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Abiotic Controls on the Tropic Status of Oligotrophic Water

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Final Report for Period: 09/2007 - 08/2008**Submitted on:** 10/16/2008**Principal Investigator:** Norton, Stephen A.**Award ID:** 0415348**Organization:** University of Maine**Submitted By:**

Norton, Stephen - Principal Investigator

Title:

Abiotic Controls on the Tropic Status of Oligotrophic Water

Project Participants**Senior Personnel****Name:** Norton, Stephen**Worked for more than 160 Hours:** Yes**Contribution to Project:****Name:** Fernandez, Ivan**Worked for more than 160 Hours:** Yes**Contribution to Project:****Name:** Amirbahman, Aria**Worked for more than 160 Hours:** Yes**Contribution to Project:****Name:** Webster, Katherine**Worked for more than 160 Hours:** No**Contribution to Project:**

Webster, a limnologist in the Department of Biology, oversaw one undergraduate student who assessed the impact of artificial stream acidification on extant insect populations. The research was conducted in the fall of 2005. Data analysis is complete. The insect was too impoverished, naturally, to show significant response to the chemical manipulation.

Name: Jacobson, George**Worked for more than 160 Hours:** No**Contribution to Project:**

Jacobson is a paleoecologist in the Climate Change Institute at the University of Maine. In March 2007 he helped us obtain a 5.3 meter sediment core from oligotrophic Sargent Mountain Pond, Acadia National Park, Maine. Our NSF goals are to extend the techniques developed by graduate student Tiffany Wilson to study Al, Fe, and P speciation in sediments spanning 14,000 years. This period includes late glacial sediments, and the entire Holocene. During this period, vegetation developed (ca. 12,000 years BP). This would have caused the development of organic soils, in turn causing the export of Al (complexed with dissolved organic carbon) to the lake, followed by photo-oxidation of the Al-DOC molecules, precipitation of Al(OH)₃, sorption of dissolved PO₄, and oligotrophication.

This is a long-term validation or test of processes that we have uncovered in our current studies.

Jacobson is conducting the palynological studies. Other resources will be used for diatom (underway) and possibly chydorid analyses. This grant covered the chemical speciation and dating of the core.

Name: Simon, Kevin**Worked for more than 160 Hours:** No**Contribution to Project:**

Simon is a second year faculty member in Biology. He is a stream ecologist interested in nutrient dynamics in streams. He has conducted preliminary nutrient (P and N) addition experiments at one of our sites (the Bear Brook Watershed in Maine) and is contributing to our understanding of the controls of P in stream water. At the same time we are supplying him with discharge and water chemistry data generated from this project. He has submitted one manuscript and submitted one proposal to NSF, based on work related to this grant.

Name: Ohno, Stum

Worked for more than 160 Hours: No

Contribution to Project:

Ohno, a soil scientist, specializes in the characterization of dissolved and solid phase organic matter. Ohno participated in our group research meetings and contributed to our understanding of the DOC mobilization and stability at the Bear Brook Watershed research site.

Name: Saros, Jasmine

Worked for more than 160 Hours: No

Contribution to Project:

Saros is a specialist in paleolimnology and diatom enumeration. She has undertaken the analysis of diatoms in the long sediment core taken from Sargent Mountain Pond. Her responsibility is to test the hypothesis that the development of vegetation after deglaciation caused increase export of Al and DOC from the land to the lake, thereby fueling the scrubbing of P from the water column by precipitating $Al(OH)_3$. She received 1 week of summer salary in 2008 and will complete the project with no additional funds from this NSF grant.

Post-doc

Name: Porcal, Petr

Worked for more than 160 Hours: Yes

Contribution to Project:

Porcal received a Fulbright Fellowship through the Czech Republic. He spent 7 months at the University of Maine focusing on the photodegradation of dissolved organic compounds complexed with metals, especially Al, Fe, and P. He focused on samples from three streams in our study (by graduate students Laird, Goss, and Huntress) and a suite of lakes being studied by PhD graduate student Bjorn Lake.

Two manuscripts are in review; results of his work were presented at the BIOGEOMON2006 conference in California in June 2006 and a Baltic-Nordic Conference in 2007.

Graduate Student

Name: Holmes, Brett

Worked for more than 160 Hours: Yes

Contribution to Project:

Holmes completed his M.Sc. research in the Department of Civil and Environmental Engineering in 2007, studying the mechanisms governing the distribution and mobilization of Al, Fe, and P in forest soils. Empirical and experimental studies were included in his research. The major focus was the experimental manipulation of CO_2 pressure in soil solutions, within soil columns. He is assessing the mechanisms of mobilization of metals and phosphorus from soils. Major findings include the documentation of non-conservative behavior of inorganic dissolved carbon (DIC) and the relationship between elevated PCO_2 and mobilization of colloidal and dissolved Al, Fe, DOC, and P. One manuscript is in review (Amirbahman et al., in review). Holmes is now employed as a consulting engineer in the private sector.

Name: Lake, Bjorn

Worked for more than 160 Hours: Yes

Contribution to Project:

Lake is a fourth-year Ph.D. student in the Department of Civil and Environmental Engineering, studying the mechanism governing the flux of Al, Fe, and P to and from modern sediments in the three lakes identified in our original proposal as well as additional sites. He is currently developing our NMR capability to study the speciation of P in lake sediments, and the diagenesis of that material. He has two published manuscripts and has presented his work at three conferences.

Name: Sanclements, Michael

Worked for more than 160 Hours: Yes

Contribution to Project:

Sanclements is a third-year Ph.D. student in the Department of Plant, Soil, and Environmental Sciences, studying the distribution of Al, Fe, and P in soils, their speciation, and changes in speciation under controlled experiments. His research sites overlap with those of Holmes but also include soils from a new research site at Strengbach, France, and from Lesni Potek, Czech Republic. All soil samples have been collected, laboratory methodological methods have been improved/developed, and laboratory analyses have been completed. He recently passed his PhD written examination. He has presented his results at three national meetings of

the Soil Science Society of America. His work has demonstrated the dominating role that Al hydroxide plays in soils in controlling P sequestration and mobility. One manuscript on P speciation in soils is in review.

His support has come from this award and from DEB-0414144.

