

# **Water Research Institute Annual Technical Report FY 2001**

## **Introduction**

Introduction - Research Program

Other Institute research conducted in 2001 includes:

Long Term Monitoring of Maine Lakes and Streams (EPA, 1991-01, \$750,000 to J.S. Kahl and S.A. Norton). The University of Maine was a founding participant in the EPA LTM program begun in 1983. The program has expanded in recent years to include spring sampling of outlets on selected lakes, and now includes lakes sampled in the 1980s by the High Elevation Lake Monitoring project conducted by Kahl and Matt Scott of Maine DEP.

Inferring Regional Patterns and Responses in N and Hg Biogeochemistry Using Two Sets of Gauged Paired-watersheds (EPA, \$475,000 to Kahl et al.). This project is part of long-term ecological research using two gauged-watersheds at Acadia National Park through collaborative funding by USGS and EPA. The focus is atmospheric deposition of N and Hg, and their ecological consequences. Both elements are of major concern, both regionally and to the Park Service at Acadia. This location offers the advantages of a) co-funding for cost-effectiveness; b) a natural experimental design for the two watersheds because of a major forest fire in part of the Park in 1947; c) parallel design with the acidic deposition experiment for the two paired-watersheds at the nearby Bear Brook Watershed, Maine (BBWM); and d) prior research at Acadia and BBWM that supply background data, and provide the basis for ecosystem indicators to be applied at Acadia. Our objectives are addressing N cycling and

Source Drinking Water Protection (Maine Drinking Water Program, J. Peckenham, \$75,000). The Mitchell Center is working in partnership with the Drinking Water Program, Maine Water Utilities Association and EPA Region 1 to develop source protection methodologies for small water utilities. Work in 2001 involved a series of training workshop across the state and development of pilot projects at several small utilities. This is the beginning of a multi-year effort.

New Partnerships.

## **Research Program**

# Ecosystem-wide Effects of Roadway Runoff on Headwater Streams in Maine

## Basic Information

<b>Title:</b>	Ecosystem-wide Effects of Roadway Runoff on Headwater Streams in Maine
<b>Project Number:</b>	2000ME2B
<b>Start Date:</b>	9/1/1999
<b>End Date:</b>	8/31/2001
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	Second
<b>Research Category:</b>	Ground-water Flow and Transport
<b>Focus Category:</b>	Non Point Pollution, Surface Water, Toxic Substances
<b>Descriptors:</b>	Benthos, Bioindicators, Biomonitoring, Ecosystems, Heavy metals, Insects, Land use, Pollutants, Runoff, Streams, Water quality, Water Quality Monitoring
<b>Principal Investigators:</b>	alex.d. .hurn.1

## Publication

1. Davies, S.P., L. Tsomides, J. DiFranco and D. Courtemanch. 1999. Biomonitoring Retrospective: Fifteen year summary for Maine rivers and streams. Maine Department of Environmental Protection, Augusta, ME. DEPLW1999-26. pp. 114-117
2. Maine Department of Environmental Protection. 2000. Surface Water Ambient Toxic Monitoring Report, 1998 Final Data Report. Section 3.3 Urban Non-point Source Investigation. Maine Department of Environmental Protection, Augusta, ME. DEPLW2000-6. pp. 1-19
3. Tsomides, L, T. Woodcock, and S. Davies. 2000. Use of Biological Monitoring to Track Nonpoint Sources in Goosefare Brook, York County, Maine. Maine Dept. of Environmental Protection and University of Maine, Orono, ME. Presentation given at: New England Interstate Water Pollution Control Commission (NEIWPC) Annual Nonpoint Source Meeting. May 23-25, 2000 at URI Narragansett Bay Campus, Narragansett, Rhode Island.

## **Problem and Research Objectives:**

Routine monitoring of water quality by the Maine Department of Environmental Protection (MDEP) indicated the presence of a serious water quality problem in Goosefare Brook in the vicinity of the Maine turnpike. MDEP funded a study, beginning in 1997, of the stream to discover the source of the problem. Possibilities included the turnpike and two industrial establishments located immediately downstream of it, one of which discharges effluent to the stream. The study revealed that while the majority of the pollution stress appeared to be coming from the industrial effluent, the turnpike was also causing a decline in the health of the stream. The nature and magnitude of the ecological impact of the turnpike is the focus of this study.

It is acknowledged by the MDEP that the present level of understanding is not sufficient to provide substantive guidance to public and private groups that may be required to monitor and maintain the quality of surface waters affected by roadway activities (e.g. Maine Department of Transportation, Maine Turnpike Authority). Preliminary evidence based upon research funded by the MDEP indicates that changes in stream invertebrate communities (taxonomic richness, biomass) and ecological processes (detritus decomposition) do occur in some streams as they pass beneath the turnpike. On the basis of this preliminary information, it is clear that the potential for water quality problems because of chronic disturbances from the turnpike (e.g. heavy metals, sediments, other contaminants) should be of public concern. The goal of this research is to narrow the information gap concerning the effect of roadway runoff and non-point heavy metal pollution on streams in southern Maine by quantifying longitudinal gradients of a comprehensive suite of physical, chemical and biological variables for five streams that flow beneath the Maine Turnpike in southern Maine. These data will be used to document the potential ecosystem-wide effect of the Maine Turnpike on stream health, to assess the performance of metrics that measure ecosystem process and function in addition to structure, and to establish an information base required to document the effects of the turnpike construction that began last year.

## **Methodology:**

The specific objectives of this study are to determine and evaluate differences in the following physical and biological variables in reaches above and below the turnpike in each of the five study streams, as well as 3 industrially impacted reaches in Goosefare Brook (53 sampling stations – Figure 1). The variables are categorized into physical, chemical, and biological attributes. Biological attributes are further subdivided in those that more closely reflect ecosystem structure, and those that reflect ecosystem function. For detailed methods for each parameter, consult the original proposal, pp10-12.

### **Physical and chemical attributes of study reaches**

- water chemistry – 9 water samples planned; all have been taken as of 9/16/00. Variables measured from water samples collected upstream and downstream of the turnpike at each sampling period include nitrate-N, ammonium-N, phosphate, alkalinity, and dissolved organic carbon. Variables measured in the field at each station include pH, dissolved oxygen, and specific conductance.
- sediment chemistry – 4 sediment samples planned; only three have been taken during the course of the study, due to financial constraints. The spring sediment sample was chosen for elimination due to weather-related delays in the winter period of sediment sampling, and continuous high flows during the rainy spring that scoured surface sediments. At each sampling period, one composite of 12 core samples was taken at each station from the same locations as the benthic samples. Percent carbon and total and exchangeable concentrations of eight heavy metals were measured.
- suspended sediments (inorganic) – 9 seston samples planned; all have been taken as of 9/16/00.

- reach channel form – habitat within the channel has been documented, and an assessment of riparian habitat has been carried out in all streams. Discharge was measured above and below the turnpike during most field visits.
- catchment land-use – large-scale land use within each catchment has been assessed using a GIS (Maine GAP land use data). A summary is presented in table 1.
- temperature – hourly measurements taken upstream and downstream of the turnpike in each stream (Figure 2).

#### Ecosystem structure

- community structure (abundance, biomass) for fish and invertebrates in each study reach – benthic samples have been taken 9 times (454 samples). Identification and measuring of several hundred thousand invertebrates has been completed, including mounted chironomids. Data entry and analysis is pending. Fish sampling was carried out in July 2000.
- maximum size of macroinvertebrates (biomass, selected taxa) – Data entry and analysis is pending.
- spatial and temporal patterns of primary producers (chlorophyll *a*) – four sets of samples planned, all had been completed as of August 2000.
- spatial and temporal patterns of benthic organic matter accumulation and storage - benthic samples have been taken 9 times; all have been completed as of September 2000.

#### Ecosystem function

- macroinvertebrate growth rate (selected taxa) – Data entry and analysis is pending.
- annual macroinvertebrate production – Data entry and analysis is pending.
- transported and stored particulate organic material -9 seston samples planned; all have been taken as of 9/16/00.
- rate of leaf detritus processing – this experiment has been completed as of November 2000.
- leaf pack invertebrate community structure and biomass – Identification and measurement of specimens is ongoing.

Taxonomic work is ongoing in the laboratory. Data entry and analysis, and manuscript writing, will be ongoing through spring 2002. The data presented in this report represents the physical and chemical template on which the invertebrate secondary production data will be superimposed in order to examine ecological processes within the study streams.

#### **Principal Findings and Significance:**

Preliminary examination of water and sediment quality data, including suspended solids, nutrients, pH, specific conductance, dissolved oxygen, alkalinity, dissolved organic carbon, and heavy metal concentrations, suggests that the Maine turnpike is indeed affecting the streams, but that examination of physical and biological variables, together with chemical parameters, is necessary to elucidate the nature of these effects on stream health. Data on chemical variables alone are not conclusive.

**Suspended solids** – No clear pattern relating to the turnpike is visible in annual means of either organic or inorganic suspended solids (Figure 3). An exception is Stevens Brook, where the increase in downstream material is likely due to some widening construction activities that entailed clearing vegetation from the riparian zone and construction of some earthworks around the culvert. Increases in transported material, particularly the inorganic fraction, downstream of industrial runoff and effluent inputs in Goosefare Brook (stations 6, 7, and 8) are evident. This material is probably precipitates of iron, based on its red color and the nature of the industrial discharge.

**Water chemistry** – Parameters include dissolved oxygen, specific conductance, pH, nutrients (N and P), alkalinity, and DOC. At no time in any stream were measurements of dissolved oxygen lower than 7mg/L; typical measurements were between 8 and 11 mg/L. Trends in pH and specific conductance (Figure 4) were evident in all streams, with the exception of relatively constant pH in Branch Brook. pH values of Cascade, Goosefare, and Stevens Brooks were variable throughout the year; each of these streams drain upland bogs, and decreasing pH values in the autumn were coincident with large influxes of organic acids (see table 2, “DOC”). It is suspected that the increasing longitudinal trend in pH recorded in these streams is due to interactions with carbonate materials in cement culverts as the water passes beneath the turnpike, and natural losses of organic acids through such processes as precipitation and microbial uptake. The decreasing pH trend in Ward Brook is not easily explicable.

Specific conductance showed a clear and significant increase in all streams, beginning immediately upstream of the roadway (aerial deposition of material), and increasing further downstream (aerial deposition plus discharge of runoff). The magnitude of the increase varies with the size of the stream, and is likely related to the degree to which the chemistry of the stream is dominated by drainage from the highway. There is also a large increase in specific conductance downstream of industrial inputs in Goosefare Brook.

The turnpike does not appear to be a source of nitrogen to the streams, and phosphorus was usually below detectable levels (Table 2). Alkalinity also shows little variation due to the turnpike. DOC varies seasonally in the bog-draining streams, and is fairly constant in Ward and Branch Brooks; no stream shows consistent differences related to the turnpike.

**Heavy metals** – With the exception of the industrial inputs in Goosefare Brook, no clear gradients in either exchangeable or total metal concentrations are observed (Figures 5-9). It is clear, however, that metal concentrations have a tendency to vary together, suggesting that certain stations have characteristics that facilitate metal retention in those sediments. Possible explanations include particle size (recorded in physical habitat data), co-precipitates (iron and manganese), and organic matter content (% carbon). Examination of physical and biological variables that relate to or are affected by the metal concentrations are a major goal of this research, and will be considered in the final analyses when all data are available.

# Maine Climate Change and Water Use

## Basic Information

<b>Title:</b>	Maine Climate Change and Water Use
<b>Project Number:</b>	2000ME5B
<b>Start Date:</b>	9/1/1999
<b>End Date:</b>	8/31/2001
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	Second
<b>Research Category:</b>	Climate and Hydrologic Processes
<b>Focus Category:</b>	Climatological Processes, Drought, Economics
<b>Descriptors:</b>	Climate, Conflict management, Drought, Hydropower, Information Dissemination, Irrigation, Water Resources
<b>Principal Investigators:</b>	John M. Peckenham, Robert Lent

## Publication

1. Peckenham, J., S. Kahl and S. Vidito, 2001. Proceedings of the Maine Climate Change and Water Use/Availability Workshop, July 26, 2000. 32 p.
2. Peckenham, J., S. Kahl and S. Vidito, 2001. Planning for Future Water Use and Availability, Our Future Water Supply - Is There Cause for Concern. International Conference on the St. Lawrence River Ecosystem, Cornwall, Ont., May, 2001.

## **Problem and Research Objectives:**

### **Identifying the Problems.**

There is a link between climate change and water resources, but over a period of months to years the cause and effect relationships are unclear. Projections of water use and availability are limited by our current inability to predict the direction and magnitude of climate change combined with the natural variations in weather. We do know that water resources are affected by weather and that historical weather patterns are difficult to interpret. The purpose of this workshop is to review the state of our knowledge and identify the data gaps. Specific workshop goals include:

1. What are the predicted regional effects of climate change?
2. How will these changes affect Maine's water resources and supplies?
3. What will be our water requirements in the next two decades?
4. Do we have conflicts with current water resources and what new types of conflicts can be expected?
5. How do we evaluate the need for alternative water supplies?

### **Methodology:**

The changes in weather patterns and yearly variations of climate in Maine have a direct and measurable relationship with water resources. This includes the mass balance of the hydrologic cycle, the timing of demand and recharge, the maintenance of flowing rivers, the ability to support fisheries, hydropower production, and water-related tourism. When totaled, Maine's water resources account for billions of dollars of the state's economy. The stakeholders are not prepared to react to all the potential changes in water resources and it is expected that demands on these resources will only increase over the next decade.

The Climate Change and Water Use Workshop is the first organized attempt in Maine to look beyond problem identification and apply research to generate management objectives. This project brought together the research community, regulatory agencies, and resource managers to coordinate current information and water resource objectives in a common action plan. The potential scale of water resource change could have a tremendous negative effect on all stakeholders. The workshop participants identified how these critical resources can be shared for mutual benefit, or at least to minimize mutual loss.

Our objectives are:

*1) To identify the key researchers on regional climate change and weather patterns.*

It is essential to get as clear a prediction of decadal-scale trends as possible. The USGS is the primary provider of water resource measurements and the NWS/NOAA is the primary provider of weather and climatic data. There are researchers in Maine and the northeast who have particular expertise on climate changes and this

workshop will be the opportunity to get the most current interpretations to the stakeholders.

2) *To enhance communication among stakeholders.*

Changes to the quantity or quality of water resources will affect everyone in the state. If trends in water resources stress natural systems, then there will be secondary sociological stress. Since water resources are common to a population with often conflicting priorities and needs, this workshop will be the first step in forging new management strategies. This workshop will give key stakeholders an opportunity to work together to develop a strategic plan to respond to the stresses.

3) *To develop a draft strategic action plan.*

The University of Maine-GMC is taking the lead in water resource educational efforts in the state. The workshop will result in a draft action plan for the Drought Task Force that can be used to manage our collective response to changes in the water resources. As a management tool, it is more effective to have a response action plan with some uncertainties than no plan and a certainty of unclear action.

4) *To develop a framework for future action.*

Once this workshop is complete, a summary of proceedings and a draft action plan will be prepared. The workshop organization will be a template for future workshops if deemed necessary by the stakeholders.

**Principal Findings and Significance:**

The following is a summary of the key conclusions of the workshop.

Information Analysis-

- Maine's weather patterns are naturally variable, but the data do not indicate a consistent trend in any parameter.
- Weather patterns appear to be cyclical with periods of 2 to 30 years.
- The recent patterns reflect a slightly warmer and wetter climate near the coast and a cooler and drier climate in extreme northern Maine.
- Precipitation ranges have become more extreme along the coast due to strong coastal storms.
- Climate models suggest that Maine could become slightly warmer (+3° F) and wetter (+1 inch) over the next several decades.
- Water supply overall is adequate to meet current needs with some notable exceptions in downeast salmon rivers.
- Demand on surface water supply is expected due to agricultural demands.

Planning Guidance-

- Short cycles of 1 to 2 years duration of wet and dry years are probable.
- High intensity precipitation events are more likely.
- Earlier ice-out and peak-spring flow is likely resulting in earlier flood potential.
- Competing quantity demands in certain rivers will increase regardless of climate.
- Predicting flood or drought years is not feasible.
- Demographic changes will have an effect on water quality and quantity, especially in southern and coastal regions.

- Water conservation needs to be part of the management process.

Needs Analysis-

- Water data information collection needs to be coordinated between agencies.
- A centralized hosting of information and data is needed.
- Support is needed to maintain existing monitoring activities.
- Research is needed to understand trends in data.
- Better quality consumptive-use information is needed.
- Climate forecasting is needed but accuracy depends upon a new generation of high-resolution climate models.
- Work needs to begin on developing a comprehensive water-management policy.

# Cycling and Speciation of Mercury and Methylmercury in the Soil of Acadia National Park

## Basic Information

<b>Title:</b>	Cycling and Speciation of Mercury and Methylmercury in the Soil of Acadia National Park
<b>Project Number:</b>	2000ME8B
<b>Start Date:</b>	6/1/1999
<b>End Date:</b>	5/31/2001
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	Second
<b>Research Category:</b>	Water Quality
<b>Focus Category:</b>	Hydrogeochemistry, Toxic Substances, Water Quality
<b>Descriptors:</b>	Geochemistry, Toxic Substances
<b>Principal Investigators:</b>	aria.amirbahman.1, Jeffrey S Kahl, Terry Haines

## Publication

1. Ruck, P., A. Amirbahman, I. Fernandez, J. Kahl, and T. Haines. 2001. Manuscript in preparation for thesis and future publication.
2. Poster presented at the 2000 Maine Water Conference, Augusta, ME. "Cycling and Speciation of Hg in Soils at Acadia National Park."
3. Oral presentation at the 2001 ARIA Conference: "Cycling and Speciation of Hg in Soils at Acadia National Park."

