Annual Report to

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US EPA, CAMD, Washington DC
and US EPA, ORD, Corvallis OR

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Determining the effectiveness of the Clean Air Act and Amendments on the recovery of surface waters in the northeastern US

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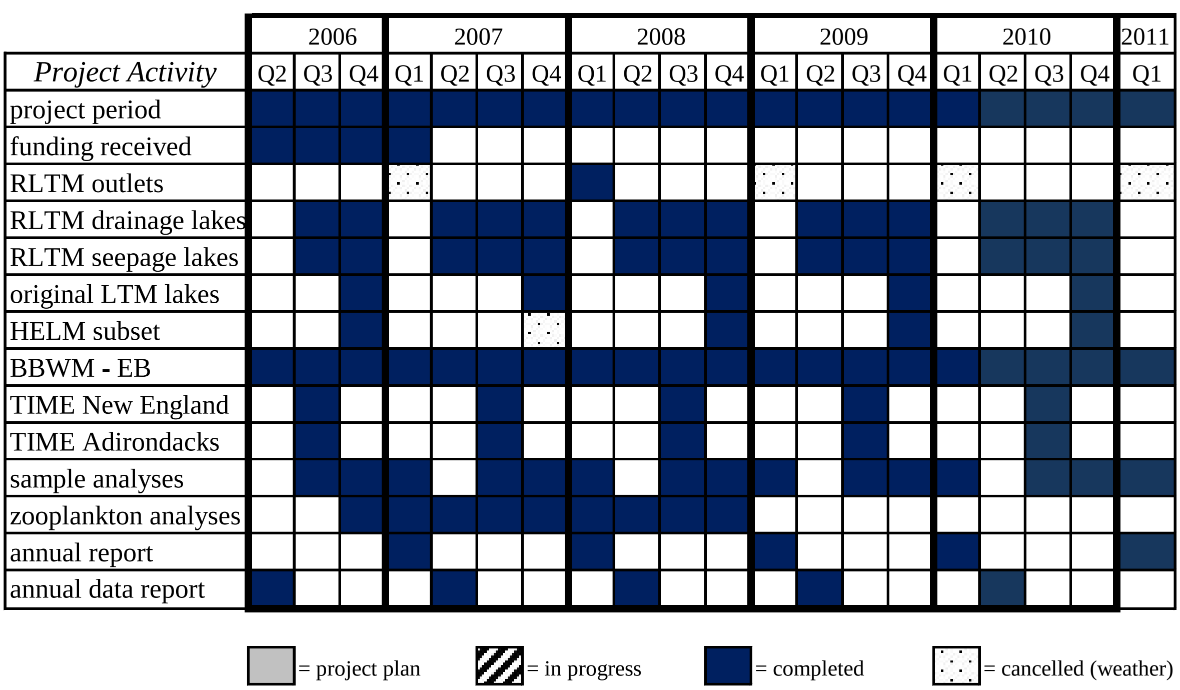
Overview of activities during 2010. A schematic summary of progress on the project plan is provided below and discussed on the following pages. We have concluded the fifth year of this five year project that supports the continuing needs of EPA for meeting the Congressional mandate for the agency to assess the effectiveness of the Clean Air Act Amendments of 1990. Field work and data assessment are on schedule, and the supplemental zooplankton component is well underway.

Project coordination is being conducted by the University of New Hampshire, with field and laboratory assistance continuing to come from the University of Maine.



Project background

Objectives. This proposed research is part of the EPA program to collect long-term data on the trends and patterns of response in surface waters sensitive to acidic deposition. The goals and methods are hierarchical from intensive site-specific to regional statistical populations. The objectives are to:

1) document the changes and patterns in aquatic chemistry for defined sub-populations and sites that are known to be susceptible to acidification or recovery;
2) evaluate linkages in changes in surface waters, if any, to changes in deposition that are related to regulatory goals;
3) characterize the effectiveness of the Clean Air Act Amendments in meeting goals of reducing acidification of surface waters and improving biologically-relevant chemistry in the northeastern US; and
4) provide information for assessment of the need for future reductions in atmospheric deposition based on the rate of recovery (or not) of the systems under study.

