}\right]$



[^24]

POPULATION DESCRIPTION PHASE II LAKE SURVEY, FAIL 1986


Min: $0.00 \quad \mathrm{Q}_{1}: 2.00 \quad \mathrm{Q}_{2}: 3.18 \quad \mathrm{Q}_{3}: 3.86 \quad \mathrm{Q}_{4}: \quad 4.46 \quad$ Max: 19.93

| Median: | 3.28 |
| :--- | :--- |
| Mean: | 5.20 |

Std. Dev.: 5.26

[^25]POPULATION DESCRIPTION PHASE II LAKE SURVEY, SPRING 1986 VARIABIE: K98 ( $\mu \mathrm{eq} / 1$ ) 10 MAY 1990


Min: $2.56 \quad Q_{1}: 6.83 \quad Q_{2}: 8.49 \quad Q_{3}: 9.21 \quad Q_{4}: 12.17 \quad \operatorname{Max}: 42.22$
Median: 9.21

Mean: 10.20
Std. Dev.: 5.46

## POPULATION DESCRIPTION PHASE II LAKE SURVEY, SUMMER 1986



Min: $1.38 \quad Q_{1}: 7.08 \quad Q_{2}: \quad 8.13 \quad Q_{3}: \quad 9.15 \quad Q_{4}: 12.50 \quad$ Max: 53.57

## POPULATION DESCRIPTION PHASE II LAKE SURVEY, FALL 1986

VARIABLE: K98 ( $\mu \mathrm{eq} / \mathrm{I})$

Sample Size: 145 \begin{tabular}{l}
O9 MAY 1990 <br>

| REGION 1 |
| :--- |
| CLUSTERS |
| $1,2, \& 3$ |

\end{tabular}

Population Size (N): 3993 SE(N): 191.5
Sample Size: 145 CLUSTERS
Lake Area (A): 354924 SE(A): 68995

DIRECT



Median:
9.90

Mean:
12.81

Std. Dev.: 9.27

Median: ..... 8.90
Mean:

10.95

Std. Dev.: 6.63

* Confidence bounds are for number and area of lakes, but have been scaled

POPULATION DESCRIPTION PHASE II LAKE SURVEY, SPRING 1986
VARIABLE. MG98 ( $\mu \mathrm{eq} / 1$ ) 10 MAY 1990


Min: $11.93 \quad Q_{1}: 32.08 \quad Q_{2}: 44.83 \quad Q_{3}: 61.86 \quad Q_{4}: 94.68 \quad \operatorname{Max}: 225.0$
Median: $\quad 49.93$

Mean: $\quad 59.98$
Std. Dev.: 29.96

POPULATION DESCRIPTION PHASE II LAKE SURVEY, SUMMER 1986
VARIABLE: MG98 ( $\mu \mathrm{eq} / 1$ ) 10 MAY 1990



* Confidence bounds are for number and area of lakes, but have been scaled.


## POPULATION DESCRIPTION PHASE II LAKE SURVEY, FALL 1986




* Confidence bounds are for number and area of lakes, but hove been scaled.

Mean: 68.71
Std. Dev.: 36.43

POPULATION DESCRIPTION PHASE II LAKE SURVEY, SPRING 1986
VARIABLE: MN11 ( $\mu \mathrm{g} / 1) \quad 10$ MAY 1990



[^26]POPULATION DESCRIPTION PHASE \| LAKE SURVEY, SUMMER 1986
VARIABLE: MN11 ( $\mu \mathrm{g} / \mathrm{I})$

Sample Size: 145 \begin{tabular}{l}
10 MAY $19 g 0$ <br>

| REGION 1 |
| :--- |
| CLUSTEFS |
| $1,2, \& 3$ | <br>

\hline
\end{tabular}

| Population Size (N): 3993 | SE(N): 191.6 |
| :--- | :--- |
| Lake Area (A): 354924 | SE(A): 68996 |$\quad$| Rample Size: 145 | CLUSTERS <br> $1,2, \& 3$ |
| :--- | :--- |




[^27]


[^28]
## POPULATION DESCRIPTION PHASE II LAKE SURVEY. SPRING 1986

VARIABLE: NA98 ( $\mu \mathrm{eq} / \mathrm{I}$ )
14 MAY ICOC

| Population Size (N):3993 | SE(N): 191.6 |
| :--- | :--- | :--- |
| Lake Area (A): 354924 | SE (A): 68996 |$\quad$ Sample Size: 145 | REGION 1 |
| :--- |
| CLUSTERS |
| $1,2, \& 3$ |


Min: $3.35 \quad Q_{1}: 33.10 \quad Q_{2}: 59.33 \quad Q_{3}: 93.39 \quad Q_{4}: 217.5 \quad \operatorname{Max}: 590.3$

## Median: <br> 69.56 <br> Mean: <br> 122.43

Std. Dev.: 123.72

Min: $3.35 \quad Q_{1}: 32.36 \quad \mathbf{Q}_{2}: 56.77 \quad \mathbf{Q}_{3}: 93.39 \quad \mathbf{Q}_{4}: 113.8 \quad$ Max: 590.3
Median:
Median:
79.78
79.78
Mean:
Mean:
106.43
106.43
Std. Dev.: 102.54
Std. Dev.: 102.54

* Confidence bounds are for number and areo of lakes, but have been scoled.

FOFULATION DESCRIPTION PHASE II LAKE SURVEY, SUMMER 1986
VARIABLE: NA98 ( $\mu \mathrm{eq} / 1$ )

Somple Size: 145 \begin{tabular}{l}
10 MAY 1990 <br>

| REGION 1 |
| :--- |
| CLUSTERS |
| $1,2, \& 3$ | <br>

\hline
\end{tabular}

Fopulation Size (N): 3993 SE(N): 191.6
Somple Size: 145
Lake Area (A): 354924 SE(A): 68996
1,2, \& 3



[^29]POPULATION DESCRIPTION PHASE II LAKE SURVEY, FALL 1986
VARIABLE: NA98 ( $\mu \mathrm{eq} / 1) \quad 09$ MAY 1990

Population Size (N): 3993 SE(N): 191.6 Sample Size: 145
Lake Area (A): 354924 SE(A): 68996

REGION 1 CLUSTERS 1,2 , \& 3


POPULATION DESCRIPTION PHASE II LAKE SURVEY, SPRING 1986
VARIABLE: NH498 ( $\mu \mathrm{eq} / 1$ ) 10 MAY 1990


Min: $0.00 \quad Q_{1}: 0.00 \quad Q_{2}: 0.00 \quad Q_{3}: 0.05 \quad Q_{4}: 1.28 \quad$ Max: 13.92

| Median: | 0.00 |
| :--- | :--- |
| Mean: | 0.78 |
| Std | 2.03 |

* Confidence bounds ore for number and area of lakes, but have been scoled.

POPULATION DESCRIPTION PHASE II LAKE SURVEY, SUMMER 1986



* Confidence bounds are for number and area of lakes, but have been scaled.

