

# State of New Hampshire

## Inter-Department Communication

**Date:** July 17, 2003

**From:** Phil Trowbridge  
Coastal Scientist

**At (Office):** Environmental Services  
Watershed Management

**Subject:** Power Analysis for the Acid Lake Outlet Monitoring Program

**To:** Bob Estabrook, Chief Aquatic Biologist  
Gregg Comstock, Supervisor, Water Quality Planning Section

### Introduction

The DES Acid Lake Outlet Monitoring Program has collected yearly data at 46 lake outlets across New Hampshire for 20 years. The Program would like to analyze the data from these stations to determine if there have been any significant trends over time. In addition, the Watershed Management Bureau is developing a Comprehensive Monitoring Strategy, which would include any changes to the acid lake outlet monitoring design in order to increase statistical power.

For this report, the acid lake outlet data from 1983 to 2002 have been reviewed to determine the power for detecting trends given the variability in each parameter. This information will identify parameters for which there is sufficient power to detect trends with the existing dataset (and, conversely, parameters with insufficient power). The power analyses can also be used to optimize the sampling design for detecting trends. Recommendations for changes to the sampling design will be considered as part of the Comprehensive Monitoring Strategy.

### Project Goals and Objectives

The objectives for this project are:

- Calculate descriptive statistics for parameters measured by the Acid Lake Outlet Monitoring Program.
- Predict the power for detecting important trends in each parameter given the variability documented in the first objective.
- Determine whether there are any significant trends for the 20 lakes that have been monitored twice per year.
- Draw conclusions and make recommendations.

### Methods

#### *Software*

All calculations were performed using SYSTAT version 10 statistical software and Crystal Ball 2000 Monte Carlo simulation software.

#### *Data Handling*

The data were handled in the following way.

- Obtained data for acid lake outlets. The data used for this study were the twice yearly measurements at 20 acid lake outlet ponds plus yearly measurements at 26 remote ponds from 1983 to 2002.

- Eliminated parameters for which >30% of the results were censored (Al, NO<sub>3</sub>, Cl). Censored data can throw off statistics and misrepresent the variability in the parameter.
- Eliminated other parameters with minimal records because sampling only began in 2000 (Mg, Na, K).
- Eliminated color as a parameter of interest because it is best used as covariate.
- Converted 44 “below detection limit”(BDL) censored values for calcium to 0.5 mg/l (a lower value than the rest of the calcium values in the dataset). Converted 3 BDL censored values for sulfate to 0.25 mg/l (a lower value than the rest of the sulfate values in the dataset).
- The following parameters were retained: pH, alkalinity, conductivity, calcium, and sulfate.

#### *Calculation of Descriptive Statistics*

- Calculated the average statistics for each parameter. For predicting the power to detect trends over time at a single station, the variability of interest is the intra-annual variability at each station. However, with only one or two measurements at each station per year, it is impossible to calculate a standard deviation for each lake for each year. Therefore, all the data from each lake over the 20 year period were used to calculate the mean and standard deviation for each parameter. This approach will overestimate the variability within years because it will include the variability associated with any trends over time. The inflated variability will make the predictions of minimum detectable trends higher than what could, in fact, be detected.
- The basic statistics were calculated from the raw data using the by groups command for LAKES\$ in SYSTAT. This command generated a table of sample size, mean, and standard deviations for each lake. Between 9 and 40 measurements were used to calculate the statistics for each lake. The statistics from all 46 lakes were averaged for each parameter to derive a central tendency estimate of the mean value and standard deviation for each parameter at a typical lake.
- Determined the distribution type for each parameter based on shape of histograms and size of the coefficient of variability. Parameters were either considered to be normal or lognormal. In general, if the coefficient of variability ( $CV = \text{stdev}/\text{mean}$ ) was >0.3, the parameter was assumed to be lognormal. For pH, conductivity, calcium, and sulfate, the CV was less than 0.2 so these parameters were considered to be normally distributed. The CV for alkalinity was close to 0.3 so a lognormal distribution may be more appropriate for this parameter. However, alkalinity can have both negative and positive values and lognormal distributions cannot have negative values. Therefore, alkalinity was assumed to be normally distributed as well.

#### *Definitions of parameters for power calculations*

- Determined trend analysis methods for study. Samples are collected one or two times during the year at the lake stations. The trends are not expected to be linear. Therefore, the appropriate test for trends is the non-parametric Mann-Kendall Test (MKT) using the median of the samples collected during the year.
- Determined the magnitude of “important trends”. In order to test for power, a trend of known magnitude must be specified and tested. After consulting with the program manager, it was decided that a change of 10% over 10 years would be the minimum trend of interest for pH (equivalent to a 300% change in hydrogen ion concentrations). For the other parameters, a 50% increase of the parameter over 10 years was chosen arbitrarily as the trend worth being able to detect.
- Determined period for trend detection. Five, 10, and 20 year periods were selected for the trend analysis. The power for detecting trends over 20 years will be indicative of which parameters should be analyzed for trends using the existing 20 year record. Detecting trends over a 5-10 year period is preferable for management purposes because it would be important to detect trends leading toward a water quality violation before a violation actually occurs.

### *Power Calculations*

- Statistical power was calculated using Monte Carlo simulations and the definitions of the MKT and SKT from Gilbert (1987). The central tendency mean and standard deviation of the concentration for each parameter was used to simulate a distribution of possible results. Five, 10, and 20 year records of sampling results were generated by randomly sampling from this distribution with a linear trend superimposed. The MKT and SKT statistical tests were run on the simulated records. The simulation was run 500 times for each parameter. The fraction of the simulations that predicted a significant (i.e.,  $p < 0.05$ , one tail or  $p < 0.10$ , two tails) trend represented the power for detecting that trend given the variability within the data.

### *Trend Analysis*

- To verify the results of the power analyses, the 20 year datasets for the 20 lakes that have been sampled twice per year were analyzed for trends using the MKT following procedures from Gilbert (1987). The two samples from each year were averaged to derive a central tendency value for each year. Trends were considered significant for  $p < 0.05$  (one tail) or  $p < 0.10$  (two tails). The slope of the trend was calculated using the Sen Slope Estimator (Gilbert, 1987) and then compared to the predicted minimum detectable slope from power analyses for a 20 year dataset.

## Results and Discussion

### *Data Handling*

Of the 12 parameters monitored at the acid lake outlets, only 5 met all the data handling criteria for this analysis. Three of the parameters listed below could not be analyzed because most of their results were listed as “below detection level”.

- Aluminum (513 out of 1164 qualified, 44%)
- Nitrate (710 out of 971 qualified, 73%)
- Chloride (525 out of 921 qualified, 57%)

### *Descriptive Statistics*

The descriptive statistics for the 5 parameters analyzed for this study are listed in Table 1.

**Table 1: Average mean value and standard deviation for each parameter in each lake.**

Parameter	Units	Number of lakes	Mean of Mean values	Mean of Standard Deviation values	Coefficient of Variation	Distribution Type
PH	Unitless	46	5.89	0.23	0.04	Normal
Alkalinity	mg/l	46	1.89	0.52	0.28	Normal
Conductivity	uS/cm	46	30.00	4.42	0.15	Normal
Calcium	mg/l	46	1.83	0.33	0.18	Normal
Sulfate	mg/l	46	4.09	0.79	0.19	Normal

### *Power Analyses*

The results of the power analyses are summarized in Table 2. By convention, a power of 0.80 or greater is considered acceptable. The tests that have a power in this range are highlighted. Using the sampling scheme of collecting two samples each year, pH, conductivity, calcium, and sulfate have sufficient power

to detect “important trends” with 10 years of data. There is insufficient power to detect these trends over 10 years if only one sample is collected from the lake each year. None of the parameters have sufficient power to detect trends over 5 years with the existing sampling scheme. All the parameters have sufficient power to detect trends with 20 years of data, even if only one sample was collected from the lake each year.

**Table 2: Power for detecting “important trends” for each parameter**

<b>(A) Power with 5 years of data</b>		Power		
Parameter	"Important Trend"	1 sample/year over 5 years	2 samples/year over 5 years	3 samples/year over 5 years
pH	10% decrease from baseline concentration over 10 years.	NA	0.24	0.31
Alkalinity	50% decrease from baseline concentration over 10 years.	NA	0.17	0.22
Conductivity	50% decrease from baseline concentration over 10 years.	NA	0.32	0.49
Calcium	50% decrease from baseline concentration over 10 years.	NA	0.26	0.37
Sulfate	50% decrease from baseline concentration over 10 years.	NA	0.24	0.35

<b>(A) Power with 10 years of data</b>		Power		
Parameter	"Important Trend"	1 sample/year over 10 years	2 samples/year over 10 years	3 samples/year over 10 years
pH	10% decrease from baseline concentration over 10 years.	0.57	0.85	0.85
Alkalinity	50% decrease from baseline concentration over 10 years.	0.37	0.57	0.59
Conductivity	50% decrease from baseline concentration over 10 years.	0.78	0.95	0.96
Calcium	50% decrease from baseline concentration over 10 years.	0.61	0.88	0.89
Sulfate	50% decrease from baseline concentration over 10 years.	0.57	0.86	0.88

<b>(A) Power with 20 years of data</b>		Power		
Parameter	"Important Trend"	1 sample/year over 20 years	2 samples/year over 20 years	3 samples/year over 20 years
pH	10% decrease from baseline concentration over 10 years.	1.00	1.00	1.00
Alkalinity	50% decrease from baseline concentration over 10 years.	1.00	1.00	1.00
Conductivity	50% decrease from baseline concentration over 10 years.	1.00	1.00	1.00
Calcium	50% decrease from baseline concentration over 10 years.	1.00	1.00	1.00
Sulfate	50% decrease from baseline concentration over 10 years.	1.00	1.00	1.00

### *Trend Analysis*

The power analyses indicated that important trends can be detected for all five parameters with 20 years of data. Therefore, the datasets for the 20 lake outlets that have been monitored twice per year were analyzed for trends using the MKT.

Significant trends were detected for all the parameters.

- For pH, two lakes had decreasing trends, 4 lakes had increasing trends and the remaining 14 lakes did not have any significant trends.
- For alkalinity, 12 of the 20 lakes had increasing trends and only one lake had decreasing trends.
- For conductivity, 10 of the 20 lakes had increasing trends and six lakes had decreasing trends. The increasing trends at Echo Lake, Granite Lake, Loon Pond, Millen Pond, and Pleasant Lake were an order of magnitude higher than for the other lakes.
- For calcium, six lakes had increasing trends while only two lakes had decreasing trends.
- For sulfate, only one lake had an increasing trend (Granite Lake) while nine lakes had decreasing trends.
- In terms of the effects of acid rain, Granite Lake has the most troubling trends. Not only is pH decreasing but alkalinity is also decreasing and sulfate is increasing.

For each parameter, the minimum slope for a significant trend and the maximum slope for a non-significant trend were averaged to approximate the minimum detectable slope for the dataset. Comparisons between this average and the predicted minimum detectable slopes from the power analyses were favorable (see bottom rows in Table 3). Therefore, the results of the trend analysis confirmed the predictions from the power analyses.

Table 3 contains a summary of all the trends for the 20 lakes studied. Line plots of the yearly average concentrations at each lake for pH, alkalinity, calcium, and sulfate are presented in an appendix.

**Table 3: Summary of Trends in Acid Outlet Ponds**

Lake	Years	pH		Alkalinity (mg/l)		Conductivity (uS/cm)		Calcium (mg/l)		Sulfate (mg/l)	
		Trend	Slope	Trend	Slope	Trend	Slope	Trend	Slope	Trend	Slope
Bow Lake	20	NS	0.000	NS	0.037	Increasing	0.41	Increasing	0.018	NS	0.000
Center Pond	20	Increasing	0.009	Increasing	0.035	Increasing	0.35	NS	-0.003	Decreasing	-0.071
Cold Spring Pond	20	NS	0.000	NS	0.009	NS	0.30	Decreasing	-0.017	Decreasing	-0.029
Conner Pond	20	NS	0.000	Increasing	0.029	NS	-0.06	NS	0.000	Decreasing	-0.013
Cooks Pond	20	NS	0.000	Increasing	0.065	Increasing	0.18	Increasing	0.027	NS	0.000
Dublin Pond	20	NS	0.000	Increasing	0.108	Decreasing	-0.56	NS	0.000	Decreasing	-0.071
Echo Lake	20	NS	-0.010	NS	-0.037	Increasing	3.38	NS	0.045	Decreasing	-0.083
Granite Lake	20	Decreasing	-0.018	Decreasing	-0.043	Increasing	1.73	Increasing	0.033	Increasing	0.156
Long Pond	20	Increasing	0.012	NS	0.005	Decreasing	-0.26	NS	-0.008	Decreasing	-0.100
Loon Lake	20	NS	0.000	Increasing	0.038	Decreasing	-0.09	NS	-0.004	Decreasing	-0.050
Loon Pond	20	NS	0.000	NS	0.047	Increasing	1.99	Increasing	0.028	NS	-0.029
Millen Pond	20	Decreasing	-0.020	NS	-0.019	Increasing	2.86	Increasing	0.047	NS	-0.063
Nubanusit Lake	20	NS	0.004	Increasing	0.033	Decreasing	-0.19	NS	-0.007	Decreasing	-0.070
Pleasant Lake	20	Increasing	0.016	Increasing	0.075	Increasing	1.39	Increasing	0.018	NS	0.000
Russell Pond	19	NS	0.000	Increasing	0.044	Decreasing	-0.14	NS	-0.001	Decreasing	-0.083
Silver Lake	20	NS	0.000	Increasing	0.043	NS	0.11	NS	0.000	Decreasing	-0.050
Spectacle Pond	20	Increasing	0.017	Increasing	0.060	NS	-0.11	NS	0.001	Decreasing	-0.067
Stinson Lake	20	NS	-0.006	NS	0.011	Decreasing	-0.14	Decreasing	-0.023	Decreasing	-0.100
Stone Pond	20	NS	0.000	Increasing	0.042	Increasing	0.06	NS	0.000	NS	-0.025
White Lake	20	NS	0.000	Increasing	0.027	Increasing	0.13	NS	0.001	NS	-0.063
Minimum Significant Trend			0.009		0.027		0.06		0.017		0.013
Maximum Non-Significant Trend			0.01		0.047		0.3		0.045		0.063
<b>Approx. Min. Detectable Trend</b>			<b>0.01</b>		<b>0.04</b>		<b>0.2</b>		<b>0.03</b>		<b>0.04</b>
<b>Predicted Min. Detectable Trend</b>			<b>0.02</b>		<b>0.04</b>		<b>0.3</b>		<b>0.03</b>		<b>0.06</b>

\* Slopes are expressed in terms of units/year

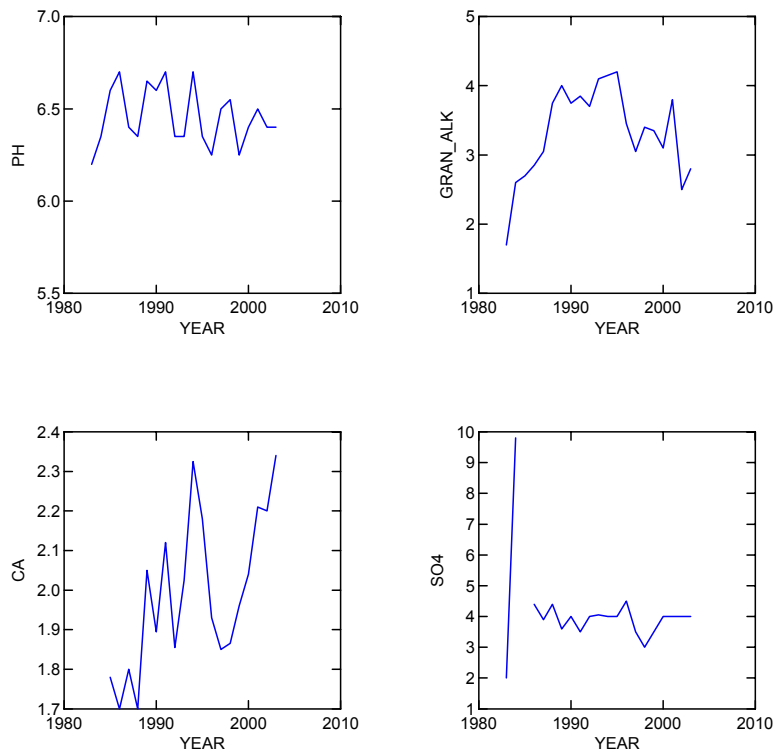
## Conclusions and Recommendations

- The analytical methods for the parameters with mostly censored results (aluminum, nitrate, chloride) should be investigated to determine if lower detection limits are achievable. With the current detection limits, these variables cannot be analyzed for trends.
- Using the existing sampling scheme of collecting two samples each year, pH, conductivity, calcium, and sulfate have sufficient power to detect “important trends” with 10 years of data and alkalinity can detect important trends with 20 years of data (maybe in as few as 15 years).
- Lakes that are sampled once per year will have sufficient power to detect “important trends” after 20 years.
- None of the parameters have sufficient power to detect trends after 5 years.
- Increasing the sample size to three samples per year does not add enough statistical power to justify the additional laboratory and personnel costs.
- Trend analysis on the 20 year datasets for 20 lakes identified significant trends for all parameters. In general:
  - Most lakes do not have a significant trend for pH, but the majority of those that do have increasing trends.
  - Alkalinity is increasing in most lakes and decreasing only in Granite Lake.
  - An equal number of lakes have increasing and decreasing trends for conductivity. Several lakes have strongly increasing trends.
  - Most lakes do not have a significant trend for calcium, but the majority of those that do have increasing trends.
  - Almost all of the lakes have decreasing trends for sulfate, but sulfate is increasing in Granite Lake.
- Trend analysis on the 20 year datasets for 20 lakes confirmed the predictions of the power analysis for the minimum detectable trend.
- The Acid Lake Outlet Monitoring Program should undertake a structured planning process to determine what magnitude of trend is important to detect over a specified time frame (5 years? 10 years?). The “important trends” tested in this analysis were arbitrary chosen. These trends may not reflect the priorities of the program.

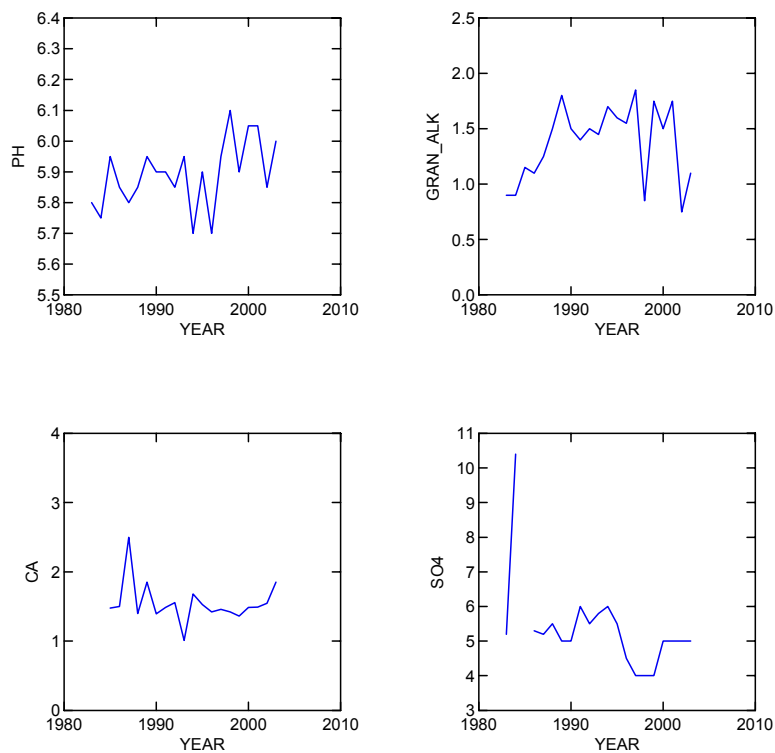
## References

Gilbert, RO (1987) Statistical Methods for Environmental Pollution Monitoring. Van Nostrand Reinhold, New York. 320 pp.