We continue to explore changes in biological condition using zooplankton collected in 2004 under separate funding from 145 ELS-II lakes in the northeast, as part of our 20th anniversary re-analysis of the Eastern Lake Survey (see Rosfjord *et al*., 2007). This re-sampling included total and methyl mercury analyses for lake water, GIS analyses of lake context, and creation of an integrated GIS-chemistry database for the 1986 ELS-II lakes and 2004 re-sampling data. Zooplankton size metrics are now in the electronic, coordinated database and final compatibility checks of taxa names across decades are in progress. Initial analyses are in progress by K. Webster in consultation with the project team. In addition to a peer-reviewed journal article in preparation (Nelson et al. 2011), the mercury and methylmercury database was recently included in USGS scientist D. Krabbenhoft's work to develop national Hg sensitivity maps and models. The lakes in the 2004 re-sampling were unique in their statistical sampling design, collection during the same time period, and inclusion of all major geochemical variables. The lakes from this work represent ~10% of the entire national database used by Krabbenhoft in sensitivity modeling. Krabbenhoft is using the dataset and modeling framework to assess Hg sensitivity in National Parks at the request of the National Park Service.

Approach. The schedule of tasks ranges from weekly to annual, continuing data records that now range from 16 to 29 years. We evaluate chemistry on a weekly basis year-round at the small watershed-scale at BBWM, weekly during the spring melt period at LTM lake outlets when seasonal conditions warrant, quarterly in LTM, and annually during the historical index period for the HELM and TIME lakes. These project components provide a *statistical framework* for inferring regional chemical patterns using TIME and LTM (and ELS-II under separate funding). The *long-term records* of LTM, HELM and BBWM provide information on seasonal and annual variability, and thus provide a seasonal context for the annual surveys.

Expected Results. This information is fundamental for EPA to meet the Congressional mandate for reporting on the effectiveness of the Clean Air Act Amendments (CAAA). The combination of site-specific data within the regional context will provide for an effective assessment of the effects of declining pollutant emissions on SO_4 concentrations, base cation depletion, and changes in N-saturation or DOC contributions to acid-base status. The results are also central to the decisions on additional emission reductions that may be needed to produce recovery.

LTM/TIME annual field schedule

LTM-Maine	Apr				May				Jun				Jul				Aug				Sep				Oct				Nov
1 Bean					X												X									w/ HELM			
2 Partridge				X											X													X	
3 Jellison Hill				X											X													X	
4 Crystal				X											X												X		
5 Duck				X											X												X		
6 Bracey				X											X												X		
7 Newbert			X												X														X
8 Wiley					X												X										X		
9 Abol					X												X										X		
10 Mud					X											X												X	
11 Salmon					X											X												X	
12 Tunk outlet					X											X												X	
13 Second					X											X												X	
14 Little Long																												X	
15 Tilden																													
16 Anderson																													
TIME-Maine																													
1 Round Pond				w/ TIME NH															X										
2 Mountain Pd				fly with HELM																						fly w/ HELM			
3 Bog Pd Hartland				w/ Bean in spring and summer														X											
4 East Branch Lake				[Penobscot Nation sample]														X											
TIME NH																			X	X	X								
TIME New Engl																				X	X								
TIME NY																				X	X	X	X	X					
HELM																										X	X		

Spring weekly drainage lake samples: weather and snowcover dependent

Project Status: Water Chemistry

Field sampling. All project field objectives in 2010 were accomplished as planned with the exception of the spring drainage lake samples. Maine experienced an extremely wet spring making spring sampling logistically difficult and potentially unsafe for field crews.

Analytical. Analyses are complete for all samples collected through 2010. All laboratory analyses for TIME, RLTM, and HELM are conducted at the University of New Hampshire Water Quality Analysis Laboratory (WQAL) except for aluminum. Total and organic aluminum samples are processed on an ICP at the USDA Forest Service Region 1 laboratory in Durham, NH. All analyses for TIME, RLTM, and HELM continue to be conducted by, or under the supervision of, Adam Baumann as it has been since 2006.

Samples from East Bear Brook at BBWM, which are collected on a regular basis year around, continue to be analyzed at the University of Maine Sawyer Environmental Chemistry Research Lab.