POPULATIOH DESCRIF IION PHASE II LAKE SURVEY, FALL 1986



[^30]

$$
\text { Min: } 0.00 \quad Q_{1}: 1.71 \quad Q_{2}: \quad 4.43 \quad Q_{3}: 6.78 \quad Q_{4}: 14.61 \quad \operatorname{Max}: 47.16
$$

| Median: | 5.81 |
| :--- | :--- |
| Mean: | 7.44 |

Mean: $\quad 7.44$
Std. Dev.: 7.25



[^31]POPULATION DESCRIPTION PHASE II LAKE SURVEY, FALL 1986


Min: $0.03 \quad Q_{1}: 0.32 \quad Q_{2}: 0.70 \quad Q_{3}: 1.77 \quad Q_{4}: 8.40 \quad \operatorname{Max}: 18.84$

Median:
1.74

Mean: $\quad 3.55$
Std. Dev.: 4.60

* Confidence bounds are for number and area of lakes, but have been scaled.

POPULATION DESCRIPTION PHASE \| LAKE SURVEY, SPRING 1986

| VARIABLE: PHO2 | O9 MAY 1990 <br> Population Size (N): 3993 <br> Lake Areo (A): 354924 |
| :--- | :--- |
| SE(N): 191.6 <br> SE(A): 68997 | Sample Size: 145RLUSTERS <br> $1,2, \& 3$ |




[^32]POPULATION DESCRIPTION PHASE II LAKE SURVEY, SUMMER 1986
VARIABLE: PHO2 09 MAY 1990
$\begin{array}{lll}\text { Population Size }(N): 3993 & \text { SE(N): } 191.6 \\ \text { Lake Area (A): } 354924 & \text { SE(A): 68995 }\end{array} \quad$ Sample Size: $\left.145 \begin{array}{|l}\text { REGION } 1 \\ \text { CLUSTERS } \\ 1,2, \& 3\end{array}\right]$

Min: $4.50 \quad Q_{1}: 5.92 \quad Q_{2}: 6.46 \quad Q_{3}: 6.73 \quad Q_{4}: \quad 6.98 \quad \operatorname{Max}: 9.08$

| Median: | 6.53 |
| :--- | :--- |
| Mean: | 6.47 |
| Std. Dev. : | 0.74 |


6.73

Std. Dev.:
0.53

* Confidence bounds are for number and area of lakes, but have been scaled.

POPULATION DESCRIPTION PHASE II LAKE SURVEY, FALL 1986
VARIABLE: PHO2

Sample Size: 145 \begin{tabular}{l}
O9 MAY 1990 <br>

| REGION 1 |
| :--- |
| CLUSTERS |
| $1,2, \& 3$ | <br>

\hline
\end{tabular}




| Median: | 6.69 |
| :--- | :--- |
| Mean: | 6.51 |
| Std. Dev.: | 0.67 |



$\begin{array}{ll}\text { Median: } & 6.84 \\ \text { Mean: } & 6.78\end{array}$
Std. Dev.: 0.46
POPULATION DESCRIP*ION PHASE II LAKE SURVEY, SPRING ; 186
VARIABLE: PTL11 ( $\mu \mathrm{g} / \mathrm{I})$
10 MAY 1990
Population Size ( $N$ ): 3993 SE(N): 191.5 Sample Size: 145
Lake Areo (A): 354924
SE(A): 68995
REGION 1
CLUSTERS
$1,2, \& 3$


| Min: 0.00 | $Q_{1}:$ | 4.00 | $Q_{2}:$ | 8.00 | $Q_{3}: 10.00$ | $Q_{4}: 13.00$ |
| :--- | ---: | ---: | ---: | ---: | ---: | ---: |
|  |  |  | Max: 52.00 |  |  |  |
| Median: |  | 9.00 |  |  |  |  |
| Mean: | 10.87 |  |  |  |  |  |
| Std. Dev.: | 9.71 |  |  |  |  |  |
|  |  |  |  |  |  |  |



* Confidence bounds are for number and area of lakes, but nave deen suuleu.

POPULATION DESCRIPTION PHASE II LAKE SURVEY. SUMMER 1986


$\operatorname{Min}: 0.40 \quad Q_{1}: 2.70 \quad Q_{2}: 4.20 \quad Q_{3}: 6.10 \quad Q_{4}: 10.00 \quad \operatorname{Max}: 137.0$

$$
\begin{array}{ll}
\text { Median: } & 6.00 \\
\text { Mean: } & 7.29
\end{array}
$$

$$
\text { Std. Dev.: } 9.48
$$

POPULATION DESCRIPTION PHASE II LAKE SURVEY, FALL 1986
VARIABLE: PTL11 ( $\mu \mathrm{g} / \mathrm{I})$
O9 MAY 1990

| REGION 1 |
| :--- |
| CLUSTERS |
| $1,2, \& 3$ |

Lake Area (A): 354924 SE(A): 68995
Sample Size: 145 CLUSTERS $1,2, \& 3$

Min: $1.00 \quad Q_{1}: 4.90 \quad Q_{2}: 6.90 \quad Q_{3}: 10.30 \quad Q_{4}: 15.50 \quad \operatorname{Max}: 54.30$

| Median: | 8.00 |
| :--- | ---: |
| Mean: | 10.99 |
| Std. Dev.: | 8.73 |



## Median: <br> 5.40

Mean: 6.97
Std. Dev.: 5.09

* Confidence bounds are for number and area of lakes, but have been scaled

POPULATION DESCRIPTION PHASE II LAKE SURVEY. SPRING 1986



POPULATION DESCRIPTION PHASE II LAKE SURVEY, SUMMER 1986
VARIABLE: SECME98 (m) 10 MAY 1990


Min: $0.55 \quad Q_{1}: 2.75 \quad Q_{2}: 3.80 \quad Q_{3}: 4.60 \quad Q_{4}: \quad 5.90 \quad$ Max: 12.60

[^33]POPULATION DESCRIPTION PHASE II LAKE SURVEY, FALL 1986


Min: $0.55 \quad Q_{1}: 2.35 \quad Q_{2}: 2.60 \quad Q_{3}: 3.35 \quad Q_{4}: 5.00 \quad \operatorname{Max}: 10.90$

Median: $\quad 3.00$
Mean: $\quad 3.56$
Std. Dev.: 1.73
POPULATION DESCRIPTION PHASE II LAKE SURVEY, SPRING 1986
VARIABIE: SIO211 (mg/I)
10 MAY 1990

| Fopulation Size (N): 3993 | SE (N): 191.6 |
| :--- | :--- | :--- |
| Lake Area (A): 354924 | SE(A): 68997 |$\quad$ Sample Size: \(145\left[\begin{array}{l}REGION 1 <br>

CLUSTERS <br>
1,2, \& 3\end{array}\right.\)



## Median: <br> 3.18

Mean: 3.22
Std. Dev.: 1.69


Min: $0.00 \quad Q_{1}: 2.34 \quad Q_{2}: 3.05 \quad Q_{3}: 4.36 \quad Q_{4}: \quad 5.66 \quad$ Max: 7.13
Median: $\quad \mathbf{3 . 4 6}$

## POPULATION DESCRIPTION PHASE II LAKE SURVEY, SUMMER 1986

VARIABLE: SIO211 (mg/I)
10 MAY 1990


Min: $0.03 \quad Q_{1}: 1.20 \quad Q_{2}: 1.59 \quad Q_{3}: 2.35 \quad Q_{4}: 4.23 \quad$ Max: 5.81

## Median: <br> 2.01

Mean: 2.54
Std. Dev.: 1.62

* Confidence bounds are for number and area of lakes, but have been scoled.