## APPENDIX A: LINE GRAPHS BOW LAKE

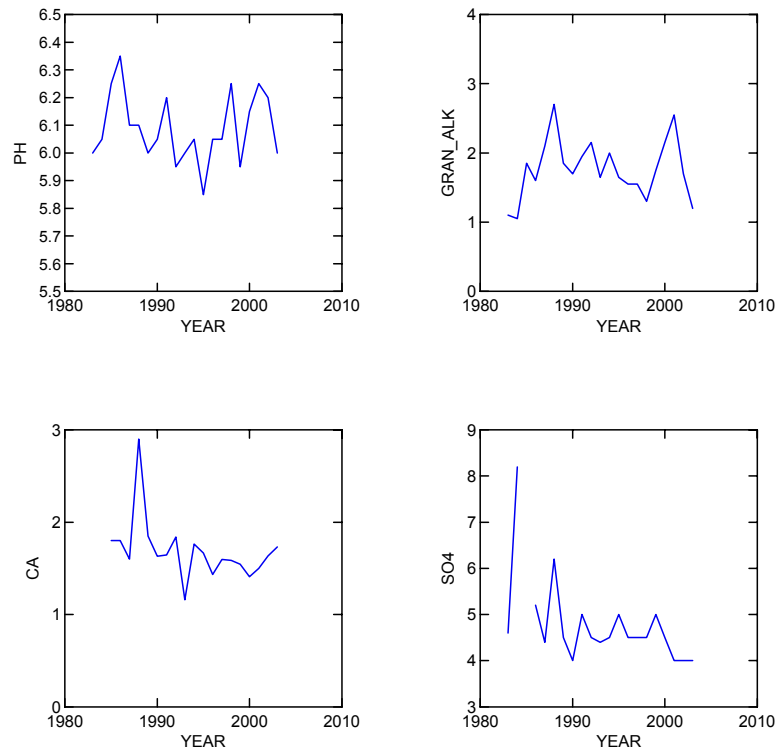


## CENTER POND

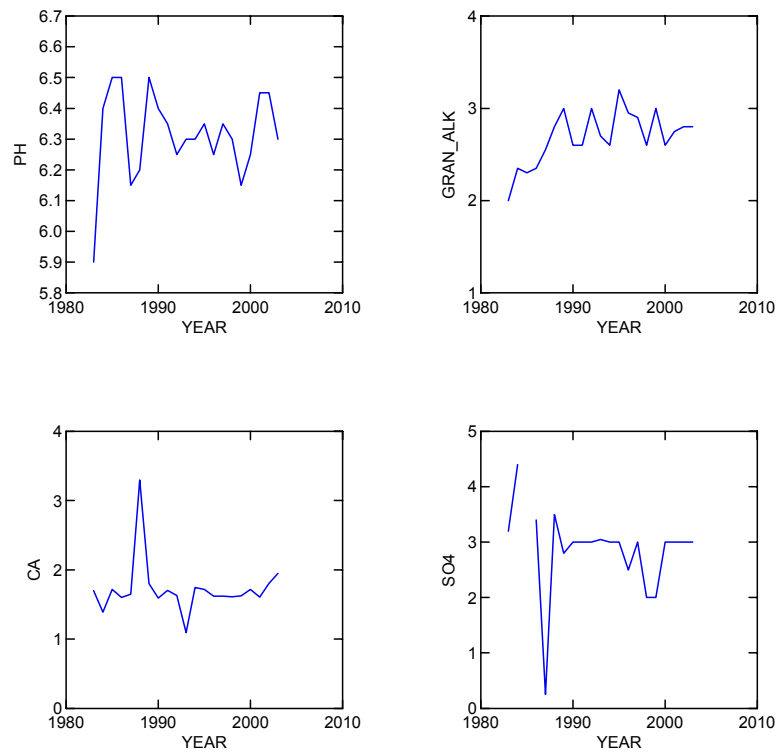




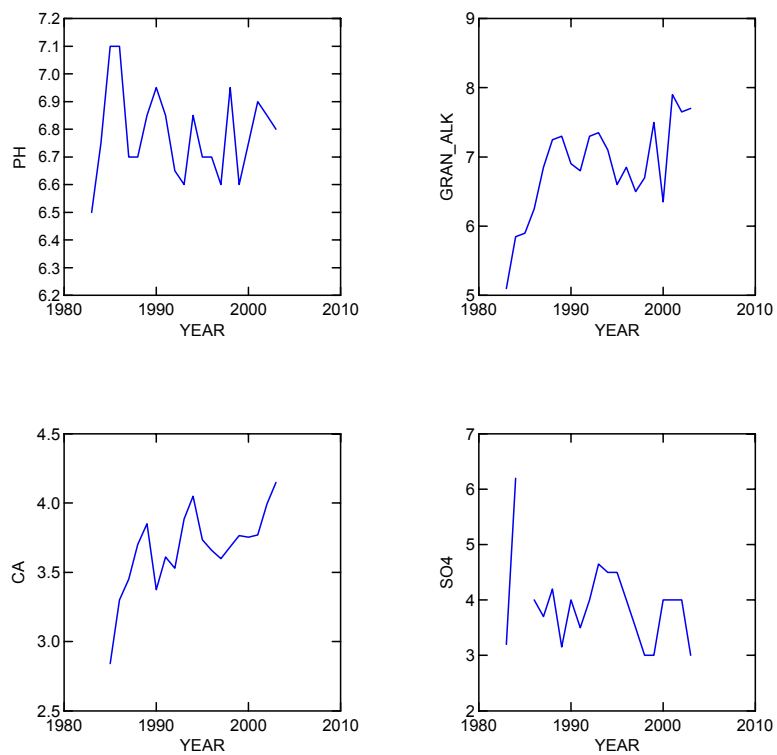
## COLD SPRING POND



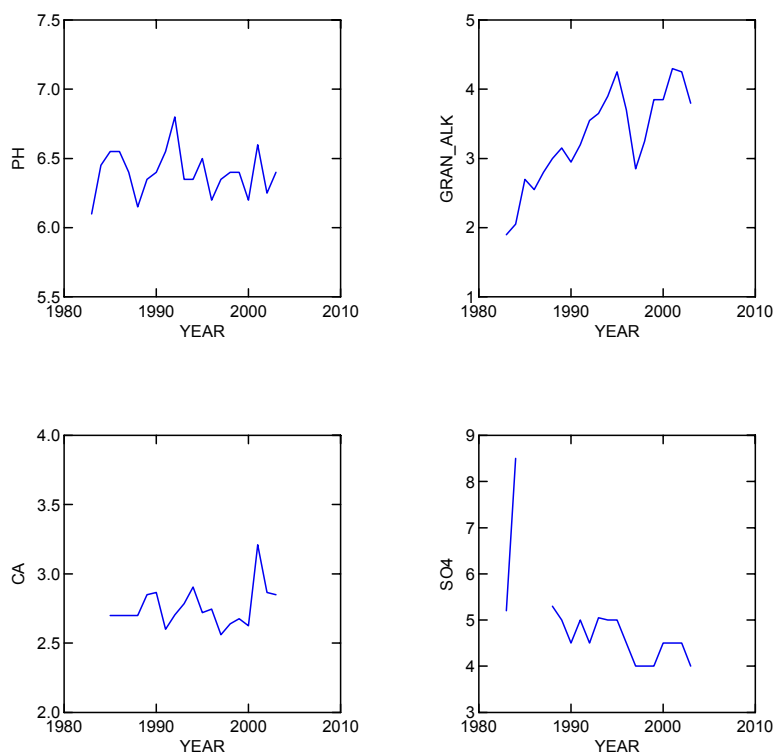
## CONNER POND



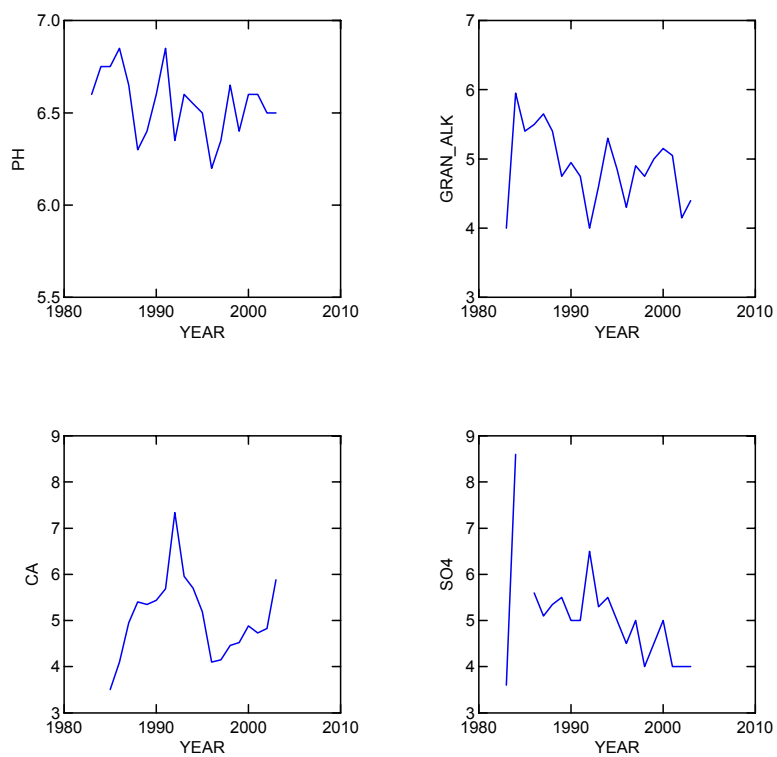
## COOKS POND



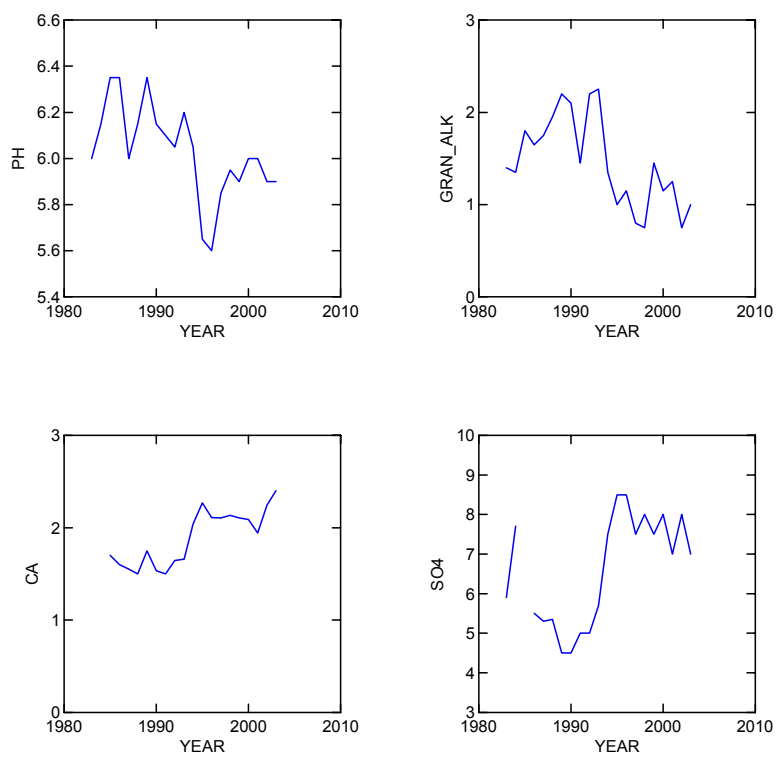
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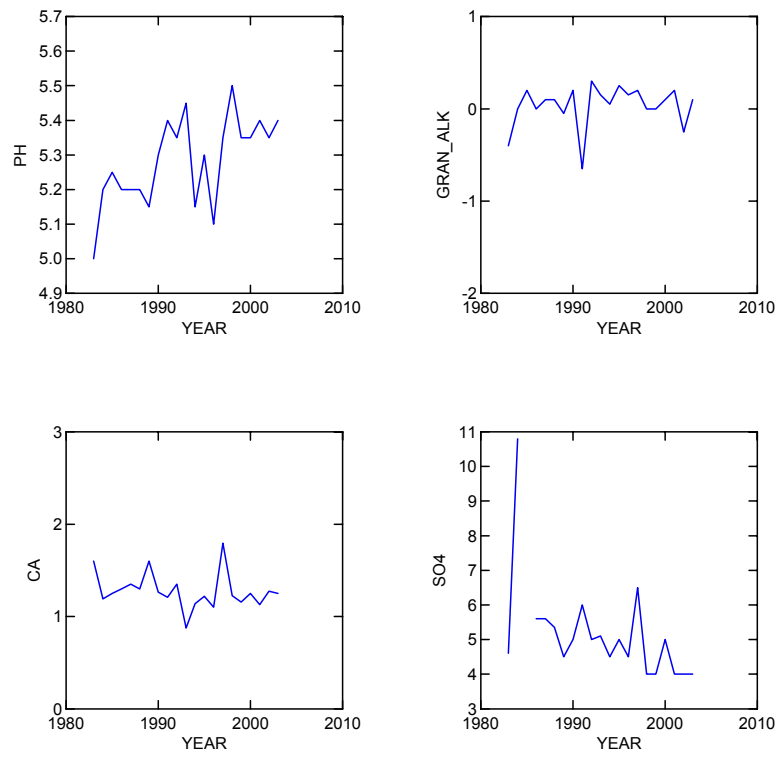
## ECHO LAKE



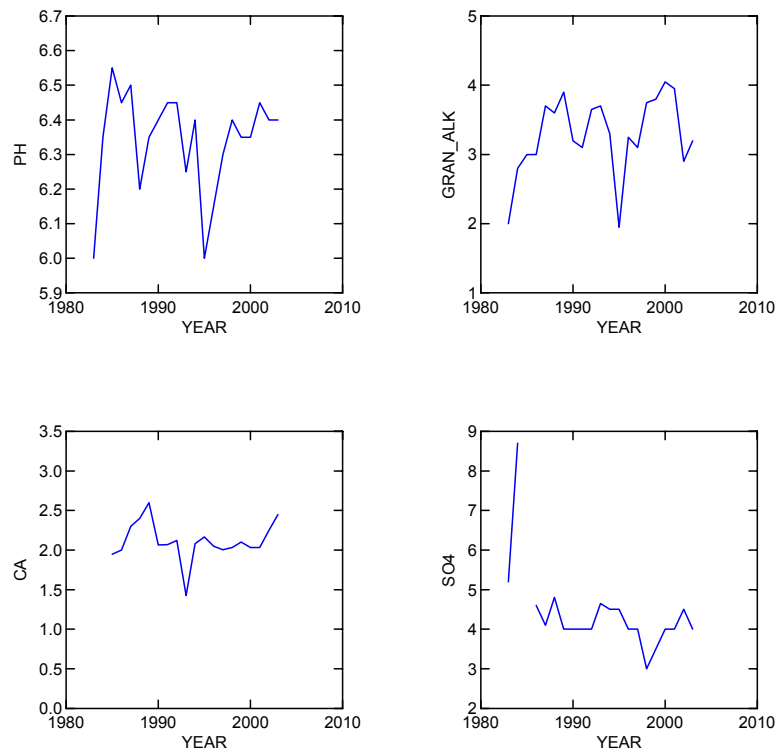
## GRANITE LAKE



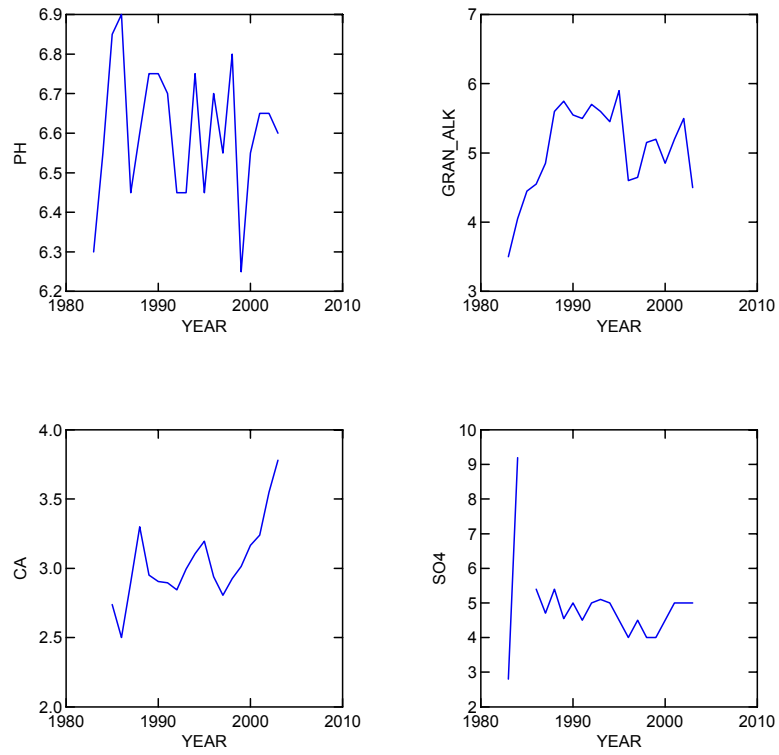
## LONG POND



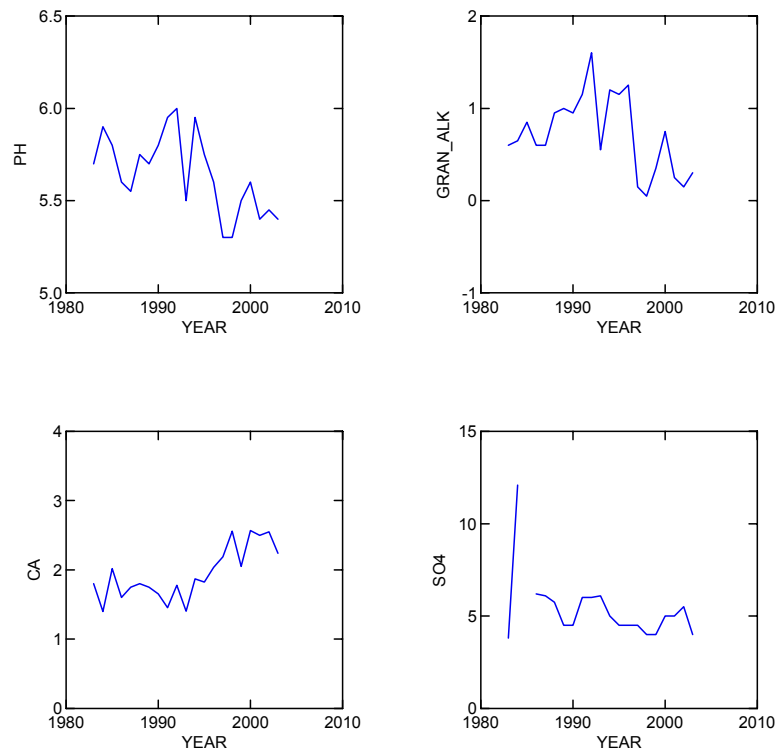
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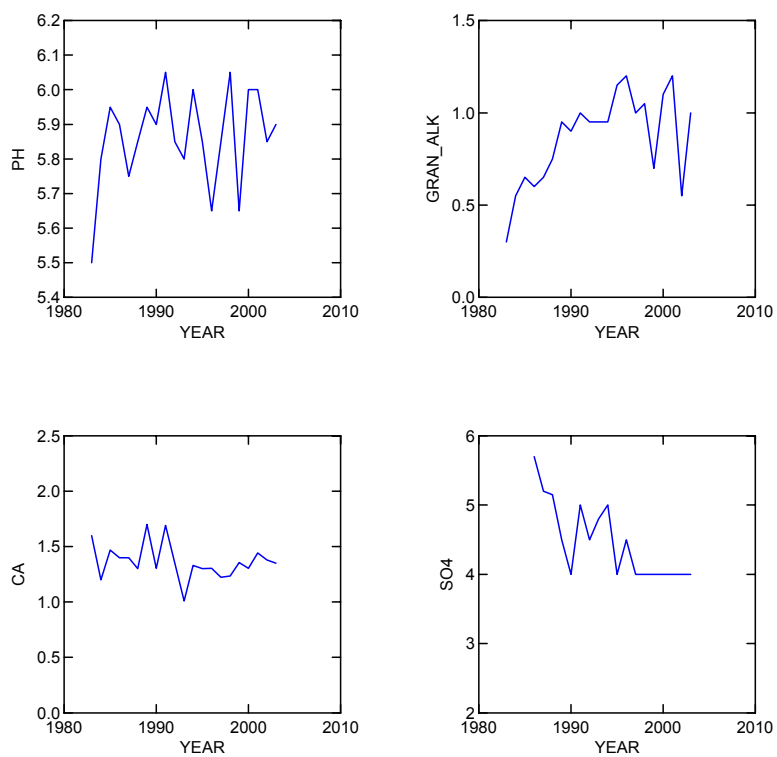
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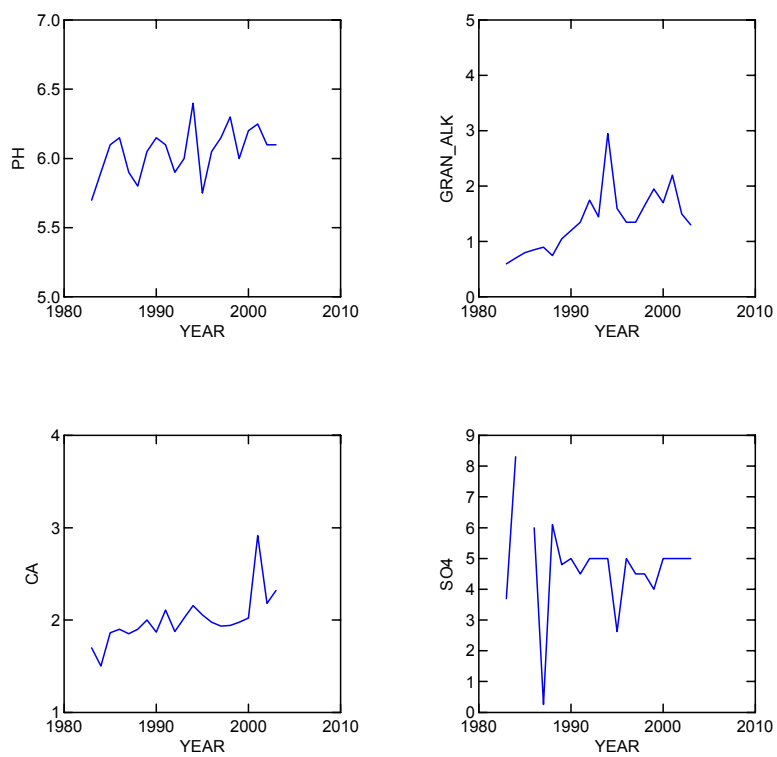
## MILLEN POND