Name: Goss, Heather

Worked for more than 160 Hours: Yes

Contribution to Project:

Goss completed her M.Sc. in the Department of Earth Sciences in 2007. She focused on in-stream artificial acidification experiments at the four US sites in the research plan, plus one site in the Czech Republic (an international add-on to our original grant). The goal is to assess Al-Fe-P dynamics between stream substrates and stream water (with initially different pHs) during acidification. All experiments have been completed, Goss successfully completed her thesis, and has one manuscript in print. Results from her work were presented at the international Acid Rain Prague Conference in 2005 and BIOGEMON2006 conference in California in June 2006. She is currently employed by the U.S. EPA in Washington.

Name: Laird, Mollie

Worked for more than 160 Hours: Yes

Contribution to Project:

Laird completed her M.Sc. degree in 2006 in the Department of Earth Sciences. She focused on the dynamic chemical differences along the thread of four first order streams, through periods of high discharge. The goal is to understand the spatial and temporal controls on Al, Fe, and P export from headwater watersheds with surface waters of variable pH. Her field work covered two seasons. She studied events at four streams (3 in Maine and one in West Virginia).

Results from her research were presented in June 2006 at the international BIOGEMON2006 conference in California. Her results are being combined with a second thesis (D. Huntress) on this topic for publication.

Name: Wilson, Tiffany

Worked for more than 160 Hours: Yes

Contribution to Project:

Wilson was a part-time student. She was responsible for trace metal analyses in our environmental chemistry laboratory. She finished her M.Sc. in the Ecology and Environmental Sciences Program. She focused on the chemical analysis of ²¹⁰Pb-dated short cores from our three study lakes in Maine. She determined the history of deposition of, and speciation of, Al, Fe, and P in these cores, linking her findings to those of graduate student Bjorn Lake. The three lakes underwent minor acidification over the last 100 years from acid rain and are now in recovery. The dynamics of Al during acidification and recovery are particularly important to understand as a control on P mobility. Major findings include the development of a model of diagenesis of P species in lake sediment, indicating that the chemical half life of organically bound P is about 15-20 years. She has confirmed hypotheses by Kopacek (Czech Republic) concerning the strong control that Al plays in sediment binding and release of P. Wilson has also played a key role in the development of analytical methods for water chemistry (Al speciation) and sediment chemistry (Al speciation). Results from her work were presented at the international BIOGEMON2006 conference in California, in June 2006; one manuscript is published and one is in review.

Name: Huntress, David

Worked for more than 160 Hours: Yes

Contribution to Project:

Huntress completed his M.Sc. in 2007 in Civil and Environmental Engineering. He focused on the behavior of Al, Fe, and P (and a myriad of other trace elements) during high discharge events in headwater streams. His work supplements and extends that of Mollie Laird. His work will be synthesized with Laird's and submitted for review this fall. A second manuscript is under construction with Professor Shaleen Jain (Department of Civil and Environmental Engineering). The manuscript concerns meteorology, antecedent conditions, stream discharge, and stream chemistry.

Name: Fatemi, Farrah

Worked for more than 160 Hours: Yes

Contribution to Project:

Fatemi has completed her second year as a PhD student in the Department of Plant, Soil, and Environmental Sciences. She is focusing on the characterization and transformation of Al, Fe, P, and trace metal species in soils and soil solutions from our research sites, with most emphasis on the Bear Brook watershed in Maine. She is supported primarily from another NSF grant, DEB-0414144 (Fernandez et al.).

Name: Perry, Randall

Worked for more than 160 Hours: Yes

Contribution to Project:

Perry was employed full-time during the summer 2007 to conduct experiments on weathering of granite, and then continued as a graduate student supported by this grant. The focus is to understand the dynamics between Al and P released or sequestered during the weathering process. We hope to simulate the development of spodosol horizons. His experiments are yielding interesting solution trajectories early in the weathering process, including unusual non-congruent Pb isotopic variations. He is completing his M.Sc. this Fall, or early next spring.

Undergraduate Student

Name: Laracy, Ryan

Worked for more than 160 Hours: No

Contribution to Project:

Laracy graduated from the Department of Earth Sciences. He was employed full-time during the summer of 2005, serving as a field and laboratory assistant to three graduate students (Laird, Wilson, and Goss).

Name: Lynch, Benjamin

Worked for more than 160 Hours: No

Contribution to Project:

Lynch was an undergraduate in the Department of Plant, Soil, and Environmental Sciences. He worked full-time for the summer of 2005, assisting in soil sample collecting at the US sites, and laboratory processing of those samples.

Name: Southwick, Janet

Worked for more than 160 Hours: Yes

Contribution to Project:

Southwick graduated from Civil and Environmental Engineering. She assisted graduate student Bjorn Lake in his field and laboratory investigations during the 2005 summer (full time), and part time until summer 2006.

Name: Martin, Mikaela

Worked for more than 160 Hours: Yes

Contribution to Project:

Martin graduated (May 2007) with high honors from Civil and Environmental Engineering. She developing expertise in NMR assessment of speciation of phosphorus in natural samples (soils, sediments, groundwater, and stream water). Her honors thesis explored the dynamic behavior of P species in recently deposited lake sediment. One manuscript (with Bjorn Lake) is in preparation.

Name: Roy, Samuel

Worked for more than 160 Hours: Yes

Contribution to Project:

Roy was hired as a research assistant, working 10 to 15 hours per week for the academic year. He has been very helpful in field and laboratory studies involving water sampling, sediment coring, and water quality measurements. He completed his work at Orono, and now is completing an M.Sc. at Indiana University.

Name: Harrington, Robert

Worked for more than 160 Hours: Yes

Contribution to Project:

Harrington started on our project 1.5 years ago. He is between his second and third year, majoring in Earth Sciences. His interest is geochemistry. He worked closely with Perry, Lindsey, and Landis on a set of experiments exploring weathering of granite and the release of P during that process.

He has been assisting us in the preparation of sediment cores, for the study of speciation of Al, Fe, and P. His CAPSTONE project is a study of a chain-of-lakes (3) study of P speciation in lake sediment, supported by this grant.

Technician, Programmer

Name: Szillery, Johanna

Worked for more than 160 Hours: Yes

Contribution to Project:

Szillery, was a technician in charge of organizing and conducting all soil collections and the in-laboratory processing of the samples from all localities. Additionally, she participated in development and testing of sequential soil extraction procedures for assessing the abundance and speciation of Al, Fe, and P in forest soils. She left our program in June of 2006 to take a job in the private sector.