POPULATION DESCRIPTION PHASE II LAKE SURVEY, FALL 1986


Min: $0.01 \quad Q_{1}: 1.36 \quad Q_{2}: \quad 2.50 \quad Q_{3}: 3.40 \quad Q_{4}: \quad 6.04 \quad \operatorname{Max}: 7.25$

## Median: $\quad 2.52$ <br> Mean: 3.28

Std. Dev.: 2.03

* Confidence bounds are for number and areo of lakes, but have been scaled.

POPULATION DESCRIPTION PHASE II LAKE SURVEY, SPRING 1986



$$
\text { Min: } 25.86 \quad Q_{1}: 82.43 \quad Q_{2}: 92.25 \quad Q_{3}: 110.4 \quad Q_{4}: 126.7 \quad \operatorname{Max}: 289.1
$$

```
Median: 99.44

POPULATION DESCRIPTION PHASE II LAKE SURVEY, SUMMER 1986
VARIABLE: SO498 ( \(\mu \mathrm{eq} / 1\) )
Sample Size: 145 \begin{tabular}{l} 
O9 MAY 1990 \\
\begin{tabular}{l} 
REGION 1 \\
CLUSTERS \\
\(1,2, \& 3\)
\end{tabular} \\
\hline
\end{tabular}


* Confidence bounds ore for number and area of lakes, but have been scaled

Std. Dev.: 38.18

\section*{POPULATION DESCRIPTION PHASE II LAKE SURVEY, FALL 1986}



Min: \(28.94 \quad Q_{1}: 73.12 \quad Q_{2}: 88.38 \quad Q_{3}: 107.8 \quad Q_{4}: 130.8 \quad\) Max: 327.9
Median:
97.44
Mean: 105.02

Std. Dev.: 41.88
* Confidence bounds are for number and area of lakes, but have been scaled.

POPULATION DESCRIPTION PHASE II LAKE SURVEY. SPRING 1986
VARIABLE: SOBC98 ( \(\mu \mathrm{eq} / \mathrm{I}\) ) 14 MAY 1990

Populotion Size (N):3993 SE(N): 191.6 Sample Size: 145
Lake Areo (A): 354924 SE(A): 68995
\begin{tabular}{l} 
REGION 1 \\
CLUSTERS \\
\(1,2, \& 3\) \\
\hline
\end{tabular}


Min: \(52.23 \quad Q_{1}: 193.1 \quad Q_{2}: 267.7 \quad Q_{3}: 350.8 \quad Q_{4}: 472.0 \quad \operatorname{Max}: 1101\)
\begin{tabular}{ll} 
Median: & 300.97 \\
Mean: & 356.15 \\
Std. Dev.: & 199.80
\end{tabular}

\begin{tabular}{lrrrrrr} 
Min: 52.23 & \(Q_{1}: 234.3\) & \(Q_{2}: 256.4\) & \(Q_{3}: 409.1\) & \(Q_{4}: 477.7\) & Max: 1101 \\
Median: & 304.24 & & & & \\
Mean: & 356.49 & & & & \\
Std. Dev.: & 165.56 & & & &
\end{tabular}
* Confidence bounds are for nurnber and area of lakes, but have been scaled

POPULATION DESCRIPTION PHASE II LAKE SURVEY, SUMMER 1986




Median:
345.62

Mean: 394.39
Std. Dev.: 183.52

\begin{tabular}{|c|c|c|c|}
\hline VARIABLE：SOBC98（ \(\mu \mathrm{eq} / 1)\) & & & 09 MAY 1990 \\
\hline & & & REGION 1 \\
\hline Population Size（N）： 3993 & SE（ N\(): 191.6\) & Sample Size： 145 & CLUSTERS \\
\hline Lake Area（A）： 354924 & SE（A）： 68995 & & 1．2，\＆ 3 \\
\hline
\end{tabular}

Min：61．72 \(Q_{1}: 221.8 \quad Q_{2}: 340.8 \quad Q_{3}: 411.3 \quad Q_{4}: 573.0 \quad\) Max： 1230
\begin{tabular}{ll} 
Median： & 370.31 \\
Mean： & 417.41 \\
Std．Dev．： & 234.30
\end{tabular}

Median：\(\quad 383.10\)
Std．Dev．： 198.89

\section*{APPENDIX B}

\section*{LISTING OF LAKES SAMPLED IN ELS-II}

Table B-1 presents a list of the \(\mathbf{1 4 5}\) target lakes sampled during Phase II of the Eastern Lake Survey (ELS-II). Lakes are ordered by state location and sorted by Lake ID within each state. A more complete description of the sample lakes (latitude, longitude, physical characteristics, etc.) can be found in volumes II and III of the Eastern Lake Survey - Phase I data report (Overton et al., 1986; Kanciruk et al., 1986).

Table B-1. Target lakes sampled in Phase-II of the Eastern Lake Survey.
\begin{tabular}{|c|c|c|c|c|c|c|}
\hline State & Lake ID & Lake Name & ELS-II Cluster & Modif. ELS-I Weight & ELS-II Cond. Weight & ELS-II Sample Weight \\
\hline CT & 1B3-056 & RIGA LAKE & 1 & 27.209 & 1.0000 & 27.209 \\
\hline CT & 1D3-025 & LONG POND & 3 & 19.426 & 2.4954 & 48.477 \\
\hline CT & 1D3-029 & KILLINGLY POND & 1 & 19.426 & 1.0000 & 19.426 \\
\hline CT & 1D3-033 & (NO NAME) & 3 & 19.426 & 2.4954 & 48.477 \\
\hline MA & 1C1-068 & LINCOLN POND & 1 & 7.822 & 1.5706 & 12.285 \\
\hline MA & 1C1-070 & PACKARD POND & 2 & 7.822 & 2.8181 & 22.043 \\
\hline MA & 1C2-050 & MOORES POND & 2 & 10.743 & 2.0518 & 22.043 \\
\hline MA & 1C2-054 & LAKE WAMPONOAG & 1 & 10.743 & 1.1436 & 12.285 \\
\hline MA & 1D1-014 & HAMILTON RESERVOIR & 3 & 6.572 & 7.5402 & 49.554 \\
\hline MA & 1D1-031 & KINGS POND & 1 & 6.572 & 1.8694 & 12.285 \\
\hline MA & 1D1-034 & ROCKY POND & 1 & 6.572 & 1.8694 & 12.285 \\
\hline MA & 1D1-037 & EZEKIEL POND & 1 & 6.572 & 1.8694 & 12.285 \\
\hline MA & 1D1-046 & ROBBINS POND & 1 & 6.572 & 1.8694 & 12.285 \\
\hline MA & 1D1-054 & UPPER MILLPOND & 2 & 6.572 & 3.3541 & 22.043 \\
\hline MA & 1D1-056 & LITTLE WEST POND & 1 & 6.572 & 1.8694 & 12.285 \\
\hline MA & 1D1-068 & LITTLE SANDY POND & 1 & 6.572 & 1.8694 & 12.285 \\
\hline MA & 1D2-025 & LITTLE QUITTACAS POND & 2 & 6.905 & 3.1342 & 21.642 \\
\hline MA & 1D2-027 & SANDY POND & 1 & 6.905 & 1.7468 & 12.062 \\
\hline MA & 1D2-036 & MICAH POND & 1 & 6.905 & 1.7468 & 12.062 \\
\hline MA & 1D2-074 & STETSON POND & 2 & 6.905 & 3.1342 & 21.642 \\