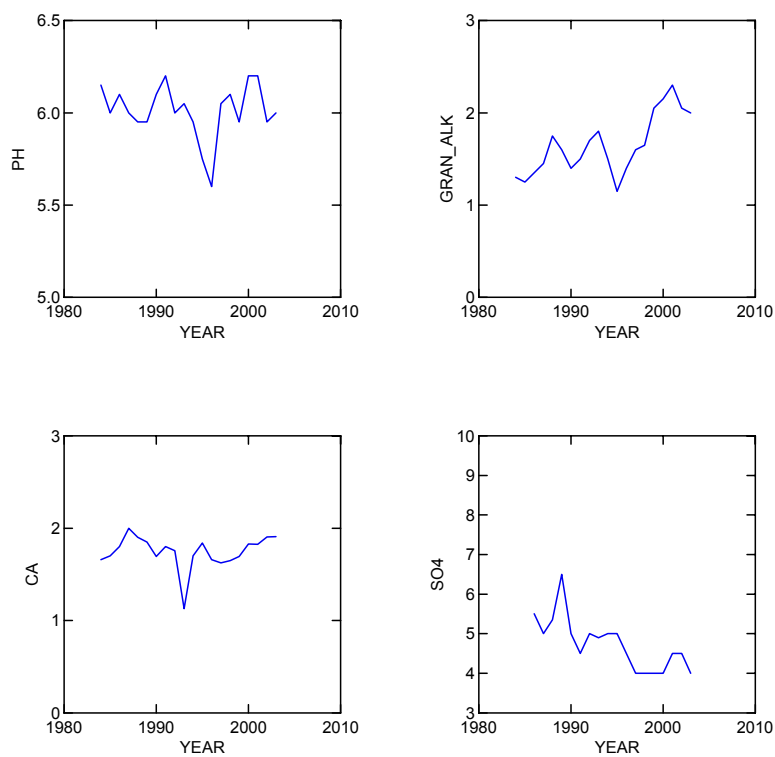
## NUBANUSIT LAKE



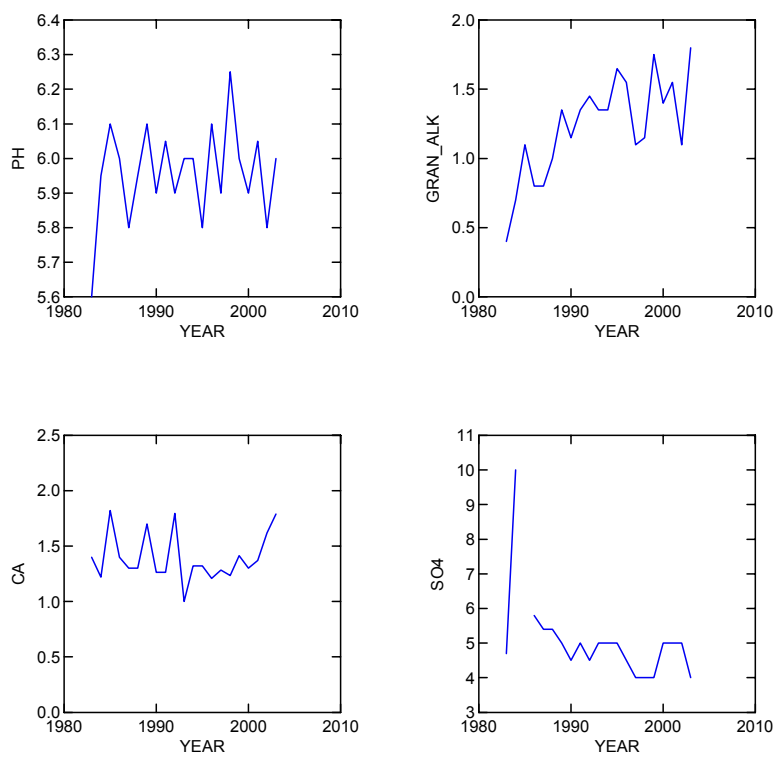
## PLEASANT LAKE



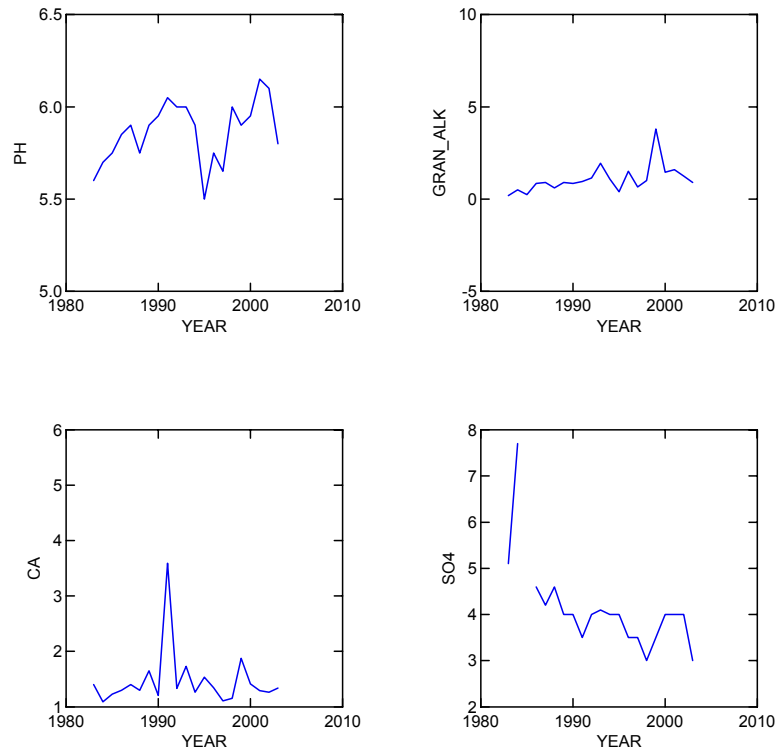
## RUSSELL POND



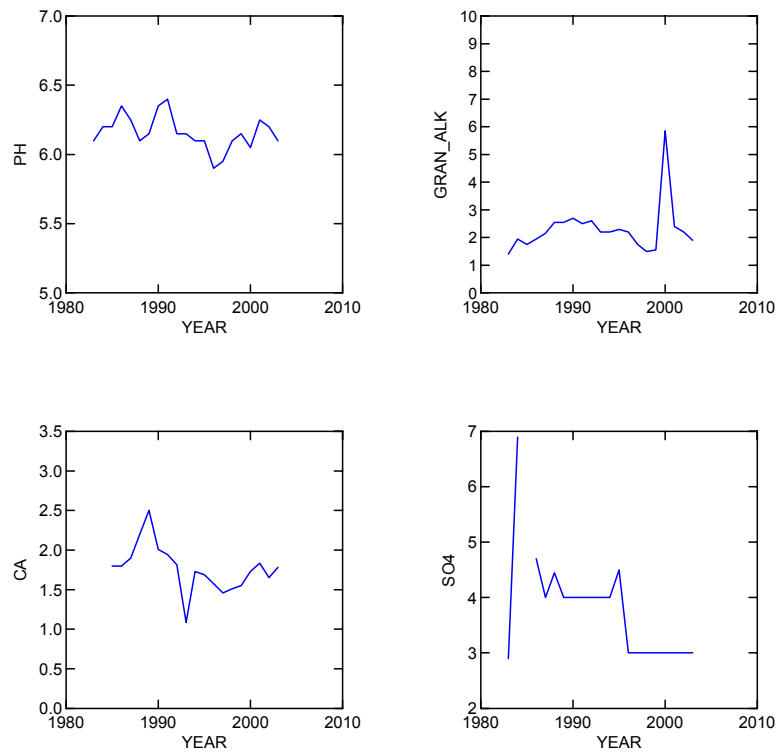
## SILVER LAKE



## SPECTACLE POND

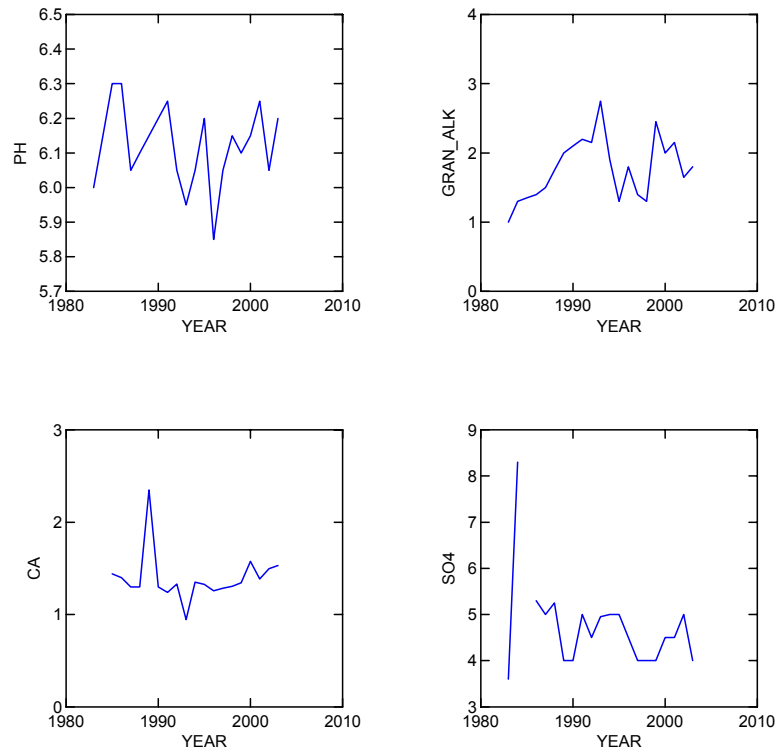


## STINSON LAKE

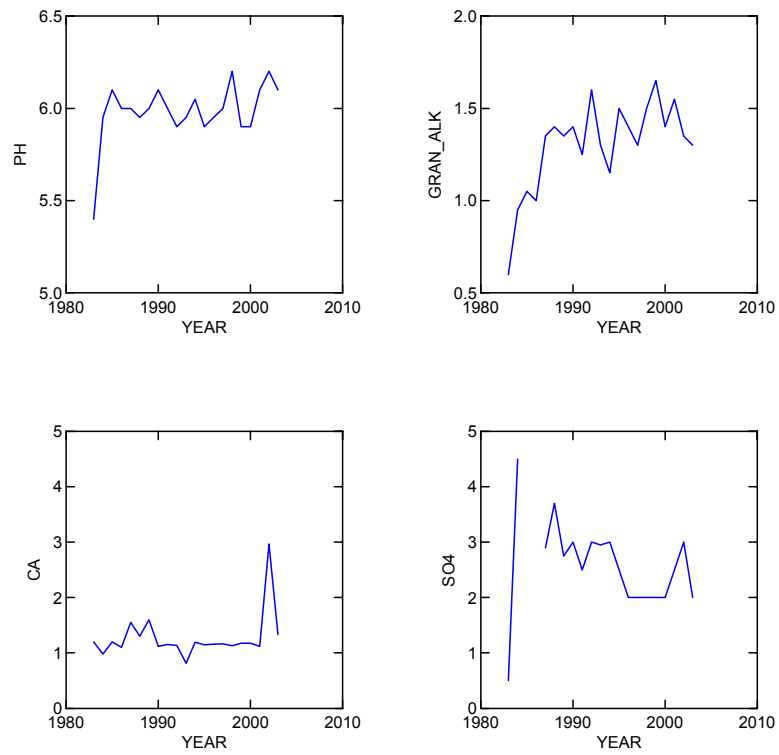




## STONE POND



## WHITE LAKE



# State of New Hampshire

## Inter-Department Communication

**Date:** July 30, 2004

**From:** Phil Trowbridge  
Coastal Scientist

**At (Office):** Environmental Services  
Watershed Management

**Subject:** Power Analysis for the Volunteer Lake Assessment Program

**To:** Bob Estabrook, Chief Aquatic Biologist  
Gregg Comstock, Supervisor, Water Quality Planning Section

### Introduction

The DES Volunteer Lake Assessment Program (VLAP) collects summer water quality data at dozens of lakes across New Hampshire. DES would like to analyze the data from these lakes to determine if there have been any significant trends over time. In addition, the Watershed Management Bureau is developing a Comprehensive Monitoring Strategy, which would include any changes to the lake monitoring design in order to increase statistical power for trend detection.

For this report, the water quality data from six VLAP lakes from 1985 to 2003 have been reviewed to determine the power for detecting trends given the variability in each parameter. This information will identify parameters for which there is sufficient power to detect trends with the existing dataset (and, conversely, parameters with insufficient power). The power analyses can also be used to optimize the sampling design for detecting trends. Recommendations for changes to the sampling design will be considered as part of the Comprehensive Monitoring Strategy.

### Methods

The six VLAP lakes used for this study were: Beaver Lake; Blaisdell Lake; Kezar Lake; North Mountain Lake; Mountainview Lake; and Pawtuckaway Lake. Water quality data for these lakes from 1985 to 2003 were provided by Scott Ashley of the DES Biology Bureau. The following parameters were included in the dataset: pH; Alkalinity; Total Phosphorus; Specific Conductivity; Turbidity; Chlorophyll-a; Secchi Depth; and Dissolved Oxygen (in the hypolimnion). The data were cleaned by removing values reported as "less than detection limit" and obvious outliers. One half the method detection limit was substituted for values reported as less than the detection limit.

Ditplot histograms were generated for each parameter for each lake and each layer. The diplots were useful for identifying outlier values and for determining the shape of the concentration distribution for each parameter. The only obvious outlier was a value for 786 units for conductivity on 7/17/00 for Mountainview Lake, which was removed. Two less glaring outliers were also removed: Zero value for pH for Blaisdell Lake hypolimnion on 8/26/03 and 9.19 pH value for pH for Kezar Lake epilimnion on 8/4/88.

Descriptive statistics were calculated for each parameter for each year for each layer for each lake (approximately 1000 combinations). These statistics were averaged first over each lake and then over all the lakes together in order to obtain an estimate of the overall mean and standard

deviation for each parameters. Statistics from years in which less than three samples were collected from a given lake were excluded from the calculation. Likewise, only lakes that had five years of complete data were included in the overall average. The overall mean and standard deviation values for each parameter across all years and all lakes are shown in Appendix A. Parameters with a coefficient of variation  $>0.3$  were treated as lognormally distributed. Turbidity, chlorophyll-a, phosphorus, and dissolved oxygen in the hypolimnion met this criterion. The remaining variables were assumed to be normally distributed.

The overall mean and standard deviation of the concentration for each parameter and the distribution type were used to simulate random variability in the concentrations using Monte Carlo simulation software. Ten year records of sampling results were generated by randomly sampling from this distribution with a linear trend superimposed. The Mann-Kendall statistical tests for trend were run on the simulated records to try to detect the linear trend. The simulation was run 500 times for each parameter. The fraction of the simulations that detected a significant (i.e.,  $p < 0.05$ , one tail or  $p < 0.10$ , two tails) trend represented the power for detecting that trend given the variability within the data. By convention, a power of greater than 0.80 was considered acceptable for trend detection.

VLAP lakes are currently monitored three times during the summer months. Therefore, the simulations tested the power to detect trends based on three samples per year. Simulations were also run for the power to detect trends with one and five samples per year.

Three different trends were superimposed on the randomly generated concentrations: 25% change from average values over 10 years; 50% change from average values over 10 years; and 100% increase from average values over 10 years.

## Results

The statistical power to detect the superimposed trends for each parameter are shown in Table 1. The results for each parameter are grouped together in three consecutive rows. Each row contains the power analysis results for one superimposed trend that is sampled at frequencies of one sample per year, three per year (the current program), and five per year. Cells with sufficient power ( $>0.80$ ) to detect the trend are highlighted in yellow. The absolute magnitude of the trend plus the average value of the parameter are listed in the right hand columns of the table. The column on the far right side of the table denotes whether the statistics for the epilimnion or hypolimnion were used in the calculation. For most cases, there was no appreciable difference in the coefficient of variation between the layers for a given parameter.

The seven VLAP parameters fell into three groupings according to their power to detect different magnitudes of trends.

Specific conductivity and pH were shown to have excellent power for detecting trends under the current sampling design. These parameters could be measured only once per year and still be able to detect trends of less than 25% change over ten years.

Alkalinity and Secchi depth have sufficient power to detect moderate trends of  $>50\%$  change over ten years with the current sampling design. In fact, if this level of trend detection is sufficient for management purposes, these parameters could be monitored once per year and still able to detect this magnitude of trend. Both of these parameters could detect trends of 25% change over ten years if five or more samples were collected each year.

Finally, chlorophyll-a, phosphorus, and turbidity only have power to detect trends of 100% change over 10 years with the current sampling design. Trends of 50% change over ten years could be detected if five samples were collected each year. The concentrations of these three parameters are lognormally distributed which produces greater variability than the normally distributed parameters.

The power for detecting trends in dissolved oxygen concentrations in the hypolimnion was not calculated in this report. Only one lake had sufficient data on dissolved oxygen in the hypolimnion (Kezar Lake) and the coefficient of variation for this lake was very high. These data did not seem representative of state-wide conditions.

