New York State Energy Research and Development Authority

# Assessment of Long-Term Monitoring of Nitrogen, Sulfur, and Mercury Deposition and Environmental Effects in New York State

Final Report

August 2012

No. 12-21

nyserda
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# ASSESSMENT OF LONG-TERM MONITORING OF NITROGEN, SULFUR, AND MERCURY DEPOSITION AND ENVIRONMENTAL EFFECTS IN NEW YORK STATE

Final Report

Prepared for the
**NEW YORK STATE**
**ENERGY RESEARCH AND**
**DEVELOPMENT AUTHORITY**

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# 1. Introduction

## 1.1 Report Objectives

Air pollutants such as nitrogen oxides (NOx), sulfur dioxide ($SO_2$), and mercury (Hg) have had significant impacts on lakes, rivers, soils, fauna, and tree health throughout the northeastern U.S. Some areas of New York are particularly susceptible to environmental degradation, such as the Adirondack and Catskill regions, which receive some of the highest rates of acidic deposition in the country (Burns et al. 2008, Driscoll et al. 2003). Long-term monitoring efforts in New York have produced data sets that have been valuable for evaluating changes over time in air pollution loads and effects on the environment. These monitoring efforts include projects carried out by a variety of federal and state agencies, private non-profit organizations, and academic institutions.

Data collected by monitoring programs in New York have been used to develop and evaluate air and water pollution control policies. In the 1970s, policy needs regarding environmental quality were identified, providing the impetus for several long-term monitoring programs initiated in the 1980s and 1990s. These monitoring efforts in New York were implemented at different times, sometimes with different research and policy goals in mind. As a result, there are few sites where precipitation, surface waters, soils, vegetation, and fauna are monitored simultaneously. Co-locating monitoring efforts increases the value of the individual data sets because they can be used in linked analyses.

Many of the monitoring programs in New York relate to current and upcoming federal and state requirements. For example, regulations enacted within the last two years that will affect acidic and Hg deposition in the future include: 1) the Mercury and Toxics Rule for power plants;

2) the Cross-State Air Pollution Rule (CSAPR) designed to reduce emissions of $SO_2$ and NOx from power plants in Eastern U.S.; 3) the EPA Pilot NOx/SOx Secondary Standard Monitoring Program, which calls for three to five monitoring sites (likely with one site located in New York) to be established in 2012 to run for five years to evaluate methods for sulfur and nitrogen oxides, dry deposition measurements and algorithms, and the application and usefulness of the aquatic acidification index (AAI); and 4) the New York law that requires ultra-low sulfur fuel for residential use. These requirements could have significant implications for monitoring programs in New York.

It is important to evaluate long-term monitoring programs periodically to ensure that these programs remain efficient and effective. To our knowledge, a comprehensive evaluation of long-term environmental monitoring has never been undertaken in New York. Such an analysis is necessary to identify possible improvements in sampling designs to maximize information gained relative to the resources required for data collection.

Long-term monitoring can be described as a pyramid (CENR 1997). At the base of the pyramid are broad monitoring programs, such as monitoring certain forest characteristics using remote sensing. At the second level of the pyramid are broad-scale surveys and multi-site networks that can be used to assess spatial patterns and statewide ecological variables. At the top level of the pyramid are a few sites where intensive, integrated monitoring is done at a fine scale to assess ecological processes and responses to ecological change. In this report, the middle and top portions of the pyramid are discussed. There are currently no broad statewide monitoring programs that use remote sensing technology in New York.

In this report, long-term monitoring of acidic and Hg deposition and the impacts of these pollutants on streams, lakes, vegetation, soils, and fauna in New York are evaluated. The objectives of this project were to:

- Provide a compendium of past and current research activities and monitoring efforts in New York relating to the study of acidic and Hg deposition.
- Analyze monitoring efforts to characterize the efficiency of monitoring and to identify redundancies and gaps in coverage. This report focuses on a few of the larger data sets that lend themselves to in-depth analysis. A full list of relevant research activities in New York can be found in the compendium.
- Provide guidance for data users, funders, and cooperators to use for informed discussions on how to modify existing monitoring programs most effectively to meet the policy and science needs of tomorrow, given the resource constraints of today.

## 1.2 Agencies and Programs

Long-term monitoring programs in New York are administered by a variety of agencies. A list of agencies and programs referenced in this report is shown in Table 1.1.

Table 1.1. Agency and program abbreviations referenced in this report are provided below. Programs are listed with the agencies that administer them. Details on the specific data sets used in these analyses can be found in the accompanying compendium of research activities.

| **Agency** | **Abbreviation** | **Program** | |
|---|---|---|---|
| Adirondack Lakes Survey Corporation | ALSC | Adirondack Long Term Monitoring Project* | ALTM |
| Biodiversity Research Institute | BRI | | |
| Cary Institute of Ecosystem Studies | CIES | | |
| Darrin Freshwater Institute | DFWI | Adirondack Effects Assessment Program | AEAP |
| Environmental Protection Agency | EPA | Clean Air Status and Trends Network<br>Long Term Monitoring Project*<br>Temporally Integrated Monitoring of Ecosystems | CASTNet<br>LTM<br>TIME |
| National Atmospheric Deposition Program | NADP | Ammonia Monitoring Network<br>Atmospheric Integrated Research Monitoring Network<br>Atmospheric Mercury Network<br>Mercury Deposition Network<br>National Trends Network | AMoN<br>AIRMoN<br>AMNet<br>MDN<br>NTN |
| New York State Department of Environmental Conservation | DEC | Rotating Integrative Basin Studies<br>Atmospheric Deposition Monitoring Network | RIBS<br>ADMN |
| New York State Energy Research and Development Authority | NYSERDA | | |
| Northeast Soils Monitoring Cooperative | NESMC | | |
| State University of New York | SUNY | | |
| U.S. Geological Survey | USGS | | |

* The ALSC ALTM program is a subset of the EPA LTM program. The ALSC also carries out additional monitoring programs in the Adirondacks.

## 1.3 Data Analysis Methods, Results, and Conclusions

In this report, the data analysis methods used depended on the structure of the data sets shown in Table 1.2. When analyzing data sets that included multiple sites monitored over multiple sampling times, repeated-measures mixed-effects models were used. These models describe an estimate of average values and a model error associated with a group of sites over the period of time in which measurements were recorded. The model mean estimate and model error are affected by either the subsampling sites or dates, indicating how the program would be affected by altered sampling regimes are described.

The methods and results for the individual analyses are described together. The results of the analyses are drawn upon to detail the main findings and conclusions at the end of each section. The findings and conclusions include results derived from the analyses, as well as information based on expert opinion drawn from interviews conducted with researchers involved in environmental monitoring in New York. When expert opinions are cited in the findings and conclusions, the person from whom the information is cited and their affiliation is included.

When analyzing data sets that included multiple sites but not multiple time periods, an analysis of detectable difference was used. This analysis can be used to guide decisions about future monitoring efforts by indicating the number of samples needed to detect a change in the mean of a specified magnitude. This has implications for deciding how many samples to fund, as well as the timing of future monitoring efforts. For example, if large numbers of samples are required to detect a significant change within a short time period, it may be more efficient to wait until larger change is expected when a smaller number of samples are needed.

For data sets that included time series, Mann Kendall or Seasonal Mann Kendall trends tests and general linear models are used to assess the standard error of the slope. These tests are commonly used to assess trends over time. Although these analyses to linear regressions were applied, the same approach would also be applicable to nonlinear regressions. Table 1.2 shows examples from the report to describe the details of these analytical approaches.

Table 1.2. Data analysis method used for different available data sets.

| Model Type | Time Series | Multiple Sites |
|---|---|---|
| Repeated measures mixed effects model | X | X |
| Detectable difference analysis | | X |
| Mann Kendall trends test and General Linear Model | X | |

### *1.3.1 Repeated Measures Mixed Effects Models*

One example of the use of the repeated measures mixed effects model is to assess how a reduction in the number of acidic deposition collectors in the DEC Acid Deposition Monitoring Program (ADMP) would affect the mean estimate and standard error. The model estimate and model standard error for a variety of reduced sampling schemes using a repeated-measures mixed-effects model were determined. In this example, the reduced sampling schemes were scenarios where randomly-selected collectors were removed from the data set. The mixed-effects model is a generalized linear model that can include both random and fixed effects. A fixed effect refers to a non-random explanatory variable. The models used in this report did not include any fixed effects, because all the sites (lakes, deposition collectors, etc.) in each of the models were unique. The random effect in these models was the site, since those included in these studies are chosen from a larger population of potential sites so they are considered random. The random effects for the deposition example are the individual deposition collectors. Although in some monitoring programs, sites may be chosen for particular reasons and are not randomly selected. The designation as a random effect is appropriate because the time series within each site was treated as a repeated measure. The correlation structure was specified based on the sampling scheme, as follows. When samples were uniformly spaced (e.g. monthly sampling), a first-order autoregressive structure was used. In the case of the deposition analysis, a first-order autoregressive structure was used because the data was collected weekly. As the model is able to handle missing values, they were left blank. When samples were not uniformly spaced (e.g. multiple samples collected in the summer of each consecutive year), the autoregressive structure was specified for that sampling regime. Chemical analytes were analyzed in separate models. For the deposition analysis, three separate models were used to assess three analytes: $SO_4$, $NO_3$, and $NH_4$.

To describe the effect of sampling intensity, subsamples of sites were randomly selected to generate sampling schemes that were 10, 20, 40, 60, 80, or 90 percent of current sampling effort. In the case of the deposition example, sampling schemes that had 22, 20, 18, 13, 9, 4, and 2 collectors were simulated. When generating subsamples, sites were randomly sampled without replacement. The number of iterations ranged from 50-500 per intensity class; the number of iterations was consistent across intensity classes for each analysis. The average of these random iterations are reported. The model could be also be run for specific subsampling scenarios for future planning purposes, for example to compare the model for a specific subsampled group of deposition collectors to the collector network that is currently in operation.

In some cases, it is efficient to sample sites that are in close proximity in a single trip. These groups of nearby sites are referred to as “visitation groups.” In these cases, it was realistic to simulate reduced sampling by removing an entire group rather than by randomly removing individual observations. When this method of subsampling is used, random sampling was not needed because the number of possible combinations was small enough that all combinations were run.

To compare the effect of different sampling intensities on uncertainty in estimates, the Least Squares Means (LSM) model estimate and model standard error was used. The LSM model estimate is an average estimate of a parameter for all sites over the time period but it does not describe change over time. For example, the parameters described in the deposition example are solute concentrations. Reducing sampling effort does not consistently change the model estimate, but it increases the confidence interval around the estimate, represented by the standard deviation of the results of each subsample within each sampling intensity category. The uncertainty in the estimates using the LSM model standard error was described.

Interpreting these analyses in terms of acceptable reductions in sampling effort depends on the degree of certainty desired for research or policy needs. These data are used for many types of applications, and the acceptable level of uncertainty differs depending on the application.  Our goal is to describe the consequences of reduced sampling schemes; there is not a single answer as to the optimal sample size or number.

All repeated measures mixed effects tests were done in SAS 9.3 (SAS Institute Inc., Cary, NC, USA).

### *1.3.2 Detectable Difference Analyses*

When analyzing data from a one-time survey, the ability to detect significant changes in a future survey is illustrated. One application of this method is to detail the detectable difference in the variables measured by the loon survey conducted by the Biodiversity Research Institute from 2003-2004. In a detectable difference analysis, the input variables include the sample size and standard deviation of the original survey and an alpha and power level. For the case of loon egg Hg concentrations, the sample size was the number of lakes sampled (29 lakes), and the standard deviation was 0.46 ppm total mercury (THg). In all cases, an alpha of 0.05 and a power of 0.8 was used. These are commonly accepted values for alpha and power (Lenth 2001). The detectable difference δ for a two-sample t-test is:

$$\delta = (s / \sqrt{n/2})(t_{\alpha,\upsilon} + t_{\beta,\upsilon})$$

where n = sample size, $\nu = 2n-2$ degrees of freedom, $\alpha$ is the probability of a Type I error, and $\beta$ is the probability of a Type II error. When using a paired test, $\sqrt{(n/2)}$ was replaced with $\sqrt{(n)}$ (Yanai et al. 2003).

These tests require certain assumptions. The first is that the variance (standard deviation) of the initial sampled population remains the same between sampling periods. For example, in the case of loon egg concentrations, this means it is assumed the population of loon eggs sampled in the future would have the same variance as those during the 2003-2004 survey. A different variance could be assumed, but there is no basis for predicting a change towards higher or lower variance. Second, the future sample is either paired or unpaired, depending on whether the same units (i.e. the 29 lakes) are re-measured at the second date. The paired test can detect smaller differences, and it was presumed that this would be used if the sampling intensity is not greater than in the past. Clearly, if samples are added, these cannot be paired with previous measurements, and an unpaired analysis would be needed. Because of this, the detectable difference for both paired and unpaired tests in figures describing the results of these tests are included.

The results of the detectable difference analyses are displayed as a percentage of the percent of the mean value of the original survey were tested. In the case of paired tests, samples sizes of 10, 25, 50, and 100 percent, where 100 percent represents the sampling effort of the original survey. For the loon egg example, this corresponds to sample sizes of 29, 15, 7, and 3 lakes. When testing the detectable difference of unpaired tests, sampling efforts representing 200 percent (58 lakes) and 300 percent (87 lakes) of the sampling effort of the original survey were included. It is always best to pair future survey sites when possible, as this always provides for greater power to detect change. Sites are paired at the experimental unit, for example a forest stand, lake, or stream.

These analyses can be used as guides for future sampling efforts. If a change in loon egg THg concentration is detectable only with a 50 percent change, surveys may be scheduled when a change of that magnitude is expected. In other cases, a change of a specific magnitude based on new legislation may be expected, and these figures can be used as a guide to assess how many samples might be need for a significant change to be detected.

All the detectable difference tests were done in Minitab 16 (Minitab Inc., State College, PA, USA).

### *1.3.3 Assessing Long-Term Trends*

When assessing long-term trends over time, a variety of methods was used. A Mann Kendall test to test for monotonic trends in time series based on the Kendall rank correlation was used. When sampling took place throughout the year and seasonal trends were present, such as the data collected once per month from 52 lakes in the ALTM study, a Seasonal Mann Kendall trend test was used. The Mann Kendall tau and p-value for these tests was reported. Also a general linear regression and the standard error of the slope was used to assess the uncertainty in trends and to rank sites by their standard error to determine which sites exhibit the most consistent trends. All regression and Mann Kendall tests were done in R64 using the Kendall package (R Foundation for Statistical Computing, Vienna, Austria).

## 1.4 Defining Acid-Sensitive Areas of New York

Acidic deposition affects soils by displacing nutrient and base cations on exchange surfaces. These cations, which are valuable nutrients for plants and other soil organisms, can then be leached from the system, resulting in nutrient loss from soils. Some soils however, are less sensitive to base cation leaching caused by acidic deposition. Alkaline soils, such as those rich in limestone, calcium carbonate, have greater acid neutralizing capacity and thus can better mitigate the effects of acidic deposition on ecosystems.

Acid-sensitive sites in New York are referred to throughout many sections of this report. The sensitive areas of the state include the Adirondacks, Catskills, Hudson Highlands, Rensselaer Plateau and parts of Long Island (DEC, "Acid Rain," http://www.dec.ny.gov/chemical/283.html). Other regions, including western parts of the state, have carbonate soils with high buffering capacities and are less sensitive to acidic deposition. These areas have been defined by surface water alkalinities as well as soil parent material. Acid-sensitive areas of New York are designated by water chemistry alkalinities less than 200 μeq/L and by areas of sensitive geology and soils (SADCA FEIS August 1984).

It should be noted that there is high variability in soils even in the sensitive regions and that gradients of sensitivity exist at very small spatial scales. It is essential to maintain some long-term deposition chemistry monitoring efforts in areas that have soils that are not particularly sensitive to acid deposition for several reasons, including: (1) fairly large population centers and potential environmental justice concerns in the New York City metro area (2) anticipated regional and federal emissions reductions from the utility sector and the need to measure the effects on acidic and Hg deposition from upwind states, and (3) current and possible future oil and gas extraction in the western part of the state. Because of this, it is important to maintain some deposition chemistry monitoring efforts, throughout the state and in a range of urban, suburban, and rural sites.

# 2. Atmospheric Deposition

## 2.1 Status

### *2.1.1 Acidic Deposition Monitoring*

The DEC has been measuring atmospheric deposition across the state under the Acid Deposition Monitoring Program (ADMP) since 1987. Currently, there are 16 sites being monitored (Figure 2.1). The DEC program collects cumulative precipitation samples on a weekly basis. The DEC also has a separate $SO_2$ air monitoring network. There are currently 23 $SO_2$ monitors operated by the DEC, including monitors at each wet deposition site except Wanakena. In addition to air monitoring related to acidic deposition, the DEC also monitors a wide range of air pollutants at more than 80 sites across the state.

In addition to monitoring by the DEC, the National Atmospheric Deposition Program (NADP) operates two monitoring programs focused on acidic deposition: the National Trends Network (NTN) and the Atmospheric Integrated Research Monitoring Network (AIRMoN). These sites are generally located in rural areas. There are 11 NTN sites in New York as shown in Figure 2.1. There is one AIRMoN site, located in Ithaca. Samples from the NTN sites are collected weekly, while the AIRMoN samples are collected on an event basis.

Some NTN sites are co-located with current DEC acidic deposition collectors. An analysis by Civerolo and Lewis (2009, poster presented at EMEP meeting) found that the levels of acidic deposition currently measured by the DEC network are generally consistent with those at the matching NADP sites. Some differences between co-located collectors were observed due to differences in topography and network operating procedures, but it appears that in general, these co-located collectors are redundant and may provide a means of reducing the DEC sample load with minimal impact to spatial coverage. There are some important differences in the standard operating procedures between the DEC and NADP programs, and thus the data are not entirely substitutable, but general trends observed at nearby sites are quite similar (Civerolo and Lewis 2009).

The EPA NCore program monitors air concentrations of nitric oxide (NO), total reactive nitrogen ($NO_y$), and $SO_2$, in addition to measurements of other air particles, pollutant gasses, and meteorology. This nationwide program has been in operation since 2011 and includes sites in New York at Pinnacle State Park and Rochester. There are additional acidic deposition collectors operated by private institutions and other organizations throughout the state. SUNY Albany measures air concentrations at the Whiteface Summit and at Pinnacle State Park. Urban air concentrations of NO, $NO_2$, ozone ($O_{3)}$, particle matter concentrations, carbon monoxide (CO), and carbon dioxide ($CO_2$ )have been monitored since 2010 at two sites in the city of Syracuse in cooperation with Clarkson University, SUNY College of Environmental Science and Forestry (SUNY-ESF), and Cornell University. The Cary Institute monitors wet deposition and air concentrations at their headquarters in Millbrook, NY (co-located with NADP NY16). NY16 is one of two Ammonia Monitoring Network (AMoN) sites in New York, along with NY67, near Ithaca, where atmospheric $NH_3$ concentrations are measured. Additionally, there are three EPA CASTNET sites located at Huntington, Claryville, and Ithaca, which measure $O_3$ concentrations as well as gaseous and particulate sulfur and nitrogen concentrations, which are used to calculate dry deposition fluxes.

Another important acidic deposition monitoring program is the Whiteface Cloud Monitoring program administered by the Adirondack Lakes Survey Corporation. In June 2001, the ALSC began monitoring cloud water from the Whiteface summit, as a follow-up to earlier research at the site conducted under the Mountain Cloud Acid Deposition Program, administered by CASTNet, from 1994-1999. The ALSC has continued to operate the cloud-monitoring program as it was run by the CASTNet program, and the program is still in operation. The sensors collect cumulative samples of cloud water from non-precipitating clouds.

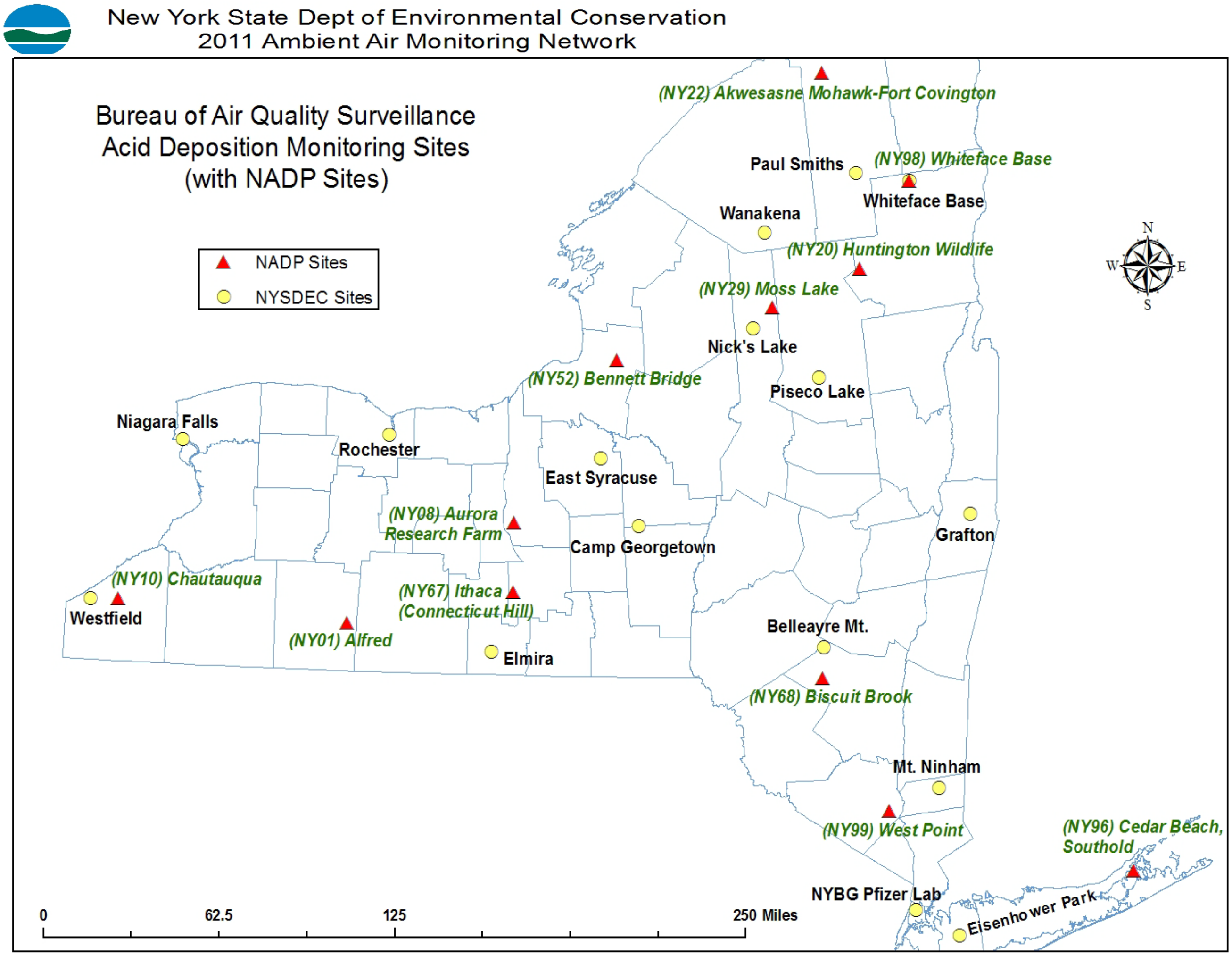


Figure 2.1. NADP NTN, AIRMoN, and DEC Acid Deposition Monitoring sites located in New York (in operation as of January 2012; map courtesy of DEC). Note that NY67 has AIRMoN only.

## 2.2 Analyses and Results

### *2.2.1 Seasonal Mann Kendall Trends*

Data from the DEC ADMP were used for these analyses. This dataset was chosen because the network has provided very valuable data in the past on long-term deposition trends. A revamping of the network is being considered, and the effects that a reduction in sites might have was a question of interest. All the data was used from the earliest date through 2007. In some cases, sites were moved to a nearby location, and these records are considered continuous in these analyses. Although closed in 2010, the sites at Altmar, Buffalo, Loudonville (primary and co-located), and White Plains are included in this analysis.

A Seasonal Mann Kendall test was used to assess significant ($p<0.05$) long-term trends in precipitation and concentrations of $H^+$, $SO_4$, $NO_3$, and $NH_4$. The slope and the standard error of the slope were calculated (Tables 2.1-2.5). The sites were then ranked by standard error, reflecting the statistical confidence in the trends in precipitation volume and solute concentration over time. The SE of the slope was chosen rather than the slope itself because the confidence in the trend was of interest, rather than in the trend itself. The site with the lowest SE for precipitation volume or concentration was given a score of one and the site with the highest SE was given a score of 22. The rankings for precipitation volume and the four solutes were summed to give each site a score. The sites with the smallest scores have the greatest ability to detect long-term trends (Table 2.6). A multiple linear regression was fit to the scores using start date, location (urban, suburban, or rural), latitude, longitude, and elevation as predictor variables. None of these factors were significant in predicting the confidence of observing long-term trends at these sites.

Table 2.1. Trends in precipitation (mm yr$^{-1}$) in DEC Acid Deposition Monitoring sites. Sites are arranged from those showing the highest confidence in the long-term trend (smallest SE) to those showing the lowest confidence (largest SE). Sites in red were closed in December 2010, and sites that were relocated are indicated with an asterisk. Significant trends based on a Mann Kendall trends test are highlighted in gray. Significance levels are indicated with asterisks: * indicates p <0.05, ** indicates p<0.01, *** indicates p<0.001, and **** indicates p<0.0001.

| | **Start Date** | **Loc. Descr.** | **Lat.** | **Long.** | **Elevation (ft)** | **Mann-Kendall tau** | **Mann-Kendall p-value** | **Mann-Kendall sig. level** | **Slope (mm yr$^{-1}$)** | **Slope SE (mm yr$^{-1}$)** |
|---|---|---|---|---|---|---|---|---|---|---|
| **Mt Ninham** | 1987 | Rural | 41.46 | -73.71 | 605 | 0.00001855 | <0.0001 | **** | 0.0079 | 0.0742 |
| **East Syracuse*** | 1986 | Suburban | 43.05 | -76.06 | 415 | -0.0001172 | 0.760 | | 0.2283 | 0.0843 |
| **Rochester*** | 1986 | Urban | 43.15 | -72.55 | 424 | 0.000005013 | 0.47 | | -0.0095 | 0.0905 |
| **Buffalo** | 1987 | Urban | 42.88 | -78.81 | 600 | -0.00005404 | 0.23 | | 0.0458 | 0.0906 |
| **Westfield** | 1987 | Rural | 42.29 | -79.59 | 1030 | -0.00008968 | 0.02 | * | 0.1648 | 0.0950 |
| **Wanakena** | 1987 | Rural | 44.15 | -74.90 | 1510 | -0.00001686 | 0.003 | ** | 0.0740 | 0.0955 |
| **Camp Georgetown** | 1987 | Rural | 42.73 | -75.78 | 1570 | -0.0002 | 0.06 | | 0.5013 | 0.0979 |
| **Loudonville (primary)** | 1987 | Suburban | 42.68 | -73.76 | 330 | -0.00007875 | 0.0006 | *** | 0.1997 | 0.0984 |
| **Elmira*** | 1987 | Urban | 42.11 | -76.80 | 837 | 0.00001767 | 0.01 | * | -0.0211 | 0.1013 |
| **Niagara Falls*** | 1986 | Urban | 43.08 | -79.00 | 571 | -0.00007991 | 0.49 | | 0.1558 | 0.1078 |
| **Loudonville (colo)** | 1989 | Suburban | 42.68 | -73.76 | 1565 | -0.00006789 | 0.003 | ** | 0.2134 | 0.1114 |
| **Belleayre Mt** | 1986 | Rural | 42.14 | -74.49 | 2000 | -0.0001204 | 0.0002 | *** | 0.3843 | 0.1129 |
| **Altmar** | 1989 | Rural | 43.51 | -75.99 | 530 | -0.00002459 | 0.02 | * | 0.0247 | 0.1222 |
| **Nicks Lake** | 1987 | Rural | 43.69 | -74.99 | 1715 | -0.00006329 | 0.09 | | 0.1272 | 0.1261 |
| **Grafton (primary)*** | 1988 | Rural | 42.78 | -73.46 | 1565 | -0.000143 | 0.50 | | 0.3389 | 0.1263 |
| **Whiteface Mt** | 1989 | Rural | 44.39 | -73.86 | 2050 | -0.00000447 | 0.08 | | 0.6688 | 0.1278 |
| **Piseco Lake** | 1988 | Rural | 43.45 | -74.52 | 1704 | -0.0001121 | 0.02 | * | 0.1414 | 0.1379 |
| **Eisenhower Park** | 1987 | Urban | 40.74 | -73.59 | 90 | -0.00008063 | <0.0001 | **** | 0.1782 | 0.1405 |
| **White Plains** | 1987 | Suburban | 41.05 | -73.76 | 195 | -0.0001956 | 0.61 | | -0.0407 | 0.1606 |
| **NY Botanical Gardens*** | 1990 | Urban | 40.87 | -73.88 | 85 | -0.0001055 | <0.0001 | **** | 0.4642 | 0.1767 |
| **Grafton (colo)** | 1988 | Rural | 42.78 | -73.46 | 837 | 0.003431 | 0.34 | | 1.2523 | 0.8023 |
| **Paul Smiths** | 2003 | Rural | 44.43 | -74.25 | 1631 | 0.002518 | 0.90 | | 0.9191 | 1.5133 |

Table 2.2. Trends in precipitation concentrations of H+ (μmol L$^{-1}$) in DEC Acid Deposition Monitoring sites. Sites are arranged from those showing the highest confidence in the long-term trend (smallest SE) to those showing the lowest confidence (largest SE). Sites in red were closed in December 2010, and sites that were relocated are indicated with an asterisk. Significant trends based on a Mann Kendall trends test are highlighted in gray. Significance levels are indicated with asterisks: * indicates p <0.05, ** indicates p<0.01, *** indicates p<0.001, and **** indicates p<0.0001.

| | Start Date | Loc. Descr. | Lat. | Long. | Elevation (ft) | Mann-Kendall tau | Mann-Kendall p-value | Mann-Kendall sig. level | Slope (μmol L$^{-1}$ yr$^{-1}$) | Slope SE (μmol L$^{-1}$ yr$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|
| **Wanakena** | 1987 | Rural | 44.15 | -74.90 | 1510 | 5.115E-07 | <0.0001 | **** | -1.3612 | 0.1429 |
| **Whiteface Mt** | 1989 | Rural | 44.39 | -73.86 | 2050 | 2.756E-07 | <0.0001 | **** | -1.5264 | 0.1462 |
| **Niagara Falls*** | 1986 | Urban | 43.08 | -79.00 | 571 | 5.294E-07 | <0.0001 | **** | -1.7914 | 0.1593 |
| **East Syracuse*** | 1986 | Suburban | 43.05 | -76.06 | 415 | 4.355E-07 | <0.0001 | **** | -1.1584 | 0.1668 |
| **Piseco Lake** | 1988 | Rural | 43.45 | -74.52 | 1704 | 6.226E-07 | <0.0001 | **** | -2.2129 | 0.1707 |
| **Belleayre Mt** | 1986 | Rural | 42.14 | -74.49 | 2000 | 4.098E-07 | <0.0001 | **** | -1.4402 | 0.1709 |
| **Buffalo** | 1987 | Urban | 42.88 | -78.81 | 600 | 0.000000751 | <0.0001 | **** | -2.5490 | 0.1791 |
| **Westfield** | 1987 | Rural | 42.29 | -79.59 | 1030 | 6.193E-07 | <0.0001 | **** | -1.6810 | 0.1919 |
| **Nicks Lake** | 1987 | Rural | 43.69 | -74.99 | 1715 | 2.956E-07 | <0.0001 | **** | -1.4003 | 0.1982 |
| **Loudonville (primary)** | 1987 | Suburban | 42.68 | -73.76 | 330 | 7.714E-07 | <0.0001 | **** | -2.8043 | 0.2168 |
| **Elmira*** | 1987 | Urban | 42.11 | -76.80 | 837 | 7.212E-07 | <0.0001 | **** | -1.9084 | 0.2206 |
| **Loudonville (colo)** | 1989 | Suburban | 42.68 | -73.76 | 1565 | 5.683E-07 | <0.0001 | **** | -2.4328 | 0.2281 |
| **Mt Ninham** | 1987 | Rural | 41.46 | -73.71 | 605 | 0.000001156 | <0.0001 | **** | -3.6575 | 0.2281 |
| **Camp Georgetown** | 1987 | Rural | 42.73 | -75.78 | 1570 | 5.836E-07 | <0.0001 | **** | -1.8718 | 0.2559 |
| **NY Botanical Gardens*** | 1990 | Urban | 40.87 | -73.88 | 85 | 4.357E-07 | <0.0001 | **** | -1.9160 | 0.2642 |
| **Rochester*** | 1986 | Urban | 43.15 | -72.55 | 424 | 7.762E-07 | <0.0001 | **** | -2.0764 | 0.2789 |
| **Grafton (primary)*** | 1988 | Rural | 42.78 | -73.46 | 1565 | 3.283E-07 | <0.0001 | **** | -1.4409 | 0.2819 |
| **White Plains** | 1987 | Suburban | 41.05 | -73.76 | 195 | 4.335E-07 | <0.0001 | **** | -1.5626 | 0.2892 |
| **Eisenhower Park** | 1987 | Urban | 40.74 | -73.59 | 90 | 5.531E-07 | <0.0001 | **** | -2.3093 | 0.3138 |
| **Altmar** | 1989 | Rural | 43.51 | -75.99 | 530 | 3.758E-07 | <0.0001 | **** | -2.0761 | 0.4059 |
| **Grafton (colo)** | 1988 | Rural | 42.78 | -73.46 | 837 | -4.753E-06 | 0.083067 | | -1.7212 | 0.7800 |
| **Paul Smiths** | 2003 | Rural | 44.43 | -74.25 | 1631 | -7.159E-06 | 0.029234 | * | -2.5925 | 1.0082 |

Table 2.3. Trends in precipitation concentrations of $SO_4$ (mg $L^{-1}$) in DEC Acid Deposition Monitoring sites. Sites are arranged from those showing the highest confidence in the long-term trend (smallest SE) to those showing the lowest confidence (largest SE). Sites in red were closed in December 2010, and sites that were relocated are indicated with an asterisk. Significant trends based on a Mann Kendall trends test are highlighted in gray. Significance levels are indicated with asterisks: * indicates p <0.05, ** indicates p<0.01, *** indicates p<0.001, and **** indicates p<0.0001.

| | **Start Date** | **Loc. Descr.** | **Lat.** | **Long.** | **Elevation (ft)** | **Mann-Kendall tau** | **Mann-Kendall p-value** | **Mann-Kendall sig. level** | **Slope (mg $L^{-1}$ $yr^{-1}$)** | **Slope SE (mg $L^{-1}$ $yr^{-1}$)** |
|---|---|---|---|---|---|---|---|---|---|---|
| **Whiteface Mt** | 1989 | Rural | 44.39 | -73.86 | 2050 | 0.00002066 | <0.0001 | **** | -0.0392 | 0.0074 |
| **Wanakena** | 1987 | Rural | 44.15 | -74.90 | 1510 | 0.00001969 | <0.0001 | **** | -0.0564 | 0.0080 |
| **Westfield** | 1987 | Rural | 42.29 | -79.59 | 1030 | 0.00002713 | <0.0001 | **** | -0.0848 | 0.0091 |
| **Piseco Lake** | 1988 | Rural | 43.45 | -74.52 | 1704 | 0.00002019 | <0.0001 | **** | -0.0681 | 0.0093 |
| **Grafton (primary)*** | 1988 | Rural | 42.78 | -73.46 | 1565 | 0.00001821 | <0.0001 | **** | -0.0592 | 0.0094 |
| **Niagara Falls*** | 1986 | Urban | 43.08 | -79.00 | 571 | 0.00002607 | <0.0001 | **** | -0.0898 | 0.0095 |
| **Belleayre Mt** | 1986 | Rural | 42.14 | -74.49 | 2000 | 0.0000218 | <0.0001 | **** | -0.0795 | 0.0096 |
| **Camp Georgetown** | 1987 | Rural | 42.73 | -75.78 | 1570 | 0.00002685 | <0.0001 | **** | -0.0797 | 0.0097 |
| **Nicks Lake** | 1987 | Rural | 43.69 | -74.99 | 1715 | 0.00001642 | <0.0001 | **** | -0.0689 | 0.0097 |
| **East Syracuse*** | 1986 | Suburban | 43.05 | -76.06 | 415 | 0.00002402 | <0.0001 | **** | -0.0690 | 0.0102 |
| **Rochester*** | 1986 | Urban | 43.15 | -72.55 | 424 | 0.00003401 | <0.0001 | **** | -0.0923 | 0.0109 |
| **Altmar** | 1989 | Rural | 43.51 | -75.99 | 530 | 0.00002056 | <0.0001 | **** | -0.0756 | 0.0121 |
| **Loudonville (primary)** | 1987 | Suburban | 42.68 | -73.76 | 330 | 0.00003238 | <0.0001 | **** | -0.1080 | 0.0122 |
| **Buffalo** | 1987 | Urban | 42.88 | -78.81 | 600 | 0.00002835 | <0.0001 | **** | -0.0716 | 0.0123 |
| **Eisenhower Park** | 1987 | Urban | 40.74 | -73.59 | 90 | 0.00003031 | <0.0001 | **** | -0.1168 | 0.0125 |
| **Elmira*** | 1987 | Urban | 42.11 | -76.80 | 837 | 0.00002139 | <0.0001 | **** | -0.0605 | 0.0127 |
| **Loudonville (colo)** | 1989 | Suburban | 42.68 | -73.76 | 1565 | 0.00002417 | <0.0001 | **** | -0.0885 | 0.0128 |
| **White Plains** | 1987 | Suburban | 41.05 | -73.76 | 195 | 0.00001142 | <0.0001 | **** | -0.0921 | 0.0144 |
| **NY Botanical Gardens*** | 1990 | Urban | 40.87 | -73.88 | 85 | 0.00001735 | <0.0001 | **** | -0.0768 | 0.0146 |
| **Mt Ninham** | 1987 | Rural | 41.46 | -73.71 | 605 | 0.00003168 | <0.0001 | **** | -0.0748 | 0.0154 |
| **Grafton (colo)** | 1988 | Rural | 42.78 | -73.46 | 837 | 0.00001072 | 0.71858 | | 0.0039 | 0.0438 |
| **Paul Smiths** | 2003 | Rural | 44.43 | -74.25 | 1631 | -0.0006369 | 0.0025317 | ** | -0.2325 | 0.0721 |

Table 2.4. Trends in precipitation concentrations of NO$_3$ (mg L$^{-1}$) in DEC Acid Deposition Monitoring sites. Sites are arranged from those showing the highest confidence in the long-term trend (smallest SE) to those showing the lowest confidence (largest SE). Sites in red were closed in December 2010, and sites that were relocated are indicated with an asterisk. Significant trends based on a Mann Kendall trends test are highlighted in gray. Significance levels are indicated with asterisks: * indicates p <0.05, ** indicates p<0.01, *** indicates p<0.001, and **** indicates p<0.0001.

| | **Start Date** | **Loc. Descr.** | **Lat.** | **Long.** | **Elevation (ft)** | **Mann-Kendall tau** | **Mann-Kendall p-value** | **Mann-Kendall sig. level** | **Slope (mg L$^{-1}$ yr$^{-1}$)** | **Slope SE (mg L$^{-1}$ yr$^{-1}$)** |
|---|---|---|---|---|---|---|---|---|---|---|
| **Whiteface Mt** | 1989 | Rural | 44.39 | -73.86 | 2050 | -3.468E-08 | <0.0001 | **** | -0.0209 | 0.0061 |
| **Belleayre Mt** | 1986 | Rural | 42.14 | -74.49 | 2000 | 0.000007598 | <0.0001 | **** | -0.0339 | 0.0065 |
| **Wanakena** | 1987 | Rural | 44.15 | -74.90 | 1510 | 0.000007768 | <0.0001 | **** | -0.0259 | 0.0065 |
| **Camp Georgetown** | 1987 | Rural | 42.73 | -75.78 | 1570 | 0.00001349 | <0.0001 | **** | -0.0411 | 0.0066 |
| **Niagara Falls*** | 1986 | Urban | 43.08 | -79.00 | 571 | 0.00001169 | 0.10271 | | -0.0379 | 0.0070 |
| **Grafton (primary)*** | 1988 | Rural | 42.78 | -73.46 | 1565 | 0.000002446 | 0.0018165 | ** | -0.0162 | 0.0070 |
| **Piseco Lake** | 1988 | Rural | 43.45 | -74.52 | 1704 | 0.000009317 | <0.0001 | **** | -0.0354 | 0.0074 |
| **Rochester*** | 1986 | Urban | 43.15 | -72.55 | 424 | 0.00001336 | <0.0001 | **** | -0.0397 | 0.0077 |
| **Elmira*** | 1987 | Urban | 42.11 | -76.80 | 837 | 0.000004458 | 0.047245 | * | -0.0116 | 0.0083 |
| **Loudonville (primary)** | 1987 | Suburban | 42.68 | -73.76 | 330 | 0.00001545 | <0.0001 | **** | -0.0513 | 0.0084 |
| **Nicks Lake** | 1987 | Rural | 43.69 | -74.99 | 1715 | -0.00000216 | <0.0001 | **** | -0.0153 | 0.0088 |
| **Loudonville (colo)** | 1989 | Suburban | 42.68 | -73.76 | 1565 | 0.000007538 | <0.0001 | **** | -0.0316 | 0.0095 |
| **Westfield** | 1987 | Rural | 42.29 | -79.59 | 1030 | 0.000002455 | 0.00092814 | *** | -0.0102 | 0.0096 |
| **Mt Ninham** | 1987 | Rural | 41.46 | -73.71 | 605 | 0.000001968 | 0.0076495 | ** | -0.0039 | 0.0107 |
| **Buffalo** | 1987 | Urban | 42.88 | -78.81 | 600 | 0.000006203 | 0.031059 | * | -0.0018 | 0.0107 |
| **Eisenhower Park** | 1987 | Urban | 40.74 | -73.59 | 90 | 0.00001387 | <0.0001 | **** | -0.0614 | 0.0108 |
| **Altmar** | 1989 | Rural | 43.51 | -75.99 | 530 | 0.000007049 | 0.0020383 | *** | -0.0359 | 0.0110 |
| **East Syracuse*** | 1986 | Suburban | 43.05 | -76.06 | 415 | 0.00001218 | <0.0001 | **** | -0.0322 | 0.0112 |
| **White Plains** | 1987 | Suburban | 41.05 | -73.76 | 195 | 0.000003374 | <0.0001 | **** | -0.0222 | 0.0122 |
| **NY Botanical Gardens*** | 1990 | Urban | 40.87 | -73.88 | 85 | 0.00000907 | 0.0018154 | ** | -0.0406 | 0.0128 |
| **Grafton (colo)** | 1988 | Rural | 42.78 | -73.46 | 837 | -0.0003046 | 0.0020095 | ** | -0.1112 | 0.0356 |
| **Paul Smiths** | 2003 | Rural | 44.43 | -74.25 | 1631 | -0.0006711 | 0.00066119 | *** | -0.2450 | 0.0712 |

Table 2.5. Trends in precipitation concentrations of $NH_4$ (mg $L^{-1}$) in DEC Acid Deposition Monitoring sites. Sites are arranged from those showing the highest confidence in the long-term trend (smallest SE) to those showing the lowest confidence (largest SE). Sites in red were closed in December 2010, and sites that were relocated are indicated with an asterisk. Significant trends based on a Mann Kendall trends test are highlighted in gray. Significance levels are indicated with asterisks: * indicates p <0.05, ** indicates p<0.01, *** indicates p<0.001, and **** indicates p<0.0001.