Data reporting. All data collected through 2009 have been delivered to EPA. The next delivery of data to EPA is expected in June 2011, after evaluation of inter-laboratory comparisons and regular QA analyses by UNH and UMaine.

Presentation of findings. Several publications and presentations have resulted from this project since the final report for the previous LTM/TIME grant, listed at the end of this report. The completion of Adam Baumann's M.S. thesis work is expected in July and will yield multiple publications focusing on results from the HELM project (see appendix).

New developments: We requested and were awarded funding to continue our work on the previously outlined objectives through FY2011. During the next sampling year group to explore climate related research objectives such as DOC quality using SUVA and fluorescence analysis, as well as dissolved greenhouse gases (CH_4, CO_2, and N_2O) in surface waters.

***Recent publications** using related project information*

Nelson, S.J., W.H. Halteman, J.S. Kahl, N.C. Kamman, D.P. Krabbenhoft, 2011. Predicting mercury concentrations in northeast lakes using hydrogeomorphic features, landscape setting, and chemical co-variates. Intended for: Environmental Science and Technology. In final prep. May, 2011.

Fernandez, Ivan; Stephen, Norton, 2010, The Bear Brook Watershed in Maine: The Second Decade: Preface. Environmental Monitoring and Assessment, 171(1-4): 1-2(2)

Norton, S.; I. Fernandez; J. Kahl; L., Rustad; Tomas, Navratil; H., Almquist, 2010, The evolution of the science of Bear Brook Watershed in Maine, USA. Environmental Monitoring and Assessment, 171(1-4): 3-21.

Navrátil, T., S.A. Norton, I.J. Fernandez, S.J. Nelson, 2010. Twenty-year inter-annual trends and seasonal variations in precipitation and stream water chemistry at the Bear Brook Watershed in Maine, USA. Environ. Monit. Assess. 171:3-21.

Kim, Jong-Suk; Shaleen, Jain; Stephen, Norton, 2010, Streamflow variability and hydroclimatic change at the Bear Brook Watershed in Maine (BBWM), USA, Environmental Monitoring and Assessment, 171(1-4): 47-58.

Laudon, Hjalmar; Stephen, Norton, 2010, Drivers and evolution of episodic acidification at the Bear Brook Watershed in Maine, USA, Environmental Monitoring and Assessment, 171(1-4): 59-69.

Porcal, Petr; Aria, Amirbahman; Jiri, Kopacek; Stephen, Norton, 2010. Experimental photochemical release of organically bound aluminum and iron in three streams in Maine, USA, Environmental Monitoring and Assessment, 171(1-4): 71-81.

Simon, Kevin; Michael, Chadwick; Alexander, Hury; H.,Valett, 2010, Stream ecosystem response to chronic deposition of N and acid at the Bear Brook Watershed, Maine, Environmental Monitoring and Assessment, 171(1-4): 83-92.

Amirbahman, Aria; Brett, Holmes; Ivan, Fernandez; Stephen, Norton, 2010, Mobilization of metals and phosphorus from intact forest soil cores by dissolved inorganic carbon, Environmental Monitoring and Assessment, 171(1-4): 93-110.

SanClements, Michael; Ivan, Fernandez; Stephen, Norton, 2010, Soil chemical and physical properties at the Bear Brook Watershed in Maine, USA, Environmental Monitoring and Assessment, 171(1-4): 111-128.

Elvir, Jose; G. Wiersma; Suzanne, Bethers; Peter, Kenlan, 2010, Effects of chronic ammonium sulfate treatment on the forest at the Bear Brook Watershed in Maine, Environmental Monitoring and Assessment, 171(1-4): 129-147.

Fernandez, Ivan; Mary, Adams; Michael, SanClements; Stephen, Norton, 2010, Comparing decadal responses of whole-watershed manipulations at the Bear Brook and Fernow experiments, Environmental Monitoring and Assessment, 171(1-4): 149-161.

Baumann, A.J. and J.S. Kahl, 2007. Chemical trends in Maine High Elevation Lakes. LakeLine 27:30-34.

Campbell, J, J. Hornbeck, M. Mitchell, M. Adams, M. Castro, C. Driscoll, J.S. Kahl, and others, 2004. Input-output budgets for inorganic nitrogen for 24 watersheds in the northeastern United States. Water Air Soil Pollut., 151:373-396.