Name: Anderson, Denis

Worked for more than 160 Hours: Yes

Contribution to Project:

Anderson is a diatomist who analyzed the diatom assemblages in the three dated sediment cores (for Wilson's thesis) we collected. We believed that diatom assemblages reflected chemical changes (in addition to known relationships with pH) in the lake water column caused by varying fluxes of Al and P, induced by acidification from acid rain, and subsequent recovery. Diatom enumeration is complete. The major findings were that the recent cores fit stratigraphically with cores taken in ca. 1980, that slight recovery of pH has occurred in one of three lakes and the other two are stable, and the near-steady state of the diatom assemblages is consistent with Al, Fe, and P speciation in the sediment. One manuscript has been published (Wilson et al., 2008)

Other Participant

Name: Vesely, Josef

Worked for more than 160 Hours: No

Contribution to Project:

Vesely was an environmental geochemist at the Czech Geological Survey in Prague. He was identified as the contact person in the original NSF proposal. He arranged field and laboratory logistics for our Czech-based efforts, identified in the proposal. He submitted a proposal to the Czech National Academy for additional funding to supplement the Czech research component associated with this grant. This proposal was funded. Unfortunately, Vesely died in April 2006. The research is being conducted by Dr. Tomas Navratil, who will spend a half year with us, starting in the Fall of 2007.

Name: Kopacek, Jiri

Worked for more than 160 Hours: No

Contribution to Project:

Kopacek and PI Norton collaborated on 6 published manuscripts during this grant, and have two in review. We are planning joint research in support of the goals of this funded research. Kopacek participated in the field work at one research site in the Czech Republic and oversaw laboratory analyses of water samples from that site. He submitted (and successfully was funded) a proposal to Czech authorities to study photodegradation of Al and Fe complexed with dissolved organic matter, and effects on P mobility. These studies are parallel to those on our grant. Our collaboration has been extended to the study of non-congruent release of Pb isotopes during early weathering after deglaciation. A manuscript is under construction. Kopacek spent one week here in 2006 at the University of Maine, working with our graduate students, and the 3 PIs.

Name: Navratil, Tomas

Worked for more than 160 Hours: Yes

Contribution to Project:

Navratil and PI Norton have collaborated on three projects over the last 6 years. Navratil assisted us in conducting an in-stream acidification experiment at Lesni Potek catchment in the Czech Republic and in the collection of soil samples from Lesni Potok watershed. Navratil and Norton collaborated on a presentation at BIOGEMON2006 (California, Santa Cruz) in June where we suggested a new mechanism in soils for the control of Al and SO₄ in streams and lakes. A manuscript is in review. Navratil continued the collaborative research efforts initiated by Dr. Josef Vesely (deceased). Navratil recently successfully competed for a Fulbright Fellowship and spent 8 months with us, starting in the Fall, 2007. Here, he focused on secondary mineral development in soils of our study sites, particularly phases that control Al dissolution and mobility. He is developing three manuscripts relating to Bear Brook Watershed in Maine, on of our study sites for this grant.

Name: Pierret, Marie-Claire

Worked for more than 160 Hours: No

Contribution to Project:

Pierret is Director of Research at a site (Strengbach, France) that we have added to our research design. She is an isotope geochemist and assisted us in field collections of soil and stream samples at Strengbach. She will oversee the analysis of the stream samples in her laboratory. Soil samples were collected in June, 2006 and analysis of them has been completed. The stream

water study (a high discharge event) is still in the planning stage.

Name: Adams, Mary-Beth

Worked for more than 160 Hours: No

Contribution to Project:

Adams, Director of the USDA Fernow, West Virginia research site, hosted PI Norton for a site visit in April 2005 and assisted us in organizing our stream acidification experiment, and high discharge sampling. We completed our studies in 2005, courtesy of the Fernow site. Additionally, we supplied them with more field samplers and they collected a suite of stream samples during a second high discharge event, to supplement the data gathered by graduate student Mollie Laird. Field collections and analysis of soils from Fernow have been completed.

Research Experience for Undergraduates

Organizational Partners

Department of Interior National Park Service

Park personnel at Acadia National Park, Maine have assisted in site selection, permitting processes, and access to data. Water samples from a headwater stream during high discharge events, soil collections are complete, and lake sediment collection are complete. All analyses are complete. In March 2007, we recovered a 5.3 m sediment core from Sargent Mountain Pond, spanning at least the last 13,500 years of history of the site. This will provide a chronology of the development of the Al control on the trophic status of the now-oligotrophic lake. Other resources will enable the reconstruction of vegetation (pollen), water chemistry (diatoms), fire (charcoal), and possibly macroflora and fauna.

Department of Agriculture USDA Research Laboratories

Dr. Mary-Beth Adams at the Fernow Research site, West Virginia assisted us in site selection, permitting, data acquisition, and water sampling. She and her staff collaborated on in-stream experiments, soil collections, and stream water collections. Adams is collaborating on at least two manuscript that compare data from Fernow with other sites in our study.

Louis Pasteur University, Strassbourg, Fr

Dr. Marie-Claire Pierret, Director of the Strengbach Research site in France, assisted us in field sampling of soils in 2006 and stream waters in 2008. The site is run by Louis Pasteur University. All chemical analyses have been completed and comparative (US sites and France and the Czech Republic) papers are under construction. Pierret will likely spend a sabbatical with us at the University of Maine in 2009, as a consequence of our collaboration.

Czech Geological Survey

Dr. Tomas Navratil assisted us in site location of soil (complete) and water sampling (complete), and conducting two in-stream acidification experiments. Navratil has completed chemical analysis of water samples at the Czech survey.

Hydrobiological Institute, Czech Academy

Dr. Jiri Kopacek has collaborated on eight manuscripts with PI Norton and co-PI Amirbahman. Kopacek has also written a successful proposal to supplement our results and effort in the C.R. One of his former students, Dr. Petr Porcal, received a Fulbright Fellowship and worked with us in Maine (11/05-05/06). Kopacek spent one week in Maine working with the PIs and graduate students on this grant.

