Acid Rain Monitoring Project

FY10 End of Fiscal Year Report

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Bureau of Waste Prevention

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Introduction

This report covers the period July 1, 2009 to June 30, 2010, the ninth year of Phase IV of the Acid Rain Monitoring Project. Phase I began in 1983 when about one thousand citizen volunteers were recruited to collect and help samples from nearly half the state's surface waters. In 1985, Phase II aimed to do the same for the rest of the streams and ponds in Massachusetts. The third phase spanned the years 1986-1993 and concentrated on a subsample of streams and ponds to document the effects of acid deposition to surface waters in the state. Over 800 sites were followed in Phase III, with 300 citizen volunteers collecting samples and doing pH and ANC analyses. In 2001, the project was resumed on a smaller scale: about 50 volunteers are involved to collect samples from approximately 150 sites, 26 of which are long-term sites with ion and color data dating back to Phase I. In Phase IV (2001-2003), 161 lakes were monitored for 3 years. Since fall 2003 (Phase V), the project has been monitoring 151 sites, mostly streams, except for the 26 long-terms sites which are predominantly lakes.

Goals

The goals of this project are to determine the overall trend of sensitivity to acidification in Massachusetts surface waters and whether the 1990 Clean Air Act Amendment has resulted in improved water quality.

Methods

Methods were mostly unchanged from previous years: Volunteer collectors are contacted a month before the collection to confirm participation. Clean sample bottles are sent to them in the mail or via UPS, along with sampling directions, a field sheet/chain of custody form, and directions to the sampling sites if necessary. Collectors visit their site(s) twice a year, in April and October, when they collect a surface water sample from the bank or wading a short distance into the water body. They collect upstream of their body after rinsing their sample bottle 3 times with sample lake or stream water. If collecting by a bridge, they collect upstream of the bridge unless safety and access do not allow it. They fill in their field data sheet with date, time, site code information, place their samples on ice in a cooler and deliver the samples to their local laboratory right away. They are instructed to collect their samples as close to the lab analysis time as possible. In a few cases, samples are collected the day prior to analysis because the lab is not open on traditional "ARM Sunday." Previous studies by our research team has established that pH does not change significantly when the samples are refrigerated and stored in the dark.

Volunteer labs are sent any needed supplies (sulfuric acid titrating cartridge, electrode, buffers), 2 quality control (QC) samples, aliquot containers for long-term site samples, and a lab sheet one week to ten days before the collection. They analyze the first QC sample in the week prior to the collection and call in their results to the Statewide Coordinator. If QC results are not acceptable, the volunteer analyst discusses possible reasons with the Statewide Coordinator and the Lab Director and makes modifications until the QC sample gives acceptable results. On Collection day, volunteer labs analyze the second QC sample before and after the regular samples, and report the results on their lab sheet along with the regular samples. Analyses are done on their pH-meters with KCl-filled combination pH electrodes. Acid neutralizing capacity (ANC) is measured with a double end-point titration to pH 4.5 and 4.2. Most labs use a Hach digital titrator for the ANC determination, but some use traditional pipette titration equipment. Aliquots are taken from the 26 long-term sites to fill one 60mL bottle and one 50mL tube for later analysis of ions and color. These aliquots are kept refrigerated until pick-up from UMass staff.

Aliquots, empty bottles, and results are collected by ARM staff a day or two after the collection. The Cape Cod lab mails those in, with aliquot samples refrigerated in a cooler with dry ice.

The Statewide Coordinator reviews the QC results for all labs and flags data for any lab results that do not pass Data Quality Objectives (within 0.3 units for pH and within 3mg/L for ANC). pH and ANC data are entered by one ARM staff and proofed by another. Data are uploaded into the web-based database at http://umatei.tei.umass.edu/ColdFusionProjects/AcidRainMonitoring/ and posted on the ARM web page at http://www.umass.edu/tei/wrrc/arm/.

Aliquots for 26 long-term sites are analyzed for color on a spectrophotometer within one day; anions within one month on an Ion Chromatograph; and cations within 6 months (but usually 2 months) on an ICP at the Environmental Analysis Lab (EAL) on the UMass Amherst campus. The data is sent via MS Excel spreadsheet to the Statewide Coordinator who uploads it into the web-based database.