Dupont, J., T. Clair, C. Gagnon, D. Jeffries, J.S. Kahl, S. Nelson, and J Peckenham, 2005. Estimation of critical loads of acidity in the northeastern US and eastern Canada. Environ. Monit. Assess. 109:275-291.

Hunt, K., J.S. Kahl, J. Rubin, and D. Mageean, 2007. Assessing the science-based needs of stakeholders; a case study on acid rain research and policy. Journal of Contemporary Water Research and Education, 136: 68-79.

Kahl, J.S., J. Stoddard, R. Haeuber, S. Paulsen, R. Birnbaum, F. Deviney, D. DeWalle, C. Driscoll, A. Herlihy, J. Kellogg, P. Murdoch, K. Roy, W. Sharpe, S. Urquhart, R. Webb, and K. Webster, 2004. Response of surface water chemistry to changes in acidic deposition: implications for future amendments to Clean Air Act. Environmental Science and Technology, Feature Article 38:484A-490A.

Lawler, J., J. Rubin, B.J. Cosby, I. Fernandez, J.S. Kahl, S. Norton, 2005. Predicting recovery from acidic deposition: Applying a modified TAF (Tracking Analysis Framework) Model to Maine High Elevation Lakes, Water Air Soil Pollut. 164:383-389.

Norton, S., I. Fernandez, J.S. Kahl, and R. Reinhardt, 2004. Acidification trends and the evolution of neutralization mechanisms through time at the Bear Brook Watershed, Maine, USA. Water, Air, Soil, Pollution Focus 4:289-310.

Rosfjord, C., K. Webster, J.S. Kahl, S.A. Norton, I. Fernandez, and A. Herlihy, 2007. Anthropogenically-driven changes in chloride complicate interpretation of base cation trends in lakes recovering from acidic deposition. Environ Sci Technol, 41:7688 -7693.

Rosfjord, C., J.S. Kahl, K. Webster, S. Nelson, I. Fernandez, L. Rustad, and R. Stemberger. 2006. Acidic deposition-relevant changes in lake chemistry in the EPA Eastern Lake Survey, 1984-2004. Final report to USDA NSRC, Durham, NH. 69 p.

Recent presentations using project information

Baumann, A.J., and J.S. Kahl, 2009. Assessing the effectiveness of federal acid rain policy using remote and high elevation lakes in northern New England. North American Lake Management Society International Symposium, Hartford, CT, October 29, 2009.

Kahl, J.S., 2009. Changes in base cations related to long-term changes in Cl distribution in northeastern lakes. Gordon Research Conference, Forested Catchments, July 12-17, 2009, Proctor Academy, NH.

Kahl, J.S., 2008 (invited). Twenty year changes in spatial patterns of Cl distribution in the northeastern US. NH Water Conference, April, 2008.

Kahl, J.S., 2007 (invited). Using societal-based incentives to address new threats to New England Lakes. Day-long short course in New England Lake Science Academy, Camp Kieve, Maine. July, 2007.

Kahl, S., K. Webster, D. Sassan, C. Rosfjord, S. Nelson, M. Greenawalt-Yelle, 2007. Increasing Cl in northeastern surface waters: an indicator of increasing development pressure. Maine Water Conference, Augusta, ME, March 21, 2007.

Kahl, J.S. 2006 (invited). Acid rain in New England: using high elevation lakes as sentinels of change. Maine Mountain Conference, October 21, 2006. Rangeley, Maine

Kahl, J.S., *et al*., 2006 (invited). The design of a national mercury monitoring network: Learning from the EPA acid rain experience. The Eighth International Mercury Conference, Madison WI, August 8, 2006.

Kahl, J.S. *et al*., 2006. Obfuscation of trends in base cations by regional salt contamination. Hubbard Brook Committee of Scientists annual meeting, July 12, 2006.

Kahl, J.S., 2006 (invited). 'Natural and human-derived sources of acidity in Maine Atlantic Salmon Rivers'. Atlantic Salmon Commission workshop on acidity, Bangor ME. April 10, 2006.

Kahl, J.S., 2005 (invited). The intersection of environmental science and environmental policy. NH Charitable Foundation Lakes Region annual meeting, Meredith, NH, September, 2005.