Maine Department of Environmental Protec

Maine DEP has been very helpful in providing us with water auto-sampling equipment and working with our students on site selection, especially for the lake water-lake sediment aspects of the proposed research. Maine DEP funded preliminary research in 2002-2004 that led to the development of this funded NSF proposal. Roy Bouchard has been very helpful in lake selection, and procurement of field gear. We have supplied Maine DEP with highly specialized sediment analyses (methods developed within this proposal) for their studies on eutrophication and P-loading of lakes.

U S Geological Survey

The US Geological Survey (Hydrologic Division, Augusta, Maine) runs the gauging stations at two of our research sites - Bear Brook and Hadlock Brooks, Maine. We share the expense of these stations (funds not from this grant). The data made available on-line and in real time have been of great value to our studies involving the chemistry of high discharge events.

Other Collaborators or Contacts

1. The addition of a research site at Strengbach, France, was supported by a Request for Supplementary Funding, submitted in April of 2005 to the NSF. This request was supported. We started a collaboration with scientists at the Louis Pasteur Institute. Soil and stream water sampling and analyses are complete.
2. In May 2007, Norton participated in a grant proposal to the Bailey Foundation. The goal is to conduct stream-side experiments with Atlantic salmon and limed, high DOC, acidic, Al-rich water. Ultimately the goal is to design an ecosystem-scale liming project. Partners in this work include NOAA, USGS, Maine Department of Environmental Protection, and Norton.

Activities and Findings

Research and Education Activities:

Our research combined laboratory and whole-ecosystem experiments with a suite of empirical observations to look at the dynamics of Al, Fe, and P. Studies occurred at 3 watersheds and 4 lakes in Maine, one in West Virginia and one each in the Czech Republic and France. The field studies link specific studies on soil and soil water, stream substrates and stream water, and lake water and lake sediment in a continuum of studies. The major goal is to understand the controls on P mobility and bioavailability in relatively unproductive (oligotrophic) systems.

A unique spectrum of ecosystems [based on stream pH (ranging from high 4s to mid-6s) and soil type] in Maine, West Virginia, France, and the Czech Republic is providing the framework to test these hypotheses. These sites include paired watersheds subject to whole ecosystem chemical manipulations with nitrogen and sulfur (Maine and West Virginia) that provide a uniquely robust design for testing these hypotheses. Our studies will determine: (1) soil properties influencing Al, Fe, and P mobility; (2) stream chemistry draining these soils during varying stream discharge; (3) the interactions of the stream water with stream sediments, and interactions between lake and lake sediment; and (4) the long-term record in lake sediments, derived from the same streams, for metals including Al, Fe, and P (and their speciation), and diatoms. Four streams have been artificially acidified from this matrix of study sites to determine mechanisms of retention and release of Al, Fe, and P. We also manipulated soil CO₂ and pH in soil columns to assess mechanisms of mobilization of P.

We have obtained a 5.3 meter core from currently oligotrophic Sargent Mountain Pond in Acadia National Park, Maine. This activity was not part of the original goals of the grant but our short-core studies pointed the way to this sub-project. The core has been studied to determine how processes of P sequestration in sediment have changed as vegetation was established after deglaciation and lake water chemistry evolved. We have other support for palynological, diatom, and possibly chydorid analyses. This NSF grant supports the chemical speciation studies as well as ¹⁴C and ²¹⁰Pb dating. The core spans at least 13,500 years.

We are conducting some short-term weathering experiments on granites to explore the role of rising pH on the congruency of weathering reactions, and the interplay of secondary Al phases and P mobility. The experiments are being conducted by a team of a high school student, a high school teacher, one undergraduate student, and a graduate student.

Findings:

All the major objectives of the proposal have been accomplished with regard to sampling sites, experiments, analyses, educational opportunities, collaborations, etc.

1. Lengthy exchange between PI Norton and Drs. Jiri Kopáček and Josef Vesel² (both from the Czech Republic)(Vesely now deceased) has resulted in three major developments:

1a. Dr. Petr Porcal (Czech Republic) received a Fulbright Fellowship and spent 7 months as a post-doctoral fellow with us at the University of Maine working on this research. He brought new expertise in the chemistry and photo-chemistry of Al-DOC and Fe-DOC complexes in fresh water to our University. This area of research was not included in our original research design but likely is a fundamental component of controlling mechanisms on P mobility in these ecosystems. Adding this expertise strengthens our approach considerably. Dr. Tomas Navratil (Czech Republic) joined us (2007-2008) to help us synthesize some of our data, and perform experiments on Al-P mobility in stream sediment.

1b. Dr. Josef Vesel² (now deceased) and Dr. Jiri Kopáček wrote proposals to the Czech authorities (both funded) for additional resources for research that complements and supplements our research activities. Vesel²'s focused on the role of dissolved Si in controlling Al in soil solutions and surface waters. Dr. Tomas Navratil (Czech Geological Survey, and Academy of Sciences) continued the studies. Kopáček focused on additional studies of photo-degradation of Al-DOC and Fe-DOC, long-core paleolimnological assessments of organic and inorganic Al and Fe controls on P availability in lakes, and Pb isotopes in long cores. Navratil joined us on a Fulbright Fellowship in the Fall of 2007, for 8 months.

1c. Dr. Jiri Kopáček and PIs Norton and Amirbahman have collaborated on eight highly relevant manuscripts since October 2004 (see publications, below); six are published, two in review. Dr. Josef Vesel² and PI Norton collaborated on a manuscript (published) on 'Increasing silicon concentrations in Bohemian Forest lakes, Czech Republic'. This manuscript links Si and Al in soil waters to changes in down-stream lakes.

