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Mechanisms Controlling Metal and Phosphorus Dynamics in an Experimentally Acidified Watershed in Maine

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Final Report for Period: 08/2008 - 07/2009

Submitted on: 07/06/2009

Principal Investigator: Fernandez, Ivan J.

Award ID: 0414144

Organization: University of Maine

Submitted By:

Fernandez, Ivan - Principal Investigator

Title:

Mechanisms Controlling Metal and Phosphorus Dynamics in an Experimentally Acidified Watershed in Maine

Project Participants

Senior Personnel

Name: Fernandez, Ivan

Worked for more than 160 Hours: Yes

Contribution to Project:

Dr. Fernandez is the lead PI on the project and as such, oversees the coordination of all project planning and organization. His area of expertise is soil biogeochemistry and he oversees the soil and vegetation sampling in this project. His time towards meeting the goals of the project is supported by University of Maine and Maine Agricultural and Forest Experiment Station funds for salary along with summer salary support from this project. He is also lead PI on complimentary grants from USDA that are providing information on soil chemistry, fine root biomass, and soil respiration that will directly support the goals of this project. He coordinates all research at the BBWM site, and serves as the University of Maine contract representative with the land owners at the site of the BBWM.

Name: Norton, Stephen

Worked for more than 160 Hours: Yes

Contribution to Project:

Dr. Norton has been actively involved in planning the research, in recruiting students and staff for the project, and in providing input and guidance to student activities that are supported by this project. His focus in the project is the development of an understanding of the linkages between the laboratory studies, terrestrial findings, and how they govern the associated chemistry of BBWM streams. Dr. Norton also serves as lead PI on a closely related project (award number 0415348) and works closely with Dr. Fernandez in maximizing the integration and synergy between contracts. Dr. Norton's salary support is from the University of Maine with summer salary from this contract.

Name: Cosby, Bernard

Worked for more than 160 Hours: No

Contribution to Project:

Because data collection for this initiative has not yet begun, there has been no significant activity on the modeling component of the project. Dr. Cosby has complete his first site visit to Maine in March as part of this project where he worked with the project staff to plan for model development work this summer and fall. Because of the timing of the beginning of the first contract year, his initial contributions have not been >160 hours in this last reporting cycle. In the coming year he will be fully involved with the modeling phases of the project in collaboration with the other PIs, students and staff.

Name: Rustad, Lindsey

Worked for more than 160 Hours: Yes

Contribution to Project:

Dr. Rustad has been involved directly in the planning of the upcoming field activities, and is also an active co-PI on complimentary research projects that are providing information on soil chemistry, fine roots, and soil respiration. Her salary support is from the USDA Forest Service and some staff and laboratory support from the USDA Forest Service facilities in Durham, New Hampshire under her guidance and management has been and continues to be critical to the overall BBWM research program.

Name: Amirbahman, Aria

Worked for more than 160 Hours: Yes

Contribution to Project:

Dr. Amirbahman is a PI and faculty in Civil and Environmental Engineering who has recently joined the BBWM PI group on a number of research contracts including this project. He has been directly involved in discussions of research plans for the first field season, and he oversees as major advisor Brett Holmes, an MS student on this project. Dr. Amirbahman is directly

responsible for laboratory soil leaching studies and the integration of highly controlled experiments with the field research program. His salary support is from the University of Maine, with summer salary from this project.

Post-doc

Graduate Student

Name: SanClements, Michael

Worked for more than 160 Hours: No

Contribution to Project:

Michael SanClements began his doctoral program in Ecology and Environmental Sciences April 1, 2005 and is partially funded through this contract. He is also partially supported by a companion NSF contract looking at soil metal and P processes across a range of watersheds. His focus was on soil P chemical fractionation. He completed his PhD in May 2009 and has worked as a post-doctoral fellow during the summer 2009 completing publications and data management tasks related to this research.

Name: Holmes, Brett

Worked for more than 160 Hours: Yes

Contribution to Project:

Brett Holmes completed his Masters of Science in Environmental Engineering in May 2007. He was partially supported by this contract, and worked on the soil column leaching experiments under this contract.

Name: Bethers, Suzanne

Worked for more than 160 Hours: No

Contribution to Project:

Suzanne Bethers is developing a project at BBWM for her MS degree to study forest physiological response to treatments. As such, her work will be partly integrated with the foliar chemistry components of this project.

Name: Fatemi, Farrah

Worked for more than 160 Hours: Yes

Contribution to Project:

This is a new graduate student to the project beginning her doctoral program. She receives departmental support supplemented by this grant. Her focus is on carbon, nitrogen and phosphorus linkages to date.

Name: Huntress, David

Worked for more than 160 Hours: Yes

Contribution to Project:

This graduate student completed his MS degree in 2007, supported by complimentary NSF funding, and studying stream dynamics at BBWM and other watersheds.

Name: Burke, Andrea

Worked for more than 160 Hours: Yes

Contribution to Project:

This is a new graduate student who will be increasingly involved with using project data in modeling for her research. She will also be helping in the field. Her assistantship is funded through the University of Maine.

Name: Raymond, Jay

Worked for more than 160 Hours: Yes

Contribution to Project:

A new graduate student to the Bear Brook program who assisted in some field logistical support activities during his orientation to our overall program.

Undergraduate Student

Name: Lynch, Benjamin

Worked for more than 160 Hours: Yes

Contribution to Project:

Benjamin Lynch is an undergraduate student worker in the forest soils program who is involved in lysimeter installation and soil sampling as part of this contract.

Name: Rackley, Sean

Worked for more than 160 Hours: No

Contribution to Project:

Sean Rackley is an undergraduate student worker in the forest soils program who is involved in lysimeter installation and soil sampling as part of this contract.