Kahl, J.S., 2005 (invited). Tracking response and recovery in surface waters in the northeastern US. Annual meeting of the Ecological Society of America, Montreal, August, 2005.

Kahl, J.S., and Catherine Rosfjord, 2005 (invited). Acid rain and the Clean Air Act in the northeastern US. Annual meeting of the NH-ME Androscoggin River Watershed Council, Bethel, June, 2005

Kahl, J.S., 2005 (invited). Developing a lake research agenda for NH. NSF workshop on lake research infrastructure in the northeast, Colby Sawyer College, April 2005.

Kahl, J.S., S. Nelson, and A. Grygo, 2004. Surface water chemistry data for the northeastern US for interpreting climate and acid rain trends. Northeast Ecosystems Research Consortium meeting, Durham, NH, October, 2004.

Kahl, J.S., K. Webster, M. Diehl, and C. Rosfjord, 2004. Successes of the Clean Air Act Amendments of 1990. Maine Water Conference invited plenary talk, Augusta, ME, 2004.

Kahl, J.S. and K. Johnson, 2004. Acid-Base Chemistry and Historical Trends in Downeast Salmon Rivers. Maine Water Conference, Augusta ME, April 2004.

Kahl, J.S., 2004 (invited). The Clean Air Act Amendments of 1990; testing a program designed to evaluate environmental policy. Lecture, Colby College. April, 2004

S.J. Nelson, J.S. Kahl, N.C. Kamman, D.P. Krabbenhoft, W.H. Halteman, 2009. (Poster) Predicting mercury concentrations in northeast lakes using hydrogeomorphic features, landscape setting and chemical co-variates. Gordon Research Conference, Forested Catchments, July 12-17, 2009, Proctor Academy, NH.

Nelson, S.J., I. Fernandez, S. Norton, B. Wiersma, L. Rustad , J.S. Kahl, 2008. The Bear Brook Watershed in Maine: Long-term research supporting climate change inquiry. Hydroclimatic effects on ecosystem response: participant workshop, Syracuse, NY, September 19, 2008.

Nelson, S.J., N. Kamman, D. Krabbenhoft, J.S. Kahl, K. Webster, 2008. Evaluating spatial patterns in mercury and methyl mercury in northeastern lakes: Landscape setting, chemical climate, and human influences. Northeastern Ecosystem Research Cooperative Conference, Durham, NH, November 12-13, 2008.

Nelson, S.J. 2008. Evaluating spatial patterns in mercury and methyl mercury in northeastern lakes: landscape setting, chemical climate, and human influences. Maine Water Conference, Augusta, ME, March 19, 2008.

Appendix I. Draft abstract from MS candidate Baumann thesis (partially supported by this IAG).

Changes in surface water chemistry in Maine high elevation lakes in response to the 1990 Clean Air Act Amendments

ABSTRACT:

The 1990 U.S. Clean Air Act Amendments (CAAA) set target reductions for both sulfur and nitrogen emissions to reduce acidic deposition and improve the biological status of low alkalinity surface waters in the United States. The Maine High Elevation Lake Monitoring (HELM) project was designed to complement assessments from other acid rain monitoring programs in the northeast that had underestimated the number of acidic lakes. HELM lakes are more susceptible to the effects of acid deposition than lowland lakes typically included in other surveys because they receive higher amounts of precipitation, and the watersheds are less able to neutralize acidic inputs because of steep slopes, shallow soils, and resistant bedrock. Since 1986, decreases in HELM surface water SO4 concentrations of 1.6µeq/L/yr. combined with lesser decreases in base cations (0.68 µeq/L/yr.) have led to significant increases in ANC (0.58µeq/L/yr.) and significant decreases in hydrogen ion (-0.05µeq/L/yr.). These improvements have led to a 50% decrease in the number of acidic (ANC <0) HELM lakes since 1986-87, and a 10% increase in the number of lakes projected to resist spring acidification (baseflow ANC > 30). Toxic inorganic aluminum comprises 9% less of the total aluminum in HELM lakes today than in 1986-87, due to the decrease in acidity and a 0.03mg/L/yr. increase in DOC which complexes inorganic Al. At current rates of change in both surface waters and deposition, we predict a recovery scenario for 2025 in which HELM lakes reach a background 24µeq/L SO_4 and non-dystrophic lakes have pH ≥ 6 and ANC ≥ 30µeq/L as depositional SO_4 becomes undetectable.