2. PIs Fernandez and Norton have been in lengthy discussions with Drs. Marie-Claire Pierret and Bertrand Fritz of the Louis Pasteur University, Strasbourg, France. Pierret currently is the Site Research Director for the Observatoire Hydro-Géochimique de l'Environnement (OHGE). The OHGE is a calibrated watershed (<http://ohge.u-strasbg.fr/>), similar to Fernow, West Virginia in bedrock chemistry (OHGE being on granite and Fernow on quartzo-feldspathic sandstones) and similar to Bear Brook, Maine in bedrock chemistry and watershed instrumentation. OHGE is located about 50 km northeast of Strasbourg. The bedrock is largely granite with minor sillimanite gneiss. Ultisol soils are well-developed and are pre-glacial (at least pre-Wisconsinan) (as at Fernow). The soils are Ca and Mg deficient and this is a focus of research at their site, as it has been at BBWM and Fernow. The watershed is 97% forested (largely conifer). Elevation ranges from 883 to 1146. Total precipitation ranges from about 1 to 1.5 m, while runoff is about 65% of input. Mean annual temperature is 6°C (as at Bear Brook). Chemical and hydrologic budgets have been monitored since 1986. Input precipitation pH is ~4.1 while runoff is ~6.1, similar to Fernow. Pierret and Fritz have expressed a desire to have us extend our Al-Fe-P research to Strengbach (see attached letter). They have given us access to the 17-year record of atmospheric chemistry and deposition, soil solution chemistry, and stream chemistry. These Louis Pasteur University scientists have already visited the University of Maine as part of an emerging collaboration between our institutions, and they were selected to represent their institution because of the similar interests evident in their, and our, watershed studies. This research provides a tangible opportunity to formalize this collaboration and to expand our matrix of research watersheds to include a European counterpart to the highly weathered, coniferous watershed characteristics from the existing matrix of sites.

3. The role of stream sediment - stream water interaction was explored through three acidification experiments in the US and two in the Czech Republic. Acid neutralization mechanisms ranged from only titration of alkalinity in stream water, to massive desorption of base cations and Al from sediment. The main variables controlling response of streams to acidification was surface area of substrate, concentration of dissolved organic carbon and alkalinity, and pH.

4. Natural episodic stream acidification in streams was explored by two graduate students. They found that most of the P that leaves the oligotrophic systems we studied does so at high flow, because of the higher flux of water AND enormously higher concentration of particulate P in that water. Dissolved P tends to remain relatively low as a result of sorption of most dissolved inorganic Al by Al(OH)₃ particulate material.

5. Lake sediments record the geochemistry of Al, Fe, and P through time. We have found that the majority of P in oligotrophic lake sediments is associated with an Al-extracted phase. The paradigm of Fe controlling P in lakes is false for oligotrophic lakes. The strong relationship between extractable Al and P in lake sediments throughout the Holocene indicates a mechanism of mobilization and transport of these two elements that is unrelated to anthropogenic acidification of lakes. The mechanism apparently is mobilization of Al and Fe from soils by dissolved organic carbon, followed by photo-oxidation of the Al-DOC and Fe-DOC bonds, producing inorganic Al and Fe that then precipitates. These hydroxide precipitates scavenge PO₄ from the water column. If the Al:Fe ratio exceeds 3 in sediment, the sorption is irreversible and recycling of P from sediment during anoxia is curtailed. This mechanism appears to be highly significant in causing the oligotrophic conditions of broad areas in Maine, New Brunswick, Nova Scotia, and Sweden, at least.

6. We explored various speciation schemes for soils and sediments and resolved that the Psenner extraction (Psenner and Psucko 1988) would be used for all solids. Interestingly, soils, stream sediments, and lake sediments have very common speciation for Al, Fe, and P, indicating a continuum of processes linking the terrestrial with the aquatic environments (SanClements et al., in review).

7. An exciting finding is the sediment archived record (from Sargent Mountain Pond in Maine) of the incongruity of Pb isotopes created during weathering shortly after deglaciation. The record is consistent with that of deep-sea North Atlantic sediments, but with far greater resolution.

8. The changes in sediment speciation in long cores spanning early post-glacial conditions, suggested that weathering reactions undergo dramatic and rapid changes, as runoff goes from high available P, high pH, and high alkalinity to low P, low pH, and low alkalinity.

9. Experiments with intact soil cores, using manipulation of PCO₂, indicate that disturbance of soil with high CO₂ pressure can cause massive loss of colloidal Al and Fe, and high dissolved P from the soil column.

Training and Development:

Eleven graduate students and six undergraduates have been supported to varying degrees in their research activities. Eleven graduate students have made one or more professional presentations at national/international meetings (a total of 28) and they were co-authors on many others.

Seven students (Tiffany Wilson, David Huntress, Heather Goss, Mollie Laird, Brett Holmes, Jessica Sherman, and Melinda Diehl) have completed their M.Sc. degrees in Earth Sciences, Plant, Soil, and Environmental Sciences, Civil and Environmental Engineering, and Ecology

and Environmental Sciences. One M.Sc. degree in Earth Sciences will be earned this Fall (Randall Perry). Three Ph.D. students are finishing their degrees within either one or two years (Farrah Fatemi, Bjorn Lake, Michael SanClements).

Six undergraduate students were employed for part-time in the school year and full-time for the summer. One high school teacher joined our team and spent three years with us. Four highly motivated high school students (all women) spent 1 or two summers with us.

Two post-doctoral fellows were attracted from the Czech Republic to work on our project: Drs. Tomas Navratil and Petr Porcal.

Our studies of speciation of P in soil, and stream and lake sediment have depended on operationally-defined procedures. We have had some difficulty distinguishing speciation of P in a matrix of sediment rich in Al, Fe, and organic matter. Consequently we have been exploring the use of NMR to study the bonding of P to various phases. We applied successfully to develop an NMR facility that will be supportive of the NSF research goals: [Amirbahman, A., Lake, B.A., and Bishop, K., Norton, S.A., and Bouchard, R., 'A ³¹P NMR investigation of phosphorus speciation in sediments of two shallow lakes in Maine, USA.' Project funded by the USGS-WRRI. Direct cost: \$10,100 (+2:1 non-Federal match). February 2007 - January 2008.]

Two successful grants were developed by Czech Colleagues, in collaboration with us, to explore other aspects of the control of trace metals on P mobility.

Outreach Activities:

PI Norton continues to work with the Atlantic Salmon Commission and the Downeast Salmon Federation to help them understand the dynamics of Al in eastern Maine streams where Atlantic Salmon populations are threatened. There are issues of low productivity (related to low P), high acidity (from high DOC and low Ca), and high Al (caused by a combination of high DOC and low pH).

Those activities have adopted the collection and analysis protocols that we developed for Al speciation, with a substantial increase in reliability of data.