**Table 1: Power analysis results for VLAP parameters**

Parameter	10 Year Trend	10 yr n=1	10 yr n=3	10 yr n=5	Slope (uni)	Mean	Layer
Alkalinity	25% change	0.38	0.68	0.83	0.164	6.55	Epilimnion
Alkalinity	50% change	0.86	1	1	0.328	6.55	Epilimnion
Alkalinity	100% change	1	1	1	0.655	6.55	Epilimnion
Chlorophyll-a	25% change	0.16	0.17	0.27	0.112	4.6	Epilimnion
Chlorophyll-a	50% change	0.27	0.49	0.65	0.232	4.6	Epilimnion
Chlorophyll-a	100% change	0.68	0.91	1	0.465	4.6	Epilimnion
pH	25% change	1	1	1	0.162	6.485	Hypolimnion
pH	50% change	1	1	1	0.324	6.485	Hypolimnion
pH	100% change	1	1	1	0.649	6.485	Hypolimnion
Phosphorus	25% change	0.16	0.19	0.31	0.0004	0.015	Hypolimnion
Phosphorus	50% change	0.31	0.55	0.73	0.001	0.015	Hypolimnion
Phosphorus	100% change	0.72	0.97	1	0.002	0.015	Hypolimnion
Secchi Depth	25% change	0.33	0.6	0.77	0.0856	3.422	Epilimnion
Secchi Depth	50% change	0.79	0.98	1	0.171	3.422	Epilimnion
Secchi Depth	100% change	1	1	1	0.342	3.422	Epilimnion
Specific Conductivity	25% change	0.97	1	1	2.489	99.57	Hypolimnion
Specific Conductivity	50% change	1	1	1	4.978	99.57	Hypolimnion
Specific Conductivity	100% change	1	1	1	9.957	99.57	Hypolimnion
Turbidity	25% change	0.17	0.22	0.35	0.0196	0.7825	Epilimnion
Turbidity	50% change	0.35	0.61	0.77	0.0391	0.7825	Epilimnion
Turbidity	100% change	0.78	1	1	0.0783	0.7825	Epilimnion

### Recommendations

The VLAP staff should review the relative and absolute magnitudes of the trends that the current VLAP sampling design is able to detect and determine whether these trends are acceptable for their management purposes. Specifically:

- The current sampling design is only capable of detecting trends of chlorophyll-a and phosphorus if the concentrations have doubled over a decade. Monitoring these parameters five times per year instead of three would allow for managers to detect trends on the order of 50% increase over ten years.
- Conversely, alkalinity, Secchi depth, pH, and specific conductivity could be monitored for trend detection as effectively with one sample per year instead of three per year. However, multiple samples per year may be needed for these parameters for §305(b) assessment purposes or lake studies.

# State of New Hampshire

## Inter-Department Communication

**Date:** July 29, 2003

**From:** Phil Trowbridge  
Coastal Scientist

**At (Office):** Environmental Services  
Watershed Management

**Subject:** Power Analysis for the Fish Mercury Trend Monitoring Program

**To:** Bob Estabrook, Chief Aquatic Biologist  
Gregg Comstock, Supervisor, Water Quality Planning Section

### Introduction

Starting 1998, the Department of Environmental Services (DES) added a program to monitor trends in fish tissue mercury ("fish-Hg") using a systematic monitoring program. The goals of the program were to allow for trend detection over time and to generate the data needed to test whether certain lake characteristics (lake color, acidity, and dissolved oxygen) had an effect on the fish-Hg levels. Two fish species in particular were chosen for the program: largemouth bass (LMB) and yellow perch (YLP). The State tests many fish for mercury each year. However, most of these samples are collected on an *ad hoc* basis, which prevents their use in statistical analyses. By conducting a small, standardized sampling program, the Department hoped to be able to document any trends in fish-Hg levels and to understand the why there was variability between lakes.

### Project Goals and Objectives

The objectives for this project are:

- Determine whether the experimental design for fish-Hg sampling will provide data to answer the research questions.
- Predict the statistical power of the sampling design to detect trends over time or the effects of lake characteristics on fish-Hg.

### Methods

#### *Software*

- All calculations were performed using SYSTAT version 10 statistical software.

#### *Data Handling*

- Data on fish-Hg from the first five years of the program (1998-2002) were reviewed for completeness. Descriptive statistics of fish-Hg (mean and standard deviation) were calculated with all the samples of each species. Mean values and confidence limits for each lake were also calculated.

#### *Definitions of parameters for power calculations*

- Determined trend analysis methods for study. Five fish samples are collected from each lake once every five years. With this sample design, the appropriate test to evaluate changes over time at an

individual lake is the 2 sample t-test or the nonparametric Wilcoxon rank sum test. Both tests have similar statistical power so the power predictions for the 2 sample t-test were used.

- Determined statistical methods to evaluate the effects of lake characteristics on fish-Hg. The study design seeks to evaluate the effects of lake acidity, lake color, dissolved oxygen and fish species on fish-Hg. However, there are not enough lakes in the “oxic” category to evaluate the dissolved oxygen factor. Excluding the dissolved oxygen factor, the effects of the remaining factors can be evaluated using 2x2 Analysis of Variance (ANOVA) for each fish species. The power predictions for this model were calculated using SYSTAT software.
- Determined magnitude of trend and effect of interest. In order to test for power, a trend or effect of known magnitude must be specified and tested. A change of 10% over five years or an effect of 10% difference was arbitrarily chosen as the smallest trend or effect of interest.

#### *Power Calculations*

- Statistical power for detecting trends using a 2 sample t-tests was calculated using SYSTAT software and the mean and standard deviation of fish-Hg for each species.
- Power for detecting differences due to lake characteristics using a 2x2 ANOVA was calculated with SYSTAT software using the standard deviation for each species and the average standardized squared effect equal to 10%\*mean/stddev.

### Results and Discussion

#### *Experimental Design*

One aspect of the monitoring program is to investigate the effects of lake properties on fish-Hg. The three factors being considered are: lake acidity, lake color, and lake dissolved oxygen levels. A fourth factor implicit in the design is fish species. This would result in 16 possible permutations of lakes with these four properties. The current sample design only covers 10 of these permutations. The six missing cells all relate to oxygenated lakes. Therefore, the research question about the effect of lake dissolved oxygen levels cannot be answered with the existing experimental design. The planned sampling design is shown below in Table 1.

**Table 1: Planned experimental design**

Species and Acidity Factors		Color and Dissolved Oxygen Factors			
		Colored		Clear	
		Anoxic	Oxic	Anoxic	Oxic
LMB	Acid	Turtle Pond		Cass Pond	
	Not Acid	Gorham Pond		Forest Lake	Crystal Lake
YLP	Acid	Hubbard Pond		Crooked Pond	
	Not Acid	Harvey Lake		Clement Pond	Spectacle Pd

A further complication is that the actual sample collection has deviated from the planned design. The actual experimental design through the first five years of the program is shown below in Table 2.

**Table 2: Actual experimental design (1998-2002)**

Species and Acidity Factors		Color and Dissolved Oxygen Factors			
		Colored		Clear	
		Anoxic	Oxic	Anoxic	Oxic
LMB	Acid	Turtle Pond		Cass Pond, Crooked Pond	
	Not Acid	Gorham Pond, Harvey Lake		Forest Lake, Clement Pond	Crystal Lake
YLP	Acid	Hubbard Pond, Turtle Pond			
	Not Acid	Harvey Lake, Gorham Pond		Clement Pond, Forest Lake	Spectacle Pd, Crystal Lake

The deviations from the experimental design can be summarized as:

- Crooked Pond was sampled for LMB instead of YLP.
- Turtle Pond, Gorham Pond, Harvey Lake, Forest Lake, Clement Pond, and Crystal Lake were all sampled for both YLP and LMB.

The result of the deviations from the experimental design is that the missing data on YLP in Crooked Pond disrupts the ability to test for differences due to lake color for YLP. The extra samples in Turtle Pond, Gorham Pond, Harvey Lake, Forest Lake, Clement Pond, and Crystal Lake add more statistical power for detecting changes between factors and make more trend analyses possible if the extra sampling is continued in the future.

### *Descriptive Statistics for Fish-Hg*

The fish-Hg concentrations from the first five years show that mean fish-Hg concentrations are higher for LMB (0.42 mg/kg) than YLP (0.28 mg/kg). The mean values and 95<sup>th</sup> percentile confidence limits for each species in each lake are listed in Table 3. The statistics for all lakes combined were used in the power calculations because these statistics conservatively incorporate extra variance from the factors.

**Table 3: Descriptive statistics for fish-Hg (mg/kg wet weight)**

Lake	Year	LMB			YLP		
		Mean	95%ile CI	Stdev	Mean	95%ile CI	Stdev
CASS POND	2001	0.56	0.32 -- 0.80	0.193			
CLEMENT POND	1998	0.34	0.19 -- 0.48	0.118	0.15	0.13 -- 0.17	0.020
CROOKED POND	2000	0.50	0.39 -- 0.61	0.088			
CRYSTAL LAKE	2002	0.39	0.19 -- 0.59	0.162	0.26	0.12 -- 0.40	0.115
FOREST LAKE	2001	0.33	0.16 -- 0.51	0.142	0.33	0.28 -- 0.39	0.045
GORHAM POND	1998	0.44	0.22 -- 0.65	0.173	0.22	0.10 -- 0.33	0.093
HARVEY LAKE	2001	0.36	0.31 -- 0.41	0.041	0.26	0.19 -- 0.33	0.058
HUBBARD POND	2000				0.29	0.18 -- 0.40	0.090
SPECTACLE POND	2002				0.32	0.20 -- 0.44	0.100
TURTLE POND	2000	0.46	0.32 -- 0.59	0.108	0.42	0.32 -- 0.53	0.084
ALL LAKES		0.42	0.38 -- 0.47	0.145	0.28	0.25 -- 0.32	0.106

1. Five fish sampled per lake. A total of 40 fish from each species averaged for last row.

2. 95%ile CI = 95th percentile confidence limits of the mean. Assuming normality.

### Power Analyses

At each lake, five fish samples are collected every 5 years. Trends over time will be expressed as statistically significant differences between the mean fish-Hg of the first and second set of samples. The statistical test for this analysis is a 2 sample t-test.

The power analysis for a 2 sample t-test showed that there is sufficient power to detect changes of 10% with the existing sampling design of five samples per year. Table 4 shows the power to detect trends of different magnitudes. By convention, acceptable power is greater than 0.80. The shaded cells in this table have power >0.80.

**Table 4: Power to detect different trends using a t-test**

Species	5% change	7.5% change	10% change
LMB	0.52	0.86	0.98
YLP	0.45	0.78	0.95

1. Significance level (alpha)=0.05

2. Assumes five fish collected from each lake.

3. % change defined as difference between the mean and the mean\*XX%/100.

To investigate whether lake acidity, lake color, and fish species have an effect on fish-Hg, a two-way Analysis of Variance (ANOVA) can be conducted for each species with the factors of acidity and color. Power analyses for the two-way ANOVA calculations showed that at least 8 LMB and YLP would be needed from each cell (i.e., unique combination of lake color, lake acidity, and species) to detect differences of 10% between cells with power >0.8 (and a significance level of 0.05). There are almost this many fish samples in each cell right now. The current numbers of fish in each cell is shown in Table 5.

**Table 5: Number of fish collected in first five years (1998-2002)**

		Colored		Clear	
		Anoxic	Oxic	Anoxic	Oxic
LMB	Acid	5		10	
	Not Acid	10		10	5
YLP	Acid	10			
	Not Acid	10		10	10

Effects smaller than 10% could probably be detected if the variance due to fish length and weight were removed but changes of less than 10% over 5 years are probably not meaningful in a biological context.

### Conclusions and Recommendations

- In order to test for the effects of dissolved oxygen, six more lakes need to be added to the program.
- In order to test for the effects of color, the data on YLP from Crooked Pond are needed
- If 5 LMB are collected from Turtle Pond and 10 YLP are collected from Crooked Pond, there would be enough data to test for the effects for color and lake acidity on fish-Hg. There is no need to wait for the next 5 year cycle of lake surveys to be complete.
- After the next five years of sampling, it will be possible to test for changes over time at the individual lakes. The experimental design has sufficient power to detect changes as small as 10% change over 5 years.
- Collection of both LMB and YLP samples from each lake should be continued if possible.



# State of New Hampshire

## Inter-Department Communication

**Date:** June 30, 2003

**From:** Phil Trowbridge  
Coastal Scientist

**At (Office):** Environmental Services  
Watershed Management

**Subject:** Power Analysis for the Ambient Rivers Monitoring Program

**To:** Gregg Comstock, Supervisor, Water Quality Planning Section  
Paul Piszczek, ARMP Coordinator

### Introduction

The DES Ambient Rivers Monitoring Program (ARMP) has collected yearly data at 17 trend monitoring stations across New Hampshire for over a decade. The Program would like to analyze the data from these stations to determine if there have been any significant trends over time. In addition, the Watershed Management Bureau is developing a Comprehensive Monitoring Strategy, which would include any changes to the ARMP monitoring design in order to increase statistical power.

For this report, the ARMP data from 1990 to 2002 have been reviewed to determine the power for detecting trends given the variability in each parameter. This information will identify parameters for which there is sufficient power to detect trends with the existing dataset (and, conversely, parameters with insufficient power). The power analyses can also be used to optimize the ARMP sampling design for detecting trends. Recommendations for changes to the ARMP sampling design will be considered as part of the Comprehensive Monitoring Strategy.

### Project Goals and Objectives

The objectives for this project are:

- Calculate descriptive statistics for parameters measured by the ARMP program.
- Predict the power for detecting important trends in each parameter given the variability documented in the first objective.
- Draw conclusions and make recommendations.

### Methods

#### *Software*

All calculations were performed using SYSTAT version 10 statistical software and Crystal Ball 2000 Monte Carlo simulation software.

#### *Data Handling*

The data were handled in the following way.

- Queried all ARMP data for the 17 trend sites from the WQD (1990-2002, 658 records)
- Eliminated parameters with measurements for <10% of the records (algal growth, fecal streptococcus, flow, Mg, Mn, Hg, N-NO<sub>3</sub>+NO<sub>2</sub>-20, Secchi Depth, Total Coliforms, Total Fecal Coliforms, water appearance, water level, water odor, weather).

- Eliminated parameters with measurements for >10% of the records for which the majority of the results were censored. Censored data can throw off statistics and misrepresent the variability in the parameter. (As, Cd, COD, Cr, Ni, Se, BOD, Cu, Pb, N-Ammonia, Zn)
- Eliminated other parameters with minimal records which had been discontinued from the ARMP sampling design (chloride, iron, sulfate).
- Removed 40 duplicate/replicate records. The record with the most measurements was retained. If both record had measurements for all the parameters, the first record was arbitrarily chosen.
- Converted all “below detection limit” censored values to one half the reported value. There was only one sample that was censored as “above detection limit”. The upper detection limit reported for this measurement was retained as the actual value.

#### *Calculation of Descriptive Statistics*

- Calculated the average statistics for each parameter. For predicting the power to detect trends over time at a single station, the variability of interest is the intra-annual variability at each station. Therefore, the basic statistics were calculated from the raw data using the by groups command for PARAMETER\$, STATION\$, and YEAR in SYSTAT. This command generated a table of sample size, mean, and standard deviations for each unique station-year (i.e., one year of monitoring at one station). The values from all the station-years with at least 3 measurements were averaged for each parameter to derive a central tendency estimate of the mean value and standard deviation for each parameter at a typical station.
- Determined the distribution type for each parameter based on shape of histograms and size of the coefficient of variability. Parameters were either considered to be normal or lognormal. In general, if the coefficient of variability (stdev/mean) was >0.3, the parameter was assumed to be lognormal.

#### *Definitions of parameters for power calculations*

- Determined trend analysis methods for study. ARMP samples are collected three times during the summer at the trend stations. Most of the parameters were lognormally distributed. Therefore, the appropriate test for trends is the non-parametric Mann-Kendall Test (MKT) using the median of the three samples collected during the summer season. The power of the Seasonal Kendall Test (SKT) to detect trends from monthly samples throughout the year was also estimated.
- Determined the magnitude of “important trends”. In order to test for power, a trend of known magnitude must be specified and tested. For the parameters with water quality standards, the trend of interest was defined as one that would increase or decrease from the mean value to the water quality standard over 10 years. For parameters without standards, a 50% increase of the parameter over 10 years was chosen arbitrarily as the trend worth being able to detect.
- Determined period for trend detection. Five year and 10 year periods were selected for the trend analysis. The power for detecting trends over 10 years reflects on which parameters should be analyzed for trends using the existing 12 year record. Detecting trends over a 5 year period is preferable for management purposes because it would be important to detect trends leading toward a water quality violation before a violation actually occurs.

#### *Power Calculations*

- Statistical power was calculated using Monte Carlo simulations and the definitions of the MKT and SKT from Gilbert (1987). The central tendency mean and standard deviation of the concentration for each parameter was used to simulate a distribution of possible results. Five and ten year records of sampling results were generated by randomly sampling from this distribution with a linear trend superimposed. The MKT and SKT statistical tests were run on the simulated records. The simulation

was run 500 times for each parameter. The fraction of the simulations that predicted a significant (i.e.,  $p < 0.05$ , one tail or  $p < 0.10$ , two tails) trend represented the power for detecting that trend given the variability within the data.

## Results and Discussion

Of the 44 parameters pulled from the Water Quality Database, only 16 met all the data handling criteria for this analysis. For example, the 11 parameters listed below could not be analyzed because most of their results were listed as “below detection level”.

- Arsenic (107 of 111 records qualified)
- Cadmium (134 of 144 records qualified)
- COD (38 of 48 records qualified)
- Chromium (111 of 111 records qualified)
- Nickel (95 of 110 records qualified)
- Selenium (111 of 111 records qualified)
- BOD (336 of 423 records qualified)
- Copper (264 of 377 records qualified)
- Lead (250 of 347 records qualified)
- N-Ammonia (391 of 479 records qualified)
- Zinc (203 of 380 records qualified)

The descriptive statistics for the 16 parameters analyzed for this study are listed in Table 1. Histograms showing the distribution of all the data for each parameter are presented in an appendix.

**Table 1: Average mean value and standard deviation for each parameter in each “station-year”.**

Parameter	Units	Number of station-years	Mean of Mean Values	Mean of Standard Deviation Values	Mean of CV Values	Distribution
ALKALINITY	mg/l	89	11.94	4.28	0.35	LogNormal
ALUMINUM	mg/l	47	0.10	0.06	0.58	LogNormal
CHLORA	ug/l	16	3.06	1.50	0.43	LogNormal
DO	mg/l	158	8.47	0.87	0.10	Normal
DOSAT	%	93	93.41	7.33	0.08	Normal
ECOLI	MPN	165	194.15	271.30	0.79	LogNormal
HARDNESS	mg/l	50	18.31	4.07	0.21	Normal
TKN	mg/l	132	0.30	0.10	0.36	LogNormal
NO4	mg/l	122	0.26	0.12	0.43	LogNormal
PH		152	6.90	0.30	0.04	Normal
PHOSPHORUS	mg/l	147	0.04	0.02	0.36	LogNormal
SPCONDUCT	mg/l	157	96.36	25.12	0.26	Normal
TEMP	degC	161	20.76	2.66	0.13	Normal
TOTSOLIDS	mg/l	86	64.24	11.42	0.16	Normal
TSS	mg/l	98	3.19	2.71	0.78	LogNormal
TURBIDITY	NTU	122	1.55	0.70	0.40	LogNormal

In Table 2, the coefficient of variation (CV) for each parameter is listed for different levels of data aggregation. The greatest variation is shown for a combination of variability between stations, between years, and within years (right hand column). The least variation is shown for within years variability at a single station (left hand column). This result is expected. Removing sources of variability should result in lower CV values. However, it is worth noting that the intra-annual CV values are still high for many parameters. This residual variability could be reduced if other sources of variability, such as flow and precipitation, were also removed.

**Table 2: Average coefficient of variation for each parameter**

	Average Coefficient of Variation		
	Just Intra-Annual Variation at a Single Station	Combination of Intra- and Inter- Annual Variation at a Single Station	Combination of Intra- and Inter- Annual Variation at all Stations
ALKALINITY	0.35	0.42	0.75
ALUMINUM	0.58	0.64	0.77
CHLORA	0.43	0.45	0.81
DO	0.10	0.13	0.14
DOSAT	0.08	0.10	0.11
ECOLI	0.79	2.27	6.73
HARDNESS	0.21	0.22	0.56
TKN	0.36	0.47	0.56
NO4	0.43	0.72	0.93
PH	0.04	0.06	0.07
PHOSPHORUS	0.36	0.57	1.03
SPCONDUCT	0.26	0.32	0.58
TEMP	0.13	0.14	0.16
TOTSOLIDS	0.16	0.22	0.43
TSS	0.78	1.04	1.15
TURBIDITY	0.40	0.66	0.92

In Table 3, the results of the power analyses have been summarized. By convention, a power of 0.80 or greater is considered acceptable. The tests that have a power in this range are highlighted. Using the existing sampling scheme of collecting three samples each summer season, only dissolved oxygen, hardness, temperature, total solids, and turbidity have sufficient power to detect the “important trend” with 10 years of data. None of the parameters have sufficient power to detect trends over 5 years with the existing sampling scheme. If a monthly sampling scheme were adopted (i.e., 12 samples per year), dissolved oxygen, temperature, total solids, and turbidity would have sufficient power to detect the “important trend” after 5 years.