\hline MA & 1D2-084 & GOOSE POND & 3 & 6.905 & 7.0459 & 48.652 \\
\hline MA & 1D2-093 & ASHLAND RESERVOIR & 3 & 6.905 & 7.0459 & 48.652 \\
\hline MA & 1D2-094 & SNOWS POND & 1 & 6.905 & 1.7468 & 12.062 \\
\hline MA & 1D3-002 & DYKES POND & 1 & 19.426 & 1.0000 & 19.426 \\
\hline MA & 1D3-003 & SANDY POND & 3 & 19.426 & 2.4954 & 48.477 \\
\hline ME & 1-1-017 & WELHERN POND & 3 & 7.822 & 6.3352 & 49.554 \\
\hline ME & 1C1-018 & DECKER PONDS (EASTERN) & 3 & 7.822 & 6.3352 & 49.554 \\
\hline ME & 1C1-021 & CLEAR POND & 3 & 7.822 & 6.3352 & 49.554 \\
\hline ME & 1C1-031 & HUNT POND & 2 & 7.822 & 2.8181 & 22.043 \\
\hline ME & 1-2-002 & IRON POND & 2 & 10.743 & 2.0518 & 22.043 \\
\hline ME & 1-2-012 & BLACK POND & 2 & 10.743 & 2.0518 & 22.043 \\
\hline ME & 1-2-016 & TRAFTON POND & 3 & 10.743 & 4.6127 & 49.554 \\
\hline ME & 1-2-056 & DRURY POND & 3 & 10.743 & 4.6127 & 49.554 \\
\hline ME & 1-2-064 & HANCOCK POND & 2 & 10.743 & 2.0518 & 22.043 \\
\hline ME & 1C2-068 & QUIMBY POND & 3 & 10.743 & 4.6127 & 49.554 \\
\hline ME & 1-3-032 & BEAR POND & 3 & 8.953 & 5.5349 & 49.554 \\
\hline ME & 1E1-009 & PEEP LAKE & 1 & 8.070 & 1.5386 & 12.416 \\
\hline ME & 1E1-010 & SIX PONDS & 3 & 8.070 & 6.2059 & 50.082 \\
\hline ME & 1E1-011 & FOURTH DAVIS POND & 2 & 8.070 & 2.7605 & 22.278 \\
\hline ME & 1E1-025 & BEAN PONDS (MIDDLE) & 3 & 8.070 & 6.2059 & 50.082 \\
\hline ME & 1E1-040 & LT. GREENWOOD POND (WEST) & 2 & 8.070 & 2.7605 & 22.278 \\
\hline ME & 1E1-050 & LOWER OXBROOK LAKE & 2 & 8.070 & 2.7605 & 22.278 \\
\hline
\end{tabular}

Table B-1. Target lakes sampled in Phase-II of the Eastern Lake Survey (Continued).
\begin{tabular}{|c|c|c|c|c|c|c|}
\hline State & Lake ID & Lake Name & ELS-II Cluster & Modif. ELS-I Weight & ELS-II Cond. Weight & \begin{tabular}{l}
ELS-II \\
Sample \\
Weight
\end{tabular} \\
\hline ME & 1E1-054 & DUCK LAKE & 2 & 8.070 & 2.7605 & 22.278 \\
\hline ME & 1E1-061 & LITTLE SEAVEY LAKE & 2 & 8.070 & 2.7605 & 22.278 \\
\hline ME & 1E1-062 & LONG POND & 2 & 8.070 & 2.7605 & 22.278 \\
\hline ME & 1E1-073 & GEORGES POND & 2 & 8.070 & 2.7605 & 22.278 \\
\hline ME & 1E1-074 & CRAIG POND & 2 & 8.070 & 2.7605 & 22.278 \\
\hline ME & 1E1-077 & PARKER POND & 2 & 8.070 & 2.7605 & 22.278 \\
\hline ME & 1E1-082 & STEVENS POND & 2 & 8.070 & 2.7605 & 22.278 \\
\hline ME & 1E1-092 & GREAT POND & 2 & 8.070 & 2.7605 & 22.278 \\
\hline ME & 1E1-096 & MIDDLE CHAIN LAKE & 2 & 8.070 & 2.7605 & 22.278 \\
\hline ME & 1E1-106 & GREENWOOD POND & 2 & 8.070 & 2.7605 & 22.278 \\
\hline ME & 1E1-111 & LONG POND & & 8.070 & 1.5386 & 12.416 \\
\hline ME & 1E1-120 & (NO NAME) & 2 & 8.070 & 2.7605 & 22.278 \\
\hline ME & 1E1-123 & FIRST POND & 2 & 8.070 & 2.7605 & 22.278 \\
\hline ME & 1E2-007 & FAIRBANKS POND & 2 & 8.344 & 2.5921 & 21.628 \\
\hline ME & 1E2-016 & ROUND POND & 3 & 8.344 & 5.8271 & 48.621 \\
\hline ME & 1E2-018 & WEBSTER LAKE & 3 & 8.344 & 5.8271 & 48.621 \\
\hline ME & 1E2-030 & ROUND LAKE & 3 & 8.344 & 5.8271 & 48.621 \\
\hline ME & 1E2-038 & NELSON POND & 1 & 8.344 & 1.4447 & 12.054 \\
\hline ME & 1E2-049 & GROSS POND & 1 & 8.344 & 1.4447 & 12.054 \\
\hline ME & 1E2-054 & BRETTUNS POND & 3 & 8.344 & 5.8271 & 48.621 \\
\hline ME & 1E2-056 & PEABODY POND & 2 & 8.344 & 2.5921 & 21.628 \\
\hline ME & 1E2-063 & KALERS POND & 2 & 8.344 & 2.5921 & 21.628 \\
\hline ME & 1E3-022 & NUMBER NINE LAKE & 3 & 10.333 & 4.7957 & 49.554 \\
\hline ME & 1E3-041 & ROUND POND & 3 & 10.333 & 4.7957 & 49.554 \\
\hline ME & 1E3-042 & SAND POND & 3 & 10.333 & 4.7957 & 49.554 \\
\hline ME & 1E3-045 & MCCLURE POND & 3 & 10.333 & 4.7957 & 49.554 \\
\hline . ME & 1E3-055 & TOGUE POND & 3 & 10.333 & 4.7957 & 49.554 \\
\hline ME & 1E3-060 & MILLINOCKET LAKE & 3 & 10.333 & 4.7957 & 49.554 \\
\hline NH & 1C1-009 & UPPER BAKER POND & 3 & 7.822 & 6.3352 & 49.554 \\
\hline NH & 1C1-039 & OSSIPEE LAKE & 2 & 7.822 & 2.8181 & 22.043 \\
\hline NH & 1C1-050 & BILLINGS POND & 2 & 7.822 & 2.8181 & 22.043 \\
\hline NH & 1C1-066 & HAUNTED LAKE & 2 & 7.822 & 2.8181 & 22.043 \\
\hline NH & 1C1-084 & UPPER BEECH POND & 2 & 7.822 & 2.8181 & 22.043 \\
\hline NH & 1C1-086 & STAR LAKE & 2 & 7.822 & 2.8181 & 22.043 \\
\hline NH & 1C2-024 & LAKE WAUKEWAN & 3 & 10.743 & 4.6127 & 49.554 \\
\hline NH & 1-2-028 & SUNSET LAKE & 2 & 10.743 & 2.0518 & 22.043 \\
\hline NH & 1C2-035 & SMITH POND & 2 & 10.743 & 2.0518 & 22.043 \\
\hline NH & 1-2-037 & MENDUMS POND & 1 & 10.743 & 1.1436 & 12.285 \\
\hline NH & 1C2-041 & JUGGERNAUT POND & 1 & 10.743 & 1.1436 & 12.285 \\
\hline NH & 1-2-057 & BABBIDGE RESERVOIR & 2 & 10.743 & 2.0518 & 22.043 \\
\hline NH & 1C2-062 & PEMIGEWASSET LAKE & 2 & 10.743 & 2.0518 & 22.043 \\
\hline NH & 1C2-066 & TURTLE POND & 2 & 10.743 & 2.0518 & 22.043 \\
\hline NH & 1-3-055 & DARRAH POND & 1 & 8.953 & 1.3722 & 12.285 \\