#### Problem and Research Objectives:

Mercury is a contaminant of major concern in the northeastern United States. Fish and eagles in Acadia National Park (ANP), Maine have some of the highest Hg concentrations in the world for the sites with no point source. This is primarily due to the atmospheric input of Hg. According to the 1999 Mercury Deposition Network Annual Report, the wet-only deposition for ANP was  $8.0 \mu\text{g}/\text{m}^2$  for 1999. Dry deposition may also be a major source of Hg.

The role of soil in ANP in the accumulation and possible methylation of Hg is not fully understood. The distribution and speciation of Hg will vary depending upon the presence of organic carbon in soil and in groundwater and physical factors, such as soil drainage,. In the forested watersheds, production of  $\text{CH}_3\text{Hg}$  is expected to take place primarily in the subsurface under anaerobic conditions.

The University of Maine and the National Park Service are currently conducting a paired watershed study to gain more insight into the biogeochemistry of Hg at ANP. One watershed recently burned, with thin soils and deciduous vegetation, and one unburned, with thicker soil and coniferous vegetation are being compared. As part of this study, the concentrations of Hg and methylmercury ( $\text{CH}_3\text{Hg}$ ), loss on ignition, base cations, carbon:nitrogen ratios, and pH were measured in soils. The data collected from this study and the ongoing PRIMENET study at ANP may be incorporated into watershed models to provide a complete regional mass balance for Hg. The different vegetative covers, organic matter concentrations and groundwater chemistry should influence the distribution of Hg and  $\text{CH}_3\text{Hg}$  in the burned and the unburned watersheds in ANP.

#### Methodology:

Total Hg was extracted from soil samples by the addition of concentrated  $\text{HNO}_3$  and 30%  $\text{H}_2\text{O}_2$  to the samples followed by microwave treatment. Total Hg in soil was determined using EPA method 1631. This method involves the addition of 0.2 M  $\text{BrCl}$  to approximately 0.5g of soil sample, and subsequent reduction of Hg with 20%  $\text{SnCl}_2$ .

Methylmercury extraction from soil was performed using pre-established methods. The soil samples were suspended in 25%  $\text{KOH}$  in methanol and then placed in a  $75^\circ\text{C}$  oven.  $\text{MeHg}$  in soil was measured using ethylation, purge and trap, desorption, and cold-vapor atomic fluorescence detection. For both Hg and  $\text{CH}_3\text{Hg}$  measurements, a Brooks-Rand cold vapor atomic fluorescence spectrometer was used.

Organic carbon was determined by loss-on-ignition in a muffle furnace at  $550^\circ\text{C}$  for 5 hours. It was assumed that LOI is attributed to organic material only. Soil pH was measured in deionized water and in 0.01 M  $\text{CaCl}_2$  with a Corning 340 pH Meter, and a Corning GP combination pH electrode.

#### Principal Findings and Significance:

The fire of 1947 probably impacted the Cadillac Brook (burned) watershed significantly by raising the soil pH, and altering the vegetation, and carbon pools. Soil pH was significantly higher in all horizons of the Cadillac Brook watershed soils than in the Hadlock Brook (unburned) watershed soils. Total Hg (ng Hg/g soil) concentrations were higher in the O horizon of the Hadlock Brook watershed soils than in the Cadillac Brook watershed soils, most likely as a result of the fire. Methylmercury concentrations, both non-normalized and normalized to LOI, were higher in the Cadillac Brook watershed vs. the Hadlock Brook watershed, also most likely as a result of the fire.

Mercury adsorption isotherms were also developed for each of the soil horizons for both watersheds at different pH ranges (pH 3, 4, and 5) to establish the physical mechanisms by which Hg reacts with the soil. The amount of Total Hg adsorbed to soil was compared to Total Hg in solution at a given pH to examine

the binding capacities of soils from each watershed. Results from these isotherms indicate that at low Hg concentrations, Hg speciation is controlled by the type of organic matter in solution (DOM), rather than that bound to soil. Once the available binding capacity of the DOM is exceeded, then Hg adsorbs onto the soil surfaces. At pH 5, more dissolved organic matter is in solution, therefore more Total Hg was found to be bound to DOM. Early results indicate that as a result of the fire, the type of DOM released into solution from burned soils is less efficient at binding Hg than that of the unburned soils.

Based on findings to date, this study hopes to explain the relationships between pH, DOC, and Hg and how they affect Hg cycling and speciation in the two watersheds. Results from this study will be incorporated into the PRIMENET Acadia study to explain Hg export from the burned and unburned watersheds.

# Do Microorganisms Control Arsenic Mobility in Groundwater?

## Basic Information

<b>Title:</b>	Do Microorganisms Control Arsenic Mobility in Groundwater?
<b>Project Number:</b>	2001ME2221B
<b>Start Date:</b>	4/1/2001
<b>End Date:</b>	3/31/2003
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	Second
<b>Research Category:</b>	Water Quality
<b>Focus Category:</b>	Water Quality, Groundwater, Toxic Substances
<b>Descriptors:</b>	Trace Elements, Toxic Substances, Groundwater Management, Bacteria
<b>Principal Investigators:</b>	Jean D. MacRae, Charles Culbertson, John M. Peckenham

## Publication

1. McCaffery, K., and MacRae, J.D. 2002. Microbial arsenate reduction in anaerobic groundwater. Poster presentation at the Maine Water Conference, May, 2002.
2. McCaffery, K., and MacRae, J.D. 2002. Microbial arsenate reduction in anaerobic groundwater. Poster presentation at Arsenic in New England: a Multidisciplinary Scientific Conference, May, 2002

## **Progress Report 2002.**

### **Role of microorganisms in arsenic contamination of groundwater.**

**Jean MacRae, John Peckenham, Charles Culbertson**

#### **Publications:**

1. McCaffery, K., and MacRae, J.D. 2002. Microbial arsenate reduction in anaerobic groundwater. Poster presentation at the Maine Water Conference, May, 2002.
2. McCaffery, K., and MacRae, J.D. 2002. Microbial arsenate reduction in anaerobic groundwater. Poster presentation at Arsenic in New England: a Multidisciplinary Scientific Conference, May, 2002.

#### **Abstract:**

Arsenic contamination has emerged as a problem in groundwater drinking water supplies in Maine. Since arsenic exposure through drinking water has been linked to increased risk of cancer, this issue is of grave public health concern. Arsenic speciation affects its adsorption and mobility. The reduced inorganic form, As(III), is more mobile and more toxic than the more oxidized form, As(V).

Microorganisms can affect the redox chemistry of arsenic compounds. Under reducing conditions, which are usually encountered in groundwater, microorganisms can catalyze the reduction of As(V) to As(III) in energy-generating reactions. Other microorganisms cause the release of adsorbed arsenic through reduction and dissolution of Fe(III) and Mn(IV). These transformations result in an increase in soluble arsenic and could contribute to contamination of the groundwater.

Information on the magnitude of these microbial processes in the groundwater environment and their role(s) in As release and solubility is needed to improve As management options for water supplies.

Enrichment cultures of microorganisms that can reduce As(V) have been made from groundwater and the scrapings from a well casing. Stable cultures of arsenate-reducing bacteria have been obtained. Characterization of these cultures is ongoing. Solid and liquid samples will also be taken from contaminated wells and experiments will be conducted to characterize Fe(III), Mn(IV) and As(V) reduction and release of As from the geologic matrix. The effects of organic carbon enrichment (lactate addition) on the reduction reactions and dissolution of arsenic will also be investigated to simulate the effect of increased organic loading on water quality.

#### **Problem**

Arsenic has been recognized as a potent human toxin for well over a century. Chronic exposure to lower concentrations through drinking water also causes cancer and other adverse health effects. Approximately 10% of wells sampled in the United States by the U.S.G.S. contained  $>10 \mu\text{g/L}$  As and much of Maine is mapped as having anomalously high arsenic in groundwater. Several regions of Maine contain wells that have arsenic concentrations in the ppm range. These elevated arsenic concentrations and "hotspots" such as the towns of Northport, Buxton, and Ellsworth pose an unacceptable health risk to the exposed populations.

It is widely reported that arsenic solubility increases with decreasing redox potential. Microbial activity in the presence of organic material consumes oxygen and other oxidants, producing conditions that favor arsenic mobility. A definition of the processes that affect arsenic form and mobility will result in better management options for arsenic control. The underlying risk factors need to be established for Maine so that preventive, rather than the more expensive end-of-pipe or point-of-use control options can be developed and employed.

There are a number of ways in which arsenic may be mobilized by microorganisms, but the direct reduction of arsenic has not yet been demonstrated in groundwater. The purpose of this research is to identify the ways in which microorganisms participate in arsenic transformations and mobility in groundwater.

### **Research Objectives**

- To obtain bacterial enrichments or isolates of arsenic reducers from arsenic-contaminated wells for further study on mechanisms and controlling parameters.
- To characterize microbial reduction of Fe(III), Mn(IV) and As(V) in water and sediment slurries made from samples taken from arsenic contaminated wells.
- To evaluate the effect of addition of an easily utilizable carbon source (lactate) on Fe(III), Mn(IV) and As(V) reduction rates.

### **Methods**

*Sample Collection and Analysis.* Water samples were collected by pumping water into nitrogen-purged serum bottles to maintain sample redox potential. Solid material from a well casing was scraped off with a sterile spatula and added to reduced media under a stream of nitrogen. Arsenic was speciated in the field by ion chromatography. Other water quality parameters were measured using standard methods. Arsenic speciation in enrichments was determined by HPLC or ion-exchange chromatography and ICP analysis. For monitoring of enrichment cultures, Fe(II) will be analyzed by the oxalate extraction-ferrozine method.

*Microbiological Analysis.* Laboratory microcosms will be prepared in 125 ml serum bottles using ground bedrock from a well in Northport and groundwater (1:4 slurry). Sterile controls will also be included to account for abiotic transformations. Reduction of added iron, manganese and arsenate will be monitored over time by analysis of reduced electron acceptors in the supernatant. Sulfide will also be measured, and all species determined in both solid and liquid phases at time 0 and at the end of the experiment. Incubations will be in the dark at 22 °C. Microcosms (live and killed) will also be prepared with 5 mM lactate added (without added electron acceptors) to determine if the rates of reduction and arsenic release are affected by organic amendment.

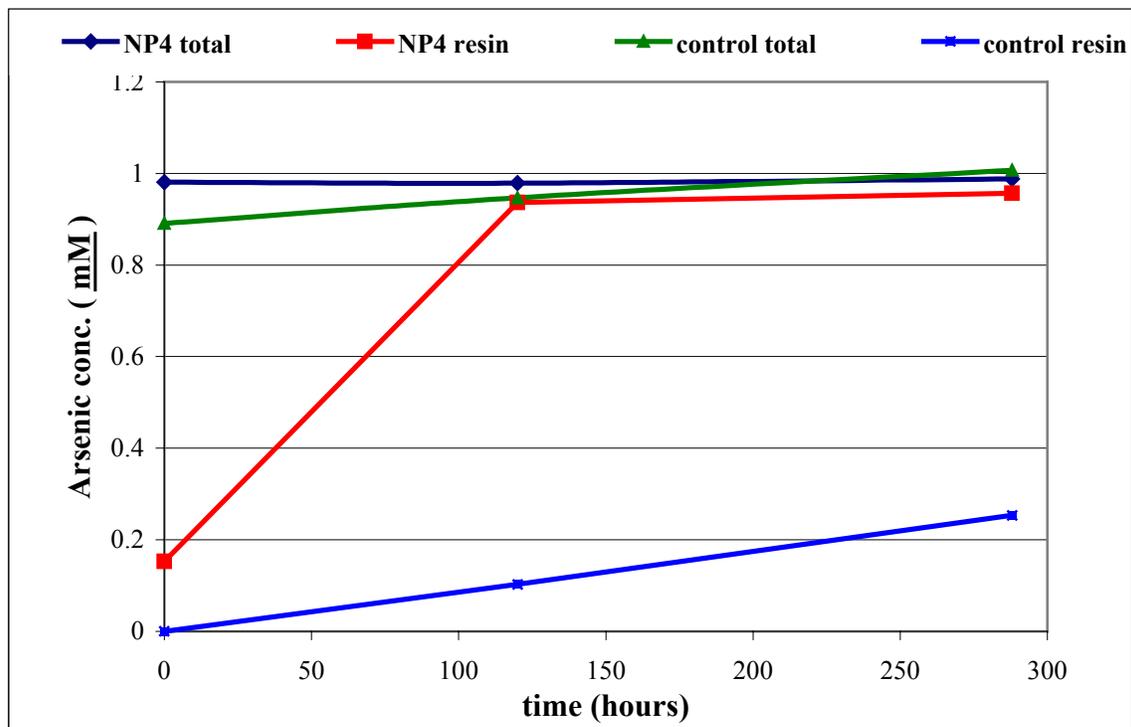
Arsenic-reducing enrichments were made by adding scrapings from the well casing to minimal media containing 5 mM sodium arsenate and 5 mM lactate as the carbon/electron source using strict anaerobic techniques. Alternatively, groundwater was supplemented with nutrients and incubated anaerobically. Stable enrichments were monitored for growth and loss of substrates and changes in electron acceptors over time. 16S rDNA from isolates will be amplified from DNA extracts by the polymerase chain reaction and sequenced for tentative identification of the strains.

## Principal Findings to Date

Early analysis of enrichment media showed that at least one culture from each site (Northport and Green Lake) could reduce As(V). A stable enrichment culture that could use arsenic (V) as an electron acceptor was obtained from the Northport groundwater samples. The use of lactate as electron donor and As(V) as electron acceptor was confirmed by HPLC analysis of the culture media over time. The growth modes of other cultures have not yet been confirmed by analysis of the media, although growth occurred and cells were observed by microscopy.

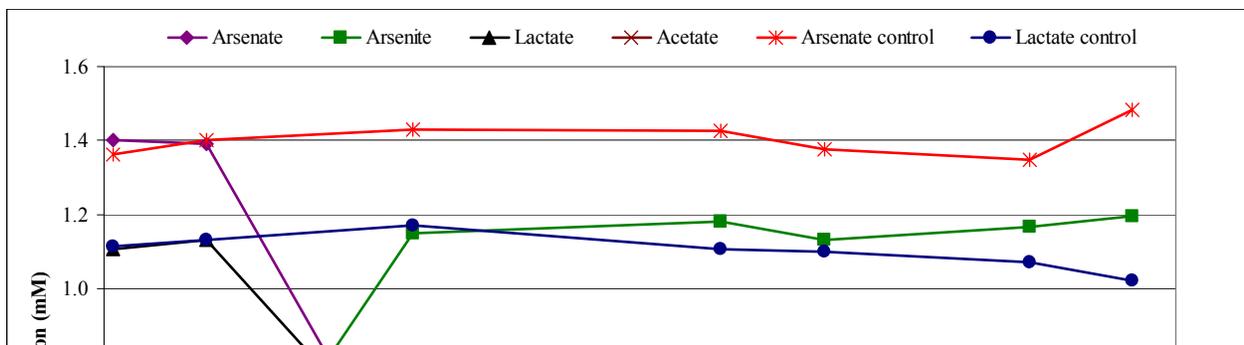
An early experiment was conducted using an enrichment culture from Northport showed that 1 mM As(V) was converted to As(III) in approximately 5 days (Figure 1).

Figure 1. As(III) and total As in NP4 culture medium with time



Another experiment was conducted using the HPLC method to analyze the culture medium for lactate, acetate, As(III) and As(V). Killed controls were also included. Figure 2 shows that as lactate and As(V) were consumed, As(III) was produced to a maximum of 90% of the total As concentration. Acetate was also produced but not with a 1:1 stoichiometric relationship. Presumably this is due to the production of biomass. The lactate and arsenate levels in the controls did not significantly change with time.

Figure 2: Growth of NP4



The enrichment is being tested to determine if it is an isolate by PCR analysis and sequencing. This will also allow us to determine the identity of the organism(s). Experiments are also underway to determine the profiles of carbon source and electron acceptor usage.

A second graduate student is beginning the incubations with bedrock material and groundwater this summer. These laboratory analyses will allow us to determine the conditions under which arsenic is released from the solid matrix.

Funding has been awarded by NSF to continue the analysis of the enrichment culture/isolate and to develop a genetic probe method to assess the relative importance of this organism in environmental samples. Additional enrichments and incubations will be made to determine the importance of indirect modes of action upon As mobility such as iron and manganese reduction. Additional funding will be sought from EPA to assess the importance of organic enrichment on As mobility, such as near landfill sites, intensive livestock rearing and composting facilities.

## **Microbial Arsenate Reduction in Anaerobic Groundwater**

Kevin A. McCaffery, Jean D. MacRae  
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Arsenic contamination has emerged as a problem in groundwater drinking water supplies in Maine. Since arsenic exposure through drinking water has been linked to increased risk of cancer, this issue is of grave public health concern. Arsenic speciation affects its adsorption and mobility. The reduced inorganic form, As(III), is more mobile and more toxic than the more oxidized form, As(V).

Microorganisms can affect the redox chemistry of arsenic compounds. Under reducing conditions, which are usually encountered in groundwater, microorganisms can catalyze the reduction of As(V) to As(III) in energy-generating reactions. Other microorganisms cause the release of adsorbed arsenic through reduction and dissolution of Fe(III) and Mn(IV). These transformations result in an increase in soluble arsenic and could contribute to contamination of the groundwater.