Journal Publications

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Kopacek, J., Borovec, J., Hejzlar, J., Ulrich, K-U., Norton, S. A., and Amirbahman, A., "Aluminum Control of Phosphorus Sorption by Lake Sediments", *Environ. Sci. Tech.*, p. 8784, vol. 39, (2005). Published,

Norton, S. A., Fernandez, I., Amirbahman, A., Coolidge, K., and Navratil, T., "Aluminum, Phosphorus, and Oligotrophy - Assembling the pieces of the puzzle", *Proc. Soc. Intern. Limnol.*, p. 1877, vol. 29, (2006). Published,

Vesely, J., Majer, V., Kopáček, J., Šafanda, J., and Norton, S. A., "Increasing silica concentrations in Bohemian Forest lakes", *Hydrol. Earth Syst.*, p. 699, vol. 9, (2005). Published,

Sherman, J., Fernandez, I. J., Norton, S. A., Ohno, T, and Rustad, L. E., "Soil aluminum, iron, and phosphorus dynamics in response to long-term experimental nitrogen and sulfur additions at the Bear Brook Watershed in Maine, USA", *Environ. Monit. Assess.*, p. 419, vol. 121, (2006). Published,

Kopáček, J., Maresová, M., Norton, S. A., Porcal, P., and Vesely, J., "Photochemical source of metals for sediments", *Environ. Sci. Tech.*, p. 4455, vol. 40, (2006). Published,

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Wilson, T. A., Norton, S. A., Lake, B., Amirbahman, A., "Sediment geochemistry of Al, Fe, and P for two oligotrophic Maine lakes during a period of acidification and recovery", *Science of the Total Environment*, p. 269, vol. 404, (2008). Published,

Lake, B., Coolidge, K., Norton, S. A., and Amirbahman, A., "Factors contributing to the internal loading of phosphorus from anoxic sediments in six Maine, USA, lakes", *Science of the Total Environment*, p. 534, vol. 373, (2007). Published,

Kopáček, J., Marešová, M., Hejzlar, J., and Norton, S. A., "Natural inactivation of phosphorus by aluminum in pre-industrial lake sediments", *Limnology and Oceanography*, p. 1147, vol. 52, (2007). Published,

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Navrátil, T., Rohovec, J., Amirbahman, A., Norton, S. A., and Fernandez, I. J., "Controls of natural amorphous aluminum hydroxide on sulfate and phosphate anions in sediment-solution systems", *Environ. Monit. and Assess.*, p. , vol. , (2008). in revision,

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Kevin S. Simon, Michael A. Chadwick, Alexander D. Huryn, H. Maurice Valett, "Stream ecosystem response to chronic deposition of nitrogen and acid at the Bear Brook Watershed, Maine", *Environ. Monit. and Assess.*, p. , vol. , (2008). Submitted,

Books or Other One-time Publications

Web/Internet Site

Other Specific Products

Product Type:

Published abstract

Product Description:

Goss, H. V., Wilson T., Boone, R., and Norton, S. A., 2005, Effects of CO₂ degassing on aluminum speciation in three streams in Maine, USA: Acid Rain 2005, 7th International Conference on Acid Rain, Prague.

Sharing Information:

Published abstract in the Proceedings, Acid Rain 2005, Prague

Product Type:

Published abstract**Product Description:**

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Published abstract

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Sharing Information:

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Sharing Information:

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Product Type:**Published abstract****Product Description:**

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Sharing Information:

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Product Type:**Published abstract****Product Description:**

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Sharing Information:

Published abstract

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Sharing Information:

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Product Description:

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Sharing Information:

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Product Description:

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Sharing Information:

Published abstract

Product Type:

Published abstract

Product Description:

Lake, B.A., Coolidge, K.M., Amirbahman, A., Norton, S.A. and Bouchard, R., 2006, Factors contributing to the internal loading of phosphorus from anoxic sediments in six Maine lakes, 30th Annual Meeting of the New England Association of Environmental Biologists, Bethel, ME.

Sharing Information:

Published abstract

Product Type:

Published abstract

Product Description:

SanClements, M., Fernandez, I., Norton, S., Amirbahman, A., and Rustad, L., 2006, Distribution of soil phosphorus fractions in acid soils of forested watersheds. (Paper 234-5). ASA-CSSA-Soil Science Society of America International Meeting, Indianapolis, Indiana, 11/12-16,2006 [CD-ROM]. ASA, CSSA, SSSA, Madison, WI.

Sharing Information:

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Product Type:

Published abstract

Product Description:

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Sharing Information:

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Product Type:**Published abstract****Product Description:**

Sherman, J., Fernandez, I. J., Norton, S. A., Ohno, T., and Rustad, L. R., 2005, Soil Al, Fe, and P dynamics after 15 years of N and S additions at the Bear Brook Watershed in Maine, USA., Acid Rain 2005, 7th International Conference on Acid Rain, Prague.

Sharing Information:

Published abstract

Product Type:**Published abstract****Product Description:**

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Sharing Information:

Published abstract

Product Type:**Published abstract****Product Description:**

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Sharing Information:

Published abstract and poster

Product Type:**Published abstract****Product Description:**

Lake B.A., A. Amirbahman, and S.A. Norton, 2006, Factors contributing to the internal loading of phosphorus from anoxic sediments in nine Maine lakes with high DOC concentration: Annual Summer Meeting of the Am. Soc. Limnol. Oceanogr., Victoria, BC.

Sharing Information:

Published abstract

Product Type:**Published abstract****Product Description:**

Kopáček J., Porcal P., Hejzlar J., and Norton S. A., 2007, Photochemical source of aluminum for lakes and its impact on phosphorus cycling. Keele Conference, Mexico.

Sharing Information:

Published abstract

Product Type:**Published abstract****Product Description:**

Lake, B., Amirbahman, A., and Norton, S., 2007, Investigating phosphorus internal loading in Maine lakes using ³¹P Nuclear Magnetic Resonance (NMR): New England Assoc. Environ. Biologists.

Sharing Information:

Published abstract

Product Type:**Published abstract****Product Description:**

Porcal P., A. Amirbahman, J. Kopáček, and S.A. Norton, 2007, Photochemical release of humic and fulvic acid-bound metals in freshwater: 11th Nordic-Baltic Symposium of International Humic Substances Society, Functioning of NOM in Environment, Joensuu, Finland.