\hline NH & 1-3-063 & MARTIN MEADOW POND & 3 & 8.953 & 5.5349 & 49.554 \\
\hline
\end{tabular}

Table B-1. Target lakes sampled in Phase-II of the Eastern Lake Survey (Continued).
\begin{tabular}{|c|c|c|c|c|c|c|}
\hline State & Lake ID & Lake Name & ELS-II Cluster & Modif. ELS-I Weight & ELS-II Cond. Weight & \begin{tabular}{l}
ELS-II \\
Sample \\
Weight
\end{tabular} \\
\hline NY & 1A1-003 & HAWK POND & 1 & 9.633 & 1.2754 & 12.285 \\
\hline NY & 1A1-008 & CEDAR RIVER FLOW & 2 & 9.633 & 2.2883 & 22.043 \\
\hline NY & 1A1-012 & WHITNEY LAKE & 1 & 9.633 & 1.2754 & 12.285 \\
\hline NY & 1A1-015 & HENDERSON LAKE & 1 & 9.633 & 1.2754 & 12.285 \\
\hline NY & 1A1-017 & CONSTABLE POND & 1 & 9.633 & 1.2754 & 12.285 \\
\hline NY & 1A1-028 & DRY CHANNEL POND & 1 & 9.633 & 1.2754 & 12.285 \\
\hline NY & 1A1-029 & MIDDLE POND & 3 & 9.633 & 5.1442 & 49.554 \\
\hline NY & 1A1-033 & KIWASSA LAKE & 3 & 9.633 & 5.1442 & 49.554 \\
\hline NY & 1A1-039 & JOHN POND & 1 & 9.633 & 1.2754 & 12.285 \\
\hline NY & 1A1-044 & LONG LAKE & 2 & 9.633 & 2.2883 & 22.043 \\
\hline NY & 1A1-049 & MIDDLE SOUTH POND & 1 & 9.633 & 1.2754 & 12.285 \\
\hline NY & 1A1-057 & HITCHCOCK LAKE & 1 & 9.633 & 1.2754 & 12.285 \\
\hline NY & 1A1-060 & SEVENTH LAKE (FULTON CHAIN) & 3 & 9.633 & 5.1442 & 49.554 \\
\hline NY & 1A1-061 & WOLF LAKE & 1 & 9.633 & 1.2754 & 12.285 \\
\hline NY & 1A1-064 & mT. ARAB LAKE & 2 & 9.633 & 2.2883 & 22.043 \\
\hline NY & 1A1-066 & WOODHULL LAKE & 1 & 9.633 & 1.2754 & 12.285 \\
\hline NY & 1A1-070 & PARADOX LAKE & 3 & 9.633 & 5.1442 & 49.554 \\
\hline NY & 1A1-073 & GULL LAKES (SOUTH) & 1 & 9.633 & 1.2754 & 12.285 \\
\hline NY & 1A2-002 & ST. JOHN LAKE & 1 & 8.338 & 1.4734 & 12.285 \\
\hline NY & 1A2-004 & DUCK LAKE & 1 & 8.338 & 1.4734 & 12.285 \\
\hline NY & 1A2-006 & LAKE FRANCES & 2 & 8.338 & 2.6437 & 22.043 \\
\hline NY & 1A2-041 & MUD LAKE & 2 & 8.338 & 2.6437 & 22.043 \\
\hline NY & 1A2-042 & NORTH BRANCH LAKE & 1 & 8.338 & 1.4734 & 12.285 \\
\hline NY & 1A2-045 & WOODS LAKE & 1 & 8.338 & 1.4734 & 12.285 \\
\hline NY & 1A2-048 & (NO NAME) & 1 & 8.338 & 1.4734 & 12.285 \\
\hline NY & 1A2-052 & CHUB LAKE & 1 & 8.338 & 1.4734 & 12.285 \\
\hline NY & 1A2-054 & TROUT LAKE & 1 & 8.338 & 1.4734 & 12.285 \\
\hline NY & 1A3-001 & NATE POND & 2 & 6.719 & 3.2807 & 22.043 \\
\hline NY & 1A3-028 & CURTIS LAKE & 1 & 6.719 & 1.8285 & 12.285 \\
\hline NY & 1А3-040 & ZACK POND & 2 & 6.719 & 3.2807 & 22.043 \\
\hline NY & 1АЗ-042 & CHENEY POND & 2 & 6.719 & 3.2807 & 22.043 \\
\hline NY & 1A3-043 & UNKNOWN POND & 3 & 6.719 & 7.3752 & 49.554 \\
\hline NY & 1А3-046 & LONG POND & 2 & 6.719 & 3.2807 & 22.043 \\
\hline NY & 1A3-048 & GRASS POND & 1 & 6.719 & 1.8285 & 12.285 \\
\hline NY & 1A3-063 & (NO NAME) & 3 & 6.719 & 7.3752 & 49.554 \\
\hline NY & 1A3-065 & SOUTH LAKE (EAST BRANCH) & 1 & 6.719 & 1.8285 & 12.285 \\
\hline NY & 1B3-032 & WIXON POND & 3 & 27.209 & 1.8212 & 49.554 \\
\hline NY & 1B3-052 & (NO NAME) & 1 & 27.209 & 1.0000 & 27.209 \\
\hline NY & 1B3-059 & ISLAND POND & 1 & 27.209 & 1.0000 & 27.209 \\
\hline NY & 1C2-048 & CRANBERRY POND & 2 & 10.743 & 2.0518 & 22.043 \\
\hline NY & 1D3-044 & MIDDLE FARMS POND & 2 & 19.426 & 1.1100 & 21.563 \\
\hline
\end{tabular}

Table B-1. Target lakes sampled in Phase-II of the Eastern Lake Survey (Continued).
\begin{tabular}{|c|c|c|c|c|c|c|}
\hline State & Lake ID & Lake Name & \begin{tabular}{l}
ELS-II \\
Cluster
\end{tabular} & \begin{tabular}{l}
Modif. \\
ELS-I \\
Weight
\end{tabular} & ELS-II Cond. Weight & ELS-II Sample Weight \\
\hline PA & 181-010 & GANOGA LAKE & 1 & 3.192 & 3.8488 & 12.285 \\
\hline PA & 1B1-023 & TWIN LAKES (BRINK POND) & 2 & 3.192 & 6.9057 & 22.043 \\
\hline PA & 181-029 & NO NAME(WILSON CREEK DAM) & 3 & 3.192 & 15.5245 & 49.554 \\
\hline PA & 1B1-043 & PENN LAKE & 1 & 3.192 & 3.8488 & 12.285 \\
\hline PA & 1B1-055 & ROCK HILL POND & 2 & 3.192 & 6.9057 & 22.043 \\
\hline PA & 1B1-064 & MILLPOND NO. 1 & 2 & 3.192 & 6.9057 & 22.043 \\
\hline PA & 1B2-028 & MILL CREEK RESERVOIR & 1 & 1.477 & 8.4786 & 12.523 \\
\hline PA & 1B3-012 & LITTLE BUTLER LAKE & 3 & 27.209 & 1.8212 & 49.554 \\
\hline PA & 1B3-019 & HARTLEY POND & 3 & 27.209 & 1.8212 & 49.554 \\
\hline PA & 1B3-041 & EAST STROUDSBURG RESERVOIR & 2 & 27.209 & 1.0000 & 27.209 \\
\hline PA & 1B3-043 & TROUT LAKE & 3 & 27.209 & 1.8212 & 49.554 \\
\hline PA & 183-053 & NO NAME (SNOWFLAKE LAKE) & 3 & 27.209 & 1.8212 & 49.554 \\
\hline PA & 1B3-060 & SLY LAKE & 3 & 27.209 & 1.8212 & 49.554 \\
\hline PA & 1B3-062 & BASSETT POND & 3 & 27.209 & 1.8212 & 49.554 \\
\hline RI & 1D1-027 & SCHOOL HOUSE POND & 2 & 6.572 & 3.3541 & 22.043 \\
\hline Rl & 1D1-067 & ROUND POND & 1 & 6.572 & 1.8694 & 12.285 \\