**Table 3: Power for detecting “important trends” for each parameter**

Parameter	"Important Trend"	Power	
		3 summer samples over 10 years	Monthly samples over 5 years
ALKALINITY	Increase from baseline (11.9 mg/l) to chronic WQS (20 mg/l) over 10 years	0.72	0.58
ALUMINUM	50% increase from baseline concentration over 10 years.	0.31	0.27
CHLORA	50% increase from baseline concentration over 10 years.	0.37	0.30
DO	Decrease from baseline (8.5 mg/l) to WQS (5 mg/l) over 10 years.	1.00	0.96
DOSAT	Decrease from baseline (93%) to WQS (75%) over 10 years.	0.91	0.69
ECOLI	Increase from baseline (194 MPN) to WQS (406 MPN) over 10 years	0.60	0.61
HARDNESS	50% increase from baseline concentration over 10 years.	0.91	0.63
TKN	50% increase from baseline concentration over 10 years.	0.54	0.42
NO4	50% increase from baseline concentration over 10 years.	0.40	0.30
PH	Decrease from baseline (6.9) to WQS (6.5) over 10 years	0.50	0.32
PHOSPHORUS	50% increase from baseline concentration over 10 years.	0.46	0.35
SPCONDUCT	50% increase from baseline concentration over 10 years.	0.78	0.52
TEMP	50% increase from baseline concentration over 10 years.	1.00	0.97
TOTSOLIDS	50% increase from baseline concentration over 10 years.	1.00	0.80
TSS	50% increase from baseline concentration over 10 years.	0.24	0.25
TURBIDITY	Increase from baseline (1.6 NTU) by 10 NTUs (11.6 NTU) over 10 years.	1.00	1.00

## Conclusions and Recommendations

- The analytical methods for the parameters with mostly censored results should be investigated to determine if lower detection limits are achievable. With the current detection limits, these variables cannot be analyzed for trends.
- The ARMP should consider recording flow at the time of each sample collected. Flow has been shown by the USGS to be a significant covariate for concentration in river samples (Helsel and Hirsch, 2003). If the variability caused by changes in flow were removed, the ARMP monitoring would have more power to detect trends.
- Using the existing sampling scheme of collecting three samples each summer season, only dissolved oxygen, hardness, temperature, total solids, and turbidity have sufficient power to detect the “important trend” with 10 years of data. None of the parameters have sufficient power to detect trends over 5 years with the existing sampling scheme.
- If it is important to be able to detect trends after 5 years, the existing sampling scheme will have to be changed to monthly sampling throughout the year. However, this sampling design will not provide sufficient power for trend detection in all the parameters. Monthly sampling throughout the year could also mask trends that only occur in the summer. For each parameter, the ARMP should decide whether summertime trends or year-round trends are the most important indicators of water quality.
- The ARMP should undertake a structured planning process to determine what magnitude of trend is important to detect over a specified time frame (5 years? 10 years?). The “important trends” tested in this analysis were arbitrary chosen. These trends may not reflect the priorities of the ARMP.

## References

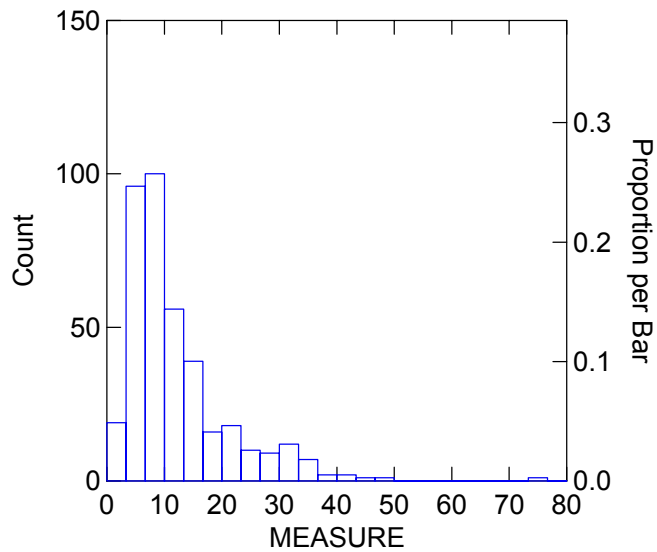
Gilbert, RO (1987) Statistical Methods for Environmental Pollution Monitoring. Van Nostrand Reinhold, New York. 320 pp.

Helsel DR and Hirsch RM. (2002) Statistical Methods in Water Resources. In Techniques of Water Resources Investigations of the USGS, Book 4, Chapter A3. U.S. Geological Survey, Reston VA. Online at <http://water.usgs.gov/pubs/twri/twri4a3/>.

## APPENDIX: HISTOGRAMS OF ALL DATA FOR EACH PARAMETER

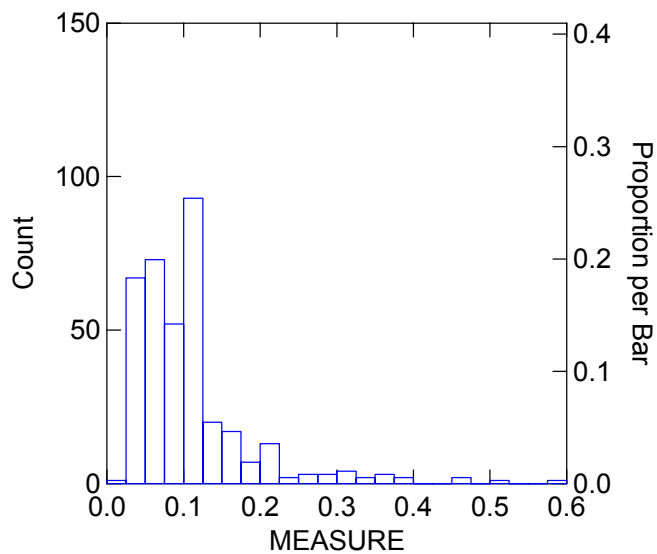
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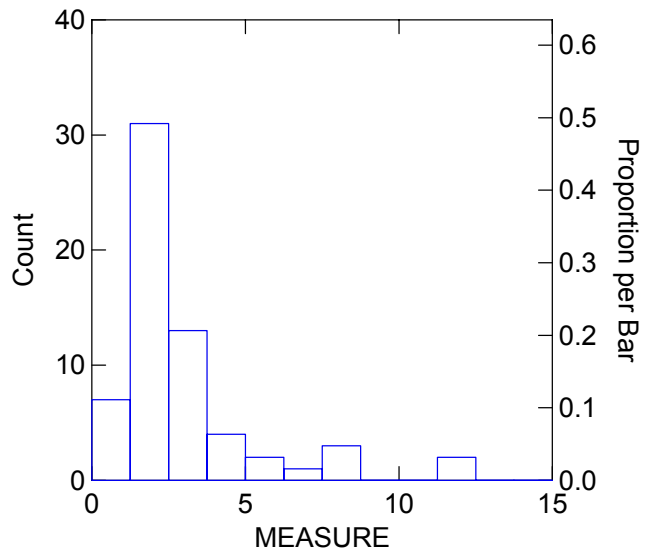


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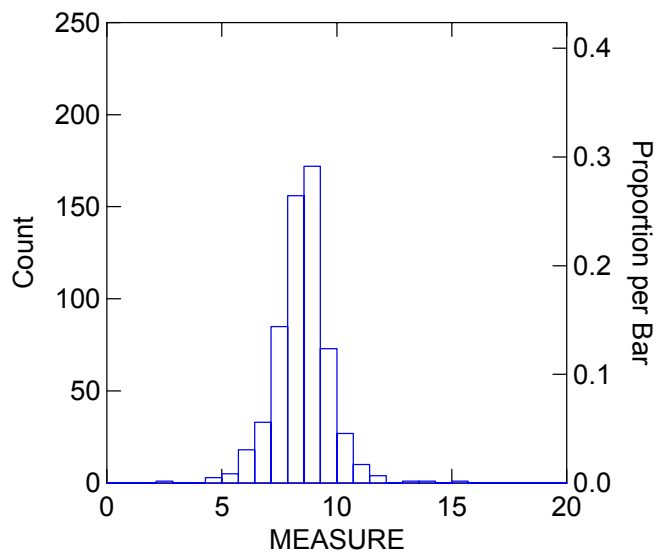
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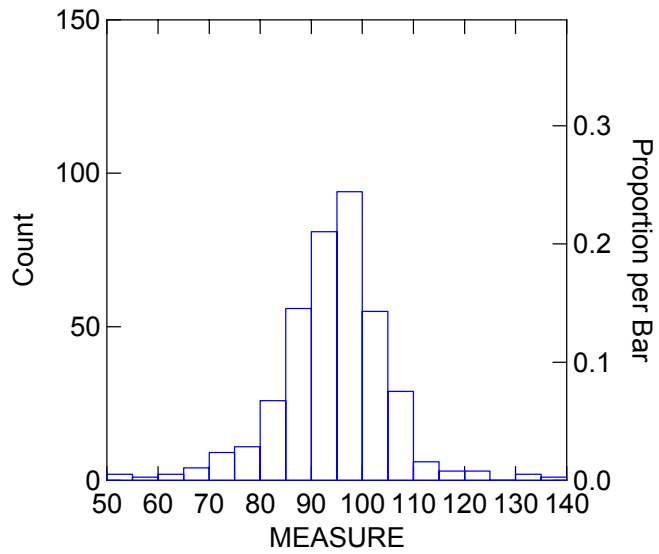


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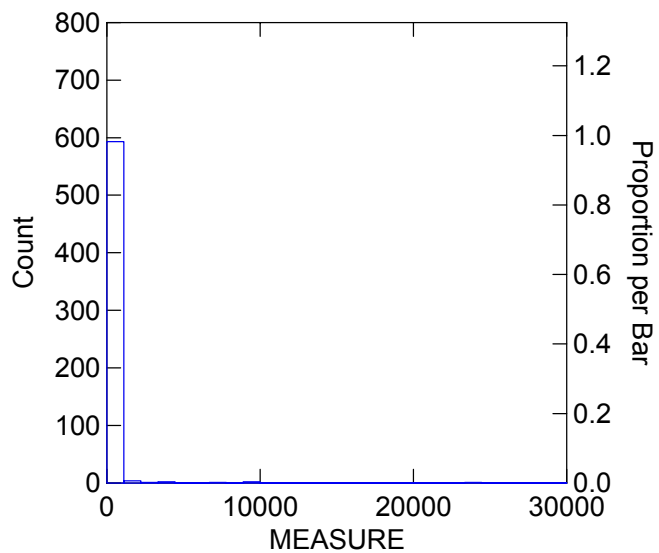




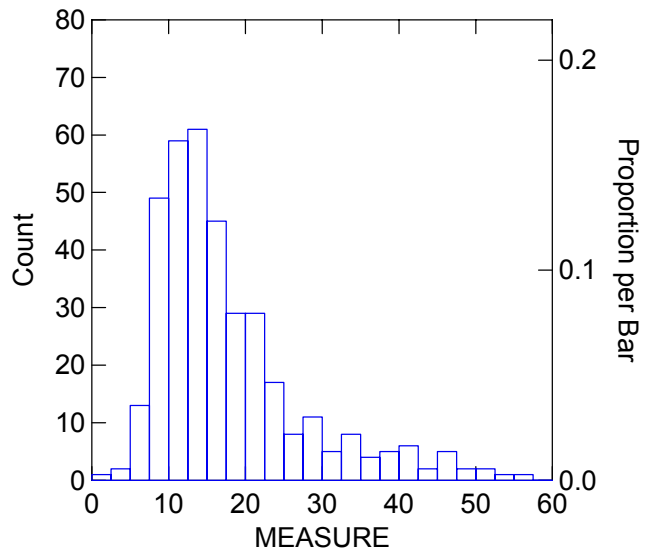
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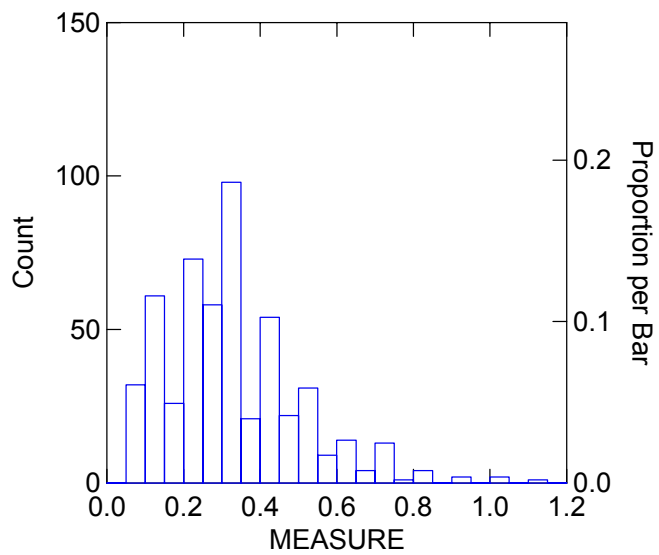
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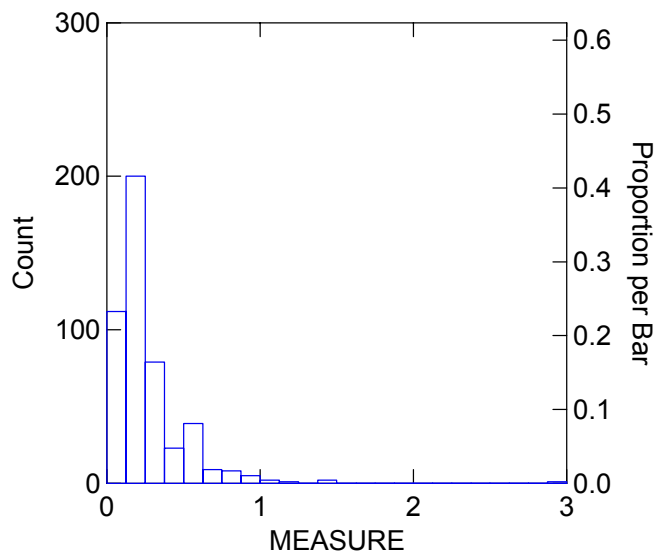
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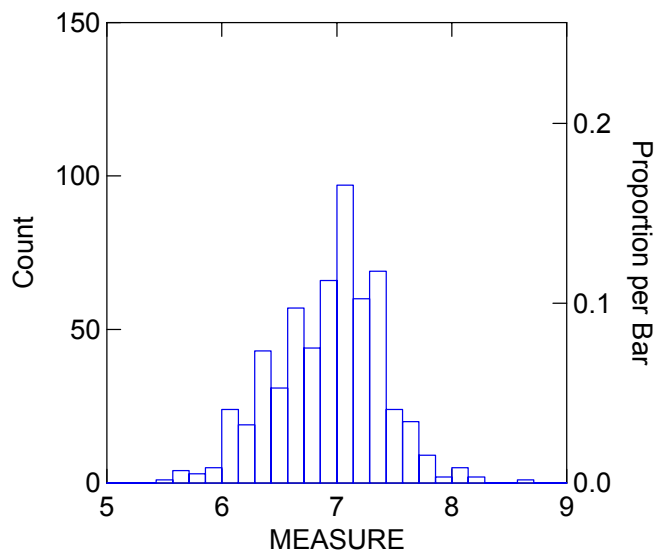
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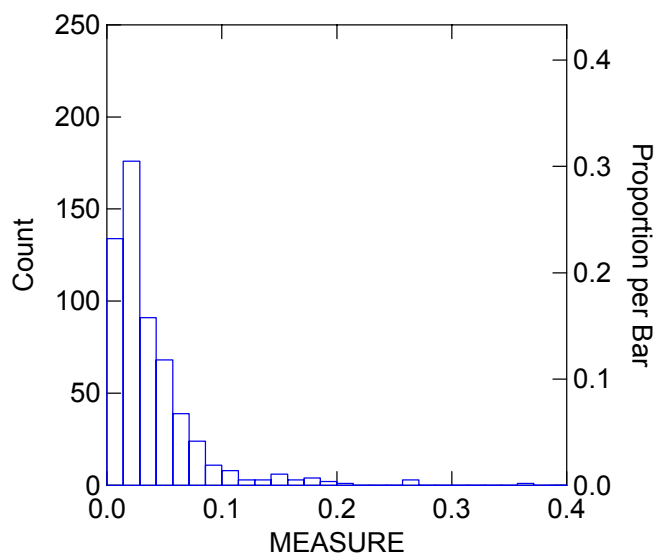
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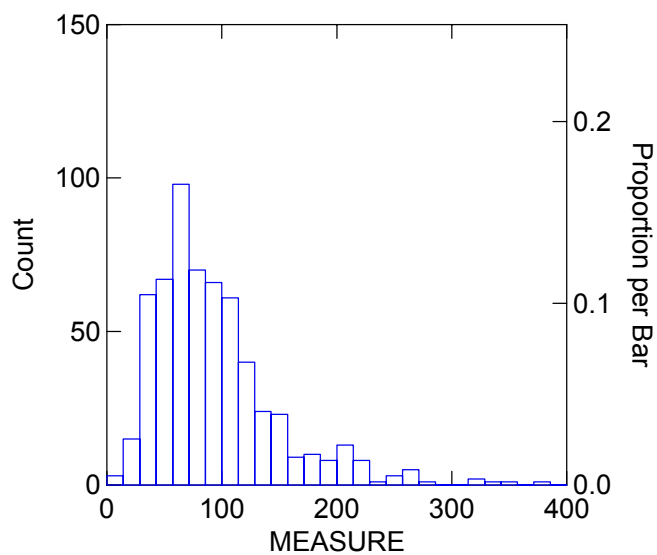
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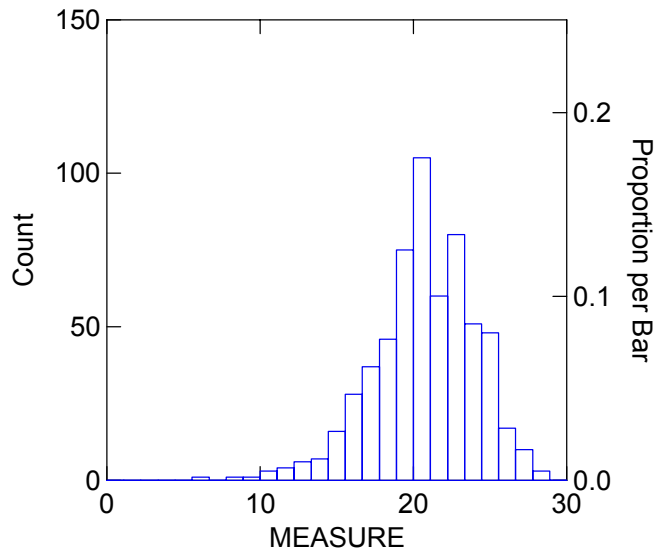
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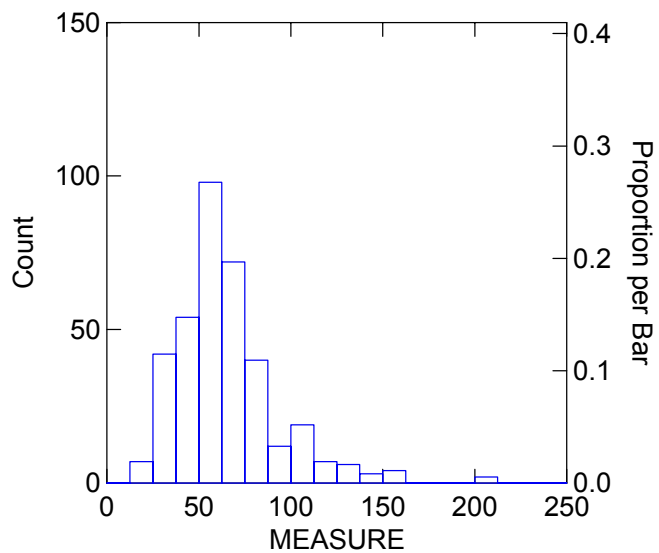
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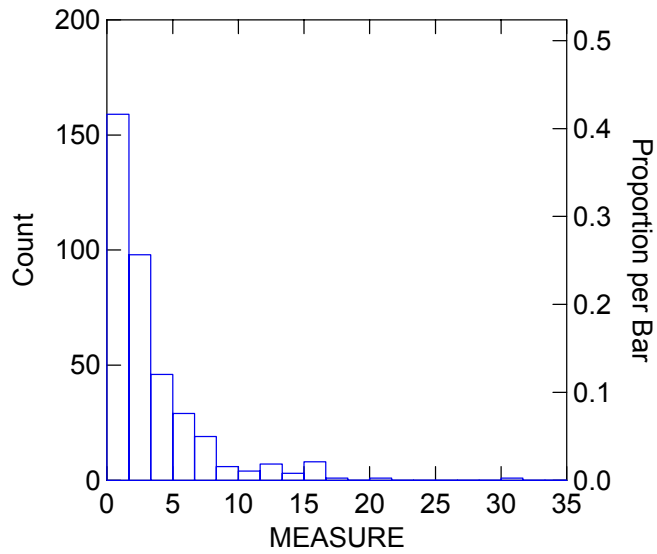
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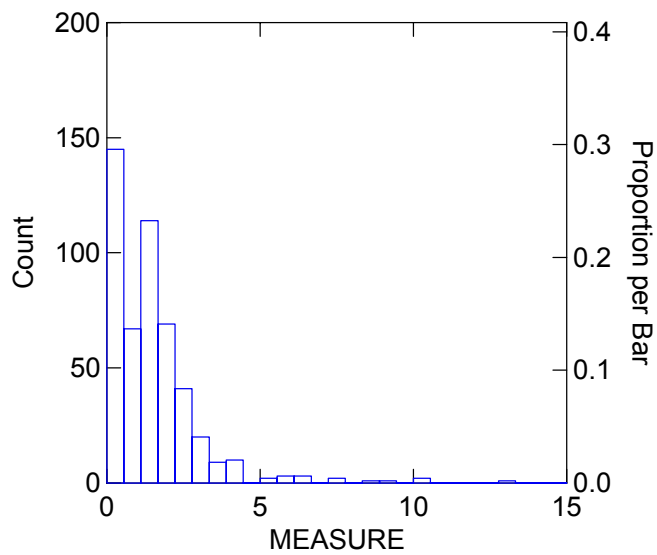
The following results are for:  
PARAMETER\$ = TOTSOLIDS