Sharing Information:

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Product Type:**Thesis****Product Description:**

Jessica Sherman, 2005, Soil Iron, Aluminum and Phosphorus Dynamics in Response to Thirteen Years of Nitrogen and Sulfur Additions at the Bear Brook Watershed in Maine (M.Sc., Department of Plant, Soil, and Environmental Science: advisor Fernandez)

Sharing Information:

University of Maine Library

Product Type:**Thesis****Product Description:**

Heather V. Goss, 2006, Contrasting chemical response to experimental acidification of five acid-sensitive streams. (M. Sc., Department of Earth Sciences; advisor Norton)

Sharing Information:

University of Maine Library

Product Type:**Thesis****Product Description:**

Molly Laird, 2006, Spatial and temporal changes in stream chemistry at three watersheds during high discharge episodes. (M. Sc., Department of Earth Sciences; advisor Norton).

Sharing Information:

University of Maine Library

Product Type:**Undergraduate Honors Thesis****Product Description:**

Mikaela Martin, 2007, Lake hypolimnetic P release: Undergraduate High Honors Thesis, University of Maine. (B. Sc., Department of Civil and Environmental Engineering; advisor Amirbahman).

Sharing Information:

University of Maine, Honors College

Product Type:**Thesis****Product Description:**

Brett Holmes, 2007, Mobilization of metals and phosphorus from intact forest soil cores by dissolved inorganic carbon: A laboratory column study. (M. Sc., Department of Civil and Environmental Engineering, advisor Amirbahman)

Sharing Information:

University of Maine Library

Product Type:**Thesis**

Product Description:

Melinda Diehl, 2006, Using Stream Chemistry to Evaluate Experimental Acidification and Natural Recovery in the Paired Catchments at the Bear Brook Watershed in Maine (Ecology and Environ. Science)

Sharing Information:

University of Maine Library

Product Type:**Published Report****Product Description:**

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Sharing Information:

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Product Type:**Published abstract****Product Description:**

Wilson, T. and Lindsey, E., 2006, Important modifications of an aluminum speciation technique for surface waters: Geological Society of Maine Annual Meeting.

Sharing Information:

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Product Type:**M.Sc. Thesis****Product Description:**

David Huntress (Civil and Environ. Engineering), 2008 (co-advisor with Professor Aria Amirbahman), Chemical dynamics during high discharge events at three forested catchments in eastern Maine, USA

Sharing Information:

University of Maine, Fogler Library

Product Type:**M.Sc. Thesis****Product Description:**

Tiffany Wilson (M.Sc. ? Ecol. Environ. Sciences), 2008, A Paleolimnological Assessment of Three Oligotrophic Watersheds in Maine

Sharing Information:

University of Maine, Fogler Library

Product Type:**Published abstract****Product Description:**

Perry, R. H., Norton, S. A., Koons, P. O., 2008, Post-Wisconsinan Chemical Weathering Rates and Trajectories From a 13,400-Year Sediment Core Record of Lead Isotopic Ratios in Maine: Am. Geophys. Union Ann. Mtg., San Francisco.

Sharing Information:

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Product Type:**Published abstract****Product Description:**

SanClements, M. D., Fernandez, I. J., and Norton, S. A., 2008, Evolution of phosphorus fractions from an upland watershed to lake sediments. Abstract and presentation at the 11th North American Forest Soil Conference. Blacksburg, VA. p.100.

Sharing Information:

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Product Description:

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Sharing Information:

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Product Type:

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Product Description:

Fatemi, F. A., Fernandez, I. J., Rustad, L. R., Simon, K. S., and Norton, S. A., 2008, The effects of N-enrichment on forest CNP stoichiometry at the Bear brook Watershed in Maine: North American Forest Soils Ann. Mtg.

Sharing Information:

Published abstract

Product Type:**Published abstract****Product Description:**

SanClements, M. D., Fernandez, I. J., Norton, S. A., Adams, M. B., Rustad, L. E., 2007, Soil Phosphorus Fractions from Six Acidic Forested Watersheds in the U.S. and Europe: Gordon Conference - Interactions of Hydrology, Biology & Geochemistry.

Sharing Information:

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Product Type:**Abstract****Product Description:**

Huntress, D., Norton, S. A., Laird, M., Amirbahman, A., 2007, Spatial and Temporal changes in Aluminum, Iron, and Phosphorus during Acidic Episodes at East Bear Brook, Maine USA: Gordon Conference - Interactions of Hydrology, Biology & Geochemistry.

Sharing Information:

Available from the authors at the University of Maine

Product Type:**abstract****Product Description:**

Norton, S. A., Kopáček, J., Fernandez I. J., Porcal, P., Amirbahman, A., Wilson, T., Lake, B., SanClements, M., Huntress, D., 2007, Al-Fe-DOC-P Coupling in Forested Ecosystems: Gordon Conference - Interactions of Hydrology, Biology & Geochemistry.

Sharing Information:

Available from the authors at the University of Maine

Product Type:**Published abstract****Product Description:**

Lake B.A., A. Amirbahman, and S.A. Norton, 2008, How might global warming affect internal P cycling in Maine lakes. Maine Water Conference, Augusta, ME, April 2008. Published and orally presented material (abstract)

Sharing Information:

Lake B.A., A. Amirbahman, and S.A. Norton, 2008, How might global warming affect internal P cycling in Maine lakes. Maine Water Conference, Augusta, ME, April 2008.

Product Type:**Published abstract****Product Description:**

Orally delivered and published abstract.

Sharing Information:

Fatemi, Farrah R., Ivan J. Fernandez, Kevin S. Simon, D. Bryan Dail, and Lindsey E. Rustad. 2008. Response of forest soil CNP dynamics to N enrichment at the Bear Brook Watershed in Maine: Clues from extracellular enzyme activities. (Paper 596-4). Presented at the ASA-CSSA-SSSA International Meetings. Houston, Texas. October 5-9. [CD-ROM]. ASA, CSSA, SSSA, Madison, WI.

Product Type:**Published abstract****Product Description:**

Orally delivered and published abstract

Sharing Information:

Fernandez, Ivan J., Stephen A. Norton, Lindsey E. Rustad, G. Bruce Wiersma, and Kevin S. Simon. 2008. New challenges for the third decade of whole-ecosystem experimental manipulations at the Bear Brook Watershed in Maine (BBWM). (Paper 699-20). Presented at the ASA-CSSA-SSSA International Meetings. Houston, Texas. October 5-9. [CD-ROM]. ASA, CSSA, SSSA, Madison, WI.