\hline RI & 1D2-049 & SPRING GROVE POND & 3 & 6.905 & 7.0459 & 48.652 \\
\hline RI & 1D3-026 & ARNOLD MILLS RESERVOIR & 3 & 19.426 & 2.4954 & 48.477 \\
\hline
\end{tabular}

\section*{APPENDIX C}

\section*{CHI-SQUARE ANALYSES OF ELS-II POPULATION DIFFERENCES}

One way to test whether two populations are different (e.g., spring 1986 ANC versus fall 1986 ANC) is to do a chi-square test as shown in the top box in Figure C-1. In this one degree of freedom sign test, the number of samples above the \(1: 1\) line is compared to the number of samples below the 1:1 line to see if the observed differences are significantly different than random chance. If the chisquare value for this sign test is \(>3.84\), we are \(95 \%\) confident that these two populations are different. Chi-square values for the sign test for the fall 1984/fall 1986 comparison are summarized in Table C-1; values for the spring 1986/fall 1986 comparisons are summarized in Table C-2. Another question evolving from these comparisons is whether or not the population differences are independent across the range of concentrations in the cluster. To address this question, the population is divided in half (using the cluster median of the pair sums) or in quarters (using cluster quartiles of the pair sums) along the \(1: 1\) line to construct a \(2 \times 2\) and a \(2 \times 4\) contigency table as depicted in the lower two boxes in Figure C -1. If the sign test indicates that there is a significant difference between the two populations \(\mathrm{p}=\) 0.05 ), then a line is drawn parallel to the \(1: 1\) line offset by the median of the pair differences to divide the population in half (see Figure \(\mathrm{C}-1\) ). If the populations are not significantly different, then no offset line is used. If the chi-square test on these contigency tables indicates a significant difference from random chance, we can conclude that the population differences are not independent of concentration. The independence tests associated with each sign test are summarized in Tables C-1 and C-2.

Points that fall on the \(1: 1\) line, the median value, or the quartile values were excluded from the analysis. These analyses treat each lake as a unit, ignoring the ELS-II weighting factor. Thus, the chisquare tests were done separately for each cluster, because ELS-II weights are nearly equal within each cluster. A more complete discussion of the Chi-square analyses for ELS-II data is given in Overton (1987, 1989).


ANC CLUSTER II FALL 1986 VS. FALL 1984

THE TOTAL NUMBER OF PONTTS PLOTTED: 53 NUMBER OF POINTS ON DAGONAL LINE: O

CHI-SOUARE \(=\mathbf{1 5 . 8 6 7 9 2}\) 1 DF CHI-SQUARE CRITKCAL VALUE \(=3.84\)

41
12

\section*{NUMBER OF POINTS ON SHIFTED LINE: 1} ADOTTIONAL POINTS WITH SUM EQUAL TO MEDLAN: I

CHHSOUAARE FOR INDEPENDENCE = 5.684116 1 DF CHI-SQUARE CRITICAL VALUE \(=3.84\)
\begin{tabular}{c|c}
9 & 17 \\
\hline 17 & 8
\end{tabular}

AODTIKNAL POINTS WITH SUM EQUAL TO A OUARTILE: O
CHI-SOUARE FOR NOEPENDENCE - 12.52367 3 OF CHI-SOUARE CRTICAL VALUE \(\mathbf{- 7 . 8 1 4 7 3}\)


Figure C-1. Example of the chi-square analysis for fall 1986/fall 1984 population differences for ANC in cluster 2. (Taken from Overton, 1989.)

Table C-1. Chi-Square Analysis of Between-Year (Fall 1984 vs. Fall 1986) Differences in ELS-II Population Distributions
\begin{tabular}{|c|c|c|c|c|}
\hline \multirow[b]{3}{*}{Variable} & \multirow[b]{3}{*}{Cluster} & \multicolumn{3}{|c|}{Chi-Square Values} \\
\hline & & Sign \({ }^{\text {a }}\) & \multicolumn{2}{|l|}{Independence Test \({ }^{\text {b }}\)} \\
\hline & & Test & 2×2 & \(2 \times 4\) \\
\hline \multirow[t]{3}{*}{ANC} & 1 & 0.75 & 0.09 & 4.32 \\
\hline & II & 15.9** & 5.68* & 12.5** \\
\hline & III & 26.3** & 3.27 & 6.91 \\
\hline \multirow[t]{3}{*}{pH} & 1 & 0.19 & 0.52 & 4.77 \\
\hline & II & 8.32** & 0.08 & 8.68* \\
\hline & III & 3.93 & 1.46 & 10.5* \\
\hline \multirow[t]{3}{*}{\(\mathrm{SO}_{4}{ }^{2-}\)} & II & 1.33 & 3.09 & 4.81 \\
\hline & II & 9.98** & 0.96 & 3.03 \\
\hline & III & 3.27 & 3.27 & 3.14 \\
\hline \multirow[t]{3}{*}{\(\mathrm{NO}_{3}{ }^{-}\)} & 1 & 8.33** & 5.33* & 8.00* \\
\hline & 11 & 15.1** & 6.24* & 11.3** \\
\hline & III & 23.3** & 13.1** & 17.8** \\
\hline \multirow[t]{3}{*}{Base Cations} & I & 27.0** & 8.33** & 10.0* \\
\hline & 11 & 34.9** & 12.3** & 16.3** \\
\hline & III & 29.5** & 1.46 & 3.27 \\
\hline \multirow[t]{3}{*}{DOC} & 1 & 0.08 & 0.75 & 1.59 \\
\hline & 11 & 0.47 & 0.31 & 4.72 \\
\hline & III & 0.09 & 0.09 & 6.47 \\
\hline \(\mathrm{Al}_{\text {MIBK }}\) & 1 & 2.08 & 0.09 & 0.26 \\
\hline
\end{tabular}
\({ }^{\text {a }}\) Sign test is a 1 -df chi-square test indicating if the populations are different.