We present findings that indicate dissimilatory arsenate reduction is occurring in anaerobic groundwaters of Maine. Reduction of arsenate, accompanied by oxidation of an organic carbon compound (lactate) has been observed in lab cultures obtained from contaminated groundwater samples.

# A Pilot Estuarine Component to the PEARL Database

## Basic Information

<b>Title:</b>	A Pilot Estuarine Component to the PEARL Database
<b>Project Number:</b>	2001ME2241B
<b>Start Date:</b>	4/1/2001
<b>End Date:</b>	3/31/2003
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	Second
<b>Research Category:</b>	Not Applicable
<b>Focus Category:</b>	Management and Planning, Non Point Pollution, Surface Water
<b>Descriptors:</b>	Bacteria, Beaches, Coastal Zone, Data Storage and Retrieval, Estuaries, Marine Resources, Pollutants, Public Health, Seawater, Shellfish, Water Quality Monitoring
<b>Principal Investigators:</b>	Paul Anderson, Todd Janeski, Jeffrey S Kahl, Tom Noonan

## Publication

1. PEARL Website <http://pearl.umaine.edu>

## **A Pilot Estuarine Component to the PEARL Database Final Report -July 8, 2002**

The long-term goal of the two- year, four-phase initiative was to develop a database that would allow information transfer among volunteer monitoring groups and data managers in estuaries. The project was focused on adapting the PEARL (Public Educational Access to Environmental Information) Project's database to include a larger watershed approach, using the 8 digit HUC framework and housing and providing access to data on lakes and ponds, estuaries and embayments, rivers and streams. The goal of Phases I and II of this seed project was to research and design an approach to adapt the present PEARL database to include estuarine monitoring data (*Year one*).

The results of this project were to utilize the PEARL GIS framework to build a similar database for housing water quality data related to estuaries and coastal projects. It was to establish the foundation on which to build the pilot database and to begin populating it with data from across the state. Benefits were to include: improved accessibility of the data in useful formats for agencies, community leaders, researchers, and citizens, better likelihood that volunteer-derived data is used by decision makers, and improved credibility and enhanced participation of the many volunteer monitoring programs in the state of Maine.

The following was to be accomplished in year one:

- Phase I: *Research database design and assess status and quality of volunteer data.* Research design options for improving PEARL and adapting it to include an estuarine component.
- Phase II: *Design the database.* Make recommendations for the necessary hardware and software (for delivery and for the user), data entry, data quality assurance, maintenance, costs for subsequent phases, and reevaluate timeframe for Phases III and IV.

### **The Phase I tasks were addressed as follows:**

Tasks: *Research database design and assess status and quality of volunteer data*

- Establish a Data Assessment Team (DAT) made up of PIs, representatives from MCP, UMCE, DEP and UMaine, and name a leader for the team  
The database team was active from April 2001 to November 2001. Molly Schauffler, Todd Janeski, Lee Doggett, Sarah Gladu, Paul Anderson and Esperanza Stancioff served on the DAT. Paul Anderson and then Esperanza Stancioff served as the team leader for the group  
.
- Review development options for an Internet database for coastal volunteer water quality monitoring data (e.g., VB/MO/Access; ArcIMS/Java/Oracle; Imagemaps/DBF tables); assess current PEARL technical approach for feasibility. (*Noonan*)  
Tom Noonan reviewed the Internet database options and recommended using Oracle for the future of Pearl. He assessed that Pearl had the technical ability to accommodate the coastal monitoring program within the database with expansion.

- Review existing on-line databases for similar projects, navigation assessment, data presentation, and public education value. (*Noonan; DAT*)

This information, while a review may have been conducted, was not made available to the DAT.

- Assess the existing application approach for PEARL to determine compatibility with the Shore Stewards Volunteer Monitoring data. Anticipated changes to PEARL development will be included in the assessment, including changes to any hardware and software, consideration will be given to whether or not project integration will hinder the performance or usability of any individual project (*Noonan*).

While this was verbally expressed, no written information was provided. However, it was assessed that compatibility was not a problem and anticipated changes to developing PEARL to meet the needs of the Coastal Monitoring component would not hinder the individual projects involved in PEARL.

- Interview or survey current volunteer data managers to estimate the amount and quality of volunteer data, identify compatibility and management considerations, and data storage, access, and data user needs. Summarize this information for the Technical Coordinator to incorporate into the database design (*DAT*)

The questions asked of the Maine Shore Stewards Advisory Committee in April 2001 to provide information to Tom Noonan were the following:

- ✓ Name of group/organization
- ✓ Location/region
- ✓ Time frame for data set (active or historical)
- ✓ Format of data (electronic or paper)
- ✓ What software was used
- ✓ How much data-# of records
- ✓ Station locations digitized? Mapped? Nomenclature?
- ✓ Level of quality control/quality assurance
- ✓ Parent project (CL/PIM, DMR, Watershed)
- ✓ Scope of Monitoring (tidal, estuarine, watershed)

Coastal groups were surveyed and the resulting information was entered into a table and provided to Noonan (May 14, 2001). Datasheets were gathered representing the coastal groups and a CD-ROM of the digitized sites were submitted.

*Deliverables:* Report of research findings and recommendations that specifically address the possibility of adapting PEARL to include estuarine volunteer water quality monitoring data.

Reports from Noonan were verbal.

## **Phase II: *Design the database***

Tasks:

- *Noonan* will make final determinations concerning the Internet database application design with consideration of the findings and feedback from all PIs and the Data Assessment Team.

Noonan met with the DAT to show the updated version of PEARL that he had improved. How this would apply to the coastal component to be developed and added was explained in technical language.

- Determine data formatting standards and revisions necessary to meet selected Internet database requirements. (*Noonan and Data Assessment Team*)

This was briefly discussed.

- Identify necessary equipment, hardware and software and make a recommendation to PI's and Data Assessment Team. (*Noonan*)

Noonan suggested that Oracle be used for the future of PEARL.

- Design a process for data submittal that assures the quality of the data prior to their entry in the on-line database. (*Noonan and Data Assessment Team*)

This was discussed very briefly.

- Draft a database schema or database prototype to represent the comprehensive design of the database. (*Noonan*)

This was discussed.

*Deliverables:* Prepare a final project report, including database schema, from Phases I and II that will include recommendations for the next phases (III and IV) of database development. These recommendations will be based on the most appropriate database design, specific metadata requirements, hardware and software needs, and data management systems. (*Noonan*)

See Final Report attached that Noonan submitted to the DAT.

Recommendations for the future for the Coastal On-line Database from the DAT: Phase I and Phase II, which were completed, revealed to the Data Assessment team and to the collaboration of agencies involved that the immediate needs of the coastal monitoring effort were in contrast to the immediate future of PEARL. The Data Assessment Team has opted to take this project in another direction. In the future, it would be desirable to include the coastal data in the PEARL database.

# A Seed Grant for Determining the Risk of Exposure to Dioxin and PCBs in Natural Water

## Basic Information

<b>Title:</b>	A Seed Grant for Determining the Risk of Exposure to Dioxin and PCBs in Natural Water
<b>Project Number:</b>	2001ME2261B
<b>Start Date:</b>	3/1/2001
<b>End Date:</b>	2/28/2002
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	Second
<b>Research Category:</b>	Not Applicable
<b>Focus Category:</b>	Non Point Pollution, Toxic Substances, Hydrogeochemistry
<b>Descriptors:</b>	benefit cost analysis, health effects, industrial waste water, law, model studies, pollutants, risk analysis, solute transport, toxic substances, water quality standards
<b>Principal Investigators:</b>	Howard Patterson, David Courtemanch, Jeffrey S Kahl, Rebecca Van Beneden

## Publication

**DETERMINATION OF LEVELS OF DIOXIN IN NATURAL WATER USING  
IMMUNOASSAY**

**A Report to Maine Water Research Institute Regarding Results Gathered From  
Seed Grant**

**Submitted by**

**Howard Patterson  
Professor of Chemistry  
University of Maine**

**And**

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**January 31, 2002**

**Abstract:**

**Activated carbon, C<sub>18</sub>, and carbon nanotubes all show strong affinity for organic pollutants, in particular 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) and its related congeners. We undertook to use these compounds as a sorbent matrix in extracting TCDD from distilled water samples in the one to four parts-per-quadrillion (ppq) concentration range. Here we show the efficiency of these various sorbents with carbon nanotubes and activated carbon demonstrating near equal efficiency at the 1-4 ppq range, while C<sub>18</sub> showed strong results only in the 60-80 ppq range. At 1 ppq activated carbon recovered 44.5% of the initial TCDD spike, while the carbon nanotubes demonstrated a recovery of 42%. It is our view that both activated carbon and nanotubes offer a means by which TCDD and related compounds may be removed from water samples as a necessary step toward environmental monitoring of natural water. While activated carbon and carbon nanotubes showed equal efficiency, carbon nanotubes may offer greater potential as a sorbent matrix based on the calculated high capture and potential for reuse.**

**Introduction:**

The issue of water contamination due to dioxin is a seminal topic of debate both nationally and in the state of Maine. Dioxin is part of a large family of toxic substances that resist decomposition. These compounds are fat-soluble and accumulate in organisms from dietary sources. Polychlorinated dibenzo-p-dioxins (PCDDs) are manufacturing byproducts, which bioaccumulate even in areas devoid of human habitation due to atmospheric deposition. PCDD contamination of living organisms is complicated by their slow metabolism and excretion, which produces a spectrum of toxicological responses in animals.

Generally, PCDDs exist in extremely small quantities in the environment. This creates a number of problems because dioxin is a potent toxin even at very low concentrations. For this reason we have worked on a method for detecting PCDDs in water in the 1-4 parts-per-quadrillion (ppq) concentration range.

Historically, a number of different methods have been used to overcome the inherent problems of detecting dioxin in natural water. Here in Maine, fish sampling has been used for the past ten years. This method involves catching fish from suspected areas of contamination and then analyzing their tissues for dioxin. This method is both expensive and limited in its ability to produce statistically reliable data due to variation in fish population.

Another method currently under consideration is the use of Semi-Permeable Membrane Devices (SPMDs). SPMDs are submersible filtration devices that are anchored for a period of time in a waterway suspected of dioxin contamination. They are then collected and analyzed using mass spectroscopy. These devices show promise and have the potential to be far more reliable than current fish testing methods; but they are still hampered by high cost and the inherent difficulty in standardizing the effects of water temperature, biofouling due to microorganisms, and particulate matter, which is known to affect the capture rate of dioxin.

We have entered a joint venture with the Maine based company CAPE Technologies to modify immunoassay kits in order to provide an inexpensive alternative for dioxin monitoring in natural waters. CAPE Technologies has produced effective kits for monitoring dioxin, dibenzofurans, PCBs and dioxin-like PCBs in solid waste using immunoassays. Our partnership with CAPE Technologies has developed these kits for monitoring dioxin in natural water. These kits correlate the toxic equivalent concentration (TEQ) contributed by dibenzo-p-dioxin and dibenzo-p-furan. CAPE's immunoassay kits designed to test solid waste have been shown to have high sensitivity and high specificity for toxic PCDD/F congeners. These kits have already been used for determining PCDD/F levels in solid waste such as soil for several decades, and have been shown to have high affinity for the most toxic PCDD congener 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD).

Our method has avoided these problems by offering a means of concentrating dioxin present in a relatively small sample size such as twenty liters. This method eliminates the inherent statistical limitations of fish sampling as well as the large volume sampling technique used with SPMDs. Here we use filtration columns with several types of sorbents to pass water through a column, which is then eluted and analyzed using immunoassay kits. The advantage of this method is that it is cost effective and avoids the inherent statistical limitations presented by other analytical techniques. Because our water sample is relatively small, we do not suffer from the complications of biofouling and water temperature fluctuations. Also because our method does not include biological sampling, we are not faced with the limitations of determining fish population migration.

Our project adapted current immunoassay kits produced by Cape Technologies of Maine for use in water sampling. In order for this product to function as a monitoring device for natural water, we developed a method to concentrate the dioxin present in the effluent. Our results indicate that this novel device will allow for detection of dioxin and dioxin-like compounds at 1ppq or less. Our research provides the necessary means for concentrating dioxin present in water samples. The growing concern for the quality of the natural water supply both in our state and the world will provide a broad market for this product serving both the economic and the environmental needs of the state of Maine.

### **Methods:**

In order to overcome problems associated with testing such dilute concentrations of dioxin we chose to use several types of extraction columns. Our first choice was the

commercially available Solid Phase Extraction (SPE) column by Burdick and Jackson made from C<sub>18</sub>. This collection column is approved for EPA method 525 and is made from a glass barrel column into which are packed eighteen molecule long carbon chains (C<sub>18</sub>). The carbon is sandwiched between two small-pore frits.

The second type of column was prepared by taking 0.5 g of activated carbon and packing it into a glass barrel column similar in style to the Burdick and Jackson device. The activated carbon was again packed between two small-pore frits. These columns were constructed in our laboratory at the University of Maine.

Our third type of column was made from carbon nanotubes packed in a glass barrel column such as those previously used. Carbon nanotubes were supplied by Professor C. Rao of Jawaharal Nehru Centre for Advanced Scientific Research, India and from Professor L. Dai of the University of Australia. The carbon nanotubes (0.5g) were hand-packed and held in place by small-pore size frits. Carbon nanotubes are carbon molecules in the shape of a geodesic dome (C<sub>60</sub>) that are woven together to form long tubes open at both ends. Previous researchers have found that carbon nanotubes have an extremely high capture rate for compounds such as dioxin and other organic contaminants<sup>1</sup>.

All columns were washed prior to their being used as extraction devices. This procedure used 5 mL of hexane followed by 5 mL of isopropyl alcohol and finally 5 mL of

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<sup>1</sup> Long, R., and Yang, R. *J. Am. Chem. Soc.* **2001**, 123, 2058.

deionized/distilled water. Columns were then allowed to air dry while attached to a vacuum for 10 minutes.

The Burdick and Jackson SPE C<sub>18</sub> columns were tested at 80 ppq, 16 ppq, 4 ppq and 1 ppq concentration range. For the 80 ppq and 16 ppq samples 80 pg and 16 pg of TCDD respectively were added to 5 mL of isopropyl alcohol. These individual spikes were then added to 1 L of distilled water. For the 4 ppq sample, a total of 40 pg of TCDD was added to 10 mL of isopropyl alcohol and then added to 10 L of distilled water. Water samples were stirred for 3 minutes prior to extraction. For the 1 ppq sample, 20pg of TCDD were added to 20 mL of isopropyl alcohol and then mixed with 20 L of distilled water. Again samples were stirred for 3 minutes prior to extraction. All columns were run using the KNF liquid diaphragm pump as a vacuum source.

The activated carbon columns were tested at the 4 ppq and 1 ppq concentration ranges. These experiments followed the same protocol as noted above. The carbon nanotube columns were run in the 1 ppq range by adding 20 pg of TCDD to 20 mL of isopropyl alcohol and mixing with 20 L of distilled water. In every trial, procedural blanks were run to verify the accuracy of our results.

After filtration each column was eluted with 15 mL of toluene. This was done by pressurizing each column with a syringe after toluene had been added. The elute was captured in a disposable test tube and evaporated under nitrogen gas while standing in a heat bath. The samples were then analyzed using CAPE Technologies immunoassay kit.

**Results:**

We were successful at both 4 ppq and 1 ppq using activated carbon as a sorbent material. At the 4 ppq range we were able to recover 64% to 68% of the original TCDD spike. At the 1 ppq range we were able to recover 44% to 45% of the original TCDD spike. Results were positive for each concentration range, demonstrating that activated carbon was sufficient at removing small concentrations of TCDD from water samples.

We were also successful using the carbon nanotubes as a sorbent material. Results were positive at the 1 ppq range with recovery of approximately 42% of the original TCDD spike. Data was calculated using the Calculation Module C for DF1 for low to mid pg/g quantitative analysis supplied by Cape Technologies.