| | Start Date | Loc. Descr. | Lat. | Long. | Elevation (ft) | Mann-Kendall tau | Mann-Kendall p-value | Mann-Kendall sig. level | Slope (mg $L^{-1}$ $yr^{-1}$) | Slope SE (mg $L^{-1}$ $yr^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|
| **Wanakena** | 1987 | Rural | 44.15 | -74.90 | 1510 | 5.421E-07 | 0.76895 | | -0.0003 | 0.0020 |
| **Piseco Lake** | 1988 | Rural | 43.45 | -74.52 | 1704 | 5.104E-07 | 0.030315 | * | -0.0025 | 0.0022 |
| **Whiteface Mt** | 1989 | Rural | 44.39 | -73.86 | 2050 | -3.195E-07 | 0.016855 | * | 0.0035 | 0.0024 |
| **Camp Georgetown** | 1987 | Rural | 42.73 | -75.78 | 1570 | -2.919E-07 | 0.5804 | | 0.0058 | 0.0025 |
| **Westfield** | 1987 | Rural | 42.29 | -79.59 | 1030 | 5.612E-07 | 0.38824 | | 0.0008 | 0.0025 |
| **East Syracuse*** | 1986 | Suburban | 43.05 | -76.06 | 415 | -0.00000168 | 0.5242 | | 0.0068 | 0.0029 |
| **Grafton (primary)*** | 1988 | Rural | 42.78 | -73.46 | 1565 | 5.984E-07 | 0.7704 | | 0.0027 | 0.0029 |
| **Nicks Lake** | 1987 | Rural | 43.69 | -74.99 | 1715 | 8.006E-07 | 0.064702 | | -0.0011 | 0.0030 |
| **Belleayre Mt** | 1986 | Rural | 42.14 | -74.49 | 2000 | 0.000003301 | 0.060118 | | -0.0076 | 0.0031 |
| **Rochester*** | 1986 | Urban | 43.15 | -72.55 | 424 | 8.652E-07 | 0.40685 | | 0.0010 | 0.0031 |
| **Niagara Falls*** | 1986 | Urban | 43.08 | -79.00 | 571 | 0.000004597 | 0.34034 | | -0.0076 | 0.0033 |
| **White Plains** | 1987 | Suburban | 41.05 | -73.76 | 195 | -0.00000122 | 0.74432 | | 0.0014 | 0.0033 |
| **Buffalo** | 1987 | Urban | 42.88 | -78.81 | 600 | 0.000001 | 0.53903 | | 0.0055 | 0.0035 |
| **Eisenhower Park** | 1987 | Urban | 40.74 | -73.59 | 90 | 0.000002784 | 0.0014751 | ** | -0.0071 | 0.0038 |
| **Altmar** | 1989 | Rural | 43.51 | -75.99 | 530 | 0.000001992 | 0.78699 | | -0.0005 | 0.0039 |
| **Elmira*** | 1987 | Urban | 42.11 | -76.80 | 837 | 1.258E-07 | 0.14537 | | 0.0042 | 0.0040 |
| **Mt Ninham** | 1987 | Rural | 41.46 | -73.71 | 605 | 0.000003076 | 0.048339 | * | -0.0031 | 0.0041 |
| **Loudonville (primary)** | 1987 | Suburban | 42.68 | -73.76 | 330 | 0.000001952 | 0.18835 | | -0.0003 | 0.0041 |
| **NY Botanical Gardens*** | 1990 | Urban | 40.87 | -73.88 | 85 | 0.000002656 | 0.00037176 | *** | -0.0130 | 0.0044 |
| **Loudonville (colo)** | 1989 | Suburban | 42.68 | -73.76 | 1565 | 0.000003976 | 0.06598 | | -0.0111 | 0.0050 |
| **Grafton (colo)** | 1988 | Rural | 42.78 | -73.46 | 837 | -0.00003015 | 0.49935 | | -0.0110 | 0.0209 |
| **Paul Smiths** | 2003 | Rural | 44.43 | -74.25 | 1631 | -0.00004059 | 0.1324 | | -0.0148 | 0.0285 |

Table 2.6. Rank of sites based on the standard error of the slope of long-term trends in precipitation amount and precipitation concentration. Sites were ranked by the standard error of the slope for precipitation and each solute concentration, from lowest to highest, and these rankings were summed to derive a Rank Sum for each site. Sites are arranged from those showing the highest confidence in the long-term trend (smallest SE of the slope) to those showing the lowest confidence (largest SE of the slope). Sites in red were closed in December 2010, and sites that were relocated are indicated with an asterisk.

| | **Start Date** | **Loc. Descr.** | **Lat.** | **Long.** | **Elevation (ft)** | **Rank based on the SE of the slope of $SO_4$** | **Rank based on the SE of the slope of $NO_3$** | **Rank based on the SE of the slope of $NH_4$** | **Rank based on the SE of the slope of Precip.** | **Rank based on the SE of the slope of $H^+$** | **RANK SUM** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Wanakena** | 1987 | Rural | 44.15 | -74.90 | 1510 | 2 | 3 | 1 | 6 | 1 | 13 |
| **Whiteface Mt** | 1989 | Rural | 44.39 | -73.86 | 2050 | 1 | 1 | 3 | 16 | 2 | 23 |
| **Westfield** | 1987 | Rural | 42.29 | -79.59 | 1030 | 3 | 13 | 5 | 5 | 8 | 34 |
| **Niagara Falls*** | 1986 | Urban | 43.08 | -79.00 | 571 | 6 | 5 | 11 | 10 | 3 | 35 |
| **Piseco Lake** | 1988 | Rural | 43.45 | -74.52 | 1704 | 4 | 7 | 2 | 17 | 5 | 35 |
| **Belleayre Mt** | 1986 | Rural | 42.14 | -74.49 | 2000 | 7 | 2 | 9 | 12 | 6 | 36 |
| **Camp Georgetown** | 1987 | Rural | 42.73 | -75.78 | 1570 | 8 | 4 | 4 | 7 | 14 | 37 |
| **East Syracuse*** | 1986 | Suburban | 43.05 | -76.06 | 415 | 10 | 18 | 6 | 2 | 4 | 40 |
| **Rochester*** | 1986 | Urban | 43.15 | -72.55 | 424 | 11 | 8 | 10 | 3 | 16 | 48 |
| **Grafton (primary)*** | 1988 | Rural | 42.78 | -73.46 | 1565 | 5 | 6 | 7 | 15 | 17 | 50 |
| **Nicks Lake** | 1987 | Rural | 43.69 | -74.99 | 1715 | 9 | 11 | 8 | 14 | 9 | 51 |
| **Buffalo** | 1987 | Urban | 42.88 | -78.81 | 600 | 14 | 15 | 13 | 4 | 7 | 53 |
| **Loudonville (primary)** | 1987 | Suburban | 42.68 | -73.76 | 330 | 13 | 10 | 18 | 8 | 10 | 59 |
| **Elmira*** | 1987 | Urban | 42.11 | -76.80 | 837 | 16 | 9 | 16 | 9 | 11 | 61 |
| **Mt Ninham** | 1987 | Rural | 41.46 | -73.71 | 605 | 20 | 14 | 17 | 1 | 13 | 65 |
| **Loudonville (colo)** | 1989 | Suburban | 42.68 | -73.76 | 330 | 17 | 12 | 20 | 11 | 12 | 72 |
| **Altmar** | 1989 | Rural | 43.51 | -75.99 | 530 | 12 | 17 | 15 | 13 | 20 | 77 |
| **Eisenhower Park** | 1987 | Urban | 40.74 | -73.59 | 90 | 15 | 16 | 14 | 18 | 19 | 82 |
| **White Plains** | 1987 | Suburban | 41.05 | -73.76 | 195 | 18 | 19 | 12 | 19 | 18 | 86 |
| **NY Botanical Gardens*** | 1990 | Urban | 40.87 | -73.88 | 85 | 19 | 20 | 19 | 20 | 15 | 93 |
| **Grafton (colo)** | 1988 | Rural | 42.78 | -73.46 | 1565 | 21 | 21 | 21 | 21 | 21 | 105 |
| **Paul Smiths** | 2003 | Rural | 44.43 | -74.25 | 1631 | 22 | 22 | 22 | 22 | 22 | 110 |

### *2.2.2 Results: Seasonal Mann Kendall Trends*

It appears that most DEC Atmospheric Deposition Monitoring Network sites in New York show similar trends. Of the 22 sites, 11 show statistically significant trends in precipitation over the period of measurement. Ten out of these 11 sites show an increasing trend in precipitation volume and only the Elmira site showed a decreasing trend. All 22 showed decreasing trends in $H^+$ and $SO_4$, and only the Grafton (co-located) collector showed a trend that was not significant for both solutes. Decreasing trends in $NO_3$ were also apparent in all 22 sites with only the Niagara Falls site appearing insignificant. Fewer compelling trends were detectable for $NH_4$, likely because values below detection limits were not included in this analysis and emissions of $NH_3$ (primary precursor) have not changed as much as $SO_2$ or $NO_x$ over this time period (Civerolo, DEC; pers. comm.). Piseco Lake, Eisenhower Park, Mt. Ninham, and the New York Botanical Garden sites all showed significant decreasing trends in $NH_4$, while Whiteface Mt. showed a significant increasing trend. All significance levels were derived from Seasonal Mann Kendall tests ($p<0.05$).

The sites were ranked by the standard error of the slope, from lowest to highest standard error. Concentrations of $SO_4$, $NO_3$, $NH_4$, $H^+$, and precipitation volume were ranked from 1-22 among the sites, and then added to calculate a rank sum for each site. A low rank sum indicates a site that exhibits a consistent trend in the data, and it is possible that these sites could be prioritized because they show the most consistent trends over time. The rank sums ranged from 13-110. The five with lowest rank sums were Wanakena, Whiteface Mt., Westfield, Niagara Falls, and Piseco Lake. The five with the highest rank sums were Eisenhower Park, White Plains, New York Botanical Gardens, Grafton (co-located), and Paul Smiths. Paul Smiths likely had the highest rank sum because it is the most recently added, so the trends there were typically not as consistent as the longer-running sites. Half the sites are rural and have been operational for 20 years or more. These tend to group towards the lowest rank sum, which may indicate that these sites are representative of regional sources.

### *2.2.3 PCA Analysis*

Principle Component Analysis (PCA) was used to group sites by the rate of change over time in the response variables of precipitation and pH as well as concentrations and annual loads of $H^+$, $SO_4$, $NO_3$, and $NH_4$ ($SO_4$ is shown in Figure 2.2. Additional plots can be found in the Appendix Figures 10.1.1-10.1.7). PCA is a procedure that uses an orthogonal transformation to convert a set of observations of possibly correlated variables into a set of values of linearly uncorrelated variables called principal components. The analysis used accounts for the correlation structure of the time series and allows us to see which sites tend to show similar patterns for each response variable and which are most different.  Site abbreviations used in the PCA analyses are in Table 2.7. The sites were grouped qualitatively are somewhat subjective depending on the viewer.

Table 2.7. Site abbreviations. Sites in red are no longer in operation as of January 2011.

| | |
|---|---|
| AL | Altmar |
| BG | NY Botanic Garden |
| BM | Belleayre Mt. |
| BU | Buffalo |
| CG | Camp Georgetown |
| EL | Elmira |
| EP | Eisenhower Park |
| ES | East Syracuse |
| GP | Grafton |
| LP | Loudonville |
| MN | Mt. Ninham |
| NF | Niagara Falls |
| NL | Nick's Lake |
| PL | Piseco Lake |
| PS | Paul Smiths |
| RT | Rochester |
| SP | Sodus Point |
| WE | Westfield |
| WF | Whiteface Base |
| WP | White Plains |
| WR | Wanakena |

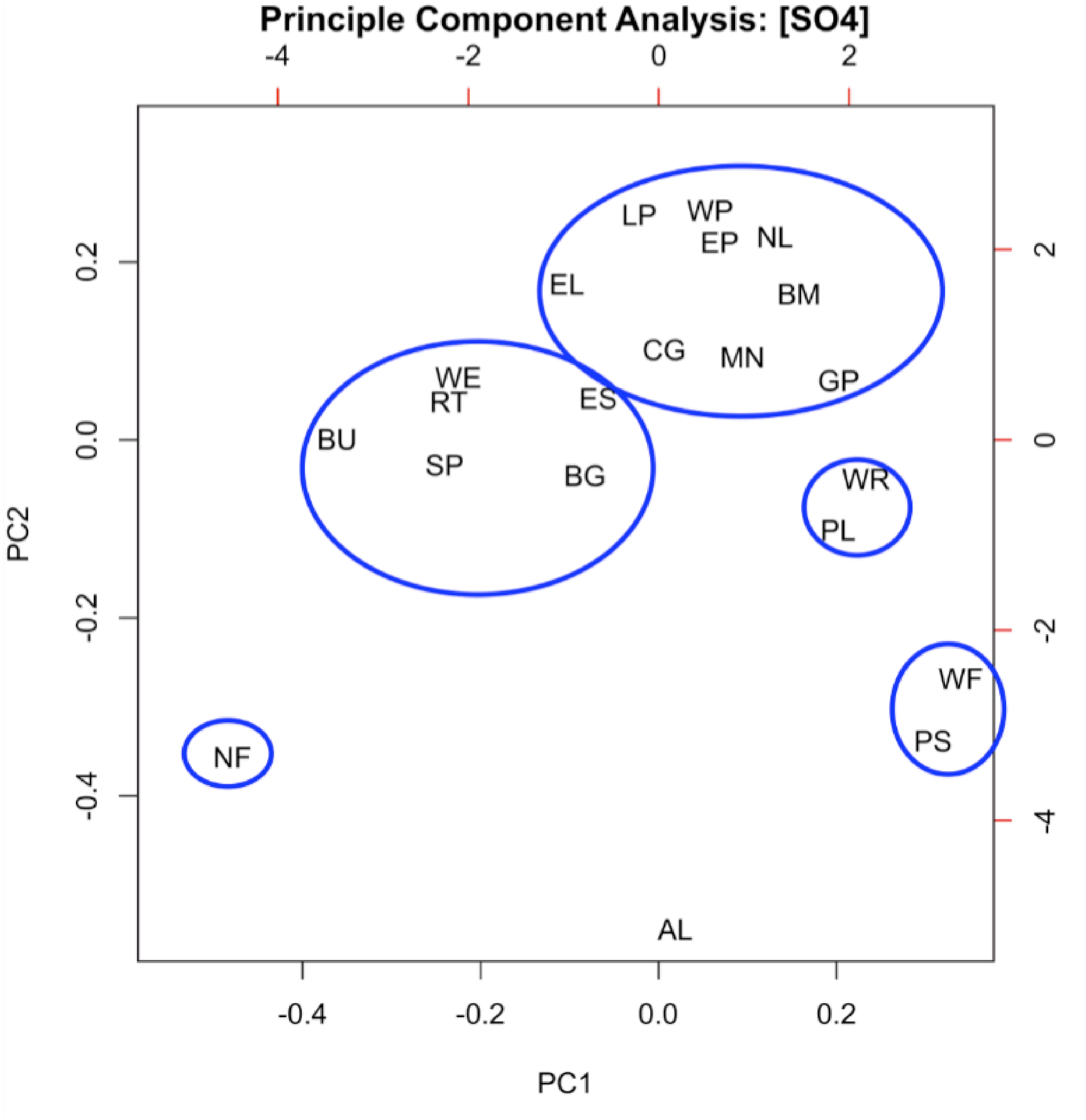


Figure 2.2 PCA analysis of showing groupings by annual average concentrations of $SO_4$ (mg $L^{-1}$ $yr^{-1}$).

### *2.2.4 Results: PCA Analysis*

Certain sites tend to be isolated in the PCA plots, indicating different trends than the other sites. This information can be used to assist in decisions regarding site closings. In some cases, distinctive sites may be desirable since they can be used to depict long-term trends that show the more extreme deposition ranges in New York. If, however, there is reason to suspect that these sites are distinctive due to local peculiarities, such as the proximity of roads or industrial activity, then the site may be a candidate for elimination under a reduced sampling scheme if the intent is to monitor large-scale regional patterns. Additionally, the PCA plots can be used to identify sites that tend to show similar long-term trends, though a similarity in trends may not be due to comparable processes among sites that group together.

Some show distinctive long-term trends based on the PCA analysis as shown in Table 2.8. The Niagara Falls site appears to be the most distinctive site and is isolated in three of the six PCA orthogonal plots. This may be due to dust inputs from a nearby road with a limestone bed (Dirk Felton, pers. comm.). The New York Botanical Garden site was isolated in two analyses and because it is the only site in New York City, it might be expected that that it would show divergent trends from other sites. In this case, if the monitoring goal includes characterizing deposition in a range of sites, it may be important to include this distinctive site.

Table 2.8. Sites isolated in PCA analyses.

| **Site** | **# of times isolated of 8 total analyses** |
|---|---|
| Niagara Falls | 3 |
| NY Botanical Gardens | 2 |
| Belleayre Mt. | 2 |
| Eisenhower Park | 2 |
| East Syracuse | 1 |
| Paul Smiths | 1 |
| Sodus Pt. (closed) | 1 |
| Westfield | 1 |
| Whiteface Base | 1 |

The PCA plots identify sites tending to exhibit similar long-term trends. Sites with the greatest similarities are listed in Table 2.9. In some cases, similar sites such as Nicks Lake and Wanakena, are close to one another in the rural Adirondacks. When other sites not in close proximity to one another such as East Syracuse and Grafton, or Elmira and Wanakena show similarities, the rationale for closing based on similarity in trends is less strong. The sites may be showing similar trends over time, but the pollution sources may not be the same, and could respond differently as pollution sources change in the future. It is interesting to note that the PCA plots for concentration and deposition of $SO_4$, $NO_3$, and $NH_4$ did not always show similar groupings. This may complicate the process of identifying redundant sites based on the PCA plots. Interpreting these findings requires expert knowledge and further statistical analyses may be necessary.

Table 2.9. Deposition sites showing a high number of similarities in PCA analyses.

| **Site 1** | **Site 2** | **Similar PCA groupings (of a total of 8)** |
|---|---|---|
| Altmar (closed 2010) | Buffalo (closed 2010) | 6 |
| Altmar (closed 2010) | Westfield | 6 |
| Buffalo (closed 2010) | Westfield | 6 |
| Elmira | Loudonville (closed 2010) | 6 |
| Elmira | Grafton | 5 |
| Elmira | Nicks Lake | 5 |
| Elmira | Wanakena | 5 |
| Eisenhower Park | White Plains (closed 2010) | 5 |
| East Syracuse | Grafton | 5 |
| Grafton | Whiteface Base | 5 |
| Mt. Ninham | Nicks Lake | 5 |
| Nicks Lake | Camp Georgetown | 5 |
| Nicks Lake | Wanakena | 5 |
| Rochester | Sodus Pt (closed 2002) | 5 |

### *2.2.5 Mixed Model Analyses to Assess Optimal Subsampling Strategies*

To assess the effect of subsampling on the ability to detect long-term trends in atmospheric deposition, a repeated-measures mixed-effects model was used. Background on the statistical model is given in Section 1.2. One hundred percent of the effort was defined to include all sites monitored as of December 2010. The sampling scheme currently in place represents ~80 percent of that effort, due to closures at Altmar, Buffalo, Loudonville, and White Plains. A bootstrap routine of 500 iterations was used to simulate subsampling at approximately 80, 60, 40, 20, and 10 percent of sampling effort. The percent effort was reduced by dropping sites from the analysis. Sites were dropped sequentially for each iteration according to an order specified by a random number generator.

For each iteration of the model, the standard error (SE) of the LSM in mg $L^{-1}$ was recorded. Box plots showing the SE of the LSM for long-term concentrations of $SO_4$, $NO_3$, and $NH_4$ are shown in figures 2.3-2.5. Table 2.10 shows the percent increase in model SE for different subsampling scenarios.

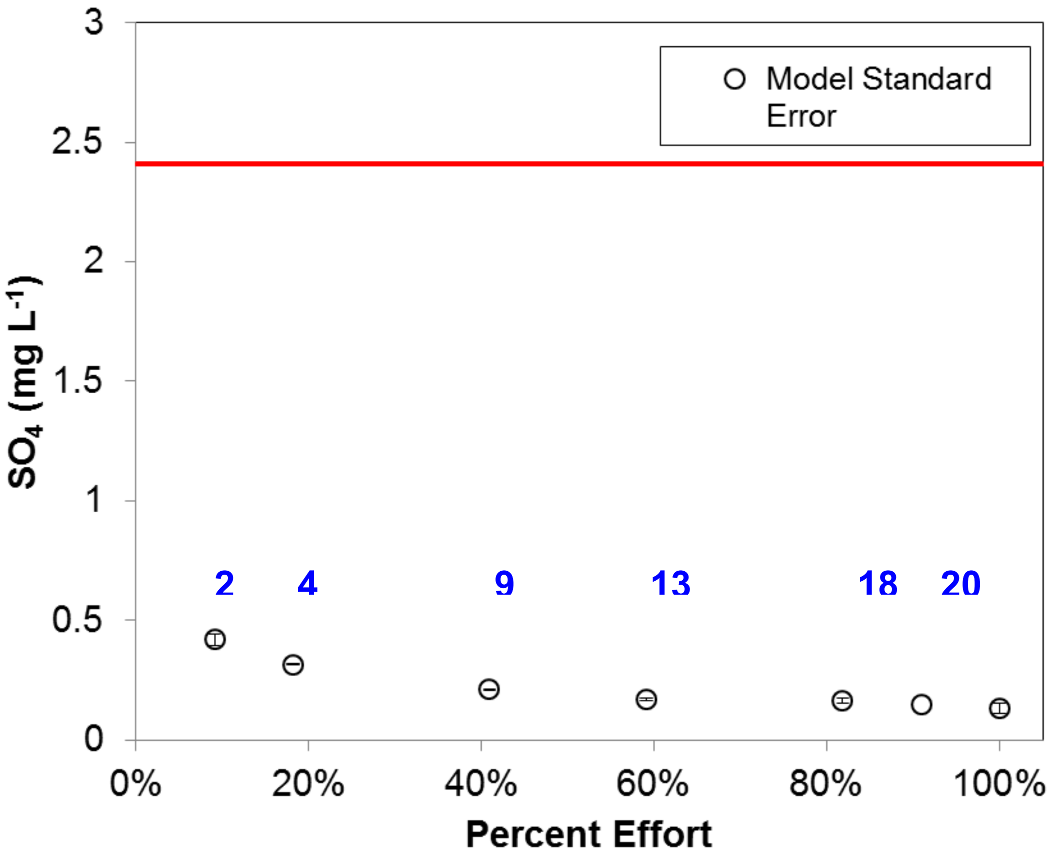


Figure 2.3. LSM estimate and LSM model SE of the repeated measures mixed effects model for concentrations of $SO_4$ (mg $L^{-1}$) in wet deposition based on 500 random iterations for each simulated subsample size (± SD of 500 iterations, which is generally quite small in this case). Data were subsampled by eliminating sites; all sampling dates for individual sites were preserved. The estimate shown above is based on a model using all available data (22 sites; 100% effort as of December 2010). The number of collectors for each subsample is shown in blue above the corresponding point.

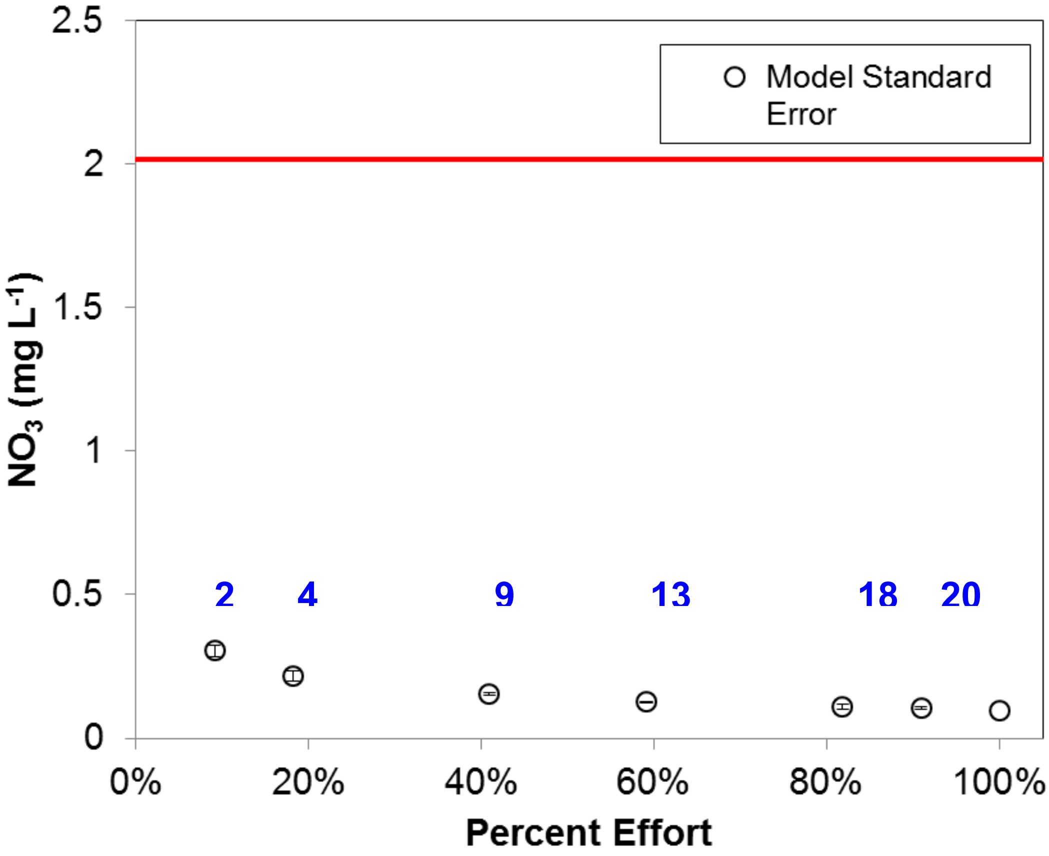


Figure 2.4. LSM estimate and LSM model SE of the repeated measures mixed effects model for concentrations of $NO_3$ (mg $L^{-1}$) in wet deposition based on 500 random iterations for each simulated subsample size (± SD of 500 iterations, which is generally quite small in this case). Data were subsampled by eliminating sites; all sampling dates for individual sites were preserved. The estimate shown above is based on a model using all available data (22 sites; 100% effort as of December 2010). The number of collectors for each subsample is shown in blue above the corresponding point.

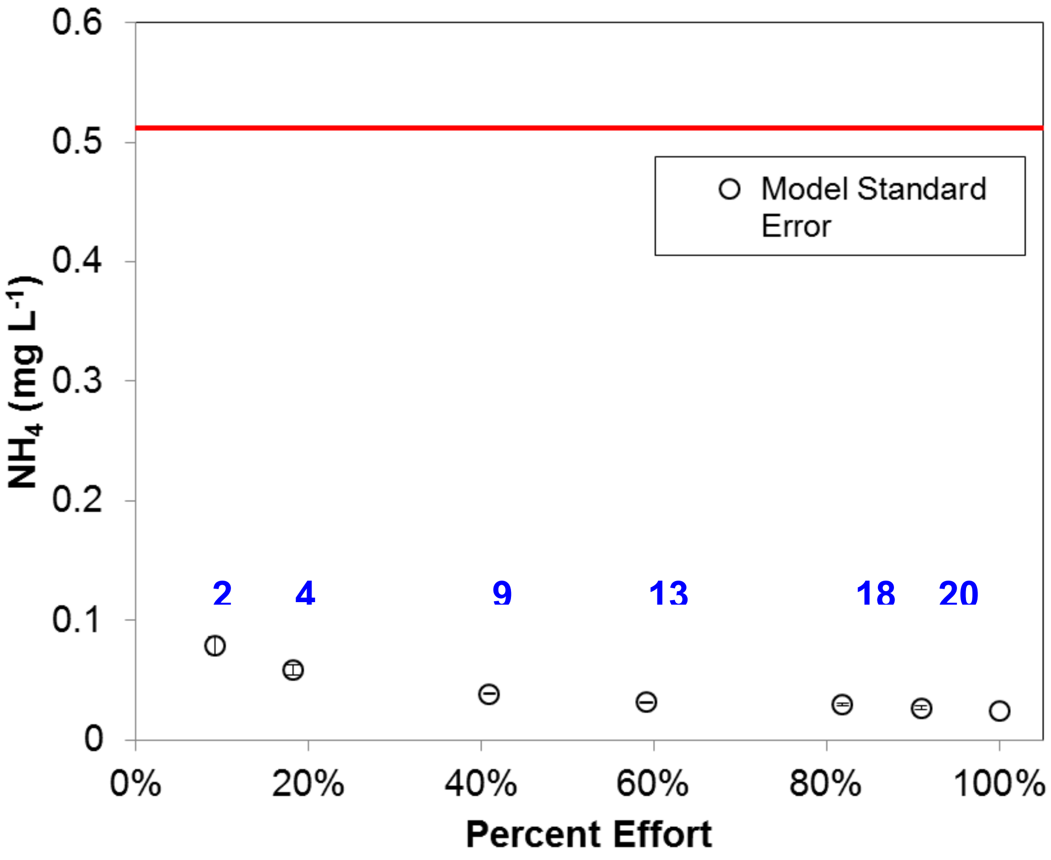


Figure 2.5. LSM estimate and LSM model SE of the repeated measures mixed effects model for concentrations of $NH_4$ (mg $L^{-1}$) in wet deposition based on 500 random iterations for each simulated subsample size (± SD of 500 iterations, which is generally quite small in this case). Data were subsampled by eliminating sites; all sampling dates for individual sites were preserved. The estimate shown above is based on a model using all available data (22 sites; 100 percent effort as of December 2010). The number of collectors for each subsample is shown in blue above the corresponding point.

### *2.2.6 Results: Mixed Model Analyses*

The repeated-measures mixed-effects models show that overall model error increases with decreased sampling effort. Table 2.10 describes the increase in model error for each subsampling scheme for $SO_4$, $NO_3$, and $NH_4$ (mg $L^{-1}$). Based on repeated-measures mixed-effects models, a closure of monitoring stations down to 60 percent of that of December 2010 would increase the standard error of models of long-term trends by ~30 percent for SO4, NO3, and NH4.

Table 2.10. Percent increase in model SE for different subsampling scenarios.

| Percent Effort (as of Dec. 2010) | Number of collectors | $SO_4$ | $NO_3$ | $NH_4$ |
|---|---|---|---|---|
| 90% | 20 | 11 | 8 | 10 |
| 80% | 18 | 26 | 12 | 23 |
| 60% | 13 | 31 | 29 | 30 |
| 40% | 9 | 60 | 59 | 59 |
| 20% | 4 | 142 | 122 | 141 |
| 10% | 2 | 225 | 207 | 230 |

## 2.3 Findings and Conclusions

- Significant trends in concentrations of $SO_4$, $NO_3$, $H^+$, and precipitation amount (regression $p<0.05$) were detectable at most of the 22 sites included in the DEC atmospheric deposition program. It would be most efficient to prioritize monitoring sensitive areas where small changes in deposition may have a larger impact on ecosystem processes. These sensitive areas include the Adirondacks, Catskills, Hudson Valley (susceptible to pollution from the New York City area), and Long Island. Areas in western New York on carbonate soils will show less susceptibility to acidification due to high buffering capacity in soils and water, but these sites provide data on the effects of pollutants transported into the state and are also important for long-term monitoring.
- During interviews, stakeholders suggested that there is a relative lack of information on acidic deposition at the highest elevations in New York. It would be valuable to measure wet deposition at one or more high elevation sites, if not year-round then perhaps seasonally, though there are practical limitations to implementing monitoring at these sites. The summit of Whiteface is a logical choice due to the historical deposition monitoring at the base of the mountain, the long-term record of cloud-water monitoring, and the fact that there are already environmental monitoring activities at the summit. Though not co-located with as much atmospheric monitoring as Whiteface Mountain,

monitoring at high-elevation sites in the Catskills would provide data in this acid-sensitive mountainous region.

- It is possible that having fewer stations would hinder estimates of deposition across the state, because sites will encompass a less diverse array of land uses and geographic areas (Figure 2.1). If modeling annual deposition loads across the state by interpolating between collectors is a priority, there will be higher uncertainty in interpolation measurements with fewer sites.
- One limitation of the PCA analysis is that neither the NTN or AIRMoN sites were included in the analysis because the networks are somewhat different. There are several NTN and DEC sites located close to one another, and if the DEC, NTN, and AIRMoN data were included in a meta-analysis of acid deposition, a clearer picture of potential redundant sampling efforts in New York might emerge.
- Consolidating stations into one network would have several benefits for monitoring atmospheric deposition in New York. Due to the more consistent and nationwide operating procedures of the NADP NTN network, it is possible that long-term trends would be easier to detect with fewer monitoring stations, and they would be consistent with those across the U.S. derived from NADP NTN data. Data could then be more easily integrated into regional models that extend beyond New York and would be more useful to the scientific community and federal policy makers who are interested in regional trends. This regional implication is important because acidic deposition in New York is affected by activities beyond the state borders.
- Stakeholders suggest that co-located equipment be used to monitor simultaneous trends in many atmospheric analytes in addition to acidic deposition, and can provide important

information on trends relative to others. Better coordination among DEC, NADP, and EPA CASTNet could help increase the breadth of measurements at particular sites. Some sites are already poised for this, including Whiteface Base, Huntington Forest, Biscuit Brook, and possibly urban sites such as the New York Botanical Gardens site in the Bronx, New York City (see Table 9.1) and the Syracuse Center of Excellence. Co-locating monitoring activities may be particularly important with regard to climate change research, which will likely be an important area of research in the future.

- The analyses in this report did not include a combined analysis of all wet deposition data collected in the state by various agencies, because the methods between programs are not directly comparable.

# 3. Lake Chemistry Monitoring

## 3.1 Status

Lakes are an important resource for New York, which contains approximately 7,600 freshwater lakes (~1800 of which have areas >1 ha), ponds and reservoirs, as well as portions of two of the five Great Lakes (DEC, “Statewide Lake Monitoring Programs”). New York lakes serve many functions, including providing drinking water for much of the state, providing habitat for wildlife, serving as a system of flood control, and supporting important economic sectors such as recreation, tourism, agriculture, manufacturing, and power generation.

Lake chemistry is monitored by a number of programs in New York. The DEC administers two such programs: the Lake Classification and Inventory Survey (LCI) and the New York Citizens Statewide Lake Assessment Program (CSLAP). The lakes in the LCI and CSLAP programs are distributed throughout the state. The LCI program includes a core set of lakes that are sampled monthly, as well as a group of lakes that rotate on an annual cycle, with each rotating group being monitored once every five years. The CSLAP program is a highly successful volunteer lake-monitoring program that has been in place since 1985. Volunteers from member-lake associations are provided supplies and training. They collect water samples and observational data bi-weekly (May-October) and send the samples to the DEC for processing. Lakes are assessed for water quality, signs of eutrophication, and invasive species, but not fish or other lake fauna. Since 1985, the CSLAP monitoring program has involved more than 1,300 volunteers on about 220 lakes throughout the state. These volunteers have collected more than 15,000 samples over this period, contributed more than 75,000 hours of time, and provided a service of close to $2 million (DEC, “Statewide Lake Monitoring Programs”).

Other lake monitoring efforts in New York have targeted areas that are particularly sensitive to acidic deposition. For several decades, the Adirondacks have been a focal point of lake research relating to acidic deposition. There are more than 3,000 lakes and ponds in this region, which is a higher density than elsewhere in the state. These lakes are especially susceptible to environmental degradation as a result of acidic deposition.

There are three major monitoring programs for lake chemistry in the Adirondacks that are somewhat overlapping. The EPA's Temporally Integrated Monitoring of Ecosystems (TIME) and Long Term Monitoring (LTM) programs were both initiated in the early 1990s. In the TIME assessment, 43 lakes were randomly selected out of a sample population of about 100 lakes with low acid neutralizing capacity (ANC) and are sampled once per year in the summer. Fifty-two acid-sensitive lakes in the LTM assessment are sampled throughout the year, with greater sampling frequency in the spring during times of high runoff. The EPA TIME/LTM program is part of a larger regional assessment designed to study acid-sensitive lakes and streams in several regions in the eastern U.S., including the Adirondack Mountains, New England, the Northern Appalachian Plateau, and the Ridge/Blue Ridge provinces. In the Adirondacks, TIME focuses on low ANC lakes while the ALTM covers a range of acid sensitivity.

The Adirondack Lake Survey Corporation (ALSC) is a not-for-profit corporation. The ALSC runs the Adirondack Long Term Monitoring (ALTM) program, which is supported by the DEC, the EPA, and NYSERDA. The ALTM program was initiated in 1982 to evaluate the chemistry of 17 Adirondack lakes. From 1984-1987, an intensive survey of 1469 lakes was undertaken to assess variability of lake chemistry within the Adirondack Park (Roy et al. 2010). Based on classification of lakes derived from this survey, a cohort of 52 lakes was selected for monthly sampling, which began in June 1992 (Baker et al. 1990). The ALSC ALTM program is a subset of the EPA LTM program. The ALSC also carries out additional monitoring programs of streams, snowpack, snowmelt, and fisheries (Figure 3.1).

The TIME sampling procedure consists of annual probability surveys. Six lakes are common in both the TIME and ALTM/LTM programs, and a recent study was conducted to determine whether trends over time are similar between the two programs (Civerolo et al. 2011). This study found that paired in time, measurements in the two studies were highly correlated, but that the TIME single annual sampling provided less of an ability to define long-term trends than the ALTM. Thus, while the two programs both have lakes in common, they serve different functions for assessing long-term lake chemistry trends in the Adirondacks. The TIME program allows for population-level statistical comparisons, while the ALTM program allows for analyses of seasonal patterns and gives finer-scale temporal data to assess lake chemistry trends over time.

The Darren Freshwater Institute's Adirondack Effect Assessment Program (AEAP) collected additional lake chemistry from 35 lakes two – three times during the 1994-2006 summer months as well as from 17 lakes in the summer of 2010. These water chemistry measurements were collected concurrently with measurements of aquatic biota. SUNY-ESF has also sampled the Arbutus Lake outlet weekly since 1991.

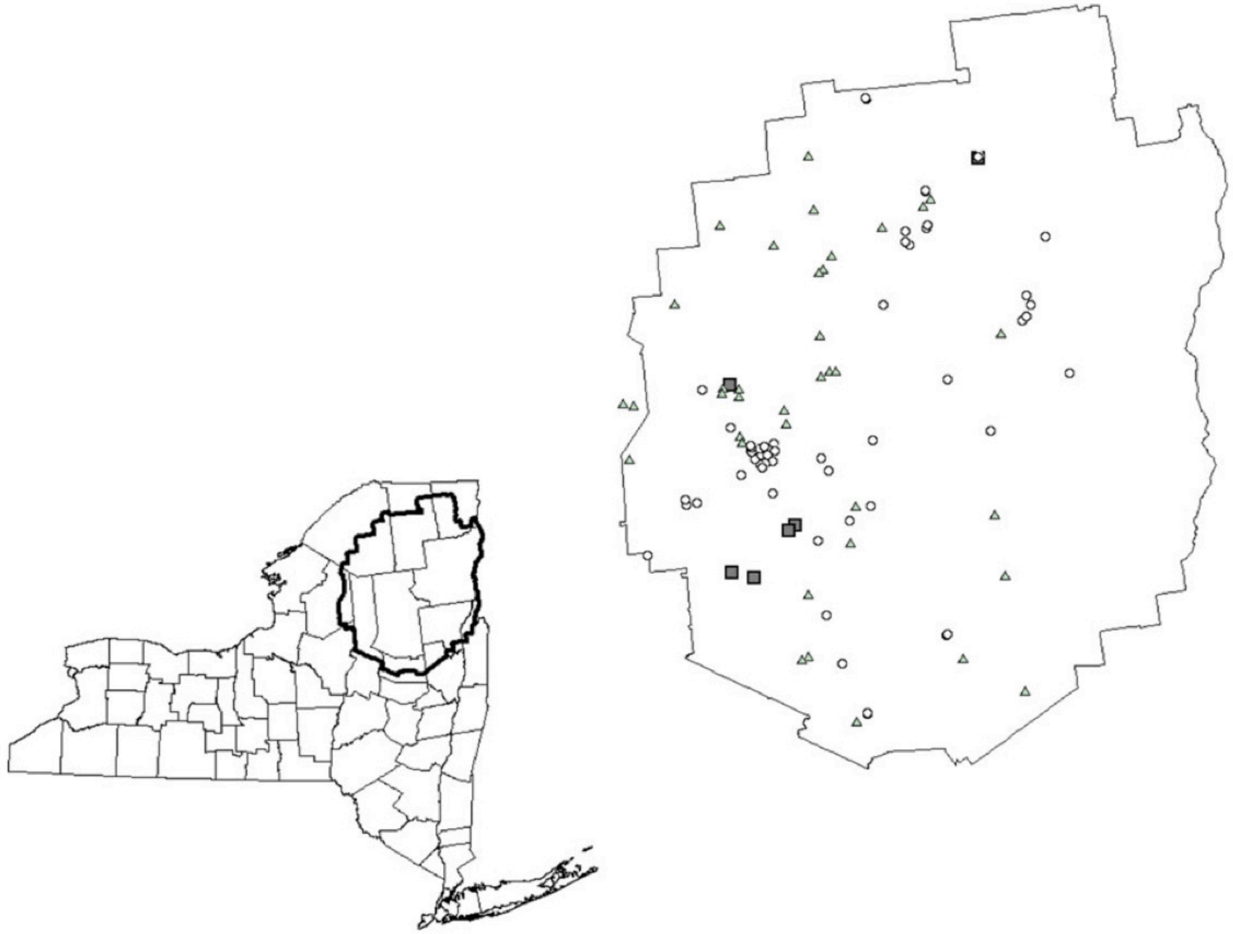


Figure 3.1. Locations of the TIME (triangles) and LTM/ALTM (circles) sites in the Adirondack Park region of New York. The six lakes common to both programs are shown as squares. This map is from Civerolo et al. 2011.

## 3.2 Analyses

### *3.2.1 Seasonal Kendall Trends and Results*

Data from the 1992-2010 ALTM long-term chemistry record were used to analyze long-term lake chemistry trends. The analyses included in this report have focused on the monitoring efficiency of the ALTM program because it is the largest dataset available for Adirondack lakes monitoring, with readily accessible and usable data sets. The results of this analysis should be transferable to other lake chemistry monitoring efforts in the Adirondack region.

A Seasonal Mann Kendall test was used to assess significant long-term trends in precipitation volume and concentrations of ANC, $H^+$, $SO_4$, $NO_3$, and Ca (see Appendix 10.2.1-

10.2.3 for results for each individual lake). Many of these lakes show significant decreasing trends for all concentrations of $SO_4$, $NO_3$, and $Ca^{2+}$ and increasing trends for ANC and pH.