\({ }^{\mathrm{b}}\) Independence test checks if the population distribution differences are independent of concentration ( \(2 \times 2\) test has \(1 \mathrm{df} ; 2 \times 4\) test has 3 df ).
\({ }^{* *}\) Significant at \(p<0.01\left(x^{2}>6.53\right.\) when \(d f=1 ; x^{2}>11.3\) when \(\left.d f=3\right)\).
\({ }^{*}\) Significant at \(p<0.05\left(X^{2}>3.84\right.\) when \(d f=1 ; X^{2}>7.81\) when \(\left.d f=3\right)\).

Table C-2. Chi-Square Analysis of Spring 1986/Fall 1986 Differences in ELS-ll Population Distributions
\begin{tabular}{|c|c|c|c|c|}
\hline \multirow[b]{3}{*}{Variable} & \multirow[b]{3}{*}{Cluster} & \multicolumn{3}{|c|}{Chi-Square Values} \\
\hline & & \multirow[t]{2}{*}{\[
\begin{aligned}
& \text { Sign }{ }^{2} \\
& \text { Test }
\end{aligned}
\]} & \multicolumn{2}{|l|}{Independence Test \({ }^{\text {b }}\)} \\
\hline & & & \(2 \times 2\) & \(2 \times 4\) \\
\hline \multirow[t]{3}{*}{ANC} & I & 8.33** & 0.33 & 2.00 \\
\hline & II & 15.9** & 1.60 & 4.91 \\
\hline & III & 44.0** & 3.27 & 6.91 \\
\hline \multirow[t]{3}{*}{pH} & 1 & 3.00 & 0.36 & 7.77 \\
\hline & II & 28.70** & 2.00 & 5.35 \\
\hline & III & 19.56** & 0.38 & 1.31 \\
\hline \multirow[t]{3}{*}{\(\mathrm{SO}_{4}{ }^{2-}\)} & 1 & 1.33 & 0.34 & 0.69 \\
\hline & 11 & 0.08 & 0.17 & 5.57 \\
\hline & III & 4.45* & 1.53 & 2.51 \\
\hline \multirow[t]{3}{*}{\(\mathrm{NO}_{3}{ }^{-}\)} & 1 & 27.0** & 33.3** & 34.0** \\
\hline & 11 & 2.28 & 3.91* & 22.6** \\
\hline & III & 9.09** & 17.8** & 21.5** \\
\hline \multirow[t]{3}{*}{Base Cations} & 1 & 3.00 & 5.69* & 6.04 \\
\hline & 11 & 45.3** & 8.67** & 11.1** \\
\hline & III & 40.1** & 1.46 & 4.73 \\
\hline \multirow[t]{3}{*}{DOC} & 1 & 3.60 & 2.65 & 3.42 \\
\hline & II & \(13.8{ }^{* *}\) & 7.07** & 9.75* \\
\hline & III & 9.09** & 1.46 & 3.27 \\
\hline \(\mathrm{AL}_{\text {im }}\) & 1 & 4.08* & 16.3** & 19.3** \\
\hline
\end{tabular}

\footnotetext{
\({ }^{\text {a }}\) Sign test is a 1 -df chi-square test indicating if the populations are different.
\({ }^{6}\) Independence test checks if the population distribution differences are independent of concentration ( \(2 \times 2\) test has \(1 \mathrm{df} ; 2 \times 4\) test has 3 df ).
**Significant at \(p<0.01\left(x^{2}>6.53\right.\) when \(d f=1 ; x^{2}>11.3\) when \(\left.d f=3\right)\).
* Significant at \(p<0.05\left(x^{2}>3.84\right.\) when \(d f=1 ; x^{2}>7.81\) when \(\left.d f=3\right)\).
}```


[^0]:    ${ }^{\text {a }}$ EPA methods are taken from U.S. EPA (1983); USGS methods are from Skougstad et al. (1979).

[^1]:    a EPA methods are taken from U.S. EPA (1983); USGS methods are from Skougstad et al. (1979).

[^2]:    a

[^3]:    ${ }^{\text {a }}$ All units are $\mu \mathrm{eq} / \mathrm{L}$ except for $\mathrm{pH}, \mathrm{DOC}(\mathrm{mg} / \mathrm{L})$, and aluminum ( $\mu \mathrm{g} / \mathrm{L}$ ). The sample size for the Seventh Lake audit was 11 in the spring, 7 in the summer, and 11 in fall; for the Big Moose Lake audit it was 10 in the spring, 12 in summer and 11 in fall.
    ${ }^{\text {b }}$ Target values represent the median of all audit samples measured in 1986 in the ELS-II, National Stream Survey, and Spring Variability Study.

[^4]:    ${ }^{\text {a }} \overline{\mathrm{X}}$ units are in $\mu \mathrm{eq} / \mathrm{L}$ except for $\mathrm{pH}, \mathrm{DOC}(\mathrm{mg} / \mathrm{L})$, and aluminum $(\mu \mathrm{g} / \mathrm{L}) . \% \mathrm{RSD}=\left(\mathrm{SD}_{\text {pool }} / \bar{X}_{G}\right) * 100 . \mathrm{SD}_{\text {pool }}$ is the pooled standard deviation $=\bar{X}$ pair variance $/ n)^{0.5}$.
    ${ }^{\text {b }}$ Data for pH expressed as $\overline{\mathrm{X}}_{\mathrm{G}} \pm$ pooled standard deviation.

[^5]:    ${ }^{\text {a }}$ Precision estimates are expressed as \%RSD (see text). Within-batch precision is based on duplicate sample pairs. Amongbatch precision is based on repeated analyses of natural audit material (SL = Seventh Lake, BML = Big Moose Lake; see Table 4-2).
    b
    pH precision is expressed in pH units as pooled standard deviation.

[^6]:    ${ }^{a} \mathrm{C}_{\mathrm{B}}=\mathrm{Ca}^{2+}+\mathrm{Mg}^{2+}+\mathrm{Na}^{+}+\mathrm{K}^{+}$.

[^7]:    ${ }^{\mathrm{a}} \mathrm{n}$ is the sample size; $\hat{\mathrm{N}}$ is the estimated number of lakes in the target population; $\hat{\mathrm{A}}$ is the estimated lake area ( $\mathrm{km}^{2}$ ) in the target population.

[^8]:    a Reference values for ANC and pH are those that are commonly used for classification purposes in acidic deposition research.
    b
    Estimates based on ELS-I chemistry measured in fall 1984 for the ELS-I target population.
    C Estimates based on ELS-I chemistry measured in fall 1984 at the 145 ELS-II lakes (population estimates made using ELS-II weights).
    d