Name: Allalemdjian, Daniel

Worked for more than 160 Hours: No

Contribution to Project:

Dan Allalemdjian is an undergraduate student worker in the forest soils program who is involved in lysimeter installation and soil sampling as part of this contract.

Name: Sinsabaugh, Jennifer

Worked for more than 160 Hours: No

Contribution to Project:

Dan Allalemdjian is an undergraduate student worker in the forest soils program who is involved in lysimeter installation and soil sampling as part of this contract.

Name: Parent, Mary Beth

Worked for more than 160 Hours: No

Contribution to Project:

This grant plus others. The student has worked mostly on laboratory sample processing, but will be working in the field with us this summer.

Name: Montgomery, Allison

Worked for more than 160 Hours: No

Contribution to Project:

This grant plus others. The student has worked mostly on laboratory sample processing, but will be working in the field with us this summer.

Name: Harrington, Robert

Worked for more than 160 Hours: Yes

Contribution to Project:

This undergraduate student joined the program this past year and is responsible for temperature and moisture data collections that are used in the work of this grant. This student is supported through a complementary NSF LTREB grant.

Name: Allen, Shaughn

Worked for more than 160 Hours: Yes

Contribution to Project:

Undergraduate student worker in the program helping with soil P extracellular and other enzyme assays.

Name: Dutton, Danielle

Worked for more than 160 Hours: Yes

Contribution to Project:

Undergraduate student worker in the program helping with soil P extracellular and other enzyme assays.

Name: Devine, Susan

Worked for more than 160 Hours: Yes

Contribution to Project:

Undergraduate student worker helping in general laboratory analyses and measurements of soil extracellular enzyme assays from the 2008 field season.

Name: Plaud, Abel

Worked for more than 160 Hours: Yes

Contribution to Project:

Undergraduate student worker helping in general laboratory analyses and measurements of soil extracellular enzyme assays from the 2008 field season.

Technician, Programmer

Name: Szillery, Johanna

Worked for more than 160 Hours: No

Contribution to Project:

Johanna Szillery began as a technician working on this project beginning in April, 2005. She has been directly involved with the methods development work, planning for sampling, lysimeter installation, and data management.

Name: Spencer, Cheryl

Worked for more than 160 Hours: No

Contribution to Project:

Cheryl Spencer is a technician that is not paid under this NSF grant, but who is involved with coordination activities in the Forest Soils program laboratory. She has been actively involved in the planning discussions and is directly involved in sample processing and analysis.

Name: Sherman, Jessica

Worked for more than 160 Hours: Yes

Contribution to Project:

This person was a graduate student under Dr. Fernandez and worked spring 2005 as a temporary technician. She has worked on a thesis and a related contract dealing with soil metal and P interactions. This person was not funded by this NSF contract. However, some of the work she has conducted contributes to the overall objectives of this NSF project. When we justified the reduced scope of work for this NSF contract in light of the reduced level of funding during the initial award, we indicated that these companion studies would be important in addressing those components of the study eliminated from the original proposal dealing with roots and soil microbiology. Her work represents some of this complimentary research.

Name: Cangelosi, John

Worked for more than 160 Hours: Yes

Contribution to Project:

This technical staff member is responsible for the watershed treatments and managing the stream gaging and coordinating with the US Geological Survey. He is funded by this project and the associated NSF LTREB grant.

Other Participant**Research Experience for Undergraduates****Organizational Partners****US Geological Survey**

The base program at BBWM includes continuous measurements of stream flow, stream chemistry, and precipitation depth and chemistry. The US Geological Survey cost shares with the University of Maine the cost of the hydrological gauging of the streams, and staff work together in the development of the stream data base.

International Paper

International Paper owned the land that the BBWM project is on, and provided access to the site through a long-term contract with the University of Maine at nominal cost. In addition, company staff provided logistical support related to site maintenance and administration. The land was sold to GMO Renewable Resources in 2004, and land management functions moved to Sustainable Forestry Initiatives at that time. SFI, now named American Forest Management, staff work with this project to facilitate road maintenance and site logistics.

GMO Renewable Resources

GMO Renewable Resources now owns the land where BBWM is located and is providing use of the site and logistical support through a contract with the University of Maine, and through local logistical support of its land management company.

USDA Forest Service - Northeastern Forest Experiment Station

One of the PIs, Dr. Lindsey Rustad, is an employee of the USDA Forest Service and provides direct contributions to the project through her efforts. In addition, Dr. Rustad has a long-term collaborative relationship and is part of the PI group at BBWM, with significant exchange in time and intellectual contributions between the project and this agency. In addition, Drs. Rustad, Fernandez, and Norton have been PIs on complementary research funded by the USDA Forest Service providing information on roots, soils, and ecosystem process that are important to the goals of this project.

Maine Agric and Forest Exp Station

The Maine Agricultural and Forest Experiment Station at the University of Maine provides significant resources to the operations of the BBWM project through staff and funding support, and directly supports PI, staff and student salaries for research efforts not directly supported by this project. These resources and support are fundamental to be able to meet project goals in the context of the overall BBWM study program.

University of Strasbourg

We have developed a scientific relationship with the Strengbach Watershed in France, under the auspices of the University Louis Pasteur in Strasbourg. Their scientists have visited BBWM and the University of Maine on several occasions, and Drs. Fernandez and Norton visited France in 2005. In 2006, as part of a complimentary NSF project with Dr. Norton as lead PI, BBWM staff sampled soils at Strengbach. Dr. Marie-Claire Pierret of the University of Strasbourg will be spending her sabbatical year in 2009-2010 at the University of Maine working with BBWM researchers as a result of this ongoing collaboration.