Contributions**Contributions within Discipline:**

Phosphorus is likely the most-studied element in fresh waters, largely because of human-induced eutrophication. Phosphorus is the most limiting nutrient in oligotrophic waters, which have low phytoplankton primary productivity and are sensitive to acidic deposition. Phosphorus is also typically the second-most limiting nutrient (N being first) to net primary productivity in forested ecosystems. Ecosystems may be oligotrophic because of low P bioavailability, despite high fluxes of total P. Aluminum and Fe geochemistry appear to be critical for controlling P mobility within ecosystems but few studies have simultaneously studied the relevant processes along the entire continuum of the hydrogeochemical pathway in the same ecosystem. Aluminum geochemistry may be the critical control on P bioavailability.

The manuscripts produced thus far indicate a major role for Al in controlling phosphorus concentrations and availability in soils, streams, and lake water. Oligotrophic lakes, in particular, are low in P because of scavenging (adsorption) of P by inorganic precipitates of Al and Fe. Subsequently Al binds the P irreversibly so that P is not released from lake sediments during periods of hypolimnetic anoxia.

We have demonstrated that, in agreement with Kopacek et al. (many recent papers), P cycling in lakes is dominated by Al(OH)₃ sorption. In headwater streams, Al mobilization is enhanced at low pH and this is typically accompanied by loss of substantial P, both dissolved and adsorbed to particulate Al(OH)₃. In high DOC surface waters, photo-oxidation causes release of organically bound Al, precipitating Al(OH)₃, and irreversible sorption of P. The dominant form of P in soil profiles is also in association with Al(OH)₃ solid phases.

This mechanism of sequestration becomes dominant in surface water as DOC increases. Consequently, in ecosystems that developed during early post-glacial times, P mobility was relatively high (with associated higher trophic conditions). As vegetation developed, DOC in runoff increased, along with accompanying organically bound Al. With time, the flux of Al from the watershed may increase, increasingly sequestering P from the water column, even as secondary Al(OH)₃ increased in watershed soils, enhancing retention of P in the soils. The result is increasing oligotrophy through time.

High rates of P release in young watersheds is suggested by weathering experiments of granite. As weathering proceeds, pH of 'runoff' declines, alkalinity declines, base cations decline, and P declines. The trajectory of declining P availability during weathering coincides with diatom evidence of declining pH and P availability. Thus there is a closely connected evolution of vegetation, soils, and water chemistry. Historically, soil scientists and aquatic sediment scientists used different operationally-defined methods to look at speciation of metals in the solid phase. Comparisons of soil, stream sediment, and lake sediment were meaningless. The number of speciation methods (extractions) literally numbered in the dozens. We researched these methods and their efficacy and found that comparison was a meaningful goal. So, we adopted a method (Psenner and Pucsko 1988) that combines aspects of both sediment and soil extractions. This led to the dramatic finding that soil P speciation looks much like lake sediment, both quantitatively and qualitatively. In retrospect, this should not be a surprise. Much of lake sediment is reprocessed soil, with in-lake processes overprinting the soil processes.

Contributions to Other Disciplines:

The manuscripts relating to sediment sequestration of P by Al(OH)₃ represent an important finding for the management of fresh water systems under threat of eutrophication from human disturbance. In essence, analysis of a sediment sample enables us to predict the general extent of P cycling in lakes that periodically become anoxic. The paradigm of the 'ferrous wheel' has been shown to be incorrect in many lake settings. Al-dominated (over Fe) waters and sediment have a high capacity to retain P under both oxic and anoxic conditions. On a molar basis, the Al:P ratio in solid secondary phases may approach 10:1; it is commonly 30-50:1 in lakes and streams, and higher in some sediments.

Contributions to Human Resource Development:

In Years One and Two of the research, we completed recruitment of eight of 11 (eventually) very capable and enthusiastic students. A ninth student joined us in year 3, as several graduated. Two more have joined us near the end of the funding period and will continue on other grants. This group met regularly with obvious synergism occurring. This is reflected in a tremendous team effort for the complicated field work, collaborative analytical approaches, and team learning. Three additional UMaine faculty, Shaleen Jain (Hydrology - Civil Engineering), Katherine Webster [limnology] and Stum Ohno [soils], joined our research group in a limited way. Undergraduate students were continuously involved in the research. One high school science teacher worked in our group for two years and contributed substantially to field and laboratory investigations. He will co-author at least one manuscript. For each of two summers, we had

three extremely capable female high school students who learned a lot, and contributed substantially to our success. Two post-doctoral Fulbright fellows from the Czech republic were attracted to our research program and they contributed additional dimensions to our research, both in the field and in the laboratory.

Contributions to Resources for Research and Education:

The development of refined methods for the determination of Al speciation in humic waters has enabled us to be helpful to the Atlantic Salmon Commission and the Downeast (Maine) Salmon Federation. Atlantic Salmon is listed as endangered in Maine (and in Nova Scotia). These organizations have considerable concern about fish restoration. We are now viewed as an important resource to them in understanding the possible role of Al in water in the demise of the fish populations, as well as poisoning the trophic status of lakes. One research project has just been funded for streamside liming experiments. We will provide the chemical know-how for that project.

Contributions Beyond Science and Engineering:

The manuscripts on sediment chemistry are a useful tool for water quality management and thus for regulatory agencies. The Maine Department of Environmental Protection (contact is Roy Bouchard, Maine DEP) is quite enthusiastic about our findings and has been very supportive in material and intellectual ways since this research started. We are providing expertise in the speciation of P, Al, and Fe in lake sediment, and thus consequently enabling them to be more predictive about P loading in lakes, and its effects.

The refinement of methods for the determination of Al speciation in surface waters, particularly high DOC water, has been important to groups interested in fish restoration in acidic waters. Eastern Maine's surface waters are oligotrophic, likely largely because of the relationships between organically-bound Al, photooxidation of that complex, precipitation of $Al(OH)_3$, and irreversible scavenging of P, thereby reducing productivity.

Categories for which nothing is reported:

Any Book

Any Web/Internet Site