Table 3.1. Summary values for statistically significant slopes of ALTM lakes (1992-2010).

| | **$SO_4$ (mg $L^{-1}$ $yr^{-1}$)** | **$NO_3$ (mg $L^{-1}$ $yr^{-1}$)** | **Ca (mg $L^{-1}$ $yr^{-1}$)** | **ANC (µeq $L^{-1}$ $yr^{-1}$)** | **$H^+$ (µmol $L^{-1}$ $yr^{-1}$)** |
|---|---|---|---|---|---|
| ***n* (of a total of 52)** | 51 | 44 | 48 | 45 | 39 |
| **Minimum value** | -4.0 | -1.4 | -3.6 | -0.71 | -610 |
| **25th quartile** | -2.8 | -0.63 | -1.4 | 0.60 | -58 |
| **Median** | -2.4 | -0.26 | -1.1 | 0.85 | -5.6 |
| **75th quartile** | -1.9 | -0.14 | -0.67 | 1.17 | 36 |
| **Maximum value** | 0.00042 | 0.38 | 2.5 | 4.7 | 147 |
| | | | | | |
| **Average** | -2.32 | -0.38 | -1.0 | 0.95 | -28 |

### *3.2.2 Mixed Model Analyses to Assess Optimal Subsampling Strategies*

To assess the effect of subsampling on the ability to detect long-term trends in ALTM lakes, a repeated-measures mixed-effects model was used. A bootstrap routine of 50 iterations was used to simulate subsampling 90, 80, 60, 40, 20, and 10 percent of lakes, as well as a model for 100 percent of effort as of December 2010. When randomly selecting lakes for simulated scenarios, lakes were stratified by ANC class to ensure that models included a representative sample. The ANC (µeq $L^{-1}$) categories used here were <0 ANC (seven lakes), 0-50 ANC (27 lakes), and >50 ANC (14 lakes). The ANC value of each lake was based on the average of the most recent three years of sampling (2008-2010). The total number of lakes in the analysis was 48, as limed lakes were not included. Also represented are subsampling scenarios where sampling is reduced by systematically eliminating months within years, rather than lakes. These subsampling scenarios are list below, and can also be found in Table 3.

- 67%: March-October
- 58%: March-September
- 50%: Even months

- 50%: Odd months
- 42%: March, April, June, September, October
- 33%: March, April, September, October
- 33%: Once per season (January, April, July, October)
- 33%: Once per season (February, May, August, November)
- 33%: Once per season (March, June, September, December)
- 8%: Each month

### *3.2.2 Results: Mixed Model Analysis*

The average standard error of the model and the standard deviation of the 50 iterations for the average concentrations of $SO_4$ and $NO_3$ are shown in figures 3.2-3.3. The subsampling scenarios, the difference in the LSM model estimate and SE of reduced models compared to the full model are described in Table 3.2.

The results of the mixed model analysis indicate that reducing sampling within years is likely to provide more useful data than reducing the number of lakes sampled. Estimates with either sampling scheme were comparable, but the error in the estimates is much lower when subsampling months. This is to be expected, because the variation among lakes is much larger than the variation among months over the sampling period (1992-2010).

Sampling only one month per year would be similar to the TIME analysis. These model simulations had low LSM standard errors due to the low variation in concentrations between months relative to the variation observed between lakes. It is important to note though, that sampling one month per year does not provide an estimate of seasonal differences.

Sampling seasonally (once every three months and in April) rather than every month might be an optimal strategy. This reduces sampling effort to 33 percent of current effort, but long-term average estimates are similar to that of the 100 percent sampling estimate, and there is little variation between the average estimates of the three possible sampling schemes tested.

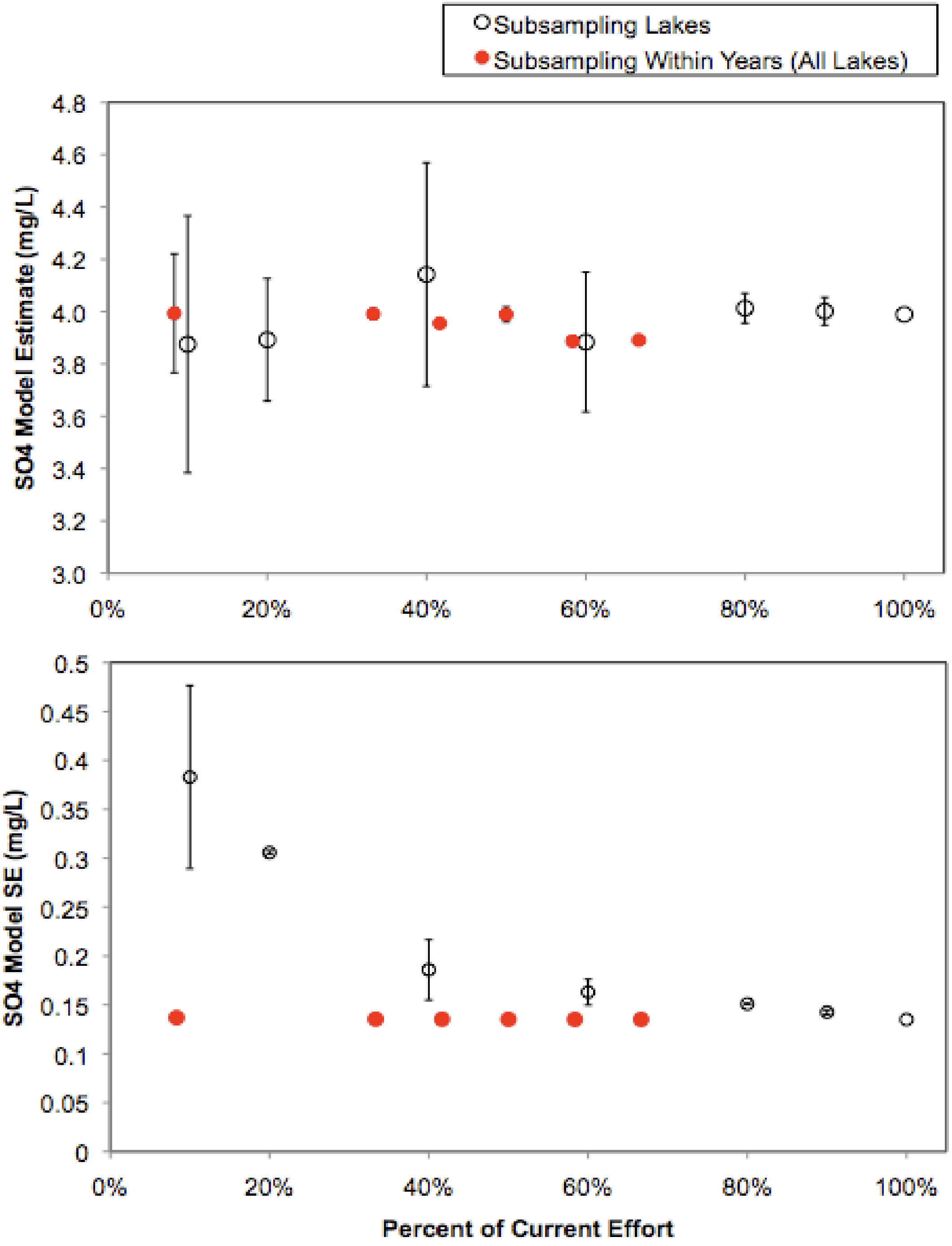


Figure 3.2. Model estimate and model standard error of long-term average concentrations of $SO_4$ (mg $L^{-1}$) based on a repeated-measures mixed-effects model using 50 random iterations for each simulated subsample size. Open symbols show models that reduced the number of lakes sampled, and red symbols show models that reduced the number of months sampled per year for all lakes.

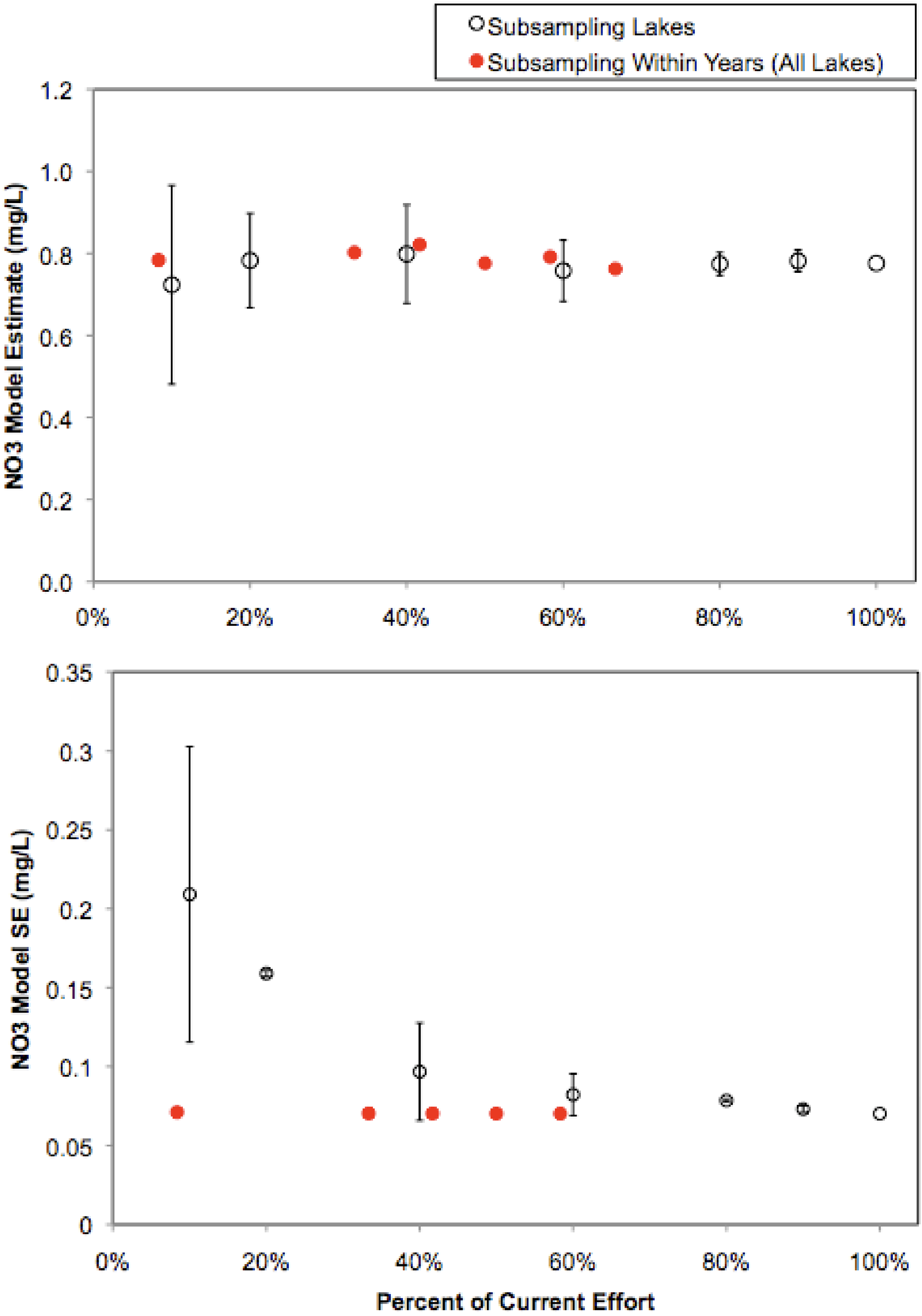


Figure 3.3. Model estimate and model standard error of long-term average concentrations of $NO_3$ (mg $L^{-1}$) based on a repeated-measures mixed-effects model using 50 random iterations for each simulated subsample size. Open symbols show models that reduced the number of lakes sampled, and red symbols show models that reduced the number of months sampled per year for all lakes.

Table 3.2. Subsampling scenarios of ALTM lakes and ratios of model SE and model estimates of $SO_4$ (mg/L) relative to the full model. For the simulated sampling schemes at 50%, 33% and 8% effort, the values listed below are the average of two, four, and 12 scenarios, respectively.

| | **Percent of Current Effort** | **Simulated Sampling Scheme** | **Ratio of reduced model SE to full model SE** | | **Ratio of reduced model estimate to full model estimate** | |
|---|---|---|---|---|---|---|
| Subsampling Lakes | | | $SO_4$ | $NO_3$ | $SO_4$ | $NO_3$ |
| | 90% | 43 lakes | 1.23 | 1.46 | 1.31 | 1.60 |
| | 80% | 38 lakes | 1.30 | 1.57 | 1.31 | 1.58 |
| | 60% | 29 lakes | 1.41 | 1.64 | 1.27 | 1.55 |
| | 40% | 19 lakes | 1.60 | 1.93 | 1.35 | 1.63 |
| | 20% | 10 lakes | 2.64 | 3.18 | 1.27 | 1.60 |
| | 10% | 5 lakes | 3.30 | 4.18 | 1.27 | 1.48 |
| Subsampling Months | 67% | Mar-Oct | 1.00 | 1.00 | 0.98 | 0.96 |
| | 58% | Mar-Sept | 1.00 | 1.00 | 0.99 | 0.99 |
| | 50% | Every other month | 1.01 | 1.01 | 1.00 | 1.00 |
| | 42% | March, April, June, September, October | 1.01 | 1.01 | 1.00 | 1.00 |
| | 33% | Four months per year | 1.00 | 1.01 | 1.00 | 1.05 |
| | 8% | One month per year | 1.01 | 1.01 | 1.00 | 1.01 |

### *3.2.3 Trends in ALTM Lake Chemistry by Month*

The argument for seasonal sampling is although lake chemistry differs by season it is relatively constant within each season. The variation over the sample period was used to assess which months have similar trends. A repeated-measures analysis of variance (ANOVA) was conducted comparing the concentrations over time among months for the 48 ALTM lakes that do not have a recent history of being limed. This was dibe for concentrations of $SO_4$, $NO_3$, and $Ca^{2+}$, $H^+$, and ANC. A Tukey range test was used to determine significant differences between months ($p<0.05$).

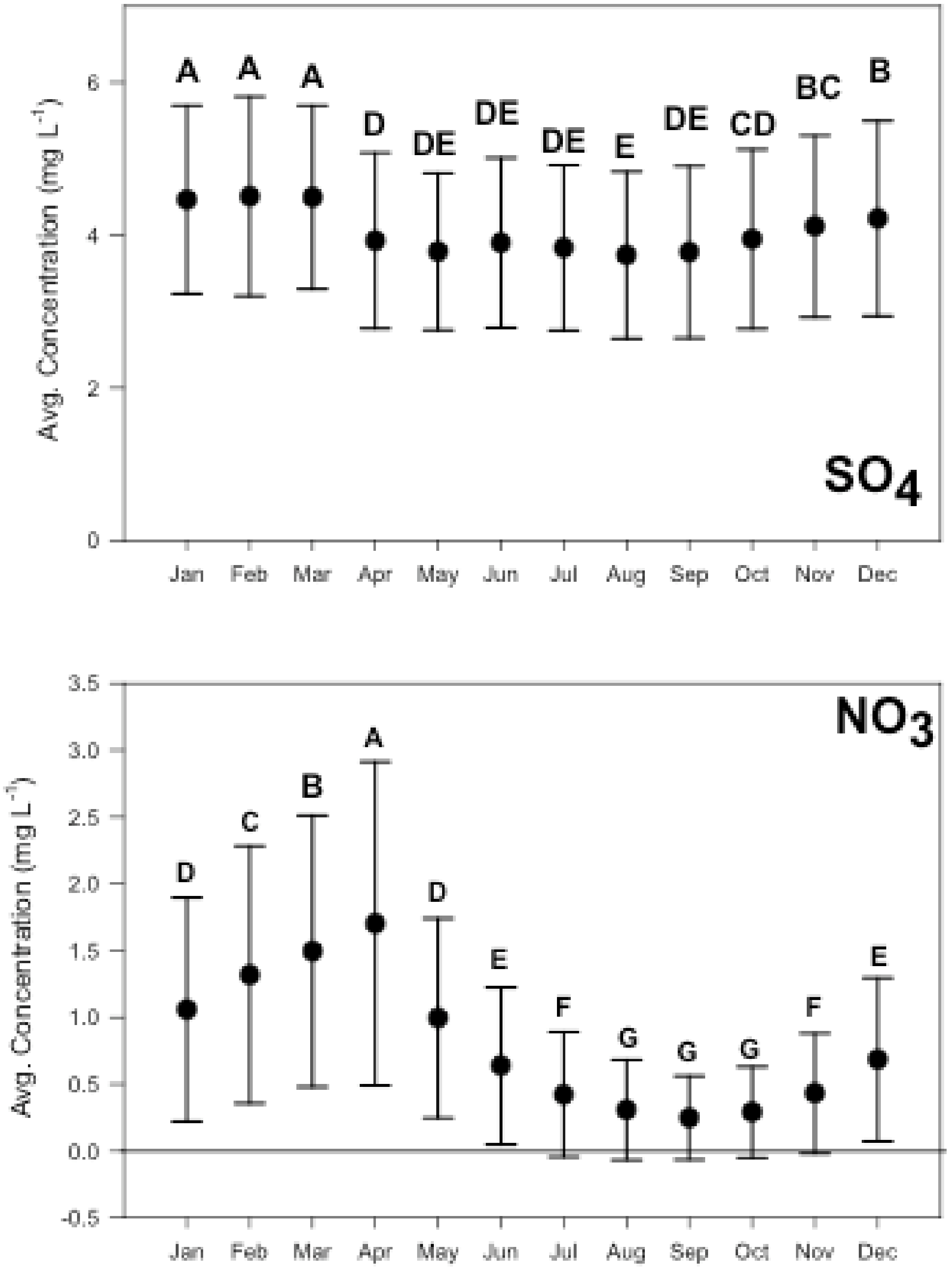


Figure 3.4a. Average monthly concentrations of $SO_4$ and $NO_3$. Letters indicate Tukey significance levels. Means that do not share a letter are significantly different.

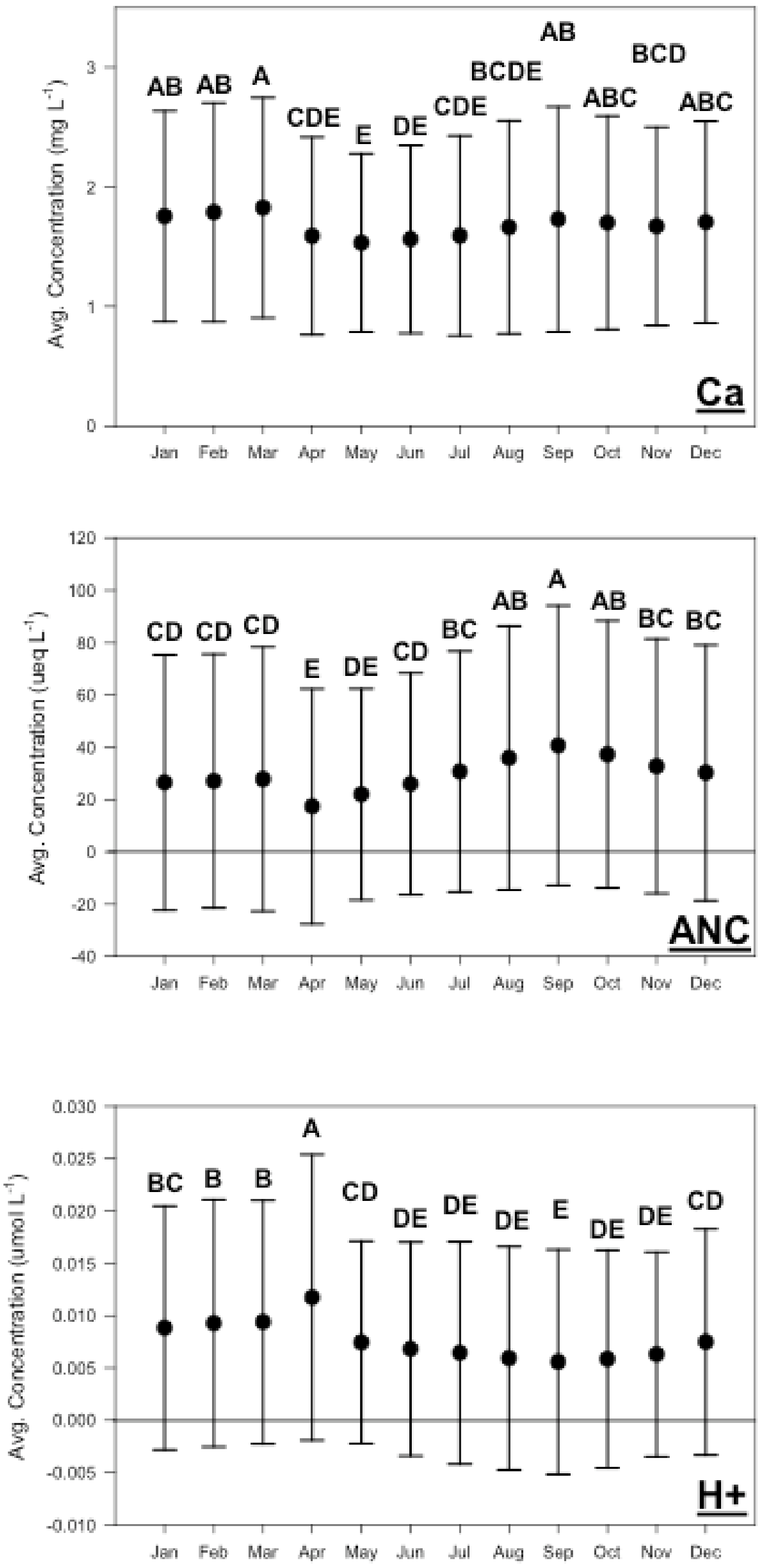


Figure 3.4b. Average monthly concentrations of Ca, $H^+$, and ANC. Letters indicate Tukey significance levels. Means that do not share a letter are significantly different.

Table 3.3. The numbers in this table indicate whether months are not statistically distinguishable for the five repeated-measures ANOVAs for concentrations of $SO_4$, $NO_3$, Ca, ANC, and $H^+$. White cells indicate whether months were similar for 0 or 1 of the 5 total tests, yellow cells indicate when months were similar for 2 or 3 tests, and pink cells indicate when months were similar for 4 or all 5 of the 5 solutes tested.

| | **Jan** | **Feb** | **Mar** | **Apr** | **May** | **Jun** | **Jul** | **Aug** | **Sep** | **Oct** | **Nov** | **Dec** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Jan** | | 4 | 4 | | 3 | 1 | 1 | 1 | 1 | 1 | 2 | 3 |
| **Feb** | | | 4 | | 1 | 1 | 1 | 1 | 1 | 1 | 2 | 2 |
| **Mar** | | | | | 1 | 1 | 1 | | 1 | 1 | 1 | 2 |
| **Apr** | | | | | 3 | 2 | 2 | 1 | 1 | 2 | 1 | 1 |
| **May** | | | | | | 3 | 2 | 2 | 1 | 1 | | |
| **Jun** | | | | | | | 4 | 3 | 2 | 2 | 3 | 3 |
| **Jul** | | | | | | | | 4 | 2 | 3 | 4 | 3 |
| **Aug** | | | | | | | | | 5 | 4 | 3 | 3 |
| **Sep** | | | | | | | | | | 5 | 2 | 1 |
| **Oct** | | | | | | | | | | | 4 | 3 |
| **Nov** | | | | | | | | | | | | 4 |
| **Dec** | | | | | | | | | | | | |

### *3.2.4 Results: ALTM Lake Chemistry by Month*

Average monthly concentrations of $SO_4$ and $NO_3$ are shown in Figure 3.4a and Ca, $H^+$ and ANC are shown in Figure 3.4b. Letters indicate Tukey significance levels. Means that do not share a letter are significantly different. These figures show the average monthly concentration across all lakes and years for each month. As a result, the time series is not reflected in the figures, but it was incorporated as a repeated factor in the ANOVA and is reflected in the Tukey significance levels. Though there is variation in long-term trends among lakes, for the purpose of this analysis, the combined data from all 48 unlimed lakes was used.

All solutes showed seasonal trends and had significant differences between months. Sulfate concentrations peak in January-March, and are lowest in May-September. Nitrate concentrations show a clear peak during spring snowmelt in April, and are lowest in August-October. Calcium concentrations are lowest in May, then increase throughout the rest of the year, reaching their peak in March. ANC is lowest in April, during spring snowmelt, and reaches its peak in September. Conversely, concentrations of hydrogen ions are lowest in September and reach their peak in April.

In order to assess which months were most similar across the solutes tested, a table displaying the number of times that a month was not significantly different from all others for the six analytes tested (Table 3.3) was used. Based on this assessment, for most solutes it appears that some months may be considered redundant, while other months appear to be unique. January, February, and March are highly similar. Only concentrations of $H^+$ were different between months. June, July, and August are generally quite similar to one another, as are September-October, and November-December. April appears to be the most unique month in the year, which is likely due to spring snowmelt. Based on this assessment, it seems that sampling a subset of lakes each month would be reasonable, and that sampling all lakes in April would add additional information on snowmelt trends. Capturing changes in snowmelt trends may also be important for future climate change research.

### *3.2.5 Effect of Subsampling Regimes on Long-Term Estimates of Concentration and Trend Detection*

To assess the differences in concentrations between a variety of sampling schemes, each of nine sampling schemes were compare over the sampled time period (1992-2010) using a one-way ANOVA (Figures 3.4a and 3.4b; sampling schemes are listed in Table 3.2, with the exception of the eight percent of sampling for individual months). The categorical variable was the sampling scheme and the sample set was the 48 ALTM lakes. The response variables included concentrations of $SO_4$, $NO_3$, $Ca^{2+}$, ANC, and $H^+$. This allowed us to compare the average estimate for each sampling scheme over the entire record. In addition, the Mann Kendall tau for each sampling scheme over the entire record (Figure 3.5a and 3.5b) was compared using a similar approach. Note that in this case, a Mann Kendall was used rather than a Seasonal Mann

Kendall test for the sampling for all months (the current sampling scheme) in order to be consistent with the other values to which the test was being compared.

In order to assess the effect that subsampling had on detecting trends over time, the number of lakes that showed significant trends for each subsampling scheme was also compared (Table 3.4). In this case, a Seasonal Mann Kendall test was used for the full sampling scheme (once per month), but used a Mann Kendall test for all subsampling schemes.

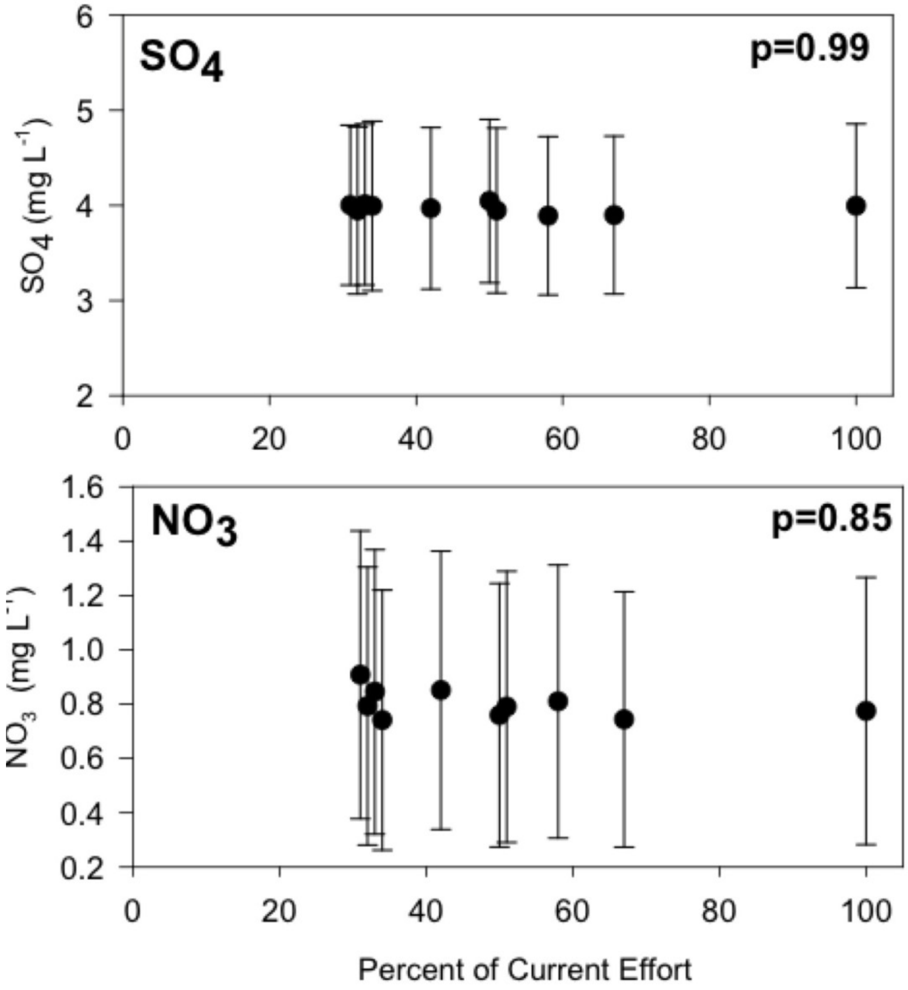


Figure 3.4a. Comparison of estimates of average concentration across lakes over the time period sampled (1992-2010). P-values of a one-way ANOVA are shown.

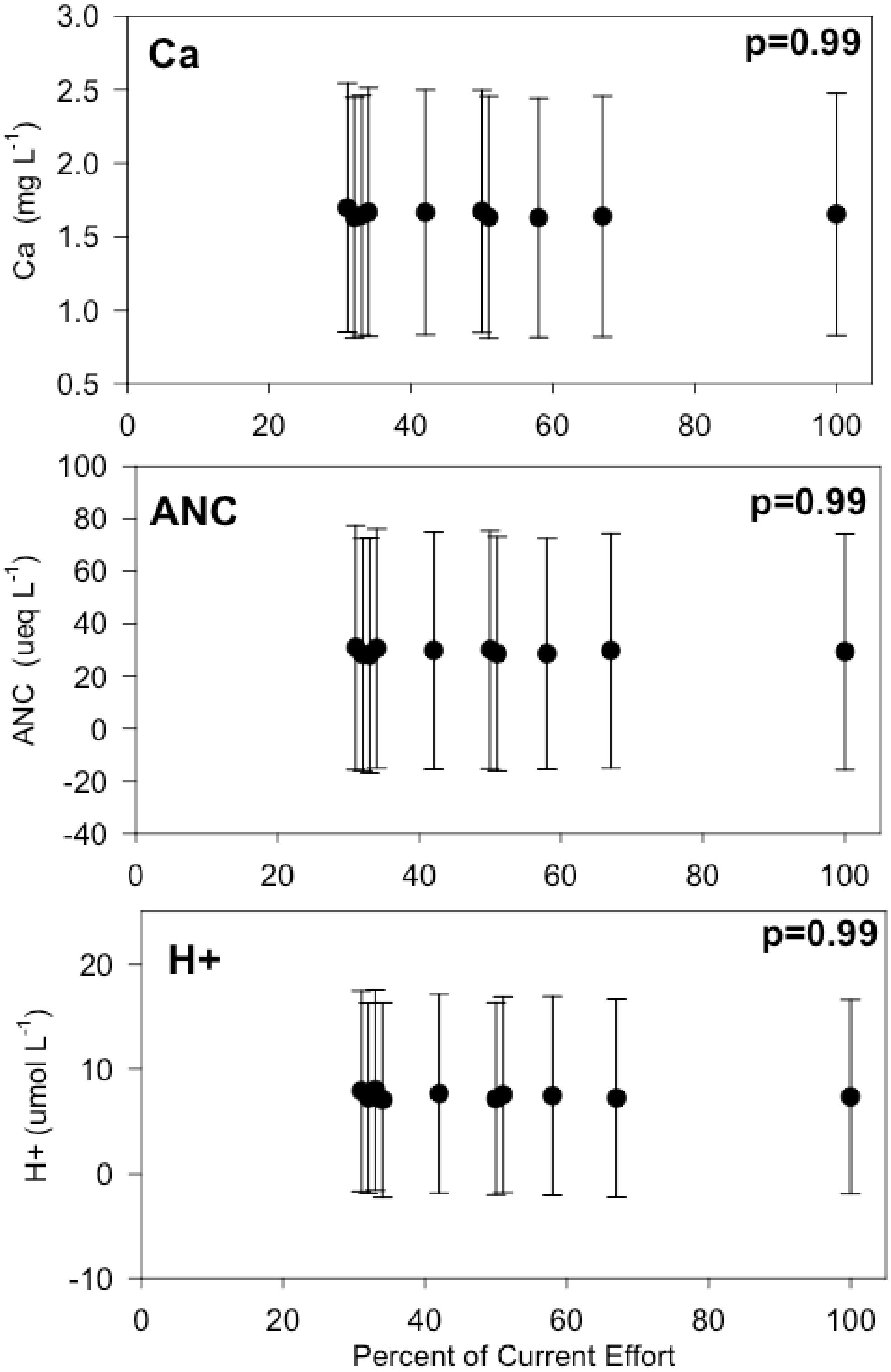


Figure 3.4b. Comparison of estimates of average concentration across lakes over the time period sampled (1992-2010). P-values of a one-way ANOVA are shown.

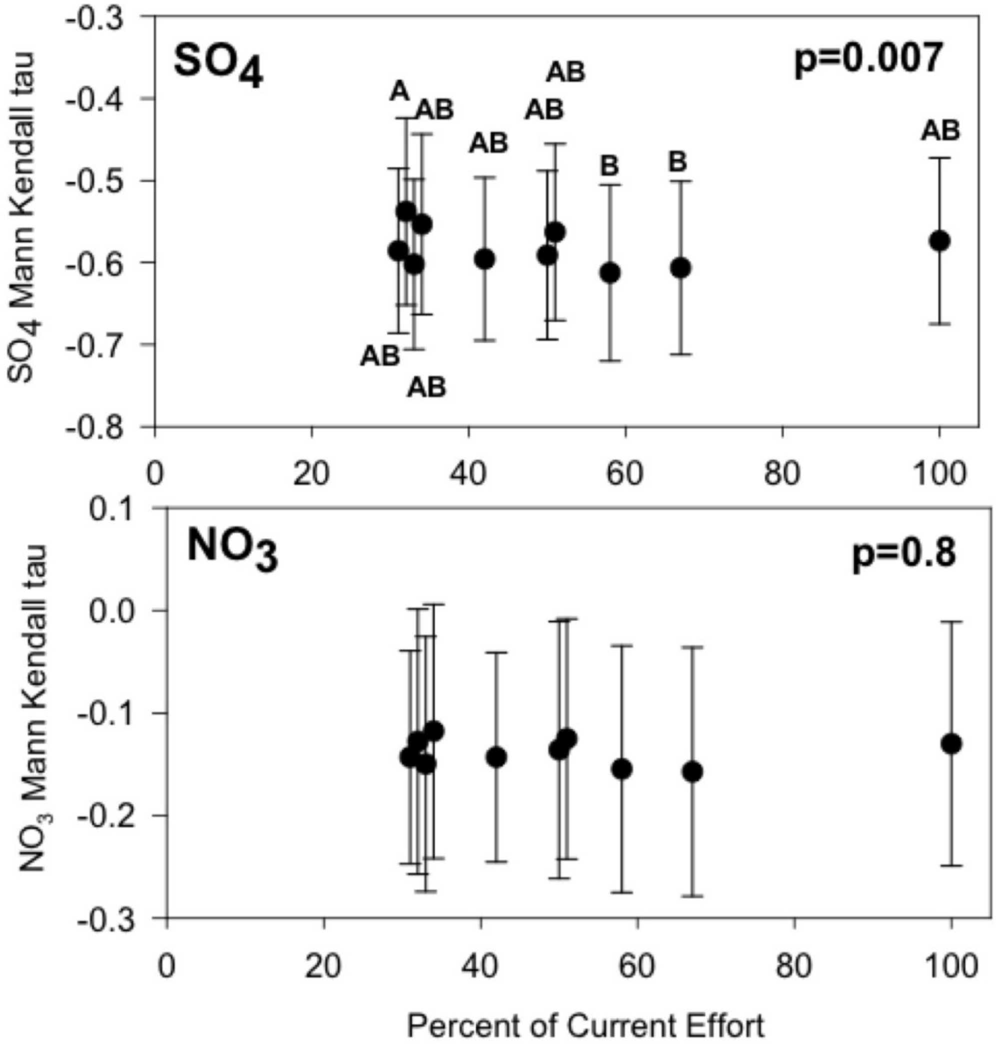


Figure 3.5a. Comparison of Mann Kendall tau values across lakes over the time period sampled (1992-2010). P-values of a one-way ANOVA are shown.

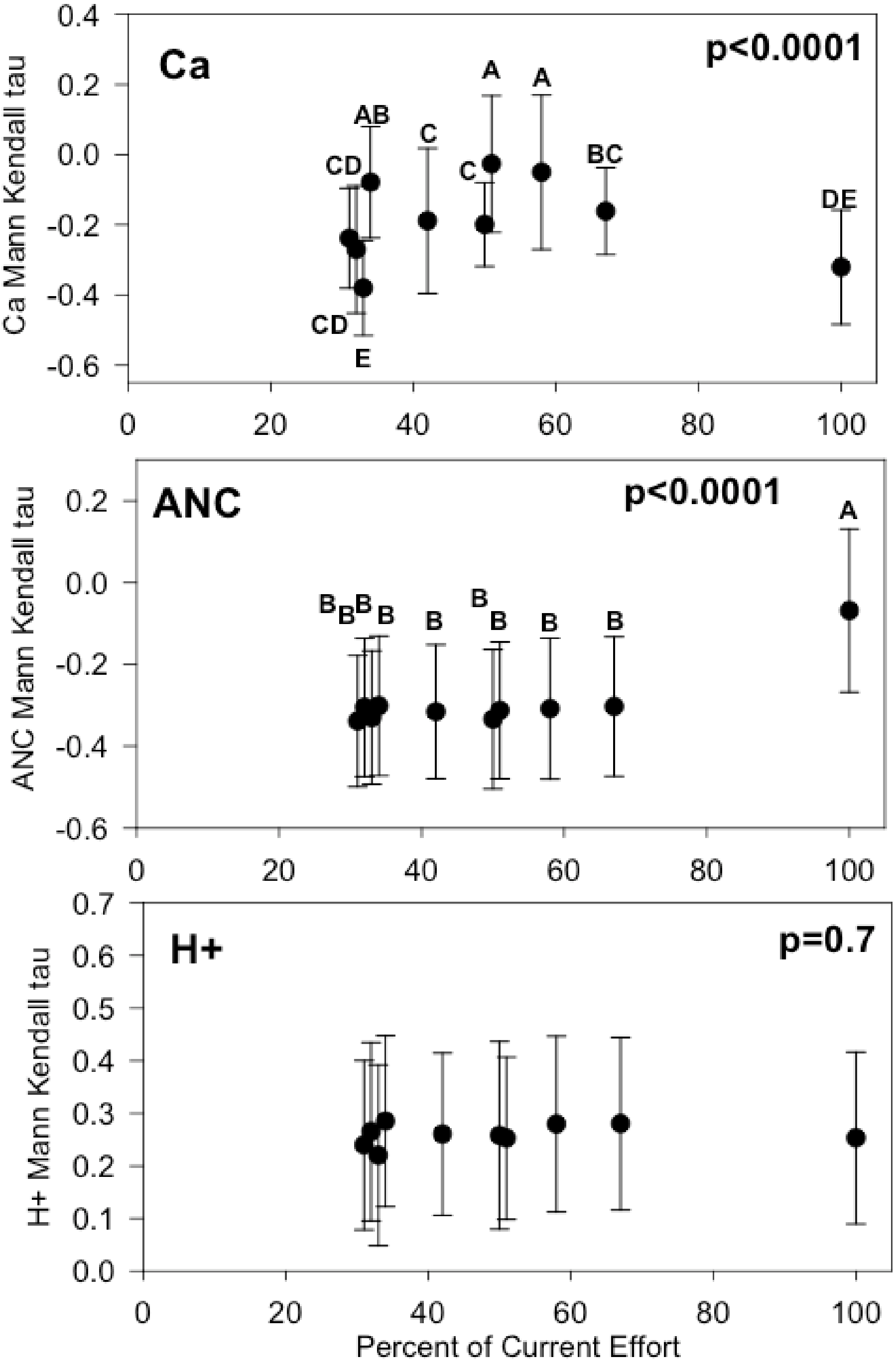


Figure 3.5b. Comparison of Mann Kendall tau values across lakes over the time period sampled (1992-2010). P-values of a one-way ANOVA are shown.

Table 3.4. Number of lakes showing significant trends over time in Mann Kendall tests. *This test was a Seasonal Mann Kendall test rather than a Mann Kendall test.

| | | **Number of Lakes Showing Significant Trends Over Time** | | | | | |
|---|---|---|---|---|---|---|---|
| **Percent of Current Sampling Effort** | **Sampling Scheme** | **$SO_4$** | **$NO_3$** | **$Ca^{2+}$** | **ANC** | **$H^+$** | **SUM** |
| 100 | All months* | 48 | 42 | 45 | 43 | 36 | 240 |
| 67 | Mar-Oct | 48 | 15 | 36 | 27 | 15 | 141 |
| 58 | Mar-Sept | 48 | 14 | 33 | 25 | 17 | 137 |
| 50 | Even months | 48 | 9 | 34 | 23 | 11 | 125 |
| 50 | Odd months | 48 | 9 | 36 | 25 | 13 | 131 |
| 42 | Mar-Apr, June, Sept-Oct | 47 | 6 | 31 | 22 | 9 | 115 |
| 33 | Seasonal (Feb, May, Aug, Nov) | 46 | 6 | 27 | 18 | 10 | 107 |
| 33 | Seasonal (Jan, Apr, July, Oct) | 48 | 6 | 29 | 15 | 7 | 105 |
| 33 | Seasonal (Mar, Jun, Sept, Dec) | 46 | 5 | 29 | 22 | 9 | 111 |
| 33 | Mar, Apr, Sept, Oct | 47 | 5 | 31 | 17 | 6 | 106 |

### *3.2.6 Results: Effect of Subsampling Regimes on Long-Term Estimates of Concentration and Trend Detection*

Average concentration estimates of the 48 unlimed ALTM lakes over the sampled time period were not significantly different for any solute or sampling scheme. Thus, it appears that the alternate sampling schemes would all provide similar estimates of average concentration in a long-term monitoring program (Section 3.2.4).

Significant differences between predicted Mann Kendall tau values and sampling schemes for several of the solutes (Section 3.2.5) were not found. For $SO_4$, the tau value was significantly different between some sampling schemes, but none of these were significantly different from the current sampling scheme. For ANC, the current sampling scheme was significantly different from all subsampling schemes, which may be a result of monthly variability not captured when months are removed. The tau for Ca for the current sampling regime was different for six of nine sampling schemes. Trends in concentrations of $NO_3$ and $H^+$ were not significantly different between sampling schemes.

In general, it appears that reducing sampling within years does decrease the ability to detect significant trends using a Mann Kendall test. For all solutes tested, as the percent of the current effort was reduced, the number of lakes with significant long-term trends detected also decreased. This general trend is reflected in the "Sum" column, and holds mostly true for each solute. A seasonal sampling scheme on average had the following effects:

- $SO_4$: 97 percent of lakes with significant trends vs. full sampling scheme
- $NO_3$: 35 percent of lakes with significant trends vs. full sampling scheme
- $Ca^{2+}$: 71 percent of lakes with significant trends vs. full sampling scheme
- ANC: 70 percent of lakes with significant trends vs. full sampling scheme
- $H^+$: 48 percent of lakes with significant trends vs. full sampling scheme

### 3.3 Findings and Conclusions

- The ALTM and TIME data sets have contributed a great deal to our understanding of lake chemistry trends in the Adirondacks through a wide range of publications and collaboration. These long-term records present important data that provide the ability to assess trends into the future and should continue to be supported.
- The AEAP provides the only long-term biological monitoring data set assessing the impacts of acidification and recovery on phytoplankton, rotifers, and crustaceans. These data compliment the ALTM lake chemistry data set. This data set is currently underutilized and has not been used in any comprehensive assessments of long-term trends or biological recovery of lakes in New York. Evaluation and publication of these

data could aid in understanding how acidification and recovery affects planktonic communities, informing the value of this long-term data set.