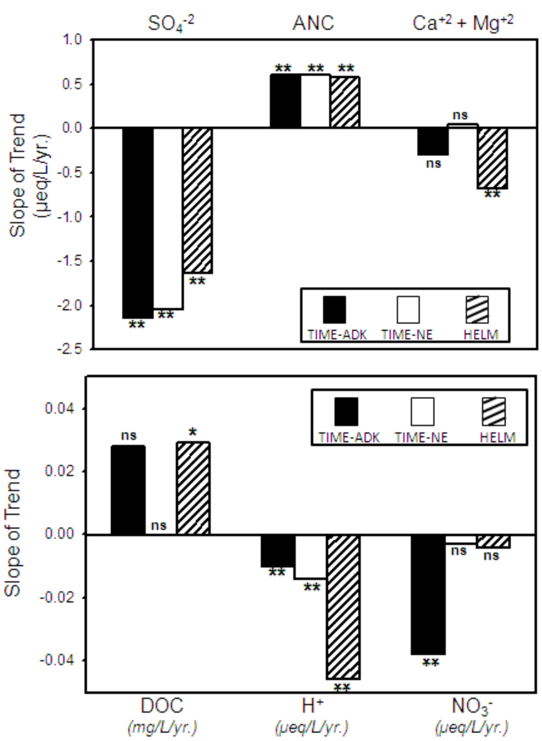


Figure 3. (a) Regional comparison of trends in biologically relevant chemistry in acid sensitive surface waters. Bars represent the median slope of the regression analysis for each individual lake. Units are noted in parentheses below each analyte. Significance is indicated by either ** ($p < 0.01$), * ($p < 0.05$) or ns ($p > 0.05$). (b) Note the change in scale of y-axis.

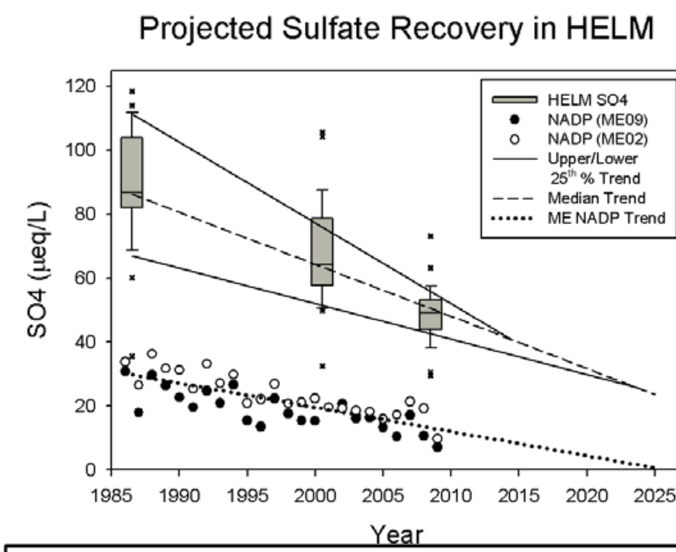


Figure 10. Estimated recovery scenario for HELM SO_4 concentration assuming continuing declines in SO_4 in atmospheric deposition. Boxplots represent HELM (n=28) data for 1986-87, 2000-01, and 2008-09 respectively. Boxes represent the 25th and 75th percentiles around the median, and error bars indicate the 10th and 90th percentiles. Solid lines show the regression for the upper and lower 25th percentiles and the dashed line represents the regression for the median. Dots indicate NADP data from Greenville (ME09) and Bridgton (ME02), ME while the dashed line represents the regression of both NADP stations together.

Appendix II. Draft abstract from MS candidate Baumann thesis (partially supported by this IAG).

Increasing organic acidity as an indicator of recovery from acid rain in Maine high elevation lakes.

ABSTRACT:

Reduced acidity in precipitation in the northeastern U.S. has led to improvements in surface water chemistry in some of the most affected waters. Nowhere is this more apparent than in Maine high elevation lakes (HELM). An important result of decreased acid rain has been an increase in the amount of dissolved organic carbon (DOC) across the northern hemisphere. This response has led to a shift in the source of acidity from anthropogenic inorganic (acid rain), to natural organic DOC sources. This shift in acidity source has minimized the long-term increase in lake pH compared to the decrease in pH in precipitation.