Czech Academy of Sciences

Personnel from the BBWM have developed a scientific collaboration with the Laboratory of Environmental Geochemistry at the Czech Academy of Sciences for a scientific exchange regarding watershed research. Specifically, the Lesni Potok watershed near Prague is a site of research similar to the work at BBWM, and scientific exchanges of samples and people have taken place between sites. In 2006 soil sampling was carried out by the University of Maine crew at the Czech watershed. During 2007-2008 Dr. Tomas Navratil of the Czech Academy of Sciences was on a Fullbright Fellowship working with us at the University of Maine. Much of his work focused on using BBWM data to develop collaborative papers and he has implemented the SAFE model on BBWM.

Other Collaborators or Contacts

Activities and Findings

Research and Education Activities: (See PDF version submitted by PI at the end of the report)

Findings: (See PDF version submitted by PI at the end of the report)

Training and Development:

During the project period there have been opportunities for six graduate students to gain experience from this research. One of these students (Jessica Sherman) completed her thesis research and then was retained in a temporary technician position to continue working on methods development during the winter of 2005. Brett Holmes began his M.S. program in January 2005 focusing his research on the soil-solution leaching studies that were completed in spring 2007. Michael SanClements completed his Ph.D. in 2009 and has been a post-doctoral fellow the last few months of the grant period. He took the lead in soil P fractionation method development, has overseen soil sampling for fractionation and acidification studies, and is involved in data aggregation and development. Farrah Fatemi began her Ph.D. program during the 2006-2007 academic year, studied soil solutions in the 2007 field season, completed a field study in 2008 at BBWM on soil extracellular enzyme activities as indicators of P and other nutrient limitations, and is carrying out a laboratory study on BBWM soils during 2009. Suzanne Bethers completed her MS degree supported by other funding studying BBWM physiology and calcium. She developed thesis projects on tree and understory responses to treatments in the BBWM. Eleven undergraduate students have been involved in laboratory and field activities.

Outreach Activities:

The project offers insights on forest ecosystem behavior that have been presented or prepared for presentation at various public and scientific forums as noted below.

SanClements, M. D., Fernandez, I. J., Norton, S. A., Rustad, L. E., Decadal responses in stream and soil Ca and Mg in an experimentally acidified and reference watershed in the northeastern United States: BIOGEOMON 2009, 7th International conference, Helsinki, Finland. June 2009.

Norton, S. A., Kopßček, J., Navrßtil, T., Fernandez, J., Amirbahman, A., Evolution of controls on phosphorus availability in aquatic ecosystems: peri-glacial to recent times: BIOGEOMON 2009, 7th International conference, Helsinki, Finland. June 2009.

Navrßtil, T., Norton, S. A., Fernandez, I. J., Seasonal and long-term variation of stream water chemistry at Bear Brook Watershed, Maine USA: BIOGEOMON 2009, 7th International conference, Helsinki, Finland. June 2009.

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). ASA-CSSA-SSSA International Meetings. Houston, Texas. October 5-9. [CD-ROM]. ASA, CSSA, SSSA, Madison, WI.

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: 11th North American Forest Soil Conference. Blacksburg, VA. p. 66.

Norton, S. A., 2008, The dominating role of Al on the trophic status of oligotrophic surface waters: Stockholm University, public lecture.

Perry, R. H., Koons, P. O., Norton, S. A., and Birkel, S., 2008, Post-LGM chemical weathering increase and atmospheric CO₂ consumption: New insights from UMISM solutions and a proposed Malaspina Glacier water chemistry study. Geol. Soc. Am. Northeast Section Annual Mtg. Buffalo, NY. Program vol. 40, #2.

SanClements, M., Fernandez, I., Norton, S., Amirbahman, A., and Rustad, L., 2008. Metal controls on Forest Floor and B Horizon Extractable Phosphorus in Forested Watersheds. (Paper 596-2). ASA-CSSA-SSSA International Meetings. Houston, Texas. October 5-9. [CD-ROM]. ASA, CSSA, SSSA, Madison, WI.

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

Kahl, J. S., Diehl, M., Fernandez, I. J., Nelson, S., Norton, S. A., and Webster, K., 2008, Decadal patterns of retention of N and S in the experimental Bear Brook Watershed in Maine: Am. Geophys. Union Ann. Mtg., San Francisco.

Fatemi, Farrah, Ivan J. Fernandez, Johanna Szillery, Stephen Norton and Lindsey E. Rustad. 2007. Insights from soil solutions on long-term acidification at the Bear Brook Watershed in Maine. (Paper 313-1). Presented at the ASA-CSSA-SSSA International Meetings. New Orleans, Louisiana. November 4-8. [CD-ROM]. ASA, CSSA, SSSA, Madison, WI.

SanClements, Michael, Ivan Fernandez, Mary Beth Adams, Stephen Norton and Lindsey Rustad. 2007. Effects of long term experimental acidification on forest soil phosphorus. (Paper 347-1). Presented at the ASA-CSSA-SSSA International Meetings. New Orleans, Louisiana. November 4-8. [CD-ROM]. ASA, CSSA, SSSA, Madison, WI.

SanClements, M.D., I.J. Fernandez, S.A. Norton, M.B. Adams, and L.E. Rustad. 2007. Soil phosphorus fractions from six acidic forested watersheds in the U.S. and Europe. Gordon Conference on Catchment Science: Interactions of Hydrology, Biology and Chemistry. Colby-Sawyer College, New London, New Hampshire. July 8-13.

Norton, S. A., J. Kopßček, I. J. Fernandez, P. Porcal, A. Amirbahman, T. Wilson, B. Lake, M. SanClements, D. Huntress. 2007. Al-Fe-DOC-P Coupling in Forested Ecosystems. Gordon Conference on Catchment Science: Interactions of Hydrology, Biology and Chemistry. Colby-Sawyer College, New London, New Hampshire. July 8-13.

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.