The following results are for:  
PARAMETER\$ = TSS



The following results are for:  
PARAMETER\$ = TURBIDITY



# **State of New Hampshire**

## **Inter-Department Communication**

**Date:** August 4, 2004

**From:** Phil Trowbridge  
Coastal Scientist

**At (Office):** Environmental Services  
Watershed Management

**Subject:** Power Analysis for the Ambient Rivers Monitoring Program

**To:** Gregg Comstock, Supervisor, Water Quality Planning Section  
Paul Piszczek, ARMP Coordinator

### Introduction

The DES Ambient Rivers Monitoring Program (ARMP) has collected yearly data at 17 trend monitoring stations across New Hampshire for over a decade. The Program would like to analyze the data from these stations to determine if there have been any significant trends over time. In addition, the Watershed Management Bureau is developing a Comprehensive Monitoring Strategy, which would include any changes to the ARMP monitoring design in order to increase statistical power.

In a previous report, Trowbridge (2003) determined that only five of the parameters measured at the ARMP stations had sufficient power to detect arbitrarily-defined “important trends” over a 10 year period. One recommendation from that report was that DES should investigate ways to reduce the variability in the data by adjusting the concentrations for changes in stream flow.

For this report, the ARMP data at one station (01-SAC) from 1990 to 2003 have been reviewed to determine the power for detecting trends if the concentrations are adjusted for changes in stream flow. The 01-SAC station was chosen because it is close to a USGS stream gage that has operated continuously during the sampling period. This analysis will determine whether it is worth the effort to associate flow data with each ARMP measurement at trend stations.

## Project Goals and Objectives

The objectives for this project are:

- Calculate descriptive statistics for parameters measured at 01-SAC.
- Determine whether there are relationships between parameter concentrations and flow.
- If such relationships exist, adjust the concentrations by removing the variability that is associated with the changes in stream flow.
- Predict the improved power for detecting important trends with flow-adjusted concentrations.
- Document any statistically significant trends in concentrations or flow-adjusted concentrations at 01-SAC.
- Draw conclusions and make recommendations.

## Methods

### *Software*

All calculations were performed using SYSTAT version 10 statistical software, MS Excel 2000, and Crystal Ball 2000 Monte Carlo simulation software.

### *Data Handling*

The data were handled in the following way.

- Queried all ARMP routine samples for the 01-SAC site from the WQD (1990-2003, 41 records, field QC samples excluded).
- Selected data for the parameters that are currently monitored by ARMP: Dissolved oxygen, temperature, specific conductivity, pH, *E.coli*, alkalinity, chlorophyll-a, hardness, total suspended solids (TSS), turbidity, nitrogen (Kjeldahl), nitrogen (nitrate+nitrite), nitrogen (ammonia), biochemical oxygen demand (BOD), phosphorus, aluminum, copper, lead, and zinc.
- Deleted four parameters because nearly all of the results were listed as “less than detection limit”: nitrogen (ammonia), BOD, copper, and lead. The method detection limits are not



sensitive enough for these parameters. Deleted the entries for chlorophyll-a because there were only data for 2002 and 2003.

- Calculated the dissolved oxygen saturation based on the dissolved oxygen concentrations (mg/l), specific conductivity, temperature, and elevation using an equation from Standard Methods.
- Combined results for three different nitrate/nitrite parameters in order to have one complete record: “NITROGEN, NITRATE (NO<sub>3</sub>) AS N RESULTS”; “NITROGEN, NITRATE + NITRITE - 20 RESULTS”; and “NITROGEN, NITRITE (NO<sub>2</sub>) + NITRATE (NO<sub>3</sub>) AS N RESULTS”. The latter two parameters were monitored in 2002 and 2003, respectively.
- Deleted six records for *E.coli* in 1990 and 1991 because these values were recorded as MPN while the rest of the records were recorded as plate counts.
- Deleted all censored values for the remaining parameters. Using censored values in trend analysis requires making assumptions about the actual (undetected) concentration. For the purposes of determining variability, it is safer to avoid these assumptions.
- Checked the data for outliers. Histograms and normal probability plots were generated for each parameter to identify anomalously high values. Two outliers were detected and removed from the dataset. On 7/18/01, the alkalinity measurement was 78.4 mg/l. The rest of the alkalinity results at this station were less than 10 mg/l. There is no logical explanation for the high alkalinity on this date. On 6/2/94, the zinc measurement was 0.130 mg/l. All the other concentrations were less than 0.022 mg/l. This value is in the 98<sup>th</sup> percentile of all zinc values recorded in the state by the ARMP program.
- Downloaded daily stream flow statistics for USGS gage 01064500 for the period 1/1/90 to 12/31/03 from USGS National Water Information System  
<http://nwis.waterdata.usgs.gov/usa/nwis/discharge>

Information on Stream gage 01064500 (Saco River Near Conway, NH)  
Carroll County, New Hampshire  
Hydrologic Unit Code 01060002  
Latitude 43°59'27", Longitude 71°05'29" NAD27  
Drainage area 385.00 square miles

Contributing drainage area 385 square miles

Gage datum 418.19 feet above sea level NGVD29

- Matched daily average stream flow at the gage to the dates of the ARMP measurements using a lookup query in MS Excel.

#### *Relationships between concentration and flow*

- Plotted histograms and normal probability plots for the water quality parameters and flow to determine whether the parameters were distributed normally. The following parameters were not normally distributed and, therefore, were transformed using the natural logarithm: Specific conductivity, *E.coli*, hardness, TSS, turbidity, TKN, phosphorus, aluminum, and zinc.
- Plotted the parameter concentrations versus flow to determine which parameters were related to flow and the nature of the relationship.
- For those parameters that were related to flow, calculated flow-adjusted concentrations by adding the residuals from the concentration-flow relationship to the average concentration.

#### *Power Calculations*

- Calculated the coefficient of variation for the raw concentrations and flow-adjusted concentrations for each parameter for years in which at least three measurements were collected. The two CV values were compared to determine the percentage of the variability that was removed by using flow-adjusted concentrations.
- Statistical power was calculated using Monte Carlo simulations and the definitions of the Mann-Kendall test from Gilbert (1987). The central tendency mean and standard deviation of the concentration for each parameter were used to simulate a distribution of possible results. The central tendency mean was taken from Trowbridge (2003). The average standard deviation was the average standard deviation listed in Trowbridge (2003) reduced by the amount calculated in the preceding paragraph. The central tendency mean and standard deviation for each parameter from Trowbridge (2003) were used so that the results of this

analysis would be comparable to the results from Trowbridge (2003). Ten year records of sampling results were generated by randomly sampling from this distribution with a linear trend superimposed. The Mann-Kendall statistical tests were run on the simulated records. The simulation was run 500 times for each parameter. The fraction of the simulations that predicted a significant (i.e.,  $p < 0.05$ , one tail or  $p < 0.10$ , two tails) trend represented the power for detecting that trend given the variability within the data.

#### *Statistically significant trends at 01-SAC*

- Checked all the parameters at 01-SAC for trends between 1990 and 2003 using simple linear regression and multivariate linear regression.

#### Results and Discussion

Figure 1 and Figure 2 show the histograms and probability plots for the ARMP parameters (minus chlorophyll-a, BOD, copper, lead, and ammonia – see page 2, third bullet) plus flow. In these plots, the values for specific conductivity, *E.coli*, hardness, TSS, turbidity, TKN, phosphorus, aluminum, zinc, and flow have already been transformed using the natural logarithm. The histograms and probability plots show that the parameters, once transformed if necessary, follow an approximate Normal distribution.

Plots of the concentrations (or log-transformed concentrations) against the natural logarithm of flow are shown in Figure 3. The blue lines on the graph are the linear regression between the variables bounded by the 95<sup>th</sup> percentile confidence limits. Nine of the 15 parameters had a statistically significant linear relationship with flow at the  $p < 0.05$  level: Dissolved oxygen, temperature, specific conductivity, *E.coli*, alkalinity, hardness, turbidity, nitrate+nitrite, and aluminum. In addition, the relationship between phosphorus and flow was significant at the  $p < 0.10$  level. Half of the parameters showed decreasing concentrations with increasing flows, presumably due to dilution. Temperature, specific conductivity, alkalinity, hardness, and nitrate all decreased with increasing flows. The other half of the parameters had concentrations that tended to increase with increasing flows: Dissolved oxygen, *E.coli*, turbidity, phosphorus, and

aluminum. The remaining five parameters (dissolved oxygen saturation, pH, TSS, nitrogen-Kjeldahl and zinc) did not show any discernable relationships with flow. None of the parameters appeared to have non-linear relationships with flow so it was not necessary to test non-linear models for significance. The linear relationships between concentration and stream flow for the 10 parameters are shown below.

Concentrations decrease with increasing flows

$$\text{TEMP} = -2.560 * \text{LN\_FLOW} + 35.495$$

$$\text{LN\_SPCOND} = -0.253 * \text{LN\_FLOW} + 5.393$$

$$\text{ALKALINITY} = -1.620 * \text{LN\_FLOW} + 14.827$$

$$\text{LN\_HARDNESS} = -0.272 * \text{LN\_FLOW} + 3.803$$

$$\text{NNO3} = -0.064 * \text{LN\_FLOW} + 0.582$$

Concentrations increase with increasing flows

$$\text{DO} = 0.529 * \text{LN\_FLOW} + 5.574$$

$$\text{LN\_ECOLI} = 1.316 * \text{LN\_FLOW} - 4.709$$

$$\text{LN\_TURBIDITY} = 0.633 * \text{LN\_FLOW} - 4.094$$

$$\text{LN\_PHOSPHORUS} = 0.172 * \text{LN\_FLOW} - 5.857$$

$$\text{LN\_ALUMINUM} = 0.318 * \text{LN\_FLOW} - 4.308$$

Flow adjusted concentrations were generated for these 10 parameters by adding the residuals from the linear relationships to the average concentration. Plots of the raw and flow-adjusted concentrations versus flow and year are shown in Appendix A and B, respectively. Descriptive statistics of the new flow-adjusted concentrations were calculated and compared to the statistics for the raw concentrations. For the log-transformed parameters, the results were converted back to normal units for the comparison. In general, the mean values did not change but the standard deviations were reduced. Table 1 shows how the coefficient of variation (stdev/mean) changed for the parameters after the flow relationships for these parameters were taken into account.

For the parameters whose concentrations decreased with increasing flows, the coefficient of variation (CV) was reduced by 45% on average after variability associated with stream flow was removed. Specifically, the CVs for temperature, specific conductivity, alkalinity, hardness, and nitrate+nitrite fell by 31%, 44%, 32%, 69%, and 47%, respectively. The relationship between concentration and flow for these parameters is most likely caused by dilution of a constant source during periods of high flows. In this case, the effect of the increasing flow should be uniform for all pollutants, which appears to be the case.

For the parameters that experience increasing concentrations with increasing flow, the changes in the CV were less consistent. The CV for dissolved oxygen was only reduced by 7%. For *E.coli* and turbidity, the CV appeared to increase after the flow adjustment was made. However, the comparisons for these parameters were based on a small and unrepresentative number of years (see footnotes on the table). Phosphorus showed a small increase in CV values. The relationship between flow and this parameter was weak so it is not surprising that the flow adjustment failed to reduce the variability. Finally, the CV for aluminum was reduced by 51%.

The disparate responses to the flow adjustment by these five parameters are likely due to a variety of different processes affecting the parameters as well as incomplete information. Increasing flows likely increase dissolved oxygen concentrations due to convection and mixing. Therefore, the amount of an increase will depend on how far below saturation the dissolved oxygen concentrations are for normal flows. If the water is generally well oxygenated, then increasing flow can only have a minimal effect on dissolved oxygen concentrations. In contrast, *E.coli*, turbidity, phosphorus, and aluminum are expected to increase with increasing flows due to stormwater loads to the river. Based on all the data at 01-SAC, there is a significant relationship between flow and these parameters. Therefore, using the flow adjusted concentrations should reduce the variability in the concentrations. A reduction in the CV was not apparent in Table 1 because comparisons had to be made between years in which at least three samples were taken. There was only one year that met this criteria for *E.coli*. Only four years met the criteria for turbidity and aluminum and these years did not appear to be representative of the whole time series. The CV for phosphorus was not affected by the flow adjustment because the relationship between this parameter and flow is weak. Therefore, it appears that the effect of flow-adjustment on the CV of dissolved oxygen and phosphorus is small, while the effect on the CV for *E.coli*, turbidity, and aluminum is likely to be significant but the precise effect cannot be quantified with the dataset from 01-SAC.

In Trowbridge (2003), the average variability of the ARMP parameters was used to calculate the power of detecting important trends over 10 year period with the existing ARMP sampling design: three summer samples per year. The Mann-Kendall nonparametric test was assumed to be the most appropriate method for measuring trends. For five parameters, there was already

sufficient power to detect these trends without removing the variability due to flow. However, for the remaining parameters, there was too much variability to detect the trends. Therefore, reducing the variability by accounting for flow would improve the trend detection.

The same power calculations from Trowbridge (2003) were re-run with the variability reduced to account for stream flow when applicable. For the five parameters that experience dilution of the concentration at high flows, the CV was reduced by 45% to symbolize the effect of using flow-adjusted concentrations. Power calculations were also redone for *E.coli*, turbidity, and aluminum with a CV reduced by 45% since these parameters have a relationship with flow but the effect could not be quantified. The trend detection power for the parameters calculated in Trowbridge (2003) and the recalculated power are shown on Table 2.

The results of the new power analyses show that, after accounting for flow variability where possible, seven of the ARMP parameters have sufficient power to detect trends with the current sampling design of three samples from the summer months. Another two parameters (*E.coli* and nitrate+nitrite) have power values slightly below the conventional target (0.80) but, in reality, have sufficient power for trend detection. Overall, the parameters that have sufficient power are those measured by field instruments (dissolved oxygen, dissolved oxygen saturation, pH, specific conductivity, temperature, and turbidity) plus alkalinity, hardness, *E.coli*, and nitrate+nitrite. The power for trend detection is still low for chlorophyll-a, Kjeldahl nitrogen, pH, phosphorus, and total suspended solids. None of these parameters exhibited a relationship with flow at 01-SAC. It is possible that the power could be improved for these parameters if data from other stations showed a relationship with flow. Finally, five parameters had effectively zero power because their concentrations were consistently below the method detection level: nitrogen-ammonia, biological oxygen demand, copper, lead, and zinc. With the current detection limits, measurements of these parameters cannot be used for trend detection.

The only two analytical measurements that have sufficient power to detect trends with the current sampling design of three summer samples are hardness and alkalinity. Therefore, it may be possible to reduce the sampling frequency for these parameters to save money while still being able to detect trends. The power analyses for these two parameters were re-run assuming

only one sample per year at each station. The results showed that collecting only one sample per year would still have sufficient power for trend detection so long as the concentrations are adjusted for changes in flow. Alkalinity is a generalized, stand-alone parameter that can be analyzed individually, whereas hardness is used in conjunction with metals analysis. Therefore, the frequency of hardness measurements should be the same as for metal measurements.

As a final check on the utility of using flow-adjusted concentrations, the raw and flow-adjusted concentrations at 01-SAC between 1990 and 2003 (14 years) were analyzed for significant trends using simple linear regression and multivariate linear regression with the log-transformed flow parameter as a covariate. The results of these tests are shown in Table 3. Time series graphs of the raw concentrations and flow-adjusted concentrations are shown in Appendix B. Statistically significant trends were detected for dissolved oxygen saturation, temperature, specific conductivity, turbidity, and zinc. The first four of these parameters are field measurements that are shown on Table 2 to have sufficient power to detect trends. Therefore, detecting trends for these parameters is not surprising. In contrast, it is unexpected to detect a trend for zinc. However, the zinc trend appears to be driven by three older measurements. The time series for zinc shows that there are three zinc measurements between 1990 and 1994, then none for 1995 through 1997, followed by multiple measurements from 1998 to 2003. The measurements from 1990 to 1994 were elevated. Because there are few elevated concentrations and they occur at the far end of the time series, these three points have a lot of leverage on the regression line, which makes the trend suspect.

### Conclusions and Recommendations

- There are statistically significant linear relationships between flow and 10 of the 20 ARMP parameters.
- For parameters that experience decreasing concentrations with increasing flow due to dilution, the variability in the concentrations can be reduced by approximately 45% if changes in stream flow are taken into account.
- For the parameters that have increasing concentrations with increasing flow, the variability is expected to be reduced but the exact amount cannot be quantified with the dataset from 01-

SAC. For planning purposes, it was assumed that 45% of the variability could be removed by using flow-adjusted concentrations.