- Not all possible future scenarios could be included in this assessment, but may be used in future analysis. For example, these analyses did not investigate the effect of adding additional lakes to current monitoring programs. The importance of monitoring limed lakes over time was not investigated. When subsampling lakes, the subsample was based on ANC category, but any other number of categories could be used (lake classification, watershed characteristics, etc.) An additional possible future analysis might include investigating what could be gained from re-sampling the 1,469 lakes included in the original ALS in 1984-1987 in one year, which could be a very valuable re-sampling survey due to the changes in deposition since the 1980s. This type of broad survey would complement the in-depth investigation of trends in the subset of 52 lakes that have been monitored over time.

*Mixed model analysis of $SO_4$ and $NO_3$:*

- It appears that reducing the number of ALTM lakes sampled would add a greater amount of error to an overall model of lake concentrations than reducing sampling within years.
- The mean estimate of concentration did not differ greatly when reduced sampling was simulated, though the standard deviation of the iterations increased as sites were removed. Thus, if reduction of lakes is considered in the future, it may be advisable to simulate the proposed scheme to identify where exactly the mean estimate falls relative to the estimate based on the current sampling scheme.

*Assessing differences in trends between months:*

- April is the most distinctive month for the majority of solutes investigated. Solute concentrations in May could be similar to those in April, but capturing lake concentrations during spring snowmelt is important if monitoring seasonal trends are a priority of the ALTM program.
- Several months show similar average concentrations across the long-term record, for example:
    - January, February, and March are highly similar
    - June, July, and August are highly similar
    - September and October are similar
    - November and December are similar

*Assessing potential subsampling schemes:*

- Based on the similarity between months as described by a repeated measures ANOVA, it seems that seasonal sampling with additional sampling during April may be a viable option.
- Estimates of average lake chemistry will not likely be different if lakes are sampled less frequently than monthly. This was demonstrated with a variety of hypothetical sampling efforts that ranged from 33-67 percent of current sampling effort.
- Though modeled least squares means estimates of average solute concentration may not change with reduced sampling, it was found that the number of lakes exhibiting significant long-term trends decreases if sampling is reduced within years. However, note that in actuality, reducing sample size in the ALTM program would not likely have as drastic of an effect shown in these models. This is because the models simulated reduced

sampling for the entire record, whereas future sampling would still contain the entire record of monthly data for the period from 1992-present. Models would likely have a greater ability to detect change than indicated in this analysis, where sampling was reduced over the entire record.

# 4. Stream chemistry monitoring

## 4.1 Status

Stream monitoring in New York has been done at several scales. At the statewide level, the DEC administers the Rotating Integrated Basin Study (RIBS), which monitors a rotating set of streams each year. The USGS is responsible for stream monitoring in the Catskill region, in which four streams are currently gauged and regularly monitored for a range of solutes, including pH, ANC, base cations, Al, P, N, and C (McHale and Siemion 2010). Additionally, some one-time surveys of stream chemistry have been completed, and these could be re-sampled in the future to allow for paired comparisons over time. Stream monitoring has generally focused on assessing the effects of acidic deposition on stream chemistry, but there is also a growing interest in monitoring N loads to the Chesapeake Bay.

With regard to long-term stream chemistry monitoring, note that the scale and expense of monitoring trends in stream concentration and trends in stream export are quite different. Monitoring stream export of nutrients requires a gauged stream where water flow is continuously recorded. These gauges must be visited regularly and properly maintained to remain functional. Continuous flow measurements are not necessary when monitoring water chemistry trends, requiring much less effort than monitoring stream export.

Areas such as the Catskills and Adirondacks, where losses to deep bedrock seepage are minimal relative to stream export channel, allow for monitoring of hydrologic export measured by the USGS in the Neversink and Rondout watersheds. Other parts of the state that lack this underlying bedrock may not be conducive to monitoring hydrologic exports, but monitoring stream chemistry regularly is still feasible.

### *4.1.1 Statewide Stream Monitoring*

The RIBS monitoring program is organized following the state's 17 major drainage basins, which are measured once every five years on a rotating schedule (Figure 4.1). The network also has 19 permanent sites that are measured six times per year between May and October. This program gives very good coverage of major waterways and generally covers the state evenly. The goals of the RIBS program include measuring water concentrations for long-term trends, focusing on characterizing background conditions of streams, and setting baseline conditions for measuring the effectiveness of restoration or protection activities or the recovery after changing pollution legislation. This makes the program quite useful for assessing effects of changes in policy on streams and rivers throughout the state, but note that the RIBS program is geared more towards evaluating changes in nutrient status of rivers and streams rather than acidification parameters.

Figure 4.1. Distribution of RIBS sampling sites in New York (Map courtesy of Alexander Smith, DEC).

### *4.1.2 Intensive Site-Specific Stream Monitoring*

USGS in Catskills:

Long-term monitoring of stream flow and chemistry in the Catskills is currently administrated by the USGS and funded by EPA. Stream sampling was significantly reduced in 2010. Originally, the sampling design included upper and lower nodes of 7 streams, and four sampling sites that were not paired (16 sites total). Records for several streams extend back to 1991, with the Biscuit Brook record going back to 1984. In 2010, sampling was reduced to four streams (Biscuit Brook, Rondout Creek, Main Branch Neversink, and Winnesook) which are monitored for continuous flow and ~38 chemistry samples per year (biweekly and event sampling). These streams were selected to represent the most sensitive region of the Catskills.

*Stream monitoring in the Adirondacks*:

Long-term stream monitoring is limited to a small number of streams in the Adirondack region. The ALSC monitors three streams in the Adirondacks: Buck Creek (at three points: one chronically acidic branch, one branch with higher ANC, and the Buck Creek main branch), Bald Mountain Brook, and Fly Pond Outlet. The Arbutus Lake inlet at Huntington Forest is also gauged and is monitored by SUNY-ESF. Sampling of Adirondack streams by the RIBS program is also very limited (Figure 4.1). Lake data have generally served to represent surface waters in the Adirondacks, though it is known that lakes and streams respond quite differently to acidic deposition. Streams are often more sensitive to acidification than lakes because stream inputs are mainly from shallow flow paths with little buffering capacity (Lawrence et al. 2008).

A large-scale survey of Adirondack streams, the Western Adirondack Stream Survey (WASS) was conducted in 2003-2005 (Lawrence et al. 2008). A random sample of 200 streams out of a possible 565 that fit the inclusion criteria were sampled within a three-day period. Sampling surveys were conducted twice during spring snowmelt, twice during summer base flows, and once during fall storms. Buck Creek was used as an index stream to contextualize variation throughout the year. The WASS represented about 20 percent of the Adirondack Park. The other 80 percent of the park was characterized in the East-Central Adirondack Stream Survey (ECASS), which took place in 2010-2011. The ECASS survey was conducted once during each of the following: spring snowmelt, summer base flow, and a fall storm.

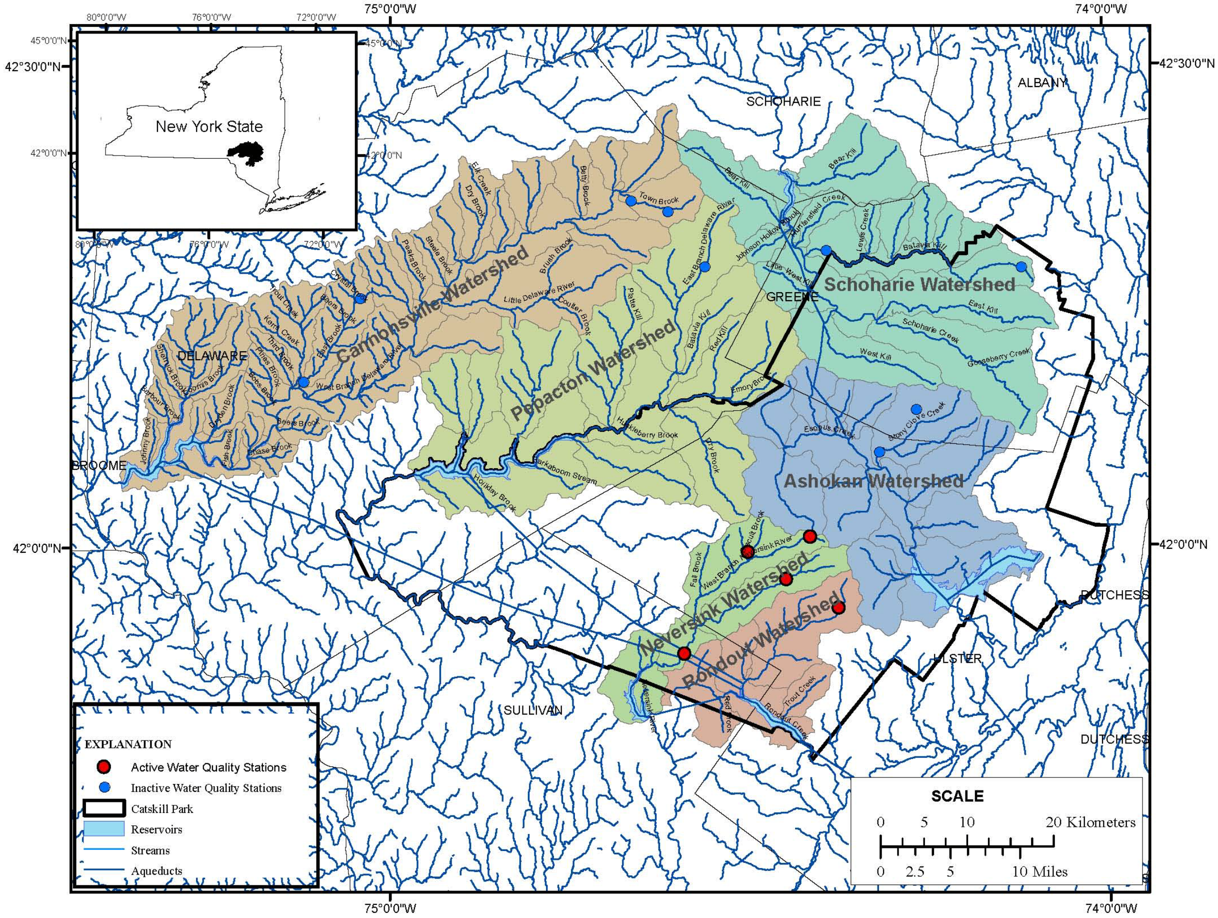


Figure 4.2. Long-term stream monitoring sites administered by the USGS in the Catskills. Monitoring at gauges marked in blue was discontinued in 2010. Gauges currently monitored (as of January 2012) are marked in red. Base map courtesy of USGS.

## 4.2 Analyses

### *4.2.1 USGS monitoring in the Catskills*

Prior to 2010, the USGS intensively monitored 16 streams in the Catskills region. In 2010, 12 of these sites were discontinued (Figure 4.2). The four remaining streams are Biscuit Brook, Neversink (Claryville), Neversink (Winnisook), and Roundout Creek. These streams are located in the Neversink and Rondout watersheds, which are the most cation-depleted and have the lowest ANC in the Catskill region. These streams were selected to represent the most sensitive region of the Catskills. Using a repeated measures ANOVA at 16 original sites, it was determined that these four sites were significantly lower than the other 12 sites in $SO_4$

($p<0.0001$), $NO_3$ ($p<0.0001$), $NH_4$ ($p<0.0001$), and total N ($p<0.0001$) concentrations over the course of the long-term record.

### *4.2.2 Detectable Differences Derived from the WASS Survey*

*Periodic stream surveys*:

Data from the 2005 spring sampling date in the WASS survey were used to assess the detectable difference for a variety of sampling intensities. The detectable difference of pH, ANC (ueq $L^{-1}$), and concentrations of $SO_4$, $NO_{3,}$ $Ca^{2+}$, and dissolved organic carbon (DOC) (umol $L^{-1}$) were investigated. There were 192 streams included in the WASS survey. These were divided into four ANC categories for this analysis: ANC <0 (57 streams), ANC of 0-50 (78 streams), ANC of 50-200 (40 streams and ANC >200 (17 streams). These are ANC categories that are typically used in studies of Adirondack surface waters (Driscoll et al. 2003). Detectable differences were derived using both a paired power analysis and a two-sample power analysis with 0.8 power for sample sizes representing 10, 25, 50, and 100 percent of the sampling effort in the 2005 survey for paired and unpaired samples, and 200 percent, and 300 percent for unpaired sample sizes. The values included in these figures are listed in Table 4.1.

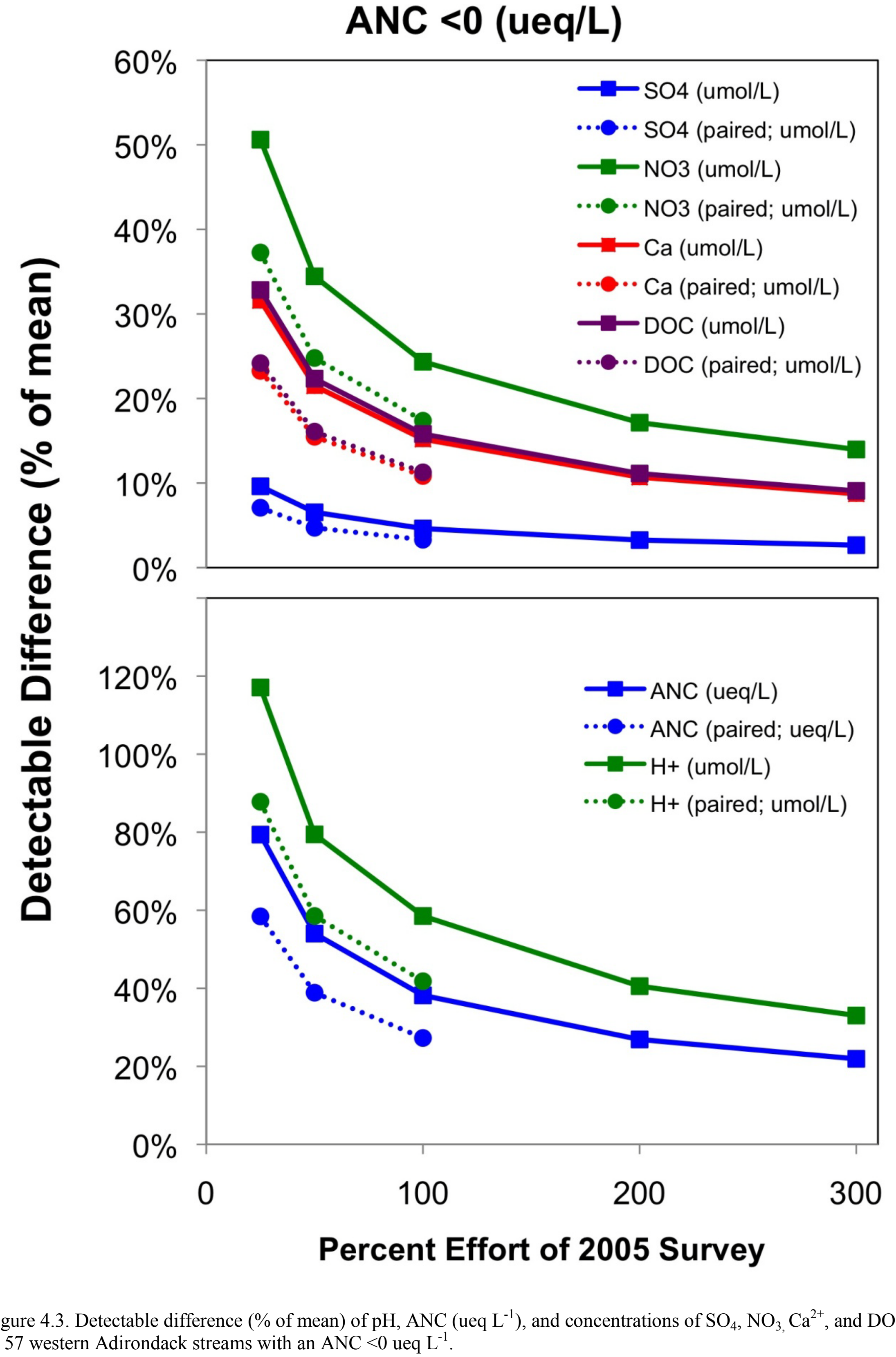


Figure 4.3. Detectable difference (% of mean) of pH, ANC (ueq $L^{-1}$), and concentrations of $SO_4$, $NO_3$, $Ca^{2+}$, and DOC (umol $L^{-1}$) in 57 western Adirondack streams with an ANC <0 ueq $L^{-1}$.

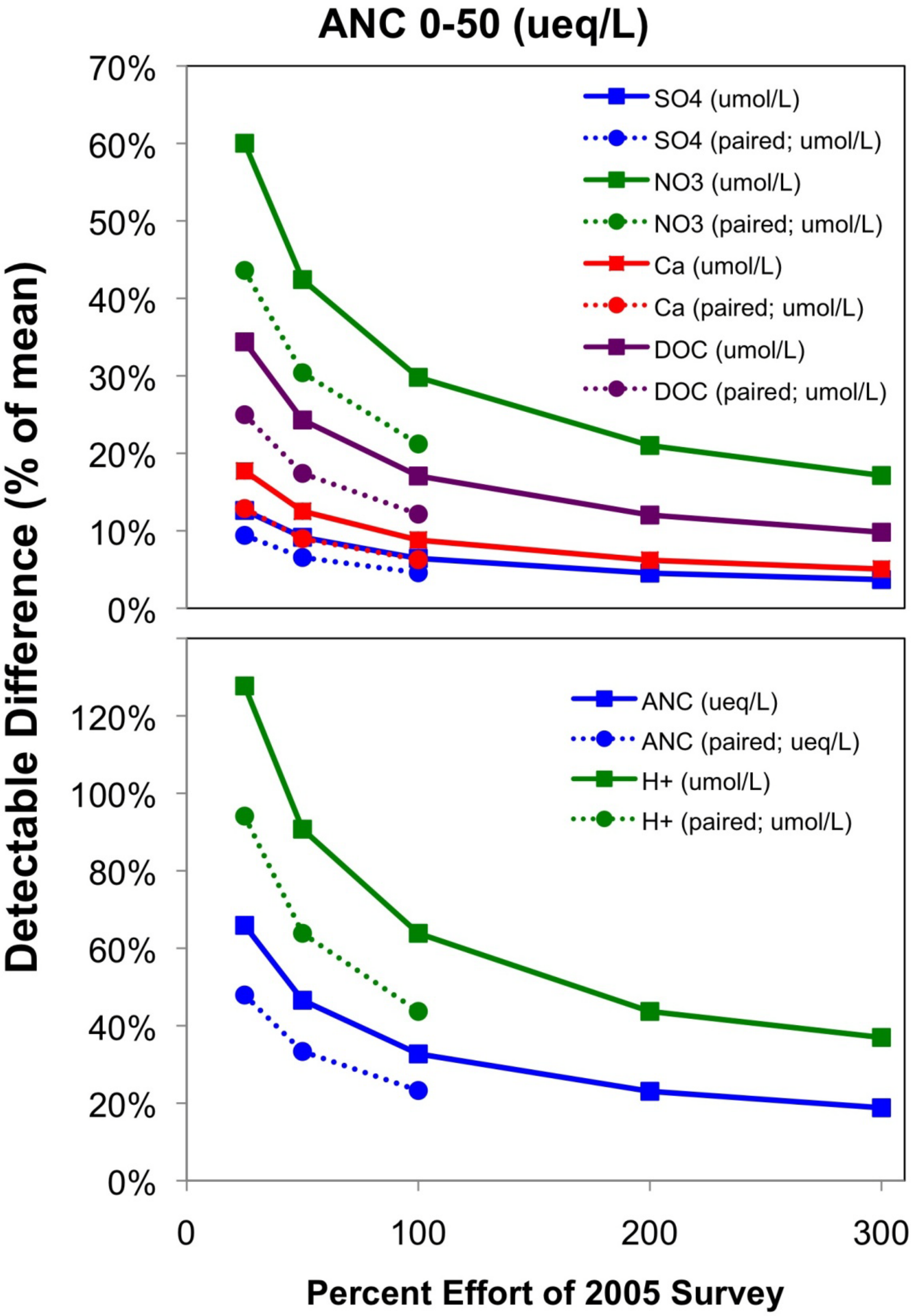


Figure 4.4. Detectable difference (% of mean) of pH, ANC (ueq $L^{-1}$), and concentrations of $SO_4$, $NO_3$, $Ca^{2+}$, and DOC (umol $L^{-1}$) in 78 western Adirondack streams with an ANC of 0-50 ueq $L^{-1}$.

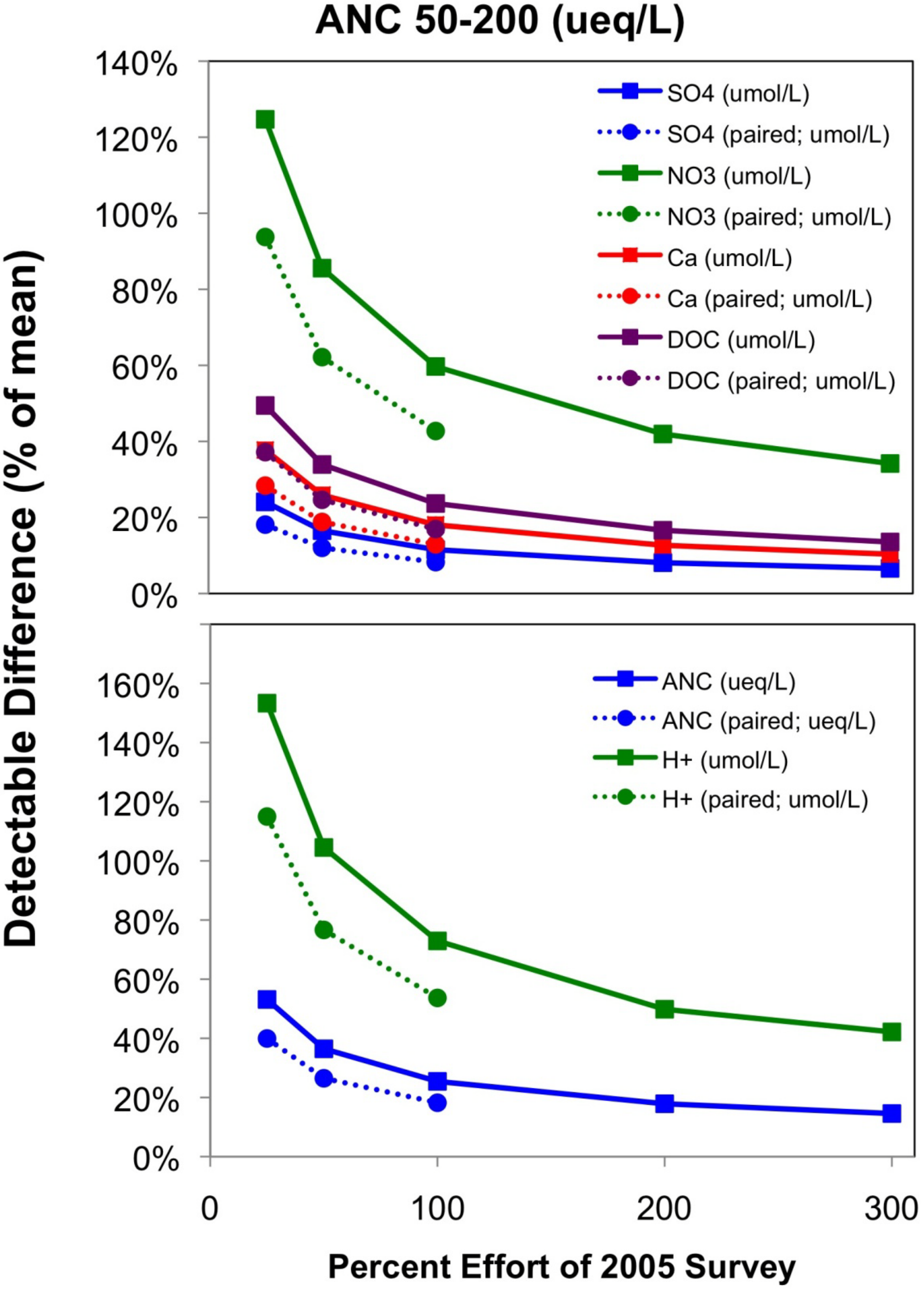


Figure 4.5. Detectable difference (% of mean) of pH, ANC (ueq $L^{-1}$), and concentrations of $SO_4$, $NO_3$, $Ca^{2+}$, and DOC (umol $L^{-1}$) in 40 western Adirondack streams with an ANC of 50-200 ueq $L^{-1}$.

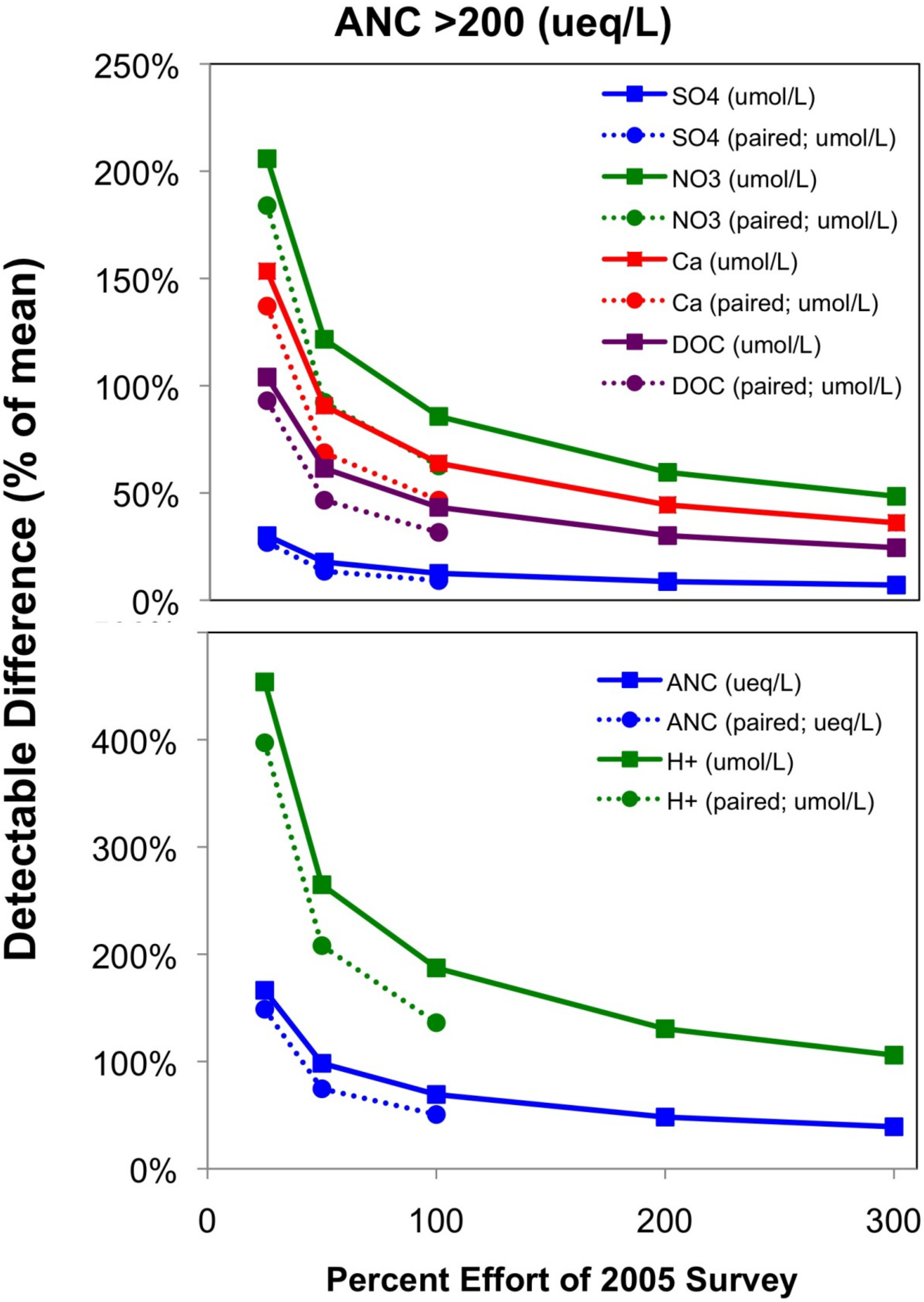


Figure 4.6. Detectable difference (% of mean) of pH, ANC (ueq $L^{-1}$), and concentrations of $SO_4$, $NO_3$, $Ca^{2+}$, and DOC (umol $L^{-1}$) in 17 western Adirondack streams with an ANC >200 ueq $L^{-1}$.

Table 4.1. Detectable change (%) in Adirondack stream chemistry based on data collected in the 2005 WASS Survey.

| | | | SO4 (umol/L) | | NO3 (umol/L) | | Ca (umol/L) | | DOC (umol/L) | | ANC (ueq/L) | | H+ (umol/L) | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **ANC Category** | ***n*** | **% Effort** | **unpaired** | **paired** | **unpaired** | **paired** | **unpaired** | **paired** | **unpaired** | **paired** | **unpaired** | **paired** | **unpaired** | **paired** |
| **ANC <0** | **57** | 25 | 10 | 7 | 51 | 37 | 32 | 23 | 33 | 24 | 79 | 58 | 117 | 88 |
| | | 50 | 7 | 5 | 34 | 25 | 21 | 15 | 22 | 16 | 54 | 39 | 79 | 59 |
| | | 100 | 5 | 3 | 24 | 17 | 15 | 11 | 16 | 11 | 38 | 27 | 59 | 42 |
| | | 200 | 3 | 2 | 17 | 12 | 11 | 8 | 11 | 8 | 27 | 19 | 41 | 29 |
| | | 300 | 3 | 2 | 14 | 10 | 9 | 6 | 9 | 6 | 22 | 16 | 33 | 23 |
| **ANC 0-50** | **78** | 25 | 13 | 9 | 60 | 44 | 18 | 13 | 34 | 25 | 66 | 48 | 128 | 94 |
| | | 50 | 9 | 7 | 42 | 30 | 13 | 9 | 24 | 17 | 47 | 33 | 91 | 64 |
| | | 100 | 6 | 5 | 30 | 21 | 9 | 6 | 17 | 12 | 33 | 23 | 64 | 44 |
| | | 200 | 5 | 3 | 21 | 15 | 6 | 4 | 12 | 9 | 23 | 16 | 44 | 32 |
| | | 300 | 4 | 3 | 17 | 12 | 5 | 4 | 10 | 7 | 19 | 13 | 37 | 26 |
| **ANC 50-200** | **40** | 25 | 24 | 18 | 125 | 94 | 38 | 28 | 49 | 37 | 53 | 40 | 153 | 115 |
| | | 50 | 17 | 12 | 86 | 62 | 26 | 19 | 34 | 25 | 36 | 26 | 105 | 77 |
| | | 100 | 12 | 8 | 60 | 43 | 18 | 13 | 24 | 17 | 25 | 18 | 73 | 54 |
| | | 200 | 8 | 6 | 42 | 30 | 13 | 9 | 17 | 12 | 18 | 13 | 50 | 36 |
| | | 300 | 7 | 5 | 34 | 24 | 10 | 7 | 14 | 10 | 15 | 10 | 42 | 30 |
| **ANC >200** | **17** | 25 | 30 | 27 | 206 | 184 | 153 | 137 | 104 | 93 | 166 | 149 | 454 | 397 |
| | | 50 | 18 | 13 | 122 | 92 | 91 | 69 | 61 | 47 | 98 | 75 | 265 | 208 |
| | | 100 | 13 | 9 | 86 | 63 | 64 | 47 | 43 | 32 | 69 | 51 | 187 | 136 |
| | | 200 | 9 | 6 | 60 | 43 | 44 | 32 | 30 | 22 | 48 | 35 | 130 | 95 |
| | | 300 | 7 | 5 | 48 | 35 | 36 | 26 | 24 | 17 | 39 | 28 | 106 | 76 |
| **Average detectable difference** | | 100 | 9 | 6 | 50 | 46 | 27 | 19 | 25 | 18 | 41 | 30 | 96 | 69 |

### *4.2.3 Results: Detectable Differences Derived from the WASS Survey*

The ability to detect differences with paired tests is always greater than with unpaired tests. Thus, maintaining the same sites for future surveys would enhance the opportunity to detect changes in stream chemistry. If all 192 sites were re-sampled, an average change of six percent in $SO_4$ (umol $L^{-1}$), 36 percent in $NO_3$ (umol $L^{-1}$), 19 percent in Ca (umol $L^{-1}$), 18 percent in DOC (umol $L^{-1}$), 30 percent in ANC (umol $L^{-1}$), and 69 percent in $H^+$ (umol $L^{-1}$; Table 4.1) could be detected.

In general, the detectable differences for all solutes were relatively high with regard to expected changes in stream chemistry in the future. A change of 30 percent of the means of all analytes in 2005 could be detected with the same number of samples as the original survey (Figures 4.3-4.6); it may be possible to see this magnitude of change in analytes such as $SO_4$ and $NO_3$, which have shown sharp downward trends over the past several years. With other analytes, such as $H^+$, a change large enough to detect may not be expected.

### *4.2.4 Maximizing Sampling Effort for Long-Term Stream Monitoring*

An alternative to reducing the number of sites sampled per year could be to monitor sites at longer intervals. The long-term record for Biscuit Brook was used as an example, which has been monitored continuously on a weekly basis since 1999, and assess how much information is lost when sampling effort is reduced to 50 percent of current effort (measured every other week), 25 percent (measured every month), or 12.5 percent (measured every other month; Figures. 4.7-4.8).

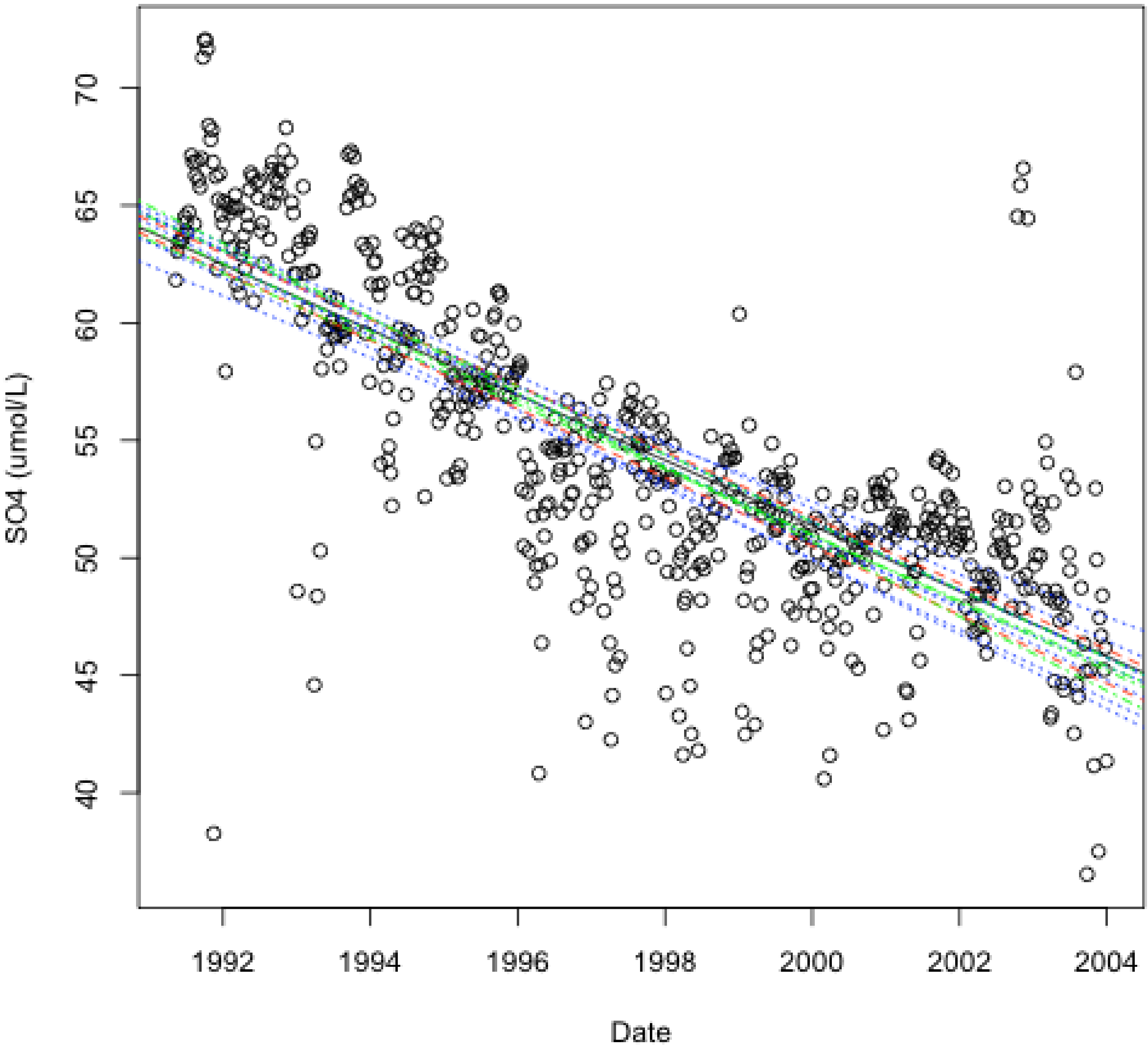


Figure 4.7. The long-term record of $SO_4$ (umol $L^{-1}$) at Biscuit Brook, measured approximately weekly from 1991-2003. The linear regression for all weeks is shown in black. The linear regressions for sampling every other week (50% sampling effort) are shown in red. The linear regressions for sampling every month (25% sampling effort) are shown in green. The linear regressions for sampling every other month (12.5% effort) are shown in blue.

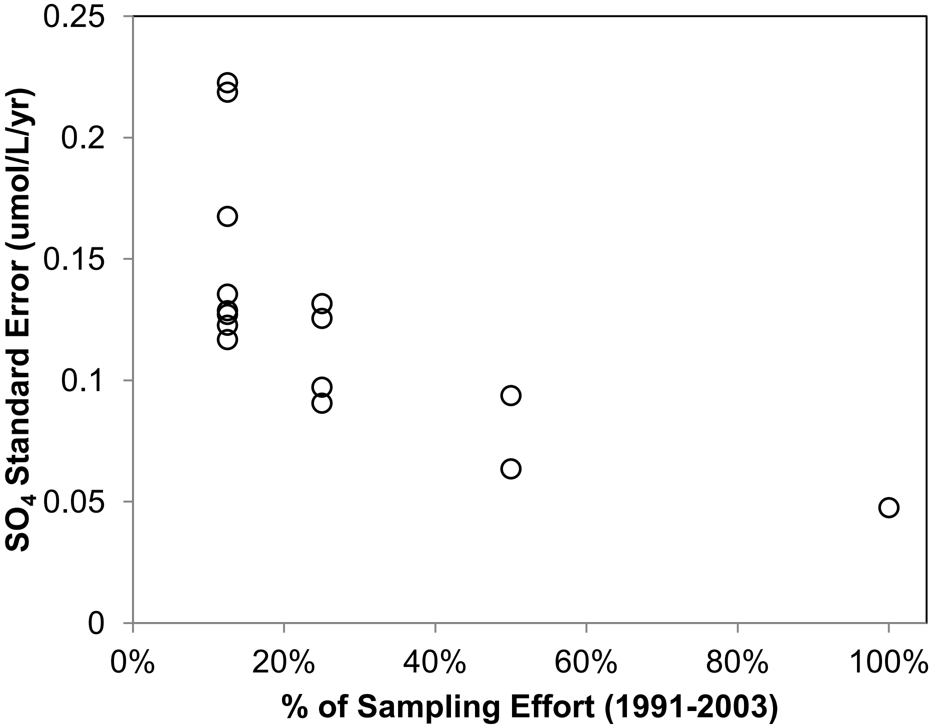


Figure 4.8. The tradeoff in sampling intensity and model error for $SO_4$ concentration measurements at Biscuit Brook when reduced sampling is simulated. A 50% sampling effort represents a biweekly sampling scheme, a 25% effort represents a monthly sampling scheme, and a 12.5% sampling effort represents a bimonthly sampling effort.

### *4.2.4 Results: Maximizing Sampling Effort for Long-Term Stream Monitoring*

This comparison of reduced sampling schemes at the Biscuit Brook site (1991-2003) showed that significant long-term trends in $SO_4$ concentrations in stream water could still be detected in all scenarios, including going to a bimonthly sampling scheme. This was not the case for all solutes, as some had trends that were not as strong as the $SO_4$ trends. Trends in $NO_3$ concentrations were significant ($p<0.05$) for a weekly and biweekly sampling scheme, for three of four monthly simulations, and for four of eight bimonthly simulations. Trends in $H^+$ concentrations were significant for a weekly sampling scheme, for one of two biweekly sampling schemes, for two of four monthly sampling schemes, and for two of eight bimonthly schemes. Trends in total monomeric Al concentrations were significant for weekly, biweekly, and monthly sampling schemes, and for seven of eight bimonthly schemes. Thus a 50 percent reduction in effort (from weekly to biweekly sampling) would still allow for significant long-term trends to be detected for the solutes tested here; not all solutes showed significant trends at longer sampling intervals in this example.

### 4.3 Findings and conclusions

- The DEC RIBS program has thorough statewide coverage for monitoring stream chemistry on a rotating basis and provides a very useful data set on long-term trends in large streams. A majority of these sites are located where water quality is affected by land use, such as agricultural and urban areas. A small number of RIBS sites are located in areas with minimal human influence and would be useful for assessing effects of changes in air quality policies; however, these sites have not been used previously to address trends in acid rain effects on streams. These data sets could be useful for future monitoring efforts.
- The RIBS program focuses on larger streams and rivers. This leads to a sample of streams and rivers that tend not to include the most acid-sensitive streams in the state, which are often smaller-order streams. Regular monitoring of small streams for stream chemistry could supplement the RIBS data set and add additional information on those that are particularly acid sensitive.
- The USGS stream monitoring program in the Catskills has provided valuable information on this sensitive area. Additionally, this record is important because there are few gauged streams with long-term monitoring of stream concentrations and stream export in New York. In section 4.2.3, it was demonstrated that this program provides data sufficient for identifying long-term trends in stream chemistry. The program is of great value and

should be supported in the future, and possibly be expanded to include monitoring of the gauged streams that were closed in 2010.

- Though there has been extensive sampling of lakes in the Adirondacks, there is little long-term monitoring of stream hydrology or chemistry. The Adirondack region is one of the most highly sensitive regions in the state to acidic deposition, and response to declines in deposition may be less marked in lakes than streams due to their higher buffering capacity and the neutralizing effect of in-lake processes during storage. Due to the close coupling of shallow groundwater flow paths for small streams (first, second, and third order), soil conditions, belowground vegetation systems, and stream conditions can help provide an indicator of ecosystem response to decreased deposition and recovery from acidification. Thus, stream sampling in the Adirondacks should be a priority for additional long-term monitoring of both hydrology and chemistry. The RIBS program has some Adirondack sites where river chemistry is measured, but this program does not address hydrologic budgets.
- When considering optimal sampling schemes, sampling in alternate years is not a practical approach, as gauges must be visited regularly and maintained in order to function properly.
- An efficient yet extensive stream monitoring system in New York would include three levels of monitoring intensity: index streams, routine chemistry monitoring, and periodic extensive surveys.
    - *Index streams*: A minimum number of index streams where stream concentrations and export are measured. For example, in the Adirondacks locating one index stream in each quadrant of the park (NE, SE, SW, and NW) could provide broad spatial

  coverage (Lawrence, USGS; pers. comm.). Ideally, the index streams would be sampled at an intensity encompassing a range of conditions. In the Adirondacks, these could be streams that are already currently monitored, such as Buck Creek and Archer Creek (Arbutus Lake inlet). Fly Pond Outlet is less ideal because it is more representative of the Fly Pond chemistry than of a stream. Bald Mountain Brook is also less ideal because the watershed hydrology is dominated by beaver activity masking any environmental trends.