Bethers, Suzanne. June 2007. Unraveling the Physiological Effects of Elevated Acid Deposition on Sugar Maple Regeneration. Poster and abstract. North American Forest Ecosystem Workshop, Vancouver, British Columbia, Canada.

- 'Calcium Cycling: Insights from Bear Brook Watershed in Maine.' February 21, 2007. Workshop sponsored by the Center for Research on Sustainable Forests. University of Maine, Orono, Maine.
- Norton et al., 2006, The Bear Brook Watershed in Maine (BBWM): Twenty years and counting. University of Uppsala, Sweden.
- Norton, S.A., 2006, Bogs Matter: A comparison of upland and wetland aquatic chemistry. Atlantic Salmon Commission et al., Whitneyville, Maine.
- Norton, S. A., 2006, Downeast Rivers: Some unanswered questions. Atlantic Salmon Commission, Bangor, Maine.
- Wiersma, G.B. Bear Brook Watershed in Maine. September 27, 2006. Presentation. Department of Forestry, College of Agriculture, University of Kentucky, Lexington, KY.
- 'Long-term Monitoring and Data Systems: New Paradigms for Basic Research.' December 5, 2006. Workshop sponsored by the Center for Research on Sustainable Forests. University of Maine, Orono, Maine.
- SanClements, Michael, Ivan Fernandez, Stephen Norton, Aria Amirbahman, and Lindsey Rustad. 2006. Distribution of Soil Phosphorus Fractions in Acid Soils of Forested Watersheds. (Paper 234-5) Presented at the ASA-CSSA-SSSA International Meetings. Indianapolis, Indiana. November 12-16, 2006. [CD-ROM]. ASA, CSSA, SSSA, Madison, WI.
- Rustad, Lindsey, Ivan Fernandez, Steve McNulty, and Allison McGill. 2006. Linkages between fine root dynamics and soil chemistry at three long-term nitrogen manipulation experiments in the northeastern United States. (Paper 203-8) Presented at the ASA-CSSA-SSSA International Meetings. Indianapolis, Indiana. November 12-16, 2006. [CD-ROM]. ASA, CSSA, SSSA, Madison, WI.
- Diehl, M., Kahl, J. S., Fernandez, I. J., Norton, S. A., and Webster, L., 15 year response of stream chemistry to acidification and recovery at the Bear Brook Watershed, Maine: BIOGEOMON2006, 6th International conference, Santa Cruz, June 2006.
- Fernandez, I. J., Norton, S. A., and Rustad, L. E., The difficulty in defining long-term ecosystem response mechanisms with short-term experimental manipulations: BIOGEOMON2006, 6th International conference, Santa Cruz, June 2006.
- Goss, H. V., Navrtil, T., Norton, S. A., and Rohovec, J, Contrasting chemical response to artificial acidification of five acid-sensitive streams: BIOGEOMON2006, 6th International conference, Santa Cruz, June 2006.
- Laird, M., Norton, S. A., and Navrtil, T., in press, Spatial and temporal changes in aluminum, iron, and base cations for an acidic episode at East Bear Brook, Maine USA: BIOGEOMON2006, 6th International conference, Santa Cruz, June 2006.
- Navrtil, T., Norton, S. A., Fernandez, I. J., and Diehl, M., Secondary soil phases controlling the surface water chemistry during artificial acidification at Bear Brook Watershed, Maine USA: BIOGEOMON2006, 6th International conference, Santa Cruz, June 2006.
- Porcal, P., Amirbahman, A., Kopek, J., and Norton, S. A., Photochemical release of metal species in stream waters: BIOGEOMON2006, 6th International conference, Santa Cruz, June 2006.
- Fernandez, Ivan J. Acid Rain and the Health of Northern Forests û An Update on the Science. Invited presentation at Forests and the Environment: Issues and Information for Land Owners and Wood Buyers in the Northern Region. NCASI Northern Regional Meeting, Portland, Maine. May 2006.
- Norton, Stephen A. Surface water chemistry in Maine, Invited presentation at Project SHARE (Salmon Habitat and River Enhancement), Whitneyville, Maine (2006)
- Fernandez, I. J., Rustad, L. E., Norton, S. A., Wiersma, G. B., and Kahl, J. S., 2005, The Bear Brook Watershed in Maine - Decadal responses to whole forest ecosystem manipulations. NESAF Annual Meeting, Portland, Maine.
- 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.
- Fernandez, I. J., Rustad, L. E., Norton, S. A., Wiersma, G. B., and Kahl, J. S., 2005, The Bear Brook Watershed in Maine û Decadal responses

to whole-forest ecosystem manipulations: NESAF2005, Portland, Maine.

Rustad, Lindsey E. and Ivan J. Fernandez. 2005. Linkages among Soil, Foliar and Litter Chemical Response to Experimentally Elevated N and S Deposition at the Bear Brook Watershed in Maine. (Paper 6230) Presented at the ASA-CSSA-SSSA Annual Meetings. Salt Lake City, Utah. November 6-10, 2005.

Fernandez, Ivan J., Lindsey E. Rustad, Stephen A. Norton, J. Stephen Kahl, and G. Bruce Wiersma. 2005. The Bear Brook Watershed In Maine û Decadal Responses To Whole Forest Ecosystem Manipulations. Northeastern Society of American Foresters. Portland, Maine. March 17, 2005. [CD-ROM]. ASA, CSSA, SSSA, Madison, WI.

Diehl, Melinda, Katherine Webster, Ivan Fernandez, Steve Norton, and Steve Kahl. 2005. Controls on Surface Water Sulfate Concentrations at the Bear Brook Watersheds in Maine. Maine Water Conference. Augusta, Maine. March 2005.

Nowinski, N, S Trumbore, I Fernandez, A Magill, L Rustad, J Szillery. 2004. The Effects of N Addition on the belowground C Cycle in two Temperate Forests, Eos Trans. AGU, 85(47), Fall Meet. Suppl., Abstract B23A-0946.