UMass Chemistry Department's Dr. Julian Tyson and his laboratory team of graduate students run the Environmental Analysis Lab (EAL) and provide the QC samples for pH and ANC to all of the volunteer labs. EAL also provides analysis for pH and ANC for selected sampling sites.

Accomplishments

1. Monitoring was completed for 23 and 25 of our long-term group of 26 lakes and streams for pH, ANC, color and ions for the October 25, 2009 and the April 11, 2010 collections, respectively. Analysis results are presented in Tables 6 and 7 (see Appendix).

2. An additional 127 statistically representative streams were sampled to measure statewide trends in acidification (pH and ANC only). Analysis results are presented in Table 8 (see Appendix).

3. The network of volunteers was maintained and kept well informed on the condition of Massachusetts surface waters so that they would be able to participate effectively in the public debate. This was accomplished by e-mail and telephone communication, as well as through updates via an internet list-serv.

   There were 11 volunteer labs across the state, in addition to the EAL at UMass Amherst, in charge of pH and ANC analyses (Table 4).

   Table 1: Volunteer Laboratories

Analyst Name	Affiliation	Town
Joseph Ciccotelli	Ipswich Water Treatment Dept	Ipswich
Alan Christian	UMass Boston Environmental Studies Program	Boston
Cathy Wilkins	Greenfield High School	Greenfield
Sherrie Sunter	MDC Quabbin Lab	Belchertown
Dave Bennett	Cushing Academy	Ashburnham
Holly Bailey	Cape Cod National Seashore	South Wellfleet
Robert Caron	Bristol Community College	Fall River
Bob Bentley	Analytical Balance Labs	Carver
David Doe	Biology Dept. Wilson Hall WSC	Westfield
Jim Bonofiglio	City of Worcester Water Lab	Holden
Carmen DeFillippo	Pepperell Waste Water Treatment Plant	Pepperell
Chengbei Li	University of Massachusetts Environmental Analysis Lab	Amherst

   Several volunteer collectors were also recruited to replace retiring or ill collectors. As in the past, our volunteers take their responsibilities very seriously and take great pride in doing the job in full, revisiting a site if necessary. Some of our volunteers have been with the project since 1982 and are now quite advanced in age but are extremely dedicated and their experience is valuable to the project.

   A total of 72 volunteers participated in this year's program, 49 of them participating in both collections. Sixty-three of the volunteers were collectors, 12 were lab analysts, and 3 were both.

4. The ARM web site and searchable database were maintained and updated, adding new data as it became available. pH, ANC, ions and color data were added to the web database via the uploading tool created in previous years. The database was evaluated for quality control and uploading errors were corrected. The web-based program was updated to include recent years.

5. The data collected was analyzed for trends in pH and ANC for 151 sites and for color and ions for 26 sites, using the JMP® Statistical Discovery Software (http://www.jmp.com/software/). Bivariate

analyses (scatter plots, regression, and correlation) were run on pH, ANC, each ion, and color separately, predicting concentration vs. time. We looked at the data set for all seasons and for April and October separately to see if trends were dependent on season. Standard t-tests were also run on the same groups of data, comparing the current 10 years of data (2001-2010) to the older 10 years of data (1983-1993). We should note that the historical data includes collections from all months of the year rather than just April and October which are the only months we sampled in the latest phase of the project. This explains why statistics for the whole set of data are sometimes somewhat different from the results shown in separating the data into two seasons (“April” vs “October”).

Data Analysis Results

pH and ANC

Bivariate analysis for pH and ANC
Table 2 displays the number of sites out of 151 that show a significant change over time for pH or ANC. If the difference was not statistically significant ($p>0.05$), the sites are tabulated in the ‘No Change’ (not significantly different) category.

Table 2: Bivariate analysis results for pH and ANC

	All seasons		**April**		**October**	
	pH	**ANC**	**pH**	**ANC**	**pH**	**ANC**
No Change	96	120	92	105	116	123
Increased	48	22	58	44	18	15
Decreased	7	9	1	2	17	13

Table 3 displays the results of the t-test analysis, showing how many sites have a significant change in the current period compared to historical data.

Table 3: Standard t-test results for pH and ANC

	All Seasons		**April**		**October**	
	pH	ANC	pH	ANC	pH	ANC
No Change	101	113	105	107	124	125
Increased	42	21	44	44	15	15
Decreased	8	17	2	0	12	11

Those results are also graphed in figures 1 and 2.