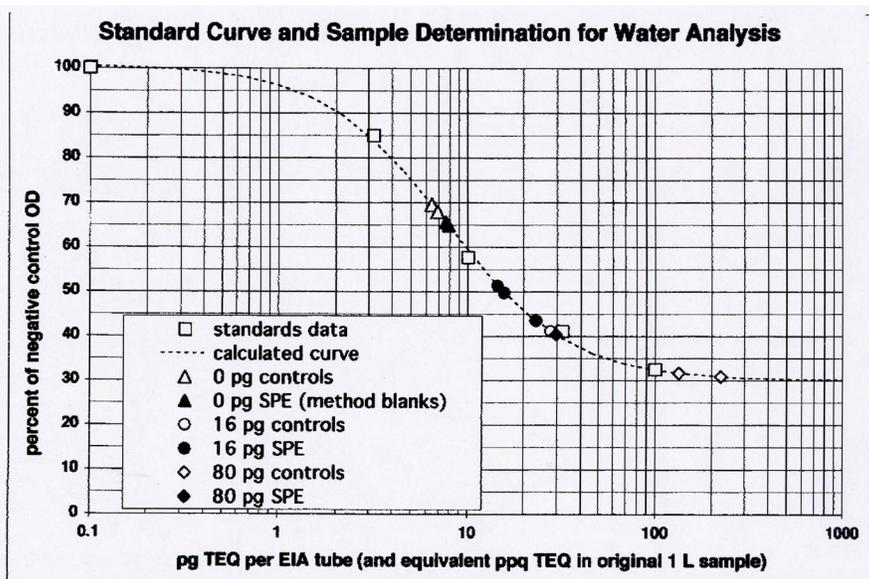
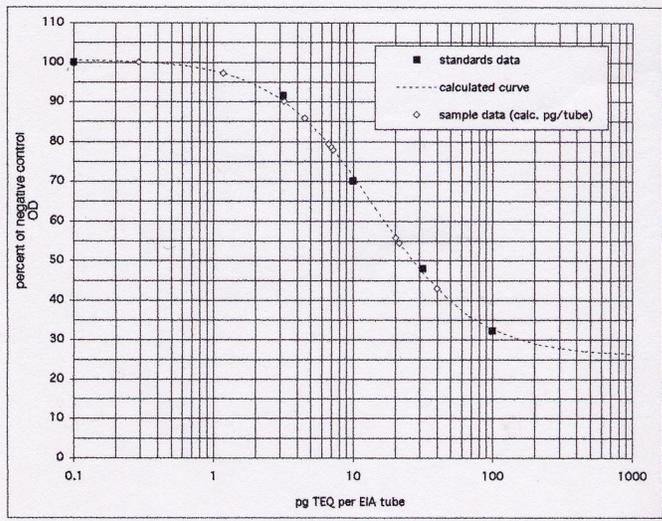


Figure 1. Data for initial tests of TCDD extraction from water samples. Distilled water was spiked with 16 pg of TCDD in 1 L of water (16 ppq) and also at 80 pg in 1 L of water (80 ppq). Data also shows two method blanks. This was calculated using the analytical module supplied by CAPE Technologies.

Figure 1 shows data from an initial test of the Burdick and Jackson SPE columns for capturing dioxin in water samples at moderate concentration levels. These tests were run using a single liter of water. The TCDD spike was first added to 5 mL of isopropyl alcohol in order to ensure the TCDD was completely dissolved. Capture rates varied from 70% to 81%. Immunoassay response curves are sigmoidal in shape. Equation 1 shows the four parameter equation used for fitting a calculated curve to the actual data. This ELISA test uses test tubes coated with anti-dioxin antibodies. The test sample is allowed to incubate in the tubes for twenty-four hours at which time a competitive conjugate is added. This competitor binds sites of the dioxin anti-body that have not already been occupied by dioxin molecules. A change in color is due to the amount of antibodies that are bound to the competitor. For this reason the CAPE Technologies immunoassay test develops a lighter chromographic response the more dioxin is present. The graph in figure 1 plots optical density (depth of color) against concentration. Samples containing higher amounts of dioxin are shown at the lower end of the curve. In other words, as the color of the tubes decreases the sample has a greater amount of dioxin.

$$Y = \frac{A - D}{1 + (X/C)^B} + D \quad \text{Equation 1}$$

Here: X= pg per immunoassay test tube (EIA); Y= normalized EIA response; A= Y value of upper asymptote; B= degree of curvature (negative slope of middle region); C= X value of midpoint curve; D= Y value of lower asymptote. These results were derived from the elution method previously described with the exception that dichloromethane was used in place of toluene. The immunoassay procedure was otherwise the same.



**Figure 2. Data collected for water samples spiked with low concentrations of TCDD. Internal standards are represented by darkened squares, experimental data is represented by open triangles. This graph includes results of both the activated carbon and carbon nanotube columns at 1 ppq and 4 ppq.**

<i>Sample ID</i>	<i>20 L x 1ppq (activated carbon)</i>	<i>20 L x 1ppq (activate carbon)</i>	<i>20 L blank</i>	<i>20 L blank</i>	<i>10 L x 4ppq (activated carbon)</i>	<i>10 L x 4 ppq (activated carbon)</i>	<i>20 L x 1ppq (nano-tubes)</i>	<i>20 L x 1ppq (nano-tubes)</i>
<i>Calc. Pg/tube</i>	7.3	7.0	0	0	21.8	20.4	40.3	6.7
<i>Expected pg based on spike</i>	16	16	0	0	32	32	16	16
<i>Percent recovery</i>	45%	44%	0	0	68%	64%	*252%	42%

**Table 1. Data from the lower concentration tests (1-4 ppq). It should be noted that the first carbon nanotube sample produced a precipitate during the experiment. This data set is marked with a \*. It is shown above, but was not used to calculated the average percentage of TCDD captured by carbon nanotubes.**

Table 1 tabulates the data taken from figure 2. It is important to note that the data in row 3 corresponds to a specific loss of eluted sample due to the immunoassay's analytical procedure. Not all of the eluted sample may be recovered due to inherent limitations of pipetting. Consequently, a fixed 20% loss is calculated based on recovery techniques. Therefore, while the 4ppq samples contain 40 pg of TCDD, only 32 pg is delivered to the EIA tube. This is the same for the 1 ppq sample that theoretically has 20 pg of TCDD, where only 16 pg make it to the EIA tube.

There is also a discrepancy with one of the carbon nanotube samples. When running the test we noticed a yellow precipitate after the column was eluted. This impurity may derive from a number of sources. This sample is marked \* and was not included in the averaged calculated recovery of TCDD from carbon nanotube columns.

### **Discussion:**

All tests were able to recover enough TCDD to successfully analyze by immunoassay. At the 1 ppq range, the activated carbon recovered on average 7.2 pg of TCDD from a spiked sample containing 20 pg (adjustments for loss of TCDD due to pipetting limitations assumes a maximum of 16 pg are present) for an average recovery of 44.5 %. At the 4 ppq range, the activated carbon recovered on average 21.6 pg from a spiked sample containing 40 pg of TCDD (again a 20 % loss of TCDD is included in the calculations). The average percent of recovery at this range was 66%. The discrepancy between the percent of recovery at the two different concentrations ranges may be due to a number of factors. It is inevitable that a portion of each TCDD sample is lost due to

glassware and other portions of the apparatus. As the concentration of TCDD decreases a greater proportion is lost by virtue of the glassware due to increased sample volumes. It is entirely possible that the greater amount of water washes some of the TCDD from the column during the filtration procedure.

The carbon nanotube column was successful at removing TCDD from water at the 1 ppq range. On average 6.7 pg of TCDD were recovered from a sample spiked with 20 pg (adjusted to 16 pg by previously described method) of TCDD for an average recovery of 42%. While carbon nanotubes have been previously shown to have a much higher affinity for TCDD compared to activated carbon, the discrepancy requires explanation. Because carbon nanotubes hold TCDD so tightly it is probable that these samples were not eluted with sufficient solvent to remove the TCDD trapped in the column. Future work must look at the solvent volume needed to completely remove any TCDD from the nanotube column. It may also be possible to heat toluene in order to increase the efficiency of elution. The advantage of the nanotube columns is their ability to capture TCDD so efficiently. With added work we should be able to develop a protocol by which the TCDD is completely freed from the nanotube column. This would allow us to use much smaller sample volumes and so greatly increase the efficiency of this method.

Our research has provided the necessary means for concentrating dioxin present in water samples. This provides a novel and reliable application for immunoassay kits. The growing concern for the quality of the natural water supply both in our state and the

world will provide a broad market for this product serving both the economic and the environmental needs of the state of Maine.

**Summary:**

We have successfully developed a method to remove dioxin from water samples at 1 ppq in sufficient quantities to perform analysis. For this purpose we have shown two sorbents to be of near equal efficiency. At the 1 ppq range activated carbon demonstrated a capture rate of 44.5 % compared to the carbon nanotubes with a capture rate of 44%.

It is our belief that the nanotubes offer greater future benefits compared to activated carbon. More needs to be done to examine the ability of the nanotubes to capture dioxin and dioxin-like toxins. Improved elution procedures will allow carbon nanotubes to attain greater capture rates compared with activated carbon and offer the additional benefit of being reusable.

This Seed Grant has allowed us develop a means of capturing dioxin at 1 ppq concentrations. These results allow for immunoassay tests to be conducted in field settings. Additional studies will have to address more complicated water samples, such as those containing particulate and organic matter. We have shown that it is possible to test natural water at 1 ppq dioxin concentrations. Further work will improve upon this method as a screening tool for dioxin in natural waters by environmental managers. In

conclusion, with this success we will seek further funds in order to develop a field tested method for screening TCDD in natural water using our concentration techniques.

# Seepage Lakes as Indicators of Climate Change: Is Maine Really Cooling?

## Basic Information

<b>Title:</b>	Seepage Lakes as Indicators of Climate Change: Is Maine Really Cooling?
<b>Project Number:</b>	2001ME2281B
<b>Start Date:</b>	6/1/2001
<b>End Date:</b>	8/31/2003
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	Second
<b>Research Category:</b>	Climate and Hydrologic Processes
<b>Focus Category:</b>	Acid Deposition, Climatological Processes, Surface Water
<b>Descriptors:</b>	climate, lakes, acid rain, drought, surface-groundwater relationships, land-water interactions, water chemistry
<b>Principal Investigators:</b>	Kathy Webster, Jeffrey S Kahl

## Publication

1. Seger, E., K. Webster, J. Kahl. 2001. Chemical Responses to Drought: Comparison of Acid-Sensitive Seepage Lakes in Maine and Wisconsin. Poster presentation at the 4th Annual Association of Graduate Students Graduate Research Exposition, April 2002, University of Maine, Orono, Maine.
2. Seger, E., K. Webster, J. Kahl. 2001. Chemical Responses to Drought: Comparison of Acid-Sensitive Seepage Lakes in Maine and Wisconsin. Poster presentation at the Maine Water Conference, May 2002, Augusta, Maine. (Award for Best Student Poster)
3. Seger, E., K. Webster, J. Kahl. 2001. Chemical Responses to Drought: Comparison of Acid-Sensitive Seepage Lakes in Maine and Wisconsin. Poster presentation at the American Society of Limnology and Oceanography Conference, June 2002, Victoria, British Columbia.

## Seepage Lakes as Indicators of Climate Change

Katherine E. Webster, Jeffrey S. Kahl

University of Maine

### Problem and Research Objectives:

Although evidence suggests that the global climate is warming, much uncertainty exists in predictions of local changes in climate, including the seasonality, direction and magnitude of changes in precipitation and temperature. As climate change is likely to be a complex set of shifts in rainfall and temperature that may have annual, seasonal, and cumulative components, we propose that lakes may provide a sensitive integrator of hydrologic effects of climate change. Prolonged climate shifts such as drought alter water balance and the pathways and transport of water and solutes, generating strong chemical signals. For example, drier and warmer periods disconnect lakes from their catchments and from local groundwater flowpaths, altering transport of substances such as dissolved organic carbon from adjacent wetlands (Magnuson et al. 1997; Schindler 1997). In addition, during drought lakes often have higher concentrations of more conservative solutes, reflecting increases in evaporation over precipitation and lower lake water levels (Webster et al. 1996; 2000). This response can be complicated in extreme cases where drought is sufficient to reverse groundwater inputs and cause decreased in-lake ion concentrations (Webster et al. 1990).

Landscape position (the position of a lake along a local hydrologic flowpath) can influence the nature of chemical responses to climatic forcing. Lakes located high in the landscape, near groundwater and surface water divides are subject to more transience in local flowpaths of groundwater and greater variability in lake water levels as climate shifts (Anderson and Cheng 1993; Cheng and Anderson 1994; Winter 1999). The hydrologic budgets of seepage lakes located high in the landscape are dominated by precipitation, evaporation, and groundwater since surface water inlets and outlets are lacking. In these lakes changes in solutes during climate shifts are a function of the relative importance of evaporative losses and groundwater inputs. This close integration between climate and hydrology make seepage lakes sensitive indicators of climate change (Winter and Rosenberry 1998; Fritz 1996).

In this study we are evaluating chemical indicators for their potential to reflect shifts in hydrologic connections between lakes and (1) groundwater inputs and (2) wetlands. We expect to find that seepage lakes located higher in the landscape, with weaker connections to groundwater flow systems are responsive to climate and thus are more sensitive indicators of climate change. Because the lakes we consider most sensitive to climate are also those most sensitive to acid deposition, examination of temporal patterns in regions of different acid loading will provide us with more ability to separate acid rain and climate driven trends. This comparison will be facilitated through access to long-term data on the chemistry of seepage lakes in Wisconsin, a region subject to lower acid-loading rates compared to Maine.

We have three general objectives for this research project:

- Determine if changes in the chemistry of seepage lakes in Maine reflect climatic shifts over the past two decades.
  - ~ Determine if chemical responses differ among lake classes defined by the degree of hydrologic connection with the groundwater system and with wetlands.
  - ~ Compare chemical responses of Maine lakes with drought-induced changes in water chemistry observed for similar seepage lakes in Wisconsin.

- ~ Interpret responses to climate in the context of decreased acid deposition over the past 20 years
- Evaluate the sensitivity of seepage lake chemistry as an indicator of climate change in Maine.
- Recommend a research program to monitor lakes for climate change in the future and to identify impacts of concern to the health of lakes and availability of water resources in the state.

In addition to these primary objectives, this study will provide basic data to increase our understanding of the ecological responses of lakes to climate. Climate change has the potential to alter physical and chemical features of lakes in ways that could dramatically change community structure of aquatic organisms and ecosystem processes. We need better information on how climate influences lake ecosystems in order to understand multiple effects of regional disturbances such as acid rain, UV radiation, and land use alteration. Placing results of both short and long-term studies in a context of climate variability greatly improves our ability to make informed decisions on policy and management actions that affect lake ecosystems.

### **Methodology:**

Water chemistry data on about 120 seepage lakes in Maine were collected in the mid-1980's and the late-1990's as part of earlier surveys. We selected a subset of 66 seepage lakes for re-sampling for this study. These lakes all have an ANC less than 100  $\mu\text{eq/L}$ , our operational definition of lakes with low groundwater influence. Lakes were then allocated to classes defined by silica (low:  $< 0.1 \text{ mg/L}$  and high:  $> 0.1 \text{ mg/L}$ ) and DOC (low, mid, high) (Figure 1). Silica was used to characterize the level of groundwater influence (Kahl et al. 1991) while DOC classes reflected the degree of wetland influence. A set of 35 seepage lakes in northern Wisconsin were classified in the same way; these lakes were sampled annually between 1987 and 2000. The Maine and Wisconsin lakes were part of the same EPA program (Long Term Monitoring), so the data are comparable in field and analytical methods.

Graduate research assistant Emily Seger sampled the 66 Maine lakes in fall 2001 and will sample them again during fall 2002. Chemical variables measured from the lakes included base cations, acid anions, DOC, true color, silica, conductance, pH, and alkalinity. All chemical analyses were performed at the Environmental Chemistry Lab at the University of Maine.

During the summer of 2002, we will develop metrics for lake classification by wetland connection and landscape position that are independent of lake chemistry. For wetland connection, we will quantify the area of wetlands adjacent to each study lake from vegetation maps. Relative lake position within the local flow system will be derived from U.S. Geologic Survey maps using information on lake elevation and distance to regional discharge points.

When lake sampling and chemical analysis are completed in winter 2003, we will relate changes in the major ion chemistry to climate variables such as precipitation and air temperature. Precipitation data were compiled from National Climate Data Center monitoring stations near locations of seepage lakes in Maine (Augusta Airport, Portland Jetport, and Grand Lake Stream) and Wisconsin (Minocqua Dam). The contrast between Maine and Wisconsin in historic trends in acid loading rates, will allow us to make more informed distinctions between patterns related to acid deposition and climate.

### **Principal Findings and Significance:**

The field sampling data for the Maine lakes corresponded to periods of (1) dry to normal in 1986-87; (2) variable, near normal in the late 1990's and (3) the lowest precipitation year on

record in 2001 (Figure 2). In spring to summer 2002 above normal precipitation reversed much of this drought although groundwater levels remain somewhat below normal. In Wisconsin, the most notable climatic event was a severe drought from 1987 to 1990 (Figure 3).

Preliminary analyses have focused on the two chemical constituents we proposed as indicators of flowpath shifts due to climate change (Figures 4-7). We assume that (1) dissolved organic carbon (DOC) levels reflect changes in wetland-lake connections and (2) changes in silica concentration reflect shifts in groundwater-lake interactions. We found that during dry periods, DOC and silica levels decreased in many Maine and Wisconsin seepage lakes, suggesting that even short-term climate shifts impact flowpath connections to these lakes and thus, their chemical environments. Patterns were more consistent across all lake hydrologic classes in Maine, while Wisconsin had stronger trends in the high DOC and silica level classes (more hydrologically connected classes).

While the data show a general trend in chemical response to drought, no particular class of lakes was consistently more responsive, and not all lakes within a class responded the same way. Perhaps a driver other than climate is affecting chemical indicators, or hydrologic classes based on the chemical constituents themselves inaccurately characterize lake types in terms of their landscape position and connection. To examine this latter possibility, other classification systems will be investigated during summer 2002. However, there is support in this preliminary examination that the chemistry of seepage lakes could be useful as a less complex indicator of hydrologic shifts due to climate change. We also plan to evaluate temporal patterns in other lake constituents for their potential as indicators of changes in hydrologic pathways.

Climate warming is a major issue for humankind globally, but the response and adaptation to climate change will occur locally. Our research addresses needs for information on the effects of climate change on aquatic ecosystems in Maine by evaluating an integrator of climate that does not rely entirely on statistical interpretations of weather variables. Use of the chemistry and hydrology of seepage lakes as early warning indicators, if successful, will provide a method for understanding the direction(s) of change in Maine's climate, and provide expectations of future impacts on water resources. Our research also addresses the need to conduct research that recognizes the impacts of multiple stressors such as acid deposition and climate change on aquatic ecosystems (Moore et al. 1997).