L.E. Rustad, I.J. Fernandez, S. McNulty, A. Magill. A Cross Site Study on the Effects of Experimentally Elevated N Deposition on Total Soil Respiration. CaRTE Symposium, Januray 21-23, 2004, Laguna Beach, CA.

L.E. Rustad, I.J. Fernandez, S. McNulty, A. Magill. 2004. The Effects of Experimentally Elevated N on Fine Root Biomass, Chemistry, and Total Soil Respiration. The Harvard Forest LTER/NIGEC Symposium, March 29, 2004, Petersham, MA.

Norton, S., Fernandez, I., Amirbahman, A., 2004, Aluminum and oligotrophy - Assembling the pieces of the puzzle: Soc. Intern. Limnol., Finland.

Journal Publications

Elvir, J.A., L. Rustad, I. Fernandez, and G.B. Wiersma., "Eleven year response of foliar chemistry to chronic nitrogen and sulfur additions at the Bear Brook Watershed in Maine", Canadian Journal of Forest Research, p. 1402, vol. 35, (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. , vol. 29, (2006). Published,

Elvir, J.A., G.B. Wiersma, M.E. Day, M.S. Greenwood, and I.J. Fernandez., "Effects of enhanced nitrogen deposition on foliar chemistry and physiological processes of forest trees at the Bear Brook Watershed in Maine", Forest Ecology and Management, p. 207, vol. 221, (2006). Published,

Wallenstein, Matthew D., Steven McNulty, Ivan J. Fernandez, Johnny Boggs, and William H. Schlesinger., "Nitrogen fertilization decreases forest soil fungal and bacterial biomass in three long-term experiments", Forest Ecology and Management, p. 459, vol. 222, (2005). Published,

Szillery, Johanna E., Ivan J. Fernandez, Stephen A. Norton, Lindsey E. Rustad, and Alan S. White, "Using ion-exchange resins to study soil response to experimental watershed acidification", Environmental Monitoring and Assessment, p. 383, vol. 116, (2006). 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:)", Environmental Monitoring and Assessment, p. 419, vol. 121, (2006). Published,

Goss, H. V. and Norton, S. A., "Contrasting chemical response to artificial acidification of three acid-sensitive streams in Maine, USA.", Science of the Total Environment, p. , vol. 404, (2008). Published,

Hunt, James F., Tsutomu Ohno, and Ivan J. Fernandez, "Influence of Foliar Phosphorus and Nitrogen Content on Chemical Properties of Water Extractable Organic Matter Derived from Fresh and Decomposed Sugar Maple Leaves", Soil Biology and Biochemistry, p. 1931, vol. 40, (2008). Published,

Ohno, Tsutomu, Ivan J. Fernandez, Syuntaro Hiradate, and Jessica F. Sherman, "Effects of soil acidification and forest type on water soluble soil organic matter properties", *Geoderma*, p. 176, vol. 140, (2007). Published,

SanClements, M. D., Fernandez, I. J., and Norton, S. A., "Soil and sediment phosphorus fractions in a forested watershed at Acadia National Park, ME", *Forest Ecology and Management*, p. , vol. , (2009). Accepted,

Kopacek, J., Hejzlar, J., Kana, J., Norton, S. A., Porcal, P., Turek, J., "Effects of soil development, atmospheric acidification, and nitrogen-saturation", *Journal of Inorganic Biochemistry*, p. , vol. , (2009). Accepted,

Laudon, H. and Norton, S. A., "Causes, drivers, and evolution of episodic acidification at the Bear Brook Watershed in Maine", *Environmental Monitoring and Assessment*, p. , vol. , (2009). Submitted,

Navrtil, T., Norton, S. A., Fernandez, I. J., Diehl, M. S., Kahl, J. S., "Assessment of secondary sulfate mineral precipitation as a mechanism of soil acid neutralizing capacity", *Environmental Monitoring and Assessment*, p. , vol. , (2009). Submitted,

Porcal, P., Amirbahman, A., Kopacek, J., and Norton, S. A., "Experimental photochemical release of organically-bound aluminum and iron in three streams in Maine", *Environmental Monitoring and Assessment*, p. , vol. , (2009). Submitted,

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Bethers, Suzanne, Michael E. Day, G. Bruce Wiersma, Ivan J. Fernandez and J. Alexander Elvir, "Effects of chronically elevated nitrogen and sulfur deposition on sugar maple saplings: nutrition, growth and physiology", *Forest Ecology and Management*, p. , vol. , (2009). Accepted,

Evans, Chris D., Christine L. Goodale, Simon J.M. Caporn, Nancy B. Dise, Bridget A. Emmett, Ivan J. Fernandez, Chris D. Field, Stuart E.G. Findlay, Gary M. Lovett, Henning Meesenburg, Filip Moldan, and Lucy J. Sheppard, "Does elevated nitrogen deposition or ecosystem recovery from acidification drive increased dissolved organic carbon loss from upland soil? A review of evidence from field nitrogen addition experiments.", *Biogeochemistry*, p. 13, vol. 91, (2009). Published,

Books or Other One-time Publications

Jessica Sherman, "Soil Iron, Aluminum and Phosphorus Dynamics in Response to Thirteen Years of Nitrogen and Sulfur Additions at the Bear Brook Watershed in Maine", (2005). Thesis, Accepted
Bibliography: M.S. Thesis
University of Maine
Orono, Maine

Melinda Diehl, "Using Stream Chemistry to Evaluate Experimental Acidification and Natural Recovery in the Paired Catchments at the Bear Brook Watershed in Maine (1989-2003)", (2006). Thesis, Published
Bibliography: MS Thesis, University of Maine, Orono, Maine

Heather V. Goss, "Contrasting chemical response to experimental acidification of five acid-sensitive streams", (2006). Thesis, Published
Bibliography: Master of Science in Earth Sciences, University of Maine

Molly Laird, "Spatial and temporal changes in stream chemistry at three watersheds during high discharge episodes", (2006). Thesis, Published
Bibliography: Master of Science in Earth Sciences, University of Maine, Orono, Maine

Kenlan, Peter H., "The Effects of Experimental Acidification on Understory Plant Communities at the Bear Brook Watershed in Maine", (2006). Thesis, Published
Bibliography: Master of Science in Forestry, University of Maine, Orono, Maine.