  - *Routine chemistry monitoring*: Chemistry grab samples collected from a range of ungauged streams. These samples could be collected quarterly and still provide ample data over a long-term period. To represent both peak and base flow, samples could be collected during snow melt in the spring and low flow in summer or autumn. These would complement the index streams where both chemistry and flow are measured.
  - *Periodic extensive surveys:* Periodic surveys of a large number of streams (>100) to collect chemistry of spring snowmelt and baseflow. These surveys would be similar to the WASS and ECASS surveys that have been carried out previously. These could either be spaced out over five to ten years or based on the expected changes in chemistry and the known detectable difference.
  - If the WASS and ECASS surveys are repeated, there will be a higher probability of detecting a significant change if the sampling sites are paired.
- Automated sampling devices are advantageous because more intensive water sampling can be triggered during hydrological events. However, switching from weekly samples collected manually to automated devices is not likely to save money. The cost of training and maintenance for technicians to operate automatic samplers is large enough that it

may be similar to the current cost of manual collection. This may be future a future option to consider as technology develops and cost of equipment and maintenance decrease.

# 5. Vegetation Monitoring

## 5.1 Status

Forests in New York and across the country are monitored by the Forest Inventory and Analysis (FIA) program of the USDA Forest Service. Data are collected to assess forest condition on plots located on a 6,000-acre grid. Plots in New York are currently inventoried on a seven-year rotating basis. Plots are distributed in forested areas throughout the state (Figure 5.1).

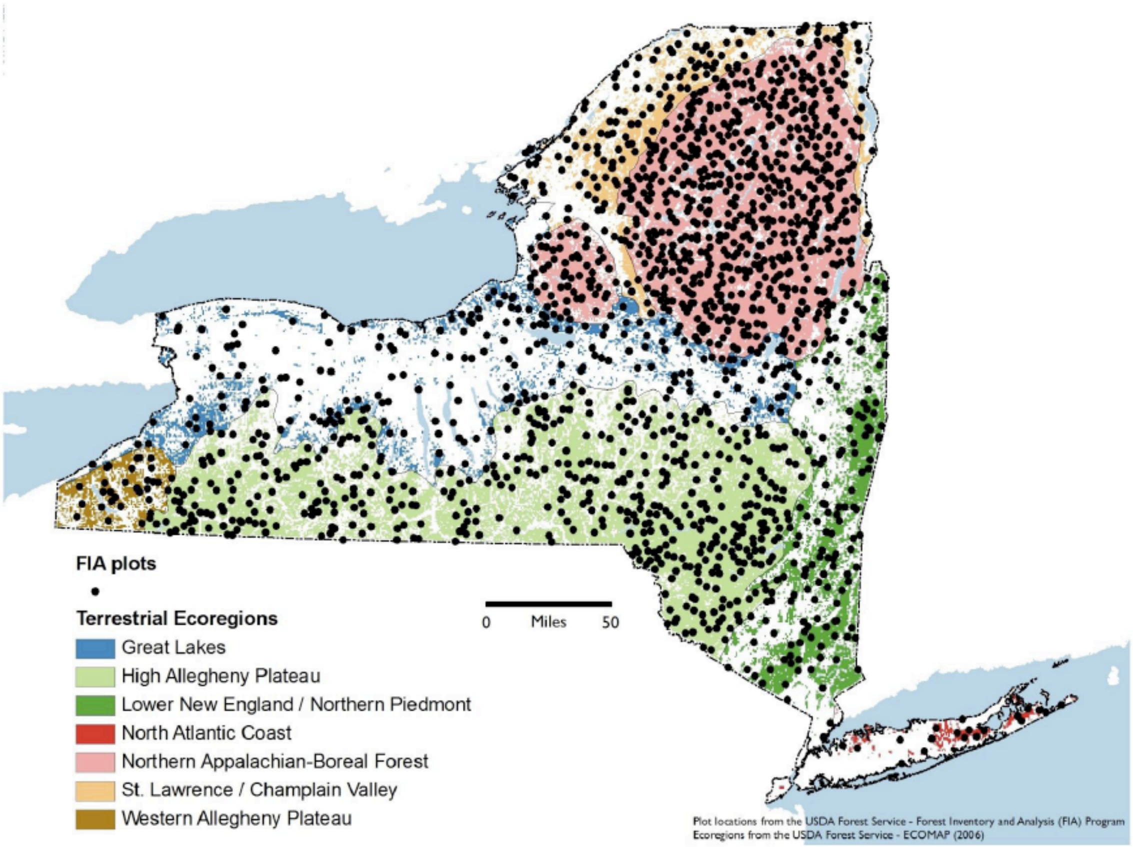
The FIA program is not specifically focused on impacts of atmospheric deposition, but many ecological variables are collected during FIA sampling that can be analyzed in conjunction with deposition from nearby DEC or NADP acidic deposition collectors. Ecological variables collected during routine plot monitoring include data on species composition, stand-level tree growth, seedling and sampling inventory, and tree health.

The FIA program includes a Forest Health Monitoring Program (Phase 3 of the FIA sampling scheme, formerly the Forest Health and Management (FHM) Program). A subset ($^{1}/_{16}$) of the FIA plots is included in Phase 3 sampling, and additional environmental variables related to forest health are collected in these plots during the routine rotating inventory. Variables measured include crown condition, soil condition (erosion, compaction, and soil physical and chemical properties), lichen communities, vegetation diversity and structure, presence and abundance of introduced exotic species, and coarse and fine woody debris (USDA 2005). These data are useful for assessing acidic deposition effects on New York forests, but not all forest variables that are important for monitoring forest response to acidic deposition are included in Phase 3 surveys (Table 5.1). Phase 3 sampling occurred in 166 plots in New York in 2002-2005, but has not been carried out since 2005 due to budget constraints.

The FIA data set is an underutilized resource with regards to long-term monitoring in New York. One of the barriers to using the FIA data is that USFS involvement is needed to obtain more data than are available on the internet, such as the locations of plots within counties. The FIA data have traditionally been used primarily for estimating timber production at a state or regional scale. Further work with these data sets investigating trends in the lesser-used categories such as lichen species, ozone-sensitive species, and seedling regeneration could be very informative.

There are other vegetation surveys in the state, some of which include permanent plots. In the Adirondacks, plots have been established at Huntington Forest (Bushey et al. 2008) and Buck Creek but a number of studies of vegetation in this region have not utilized permanent plots (McGee et al. 2007, Forrester et al. 2003, Kiernan et al. 2003, and Hurd et al. 1998). In the Catskill region, plots have been established in several watersheds which have been correlated with stream water measurements in previous studies (Lovett et al. 2002). Permanent vegetation plots have also been established in the Hudson Valley at the Cary Institute of Ecosystem Studies, specifically for the monitoring of atmospheric deposition effects on forest ecosystem processes (Lovett and Hart 2005). Additional plots in the Hudson Valley are located at Black Rock Forest.

Additional monitoring is currently being done in coordination with studies of other ecosystem components. For example, data were collected from plots in the Adirondacks with associated stream and soil measurements (Lawrence et al. 2008). Vegetation data from plots in the Hudson Valley were collected with associated deposition, soil solution, and soil metabolism measurements (Lovett and Hart 2005).



Plot locations from the USDA Forest Service - Forest Inventory and Analysis (FIA) Program
Ecoregions from the USDA Forest Service - ECOMAP (2006)

Figure 5.1. FIA plot locations with relation to forest cover and ecoregions in New York (map from Shirer and Zimmerman 2010; ecoregions from the USDA FS ECOMAP (2006), FIA plot locations from USDA FS FIA program).

Table 5.1. Important variables for long-term forest monitoring and coverage under the FIA Phase 2 and Phase 3 monitoring programs.

| **Possible Forest Monitoring Variables** | **Covered under the FIA program?** |
|---|---|
| Tree inventory (species and DBH of trees >10cm DBH) | Yes (P2) |
| Sapling inventory (species and DBH of trees >10cm DBH and >50cm tall) | Yes (P2) |
| Tree seedling inventory (species and abundance of tree seedlings <50 cm tall) | Yes (P2) |
| Ozone bioindicator species richness and abundance | Yes (P3) |
| Lichen species | Yes (P3) |
| Crown condition | Yes (P3) |
| Down woody material (coarse, fine, fuel) | Yes (P3) |
| Litter mass and chemistry | No |
| Foliar chemistry | No |
| Root biomass and chemistry | No |
| Fruit production | No |
| Herbaceous species and abundance | No |
| Monitoring of rare or endangered plants | No |
| Monitoring growth of individual trees | No |

### 5.2 Findings and conclusions

- Nearly all vegetation monitoring is of forest trees. Long-term data sets on herbaceous plants and vegetation in ecosystems are lacking. Consideration should be given to adding herbaceous plant monitoring. These could be sporadic surveys, with the early surveys serving as a baseline for future sampling. These surveys would also be highly valuable for climate change studies.
- More extensive use of FIA data could provide information on vegetation trends throughout New York for some of the less used data sets (e.g. lichen species and ozone-sensitive species).
- Like other statewide surveys, the FIA has excellent broad coverage of the state, but for ecological monitoring, it may be desirable to have areas that are monitored at specific locations within particular areas. This type of monitoring would include multiple

permanent vegetation plots where one or more variables listed in Table 5.1 would be monitored on a regular basis. Currently, permanent vegetation plots are located at the Cary Institute, Catskills, Black Rock Forest, and Huntington Forest. Additional sites that are not currently monitored could be added. These sites would add more detailed information to the broad-scale survey data provided by the FIA.

# 6. Soil Monitoring

## 6.1 Status

Forest soils are notoriously difficult to sample. They can be rocky, inaccessible, and spatially heterogeneous, making it difficult to accurately quantify soil characteristics or to quantify change over time (Kulmatiski et al. 2003). Thus sampling schemes are often inadequate detecting changes in large soil pools (Conant et al. 2001), and the number of samples required to detect a minimum change in a forest ecosystem can be quite high. For example, in an old-growth coniferous forest, Conant et al. (2003) estimated that over 60 composite samples with an area of ~2 $m^2$ and depth of 0.3 m are required to detect a change of 60 Mg C $ha^{-1}$. In a survey of 21 studies that measured change over time in the forest floor, Yanai et al. (2003) found that the study designs were incapable of detecting significant changes in forest floor mass or C content smaller than 15-20 percent. Soil coring may provide better precision than soil pits, because a larger number of samples can be collected for the same effort (Levine et al. 2012).

Detailed information on soil characteristics in New York is provided by county soil surveys. These surveys include soil classifications and detailed soil maps for each county. These surveys provide important information for management and land use planning, but they do not detail how soils are changing over time. The only statewide soil monitoring is by the USDA Forest Service as part of Phase 3 FIA.

In the Adirondacks, there have been soil surveys and repeated visits to sites in Buck Creek, which were sampled in 1997 and 2010 in conjunction with stream monitoring. Additionally, soils at Woods Lake were sampled in the 1980s and re-sampled in 2010 as part of a long-term liming experiment (Melvin and Goodale 2007). Warby et al. (2009) re-sampled soils after 17 years (from 1984-2001) in the Adirondacks and throughout the Northeast. A long-term resampling survey was undertaken by Johnson et al. (1994), who re-sampled Carl Heimburger's plots from the 1930s in 1984 and again in 2004 (Johnson et al. 2008). A comparison of soil organic matter content was executed in 1932, 1984, and 2005-06 in an array of Adirondack forests with different disturbance histories in order to asses change over a ~75 year interval (Bedison et al. 2010). This represents the longest soil resampling interval data available. There have also been studies comparing soils throughout the Adirondacks (Sullivan et al. 2006).

There have been several soil surveys in the Adirondacks that have not been revisited. Soils were sampled in conjunction with the WASS and ECASS stream surveys in several Adirondack watersheds. These soils were only sampled a single time, but the GPS locations have been archived for future resampling. Additional soil surveys have been conducted in the Oswegatchie and Black River Basins in the western Adirondack Mountains in association with the Adirondack Sugar Maple Study (Lawrence et al. 2011). In 2003, Sullivan et al. (2006) excavated soil pits at 199 locations within 44 statistically selected Adirondack lake watersheds, as well as 26 additional watersheds that are included in long-term lake water monitoring programs. Beginning in 2012, a long-term soil monitoring program will be instituted in the Catskill Mountains (Chris Johnson, Syracuse University, pers. comm).

### 6.2 Analyses: Detectable change in Adirondack Forest Soils

Under FIA's Phase 3, soil data were collected from 166 plots in New York from 2002-2005, with each plot sampled once. Forest floor and mineral soil samples were collected and analyzed separately. Soil measurements taken as part of this program include data on soil erosion, compaction, and physical/chemical characteristics. Unfortunately, due to budget constraints, the 166 plots sampled under Phase 3 for soils from 2002-2005 have not yet been resampled.

The magnitude of changes in soil chemistry that could be detected by FIA Phase 3 soil chemistry monitoring in plots located in the Adirondack region was assessed. All plots located within the 12 counties that are included in the Adirondack Park (Clinton, Essex, Franklin, Fulton, Hamilton, Herkimer, Lewis, Oneida, Saint Lawrence, Saratoga, Warren, and Washington) were used.

A paired test with a power of 0.8 was used to calculate the detectable difference as a percent of the mean for %C and %N in the forest floor, effective cation exchange capacity ($cmol_c$ $kg^{-1}$; Figure 6.1), $H^+$ (umol $L^{-1}$ in a 1:1 soil/water solution; Figure 6.2), and exchangeable Ca, K, Mg, and Na (mg $kg^{-1}$ dry soil; Figure 6.3) in the first 4 cm of mineral soil. Paired tests were used here because the FIA plots are permanently established plots that would remain consistent between surveys. These analyses allow us to assess what change as a percent of the mean is detectable within the Adirondack region.

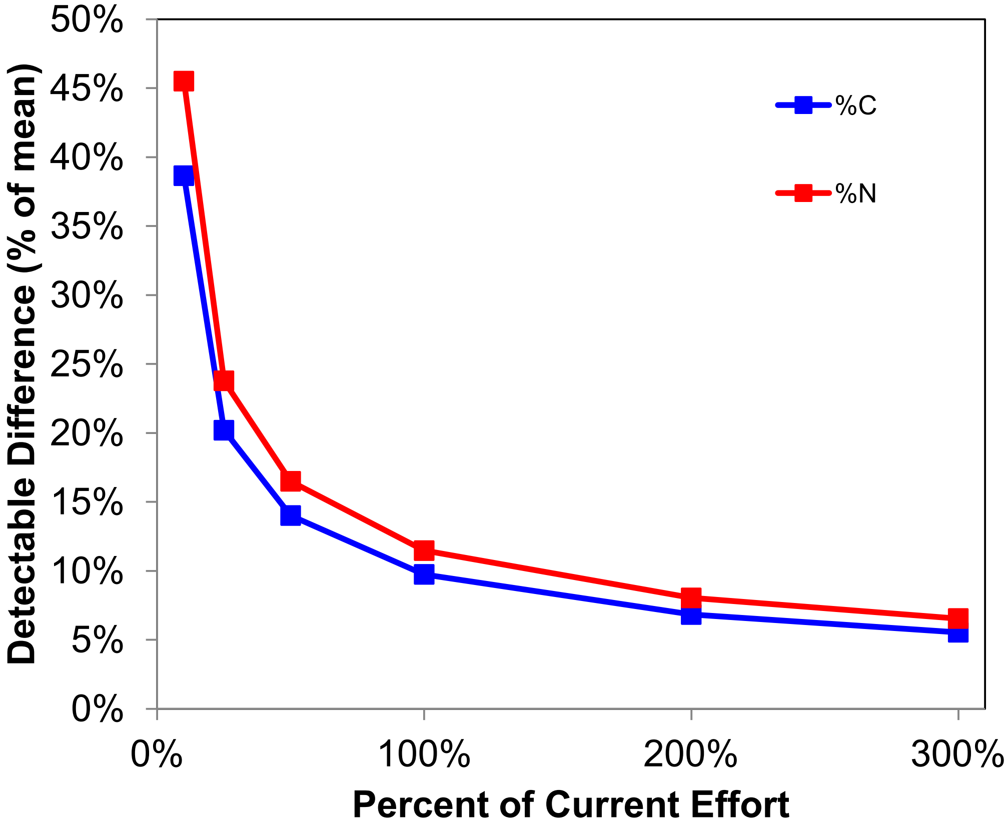


Figure 6.1. Detectable difference of %C and %N in forest floor samples collected by the FIA in 62 plots in the Adirondack region.

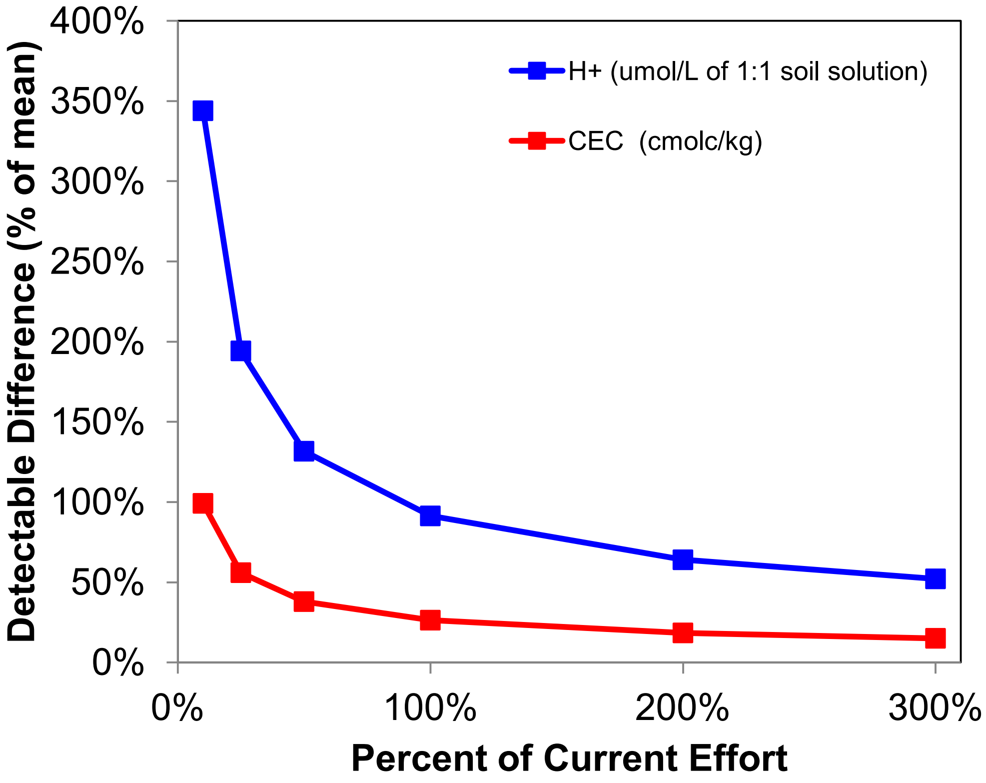


Figure 6.2. Detectable difference of H+ (umol $L^{-1}$ in a 1:1 soil/water solution) and effective cation exchange capacity ($cmol_c$ $kg^{-1}$) in mineral soil samples collected by the FIA in 56 plots in the Adirondack region.

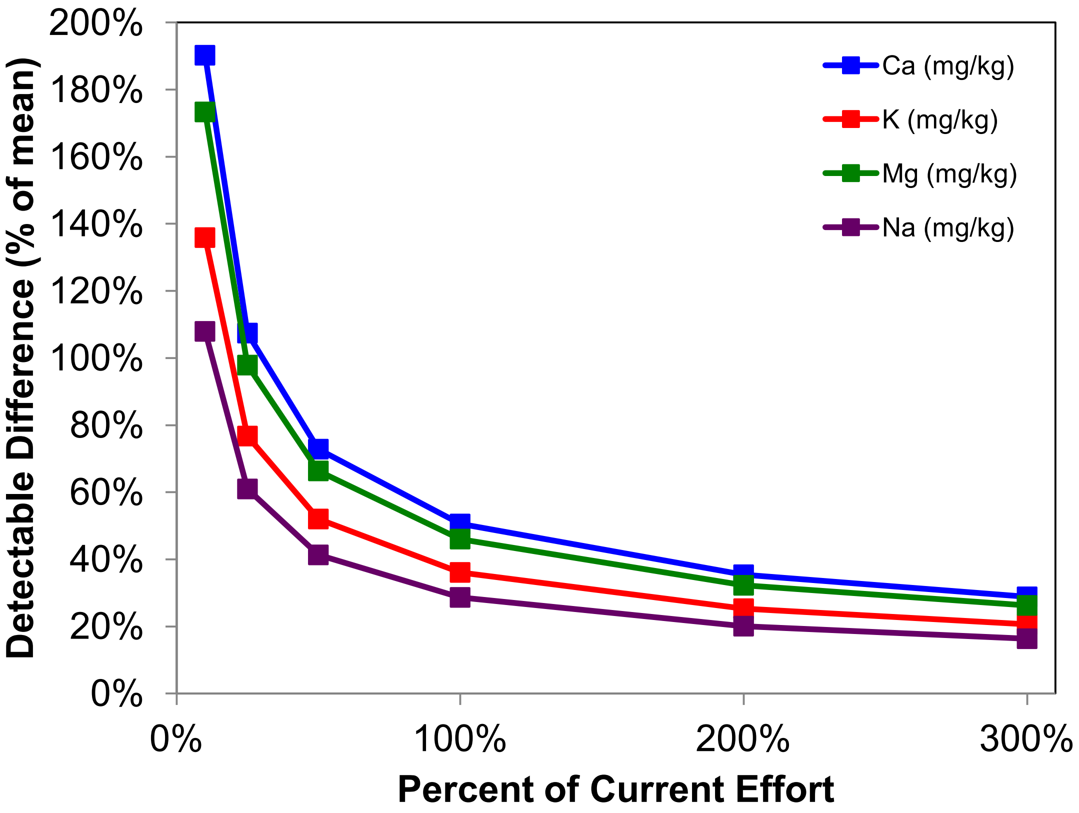


Figure 6.2. Detectable difference of exchangeable cation concentrations (mg $kg^{-1}$ dry soil) in mineral soil samples collected by the FIA in 56 plots in the Adirondack region.

With a paired resampling scheme, detectable changes in forest floor %C of nine percent of the mean and changes in forest floor %N of eleven percent of the mean could be significantly detected in future studies, which could be important for research interested in the implication of acidic deposition effects on carbon storage in forests. With the current sampling intensity, changes equaling 30-52% of mean concentrations of Ca, K, Mg, and Na in soils could be detected with 95 percent confidence. In terms of monitoring for cation depletion, a more extensive sampling program would be needed to detect smaller changes in cation concentrations in soils over time across the Adirondacks.

### 6.3 Findings and conclusions

- FIA soils dataset provides extensive information on soils throughout New York; however, this survey has only been conducted once and the data are not utilized extensively. Additional soil surveys at these or other sites of specific interest would be useful in the future.
- Soil monitoring is limited by methods that cannot describe the variation in heterogeneous soils with enough certainty to detect small changes over time (Wielopolski et al. 2010). An investment in methods development for soil monitoring would be advantageous. Supporting the ongoing work of the Northeast Soils Monitoring Cooperative (NESMC), a consortium of scientists interested in soil monitoring in the northeastern U.S., including New York, for whom methods development is of great interest would aid in data sharing and collaboration.
- Because it is difficult to detect small changes in forest soils due to high spatial variability, soil surveys using current methods require large numbers of samples. Soil coring may be more economical than soil pits, and focusing on the forest floor may be beneficial. The frequency of these surveys will be determined by policy needs, but the longer the interval, the greater the likelihood of detecting changes.
- Focusing on sensitive areas: western New York is not as relevant for monitoring effects of acidic deposition on soils due to the high buffering capacity of these soils. Soil monitoring should be focused in the most sensitive areas. Surveys are generally being carried out in these sensitive areas (Adirondack and Catskill watersheds). High elevation soils are also quite sensitive systems and the effects of deposition in these soils are not as well known as at lower elevation forested sites.

- Inclusion of soil monitoring at coordinated ecosystem monitoring sites, especially in relation to stream chemistry, would allow for better comprehension of belowground biogeochemical dynamics (See Section 9 for a further discussion of integrated monitoring).

# 7. Fauna

## 7.1 Status

Measurements of acidic deposition effects on fauna in New York are varied and extensive, and include both one-time surveys and continuous long-term monitoring projects. Studies investigating effects of acidic deposition on fauna tend to focus on aquatic animals, as they are most affected by changes in the chemistry of water bodies. Studies of songbirds, shore birds, birds of prey, bats, fish, and invertebrates have been carried out for studies of Hg, and are described in Section 8.6.

### *7.1.1 Aquatic Fauna*

*Stream macroinvertebrates*:

Under the RIBS program, the statewide stream survey conducted by the DEC, macroinvertebrate community assessments and invertebrate tissue chemistry are measured along with water quality data. Since 1980, 17 basins in the state are measured on a rotating basis, with each being measured once every five years (~6 measurements per site over the sampling period).

A project in the Catskill Mountains in 2003 re-sampled 15 sites that had previously been sampled in 1987 to assess whether spatial patterns in species composition of aquatic macroinvertebrates, fish, and periphyton had changed with decreasing acidity of surface waters in the region (Burns et al. 2006). Although the study found small improvements in the acidity of surface waters, it did not translate into large-scale changes in biological communities. This could be a site for future monitoring work as the acidity of surface waters in the region continues to decrease.

### *Fish population recovery in the Adirondacks*:

The ALTM has sampled 45 lakes to describe changes over time in fisheries in the Adirondacks. These lakes were first surveyed in 1984-87, then in 1994-2005, and a third round of surveys was initiated for 2008-2012, with added investigations of Hg in yellow perch and brook trout (Roy and Bulger 2011).

The authors found a mixed response to lake recovery in fish species in the 45 ALTM lakes between 1984 and 2005. Moderately sized lakes with pH 5.5 – 6.0 showed the greatest species gains over this period. This research also allowed for the development of fish-community sensitivity indices. Three minnow species (fallfish, fathead minnow, and bluntnose minnow) are sufficiently common and acid sensitive to serve as potential indicators. Brown trout are sensitive but not common enough to be a reliable indicator of sensitivity (Roy and Bulger 2011).

### *AEAP lake monitoring: bacterioplankton, phytoplankton, zooplankton, macrophytes, and fish*:

The Darrin Freshwater Institute, a research center of the Rensselaer Polytechnic Institute (RPI), initiated the Adirondack Effects Assessment Program (AEAP) in 1994. The AEAP currently monitors 17 lakes in the Adirondacks for bacterioplankton, phytoplankton, zooplankton, macrophytes, fish, and water chemistry (surface chemistry and deep water chemistry). Samples have been collected two times each year between June and September from 1994-2010. Results from the early years of the study were recently published (Nierzwicki-Bauer et al. 2010).

## 7.2 Analyses

### *7.2.1 AEAP aquatic biota*

Currently, the AEAP monitors 17 lakes for aquatic biota in three categories: rotifers, phytoplankton, and crustaceans. The goal of this monitoring program is to investigate trends in species richness (number of species), community composition, and the appearance and disappearance of important indicator species, particularly in connection with changes in water chemistry. To assess optimal subsampling strategies, a repeated-measures mixed-effects model is being used to assess the effect of subsampling on the estimates and model error of species richness and species diversity (Shannon Diversity Index) for each of the three biological groups (Figures 7.1-7.3). In this model, lakes are treated as random effects, and the time series for each lake is treated as repeated measures.

Due to proximity of sample lakes, the lakes are visited in specific groups twice each summer (See Appendix 10.2.4 for visitation groups). The mixed model is used to determine the estimate and standard error of species richness and diversity for all possible combinations of the seven visitation groups.

Table 7.2. Percent increase in model SE for different subsampling scenarios.

|  | % Effort | Number of lakes sampled | Sample Timing | Rotifer Richness | Rotifer Diversity | Phyto-plankton Richness | Phyto-plankton Diversity | Crustacean Richness | Crustacean Diversity |
|---|---|---|---|---|---|---|---|---|---|
| **Reducing the number of lakes** | 88% | 14 lakes | 2-3 times every year | 5 | 6 | 8 | 12 | 7 | 9 |
|  | 81% | 13 lakes | 2-3 times every year | 13 | 9 | 11 | 6 | 12 | 13 |
|  | 69% | 11 lakes | 2-3 times every year | 19 | 16 | 23 | 21 | 19 | 19 |
|  | 63% | 10 lakes | 2-3 times every year | 31 | 30 | 27 | 31 | 31 | 30 |
|  | 56% | 9 lakes | 2-3 times every year | 31 | 30 | 35 | 36 | 34 | 34 |
|  | 50% | 8 lakes | 2-3 times every year | 43 | 45 | 42 | 45 | 42 | 44 |
|  | 44% | 7 lakes | 2-3 times every year | 46 | 47 | 53 | 55 | 50 | 53 |
|  | 31% | 5 lakes | 2-3 times every year | 77 | 75 | 78 | 83 | 80 | 81 |
|  | 25% | 4 lakes | 2-3 times every year | 97 | 101 | 104 | 105 | 100 | 99 |
|  | 6% | 1 lake | 2-3 times every year | 298 | 299 | 300 | 301 | 294 | 298 |
| **Reducing sampling dates** | 52% | 16 lakes | Every other year | 2 | 2 | 9 | 13 | 1 | 2 |
|  | 45% | 16 lakes | Once per year | 3 | 2 | 11 | 15 | 1 | 2 |
|  | 23% | 16 lakes | Once per year every other year | 7 | 6 | 29 | 41 | 4 | 6 |

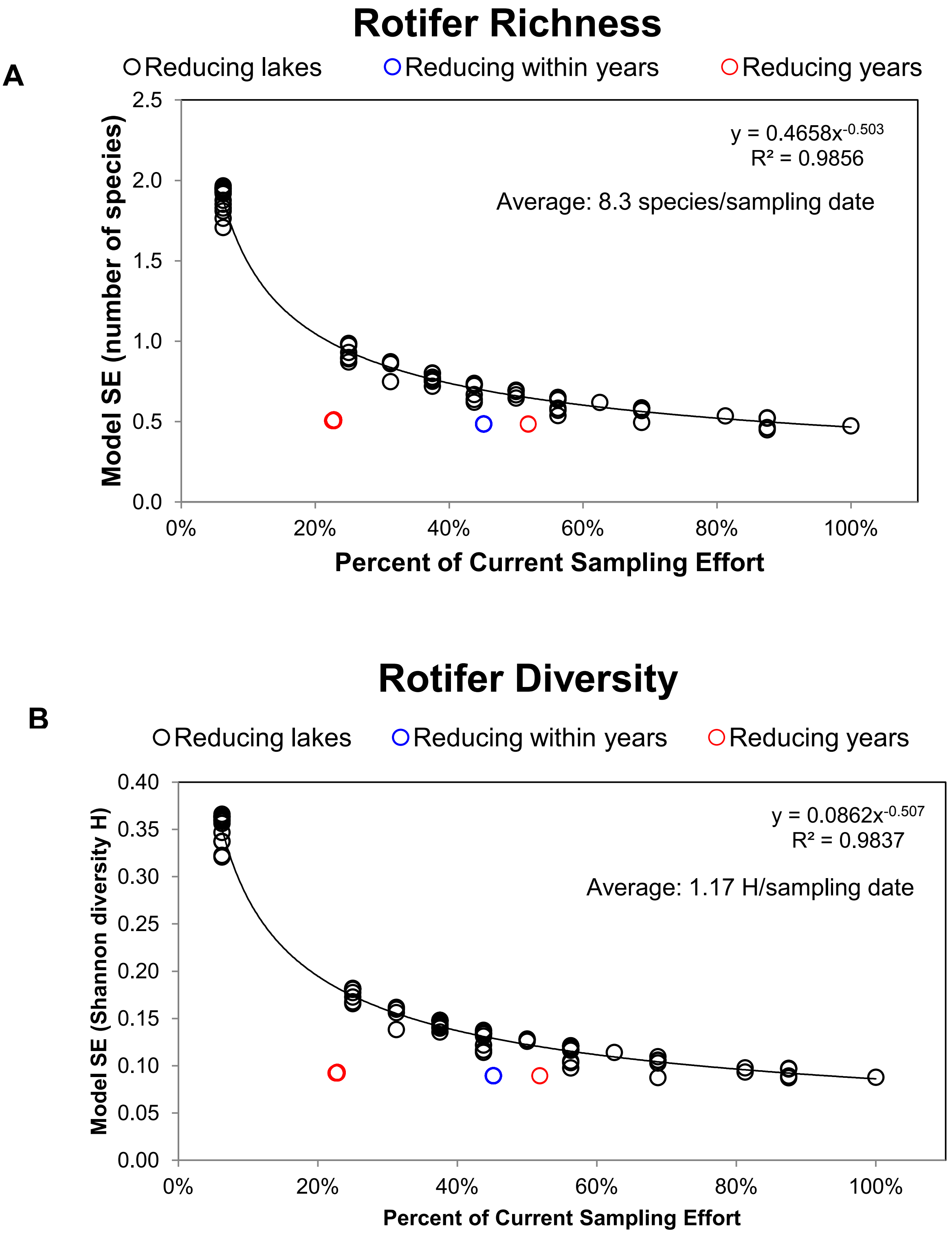
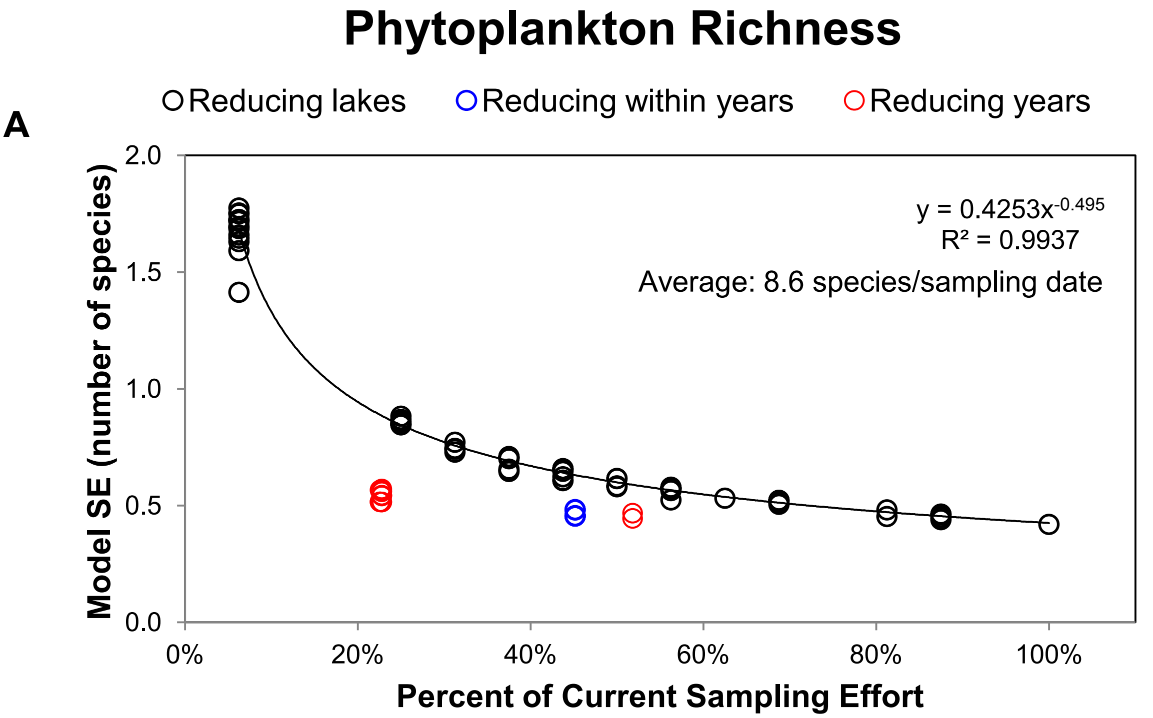


Figure 7.1. The model SE for long-term trends in rotifer richness (A) and diversity (B) increase with decreased sampling effort. Black symbols represent sampling schemes of 88% (14 lakes), 81% (13 lakes), 69% (11 lakes), 63% (10 lakes), 56% (9 lakes), 50% (8 lakes), 44% (7 lakes), 31% (5 lakes), 25% (4 lakes), and 6% (1 lake). The blue symbol represents a sampling scheme of sampling 52% (sampling 16 lakes once every other year). The red symbols represent a sampling scheme of 45% (sampling 16 lakes once per year) and 23% (sampling 16 lakes once per year every other year).



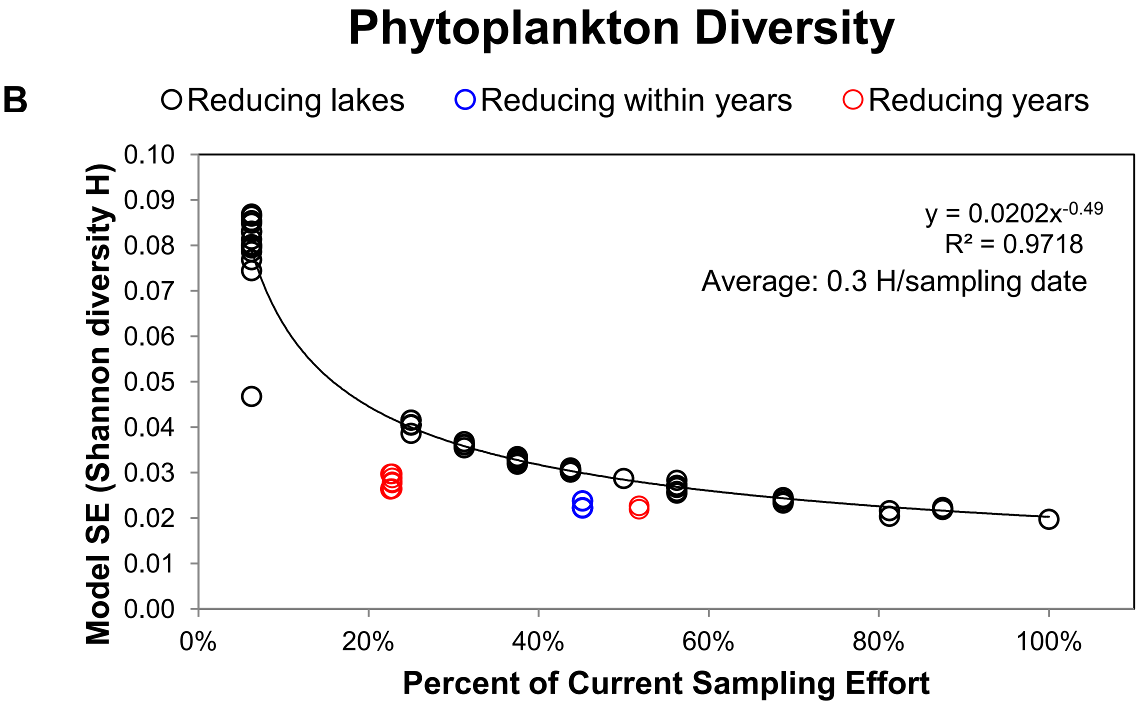


Figure 7.2. The model error as a function of decreased sampling effort for phytoplankton richness (A) and diversity (B). Black symbols represent sampling schemes of 88% (14 lakes), 81% (13 lakes), 69% (11 lakes), 63% (10 lakes), 56% (9 lakes), 50% (8 lakes), 44% (7 lakes), 31% (5 lakes), 25% (4 lakes), and 6% (1 lake). The blue symbol represents a sampling scheme of sampling 52% (sampling 16 lakes once every other year). The red symbols represent a sampling scheme of 45% (sampling 16 lakes once per year) and 23% (sampling 16 lakes once per year every other year).

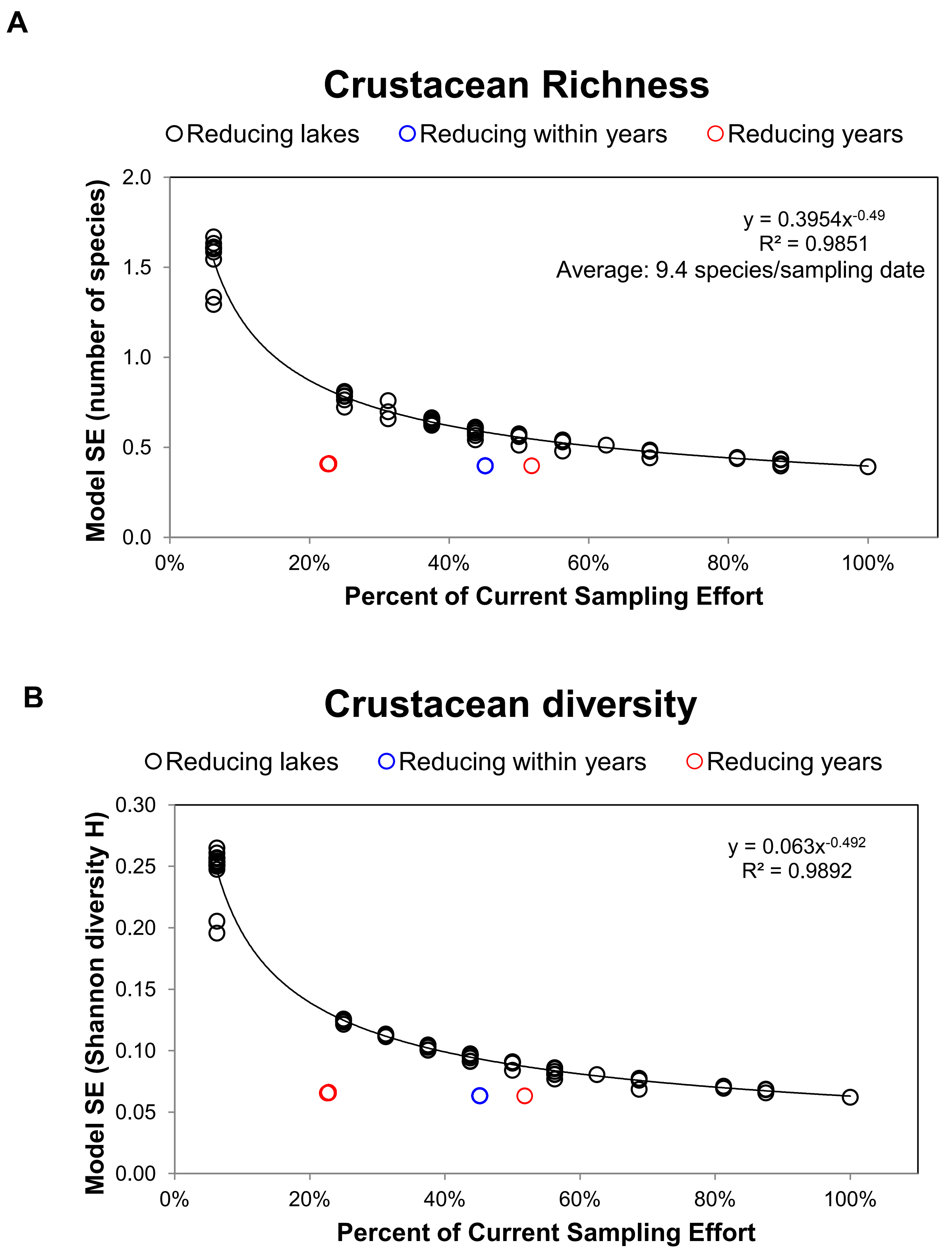


Figure 7.3. The model SE for long-term trends in crustacean richness (A) and diversity (B) increase with decreased sampling effort. Black symbols represent sampling schemes of 88% (14 lakes), 81% (13 lakes), 69% (11 lakes), 63% (10 lakes), 56% (9 lakes), 50% (8 lakes), 44% (7 lakes), 31% (5 lakes), 25% (4 lakes), and 6% (1 lake). The blue symbol represents a sampling scheme of sampling 52% (sampling 16 lakes once every other year). The red symbols represent a sampling scheme of 45% (sampling 16 lakes once per year) and 23% (sampling 16 lakes once per year every other year).