- The existing sampling design for ARMP (3 summer samples per year) has sufficient power for detecting important trends for 5 parameters using raw concentrations. Using flow-adjusted concentrations, the program would have sufficient power for two more parameters (plus two others that are close). Therefore, on balance, stream flow coincident with ARMP trend station sampling should be measured or extrapolated from existing stream gages. The effort to gather these data for the 17 trend stations for 1990 to present is worth the effort because it will make it possible to detect trends for some of the parameters at these stations at least 5 years earlier than they would be otherwise.
- There was insufficient data at 01-SAC to evaluate the relationships with flow for pH, chlorophyll-a, Kjeldahl nitrogen, phosphorus, and TSS. Data from several other ARMP trend sites should be reviewed to determine whether the trend detection power for these parameters could be improved by using flow-adjusted concentrations.
- Five of the parameters (BOD, ammonia, copper, lead, and zinc) are consistently below the detection limit. If the detection limits are not changed, these parameters cannot be used for trend detection and they should be dropped from the program to save money unless they are needed for assessing standards attainment.
- Alkalinity and hardness could be measured less frequently while still retaining sufficient power for trend detection. Only one sample per year is needed for these parameters so long as the concentrations are adjusted for flow. Hardness samples should be collected at the same frequency as metals samples. If metals are not being measured, there is no need to measure hardness.
- A longer list of metals should be monitored if low detection limits can be achieved through clean techniques. The current list of metals misses mercury which is a Gulf of Maine priority pollutant. The RCRA 8 metals (arsenic, barium, cadmium, chromium, lead, mercury, selenium, silver) would provide better coverage of the toxic metals. The increased cost of monitoring the additional metals could be offset by reducing the sampling frequency for metals to once per year. In addition, total organic carbon and important ions such as chlorides, calcium, magnesium, and sulfate should be considered for the ARMP in order to better understand the effects acid rain and roadway salt application.



- At station 01-SAC, the only trends that were apparent in the 1990-2003 dataset were increasing dissolved oxygen saturation, specific conductivity, and temperature, and decreasing turbidity and zinc. The trends were apparent in both the raw and flow-adjusted concentrations.

## References

Gilbert, RO (1987) Statistical Methods for Environmental Pollution Monitoring. Van Nostrand Reinhold, New York. 320 pp.

Trowbridge (2003) Memorandum to Gregg Comstock (NHDES) re: Power analyses for the ambient rivers monitoring program. NH Department of Environmental Services, Watershed Management Bureau, Concord, NH. June 30, 2003.

Figure 1: Histograms of the concentrations and flow measured at 01-SAC 1990-2003

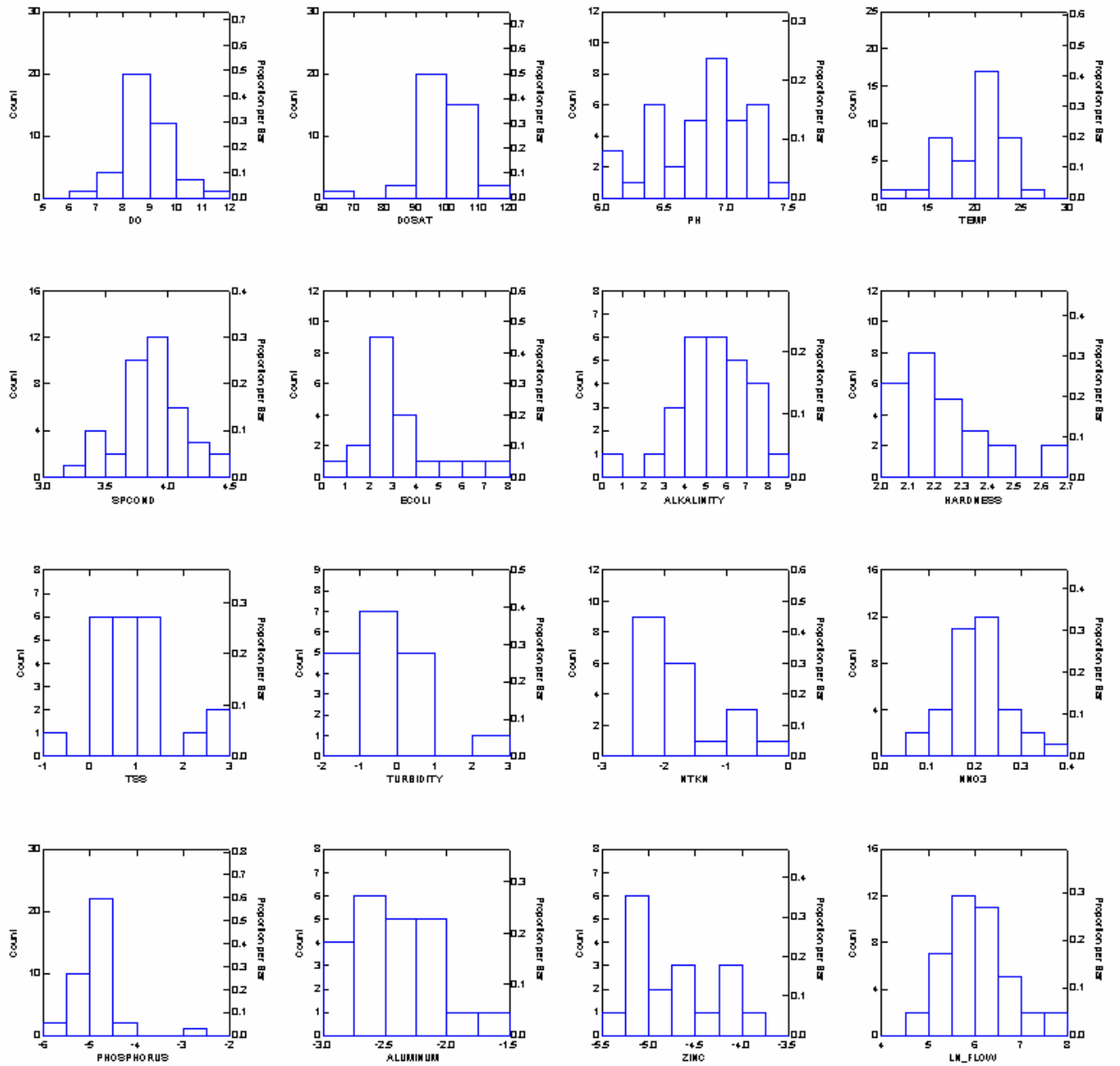


Figure 2: Normal probability plots for concentrations and flow measured at 01-SAC 1990-2003

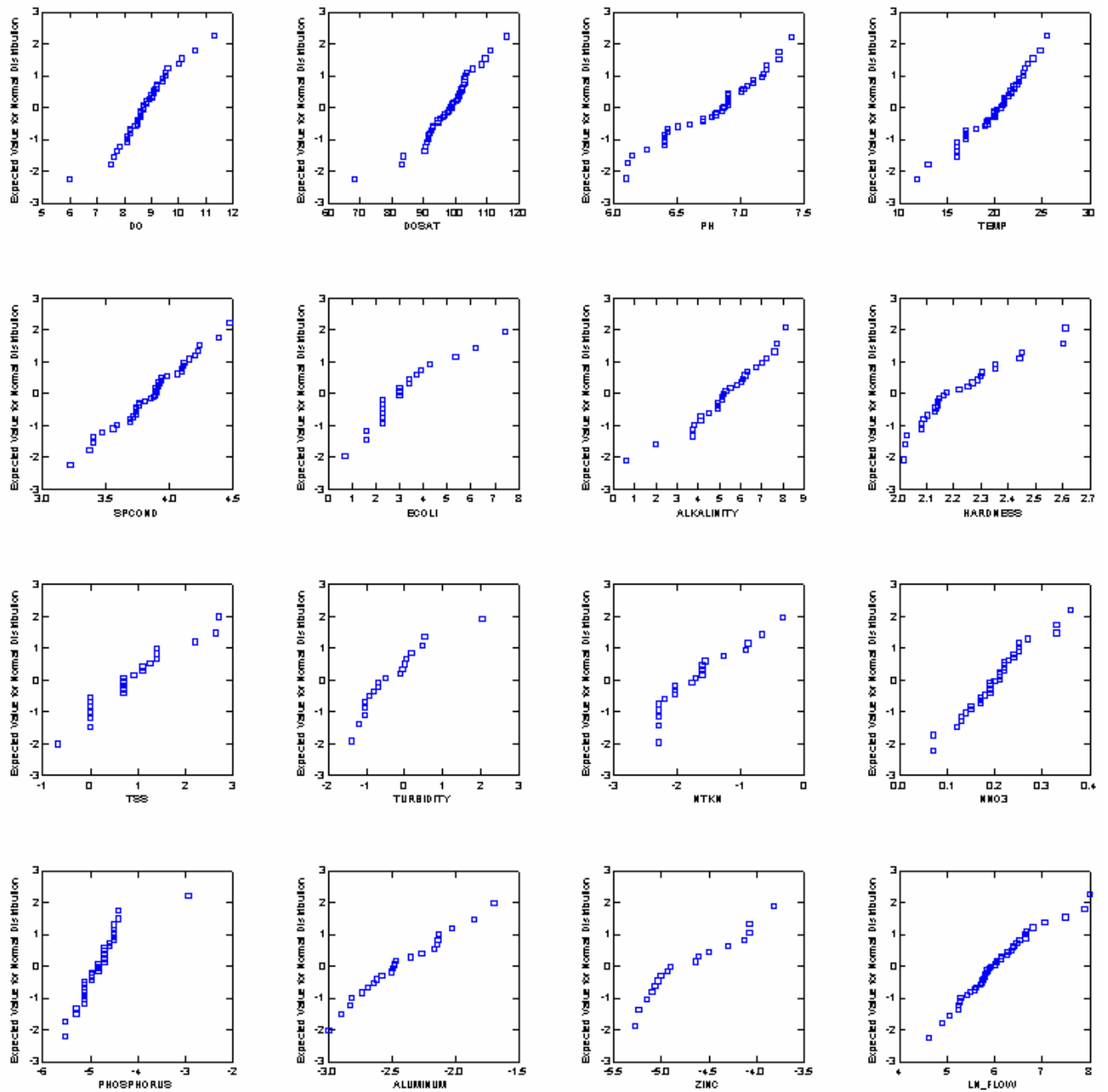
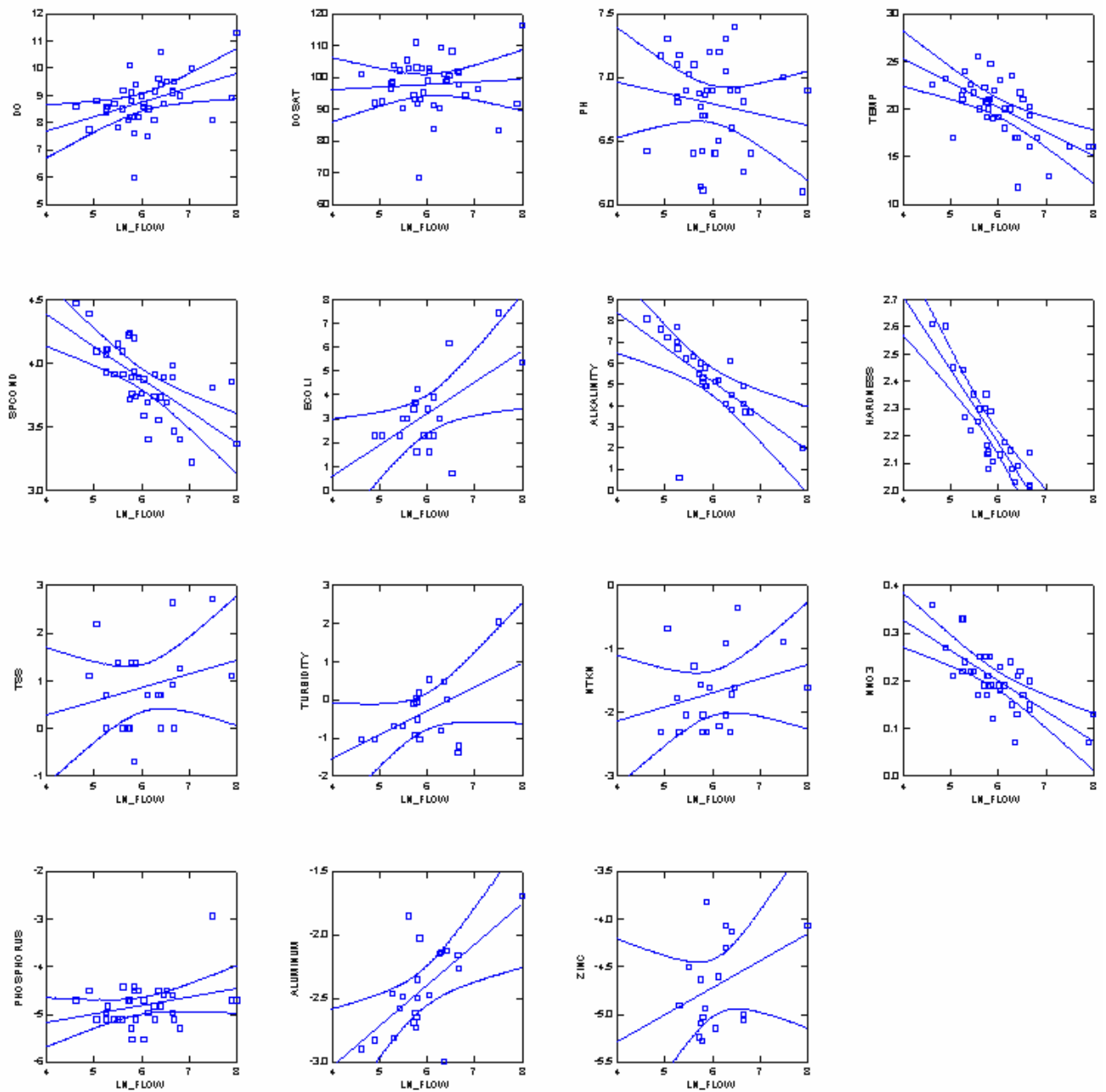


Figure 3: Relationships between parameter concentrations and stream flow at 01-SAC 1990-2003



**Table 1: Summary statistics for ARMP parameters at 01-SAC from 1990 to 2003 for years with >2 measurements**

Parameter	Data	Data2		% Reduction in CV	Comments
		Raw	Flow-adjusted		
Alkalinity (mg/l)	Count of Mean	7	7		
	Average of Mean	5.204	5.264		
	Average of Stdev	1.567	0.905		
	Average of CV	0.324	0.219	32%	
Aluminum (mg/l)	Count of Mean	4	4		
	Average of Mean	0.086	0.088		
	Average of Stdev	0.025	0.013		
	Average of CV	0.289	0.141	51%	
Dissolved Oxygen (mg/l)	Count of Mean	12	12		
	Average of Mean	8.754	8.731		
	Average of Stdev	0.806	0.740		
	Average of CV	0.092	0.085	7%	
Dissolved Oxygen Saturation (%)	Count of Mean	11			
	Average of Mean	98.214			
	Average of Stdev	7.618			
	Average of CV	0.079			
Hardness (mg/l)	Count of Mean	5	5		
	Average of Mean	9.591	9.532		
	Average of Stdev	1.701	0.501		
	Average of CV	0.170	0.053	69%	
Nitrate+Nitrite (mg/l)	Count of Mean	10	10		
	Average of Mean	0.205	0.208		
	Average of Stdev	0.060	0.031		
	Average of CV	0.286	0.152	47%	
Nitrogen, Kjeldahl (mg/l)	Count of Mean	3			
	Average of Mean	0.206			
	Average of Stdev	0.106			
	Average of CV	0.490			
pH	Count of Mean	10			
	Average of Mean	6.774			
	Average of Stdev	0.235			
	Average of CV	0.035			
Phosphorus (mg/l)	Count of Mean	9	9		
	Average of Mean	0.010	0.009		
	Average of Stdev	0.005	0.004		
	Average of CV	0.354	0.380	-7%	See note 1
Specific Conductivity (umho/cm)	Count of Mean	11	11		
	Average of Mean	50.095	49.003		
	Average of Stdev	10.537	5.652		
	Average of CV	0.212	0.119	44%	
Temperature (degC)	Count of Mean	12	12		
	Average of Mean	20.110	20.213		
	Average of Stdev	2.716	1.917		
	Average of CV	0.140	0.097	31%	
Total Suspended Solids (mg/l)	Count of Mean	3			
	Average of Mean	1.556			
	Average of Stdev	0.873			
	Average of CV	0.571			
Turbidity (NTU)	Count of Mean	4	4		
	Average of Mean	0.629	0.705		
	Average of Stdev	0.221	0.304		
	Average of CV	0.337	0.513	-52%	See note 2
Zinc (mg/l)	Count of Mean	2			
	Average of Mean	0.006			
	Average of Stdev	0.001			
	Average of CV	0.138			
E.coli (cts/100ml)	Count of Mean	1	1		
	Average of Mean	236.667	100.227		
	Average of Stdev	231.157	147.307		
	Average of CV	0.977	1.470	-50%	See note 3

Note 1: There was only a weak relationship between phosphorus and flow. The relationship might be improved if an outlier in 1992 was removed.

Note 2: Average not representative of the whole time series. Only the last four sampling years have 3 measurements per year but the flow relationship is based on data from all years. There was a major outlier in 2002 that drove the equation with streamflow.

Note 3: There was only one year with 3 E.coli measurements. Therefore, the average is only representative of one year, not the whole time series.

**Table 2: Summary of Power Analyses for ARMP Parameters**

			Power to detect "important trend" over 10 years with 3 summer samples per year	
Group	Parameter	"Important Trend"	Raw concentrations	Flow adjusted concentrations
Field measurements	Dissolved oxygen	Decrease from baseline (8.5 mg/l) to WQS (5 mg/l) over 10 years.	1.00	Same as raw
	Dissolved oxygen Saturation	Decrease from baseline (93%) to WQS (75%) over 10 years.	0.91	Same as raw
	pH	Decrease from baseline (6.9) to WQS (6.5) over 10 years	0.50	Same as raw
	Specific conductivity	50% increase from baseline concentration over 10 years.	0.70	1.00
	Temperature	50% increase from baseline concentration over 10 years.	1.00	1.00
	Turbidity	Increase from baseline (1.6 NTU) by 10 NTUs (11.6 NTU) over 10 years.	1.00	1.00
Bacteria	E.coli	Increase from baseline (194 MPN) to WQS (406 MPN) over 10 years	0.60	0.68
Nutrients	Nitrogen, Kjeldahl	50% increase from baseline concentration over 10 years.	0.54	Same as raw
	Nitrogen, nitrate+nitrite	50% increase from baseline concentration over 10 years.	0.40	0.72
	Nitrogen, ammonia	NA	Effectively 0 b/c most values are	Same as raw
	Phosphorus	50% increase from baseline concentration over 10 years.	0.46	Same as raw
Metals	Aluminum	50% increase from baseline concentration over 10 years.	0.31	0.58
	Copper	NA	Effectively 0 b/c most values are	Same as raw
	Lead	NA	Effectively 0 b/c most values are	Same as raw
	Zinc	NA	Effectively 0 b/c most values are	Same as raw
Other	Alkalinity	Increase from baseline (11.9 mg/l) to chronic WQS (20 mg/l) over 10 years	0.66	0.97
	Hardness	50% increase from baseline concentration over 10 years.	0.80	1.00
	Total suspended solids	50% increase from baseline concentration over 10 years.	0.24	Same as raw
	Biological oxygen demand	NA	Effectively 0 b/c most values are	Same as raw
	Chlorophyll-a	50% increase from baseline concentration over 10 years.	0.37	NA

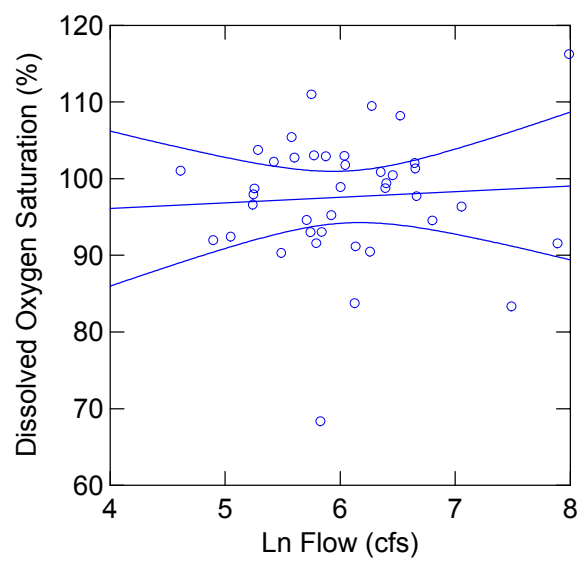
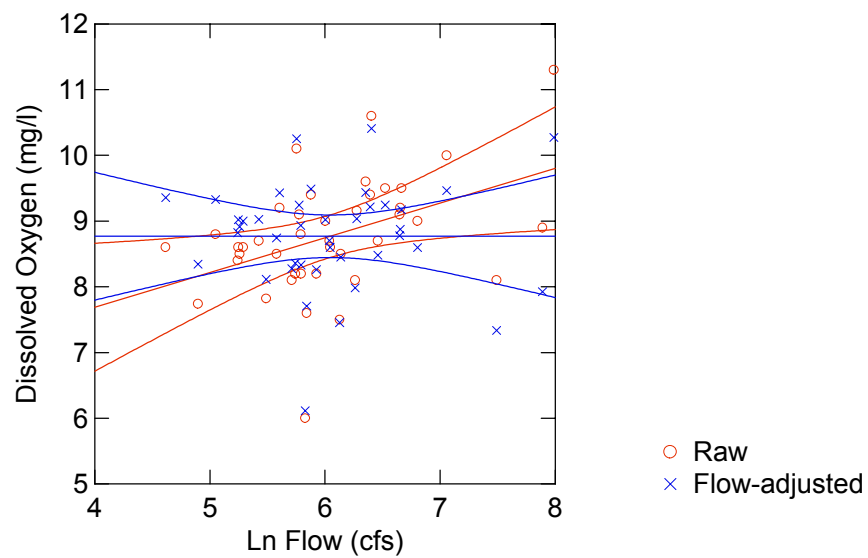
**Table 3: Summary of Trend Analyses for ARMP parameters at 01-SAC from 1990 to 2003**