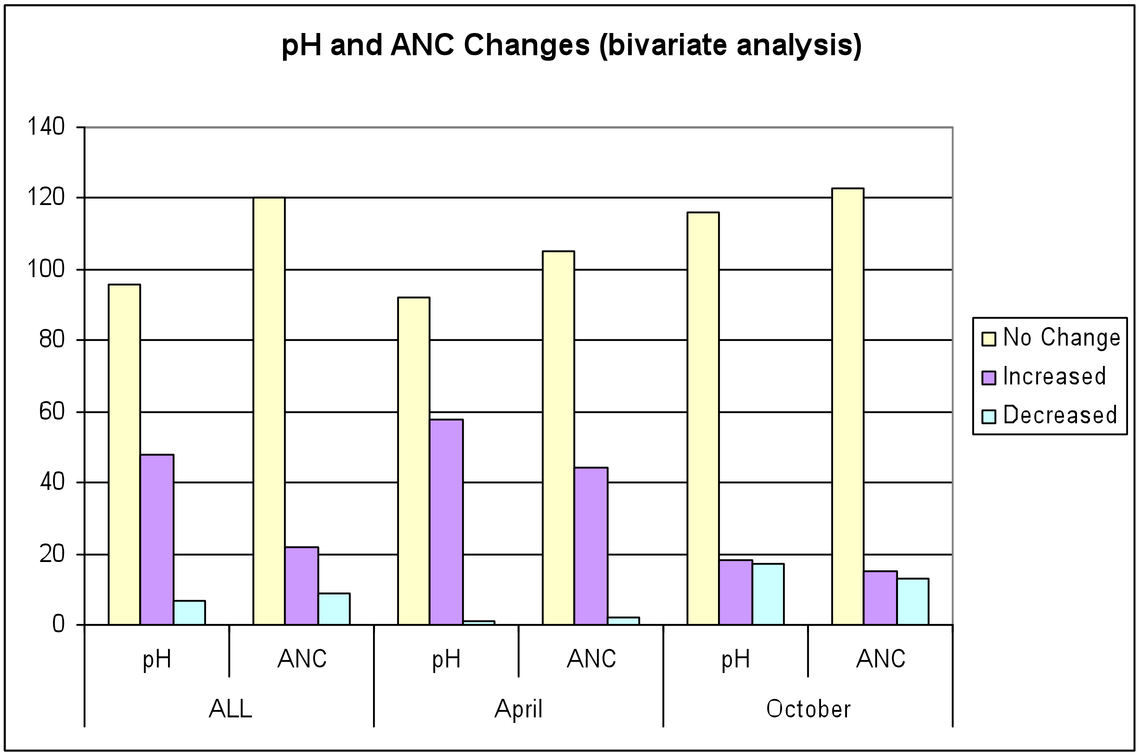


Figure 1. Changes in pH and ANC, from bivariate analysis

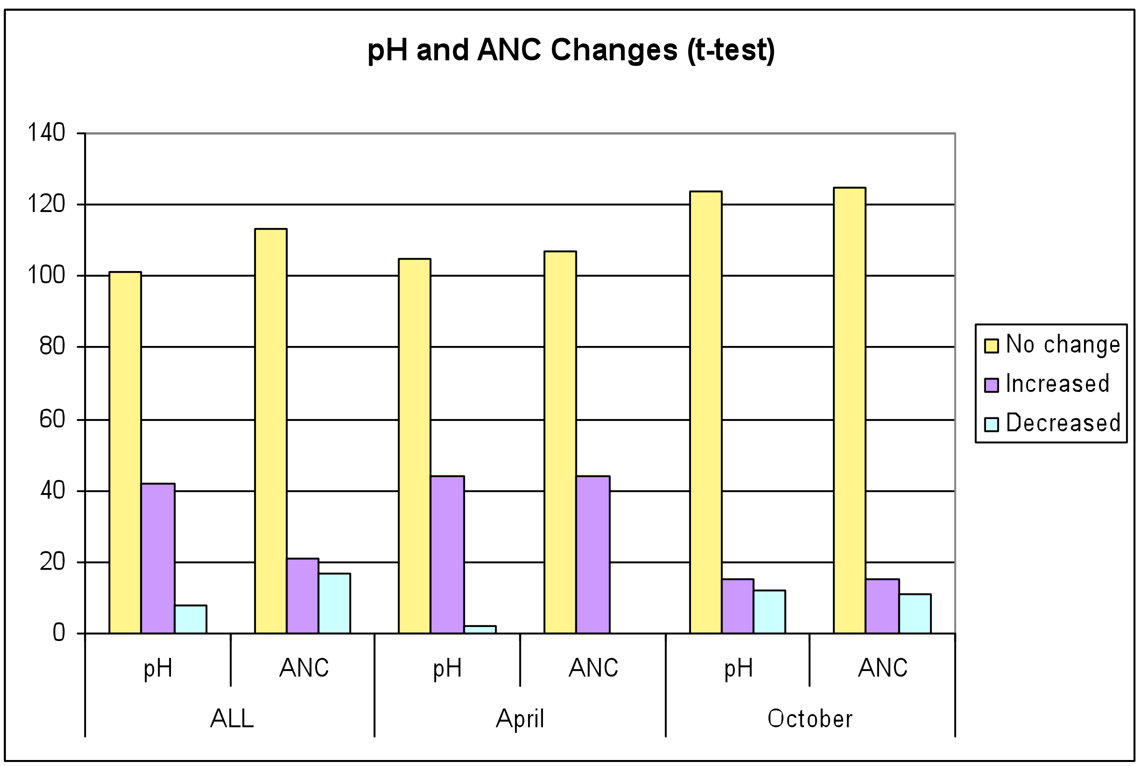


Figure 2. Changes in pH and ANC, from t-test analysis

While both types of statistical analysis give somewhat different results, they both show a similar tendency that for most sites, neither pH nor ANC has changed significantly over time. However, for those sites that show a significant change, more show an increase than a decrease in value. That is especially true for pH, with almost one third of the sites showing a statistically significant increase. ANC shows a less clear trend, except when spring