### *7.2.2 Results: AEAP Aquatic Fauna*

The results of the repeated measures mixed effects models demonstrate that overall model error increases with a decreased sampling effort. Table 7.2 describes the increase observed for rotifer, phytoplankton, and crustacean species richness and diversity. The points shown as the "6% Effort" category represent the individual lakes, and show the spread of model SE for each of the lakes tested. Future work may address trends in the individual lakes in addition to treating the lakes as samples of a population.

This sensitivity analysis shows that the error of the model increases only slightly even when sampling as little as ~40 percent of current effort. Reducing sampling dates does not increase the model error as much when the number of lakes sampled is less. When the number of sample years or dates is reduced, the model error is quite similar to when all sampling dates are included, even when sampling at 23 percent of the effort. Therefore, a reduced sampling scheme should include as many lakes as possible, with fewer samples taken per lake.

This model was not used to test the effect of increasing the number of lakes. An alternative sampling scheme at 100 percent of current effort could be to sample 32 lakes once per year rather than 16 lakes twice per year, or even 64 lakes once every other year.

In the future, reducing sample size in the AEAP monitoring program would not have as much effect on statistical power as is shown in these models. This is because the models simulated reduced sampling for the entire record, whereas future studies would make use of the existing data for the period from 1994-2006. Future models would thus have a greater ability to detect change than indicated in this analysis, where sampling was reduced over the entire record.

## 7.3 Findings and conclusions

- The ALTM surveys have been useful in examining changes in fish populations associated with decreases in acidic deposition. These surveys also demonstrated that lakes have not made a systematic recovery in this region since the 1980s. Future surveys should be continued to monitor Adirondack lake recovery. Surveys take approximately five years to complete. A possible sampling plan could be to carry out a survey every ten years from the starting date of the one previous.

*AEAP aquatic fauna*:

- For the most efficient sampling scheme addressing change over time while characterizing a range of Adirondack lake conditions representative of the region, the following two-part strategy would be effective: a small number of lakes could be sampled more frequently than the two current sampling dates, while a larger number of lakes could be sampled infrequently either annually or every other year. This would provide more data on changes in lake biological communities and their relationship to water chemistry throughout the year. It would also allow for a larger sample of lakes to be monitored over time so this sample might be considered representative of overall trends in the Adirondack region.
- As the AEAP sampling program currently stands, it appears that monitored lakes could be sampled once per summer or twice per summer in alternate years. Both of these sampling schemes would reduce sampling effort by 50 percent without considerably increasing the error associated with modeling estimates of species diversity or richness of rotifers, phytoplankton, or crustaceans. Reduction of sampling within years could create opportunities to add lakes and therefore additional spatial information to the current

group of lakes. For example, because sampling once per summer or twice per summer in alternate years results in models quite similar to sampling twice per summer, 32 lakes could be sampled once each summer for the same amount of effort as is currently expended.

- Although lakes in this analysis were categorized by current visitation groups, it is possible that they could be rearranged if lakes were eliminated under a reduced sampling scheme. If a sampling scheme involving a reduced subset of lakes is desired, choosing a stratified sample of lakes from ANC or pH class may be better than subsampling by current visitation groups.
- The AEAP monitoring program is the only program in the state that targets long-term monitoring of lake biota, but the data have not been widely used or published. The focus here is on the effect of monitoring intensity, but future work should include an investigation of the long-term trends of aquatic biota throughout the record. Additionally, making the additional trend analyses results available to researchers would help inform future work in this area.
- The RIBS program provides valuable information on the general status of river invertebrates throughout New York. The RIBS program is not very relevant for acidification assessment because smaller streams are where stronger acidification effects are observed, but the program is very valuable for Hg monitoring. This research could be supplemented with surveys in an additional population of smaller streams not captured in the RIBS survey.

# 8. Status of Mercury Monitoring in New York

There have been several studies of ecological processes and effects of Hg deposition in New York, but consistent long-term monitoring is limited. Below, long-term monitoring efforts to evaluate Hg deposition and environmental impacts are described, as well as relevant studies and surveys that have been conducted to investigate Hg cycling. Most studies of Hg processes are quite recent. Although mostly recent, these individual studies do not currently provide information regarding long-term Hg trends. They may however, serve as starting points for future environmental monitoring. Future research should focus on identifying areas that are particularly sensitive to Hg deposition in New York in order to help locate future monitoring efforts.

There is a need to refine specific Hg monitoring goals for New York. In 2008, a committee convened and developed guidelines for a national Hg monitoring network (MercNet) to track trends in Hg concentrations in land, air, water, and biota. The committee set forth the goals of this program, which were to "establish an integrated, national network to systematically monitor, assess and report on policy-relevant indicators of atmospheric Hg concentrations and deposition, and Hg levels in land, water, and biota in terrestrial, freshwater and coastal ecosystems in response to changing Hg emissions over time" (MercNet draft report, 2008). This plan proposes measurements in various categories as well as their target frequency of measurement, which ranges from continuous monitoring to sampling every three to five years. A preliminary plan for Hg monitoring in New York should include a similar list of desired measurements and target schedules as a starting point for coordinating Hg monitoring in the state among interested parties.

## 8.1. Monitoring of Atmospheric Mercury

### *8.1.1 Status of Deposition Monitoring*

Wet Hg deposition is currently monitored at four sites in New York, which are part of the NADP Mercury Deposition Network (MDN). Huntington Forest has been in operation since 1999, Biscuit Brook since 2004, and Rochester and the Bronx since 2008. The MDN site at West Point was in operation for a four-year period from 2006-2010. Wet Hg deposition is also being monitored at an urban site in Syracuse by researchers at Syracuse University but is not part of the NADP.

In addition to monitoring of wet deposition that is done through the NADP MDN program, there have also been some attempts to monitor air concentrations and dry deposition of Hg in the state. Air concentrations of Hg are currently monitored using Tekran instruments at Huntington Forest, Rochester, and the Bronx, all with records going back to 2008. The DEC operates the instruments in Rochester and the Bronx. The instrument at Huntington Forest is operated by Clarkson University. One study of dry deposition of Hg was carried out at the Black Rock Forest using the surrogate surface technique in three, three-month intervals in 2006-2008. That study found that trends in dry deposition tended to follow trends in wet deposition measured at the nearby West Point site (Anthony Carpi; John Jay College, CUNY).

Measurements of Hg concentrations in litterfall have been used to estimate total Hg deposition. NADP has initiated a pilot monitoring initiative in which NADP site sponsors collect litterfall measurements to approximate a large part of the Hg dry deposition in a forest landscape (Risch et al. 2012). Sponsor sites collect annual litterfall measurements, and samples are analyzed for THg and MeHg.

When developing the approach for MercNet, the National Mercury Monitoring Steering Committee recommended that in the category of air monitoring, the following variables be measured:

- Atmospheric Hg speciation (continuous monitoring)
- Dry deposition (continuous monitoring)
- Wet deposition (weekly cumulative collection)
- Hg evasion (monthly monitoring)

Currently, Hg in wet deposition is monitored at four sites in New York and air concentrations are monitored at a subset of these sites. There is no systematic measurement of dry deposition, total deposition, or evasion flux. A future statewide monitoring program would benefit from adding measurements of dry and total deposition. If costs are prohibitive, these variables could be monitored for a short period, during which models of dry and total deposition predicted from wet deposition trends could be developed.

### *8.1.2 Analysis of Trends in the MDN Program*

Trends in concentrations of THg (ng $L^{-1}$ $yr^{-1}$) and Hg deposition (ng $m^{-2}$ $yr^{-1}$) at four MDN sites were analyzed using a Mann Kendall trend test. The Rochester, Bronx and West Point sites did not show significant trends, which is not surprising because their records are short. Biscuit Brook and Huntington Forest showed substantial decreases in total Hg concentrations, but did not show significant trends for total Hg deposition (Table 8.1 and Appendix Table 10.3.1, Figures 8.1-8.2).

Table 8.1. Trends in Hg concentrations at MDN sites in New York. Asterisks indicate significant trends ($p<0.05$).

| | Years Active | Mann Kendall Tau | Mann Kendall p-value | Slope (ng Hg $L^{-1}$ $yr^{-1}$) | SE (ng Hg $L^{-1}$ $yr^{-1}$) |
|---|---|---|---|---|---|
| Bronx | 2008-present | -0.0718 | 0.15 | -0.535 | 0.392 |
| Biscuit | 2004-present | -0.0718 | 0.04* | -0.210 | 0.136 |
| Huntington | 1999-present | -0.0872 | 0.002* | -0.143 | 0.079 |
| Rochester | 2008-present | -0.0758 | 0.13 | -0.487 | 0.360 |
| West Point | 2006-2010 | -0.0746 | 0.14 | -0.546 | 0.384 |

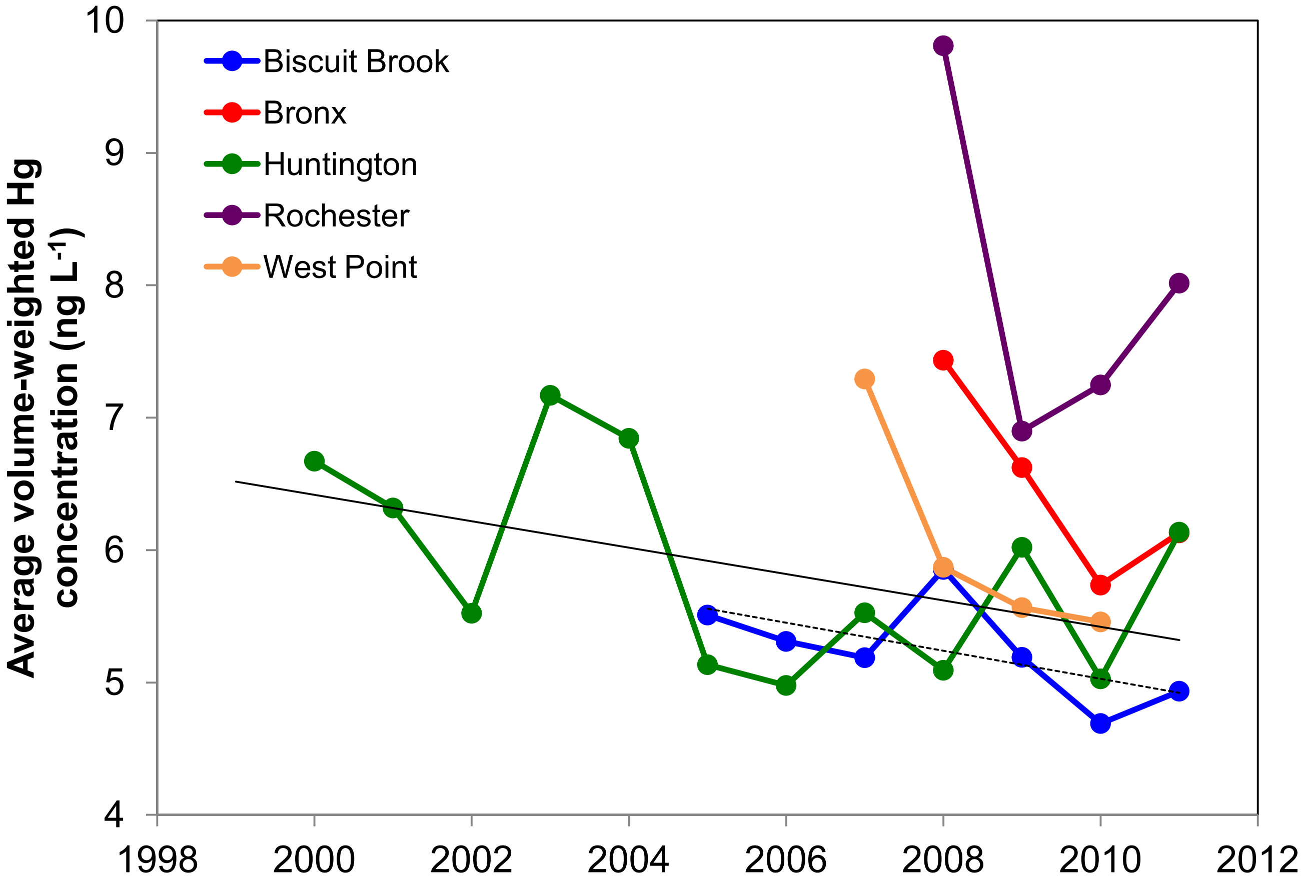


Figure 8.1. Annual average Hg concentrations (ng Hg $L^{-1}$) in precipitation at New York MDN sites. Trend lines are shown for Huntington (solid line) and Biscuit Brook (dashed line), the two sites that showed significant decreasing Seasonal Kendall trends. The other sites show non-significant decreasing trends.

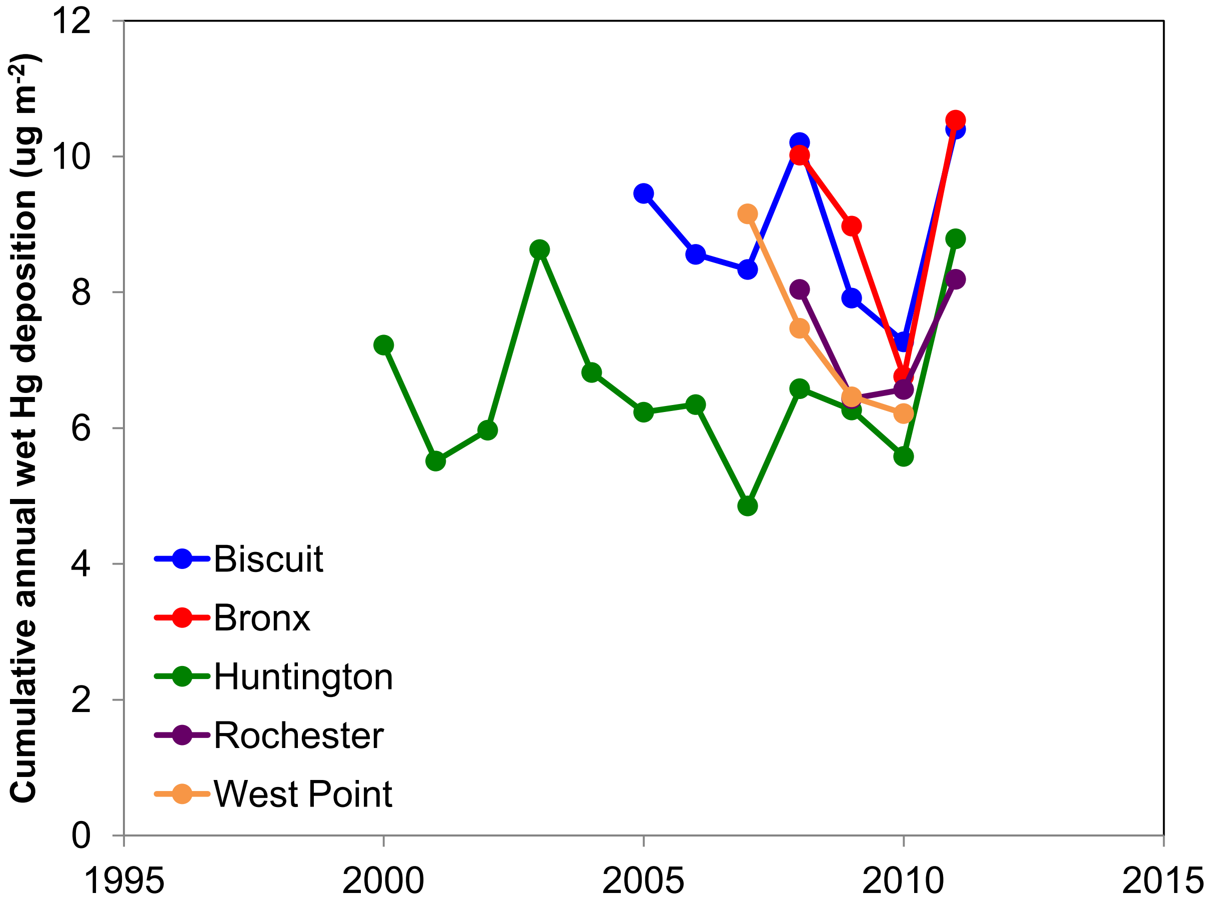


Figure 8.2. Cumulative annual wet deposition (μg Hg $m^{-2}$) at New York MDN sites. No sites showed significant Mann Kendall trends for Hg deposition.

### *8.1.3 Findings and Conclusions for Monitoring of Mercury Deposition:*

*Wet deposition*:

- The MDN network is a very useful tool for long-term Hg wet deposition monitoring. The consistency in methods across the state allows comparisons of trends among sites. Though there were no significant long-term trends observed at the sites with shorter records, it is expected that significant trends would be observed after additional years of data collection, as was observed at Huntington and Biscuit Brook, because the slopes and variances are similar. All sites however, showed decreasing trends for Hg concentration.

- Monitoring for Hg is costly, but the benefits are abundant. Monitoring should continue to be supported at the four sites that are currently in operation, as longer records tend to show significant decreasing trends. Additional Hg deposition sites in areas not currently monitored would be useful for describing trends in sensitive areas, for example coastal areas on Long Island or high-elevation sites in the Adirondacks. Additional long-term Hg monitoring sites could be co-located with other environmental monitoring efforts (see section 9 for a complete listing).

*Air concentrations and dry deposition*:

- Wet deposition is easier and less expensive to monitor than air concentrations or dry deposition. Though wet and dry deposition tend to show similar trends, dry deposition comprises a large portion of total deposition and may be more spatially and temporally variable than wet deposition. Initiating a statewide program for monitoring dry and total Hg deposition would be ideal. Any research contributing to the study of dry deposition velocities would be valuable for incorporating into models of total and dry Hg deposition.

*Total mercury deposition*:

  - Mercury in litterfall can serve as a proxy for total Hg deposition, because Hg deposited in wet and gaseous forms adheres to leaves. Co-locating litterfall measurements with wet deposition collectors and surrogate surfaces measuring dry deposition would allow for a comparison between measurements of total Hg in leaves to the sum of wet and dry deposition. Because collecting litterfall is much more cost-efficient than measuring dry deposition, establishing a model of dry-only deposition based on total Hg deposition in litterfall would be very advantageous for a long-term monitoring program. Therefore, a select number of forested New York sites should be added to the NADP litterfall Hg pilot program, particularly those that are co-located with additional monitoring activities, as funding allows.

- Huntington Forest, Rochester, and the Bronx are the three sites that are currently outfitted with the most monitoring equipment (MDN wet deposition collectors and Tekran air concentration collectors). These sites seem to be the likely candidates for expansion into dry deposition and total deposition monitoring. Huntington Forest has been proposed as a representative site for New York within the MercNet program. When selecting sites to monitor, it would be most useful to include sites that represent elevational, east-west, and urban-rural gradients.

## 8.2. Monitoring of Mercury in Aquatic Systems

### *8.2.1 Status of Monitoring of Mercury Concentrations in Surface Waters*

Monitoring of lake Hg is very important to protecting human health. Mercury deposited onto the landscape can be transformed into MeHg, a neurotoxin that bioaccumulates up the aquatic food chain. Measuring Hg in surface waters has generally been conducted in association with monitoring aquatic fauna to provide metrics for predicting concentrations of THg and MeHg in aquatic wildlife such as loons and loon prey species (Yu et al. 2011; 44 Adirondack lakes), turtles (Turnquist et al. 2011; 10 lakes and wetlands throughout New York), and fish (Dittman and Driscoll 2009; 25 Adirondack lakes, Simonin et al. 2008; 131 lakes throughout New York). The USGS, in collaboration with Syracuse University, Plymouth State University, the U.S. Forest Service, and SUNY-ESF have also been successful in using optical sensors to measure fluorescence of dissolved organic matter (FDOM) in situ as an index of Hg concentrations (Myron Mitchell, SUNY-ESF, pers. comm.).

In addition to studies that concurrently measured surface water and biotic Hg concentrations, Hg concentrations in other surface waters in the Adirondacks have been monitored less consistently for about ten years for a variety of individual research projects. Sunday Pond and Arbutus Lake have sporadic long-term records of Hg concentrations (Charles Driscoll, Syracuse University, pers. comm.).

Most surface water Hg monitoring has occurred in the Adirondack region. The Adirondacks and the Catskills have been found to have higher Hg concentrations than waters in the rest of the state (Simonin et al. 2008), but Hg levels may be high in other areas that have not well been monitored.

### *8.2.2 Detectable Change in Surface Water Mercury Concentrations*

Concentrations of THg and MeHg were measured in 131 surface waters throughout New York as part of an assessment of Hg effects on fish (Simonin et al. 2008). Repeating this survey would be a useful way to build on these data sets and may help refine models of fish Hg concentrations. The detectable change was used to assess what (as a percentage of the mean) surface water Hg concentrations would be required to produce a significant change in concentrations. Both paired and unpaired tests with a power of 0.8were used to calculate the detectable difference as a percent of the mean for THg and MeHg (Figure 8.3). Paired tests simulate sampling the same surface water as the original survey. Unpaired tests simulate sampling a different set of surface waters with an assumed variance that is the same as the original set.

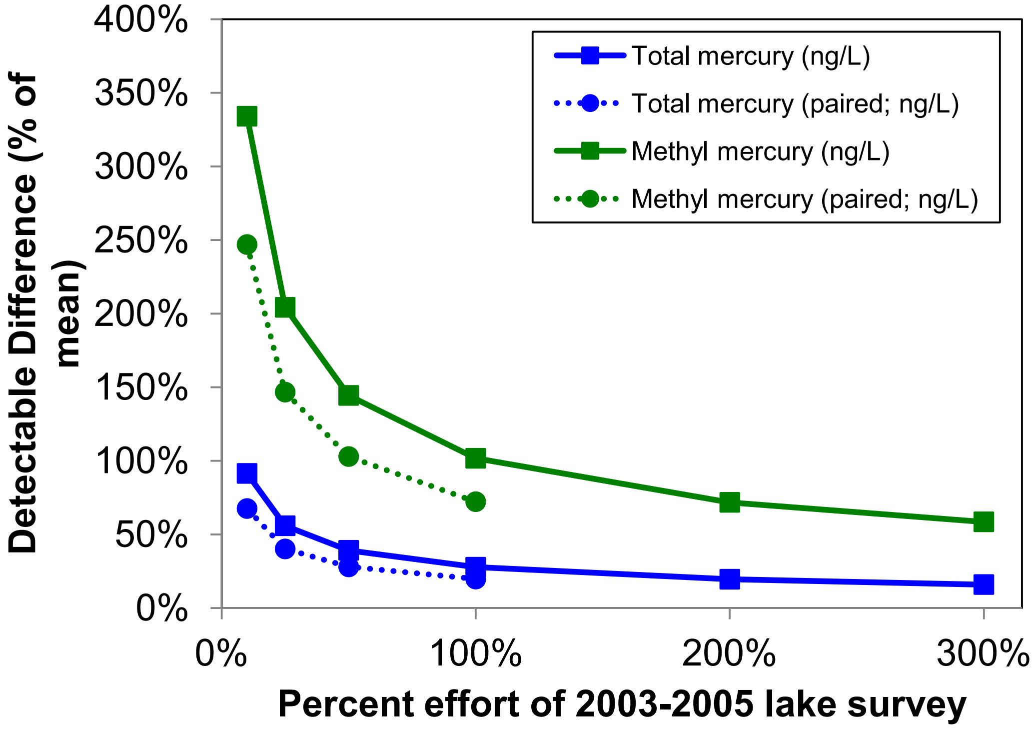


Figure 8.3. Detectable difference of surface water Hg concentrations as a percent of mean concentrations in 131 lakes sampled throughout New York from 2003-2005.

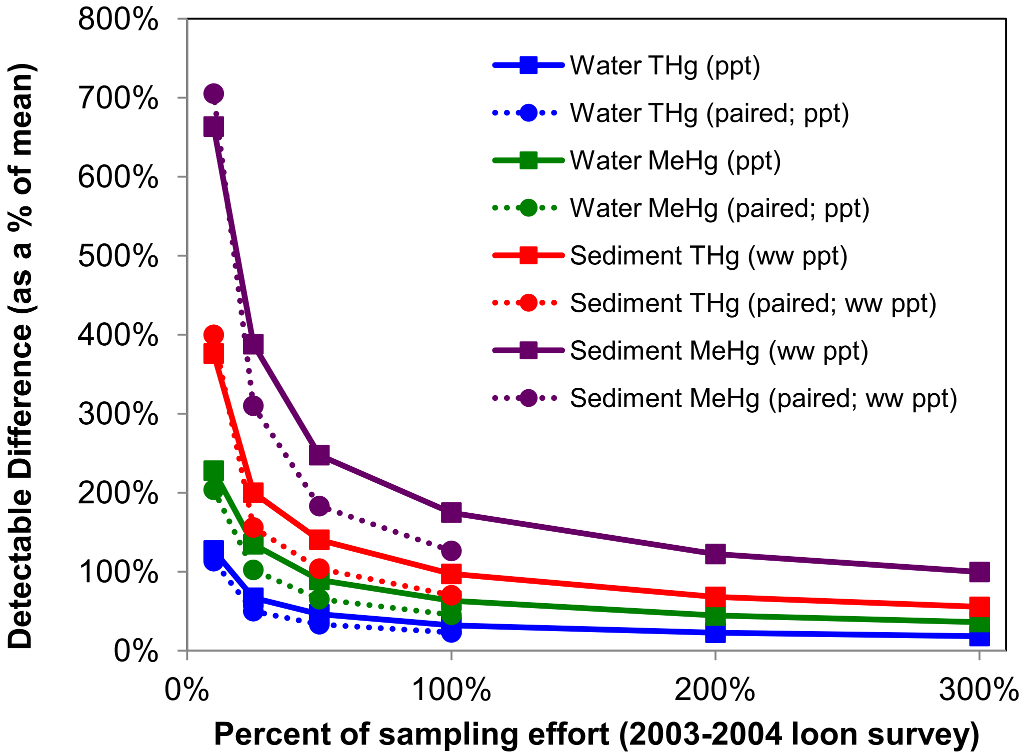


Figure 8.4. Detectable difference of surface water Hg concentrations as a percent of mean concentrations in Adirondack lakes sampled from 2003-2004.

### *8.2.3. Results: Detectable Difference of Surface Water Mercury Concentrations*

Based on the 2003-2005 study of surface water throughout New York, it was observed that by resampling the same set of 131 surface waters in the future, a 24 percent change in THg and a 9 percent change in MeHg (Figure 8.3) would be detectable. Based on the sample size and standard deviation of the data collected in the 2003-2004 survey of lake concentrations conducted to focus on loon habitat, tissue chemistry, and productivity, it was found that a resurvey of the original lakes would allow a difference of 23 percent to be detected in THg, a 45 percent difference in MeHg, a 70 percent difference in sediment THg, and a 126 percent difference in sediment MeHg (Figure 8.4).

### *8.2.4. Findings and Conclusions for Monitoring Mercury Concentrations in Surface Waters*

- Resampling the 2003-2005 survey conducted by Simonin et al. would be useful for detecting change in both fish and surface water Hg concentrations over the last decade, and would help refine current models of fish Hg concentrations. Efforts to resample some or all of the lakes included in the original study should be considered.
- Because the only long-term monitoring of surface water Hg concentrations is sporadic at Arbutus Lake, it may also be valuable to include regular monitoring at a subset of ALTM sites to assess seasonal variations in Hg monitoring and long-term trends. This would provide valuable in-depth information on trends in specific waters. Additional analysis of the datasets from Arbutus could also be undertaken to determine how long it would take to see a trend in lake Hg and to assess whether expanding monitoring would be worthwhile.

### *8.2.5 Status of Mercury Monitoring in Streams*

New York has had some long-term monitoring of stream water Hg concentrations in addition to some smaller-scale studies. Current methods, though costly, make it possible to measure THg and MeHg concentrations in streams with high accuracy.

The RIBS program measures THg concentrations routinely as part of its stream-monitoring program. However, these measurements are only occasionally above detection limits. For example, of data collected between 2001-2007, only 15 percent of measurements (409 of 2,764 samples) were above detection limits. The Hg method used by RIBS is not a very sensitive method, but the data set includes high Hg concentrations above the detection limit, which are valuable from a monitoring perspective.

Additional measurements of stream MeHg were conducted by the U.S. Geological Survey at Fishing Brook in the Adirondacks in the spring, summer, and fall of 2007-2009 (Bradley et al. 2011). Occasional measurements of stream Hg at Archer Creek have been taken as part of various research projects for about ten years.

### *8.2.6 Finding and Conclusions for Stream Mercury Monitoring*

- The RIBS program provides a large data set on THg concentrations in rivers as well as Hg concentrations in river invertebrates. This program has ample statewide coverage and the data are generally publicly available. In the future however, it may be difficult to detect changes in the long-term RIBS record because the majority of measurements are below detection limits.
- The RIBS program generally evaluates larger rivers and streams, and the majority of sampling sites are located in areas affected by human land use, such as agricultural or urban areas. Mercury in smaller streams or in stream invertebrate is less well studied but would be a valuable addition to future evaluations.

- There has been little effort to monitor stream waters or invertebrates in undisturbed, small streams in New York, or in the northeast U.S. in general. While some recent work has shown that fish in lakes respond rapidly to changes in rates of Hg deposition (Dittman and Driscoll 2009), it may not be possible to extrapolate these results to streams. Stream networks are different from lakes in that there is much less surface water area exposed to direct Hg deposition, so proportionally more of the Hg originates from the watershed soils (Doug Burns, USGS; pers. comm.). To continue researching the effects of Hg emissions policies in the U.S. and the relative roles of regional, national, and global emissions on local Hg deposition in places like the Adirondacks and Catskills, regular monitoring of Hg concentrations in surface waters as well as in aquatic biota is important.

### *8.2.7. Mercury in Aquatic Fauna*

Loon monitoring and 1998-2007 survey:

The Biodiversity Research Institute (BRI) has conducted long-term monitoring of loon tissue Hg concentrations since 1998. Results of the long-term monitoring program are detailed in NYSERDA report #12-06 (Schoch et al. 2012). In addition to regular summer monitoring of loons and water chemistry at 44 lakes in the Adirondacks, this project also conducted a study in 2003-2004 assessing Hg concentrations in loons, loon prey species such as fish and crayfish, lake sediments, and lake water chemistry.

A power analysis test was used to assess what change (as a percentage of the mean) would be detectable for Hg concentrations in loon prey (zooplankton and crayfish), yellow perch, and loon blood, feathers, and eggs (Figs. 8.4-8.7). Both a two-sample and paired test were conducted for each variable with a power of 0.8 and an alpha of 0.05. The sampling units for these analyses are lakes, not individuals.

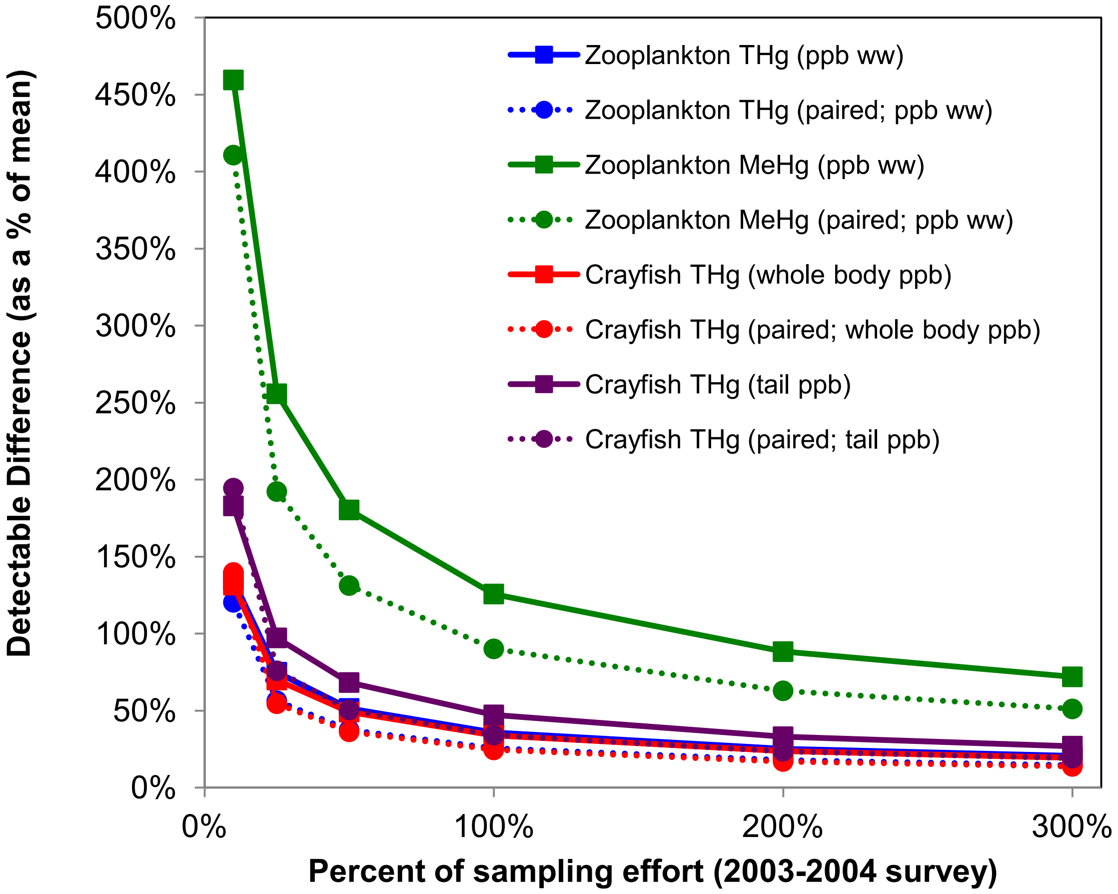


Figure 8.4. Detectable difference of zooplankton THg (n=40 lakes), zooplankton MeHg (n=38 lakes), crayfish THg (n=26 lakes), and crayfish THg (n=26 lakes).

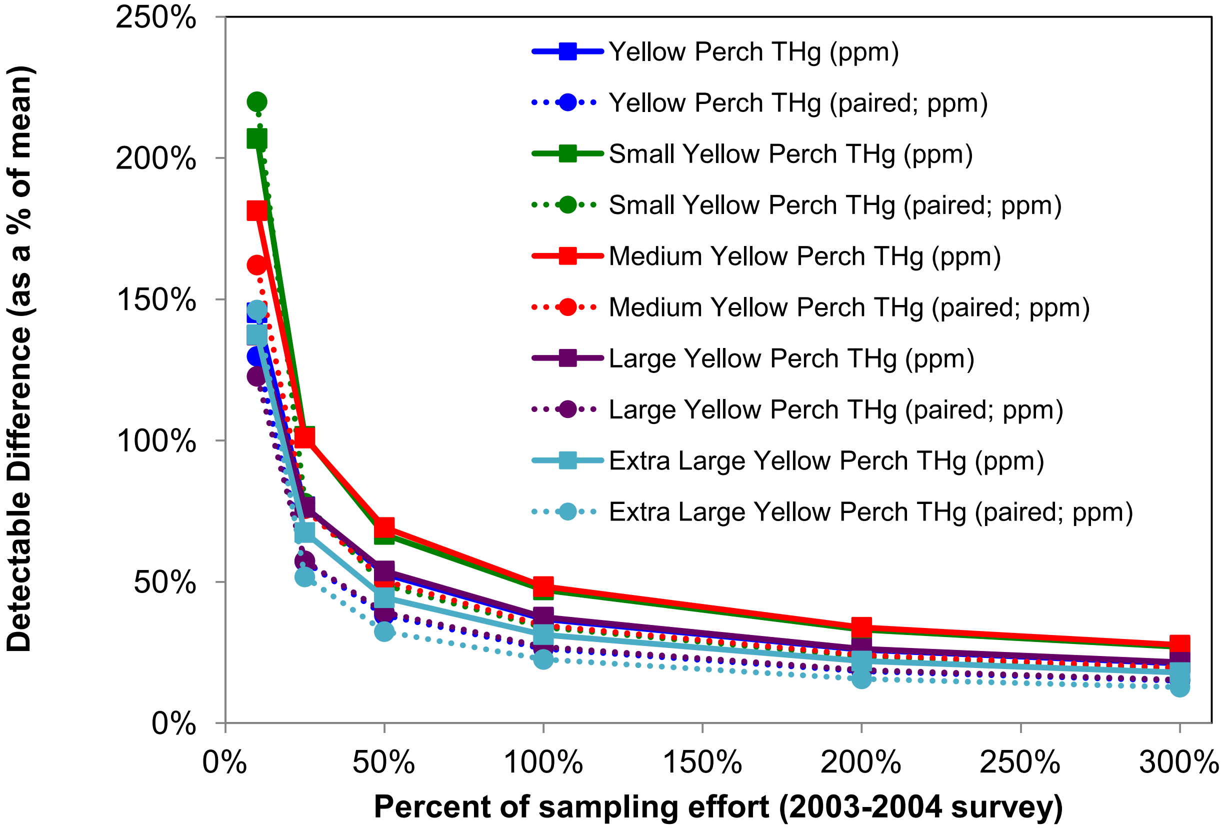


Figure 8.5. Detectable difference of yellow perch THg (n=44 lakes), and the THg of small yellow perch (n=33 lakes), medium yellow perch (n=40 lakes), large yellow perch (n=38 lakes), and extra large yellow perch (n=33 lakes).

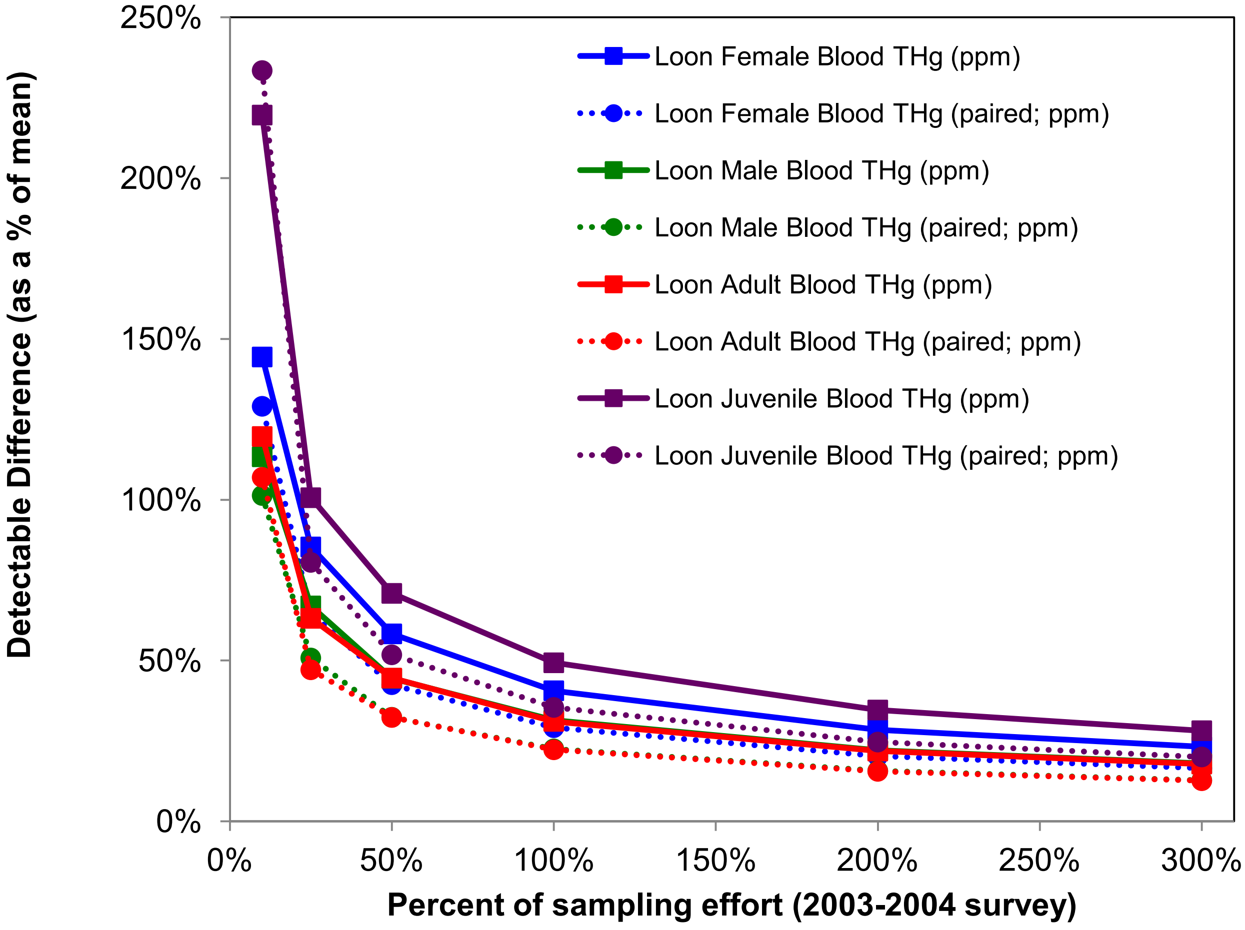


Figure 8.6. Detectable difference of loon female blood THg (n=36 lakes), male blood THg (n=37 lakes), adult (male and female combined) blood THg (n=42 lakes) and juvenile (male and female combined) blood THg (n=34 lakes).