Parameter	Units	Adjustment for Flow Effects	Probability of significant trend	Slope of trend (units/year)	Method
Dissolved Oxygen	%	None	<0.10	0.617	SLR
Dissolved Oxygen	%	Includes LnFLOW in model	<0.05	0.668	MLR
Ln Specific Conductivity	umho/cm	Includes LnFLOW in model	<0.05	0.019	MLR
Ln Specific Conductivity	umho/cm	None	<0.05	0.03	SLR
Ln Specific Conductivity	umho/cm	Flow adjusted	<0.05	0.02	SLR
Temperature	degC	None	<0.05	0.36	SLR
Temperature	degC	Flow adjusted	<0.05	0.28	SLR
Temperature	degC	Includes LnFLOW in model	<0.05	0.29	MLR
Ln Turbidity	mg/l	None	<0.05	-0.132	SLR
Ln Turbidity	mg/l	Flow adjusted	<0.05	-0.093	SLR
Ln Turbidity	mg/l	Includes LnFLOW in model	<0.05	-0.11	MLR
Ln Zinc	mg/l	None	<0.05	-0.082	SLR
Ln Zinc	mg/l	Includes LnFLOW in model	<0.05	-0.077	MLR

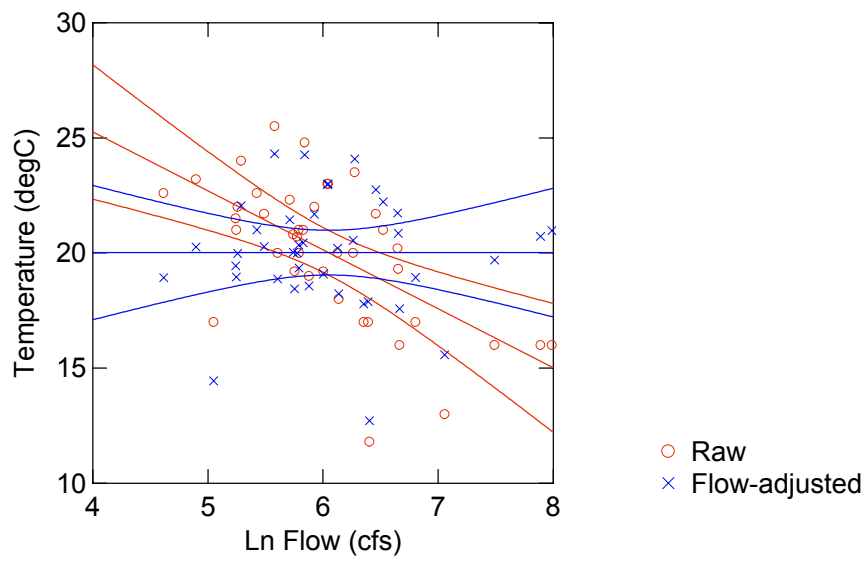
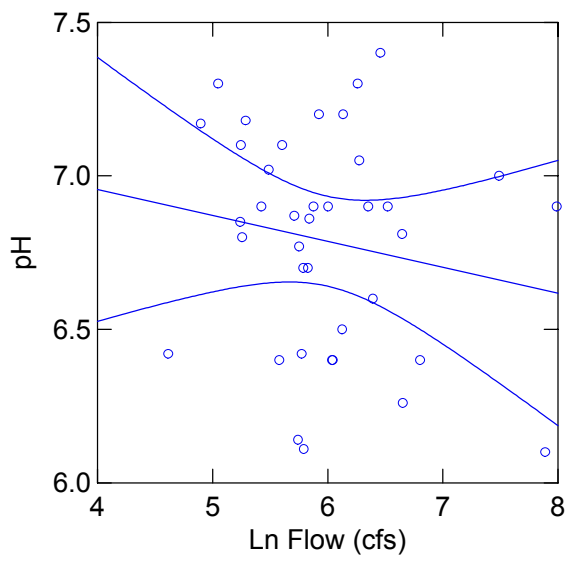
Methods: SLR=Simple Linear Regression, MLR=Multivariate Linear Regression

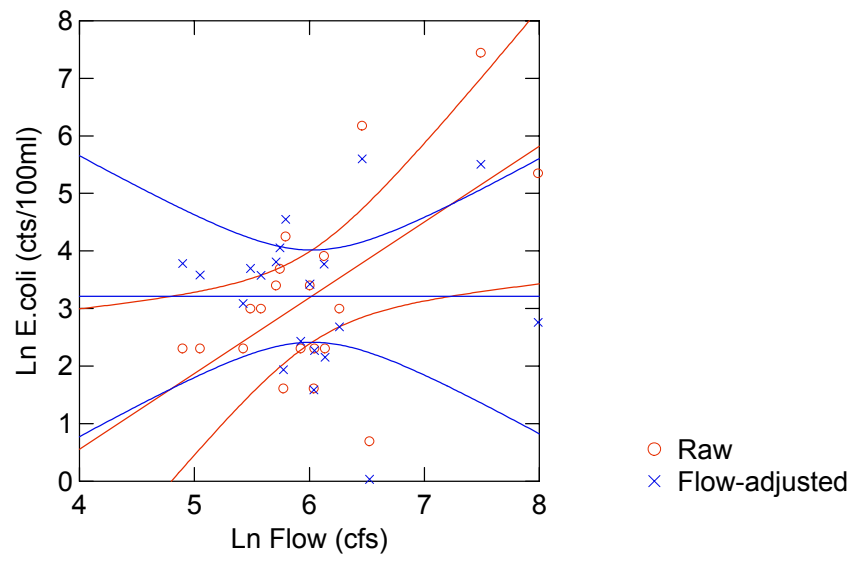
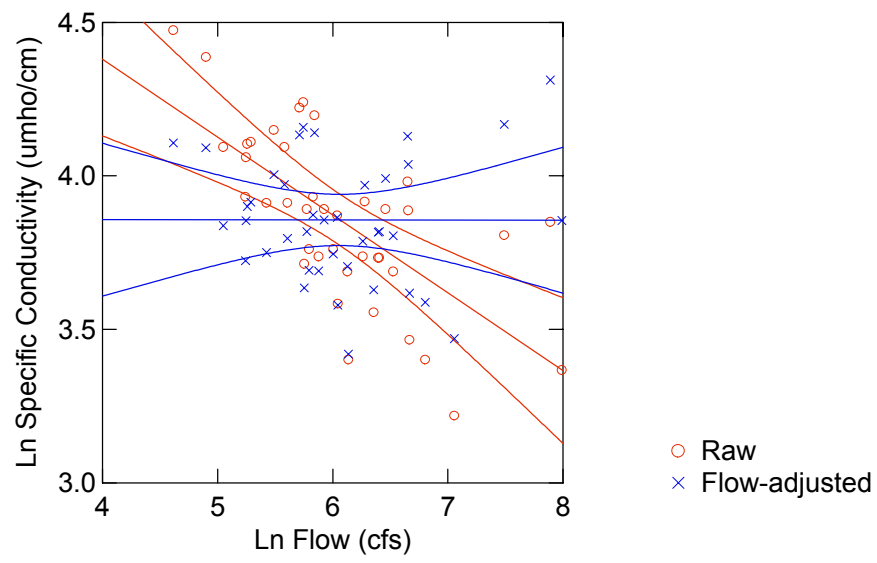
## Appendix A

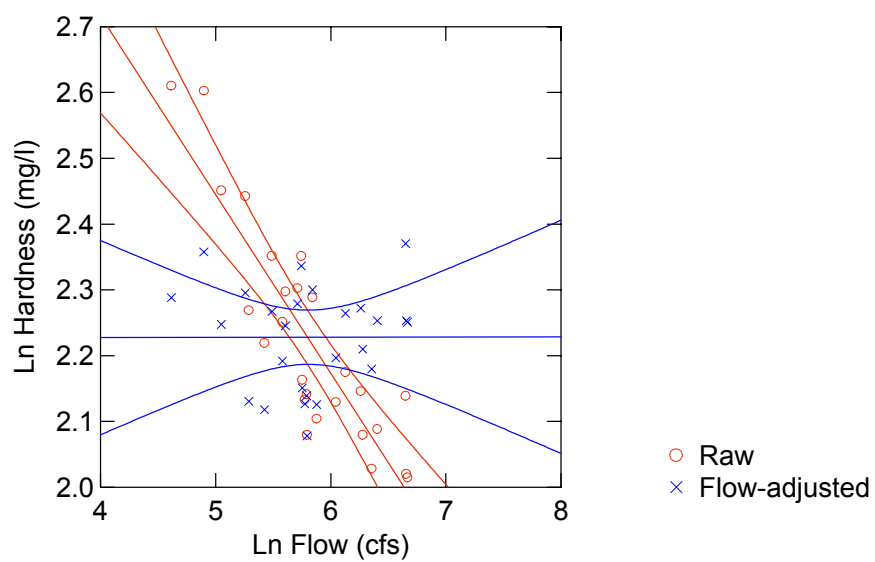
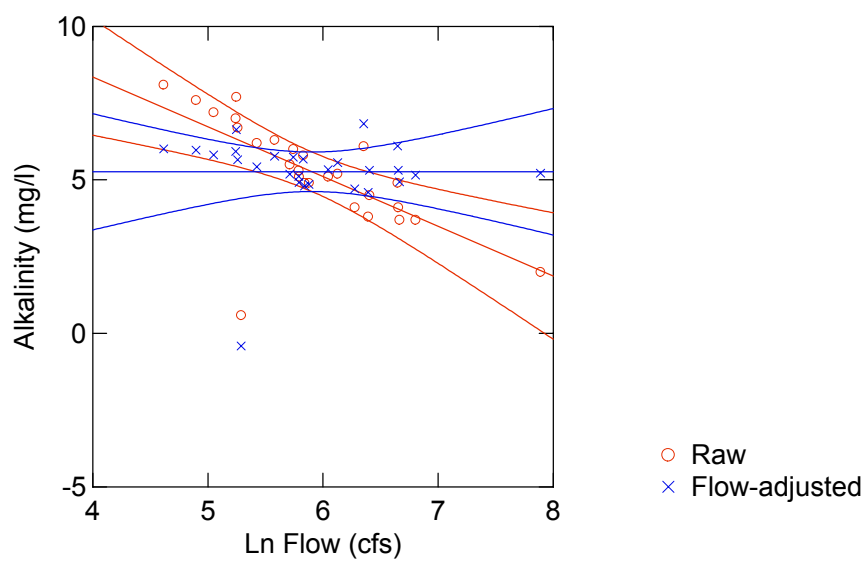
### Relationships between concentrations and flow before and after flow-adjustment

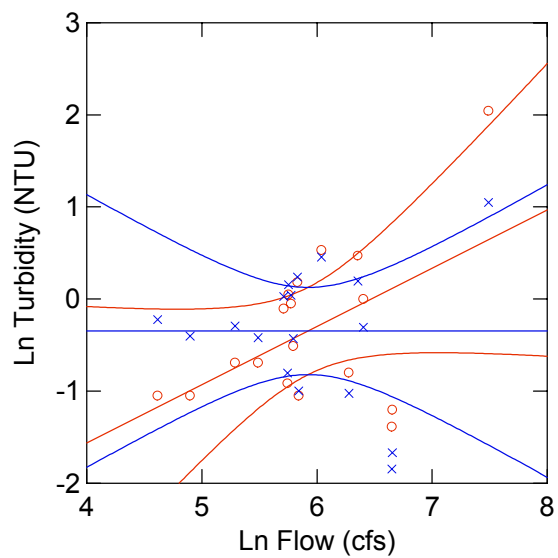
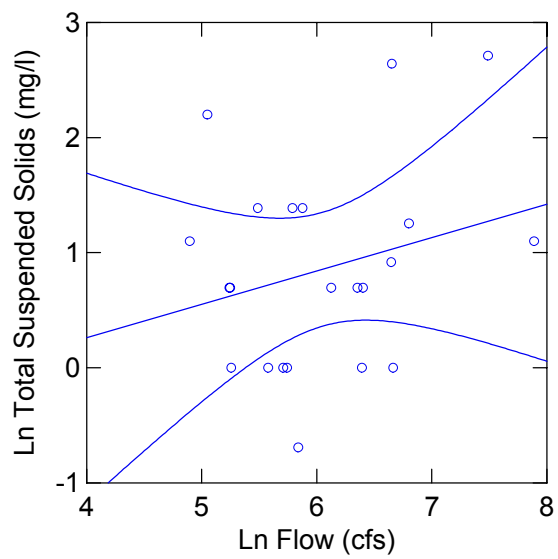




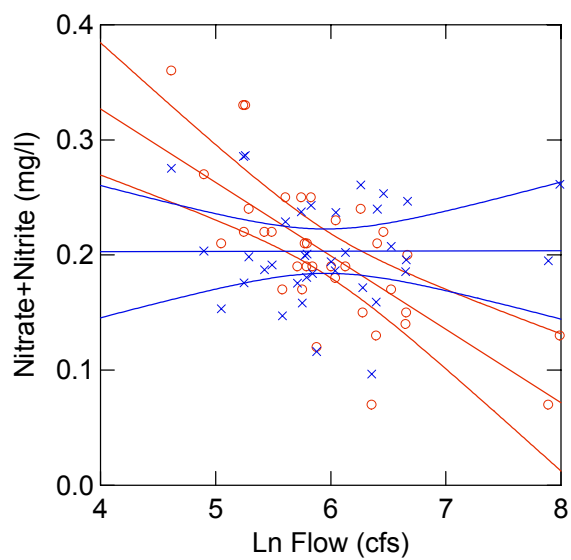
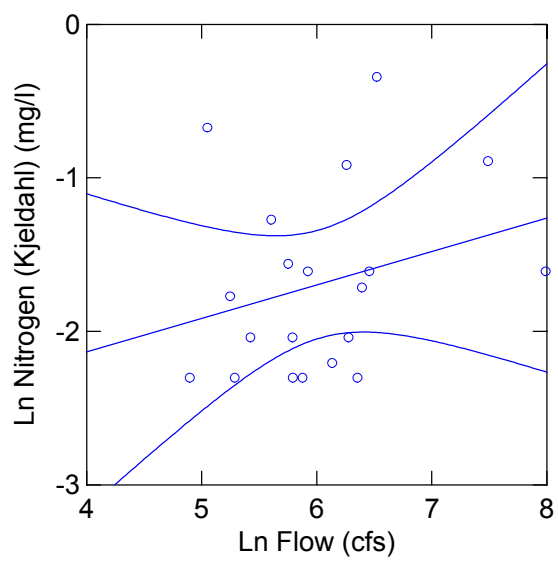




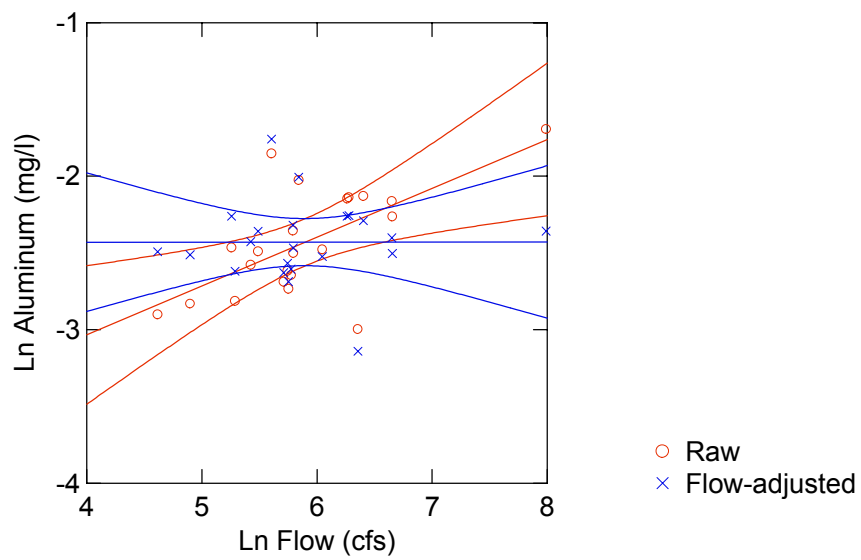
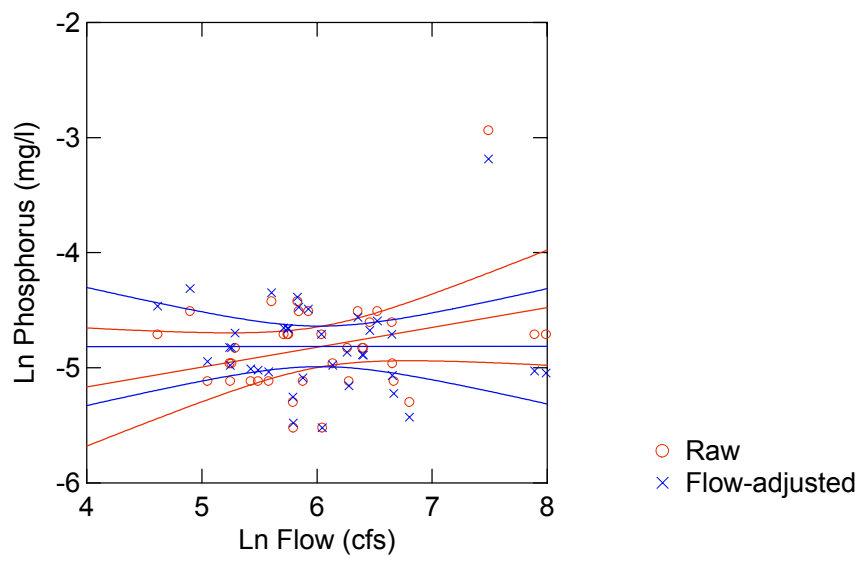


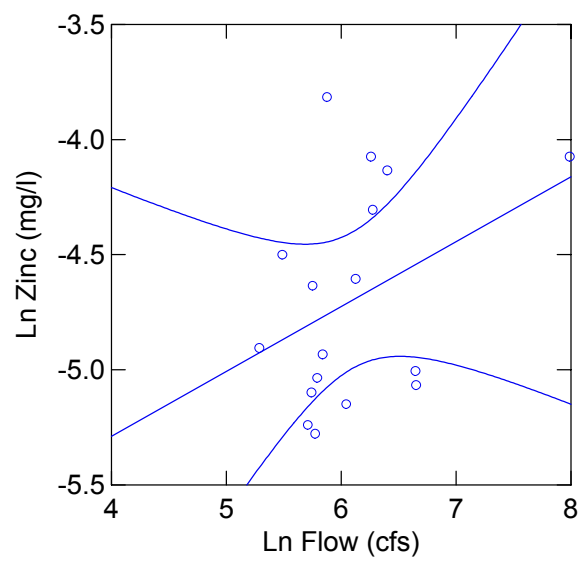


○ Raw  
× Flow-adjusted



○ Raw  
× Flow-adjusted





## Appendix B

### Time series of raw and flow-adjusted concentrations