and fall seasons are analyzed separately. In that case, many more sites show an increase in ANC in April than in October.

Ions and Color
Bivariate and standard t-test analyses were run on the 26 long-term sites that are analyzed for 10 ions and color. (In Phase V we analyze 11 ions, but Cu was not part of the cation suite in Phases I through III so no comparison can be made for that ion).

Table 4 and figure 3 show the results of the bivariate analysis for all parameters, while table 5 and figure 4 show the results of the standard t-test analysis.

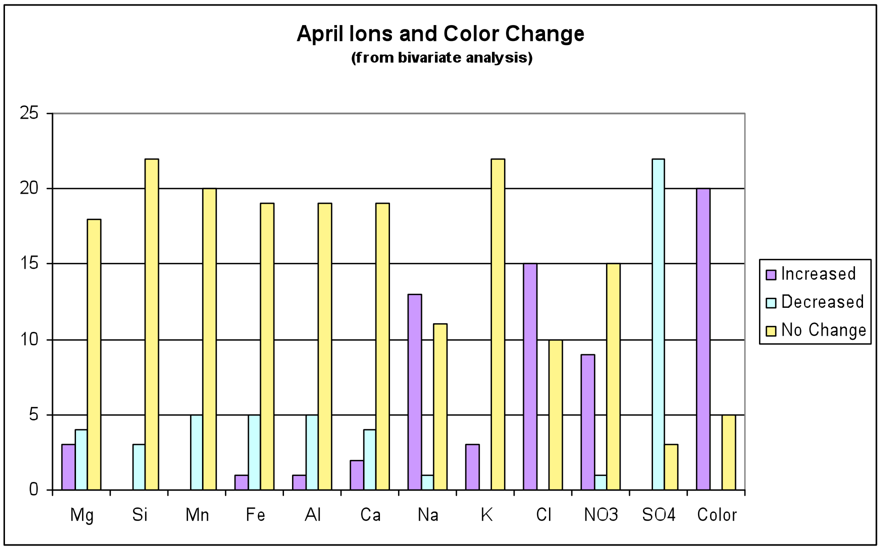
Table 4: Bivariate analysis results for ions and color