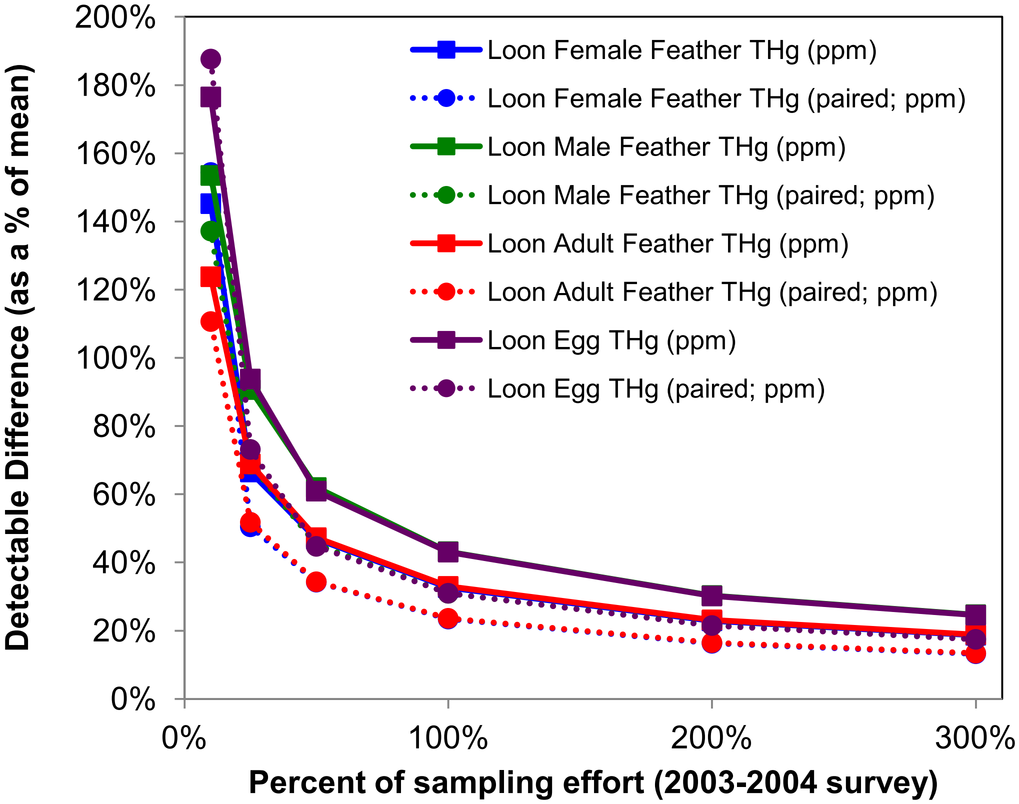


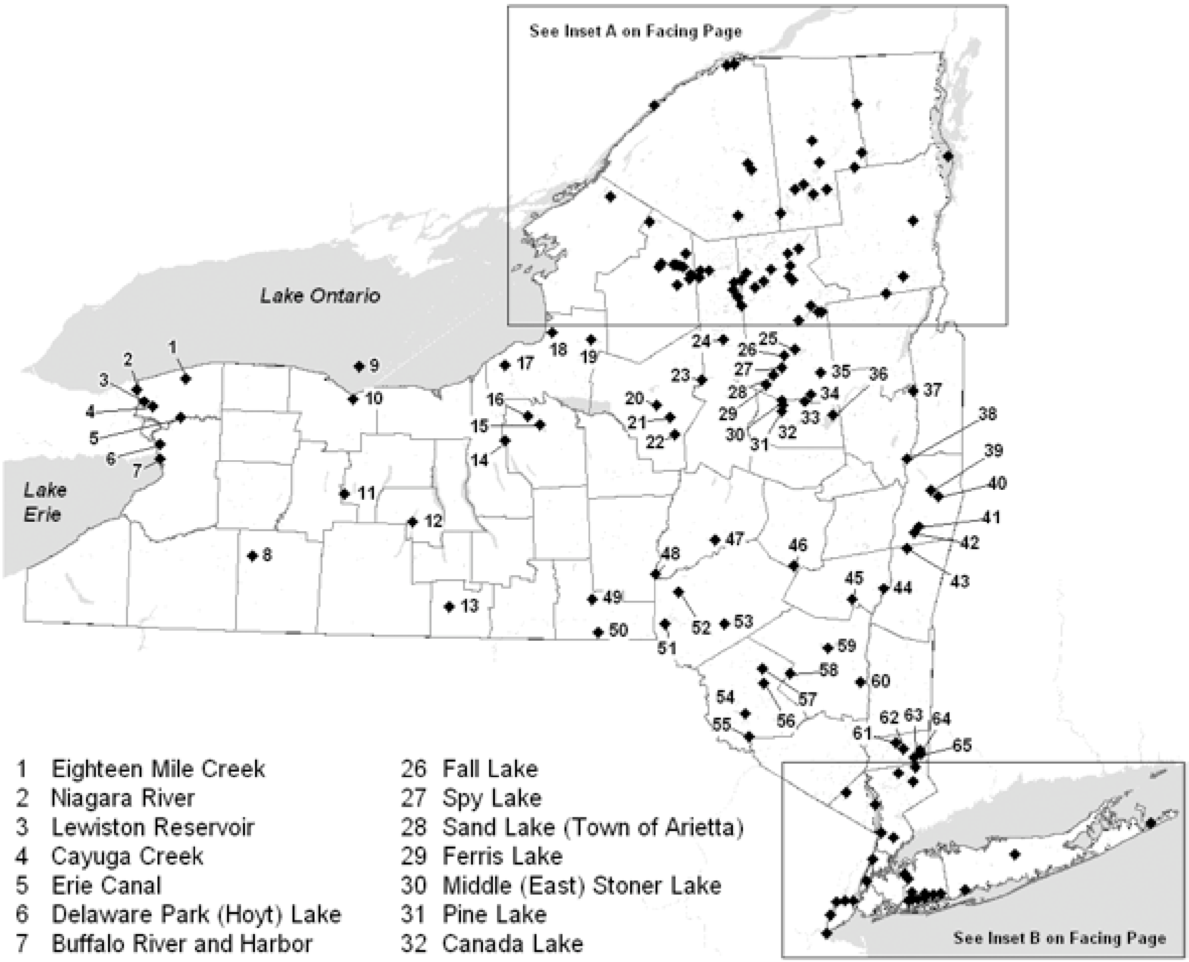
Figure 8.7. Detectable difference of loon female feather THg (n=34 lakes), male feather THg (n=36 lakes), adult (male and female combined) feather THg (n=40 lakes) and egg THg (n=29 lakes).

If the 2003-2004 loon survey were repeated, changes would be detectable if they were at least 26% in zooplankton THg, 90% in zooplankton MeHg, 24% in crayfish tissue THg, 34% in crayfish tail THg, 26% in yellow perch THg, 22% in adult loon blood THg, 35% in juvenile loon blood THg, 24% in adult loon feather THg, and 31% in loon egg THg.

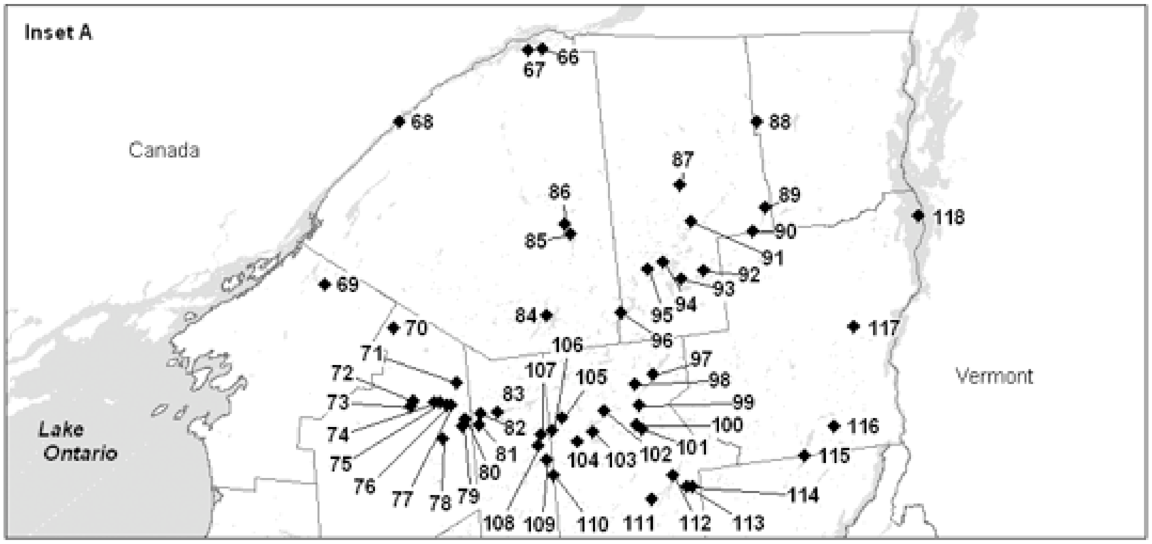
*Fish monitoring of mercury concentrations*:

Monitoring fish populations and health is an important area of research for the DEC due to ecological, recreational, and human health concerns. The DEC conducts annual surveys of fish populations along with associated water quality assessments in several creeks as well as a few associated lakes and ponds in cooperation with the New York State Department of Health. These data are used in the determination of fish consumption advisories that are provided to the public.

In addition to fish consumption advisories for particular water bodies, both the Adirondack and Catskill parks have park-wide fish consumption advisories as well. Additional fish monitoring has focused on Hg tissue concentrations and their relationship to water quality variables to help parameterize models of fish Hg concentrations based on water chemistry (Figure 8.8).



1 Eighteen Mile Creek
2 Niagara River
3 Lewiston Reservoir
4 Cayuga Creek
5 Erie Canal
6 Delaware Park (Hoyt) Lake
7 Buffalo River and Harbor
8 Rushford Lake
9 Lake Ontario
10 Irondequoit Bay
11 Canadice Lake
12 Keuka Lake
13 Koppers Pond
14 Skaneateles Creek
15 Onondaga Lake
16 Seneca River
17 Oswego River
18 Salmon River
19 Salmon River Reservoir
20 Threemile Creek
21 Mohawk River
22 Sauquoit Creek
23 Hinckley Reservoir
24 North Lake (Town of Ohio)
25 Sacandaga Lake
26 Fall Lake
27 Spy Lake
28 Sand Lake (Town of Arietta)
29 Ferris Lake
30 Middle (East) Stoner Lake
31 Pine Lake
32 Canada Lake
33 Chase Lake
34 Woods Lake
35 Willis Lake
36 Great Sacandaga Lake
37 Hudson River
38 Hoosic River
39 Dunham Reservoir
40 Dyken Pond
41 Valatie Kill
42 Nassau Lake
43 Kinderhook Lake
44 Hudson River
45 North-South Lake
46 Schoharie Reservoir
47 Goodyear Lake
48 Unadilla River
49 Chenango River
50 Susquehanna River
51 Cannonsville Reservoir
52 Herrick Hollow Creek
53 Pepacton Reservoir
54 Swinging Bridge Reservoir
55 Rio Reservoir
56 Loch Sheldrake
57 Neversink Reservoir
58 Rondout Reservoir
59 Ashokan Reservoir
60 Chodikee Lake
61 Boyds Corner Reservoir
62 West Branch Reservoir
63 Diverting Reservoir
64 Bog Brook Reservoir
65 East Branch Reservoir



66 Grasse River
67 Massena Power Canal
68 St. Lawrence River
69 Red Lake
70 Indian Lake (Fort Drum)
71 Long Pond (Croghan)
72 High Falls Pond
73 Beaver River
74 Elmer Falls Pond
75 Effley Falls Reservoir
76 Soft Maple Dam Pond
77 Soft Maple Reservoir
78 Halfmoon Lake
79 Francis Lake
80 Beaver Lake
81 Sunday Lake
82 Moshier Reservoir
83 Stillwater Reservoir
84 Cranberry Lake
85 Carry Falls Reservoir
86 Stark Falls Reservoir
87 Meacham Lake
88 Upper Chateaugay Lake
89 Union Falls Pond
90 Franklin Falls Pond
91 Osgood Pond
92 Lower Saranac Lake
93 Weller Pond
94 Polliwog Pond
95 Rollins Pond
96 Tupper Lake
97 Long Lake
98 Lake Eaton
99 South Pond
100 Blue Mountain Lake
101 Rock Pond & Lake Durant
102 Forked Lake
103 Raquette Lake
104 Brown Tract Ponds
105 Upper and Lower Sister Lakes
106 Russian Lake
107 Big Moose Lake
108 Dart Lake
109 Fourth Lake
110 Limekiln Lake
111 Lewey Lake
112 Indian Lake (Indian Lake)
113 Round Pond
114 Kings Flow
115 Schroon Lake
116 Crane Pond
117 Lincoln Pond
118 Lake Champlain

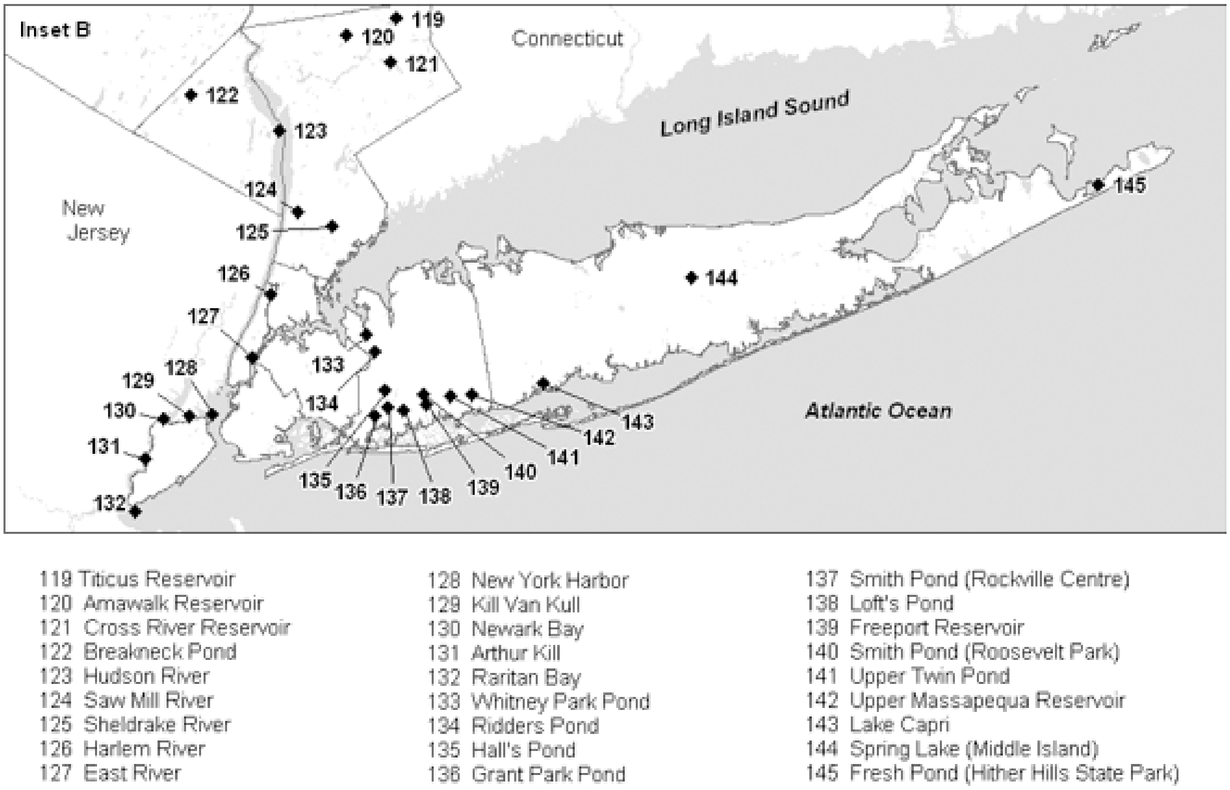


Figure 8.8. Guide to waters designated with fish consumption advisories by the NYS Department of Health. Specific consumption advisories by water body can be found on the NYS Department of Health website (http://www.health.ny.gov/environmental/outdoors/fish/health_advisories/regional/).

In addition to routine Hg monitoring of fish tissues, extensive surveys of water chemistry and watershed landscape characteristics have been completed to improve predictive models of fish Hg concentrations. One such survey was conducted in 131 lakes throughout the state in 2005 (Simonin et al. 2008). The survey used water concentrations and data on fish tissue concentration to develop models of Hg concentrations. These models are very useful because water chemistry can be monitored more easily than fish tissue chemistry, and can be used as predictor variables to assess which lakes may be in danger of having high Hg concentrations in fish.

The detectable change (as a percent of the mean) in fish Hg concentrations was determined using both a two-sample and paired test with a power of 0.8 and an alpha of 0.05

(Figures 8.9). The sample unit in this case was the lake. The sample size was different for each species and is specified in the figure caption. The predicted detectable differences depend on the accuracy and precision of the predictor models, which could change over time (Simonin et al. 2008).

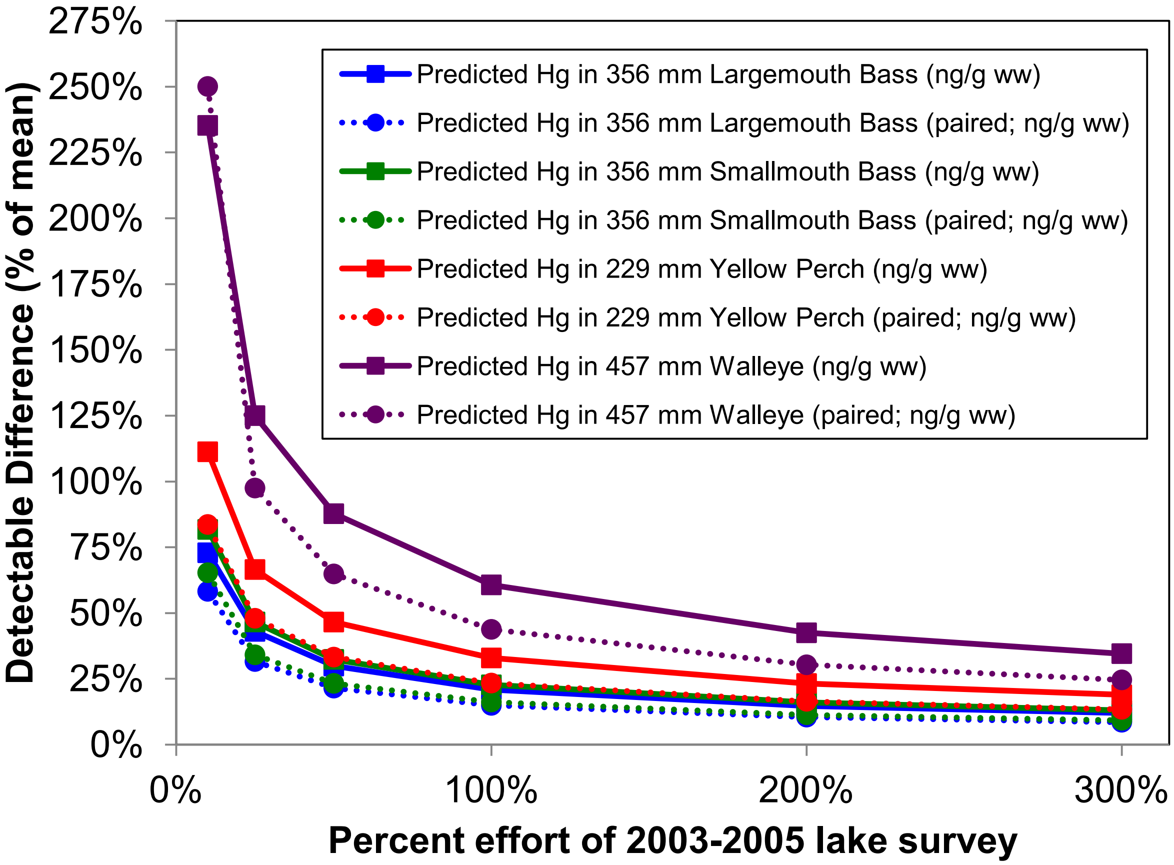


Figure 8.9. Detectable difference of modeled Hg tissue concentrations as a percent of mean concentrations in lakes sampled throughout New York (n=60 for largemouth bass, n=64 for smallmouth bass, n=103 for yellow perch, and n=26 for walleye).

Based on the variability of the modeled fish Hg concentrations and the predictor variables, in a future resampling changes would be statistically significant if they were at least 15 percent in largemouth bass, 16 percent in smallmouth bass, 23 percent in yellow perch, and 44 percent in walleye.

### *8.2.8 Findings and Conclusions for Monitoring Mercury in Aquatic Biota*

Wetlands are very important areas with regard to Hg cycling in ecosystems. There have been a small number of studies assessing Hg cycling through wetland food webs in New York, but there are no long-term monitoring programs addressing Hg deposition in wetlands. This may be an important area of research to explore in the future, as funding allows. It is important to note that this applies both to terrestrial and aquatic food webs and ecosystems.

<u>Invertebrates</u>:

- Measuring tissue concentrations of aquatic invertebrates is often used as an indicator for Hg concentrations in the substrate in which the organisms live as well as for studies of dynamics of Hg in food webs. A survey of aquatic invertebrates is currently included as a component of the statewide RIBS program. Aquatic invertebrates may be a suitable proxy for measuring water Hg concentrations, which are often so low that they cannot be detected.

<u>Aquatic birds</u>:

- In addition to their ecosystem functions, birds are important for food web studies because they are typically at high trophic levels. Current loon monitoring in the Adirondacks provides detailed information on effects of Hg on loon health and productivity and is a unique, valuable program that should be supported.

<u>Fish</u>:

- Due to human health implications with regard to fish consumption in New York, the DEC and NYS Department of Health regularly monitor fish populations and fish tissue contaminants. This program is executed within each DEC region, and thus has broad coverage throughout the state.

- Developing models of tissue concentrations based on easily measured variables, such as water chemistry, would make future fish monitoring programs more cost effective because monitoring fish tissues could be reduced to areas of concern.

## 8.3. Monitoring of Mercury in Terrestrial Systems

### *8.3.1. Status of Monitoring Mercury Effects on Vegetation*

Mercury concentrations in vegetation have not been systematically monitored at any site in New York. Mercury concentrations in vegetation have been involved in isolated studies of Hg cycling in forests, mainly in the Adirondack and Catskill Mountains. At Huntington Forest, permanent vegetation plots were established in conifer and hardwood forests, and Hg concentrations in litter inputs have been measured (Yu et al., in review). Additionally, a survey of Hg concentrations in forest floors and foliar inputs was conducted at 60 sites in the Adirondacks along an elevation gradient (Blackwell and Driscoll 2011).

### *8.3.2. Findings and Conclusions for Monitoring Mercury Effects on Vegetation*

- Monitoring concentrations of Hg in litterfall is a valuable activity because litterfall concentrations can be used as proxies for expensive measurements of THg deposition. Monitoring litterfall in coordination with other Hg deposition would provide valuable information on trends in deposition that could then be incorporated into models of total deposition for the state.
- Some research has shown that increased Hg levels may adversely affect seed germination, photosynthesis pathways, and cell division (Patra and Sharma, 2000.) Little is known about the effects of Hg deposition on plant health in northeast forests. This could be a focus of future research.

### *8.3.3. Status of Soil Mercury Monitoring*

Soils are often the largest pools of Hg in forest ecosystems and provides important input to the terrestrial food chain. Defining Hg concentrations in soils is needed to assess one essential vector of Hg into terrestrial food webs. Mercury concentrations in soils have not been systematically monitored at any site in New York, but there have been some isolated studies addressing Hg concentrations and processing in soils. Detailed soil data have been collected at Huntington Forest in both a conifer and hardwood plot (Blackwell and Driscoll 2009). Additional soil samples have been collected in the Adirondacks as part of a study on seasonal and spatial variations of Hg in the Fishing Brook Basin (Bradley et al. 2011). Forest floor samples were collected as part of one-time survey of 60 sites in the Adirondacks in a study linking forest floor Hg to Hg concentrations in foliar inputs (Blackwell and Driscoll 2011). Some work on Hg transformations in homogenized soils was done at Black Rock Forest to assess rates of Hg evasion (Anthony Carpi; John Jay College, CUNY). Additionally, data on soil Hg concentrations are being collected as part of a regional soil monitoring effort that includes the Adirondacks, the Catskills, and parts of New England (Charles Driscoll, Syracuse University).

### *8.3.4 Findings and Conclusions for Soil Mercury Monitoring*

- An enhanced monitoring program that measures soil Hg concentrations in addition to atmospheric deposition and stream water concentrations would provide insight into questions about Hg storage in watersheds. The MercNet program does not recommend any monitoring of soil Hg concentrations, but coupling soil and stream measurements in watersheds would allow for larger-scale ecosystem inferences to be made.
- As in the case of soil monitoring for acidic deposition, sampling soils with current technology requires a large number of samples and the longer the interval between sampling dates, the greater the likelihood of detecting change.

- Studies of Hg in soils have been done on a relatively small scale and mostly in the Catskills and Adirondacks. More work is needed to categorize soil Hg storage in other parts of the state. It would be of particular interest to investigate soil Hg levels in the Hudson Valley, as it appears that this part of the state receives Hg pollution inputs from sources that are different than those of the Catskill and Adirondack regions due to its proximity to New York City (Anthony Carpi; John Jay College, CUNY).

### *8.3.5 Terrestrial Bird Monitoring Surveys*

Monitoring tissue concentrations of Hg in songbirds and invertebrate bird prey species has been conducted over the last two to three years in paired upland and wetland plots in Bloomingdale Bog, Madawaska Flow, Massawepie Mire and Spring Pond Bog in the Adirondacks, as well as at some plots on Whiteface Mountain (Sauer et al. 2011). This recent intensive sampling could be considered baseline data for a future monitoring program. Additional surveys of songbird Hg concentrations have been conducted in the Hudson Valley at the Shawangunk Ridge (Amy Sauer, Syracuse University).

An additional survey of tissue concentrations of Hg in nestling and adult bald eagles was done throughout New York in 2006. Sampling in this study represented 53 percent of all occupied nesting territories and 69 percent of all territories fledging young statewide (DeSorbo et al. 2008). Blood and breast feathers were collected and analyzed for Hg.

### *8.3.6. Mercury Effects on Mammals*

Little work has been done on the effects of Hg deposition on mammal populations. Generally, studies of Hg effects on fauna are restricted to aquatic animals, but some semi-aquatic mammals may also be affected, particularly because they are top predators that consume other animals that are known MeHg vectors. One study was conducted on regional variation in total Hg in brain, liver, and fur from otter and mink collected across New York, New England, and

Nova Scotia (Yates et al. 2005). Otters were collected in New York in 1982-1985 and minks were collected from 1982-1991. Tissues collected at later dates were found to have significantly less Hg.

### *8.3.7. Findings and Conclusions for Mercury Monitoring of Terrestrial Fauna*

*Invertebrates:*

- Measuring tissue concentrations of Hg in terrestrial invertebrates can be used as an indicator for Hg concentrations in the substrate in which the organisms live as well as for studies of dynamics of Hg in food webs. There is currently no long-term monitoring of terrestrial invertebrates, though some collections have been included in other food web studies. Sporadic monitoring of Hg in terrestrial invertebrates could inform studies of a variety of other ecosystem components.

*Birds:*

- Surveys of song birds and birds of prey that have been done in the past could be re-implemented once every several years to track trends in deposition effects on bird populations and overall health throughout the state.

*Mammals:*

- Few studies of mammal tissue Hg concentrations or effects on mammal productivity have been carried out in New York. Mammals that spend large amounts of time in water bodies are exposed to high levels of MeHg in their diet and would be good candidates for a long-term monitoring project to assess effects of Hg deposition in higher trophic levels.

# 9. Integrated Monitoring Opportunities

Coordinating multiple long-term monitoring studies in a single site has many advantages. Information from co-located deposition collectors, streams, lakes, vegetation, soils, and fauna can all be integrated in statistical analyses and projection models of future climate and deposition scenarios to better quantify overall ecosystem response to changes in acid and Hg deposition rates. The establishment of integrated research sites distributed throughout the state would be of great benefit. These research sites could be based on plots or catchments. In sites underlain by impervious bedrock, for example some catchments in the Adirondacks and Catskills, hydrologic budgets can be determined based on measurements of atmospheric deposition and stream water export.

## 9.1 Routine Monitoring and Periodic Survey Activities

One approach for creating integrated forest monitoring sites in New York would be to have a statewide network with coordinated long-term monitoring protocols at each site. This would allow trends in different areas of the state to be directly compared. Logistically, this would likely involve two tiers of monitoring activities: routine monitoring and periodic survey activities. Routine monitoring would include monitoring of atmospheric deposition, stream chemistry and export, and lake monitoring. These are activities that would need to be carried out continuously each year. They could be carried out by a state or federal agency such as the DEC or the USGS, and in many cases these are measurements that are already being collected under other monitoring programs and would not require additional funds. Suggested monitoring protocols for routine monitoring activities include:

- *Atmospheric deposition:* Sites should include both wet and dry acidic deposition and wet Hg deposition monitoring. Integrating this program under the umbrella of the NADP

NTN and MDN networks would be useful due to the consistent collection and measurement protocols of these programs and the fact that this information would be useful at a regional scale as well as at a local scale. Additional measurements of total Hg deposition as well as air concentrations of Hg would be informative, but due to their expense, may not be feasible at all sites. Rather, some intensive monitoring at specific sites may be used to allow for the development of integrated models for the State.

- *Surface water monitoring:* Monitoring gauged streams allows solute export and thus ecosystem chemistry budgets to be calculated, so locating research watersheds in sites where gauges are already present would be beneficial. In some cases, such as watersheds in the Hudson Valley and in central New York, the porous shale bedrock prevents calculation of hydrologic budgets, and estimating export may not be a research priority. If estimating hydrologic budgets is not a research priority, then simply measuring stream chemistry biweekly or monthly (See Figures. 4.7-4.8) would be sufficient. Lake monitoring may not be necessary or appropriate at all designated research sites. In the Adirondacks, lakes are an important feature of the forested ecosystems, and lake processes have historically been used to assess the environmental impact of acidic and Hg deposition. In other areas (Catskills, Hudson Valley, Central NY, Long Island), lakes are less prevalent, but monitoring of other surface waters (e.g. ponds, reservoirs) may be desirable due to their implications for human health.

Periodic survey activities such as vegetation, soils, and biological monitoring would not need to be administered every year. These studies could be carried out by participating universities and research institutes if a long-term commitment to the project could be reasonably assured. Suggested monitoring protocols for occasional monitoring activities include:

- *Vegetation:* Large-scale dynamics can be characterized using vegetation surveys. These surveys should include the monitoring of tree and sapling diameter and density, and also height if desired, as well as surveys for seedlings and herbaceous plants. Vegetation surveys could be conducted on five or ten-year intervals and still provide valuable information (Section 5.2). In some cases, FIA may already be monitoring nearby sites and these data could be used instead. Additional field collections may include foliar chemistry, litterfall mass and chemistry, throughfall collections, woody debris, seed and fruit production, regeneration dynamics, and crown condition ratings. Field collections of leaves, litter, and seeds could be scheduled for two to four years in a row, with five to ten years elapsed between collections. This would allow interannual variation to be accounted for in testing for long-term trends. The sampling interval may depend on interest or funding and need not be consistent.
- *Soils:* Some sites have already had preliminary soils data collected in past surveys. In those cases, soils should be re-sampled following the methods used in the original survey. Soils that have not been surveyed previously would need to be surveyed for initial measurements. Because of the high degree of spatial heterogeneity in mineral soils, it is often difficult to detect significant changes over short periods of time. Thus, these surveys can be re-sampled at longer intervals than most other monitoring activities. It

might be reasonable to resurvey forest floor soils more frequently than mineral soils, as a smaller change is more likely to be detectable.

- *Fauna:* Focal fauna for collection will differ depending on the site. For example, songbirds that are present in the Adirondacks may not be present at other monitoring sites in the state. If direct comparisons between research sites across the state are desired, species that are common to all sites could be the focal fauna for long-term monitoring. Candidate species may include ubiquitous macroinvertebrate species (crayfish, spiders) or vertebrates such redbacked salamanders or a variety of *Lithobates* species that have ranges throughout New York.

### 9.2 Candidate Sites

Ecosystem studies should be established in sensitive areas in New York, including at least the Adirondacks and the Catskills. The Hudson Valley/Hudson Highlands, and central New York near Ithaca, should also be considered. The issue of land ownership complicates the selection process. Long-term access to private land can be uncertain, while state policy limits what research equipment can be deployed on public lands. There are several places that already have some coordinated ecosystem studies that could be expanded to long-term monitoring studies. In the Adirondacks, Buck Creek and Huntington Forest both have long histories of deposition; stream, lake, vegetation, and soil monitoring would provide a good foundation for an integrated monitoring program.

In the Catskills, Biscuit Brook has a long history of monitoring, though it may not be an ideal site due to its large size and the fact that the watershed includes private lands that may be difficult to monitor continuously. Hollow Tree Brook and Hunter Brook may also be considered.

Both sites have a history of stream chemistry monitoring, and Hollow Tree Brook is already gauged. Additionally, Rondout Creek has a gauge, a history of chemistry data, and extensive work on vegetation and biogeochemical processes. Working at this site would require negotiations with landowners, but they historically have been cooperative (Gary Lovett, Cary Institute of Ecosystem Studies; pers. comm.). The Catskill Research Consortium is interested in investing in a research site and should be included in this discussion.

In the Hudson Valley/Hudson Highlands, there are two sites that are well suited to be expanded into integrated studies. The first is at the Cary Institute, where stream chemistry, vegetation, and deposition have been monitored extensively, and the strong research ethic of the Institute and its collaborations with nearby colleges could provide the interest and labor for continued monitoring. An additional site is Black Rock Forest, where considerable monitoring of deposition and forest ecosystem processes has been carried out. There is a defunct MDN site nearby at West Point where monitoring could be resumed, which would add information on Hg trends at that site.

A possible site in central New York is the Connecticut Hill Wildlife Management Area near Ithaca, where researchers at Cornell have set up small-scale vegetation and soil surveys, current deposition monitoring, and a one-time stream chemistry survey.

If resources allow, other sites could be considered in the future. A site on Long Island could be coordinated with current air monitoring sites, and planned activities include a possible NADP MDN site for monitoring of wet deposition of Hg, as well as some monitoring of Hg in shore birds.

This program is very ambitious, but there is a high level of interest to establish a network of integrated research sites. The first step in moving forward with this approach would be to convene a small group of stakeholders and state representatives to discuss the scope of the network and the proposed schedule of regular monitoring and occasional surveys. It would be possible for each integrated study site to be administered separately, but structuring the studies as a network and coordinating research efforts would make the data more useful in the future.

Table 9.1. Current and past monitoring and surveys at candidate watersheds for integrated monitoring programs. Blank cells in this table indicate that there are no historical or current monitoring activities in that particular category. Details of the monitoring programs listed here are outlined in the compendium document accompanying this report.

| | **Adirondacks** | | **Catskills** | | **Hudson Valley/Hudson Highlands** | | |
|---|---|---|---|---|---|---|---|
| | **Huntington** | **Buck Creek and Moss Lake** | **Biscuit Brook** | **Hollow Tree Brook/ Hunter Brook/ Rondout?** | **Cary Inst.** | **Black Rock Forest** | **Connecticut Hill** |
| **Acidic deposition** | Both wet deposition (NTN site) and CASTNet sampler for dry S and N | Nicks Lake DEC deposition site is 15 km away (wet only). Moss Lake has NTN site (wet only) | NTN site; nearby CASTNet site | | Wet and dry deposition, AMoN | NTN site at West Point, (wet only) | Aurora NTN site nearby and AIRMoN site (both wet only; CASTNet site (dry); AIRMoN for event sampling), AMoN |
| **Hg deposition** | Wet deposition: long-term MDN site (longest record in the state). Dry deposition: Tekran for dry Hg | No deposition collector, but extensive Hg cycling data (Driscoll et al.) | Long-term MDN site (second-longest record in the state) | | | Wet dep: Formerly an MDN site at West Point, could be resumed. Some research on dry dep. using surrogate surfaces in 2006-2008 | |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Streams** | Gauge on Archer Creek and long-term chem data | Gauge and long-term record of two minor branches and the major branch of Buck Creek | Gauge on Biscuit Brook and long-term chem data | Gauge and long-term chem. Data on Hollow Tree Brook and Rondout Creek, sporadic measurements on Hunter Brook | Gauge and long-term chem data | Gauge and chemistry at Cascade Brook | 1-time stream chemistry survey (Goodale) |
| **Lakes** | Arbutus lakes inlet and outlet records, surface chemistry from ALSC | Long-term monitoring of Moss Lake | Not applicable | Not applicable | Not applicable | Not applicable | Not applicable |
| **Vegetation** | There have been extensive measurements done at the Huntington Forest on vegetation including permanent vegetation plots | Some vegetation plots established (McNeil 2003 foliar N survey, Lawrence sugar maple study plots) | Permanent vegetation plots | Permanent vegetation plots | Permanent vegetation plots | Permanent vegetation plots | Long-term monitoring at nearby Arnot Forest |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Soils** | There has been extensive work on soils at the Huntington Forest | Newton et al. 1987, Sullivan et al. 2003 | Repeated soil sampling in some plots (Lovett et al.) Some Hg work (Burns et al.) | Repeated soil sampling in a network of plots (Lovett et al.) | Permanent long-term monitoring plots | | Some quantitative soil pits, some organic matter studies (Goodale) |
| **Fauna** | Extensive information on faunal components (see http://www.esf.edu/aec/research/ALTEMP.htm) | Fisheries and plankton studies, no long-term monitoring. Loon monitoring | | | Extensive long-term studies of birds, small mammals, deer, and some insects | | |

# 10. Appendix

## 10.1. Atmospheric Deposition

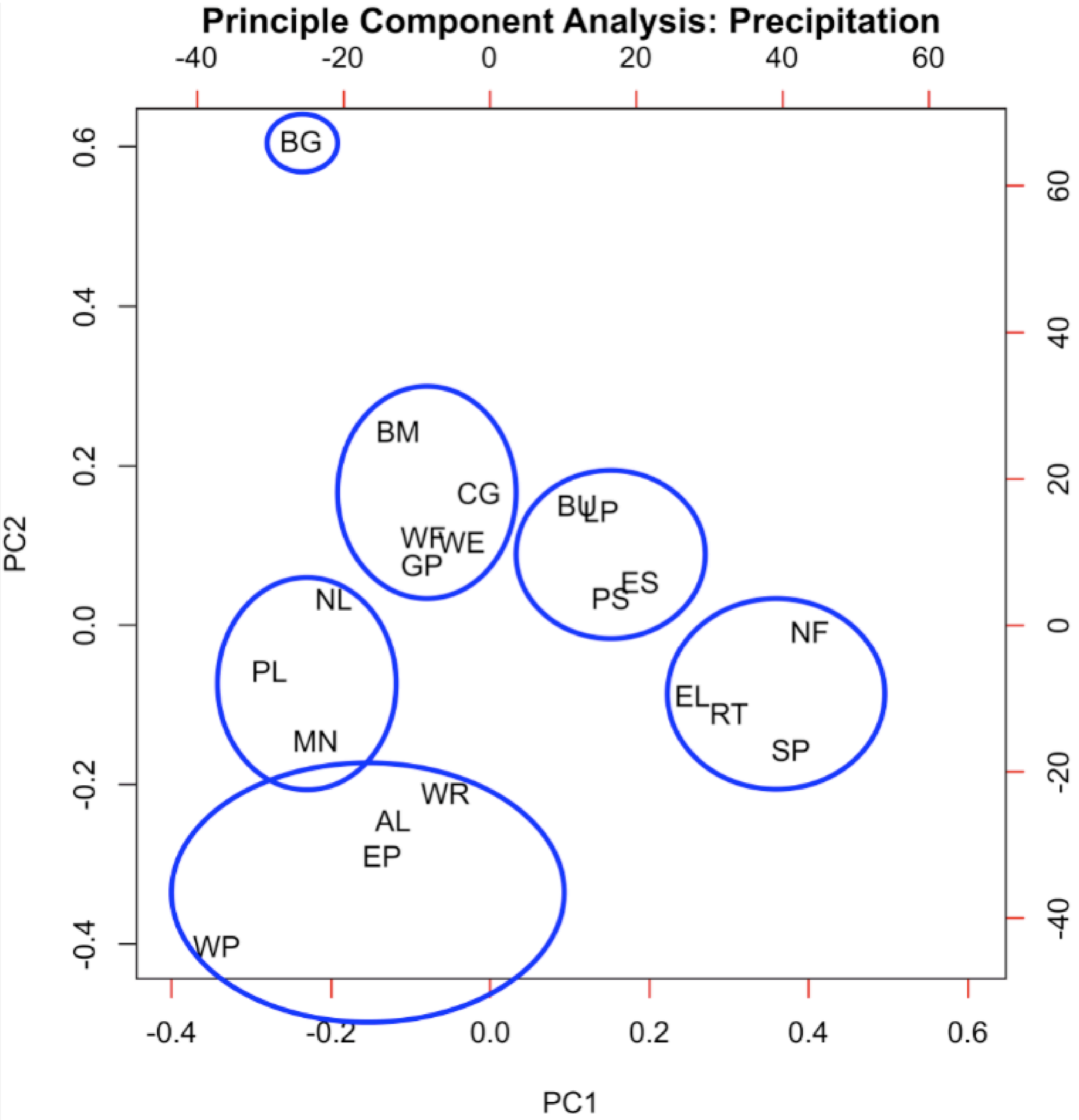


**Figure 10.1.1. PCA analysis of showing groupings by annual precipitation amount (mm yr$^{-1}$).**

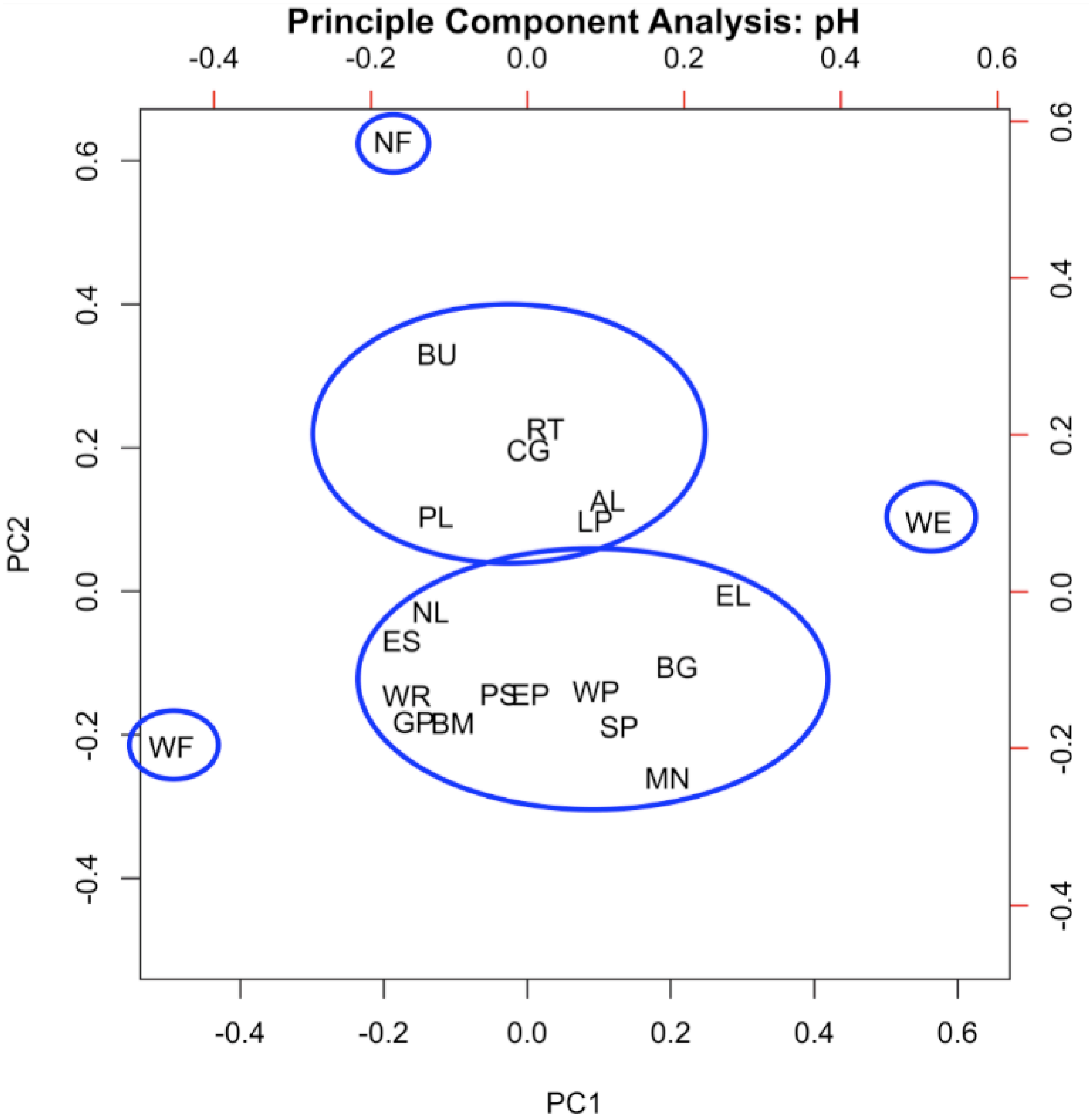


Figure 10.1.2. PCA analysis of showing groupings by annual averages of $H^+$ (μmol $L^{-1}$ $yr^{-1}$).