Michael SanClements, "The Chemistry of Acidic Soils in Humid, Temperate Forested Watersheds with emphasis on Phosphorus, Aluminum,

and Iron
", (2009). Thesis, Published
Bibliography: Doctoral Dissertation, University of Maine

Web/Internet Site

Other Specific Products

Contributions

Contributions within Discipline:

Important methodological contributions from this grant were the development of the historical basis of the P fractionation approach, and the subsequent selection and modification of P fractionation methods to best meet project goals. This has resulted in the adoption of fractionation methods suitable for the scientific questions posed in this project that also allow the research to maintain a high level of data quality. These techniques have been applied to BBWM, the subject of this contract, and a network of watersheds as part of a companion grant.

In addition, tension lysimeters within the watersheds have been re-established and collections are being added to the historical record of soil solution response showing the value and challenges of using lysimetry for defining temporal patterns in ecosystem processes. In addition, a strategy has been developed to use precipitation event based sampling of soil solutions to evaluate the evolution of solution chemistry through the ecosystem in real time.

The overall project activities have developed insights on soil, soil solution, and foliar chemistries that will be used in conjunction with, and complement, related research. Publications noted in earlier sections of this report demonstrate complementary research on soil microbiology, fine roots, soil solutions and nitrogen that will be essential for whole-ecosystem assessments of mechanisms of response to acidification. The development of methods, definition of soil chemical mechanisms, and contribution to a decadal time series of whole-watershed biogeochemistry are key contributions of this research.

Contributions to Other Disciplines:

This research has significantly increased the interactions among students and faculty in soil and earth sciences with those in engineering through our collaboration on this project. To that end, we have seen an increased awareness of the ecological context of process research conducted by engineering students, and likewise have seen ecosystem science students also grow intellectually by watching the development of engineering ideas and concepts in the quest to address ecological problems. This has been further enhanced in the past year by the development of new research components that integrate biological with geochemical insights on ecosystem P dynamics.

Contributions to Human Resource Development:

As noted in earlier sections of this report, numerous graduate students have been involved in research based on this project and involved with related activities in the BBWM program. In addition, undergraduate student workers have been involved in all phases of the field and laboratory components of the project, giving them hands-on experience in their fields of study.

Contributions to Resources for Research and Education:

The BBWM watershed project is used for illustrations in classes and is contributing to regional discussions on a variety of topics from salmon habitat to acidification to carbon sequestration and climate change as a result of the intensive and long-term nature of this research. The site has been the subject of studies by high school students and teachers as well, and data from the site forms a component of many classes both in Maine and beyond. In addition, the BBWM site has served as an example of the type of ecological observatory necessary for addressing issues like climate change, and has been widely referenced and leveraged for various initiatives, including a pending major NSF EPSCoR initiative in Maine.

Contributions Beyond Science and Engineering:

During the past year several of the PIs have been actively engaged in climate change assessment work for Maine and the region, and have developed planning for state adaptation and the research that will be needed to support knowledge to action in climate policy. The BBWM site is used as an example of the type of ecological insights that we can obtain only through a long-term, mechanistic approach. Using BBWM as an example of an ecological observatory of this type, we are engaged in planning for a broader initiative that would include and replicate the BBWM success in other sites and ecosystems.

Conference Proceedings

Categories for which nothing is reported:

Any Web/Internet Site

Any Product

Any Conference

Project Findings

We spent extensive time during the first year developing methodologies with adequate quality assurance for P fractionation of soils, and in so doing have adopted a new methodology changing from the 'Hedley' procedures to a modified 'Psenner' method that utilizes a reductant step. We believe this provides more mechanistic insight into soil Al-Fe-P dynamics and enables us to directly compare soil, stream sediment, and lake sediment chemical characteristics. Additional studies have defined the contribution of apatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH})$) to occluded P in the HCl extraction step of the fractionation procedure. Comparisons between the sum of the fractions and total soil analyses have been made to evaluate recovery by the modified Psenner fractionation procedure that we now have utilized on BBWM and seven other watersheds and recommend for soil and sediment studies of this nature. These recommendations have been detailed in several manuscripts published and in preparation.

Fractionation results have shown that the NaOH-extractable phase thought to be associated largely with Al-P accounts for the major portion of subsoil P, and there is little spatial pattern evident with distance from the stream for these soil properties with the exception of increased variability, Al, and organic matter in the near-stream zone. Forest type has a strong influence on the characteristic concentrations of P and metal fractions, and the experimental acidification has had a small but detectable effect on mobilizing Al-P from these soils. There appears to be a period of time where easily mobilized P, presumably associated with the less organized forms of $\text{Al}(\text{OH})_3$, is more biologically available and deciduous forests appear to capture some of this mobilized P that is further biocycled within the ecosystem, while coniferous forest types allowing for more net depletion of the mobilized P. This research in combination with the companion NSF funded research on additional watersheds has demonstrated a pattern of mobilization and biocycling across watersheds on two continents that can be summarized in a simple relationship between soil P and metal concentrations. The most labile P pools will eventually be exhausted by acidification leading to an impoverished soil condition. We have an emerging picture of the spatial variation of subsoil P and metal accumulations throughout the watershed, with distance from the stream, and with depth.