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Webster, K.E., A.D. Newell, L.A. Baker, and P.L. Brezonik. 1990. *Nature*. 347:374-376.

Winter, T.C. 1999. *Hydrogeology Journal*. 7:28-45.

Winter, T.C. and D.O. Rosenberry. 1998. *Clim. Change* 40:189-209.

		<b>Silica Concentrations</b>	
		Low ( $\leq .1\text{mg/L}$ )	High ( $> .1\text{ mg/L}$ )
<b>DOC Concentrations</b>	Low ( $\leq 3\text{ mg/L}$ )	<i>ME = 19 lakes</i> <i>WI = 12 lakes</i>	<i>ME = 16 lakes</i> <i>WI = 0 lakes</i>
	Mid ( $3 < 7\text{ mg/L}$ )	<i>ME = 11 lakes</i> <i>WI = 17 lakes</i>	<i>ME = 7 lakes</i> <i>WI = 4 lakes</i>
	High ( $\geq 7\text{ mg/L}$ )	<i>ME = 7 lakes</i> <i>WI = 0 lake</i>	<i>ME = 6 lakes</i> <i>WI = 2 lakes</i>

*Figure 1.* Responses to climate shifts were tracked by lake class. Classes were determined by silica and DOC concentrations from 1986/87, the beginning year of each dataset.

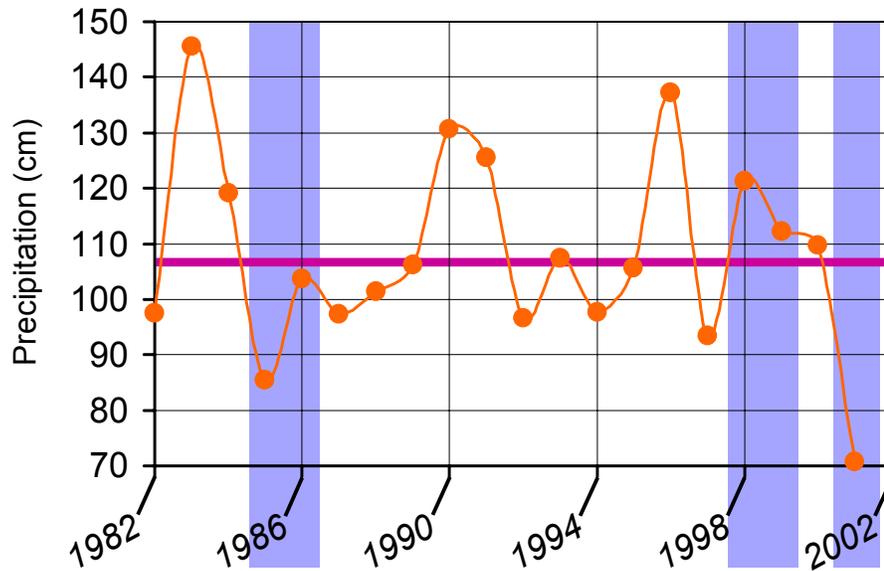


Figure 2. Maine total annual precipitation averaged over three Maine NCDC Stations. NCDC thirty year normal precipitation mean = 107.2 cm (indicated by purple line). A pattern of low to recovery, to above normal, to severely low precipitation occurred during years with data.

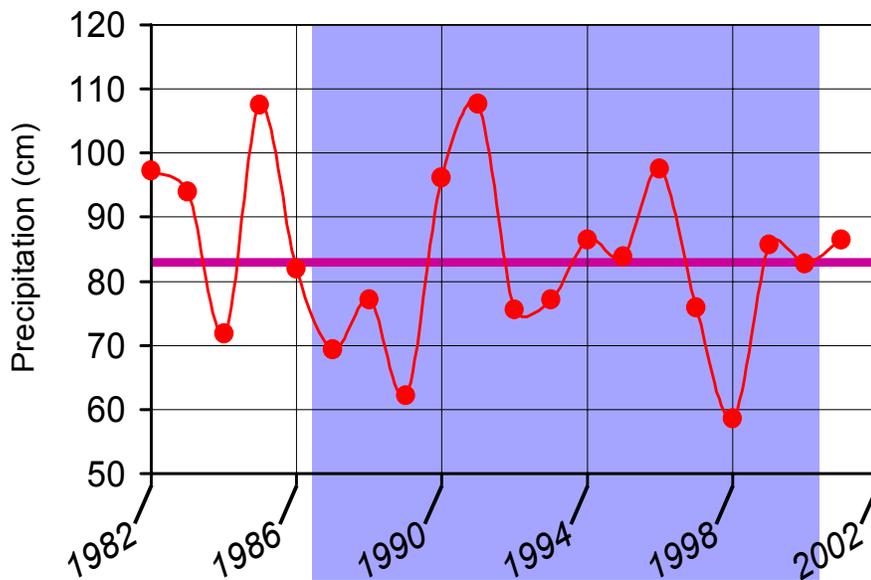
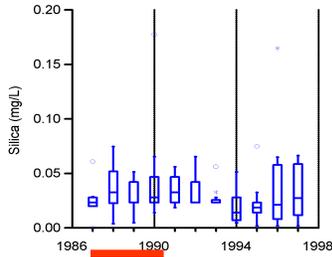


Figure 3. Wisconsin total annual precipitation at Minocqua Dam NCDC station. Shaded areas indicate years with lake data. NCDC thirty year normal precipitation mean = 82.9 cm (indicated by purple line). A severe drought occurred from 1987 to 1990, followed by a transition to above/normal precipitation.

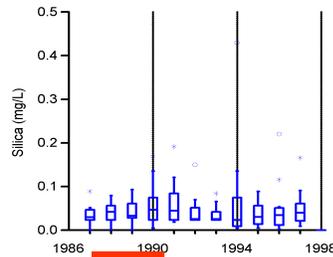
**Wisconsin Silica Trends Grouped by Lake Class. Figure 4**

Indicates drought years. See Figures 2 & 3

**Low Si & Low DOC n=12**



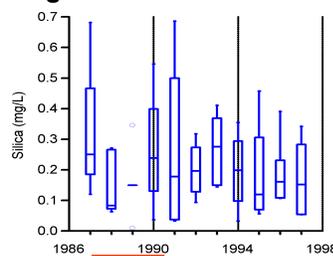
**Low Si & Mid DOC n=17**



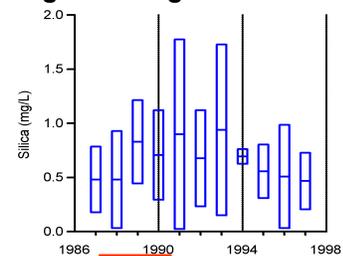
No lakes in Low Si & High DOC class.

No lakes in High Si & Low DOC class.

**High Si & Mid DOC n=4**



**High Si & High DOC n=2**

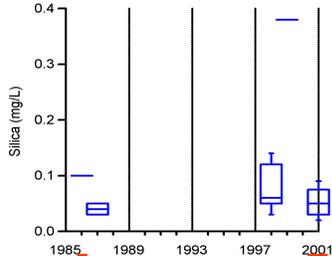


A few lakes had silica decreases during drought years, yet there were no apparent trends. However, lower silica classes had a general decrease in the slightly dry mid-90s.

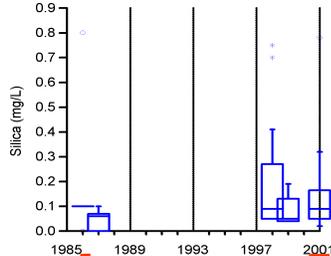
**Maine Silica Trends Grouped by Lake Class. Figure 5**

Indicates drought years. See Fig. 2 & 3.

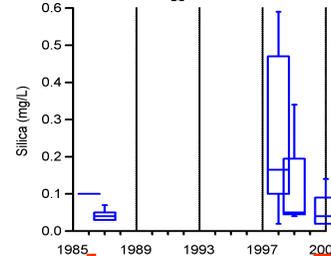
**Low Si & Low DOC n=19**



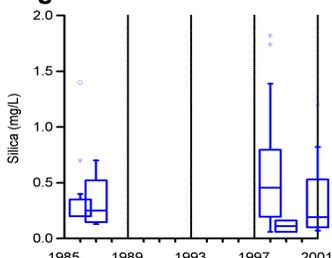
**Low Si & Mid DOC n=12**



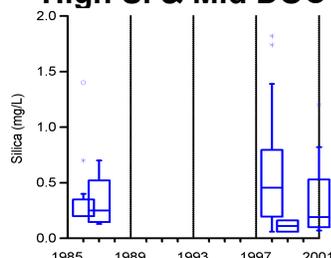
**Low Si & High DOC n=7**



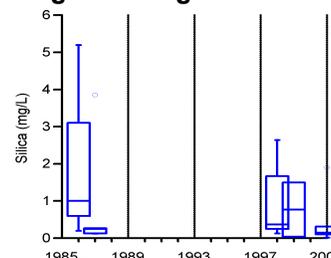
**High Si & Low DOC n=16**



**High Si & Mid DOC**



**High Si & High DOC n=6**

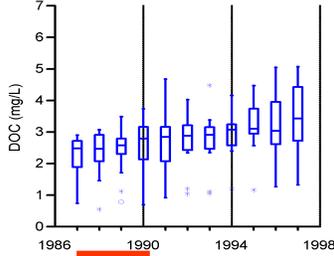


More apparent trends occurred in Maine. Both high and low silica classes had decreases in concentrations during dry years.

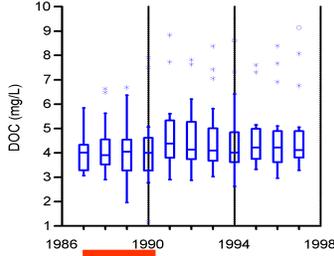
**Wisconsin DOC Trends Grouped by Lake Class. Figure 6**

Indicates drought years. See Figures 2 & 3

**Low Si & Low DOC n=12**



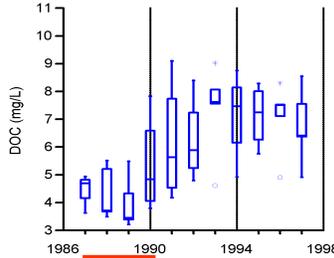
**Low Si & Mid DOC n=17**



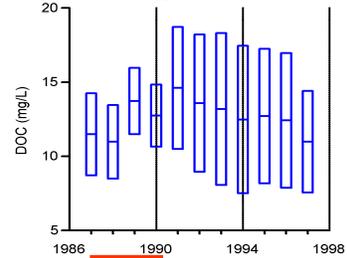
No lakes in Low Si & High DOC class.

No lakes in High Si & Low DOC class.

**High Si & Mid DOC n=4**



**High Si & High DOC n=2**

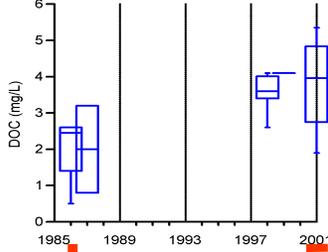


DOC decreased in some lakes of the lower DOC classes during later drought years, with increases or steady levels in recovery years. High DOC lakes were more variable.

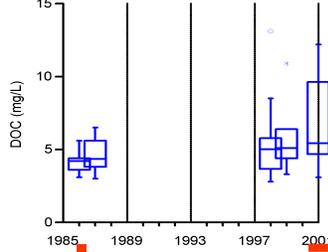
**Maine DOC Trends Grouped by Lake Class. Figure 7**

Indicates drought years. See Fig. 2 & 3.

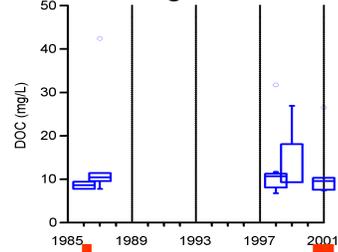
**Low Si & Low DOC n=19**



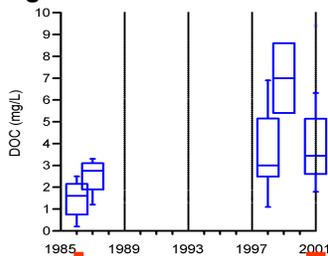
**Low Si & Mid DOC n=12**



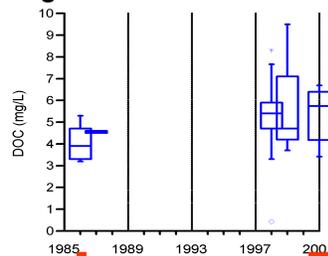
**Low Si & High DOC n=7**



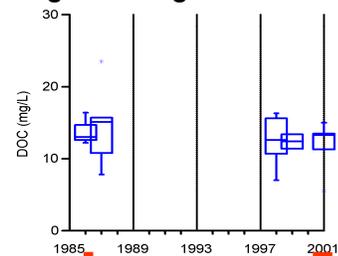
**High Si & Low DOC n=16**



**High Si & Mid DOC n=9**



**High Si & High DOC n=6**



All classes had a general increase in DOC during the first dry-to-recovery period. Yet in the later drought, higher classes and some lakes in class 1 had a decrease in DOC.

# Seed Project to Determine the Fate of MtBE in Groundwater in Maine.

## Basic Information

<b>Title:</b>	Seed Project to Determine the Fate of MtBE in Groundwater in Maine.
<b>Project Number:</b>	2001ME2401B
<b>Start Date:</b>	3/1/2001
<b>End Date:</b>	2/28/2002
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	2nd
<b>Research Category:</b>	Water Quality
<b>Focus Category:</b>	Groundwater, Toxic Substances, Water Quality
<b>Descriptors:</b>	water quality., water chemistry, organic compounds, groundwater quality,contaminant transport
<b>Principal Investigators:</b>	John M. Peckenham

## Publication

1. Peckenham, J.M. (2002) The occurrence and persistence of MtBE in groundwater in Windham, Maine, NE FOCUS Conf. On Groundwater Issues, October 3, 2002.
2. Schmitt, C. and J.M. Peckenham (2002) Source Water Protection: Linking Surface Water Quality to the Watershed. Handbook, Univ. of Maine 85 p. (includes information on MtBE)

*Seed Project to Determine the Fate of MtBE in Groundwater in Maine*

John M. Peckenham

University of Maine

**Problem and Research Objectives:**

Methyl tert-butyl ether (MtBE) was added to gasoline to lower VOC emissions from automobiles. In 1991 Maine opted into the use of reformulated gasoline that had 8% to 12% MtBE. In 1998, the State of Maine (1998) determined that 16% of public water supplies contained detectable concentrations of MtBE and reduced MtBE in gasoline from 12% to 2%. The effect of decreasing the MtBE content in gasoline on groundwater supplies is unknown. This made a unique opportunity to assess the residual effects of MtBE on groundwater quality.

This project initiated the determination of the residual risks posed to groundwater supplies by MtBE. We expected to detect changes in the distribution of MtBE (magnitude and detection rate) since 1998 (post-RFG). The geographical distribution of MtBE is a function of gasoline composition, spills, atmospheric transport, dilution/dispersion, and microbial transformation (Johnson *et al.*, 2000, Squillace *et al.*, 1999). This study provided time-sensitive data to quantify how water resources recover from ambient MtBE contamination and thus provide the basis for a more exhaustive research proposal to be submitted to an appropriate agency in the near future.

MtBE was added to gasoline in Maine from circa 1986 through 1998. The use of greater than 5% by volume MtBE was banned in 1999. This research assessed the changes in the distribution of MtBE in groundwater monitoring wells in Windham, Maine, from 1998/1999 versus 2001 (2 data years). This builds on a detailed town-wide study completed in 1999 (Nielsen and Peckenham, 2001).

**Methodology:**

Site Selection. We sampled 19 existing groundwater monitoring wells in Windham, Maine where baseline data are available (Figure 1). MtBE contamination has been detected in 35% of wells in Windham sampled in 1998 and 1999 (Nielsen and Peckenham, 2001).

Sampling Methods. This study used existing monitoring wells installed by the USGS in the Windham aquifer (Nichols and Silverman, 1998). Sampling will be based on the with USGS National Water Quality Assessment protocols for sampling groundwater wells (Koterba *et al.*, 1995). Modifications of the USGS protocols were incorporated to use the USEPA low-flow (minimal drawdown) sampling procedures (Puls and Barcelona, 1995). The monitoring-well sampling equipment setup was simplified from the USGS protocols. A submersible pump with teflon-lined tubing was used to purge wells by the USGS field personnel. Once field personnel collected a water quality sample, a clean polyethylene bailer was lowered to the top of the water table to collect a sample. A new bailer and line was used for each well.

Samples for MtBE and BTEX analyses were collected directly from the bailer into four 40 ml glass VOA vials with teflon septum tops and no air space (acidified to pH<2).

QA/QC Methods. Samples will be kept on ice and driven to the Geochemistry and Environmental Engineering Laboratory of the George Mitchell Center, Orono, Maine, for analysis. Quality-assurance samples consisted of 10% duplicate samples, plus equipment blanks, trip blanks, spiked samples, source-solution blanks, and ambient blanks (trip blank vials opened and exposed to the ambient air during sampling, then closed and sent in for analysis). Laboratory quality assurance and quality control were consistent with good laboratory practices and USEPA QA/QC guidelines. The laboratory currently operates under both USEPA and state approved laboratory plans.

Sample Analysis. Samples will be analyzed for MtBE and gasoline-range organic compounds using modified USEPA Methods (SW-846) and specialized laboratory methods including Standard Methods (5000 and 6000) and Church *et al.* (1997).