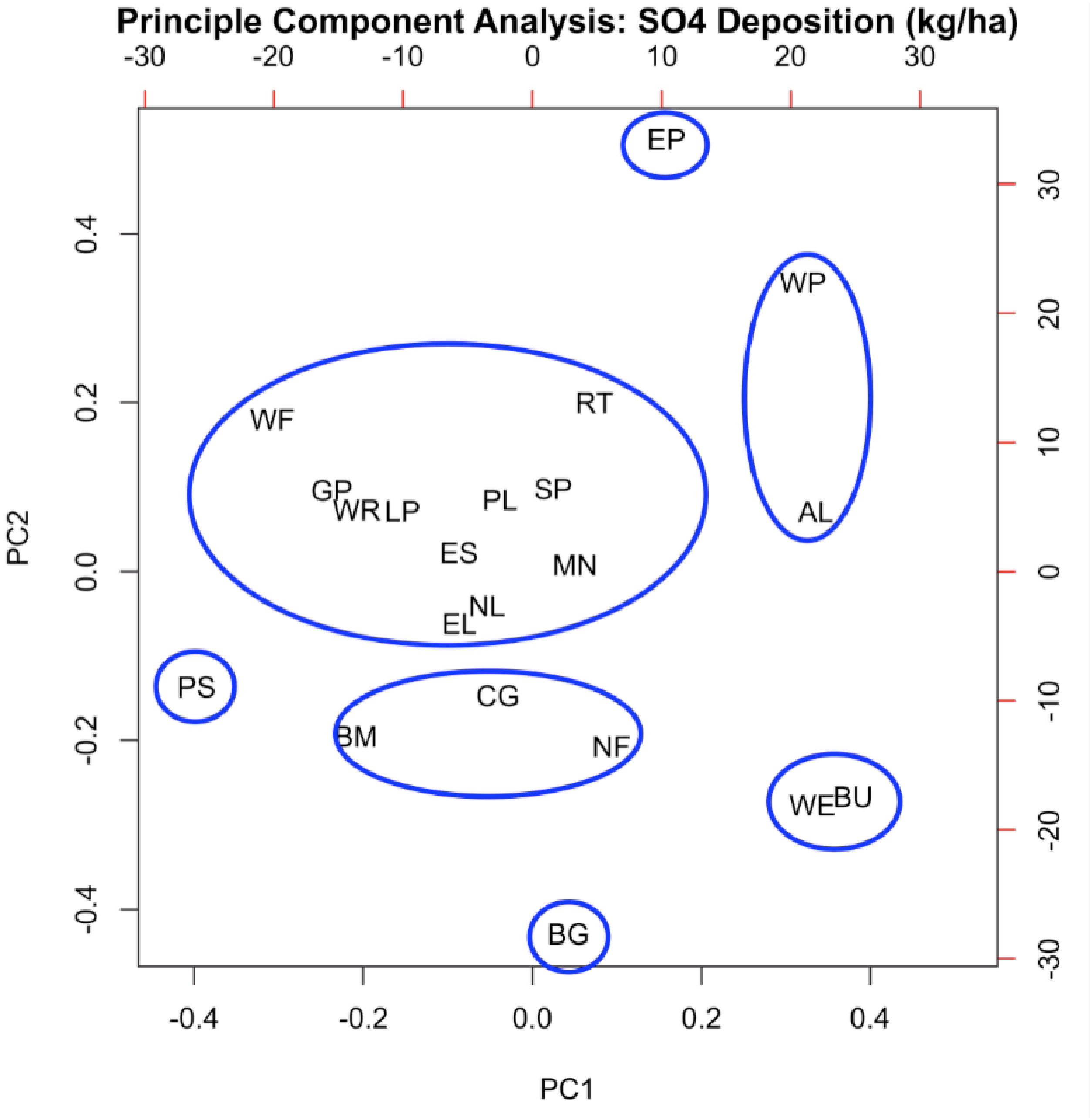


Figure 10.1.3. PCA analysis of showing groupings by annual deposition of $SO_4$ (kg $ha^{-1}$ $yr^{-1}$).

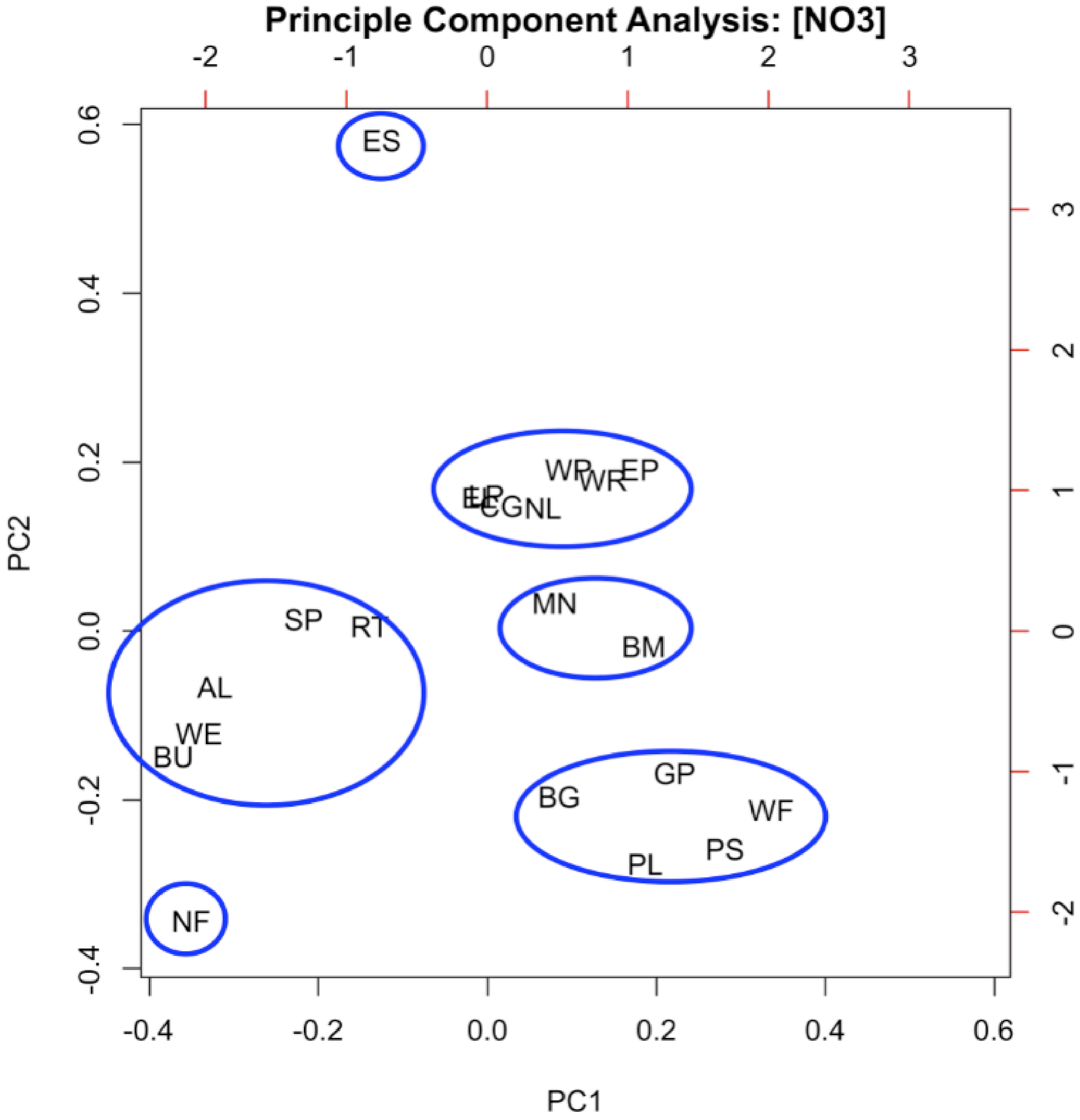


Figure 10.1.4. PCA analysis of showing groupings by annual average concentrations of $NO_3$ (mg $L^{-1}$ $yr^{-1}$).

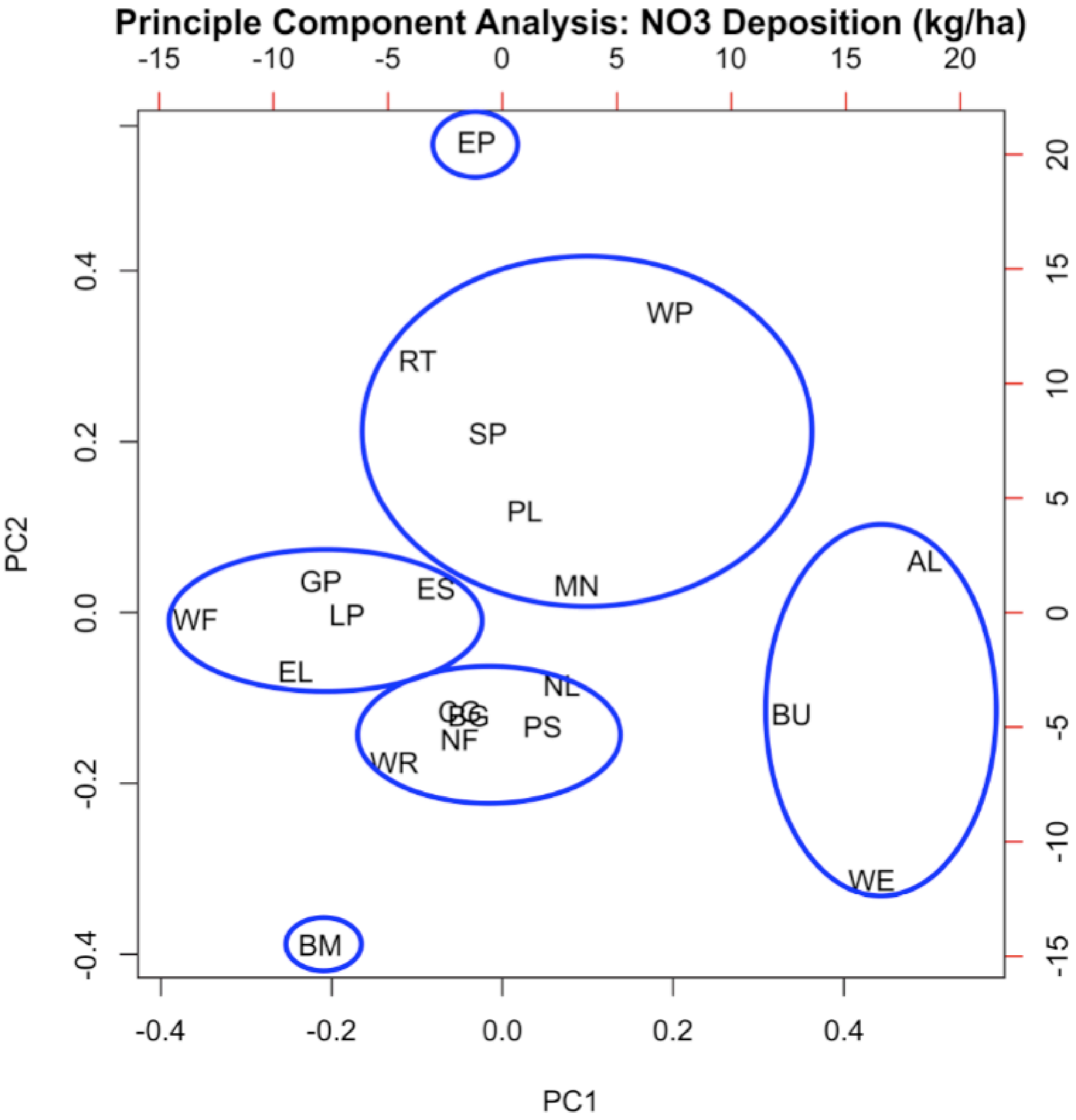


Figure 10.1.5. PCA analysis of showing groupings by annual deposition of $NO_3$ (kg $ha^{-1}$ $yr^{-1}$).

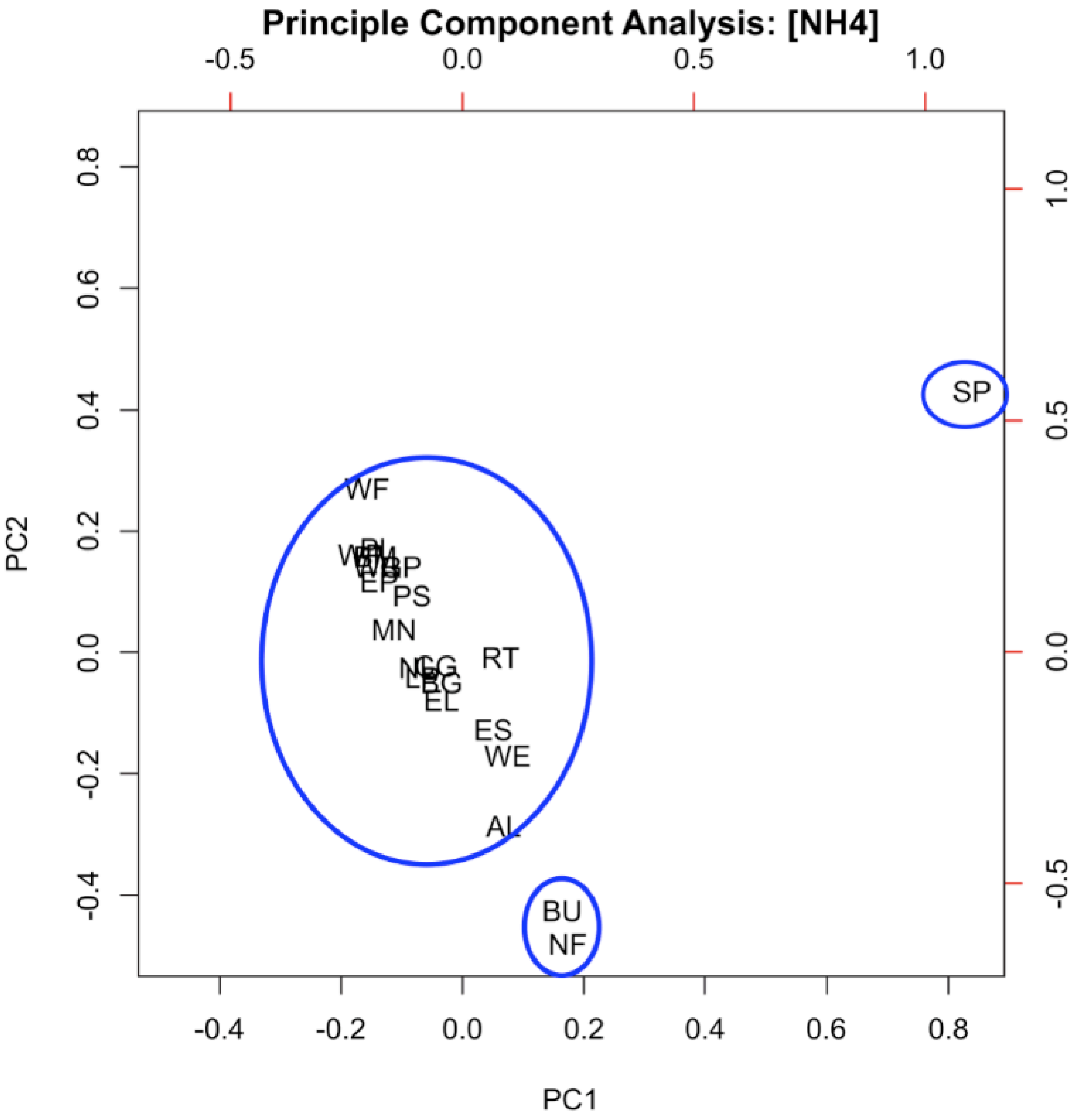


Figure 10.1.6. PCA analysis of showing groupings by annual average concentrations of $NH_4$ (mg $L^{-1}$ $yr^{-1}$).

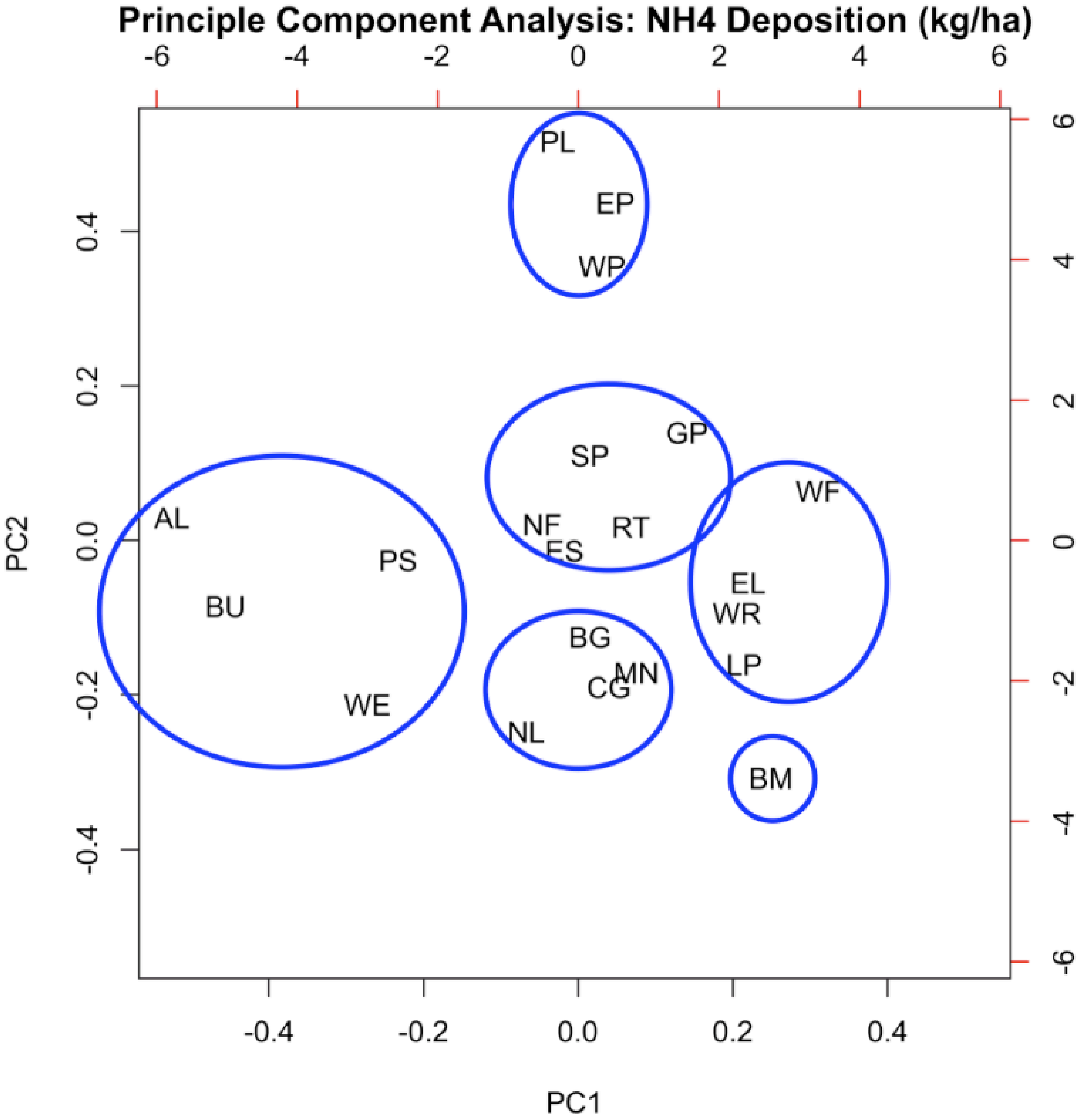


Figure 10.1.7. PCA analysis of showing groupings by annual deposition of $NH_4$ (kg $ha^{-1}$ $yr^{-1}$).

## 10.2 Lakes

Table 10.2.1. Season Kendall tau for ANC (ueq $L^{-1}$), $H^+$, and concentrations of $SO_4$, $NO_3$, $NH_4$, $Ca^{2+}$ (mg $L^{-1}$) in ALTM lakes (1992-2010). Only significant trends are shown. Gray cells indicate non-significant trends.

| | $SO_4$ (mg $L^{-1}$) | $NO_3$ (mg $L^{-1}$) | $NH_4$ (mg $L^{-1}$) | $Ca^{2+}$ (mg $L^{-1}$) | ANC (ueq $L^{-1}$) | $H^+$ (umol $L^{-1}$) |
|---|---|---|---|---|---|---|
| **Arbutus Lake** | -0.673 | -0.369 | -0.154 | -0.416 | | -0.16 |
| **Avalanche Lake** | -0.677 | -0.0968 | -0.176 | -0.461 | 0.456 | 0.343 |
| **Barnes Lake** | -0.419 | -0.228 | -0.369 | -0.763 | -0.367 | -0.522 |
| **Big Hope Pond** | -0.721 | -0.142 | -0.26 | 0.211 | 0.642 | 0.482 |
| **Big Moose Lake** | -0.824 | -0.611 | -0.18 | -0.552 | 0.579 | 0.488 |
| **Black Pond Outlet** | -0.796 | -0.164 | | -0.364 | 0.138 | |
| **Brook Trout Lake** | -0.856 | -0.328 | 0.055 | -0.645 | 0.402 | 0.324 |
| **Bubb Lake** | -0.691 | -0.244 | -0.174 | -0.508 | 0.131 | 0.134 |
| **Carry Pond** | -0.667 | -0.158 | | -0.421 | 0.568 | 0.547 |
| **Cascade Lake Outlet** | -0.645 | -0.346 | | -0.292 | 0.103 | |
| **Clear Pond** | -0.776 | | -0.19 | -0.525 | | |
| **Constable Pond** | -0.788 | -0.558 | -0.186 | -0.597 | 0.345 | 0.191 |
| **Dart Lake** | -0.824 | -0.616 | | -0.552 | 0.65 | 0.472 |
| **East Copperas Pond** | -0.465 | -0.12 | 0.12 | -0.232 | 0.268 | 0.113 |
| **G Lake** | -0.752 | -0.145 | -0.175 | -0.447 | 0.348 | 0.286 |
| **Grass Pond (030171)** | -0.672 | -0.121 | | -0.173 | 0.19 | 0.155 |
| **Grass Pond (040706)** | -0.777 | | | -0.557 | 0.147 | |
| **Heart Lake** | -0.758 | -0.2 | -0.23 | -0.569 | 0.593 | 0.482 |
| **Indian Lake** | -0.831 | -0.2 | -0.23 | -0.569 | 0.593 | 0.482 |
| **Jockeybush Lake** | -0.679 | | | -0.425 | 0.528 | 0.378 |
| **Lake Colden** | -0.81 | -0.599 | -0.0967 | -0.343 | 0.334 | 0.164 |
| **Lake Rondaxe** | -0.848 | -0.491 | | -0.445 | 0.562 | 0.483 |
| **Lime Kiln Lake** | -0.744 | | | | | |
| **Little Clear Pond** | -0.585 | | | -0.014 | 0.504 | 0.49 |
| **Little Echo Pond** | -0.731 | -0.183 | -0.157 | -0.25 | 0.482 | 0.453 |
| **Little Hope Pond** | -0.752 | -0.313 | | -0.134 | 0.19 | 0.161 |
| **Little Simon Pond** | -0.677 | -0.178 | 0.107 | -0.212 | 0.434 | 0.367 |
| **Long Pond** | -0.601 | -0.43 | -0.267 | -0.612 | 0.407 | 0.319 |
| **Loon Hollow Pond** | -0.457 | -0.294 | | -0.468 | 0.145 | |
| **Lost Pond** | -0.719 | | | -0.27 | 0.205 | 0.142 |
| **Marcy Dam Pond** | -0.689 | -0.36 | -0.104 | -0.318 | 0.146 | 0.108 |
| **Middle Branch Lake** | -0.614 | -0.147 | | -0.273 | 0.13 | |
| **Middle Pond** | -0.767 | -0.347 | -0.189 | -0.32 | 0.432 | 0.4 |
| **Middle Settlement Lake** | -0.753 | -0.464 | -0.145 | -0.443 | 0.215 | 0.109 |
| **Moss Lake** | -0.736 | -0.174 | | -0.392 | | |
| **Nate Pond** | -0.72 | -0.451 | -0.102 | -0.545 | 0.437 | 0.275 |
| **North Lake** | -0.762 | -0.152 | 0.144 | -0.495 | 0.398 | 0.278 |
| **Otter Lake Outlet** | -0.757 | 0.167 | -0.136 | -0.366 | 0.156 | 0.0719 |
| **Owen Pond** | -0.849 | -0.554 | -0.205 | -0.507 | 0.616 | 0.578 |
| **Raquette Lake Reservoir** | -0.751 | -0.459 | | -0.551 | 0.176 | |
| **Sagamore Lake** | -0.757 | -0.393 | | -0.477 | 0.196 | |
| **Sochia Pond** | -0.669 | -0.142 | | | 0.535 | 0.428 |
| **South Lake** | -0.813 | -0.542 | | -0.479 | 0.528 | 0.509 |

| | | | | | | |
|---|---|---|---|---|---|---|
| **Squash Pond** | -0.637 | -0.208 | | -0.487 | 0.413 | 0.379 |
| **Squaw Lake** | -0.835 | -0.413 | -0.145 | -0.709 | 0.462 | 0.263 |
| **Sunday Pond** | -0.368 | -0.184 | -0.145 | -0.608 | | -0.31 |
| **West Pond** | -0.601 | -0.322 | | -0.466 | 0.235 | |
| **Willis Lake** | -0.581 | | | | 0.193 | |
| **Willys Lake** | -0.846 | -0.596 | | -0.791 | 0.519 | 0.439 |
| **Windfall Pond** | -0.766 | -0.248 | -0.126 | -0.265 | 0.195 | 0.193 |
| **Woods Lake** | -0.755 | -0.301 | 0.179 | -0.651 | | |

Table 10.2.2. Slope of trend lines for $SO_4$, $NO_3$, $NH_4$, Ca, ANC, and $H^+$ in ALTM lakes (1992-2010).

| | $SO_4$ (μeq $L^{-1}$ $yr^{-1}$) | $NO_3$ (μeq $L^{-1}$ $yr^{-1}$) | $NH_4$ (μeq $L^{-1}$ $yr^{-1}$) | Ca (μeq $L^{-1}$ $yr^{-1}$) | ANC (μeq $L^{-1}$ $yr^{-1}$) | $H^+$ (meq $L^{-1}$ $yr^{-1}$) |
|---|---|---|---|---|---|---|
| **Arbutus Lake** | -2.4044 | -0.2303 | -0.0349 | -1.4303 | 0.0556 | -8.7376 |
| **Avalanche Lake** | -2.9238 | -0.0848 | -0.0543 | -1.1654 | 0.7625 | 77.2586 |
| **Barnes Lake** | -1.0288 | -0.1539 | -0.3741 | -1.7655 | -0.7097 | 145.7980 |
| **Big Hope Pond** | -2.3946 | -0.1268 | -0.1024 | 0.2862 | 1.8856 | -20.5508 |
| **Big Moose Lake** | -2.9337 | -0.9490 | -0.0566 | -1.0662 | 1.1180 | -23.7037 |
| **Black Pond Outlet** | -2.3953 | -0.1691 | -0.0052 | -1.5489 | 0.7366 | -3.0513 |
| **Brook Trout Lake** | -2.8713 | -0.5393 | 0.0185 | -1.0645 | 0.9172 | -9.1423 |
| **Bubb Lake** | -2.0037 | -0.2664 | -0.0677 | -1.1415 | 0.3763 | -2.7813 |
| **Carry Pond** | -2.7307 | -0.1537 | 0.1248 | -0.6694 | 1.5921 | 54.5593 |
| **Cascade Lake Outlet** | -1.9064 | -0.4819 | -0.0016 | -1.3870 | 0.8070 | -2.8641 |
| **Clear Pond** | -2.4820 | -0.0026 | -0.0396 | -1.9236 | -0.0866 | -1.5400 |
| **Constable Pond** | -3.3519 | -0.9633 | -0.0603 | -1.5496 | 0.9975 | -188.5846 |
| **Dart Lake** | -2.9033 | -0.8264 | -0.0112 | -1.1923 | 1.2538 | -5.5700 |
| **East Copperas Pond** | -1.3239 | -0.0788 | 0.3032 | -0.2073 | 0.5296 | -81.0847 |
| **G Lake** | -2.2006 | -0.3041 | -0.0586 | -0.9147 | 0.8231 | 146.9385 |
| **Grass Pond (030171)** | -0.6784 | -0.0257 | 0.0381 | -0.2020 | 0.2628 | -56.6931 |
| **Grass Pond (040706)** | 0.0088 | -0.0338 | 0.0514 | 0.0918 | 0.4522 | 52.3519 |
| **Heart Lake** | -2.0957 | -0.1390 | -0.0032 | -1.6682 | 0.4566 | -16.4966 |
| **Indian Lake** | -3.1116 | -0.7448 | -0.0058 | -1.5513 | 0.8548 | 55.4790 |
| **Jockeybush Lake** | -2.3474 | -0.2513 | -0.0649 | -0.9231 | 0.8530 | 32.9232 |
| **Lake Colden** | -2.6227 | -0.1446 | -0.0358 | -1.0965 | 0.7304 | 73.1014 |
| **Lake Rondaxe** | -2.5428 | -0.7728 | -0.0466 | -1.1319 | 1.4607 | -5.3529 |
| **Lime Kiln Lake** | -2.6987 | -0.4802 | -0.0150 | -0.9871 | 1.3158 | 1.1949 |
| **Little Clear Pond** | -1.3034 | -0.2103 | 0.1442 | 2.4802 | 4.6735 | -606.2961 |
| **Little Echo Pond** | -1.2585 | -0.0865 | 0.1107 | -0.0992 | 1.1129 | -297.5192 |
| **Little Hope Pond** | -2.7877 | -0.1215 | -0.0848 | -0.5484 | 1.7870 | -83.8440 |
| **Little Simon Pond** | -2.5915 | -0.5496 | -0.0175 | -0.5508 | 1.3724 | 120.1555 |
| **Long Pond** | -2.9337 | -0.0975 | 0.0184 | -0.4442 | 1.2333 | -58.5326 |
| **Loon Hollow Pond** | -2.2364 | -0.7386 | -0.1978 | -0.6470 | 0.9902 | 137.9250 |
| **Lost Pond** | -1.4988 | -0.9667 | -0.1578 | -1.3897 | 0.4600 | -61.2182 |
| **Marcy Dam Pond** | -1.9368 | 0.3787 | -0.0153 | -0.8101 | 0.5179 | 42.6394 |
| **Middle Branch Lake** | -1.6037 | -0.3083 | -0.0450 | -0.7391 | 0.6176 | 11.2503 |
| **Middle Pond** | -2.0949 | -0.1426 | -0.0871 | -0.7798 | 1.0373 | -6.9533 |
| **Middle Settlement Lake** | -1.9581 | -0.2627 | -0.0954 | -0.3604 | 1.0581 | 59.6731 |
| **Moss Lake** | -2.1535 | -0.6553 | -0.0325 | -1.3680 | 0.6917 | 1.6589 |
| **Nate Pond** | -2.7010 | -0.2136 | -0.0048 | -1.2302 | 0.3081 | 21.9488 |
| **North Lake** | -2.4356 | -0.9439 | -0.0429 | -1.1698 | 0.9968 | -38.9972 |
| **Otter Lake Outlet** | -2.5018 | -0.1260 | 0.0187 | -0.9899 | 0.7172 | -123.3930 |
| **Owen Pond** | -3.7778 | 0.2874 | -0.0527 | -1.7619 | 1.1921 | -4.2713 |
| **Raquette Lake Reservoir** | -4.0264 | -0.6291 | 0.0209 | -2.6590 | 0.1897 | -123.9081 |
| **Sagamore Lake** | -2.5999 | -0.6467 | -0.0616 | -0.9162 | 1.1038 | 46.4287 |

|  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|
| **Sochia Pond** | -1.1650 | -0.0857 | 0.0989 | -0.0471 | 1.2563 | -245.9031 |
| **South Lake** | -2.1033 | -1.0488 | -0.0244 | -0.7132 | 1.1749 | -64.1246 |
| **Squash Pond** | -2.3307 | -0.1953 | -0.0082 | -0.6565 | 0.7709 | 10.4373 |
| **Squaw Lake** | -3.2979 | -0.5119 | -0.0257 | -1.8487 | 0.8291 | 24.7007 |
| **Sunday Pond** | -0.6548 | -0.1412 | -0.0995 | -0.7784 | 0.0694 | 39.8066 |
| **West Pond** | -2.5755 | -0.2838 | -0.0152 | -1.3335 | 0.4771 | -161.6912 |
| **Willis Lake** | -1.9322 | -0.0100 | -0.0287 | -0.1410 | 1.2085 | -9.0650 |
| **Willys Lake** | -3.2873 | -1.3893 | -0.0154 | -1.4797 | 0.8515 | 27.8756 |
| **Windfall Pond** | -3.1565 | -0.4582 | -0.0315 | -1.9181 | 0.6030 | -10.7316 |
| **Woods Lake** | -3.6325 | -0.4513 | 0.0505 | -3.5861 | -0.6516 | 1.5198 |
|  |  |  |  |  |  |  |
| Min | -4.0264 | -1.3893 | -0.3741 | -3.5861 | -0.7097 | -606.2961 |
| 25th q. | -2.8295 | -0.5893 | -0.0576 | -1.4100 | 0.4975 | -47.8451 |
| Median | -2.4044 | -0.2513 | -0.0257 | -1.0645 | 0.8291 | -3.0513 |
| 75th q | -1.9474 | -0.1264 | -0.0024 | -0.6517 | 1.1465 | 36.3649 |
| Max | 0.0088 | 0.3787 | 0.3032 | 2.4802 | 4.6735 | 146.9385 |
|  |  |  |  |  |  |  |
| Avg. | -2.3231 | -0.3633 | -0.0232 | -0.9940 | 0.8646 | -22.2937 |

Table 10.2.3. The standard error of the slope for $SO_4$, $NO_3$, $NH_4$, Ca, ANC, and $H^+$ in ALTM lakes (1992-2010).

| | SO4 (μeq L-1 yr-1) | NO3 (μeq L-1 yr-1) | NH4 (μeq L-1 yr-1) | Ca (μeq L-1 yr-1) | ANC (μeq L$^{-1}$ yr$^{-1}$) | H+ (meq L-1 yr-1) |
|---|---|---|---|---|---|---|
| **Arbutus Lake** | 0.2952 | 0.2922 | 0.0037 | 0.0667 | 0.1470 | 0.0043 |
| **Avalanche Lake** | 0.4171 | 0.9867 | 0.0102 | 0.0550 | 0.0911 | 0.0811 |
| **Barnes Lake** | 0.1839 | 0.1670 | 0.0196 | 0.0307 | 0.0967 | 0.0503 |
| **Big Hope Pond** | 0.2635 | 0.2069 | 0.0094 | 0.0692 | 0.1585 | 0.0132 |
| **Big Moose Lake** | 0.2248 | 0.3717 | 0.0053 | 0.0322 | 0.0791 | 0.0745 |
| **Black Pond Outlet** | 0.1788 | 0.2966 | 0.0075 | 0.0832 | 0.2987 | 0.0010 |
| **Brook Trout Lake** | 0.2118 | 0.3953 | 0.0104 | 0.0313 | 0.1385 | 0.0781 |
| **Bubb Lake** | 0.1799 | 0.3600 | 0.0071 | 0.0359 | 0.1249 | 0.0169 |
| **Carry Pond** | 0.2798 | 0.2019 | 0.0272 | 0.0325 | 0.0982 | 0.0563 |
| **Cascade Lake Outlet** | 0.2972 | 0.4911 | 0.0037 | 0.1254 | 0.5848 | 0.0077 |
| **Clear Pond** | 0.2141 | 0.2177 | 0.0037 | 0.0664 | 0.1367 | 0.0014 |
| **Constable Pond** | 0.2838 | 0.5566 | 0.0045 | 0.0433 | 0.1813 | 0.0958 |
| **Dart Lake** | 0.1958 | 0.3111 | 0.0052 | 0.0292 | 0.0789 | 0.0403 |
| **East Copperas Pond** | 0.2370 | 0.1437 | 0.0452 | 0.0365 | 0.1587 | 0.1519 |
| **G Lake** | 0.2642 | 0.7635 | 0.0057 | 0.0327 | 0.1396 | 0.0642 |
| **Grass Pond (030171)** | 0.2581 | 0.2493 | 0.0295 | 0.0249 | 0.1329 | 0.0886 |
| **Grass Pond (040706)** | 0.3380 | 0.8059 | 0.0091 | 0.0660 | 0.2406 | 0.0559 |
| **Heart Lake** | 0.3736 | 0.3441 | 0.0059 | 0.0813 | 0.1407 | 0.0064 |
| **Indian Lake** | 0.3645 | 0.6884 | 0.0062 | 0.0400 | 0.0926 | 0.0669 |
| **Jockeybush Lake** | 0.1946 | 0.6555 | 0.0060 | 0.0285 | 0.0596 | 0.0505 |
| **Lake Colden** | 0.3477 | 0.9320 | 0.0071 | 0.0572 | 0.0629 | 0.0518 |
| **Lake Rondaxe** | 0.1820 | 0.3703 | 0.0073 | 0.0852 | 0.2626 | 0.0160 |
| **Lime Kiln Lake** | 0.3382 | 0.3060 | 0.0035 | 0.0645 | 0.1076 | 0.0189 |
| **Little Clear Pond** | 0.1874 | 0.3392 | 0.0470 | 0.1901 | 0.7053 | 0.1014 |
| **Little Echo Pond** | 0.1815 | 0.1195 | 0.0281 | 0.0384 | 0.1114 | 0.1260 |
| **Little Hope Pond** | 0.3231 | 0.2152 | 0.0128 | 0.0688 | 0.1751 | 0.0591 |
| **Little Simon Pond** | 0.3035 | 0.5026 | 0.0041 | 0.1601 | 0.4036 | 0.0418 |
| **Long Pond** | 0.3661 | 0.1233 | 0.0135 | 0.0492 | 0.1612 | 0.1663 |
| **Loon Hollow Pond** | 0.2674 | 0.4900 | 0.0185 | 0.0156 | 0.1292 | 0.0871 |
| **Lost Pond** | 0.4318 | 1.0882 | 0.0277 | 0.0643 | 0.2630 | 0.0814 |
| **Marcy Dam Pond** | 0.2393 | 0.6326 | 0.0046 | 0.0806 | 0.2349 | 0.0352 |
| **Middle Branch Lake** | 0.1958 | 0.3188 | 0.0077 | 0.0480 | 0.2141 | 0.0226 |
| **Middle Pond** | 0.2761 | 0.2164 | 0.0209 | 0.0845 | 0.3184 | 0.0038 |
| **Middle Settlement Lake** | 0.1829 | 0.2908 | 0.0196 | 0.0305 | 0.1322 | 0.0465 |
| **Moss Lake** | 0.1613 | 0.3544 | 0.0030 | 0.0510 | 0.1966 | 0.0117 |
| **Nate Pond** | 0.3080 | 0.4607 | 0.0060 | 0.0697 | 0.2342 | 0.0074 |
| **North Lake** | 0.3065 | 0.7036 | 0.0046 | 0.0346 | 0.1281 | 0.0738 |
| **Otter Lake Outlet** | 0.1893 | 0.4423 | 0.0024 | 0.0283 | 0.1014 | 0.0394 |
| **Owen Pond** | 0.4188 | 0.6468 | 0.0069 | 0.1221 | 0.4120 | 0.0024 |
| **Raquette Lake Reservoir** | 0.5608 | 0.6050 | 0.0056 | 0.0857 | 0.4383 | 0.0891 |

|  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|
| **Sagamore Lake** | 0.1685 | 0.2938 | 0.0059 | 0.0318 | 0.0754 | 0.0328 |
| **Sochia Pond** | 0.1475 | 0.1622 | 0.0345 | 0.0188 | 0.0882 | 0.1032 |
| **South Lake** | 0.1913 | 0.6162 | 0.0066 | 0.0466 | 0.1381 | 0.0799 |
| **Squash Pond** | 0.3103 | 0.5299 | 0.0127 | 0.0243 | 0.0806 | 0.1013 |
| **Squaw Lake** | 0.2570 | 0.3827 | 0.0060 | 0.0378 | 0.0791 | 0.0225 |
| **Sunday Pond** | 0.1843 | 0.1309 | 0.0083 | 0.0241 | 0.0475 | 0.0406 |
| **West Pond** | 0.3336 | 0.2695 | 0.0091 | 0.0424 | 0.1112 | 0.0946 |
| **Willis Lake** | 0.4900 | 0.1203 | 0.0062 | 0.1189 | 0.2798 | 0.0179 |
| **Willys Lake** | 0.2076 | 0.5073 | 0.0074 | 0.0227 | 0.0954 | 0.0675 |
| **Windfall Pond** | 0.3098 | 0.6590 | 0.0063 | 0.1437 | 0.3612 | 0.0111 |
| **Woods Lake** | 0.5172 | 0.6244 | 0.0043 | 0.1143 | 0.2587 | 0.0180 |
| Min | 0.1475 | 0.1195 | 0.0024 | 0.0156 | 0.0475 | 0.0010 |
| 25th q. | 0.1929 | 0.2594 | 0.0054 | 0.0320 | 0.0974 | 0.0174 |
| Median | 0.2642 | 0.3703 | 0.0071 | 0.0480 | 0.1385 | 0.0503 |
| 75th q | 0.3284 | 0.6106 | 0.0127 | 0.0751 | 0.2377 | 0.0805 |
| Max | 0.5608 | 1.0882 | 0.0470 | 0.1901 | 0.7053 | 0.1663 |
| Avg. | 0.2773 | 0.4306 | 0.0114 | 0.0601 | 0.1880 | 0.0525 |

Table 10.2.4. Sampling Groups for AEAP lake visits. Note that the sites accessed by helicopter represent 19 percent of sampling effort.

| **Visitation Group** | **Lakes included in Visitation Group** |
|---|---|
| **1** | Jockeybush, G |
| **2** | North, South |
| **3** | Moss, Cascade, Dart |
| **4** | Limekiln, Big Moose |
| **5** | Round, Wheeler |
| **6** | Sagamore, Rondaxe |
| **7** | Brooktrout, Squaw, Indian (note: lakes accessed by helicopter) |

## 10.3 Mercury Deposition

Table 10.3.1. Trends in Hg deposition at MDN sites in New York. There were no significant trends.

|  | Years Active | Mann Kendall tau | Mann Kendall p-value | Slope (ng Hg $m^{-2}$ $yr^{-1}$) | SE (ng Hg $m^{-2}$ $yr^{-1}$) |
|---|---|---|---|---|---|
| Bronx | 2008-present | -0.0192 | 0.69 | 0.95 | 10.22 |
| Biscuit | 2004-present | 0.0145 | 0.67 | -3.88 | 4.44 |
| Huntington | 1999-present | -0.0113 | 0.68 | -0.22 | 1.68 |
| Rochester | 2008-present | 0.000442 | 0.99 | 4.64 | 10.52 |
| West Point | 2006-2010 | -0.0369 | 0.45 | -4.44 | 11.14 |

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# Assessment of Long-Term Monitoring of Nitrogen, Sulfur, and Mercury Deposition and Environmental Effects in New York State

Final Report
August 2012

**State of New York**
Andrew M. Cuomo, Governor

**New York State Energy Research and Development Authority**
Francis J. Murray, Jr., President and CEO