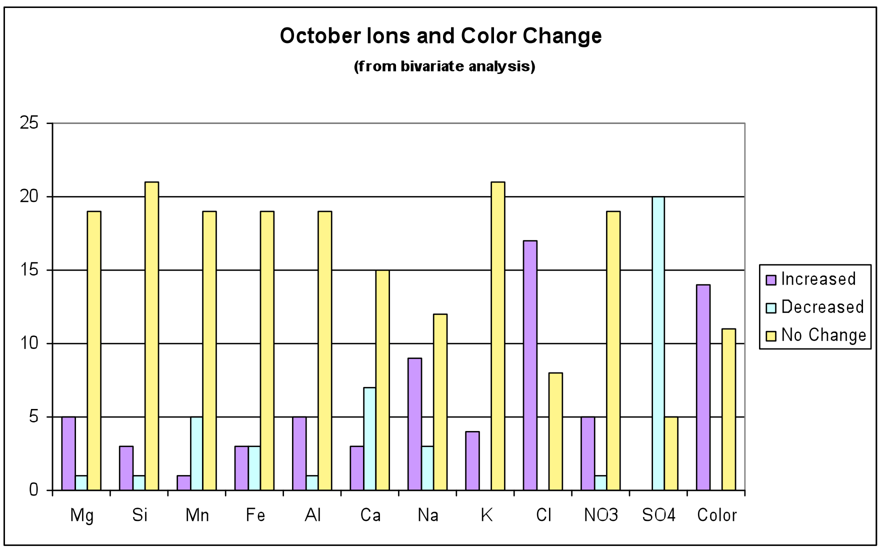
	April			October			All Seasons		
	No Change	Increased	Decreased	No Change	Increased	Decreased	No Change	Increased	Decreased
Mg	18	3	4	19	5	1	19	3	3
Si	22	0	3	21	3	1	23	1	1
Mn	20	0	5	19	1	5	19	1	5
Fe	19	1	5	19	3	3	18	4	3
Al	19	1	5	19	5	1	19	4	2
Ca	19	2	4	15	3	7	14	4	7
Na	11	13	1	12	9	3	12	12	1
K	22	3	0	21	4	0	22	3	0
Cl	10	15	0	8	17	0	6	19	0
NO3	15	9	1	19	5	1	14	10	1
SO4	3	0	22	5	0	20	8	0	17
Color	5	20	0	11	14	0	8	17	0

Table 5: T-test analysis results for ions and color

	April			October			All		
	No change	Increased	Decreased	No change	Increased	Decreased	No change	Increased	Decreased
Mg	19	4	2	20	2	3	18	3	4
Si	21	2	2	21	3	1	22	2	1
Mn	18	1	6	18	1	6	19	1	5
Fe	19	3	3	22	2	1	21	2	2
Al	23	1	1	21	1	3	20	2	3
Ca	15	5	5	18	3	4	16	3	6
Na	12	11	2	11	13	1	10	14	1
K	23	2	0	21	4	0	7	18	0
NO3	22	2	1	13	9	3	14	1	10
SO4	6	2	17	3	2	20	6	0	19
Color	14	10	1	6	19	0	8	17	0

Figure 3: Results of bivariate analysis for ions and color, all seasons, April, and October.