Surface chemistry of soils in the watersheds as related to exchangeable base cations, pH, exchangeable Al, and extractable P were also studied in soils sampled in 2006 with contrasts to earlier soil sampling, most notably in 1998. Although in 1998 there appears to have been a significant decline in the exchangeable base cation pool, particularly for Ca, a continued depletion was not evident through to 2006. Interesting, the results of this research reveal an important consequence for the ice storm of 1998 in New England that both biased our ability to see long-term trends in soil condition, while at the same time giving us the unique opportunity through this research to capture the soil response to the unusually high litter input that resulted that one year from this meteorological event.

Intact soil column leaching studies have shown the role of PCO_2 in generating bicarbonate acidity in soil solutions, and subsequent base cation, metal and P mobilization. Some of the patterns of base cation depletion mimic the results seen at the whole watershed scale as a result of acidification.

Long-term patterns of elemental composition of tree foliage are evolving and provide a link between historic soil solution and solid-phase soil studies. No publications directly from this contract resulted from the analysis of these data, but they will be included in a new initiative on the physiological and chemical phenology of trees at BBWM that will directly draw on these data for publications.

Complementary research not funded by this contract at BBWM has shown evidence of various ecosystem responses, including tree foliar chemistry, fine root biomass and chemistry, and soil microbial communities, as noted above.

Project Activities

The overall objectives of the project were to investigate the evolution of acidification in the Bear Brook Watershed in Maine (BBWM) study, focusing on base cation depletion, metal (particularly Al and Fe) mobilization, and alterations in P cycling as a result of decadal-scale whole-watershed treatments of N and S.

The original proposal objectives were:

Objective (1) Determine if the differences in soil exchangeable base cation pools (primarily Ca and Mg) between WB and EB documented in 1998 have evolved farther along the theoretical base cation depletion curve. If so, does soil horizon/depth or forest type influence the evolution of these differences?

Objective (2) Determine if there are differences between WB and EB in soil Al, Fe, and P that reflect the evolution of acid neutralization mechanisms in these watersheds implied by the time series of stream chemistry after 14 years of treatment. If so, does soil horizon/depth or forest type influence the evolution of these differences?

Objective (3) Define linkages between soil and stream water chemistry through studies of soil solution chemistry as influenced by forest type, watershed, soil moisture and distance from the stream channel.

Objective (4) To determine if potential changes in soil metal and P dynamics influence ecosystem biota as evidenced by changes in tree foliar and root chemistry, fine root biomass, microbial biomass, and microbial biomass chemical composition.

Objective (5) To determine if treatments change the characteristics of soil organic matter ligands, thereby changing metal mobility.

Objective (6) To build on the successes of the MAGIC model for predicting whole watershed acidification at BBWM by incorporating more spatial detail on soil properties with depth and mechanisms for Al, Fe, and P mobilization through time.

This contract was initiated at the end of field season 2004, and the focus during 2005 was on planning of research and assembling the research team. During 2005 project activity included (1) bringing on Brett Holmes and Michael SanClements as graduate students most directly focused on this contract, (2) continued precipitation and stream biogeochemical measurements at the reference (East Bear) and treated (West Bear) watersheds to maintain the long-term input/output record, (3) development of soil P fractionation methods, (4) development of soil column study methods and the execution of bench top studies, and (5) installation of tension lysimeters throughout the watersheds and installation of zero-tension lysimeters in the hardwood forest compartments. During field season 2006 all soil and vegetation sampling was carried out and chemical analyses of soil samples, including P fractionation, were completed in 2007 and

early 2008. Statistical analyses of these data and writing began in 2008 and is continuing, with the completion of Michael SanClements' doctoral thesis in May 2009 representing a critical compilation of findings from this research. During the 2006-2007 academic year, Farrah Fatemi joined the research group to begin her doctoral program and is focusing on linkages between C, P, and N in the BBWM ecosystem. She took the lead during the 2007 field season in soil solution studies and both doctoral students have presented their findings at a number of U.S. and international scientific conferences. Significant time was spent in 2005 and 2006 on the companion NSF contract studying metal and P dynamics across a range of watersheds (Abiotic Controls on the Tropic Status of Oligotrophic Water - DEB-0415348) with which this contract is highly integrated. In 2007 periodic and episodic solution sampling took place in tension soil solutions and stream samples and those data are being developed as part of Farrah Fatemi's doctoral thesis scheduled for completion in 2010. Her work went well beyond the original objectives of the grant through leveraging of other funding. Brett Holmes completed his MS degree in 2007 using column leaching studies to characterize soil-solution chemical dynamics related to P and metals as a function of CO₂ partial pressures. During 2008 doctoral student Farrah Fatemi initiated a major new component of this research focusing on the measurement of extracellular enzymes in the soil related to C, N, and P dynamics that will complement our emerging concepts about biogeochemical controls on P dynamics in the BBWM ecosystem.

Activity and Findings by Objectives

Objectives 1&2 - These objectives were addressed primarily by soils studies. The intensive soil sampling for this project was completed during field season 2006 and included resampling the quantitative pit network at BBWM established in 1998. A subset of sites were sampled and analyzed as part of a graduate student thesis project in 2002, and therefore scheduling soil sampling at BBWM in 2006 gave us the best opportunity to define temporal patterns of change in watershed soils. This project tested hypotheses at BBWM on a whole ecosystem basis, and provided data for the more extensive assessment of soil and stream biogeochemical processes related to P in the companion project 'Abiotic Controls on the Trophic Status of Oligotrophic Water' by this same group of PIs. Tree foliage was sampled and analyzed in 2006 and will add to the long-term record of tissue chemistry response to climate and the BBWM S and N treatments the foliage data will be incorporated into the research of a new graduate student to begin later this year under other funding.