    Estimates based on ELS-II fall seasonal survey.

[^9]:    ${ }^{2}$ All units are in $\mu \mathrm{eq} / \mathrm{L}$ except for $\mathrm{pH} \operatorname{DOC}(\mathrm{mg} / \mathrm{L})$, and aluminum ( $\mu \mathrm{g} / \mathrm{L}$ ).
    ${ }^{\text {b }}$ Fall 1984 data is from ELS-I.
    ${ }^{c} Q_{1}=25$ th percentile, $O_{3}=75$ th percentile.

[^10]:    ${ }^{\text {a }}$ All units are in $\mu \mathrm{eq} / \mathrm{L}$ except for $\mathrm{pH}, \mathrm{DOC}(\mathrm{mg} / \mathrm{L})$, and aluminum $(\mu \mathrm{g} / \mathrm{L})$.
    b Grand mean is the mean of all the triplicate means in the Fall Variability Study $(\mathrm{n}=41)$.
    C Population distribution of the standard deviation of the three lake samples collected in the Fall Variability Study.

[^11]:    a Total ELS-II population size $=3,993$ lakes, 754 in the Adirondacks, 608 in the Poconos/Catskills, and 2,631 in New England.

[^12]:    a Total ELS-ll population size $=3,993$ lakes, 754 in the Adirondacks, 608 in the Poconos/Catskills, and 2,631 in New England.

[^13]:    ${ }^{\text {a }}$ All units are in $\mu \mathrm{eq} / \mathrm{L}$ except for $\mathrm{pH}, \mathrm{DOC}(\mathrm{mg} / \mathrm{L})$, and aluminum $(\mu \mathrm{g} / \mathrm{L})$.
    ${ }^{\mathrm{b}} Q_{1}=25$ th percentile, $Q_{3}=75$ th percentile.
    c There were an estimated 346 lakes in the Adirondacks, 141 lakes in the Poconos/Catskills, and 514 lakes in New England with fall ANC $\leq 50 \mu \mathrm{eq} / \mathrm{L}$ in the ELS-II.

[^14]:    a Units are in $\mu \mathrm{eq} / \mathrm{L}$ except for pH and DOC (mg/L).
    b
    Analytical pooled standard deviation is calculated from all available ELS-II data and is based on 84 sample duplicate pairs collected from 60 different lakes. As such, it is not based on all 145 ELS-1l lakes or all 41 fall variability lakes as are the other pooled standard deviations.
    c
    Spatial pooled standard deviation is the standard deviation of all the Fall 1986 index samples.

[^15]:    a
    Units are in $\mu \mathrm{eq} / \mathrm{L}$ except for $\mathrm{pH}, \mathrm{DOC}(\mathrm{mg} / \mathrm{L})$, and $\mathrm{Al}_{\mathrm{m}}(\mu \mathrm{g} / \mathrm{L})$.
    b
    RMSE $=$ root mean square error.

[^16]:    ${ }^{\text {a }}$ All units are in $\mu \mathrm{eq} / \mathrm{L}$. Low ANC lakes were defined as those lakes with fall $1986 \mathrm{ANC} \leq 50 \mu \mathrm{eq} / \mathrm{L} . \Delta \mathrm{Af}^{+}$is the spring-fall change in inorganic monomeric aluminum concentration in $\mu \mathrm{eq} / \mathrm{L}$. Inorganic aluminum was converted from $\mu \mathrm{M}$ to $\mu \mathrm{eq} / \mathrm{L}$ based on an aluminum charge calculated from an empirical equation derived from equilibrium model speciation and National Stream Survey data ( $\mathrm{A}_{\mathrm{m}}$ charge $=7.06-\mathrm{pH}$; also see Figure 1 in Sullivan et al., 1989). $\Delta$ Org $A^{-}$is the spring-fall change in organic anion concentration in $\mu \mathrm{eq} / \mathrm{L}$. Organic anion concentration was estimated from DOC and pH using the equation of Oliver et al., (1983).

[^17]:    * Confidence bounds are for number and area of lakes, but have been scaled

[^18]:    * Confidence bounds are for number and area of lakes, but have been scaled

[^19]:    * Confidence bounds are for number and area of lakes, but have been scaled.

[^20]:    * Confidence bounds are for number and area of lakes, but have been scaled

[^21]:    Min: - $63.1 \quad Q_{1}: 30.60 \quad Q_{2}: 68.90 \quad Q_{3}: 109.2 \quad Q_{4}: 235.8 \quad$ Max: 338.3
    Median: $\quad 88.90$
    Mean: 116.96
    Std. Dev.: 93.95

[^22]:    Min: $-54.3 \quad Q_{1}: 56.80 \quad Q_{2}: 101.1 \quad Q_{3}: 181.4 \quad Q_{4}: 298.3 \quad$ Max: 461.2
    Median: 117.20

    Mean: 166.11
    Std. Dev.: 118.16

[^23]:    * Confidence bounds are for number and area of lakes, but have been scaled.

[^24]:    * Confidence bounds are for number and orea of lokes, tut mine beta se aleat

[^25]:    - Enf:tome toonds afe for rumber and area of lakes, but have been scaled

[^26]:    * Confidence bounds ate for mumber and area of lakes, but hove been scoled

[^27]:    - Confidence bounds are for number and areo of lakes, but have been scaled.

[^28]:    * Confidence bounds are for number and area of lakes, but have been scaled.

[^29]:    * Confidence bounds are for number and area of lakes, but have been scaled.

[^30]:    * Confidence bounds are for number and area of lakes, but hove been scaled.

[^31]:    - Confidence tounds are for number and area of lakes, but have been scaled

[^32]:    * Confidence bounds are for number and area of lakes, but have been scaled.

[^33]:    - ranfidence bounds are for number and area of lakes, but have been scaled.