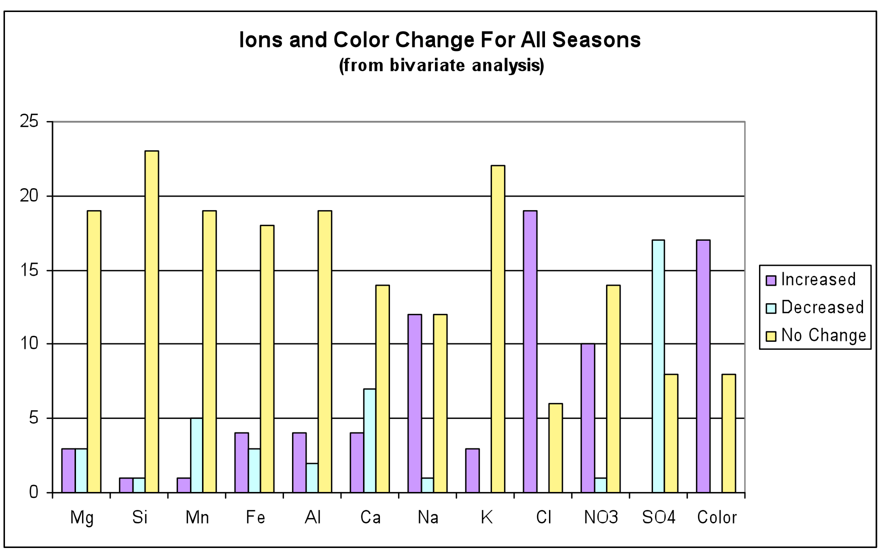
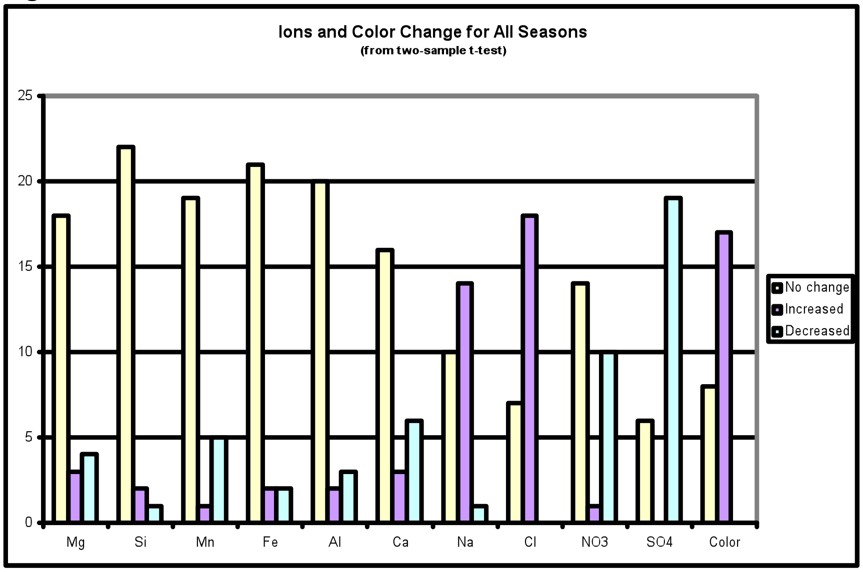
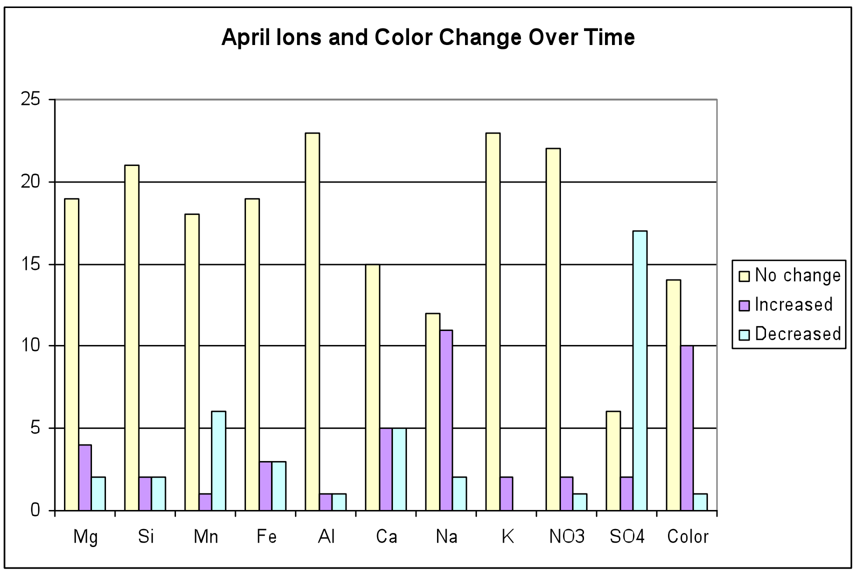
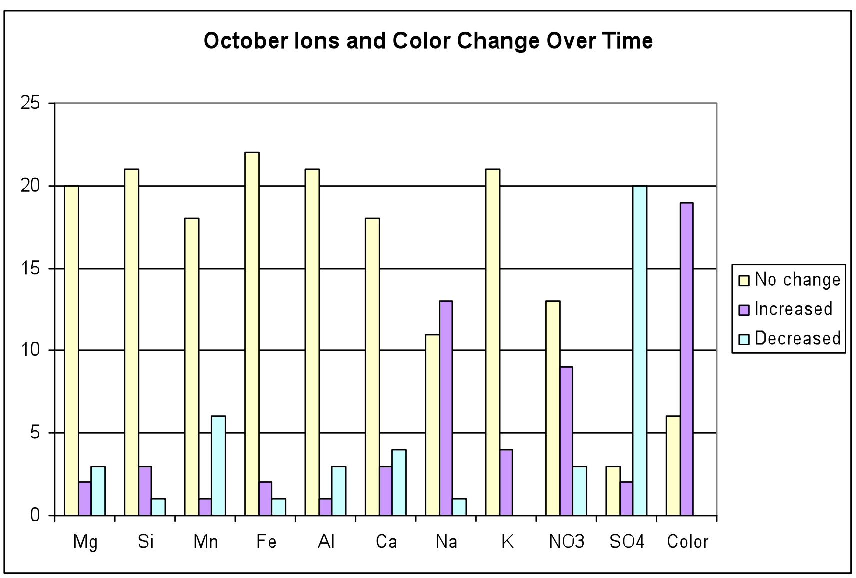