During the winter of 2005 we focused on improving data comparability in the traditional Hedley fractionation protocols. These protocols were developed using colorimetric measures of P only (not metals) and on agricultural soils with higher pH and lower labile metal concentrations. Forest soils offered additional challenges, particularly when Al and Fe concentrations in the fractions were measured. We improved the methodology to allow for use of inductively coupled plasma emission spectrometry techniques for quantifying solute concentrations on extracts from highly acidic forest soils rich in labile Al and Fe. During this process we also developed a more comprehensive as well as historical understanding of the evolution of various P fractionation

approaches in the literature. In the winter of 2006 we modified our methodology to utilize a fractionation approach (Psenner and Pucsko, 1988) with improved definition based on chemical mechanisms of separation (e.g., reducing phases and acid soluble phases), and enabling direct comparisons of the soil and sediment data. This modified approach was applied to the BBWM soils sampled in 2006 and all watersheds in the companion NSF project. Results have been presented at several international conferences, in a doctoral thesis, and in several peer reviewed scientific papers either published, in press, and in review. One of the thesis chapters directly addressed Objective 1 and defines the progression over time of soil base cation status in the acidified versus reference watersheds.

Objective 3 – New work under objective 3 required the re-establishment of a once used network of tension lysimeters at BBWM, expanding that network, and adding zero-tension lysimeters to the lysimeter system. In 2005 we re-established all of the historical tension lysimeter sites. We modified our original plans for zero-tension lysimeters because past experience has shown us that we will likely learn little by pairing zero-tension lysimeters with tension lysimeters by location. Therefore, we developed plans to install zero-tension lysimeter nests across the topographic gradient away from the stream. The intent will be to sample these zero-tension lysimeters several times during precipitation events, along with throughfall and streams, to track the chemical evolution of water as it migrates through these ecosystems. Only pilot testing of the event-based sampling has been completed under this contract. We have, however, completed a year of tension lysimeter measurements focusing on metals and P, along with other solutes. Particular attention was paid to soil solution analyses to capture low concentrations of soluble P, typically unavailable in soil solution data because P concentrations are below detection limits. Using ICP MS techniques, P data were obtained and comparisons among ecosystem compartments will be included in the chapter and publication on soil solutions being developed by Farrah Fatemi as part of her doctoral thesis.

In addition, laboratory studies using packed bed column experiments were examined in 2005 and 2006 to study specific mechanisms of metal and P mobilization under varying PCO_2 and solution chemical conditions. The initial studies used reconstructed soil profiles and suffered from unrealistically high concentrations of dissolved organic carbon as a result of the disturbance. Intact soil cores were then collected in the field and used for the soil column leaching experiments with significant improvements in performance and realism. A series of experiments under varying PCO_2 were conducted to examine the influence of the soil gas phase on metal and P mobilization. Results showed significant Al mobilization that correlated well with the inorganic carbon concentration. The mobilized Al was largely dissolved and uncomplexed with the DOC. Mobilized Fe and P, however, showed weaker correlations with inorganic carbon. A set of experiments was conducted by draining the column and rewetting it. Following rewetting, the mobilized Al contained a large fraction of particulate Al. Inorganic carbon transport was slightly retarded possibly due to sorption on soil surface sites. These studies were completed in 2006 with Brett Holmes defending his M.S. thesis research in the

spring of 2007. The highlights of this research are the insights provided on the role of DIC in P and metal displacement in these forest soils.

Objective 4 – This objective was designed to determine evidence of geochemical changes in metal and P chemistry in ecosystem biota (i.e., tree foliage, root chemistry, microbial biomass chemistry). To address the reduced budget for the award under this contract, we eliminated new root and microbial biomass studies. We did so because we were conducting research under alternate funding that included elements of root and microbial biomass chemistry that were close enough in time to this study period to be able to be utilized in testing our hypotheses. Data on microbial responses to treatments show changes in microbial community composition and phosphatase concentrations between watersheds. Nitrogen treatments also appear to reduce fine root biomass in the treated watershed with consequent higher fine root N and P concentrations related to changes in soil chemistry and fine root biomass. Under partial funding from this contract and the University of Maine, Farrah Fatemi has developed a component of her research that will expand on the microbial contributions to P dynamics through the evaluation of extracellular enzyme activities in the BBWM soil compartments. Her doctoral research on these topics includes both a field component carried out in 2008 and a microlysimeter laboratory experiment being completed during 2009. Initial investigations focus on the activities of seven extracellular enzymes involved in microbial acquisition of C, N and P (acid phosphatase, N-acetylglucosaminidase, xylosidase, α -glucosidase, β -glucosidase, phenol oxidase and peroxidase). Preliminary results suggest that the activities of most enzymes are different by treatment, forest type, and soil horizon.

Objective 5 – This objective is being addressed by insights from the intact soil core leaching studies that are complete and described above, as well as the field studies of soil solutions. The extensive work done on the role of DIC in the soil core studies limited the time available to continue on with DOC leaching as a treatment under this contract, and the findings from the DIC work are captured in a thesis and publication.

Objective 6 – Limited activity occurred in the modeling component of the project beyond early discussions and initial model evaluations in this project. The PI leading the modeling effort from the University of Virginia (B.J. Cosby) traveled to Maine and met with project staff to scope out data needs and model objectives. These discussions continued at the BIOGEOMON 2006 conference in summer 2006, and will likely continue at BIOGEOMON 2009 in Helsinki among project PIs, but deliverables will not be available within the project period. A Fulbright Fellow, Dr. Tomas Navratil, was a visiting scholar with us at the University of Maine in 2008-2009 and has worked on BBWM data including the application of the SAFE model to BBWM. The model has been parameterized for BBWM and a draft manuscript has been developed modeling scenarios of recovery, continued acidification, and the consequences of varied forest management on soil and soil solution response.