### **Principal Findings and Significance:**

The 2001 sampling data for selected wells in Windham, Maine, substantiate the persistence of MtBE in groundwater (Table I). The characteristics of the occurrences of MtBE, however, have changed since 1998. The characteristics include the statistical attributes, as well as, the spatial attributes.

The results of this seed project indicate that the mean concentration of MtBE in the groundwater in Windham, Maine, has increased significantly since 1998. The concentrations of MtBE ranged from values less than detection (0.1 µg/L) to 38.7 µg/L. The rate of detection (percentage of wells with detectable MtBE for each sample event) for 2001 (42%) was nearly the same as overall rate (43%) and both were greater than 1998 (20%) (Figure 2).

The mean concentrations of MtBE for the same set of wells has increased from 0.225 µg/L to 3.01 µg/L. This mean was calculated by setting less than detection limit values to equal 0.5 times the detection limit. The mean increased even when the highest concentration, 38.7 µg/L, was excluded from the estimate of the mean.

The median concentrations of MtBE for the same set of wells has decreased from 0.1 µg/L to 0.05 µg/L. This median was calculated by setting less than detection limit values to equal 0.5 times the detection limit. This estimate of the median implies that there are more low-level detections of MtBE with a fewer number of high concentration. However, if the median is calculated based on samples above the detection limit only then the median exhibits a steady increase from <1.0 µg/L in 1998 to 4.2 µg/L in 2001.

The statistical characteristics of the MtBE detections suggest that MtBE is still widespread in the groundwater with perhaps a greater occurrence at low concentrations. The

detection of significant concentrations in a few wells suggests that the MtBE content in gasoline is still sufficiently high to cause marked groundwater contamination.

The spatial association were analyzed using the same land-use criteria as Nielsen and Peckenham (2001): urban, low-density residential, and undeveloped. The distribution of MtBE based on these spatial landscape categories exhibited marked differences between 1998 and 2001 (Figures 3 and 4). In particular, there was a broadening of the detection ranges in the undeveloped units while the urban units exhibit little or no change.

In summary:

- The mean detectable concentration of MtBE has increased since 1998.
- The range of detection is greater in 2001 than 1998.
- There is a broader spatial occurrence in 2001 compared to 1998.
- Detections are associated with any type of land use.

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# Location of Wells in Windham, Maine

## Sand and Gravel Aquifer Boundaries from Neil (1998).

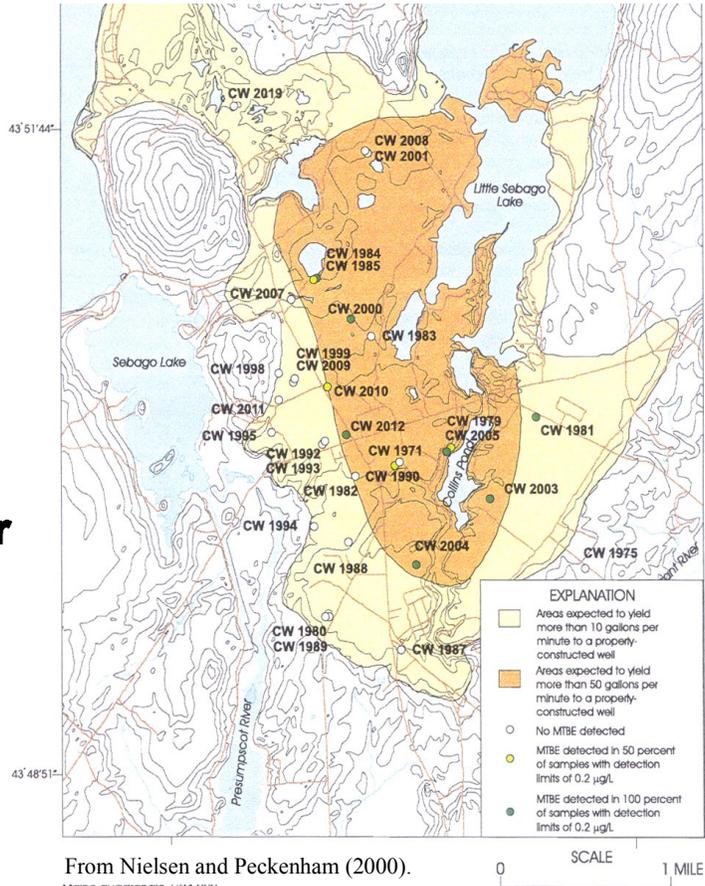
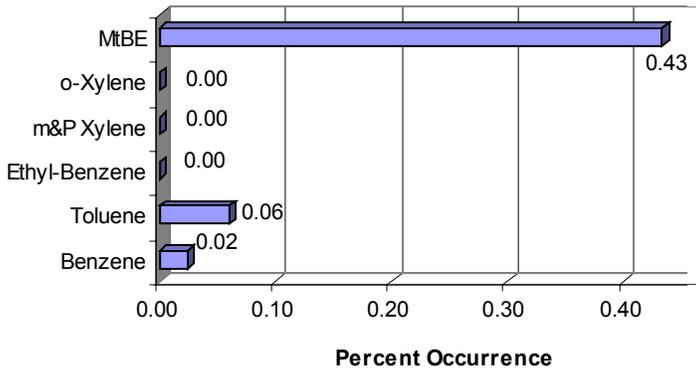
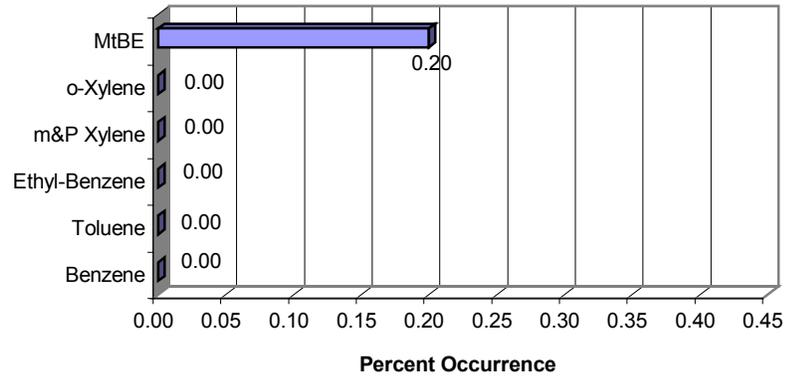


Figure 1. Study location in Windham, Maine.

**Windham, Maine 1998-2001**  
**N = 83**



**Windham, Maine Summer-1998**  
**N = 50**



**Windham, Maine 2001**  
**N = 19**

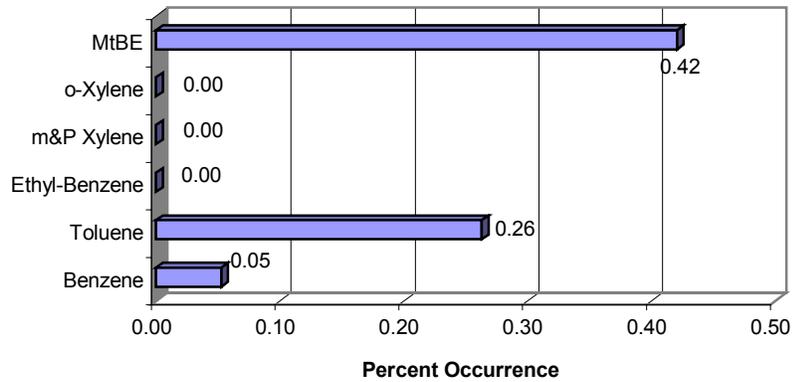


Figure 2. Frequency of occurrence for MtBE in groundwater samples for 1998 through 2001.

# Spatial Frequency of Occurrence of MtBE in Windham, Maine

## Sand and Gravel Aquifer Boundaries from Neil (1998).

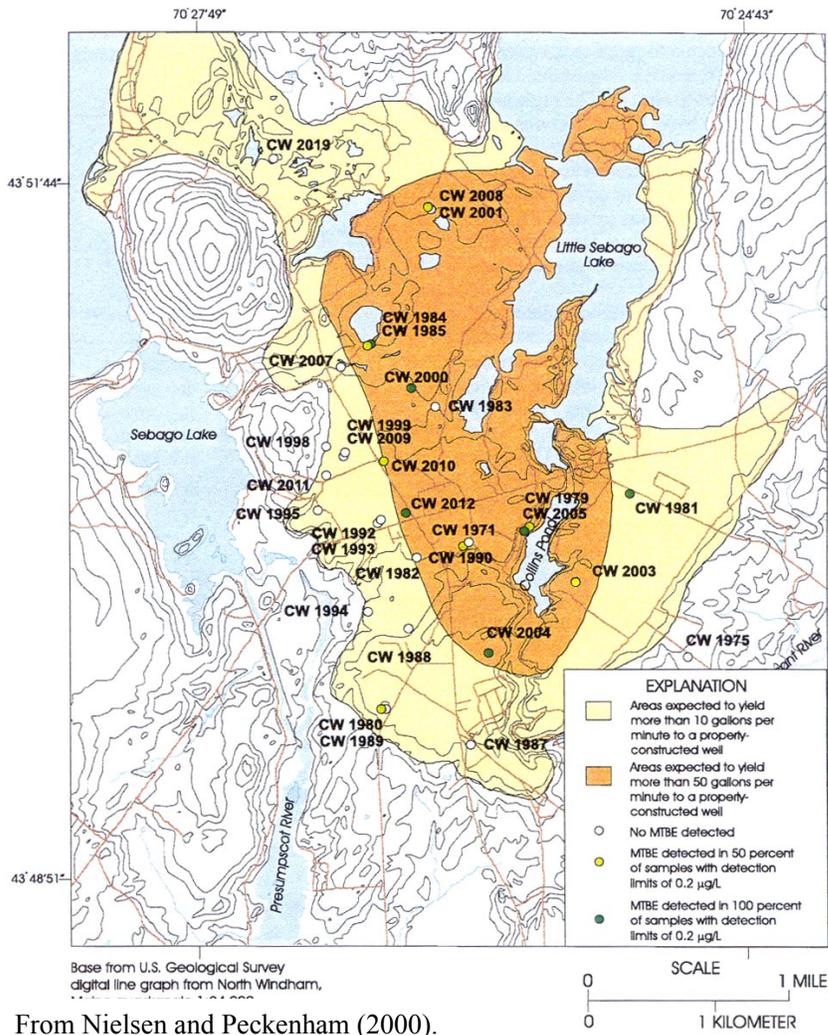


Figure 3. Spatial and temporal distribution of MtBE detections in groundwater wells.

## MtBE Concentrations Relative to Land Use

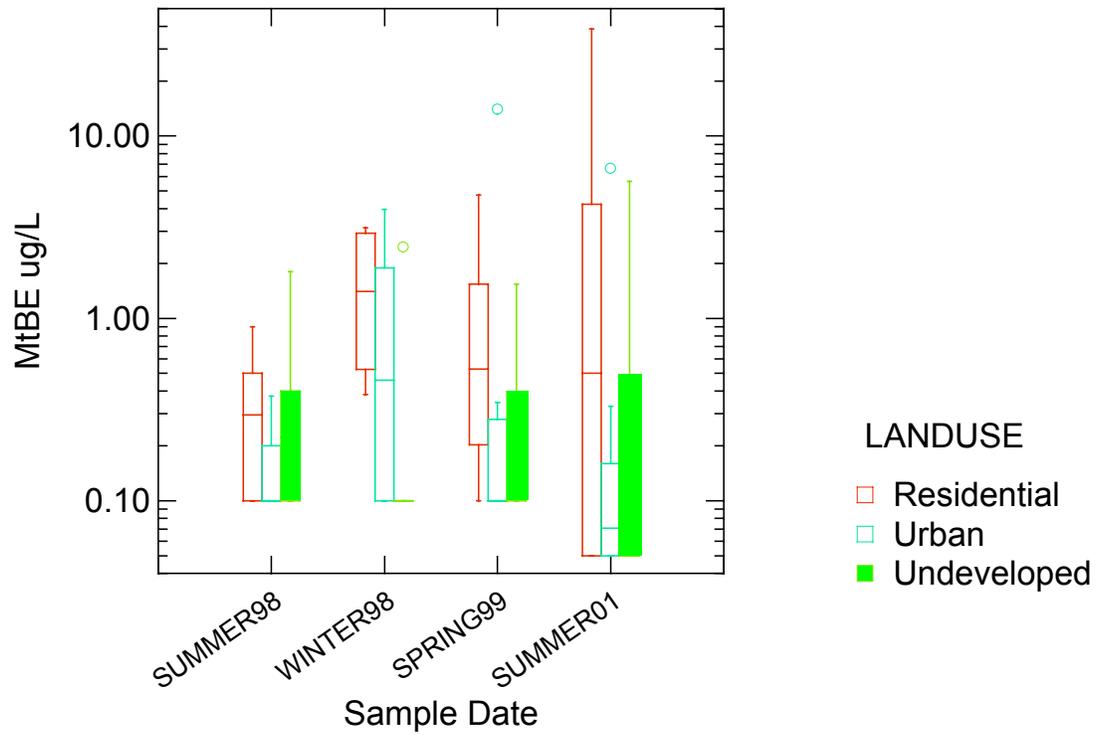


Figure 4. Spatial and statistical summary of MtBE detections in groundwater wells by land-use class.

Table I. Analytical results for MtBE analyses 1998-2001. Note that < means less than detection limit and E is estimated concentration. Data for 1998 and 1999 from Nielsen and Peckenham (2001).

Well ID	USGS ID	Sample Date		MtBE (ug/L)	
		Aug-98	Nov-98	May-99	Aug-01
ARL-1	CW 1971	<0.2		<0.2	<0.1
CPW-1	CW 1979	<0.2		0.203	0.500
MTW-1	CW 1980	<0.2			0.490
CHA-2	CW 1985	<0.5	<0.2	E0.102	<0.1
KEL-1	CW 1987	<0.2		<0.2	<0.1
ARL-2	CW 1990	<0.2		0.226	E0.01
Bent-1	CW 1992	<0.2		<0.2	<0.1
Bent-2	CW 1993	<0.2		<0.2	<0.1
Key 1	CW 1999	<0.2		<0.2	<0.1
SSW-1	CW 2000	<0.4	0.459	0.346	0.160
MPW-1	CW 2001	<0.8	<0.2	<0.2	<0.1
UWW-1	CW 2003	<1.0	0.723	0.467	E0.05
TCBY-1	CW 2004	<0.7	3.140	0.596	38.700
CPW-2	CW 2005	<1.8	2.730	1.540	4.220
MPW-2	CW 2008	<0.2		<0.2	5.650
Key 2	CW 2009	<0.2		<0.2	<0.1
MDW-1	CW 2010	<0.2		1.890	0.330
CBW-1	CW 2012	<0.75	3.960	14.000	6.640
BRW-1	CW-2011	<0.4	<0.2	<0.2	<0.1
Mean			2.202	2.409	7.086
median			<i>RFG use</i> 2.730	<i>post-RFG</i> 0.532	4.220

# Does aluminum geochemistry control the trophic status of oligotrophic lakes?

## Basic Information

<b>Title:</b>	Does aluminum geochemistry control the trophic status of oligotrophic lakes?
<b>Project Number:</b>	2001ME1481G
<b>Start Date:</b>	9/1/2001
<b>End Date:</b>	8/31/2003
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	second
<b>Research Category:</b>	Water Quality
<b>Focus Category:</b>	Acid Deposition, Water Quality, Non Point Pollution
<b>Descriptors:</b>	Oligotrophic Lakes, Metal Cycling
<b>Principal Investigators:</b>	Stephen A. Norton, Aria Amirbahman, Roy James Bouchard, Jeffrey S Kahl

## Publication

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**Mobilization of and linkages among P, Al, and Fe during high discharge episodic acidification at the Bear Brook Watershed in Maine, USA**

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## 1. ABSTRACT

Phosphorus (P), aluminum (Al), and iron (Fe) stream chemistry were assessed for high discharge snowmelt events at the Bear Brook Watershed, Maine (BBWM) during December 2001 and February 2002 and compared with results from Roy et al. (1999) from a January 1995 study of the same streams. The West Bear catchment has been subjected to artificial acidification since 1989. The East Bear catchment is the untreated reference. Most of the P export was with acid-soluble particulate Al in the 1995 event. Particulate P was co-precipitated with, occluded in, or adsorbed on acid-soluble  $\text{Al}(\text{OH})_3$ , which precipitated as emerging acidic groundwater degassed  $\text{CO}_2$  and pH rose, or as the groundwater mixed with higher pH stream water. Induced acidification of the treated catchment resulted in increased transport of Al and P from soil to the stream, leading to greater Al and P export from the treated catchment, compared to the reference (Roy et al., 1999).

Particulate Al, Fe, and P were positively correlated with discharge during the 2001-2002 events. However, dissolved P concentrations remained low ( $\leq 0.1 \mu\text{M}$ ) during high discharge events as pH decreased in both streams. For example, in 2001, total P concentration (acid-soluble) increased to  $1.7 \mu\text{M}$  during the rising limb of the hydrograph in West Bear, approximately five times the value in East Bear. In 1995, the peak was  $1.9 \mu\text{M}$  total P in West Bear, four times the value in East Bear. During the December 2001 event, dissolved Al concentrations increased to maxima of 21 and  $6.3 \mu\text{M}$  in West Bear and East Bear, respectively, lower than maxima of 43 and  $9.3 \mu\text{M}$  in 1995. Acid-soluble particulate Al concentrations in 2001 increased to 166 and  $30 \mu\text{M}$  for West Bear and East Bear, respectively, up from 1995 maxima of 155 and  $6.7 \mu\text{M}$ . Dissolved Fe

concentrations remained  $\leq 0.9 \mu\text{M}$  in both streams during all study events. However, acid-soluble particulate Fe concentrations in 2001 increased to 239 and  $4.1 \mu\text{M}$  for West Bear and East Bear, respectively, up from 9.5 and  $0.54 \mu\text{M}$  in 1995. Acid-soluble particulate Al and Fe declined parallel to total P after peaking during all study periods.