We have previously established that HELM lakes have responded rapidly to changes in deposition and are thus well suited to look at the impacts of increased DOC on recovery from acid rain. Sulfate fraction (SF, the relative contribution of SO_4 to the total anionic charge) has decreased 5% to 40% in HELM lakes since 1986-87, yet decreased H^+ is not widespread. Over the same time period, DOC has increased at 0.03mg/L/yr, the equivalent of 0.13 µeq/L/yr. We estimate that organic anions (OA^-) now contribute 10% to 15% more to anionic charge than in 1986-87.

The influence of increased OA^- is magnified because the HELM lakes are becoming increasingly dilute as acidic deposition declines and ionic leaching from watersheds decreases. Conductivity in HELM lakes has decreased from 17.6 µS/cm to 13.4 µS/cm since 1986-87. Overall, HELM lakes have experienced a shift in the SO_4:OA^- ratio from? 3.4 to 1.3 since 1986-87. We found significant differences between lakes with a small change in OA^- (low ΔOA) and those with large increases in OA^- (high ΔOA). Declines in H^+ in the low ΔOA group of 0.09 µeq/L/yr. were twice that of the population median and 10x that of the high ΔOA group. Furthermore, only the low ΔOA group exhibits a strong acidic deposition recovery pattern, with a significant decline in SF corresponding to a decrease in H^+. This means that HELM lakes are recovering in one of two ways. Low DOC lakes have experienced decreased H^+ as a direct result of decreased mineral acid inputs, while high DOC lakes have undergone a shift towards a natural organic source of acidity. While recovery in ANC may take an additional 10 to 30 years, recovery in pH is essentially complete in many lakes because their pH was not controlled by mineral acids and was relatively unaffected by acidic deposition. This conclusion is consistent with ample paleolimnological evidence from the northeastern US.

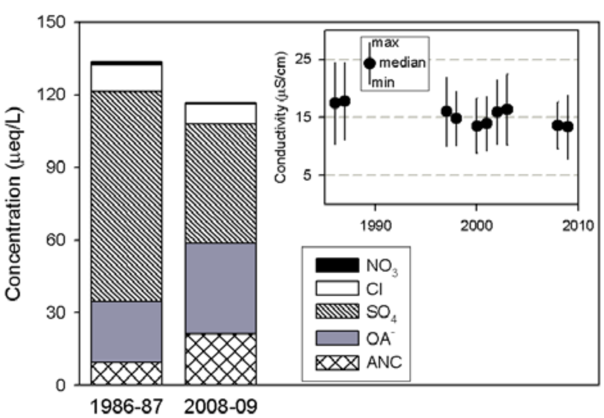


Figure 2. Shift in anion concentrations of the median HELM lake from 1986-87 to 2008-09. [inset: decrease in median HELM conductivity since 1986].

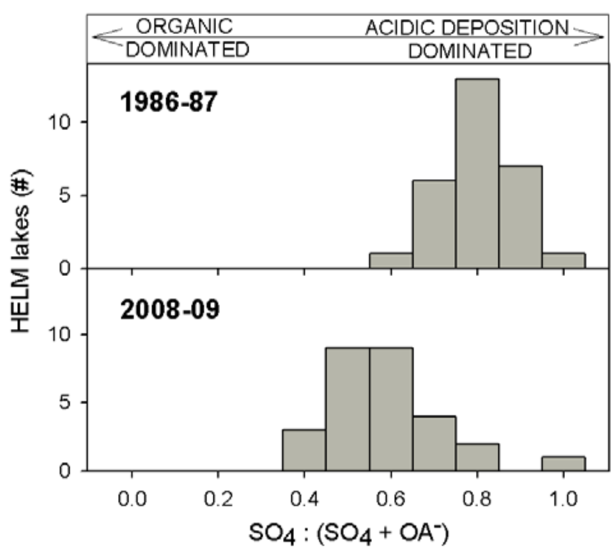


Figure 3. Shift in the relative influence of inorganic acid anions and organic anions in HELM lakes .