Figure 4: Results of standard t-test for ions and color, all seasons







Most cations show no significant change over time for the 26 sites we are following. A notable difference, however, can be seen for sodium, which increased for almost half of the sites no matter what season and with both types of statistics used.

All anions show significant changes as well. This change is seen more clearly with the bivariate analysis, which tracks concentrations continuously over time, while the t-test compares only the set of data from the first 10 years with the last 10 years of the project. Chloride never decreases with time, and increases for two-thirds of the sites. Nitrate's change is less definite, but it clearly increases for about a third of the sites and decreases for a couple of sites on average. Sulfate shows the most dramatic change, a strong decrease for over two-thirds of the sites.

Color also shows a consistent increase over time, for over two-thirds of the sites in all seasons.

Discussion

These results are mostly consistent with what we found for an earlier analysis we performed on lakes in Phase IV of this project, and with results from other research studies in the northeast. The main difference is that we now see more of an increase in pH, and we are seeing a clearer increase in nitrate in Phase V.

It is interesting to note that for both pH and ANC, more sites show an increase in April than in October, and this trend holds with both statistical tests performed. April is the time of year when we typically see the lowest pH and ANC values, most probably due to snowmelt waters that carry an important amount of nitrates into surface waters. Yet we do not see a clear corresponding trend with nitrate. On the contrary, the bivariate analysis shows more of an increase in nitrate in April than in October, though the reverse is true with the t-test analysis. An explanation might be that the reduction in sulfate is more important than the increase in nitrate, but further research or literature review should be done in order to draw a confident conclusion.

Base cations calcium and magnesium still show no sign of recovery, if anything calcium actually seems to be still declining.

Sulfate continues to show a strong and significant decline, in line with decreases in emissions of sulfur dioxide that followed the 1990 Clean Air Amendment. The increase in nitrate is also not surprising, despite a similar decrease in NOx emissions from power plants, because nitrogen emissions from vehicle sources have increased over time. Since roads in Massachusetts are often located along streams, and because roads are designed to channel water off and away from their surface, increased NOx emissions have a direct path into surface waters.

At this time we cannot confidently assess an increase or a decline in aluminum.

However, we continue to document a significant increase in sodium and especially chloride. This results very likely from road salting practices in the northeast.

The obvious increase in color is less intuitive to explain, but in New England, there is a buffer other than ANC that is rarely considered - organic acids. These natural acids make waters somewhat acidic and tea brown in color, and they act as buffers against further lowering of the pH by mineral acids. So naturally colored waters have been titrating acid deposition and becoming less colored. The increase in color we are observing would point to an increase in buffering capacity that is not measured by ANC.

In conclusion, to answer our question whether the 1990 Clean Air Act Amendment has resulted in improved water quality in Massachusetts surface waters, the answer is a cautious "somewhat." More water bodies seem to have improved than worsened, but the increase in nitrates, coupled with the lack of increase in calcium and magnesium cause concern that the improvement may not last and may even reverse in the future if NOx emissions are not curbed.

It is our recommendation to pursue this long-term monitoring of surface waters in the Commonwealth. We propose to change our sampling scheme to drop half of the streams we are currently following, and replacing them with an equal number of lakes that were monitored in Phase IV.

Acknowledgements

Thank you to all of the project's volunteers who make this project possible by collecting samples all over the state under any weather conditions, and who spend many hours in the lab analyzing samples.