Nearly all of the base cations were in dissolved form during the three events, indicating that particulate Al in West and East Bear Brooks is not associated with primary minerals such as feldspars. Particulate acid-soluble Al concentrations substantially exceeded concentrations of particulate base cations in both streams during all sampling events. We conclude that particulate Al, Fe, and P are chemically linked during transport at high discharge in these episodically and chronically acidified streams.

Key words: acidification, aluminum, episodic acidification, iron, phosphorus, watershed manipulation

## **2. INTRODUCTION**

Understanding the relationship between acid rain and phosphorus (P) mobilization in headwater systems is essential in the study of lake eutrophication. Lake eutrophication from excess P is a significant water quality problem. For example, one third of the natural water systems on Maine's threatened waters list are lakes, and 77% of those lakes are listed due to non-point pollution by P.

Particulate P increases with increasing discharge due to surface runoff and entrainment of material eroded from the stream bed or banks (Likens et al., 1977). Therefore, the bulk of annual particulate P export from northeastern U.S. forested

watersheds typically coincides with brief, high discharge events (i.e., fall rains, snowmelt). Dissolved P, on the other hand, is highly variable in relation to stream discharge among watersheds, and fluctuations may be correlated with, but not caused by, declining pH (Likens et al., 1977; Meyer and Likens, 1979; Munn and Prepas, 1986; Prairie and Kalff, 1988). Phosphorus adsorbed to secondary Al and Fe phases on soil particle surfaces may dissolve as acidified groundwater rises into the solum during high discharge (Fernandez and Struchtemeyer, 1985). Dissolution of these surface coatings would have the same net effect on the stream chemistry as transport and dissolution of the streambed material.

During catchment acidification, the accumulation of  $\text{Al}(\text{OH})_3$  and P varies episodically and reversibly in stream sediments (Norton, 1975). Aluminum (Al) mobilization is attributed primarily to the acid-catalyzed dissolution of Al-bearing secondary minerals in the soil. Aluminum mobilization from soil and subsequent precipitation downstream may reduce the concentration of dissolved P by adsorption or co-precipitation (Kopacek et al., 2000).

Mobilization of other metals, including iron (Fe), may occur naturally in some watersheds during high flow events and is promoted by acidic and anoxic soil solutions with a high  $\text{PCO}_2$ . Metal mobilization is enhanced in catchments subject to acidic precipitation, as observed in the two catchments in Bear Brook Watershed in Maine (BBWM), USA.

Release of Al, Fe, and P at BBWM was first addressed by Roy et al. (1999). They hypothesized that particulate Al, Fe, and P are chemically associated during transport, with the Al phase dominating. Roy et al. compared the chemistry of artificially

acidified West Bear Brook and untreated East Bear Brook catchments during a January 1995 high discharge event, when pH declined. The pH minimum was lower in the manipulated West Bear (4.8) than in the untreated East Bear (5.2). The pH decline was typical of episodic acidification of Maine streams (Kahl et al., 1992; Roy et al., 1999). Lower pH in West Bear Brook was attributed to higher concentrations of  $\text{NO}_3$  and  $\text{SO}_4$ , resulting from chemical manipulation, that were not wholly compensated by increased base cations. Higher concentration ranges for base cations in West Bear were attributed to cation desorption induced by the chemical manipulation. Concentrations of  $\text{NO}_3$ , DOC, and dissolved Al increased in West and East Bear Brooks, consistent with the assumption of shallow flow paths. Concentrations of total P and Al were too high to be controlled by DOC, which only increased by 1 to 2 ppm.

The covariance of particulate Al and Fe with total P during the January 1995 event suggested that P- and Al- or Fe-bearing primary acid-soluble materials were eroded from the catchment, streambed, or stream banks, or P is chemically associated with particulate Al and Fe derived from the soil (Roy et al., 1999). The molar ratios of particulate Al to total P (50:1 to 100:1) did not suggest stoichiometric precipitation of P as an essential element of some mineral phase, but rather that P is adsorbed to or co-precipitated with  $\text{Al}(\text{OH})_3$  (Norton and Henriksen, 1983; Roy et al., 1999). Iron should behave similarly to Al in the acidifying soils (Norton, 1989; Roy et al., 1999). Release and dissolution of Al and Fe particulate hydroxides from the stream bed as well as dissolution of Al and Fe adsorbed to stream substrates would occur during the rising limb of the hydrograph as pH decreases. Particulate Al and Fe may also be formed during high flow as  $\text{CO}_2$ -rich, Al- and Fe-rich groundwater emerge to the higher pH and oxygen-

rich stream and degas CO<sub>2</sub>, producing an increase in pH and precipitation of Al(OH)<sub>3</sub> and Fe(OH)<sub>3</sub>.

Particulate and dissolved Al, Fe, and P during high discharge events at BBWM in December 2001 and February 2002 have been determined and compared to those reported by Roy et al. for January 1995. From 1995 to 2002, continuous artificial acidification of the West Bear catchment has affected the mobilization rates of Al, Fe, and P in the stream. We infer mechanisms controlling P export in surface waters undergoing chronic and episodic acidification.

### 3. METHODS

BBWM is comprised of the adjacent catchments of West and East Bear Brooks with areas of 10.7 and 10.2 ha, respectively. Soils in this catchment are primarily Spodosols, Inceptisols, and Folists with subsoil accumulations of sesquioxides (Fernandez and Struchtemeyer, 1985). Bimonthly treatments of 1,800 eq (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> ha<sup>-1</sup> yr<sup>-1</sup> have been applied to the West Bear catchment since 1989. The East Bear catchment is an untreated reference.

Stream water samples were collected simultaneously at short intervals from West and East Bear Brooks during periods of high discharge in December 2001 and February 2002. We used ISCO<sup>TM</sup> automated samplers fitted with 1 L acid-washed, plastic containers. Equilibrated pH was determined on 30 ml unfiltered aliquots equilibrated with air containing 300 ppm CO<sub>2</sub> at room temperature using a Radiometer combination pH electrode (model GK273920B). Alkalinity (ANC) was determined on 50 ml aliquots

via Gran Titration using a Radiometer Titration Manager with the same electrode. Sixty ml aliquots were filtered through Fisher 0.45  $\mu\text{m}$  polyethylene filters into HDPE bottles, preserved with 2 drops of  $\text{H}_2\text{SO}_4$ , and stored at  $4^\circ\text{C}$  until analysis for dissolved organic carbon (DOC) with an OI Corporation model 1010 TOC analyzer.

Total P and dissolved P were each determined on 50 ml aliquots by colorimetry. Samples for dissolved P were filtered through a 0.45  $\mu\text{m}$  polyethylene filter prior to digestion. Total and dissolved P samples were digested by ammonium persulfate oxidation, autoclaved, and analyzed using the ascorbic acid method (Standard Method #4500 P-E) on a Thermospectronics Genesys5 Spectrophotometer. The detection limit was  $1 \mu\text{g L}^{-1}$  with a precision of  $\pm 1 \mu\text{g L}^{-1}$ .

Samples for dissolved fractions of base cations and metals were filtered through a Fisher 0.45  $\mu\text{m}$  polypropylene filter and acidified to  $\text{pH} < 2$  with  $\text{HNO}_3$ . Samples for total base cations and other metals were microwave-digested with  $\text{HNO}_3$  at  $180^\circ\text{C}$  for 15 minutes prior to analysis. The remaining sample volume in the ISCO field container was acidified to 0.5%  $\text{HNO}_3$  to dissolve any particulate Al and Fe hydroxides and associated P which had adhered to the walls of the sample container or had precipitated in the field container. The resulting concentrations using this “field total” method likely exaggerate total metal concentrations in the sample because the original volume had been reduced and any metals adsorbed on the container walls become concentrated in a smaller volume of acidified solution. Therefore, this field total method provides a maximum estimate of the concentration of metals initially in the container. Here we report total metal concentrations determined by the former method. The method of determining total metals concentrations for the December 2001 event differs from the method used for the

February 2002 events in that the aliquot for total metals was removed from the field container after the acidification for the field total method was done. Base cations (Ca, K, Mg, Na) and Al, Fe, and Si were determined using a Perkin-Elmer Optima 3300XL inductively coupled plasma optical emission spectrometer (ICP-OES) with axially-viewed plasma and a CETAC International, Inc. ultrasonic nebulizer.

#### 4. RESULTS

Stream discharge for the three events at West and East Bear Brooks are reported in Figures 1-3. Maximum discharge increased in each successive event. Discharge ranged from 0.71 to 24.85 L s<sup>-1</sup> (28 L s<sup>-1</sup> = 1 mm/h) in East Bear during the 23-26 December 2001 event (Figure 1). The hydrograph in West Bear failed. Discharge ranges in West and East Bear Brooks were 0.73 to 35.76 and 0.73 to 46.95 L s<sup>-1</sup> for the 10-12 February 2002 event (Figure 2), and 2.46 to 126.15 and 3.45 to 132.55 L s<sup>-1</sup> for the 26-28 February 2002 event (Figure 3). The minimum equilibrated pH decreased in each successive event. Equilibrated pH decreased from 6.20 to 4.99 and 6.10 to 5.60 in December 2001 in West Bear and East Bear, respectively (Figure 1). Equilibrated pH decreased from 5.5 to 4.9 and 6.1 to 5.5 in West Bear and East Bear, respectively, during the early February event (Figure 2) and from 5 to 4.7 and 5.7 to 5.2 during the late February event (Figure 3).

Dissolved P concentrations remained low ( $\leq 0.10 \mu\text{mol L}^{-1}$ ) in both streams during high discharge events during all three study periods (Figures 1-3). In December 2001, total P concentration (acid-soluble) increased to 1.7  $\mu\text{M}$  during the rising limb of

the hydrograph in West Bear compared to 0.3  $\mu\text{M}$  in East Bear (Figure 1). Acid-soluble total P concentrations reached 0.6  $\mu\text{M}$  in both streams during the early February 2002 event (Figure 2). These concentrations were 3 and 1.5  $\mu\text{M}$  during the late February event in West Bear and East Bear Brook, respectively (Figure 3).

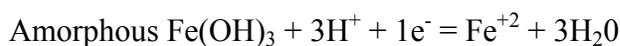
Maximum concentrations of dissolved Al increased with each successive event, consistent with the decreasing pH. Dissolved Al concentrations increased to maxima of 20.0 and 6.30  $\mu\text{M}$  in West Bear and East Bear, respectively, during the December 2001 event (Figure 1). Dissolved Al concentrations reached 28.5 and 7.04  $\mu\text{M}$  in West and East Bear, respectively during early February 2002 (Figure 2), and 40.0 and 11.5  $\mu\text{M}$  during late February 2002 (Figure 3). Acid-soluble particulate Al concentrations in 2001 increased to 186 and 35.6  $\mu\text{M}$  in West Bear and East Bear, respectively (Figure 1). Acid-soluble particulate Al concentrations reached maxima of 40.0 and 18.5  $\mu\text{M}$  during the early February 2002 event (Figure 2), and 138 and 126  $\mu\text{M}$  during the late February event (Figure 3), in West and East Bear Brooks, respectively. Thus the particulate Al maxima did not correspond to the maximum dissolved Al although the maxima could have occurred between sampling times.

Dissolved Fe concentrations remained low ( $\leq 0.895 \mu\text{M}$ ) in both streams during the three events (Figures 1-3). However, acid-soluble particulate Fe concentrations in December 2001 increased to 251 and 4.12  $\mu\text{M}$  for West Bear and East Bear, respectively (Figure 1). Concentrations of acid-soluble particulate Fe in West and East Bear Brooks reached maxima of 23.6 and 6.86  $\mu\text{M}$  during the early February 2002 event (Figure 2), and 13.4 and 20.2  $\mu\text{M}$  during the late February event (Figure 3). The particulate maximum for Fe occurred during the least acidic event, and vice versa.

Dissolved base cations comprised nearly all of the total base cations and remained relatively constant or decreased slightly as discharge increased during the three events (Table I). The difference between total and dissolved base cation concentrations was typically one to three  $\mu\text{moles L}^{-1}$ . Differences in base cation concentration ranges between West and East Bear Brook are attributed to cation desorption caused by the chemical manipulation of West Bear Brook (Norton et al., this volume). Particulate acid-soluble Al concentration also substantially exceeded concentrations of particulate base cations in both streams during each of the events. The difference between total and dissolved Al was on the order of approximately 100 micromoles per liter. From peak values, acid-soluble particulate Al and Fe declined parallel to total P during all events.

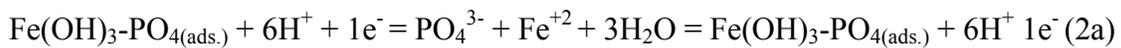
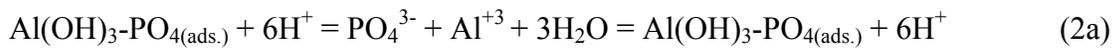
## 5. DISCUSSION

During periods of low flow, Al, Fe, and P are translocated from the mineral-rich B horizon soils to accumulate in the streambed. The particulate  $\text{Al}(\text{OH})_3$  and  $\text{Fe}(\text{OH})_3$  in stream water during high flow likely originate from the streambed and from precipitated colloids from solutions leached directly from B horizon soil. The particulate  $\text{Al}(\text{OH})_3$  and  $\text{Fe}(\text{OH})_3$  is likely formed as a consequence of increased pH caused by  $\text{CO}_2$  degassing from soil solutions emerging into the stream, and mixing with higher pH and oxygen-rich water. The generalized reactions are, within the soil:



(1b)

These reactions consume alkalinity. The anion accompanying the release of the Al and Fe is  $\text{HCO}_3^{1-}$ , which is relatively abundant even at low pH because of the high  $\text{PCO}_2$  in the soil. As the pH of the stream water rises because of  $\text{CO}_2$  degassing, mixing with higher pH water, and oxygen is introduced, the reactions reverse. Phosphorus sequestered (adsorbed and occluded) in the sesquioxide-rich forest soils is released as the Al and Fe are mobilized, and is recaptured as the Al and Fe are precipitated in the stream water. These reversed reactions consume alkalinity with no net gain for the whole process.



Induced acidification of the treated catchment resulted in increased transport of Al, Fe, and P from the treated catchment compared to the reference catchment. The positive correlation between the particulate Al and P species, discharge, and lower pH is clear. Particulate Fe is higher during high discharge but is not as strongly related as Al. Dissolved P, however, does correlate with the discharge. Roy et al. (1999) observed the same lack of relationship. However, concentrations of total Al (160  $\mu\text{M}$ ) were significantly higher compared to total Fe (10  $\mu\text{M}$ ) in West Bear Brook during the 1995 discharge event. As a result, Roy et al. (1999) concluded that most of the particulate P was associated then with  $\text{Al(OH)}_3$ , and to a lesser extent with  $\text{Fe(OH)}_3$ .

Concentrations of total Al and Fe were comparable in West Bear Brook during the 2001-2002 events. Particulate P seems to track particulate Fe more closely in time during a single event. Total Al and P concentrations observed in West Bear in 2001-2002 were comparable to those observed in 1995. However, 2001-2002 discharge events had

higher total Fe concentrations compared to the 1995 event, perhaps due to earlier selective dissolution of more labile Al phases and lower pH.

Two lines of evidence indicate that the total P is not in primary minerals. Nearly all base cations are in dissolved form (Table 1). The presence of Ca primarily in a dissolved form precludes P associated with phosphate minerals such as apatite ( $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ ) in the streams. Particulate P ranges up to  $100 \mu\text{moles l}^{-1}$  whereas particulate Ca is in the few  $\mu\text{moles L}^{-1}$  range and dissolved Ca is less than  $100 \mu\text{moles L}^{-1}$ , at all flows. Second, there is no stoichiometric relationship between P and Al or Fe or Si. By similar arguments, the particulate Al in both streams is not associated with primary minerals such as feldspars ( $\text{KAlSi}_3\text{O}_8$  or  $\text{NaAlSi}_3\text{O}_8$ ). It is too easily and quickly dissolved and little Ca occurs in the particulate fraction. Roy et al. (1999) also concluded from the January 1995 event that Al is not strongly associated with silicate minerals in the suspended material at either the West or East Bear Brook catchments on the basis of concentrations of particulate Al and base cations.

Particulate total Al was high in each of the three events, suggesting that much of the Al was derived directly from the soil as discharge increased, with relatively little intervening precipitation of Al in the stream substrates. The maximum total Fe decreased in each successive event, suggesting a slightly different mechanisms for mobilization and greater dependence on storage in the stream substrate.

Unlike dissolved Al that increased in both streams with a decreasing pH, dissolved Fe did not exhibit a dependence on pH. Dependence of dissolved Al on pH suggests relatively fast dissolution kinetics of  $\text{Al}(\text{OH})_3$  in the soil leading to equilibrium with respect to this mineral. Lack of dependence of dissolved Fe and P concentrations on

pH may relate to the high redox conditions (low solubility) of the stream as well as kinetics of precipitation. Alternatively for P, the concentration of dissolved Al may be controlled in the stream by adsorption onto colloidal Fe and Al hydroxide. Colloidal  $\text{Al}(\text{OH})_3$  and  $\text{Fe}(\text{OH})_3$  are effective adsorbents for many anions including P.

## 6.0 SUMMARY

Aluminum- and Fe-linked export of P appears to be episodic, occurring concurrently with increasing discharge and depressed pH at the Bear Brook Watershed in Maine. There are substantial difficulties in accurately determining the dissolved and particulate species because of time-dependent processes that are causing dissolved Al and Fe to precipitate. These processes include:

- Degassing of excess  $\text{PCO}_2$
- Mixing of acidic groundwater with higher pH stream water
- Increasing the  $\text{PO}_2$  as groundwater emerges into the stream

At BBWM export of Al and Fe in particulate acid-soluble form dominates the stream budget for these two elements. P is strongly associated with these particulate metals, with P in particulate form exceeding dissolved P by a factor of approximately 50. The pH does not control either dissolved Fe or P to an appreciable extent but dissolved Al is strongly controlled. Mobilization of these elements has been accelerated by progressive chronic acidification of the catchment and is particularly enhanced at high flow. Most mobilization to the stream appears to be a one-stage process from the soil to the stream water. However, temporary storage of precipitated Al and Fe, with adsorbed P, may occur in the stream substrate at lower flow. The mobilization of Al and Fe in this fashion

does not provide any net alkalinity to the system, only a removal of the solid phase from the soil. However, downstream P budgets may be substantially affected by the presence of the Al and Fe solids, both of which strongly adsorb P, thereby affecting trophic status of water.

## 7.0 ACKNOWLEDGMENTS

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### Figure Captions

Figure 1. from top to bottom: (a) equilibrated pH (EqpH) and discharge (Q) ( $L s^{-1}$ ) versus time (h) in West (WB) and East (EB) Bear Brooks from December 23-26, 2001; evolution of total and dissolved Al, Fe, and P ( $\mu\text{moles } L^{-1}$ ) versus time (h) in (b) West Bear Brook and (c) East Bear Brook. Time zero equals 1600 h on 12/23/01). Subscripts 'Tot' and 'Diss' refer to total and dissolved concentrations, respectively.

Figure 2. from top to bottom: (a) equilibrated pH (EqpH) and discharge (Q) ( $L s^{-1}$ ) versus time (h) in West (WB) and East (EB) Bear Brooks from February 10-12, 2002; evolution of total and dissolved Al, Fe, and P ( $\mu\text{moles } L^{-1}$ ) versus time (h) in (b) West Bear Brook and (c) East Bear Brook. Time zero equals 1600 h on 2/10/02. Subscripts 'Tot' and 'Diss' refer to total and dissolved concentrations, respectively.

Figure 3. from top to bottom: (a) equilibrated pH and discharge ( $L s^{-1}$ ) versus time (h) in West and East Bear Brooks from February 26-28, 2002; evolution of total and

dissolved Al, Fe, and P ( $\mu\text{moles L}^{-1}$ ) versus time (h) in (b) West Bear Brook and (c) East Bear Brook from February 26-28, 2002 (time zero = 1600 h on 2/26/02). Subscripts 'Tot' and 'Diss' refer to total and dissolved concentrations, respectively.

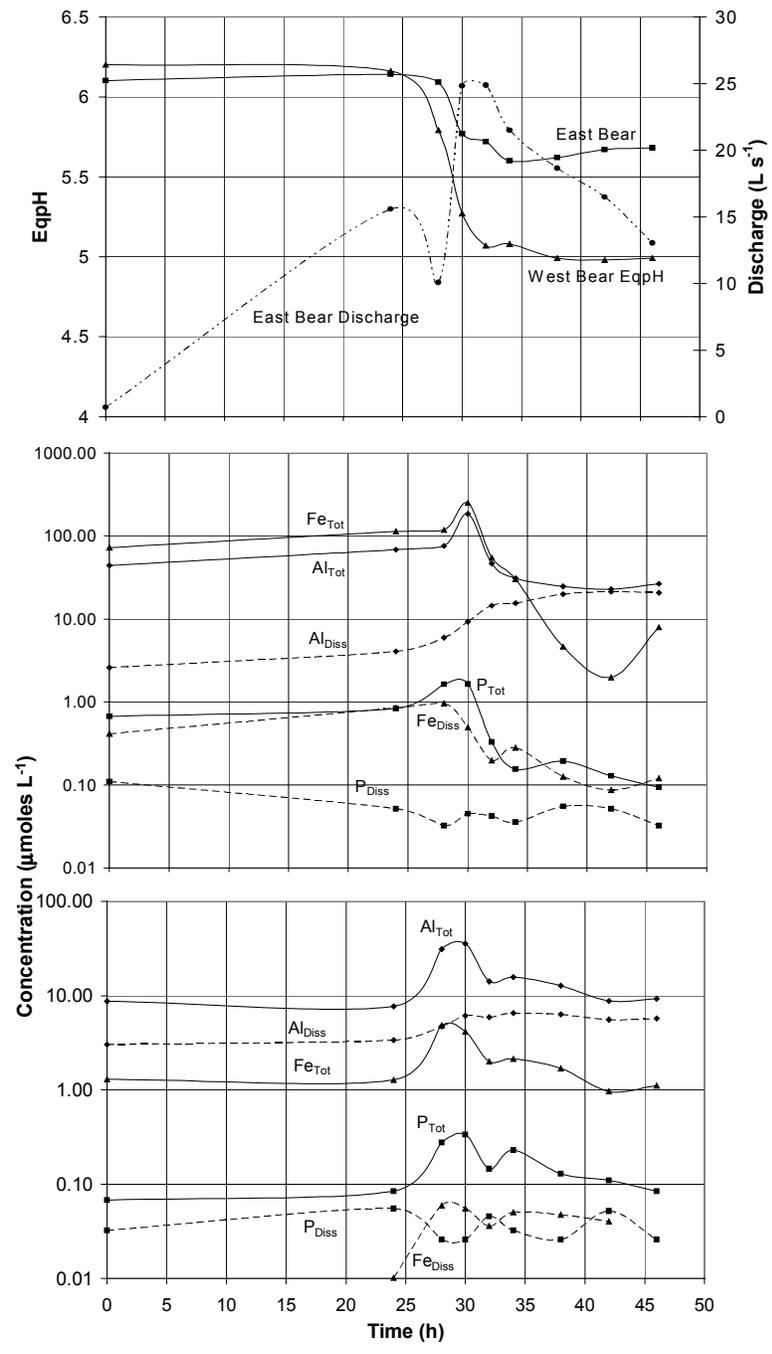


Figure 1.

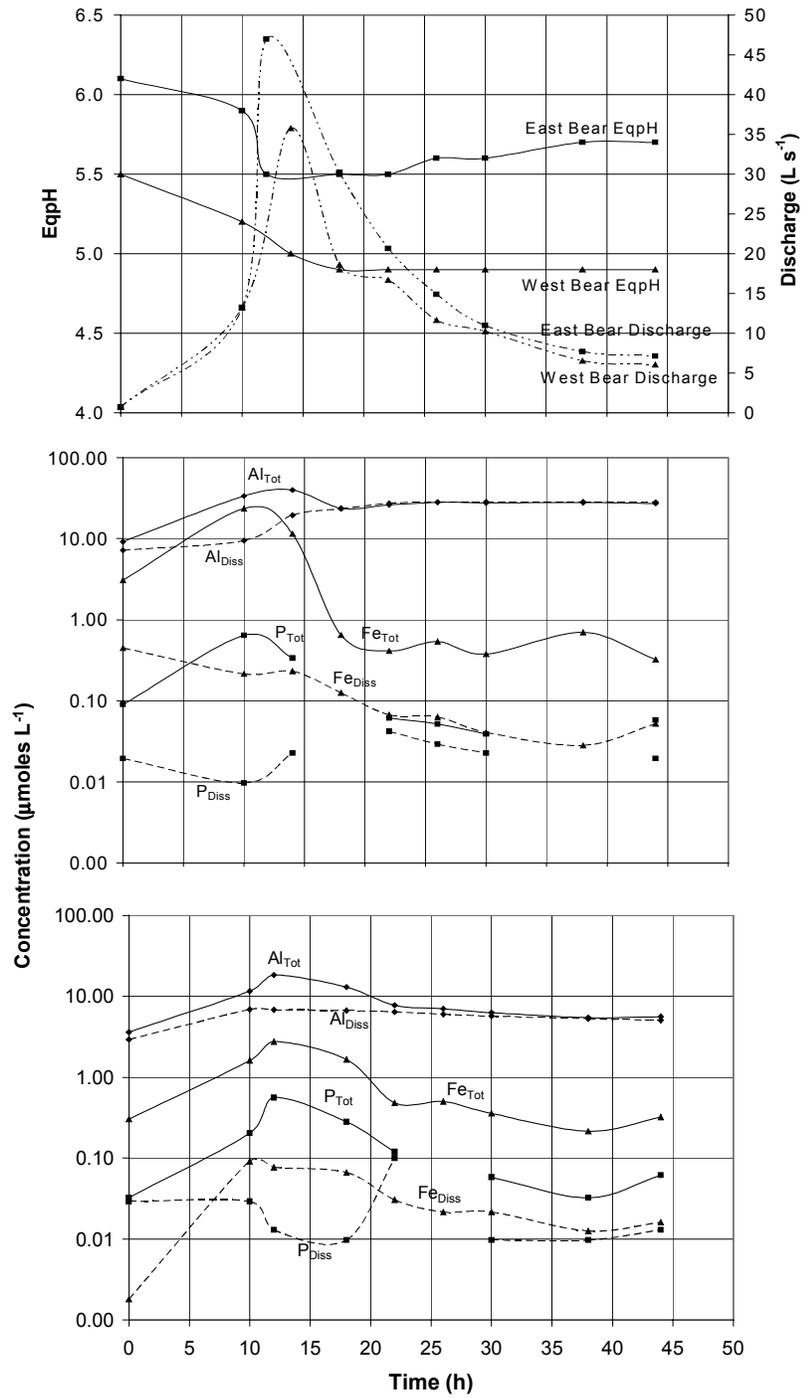


Figure 2

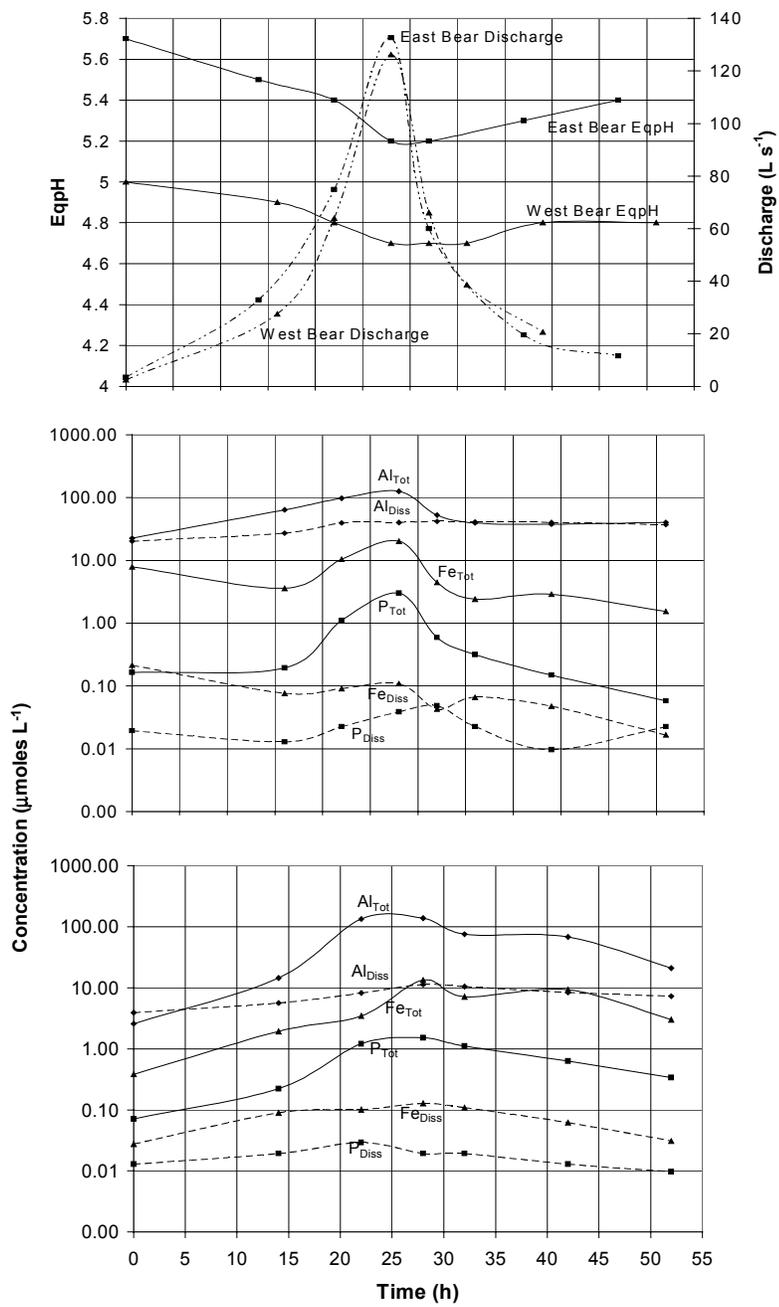


Figure 3

Table I  
West and East Bear Brook chemistry for February 26-28, 2002

Date	Time	Discharge	DOC	Ca, mM	Ca, mM	K, mM	K, mM	Mg, mM	Mg, mM	Na, mM	Na, mM
	h	L s <sup>-1</sup>	mg L <sup>-1</sup>	Total	Dissolved	Total	Dissolved	Total	Dissolved	Total	Dissolved
West Bear Brook											
26-Feb-2002	1600	2.46	1.75	0.054	0.055	0.007	0.007	0.020	0.020	0.095	0.095
27-Feb-2002	800	27.58	2.24	0.050	0.051	0.008	0.008	0.019	0.020	0.089	0.089
27-Feb-2002	1400	64.00	2.66	0.050	0.048	0.013	0.012	0.021	0.020	0.096	0.096
27-Feb-2002	2000	126.15	3.47	0.064	0.050	0.020	0.016	0.022	0.021	0.087	0.087
28-Feb-2002	0	66.09	3.08	0.052	0.051	0.014	0.013	0.021	0.022	0.084	0.084
28-Feb-2002	400	38.74	2.89	0.050	0.051	0.012	0.012	0.021	0.021	0.095	0.095
28-Feb-2002	1200	20.67	2.52	0.050	0.051	0.011	0.011	0.021	0.021	0.090	0.090
1-Mar-2002	0	11.67	2.22	0.051	0.051	0.009	0.009	0.021	0.021	0.084	0.084
East Bear Brook											
26-Feb-2002	1600	3.45	2.09	0.031	0.032	0.004	0.003	0.012	0.012	0.077	0.077
27-Feb-2002	600	32.90	2.54	0.030	0.031	0.005	0.005	0.012	0.012	0.079	0.079
27-Feb-2002	1400	74.95	3.41	0.039	0.029	0.008	0.007	0.013	0.012	0.076	0.076
27-Feb-2002	2000	132.55	4.17	0.031	0.025	0.010	0.008	0.011	0.011	0.066	0.066
28-Feb-2002	0	59.95	3.49	0.030	0.025	0.008	0.007	0.011	0.011	0.070	0.070
28-Feb-2002	1000	19.62	2.96	0.030	0.026	0.006	0.007	0.011	0.011	0.074	0.074
28-Feb-2002	2000	11.67	2.72	0.028	0.026	0.006	0.005	0.011	0.011	0.069	0.069

# Response of surface water chemistry to the Clean Air Act Amendments of 1990

## Basic Information

<b>Title:</b>	Response of surface water chemistry to the Clean Air Act Amendments of 1990
<b>Project Number:</b>	2001ME12O
<b>Start Date:</b>	10/1/1999
<b>End Date:</b>	7/31/2003
<b>Funding Source:</b>	Supplemental
<b>Congressional District:</b>	2
<b>Research Category:</b>	Climate and Hydrologic Processes
<b>Focus Category:</b>	Acid Deposition, Surface Water, Water Quality
<b>Descriptors:</b>	Clean Air Act, Acid Deposition, Surface Water Quality
<b>Principal Investigators:</b>	Jeffrey S Kahl

## Publication

1. Stoddard, John L., Jeffrey S. Kahl, Frank A. Deviney, David R. DeWalle, Charles T. Driscoll, Alan T. Herlihy, James H. Kellogg, Peter S. Murdoch, James R. Webb, and Katherine E. Webster, 2002, Response of surface water chemistry to the Clean Air Act Amendments of 1990, U.S. EPA (report number pending).

## Response of surface water chemistry to the Clean Air Act Amendments of 1990

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September 30, 2002

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## EXECUTIVE SUMMARY

### Response of surface water chemistry to the Clean Air Act Amendments of 1990

SEPTEMBER 30, 2002

**Purpose of this report.** Title IV of the 1990 Clean Air Act Amendments (CAAA) set target reductions for sulfur and nitrogen emissions from industrial sources as a means of reducing the acidity in deposition. One of the intended effects of the reductions was to decrease the acidity of low alkalinity waters and thereby improve their biological condition. *The purpose of this report is to assess recent changes in surface water chemistry in the northern and eastern U.S., in response to changes in deposition.* The regions covered in this report are New England (sites in Maine, New Hampshire, Vermont and Massachusetts), the Adirondack Mountains of New York, the Northern Appalachian Plateau (New York, Pennsylvania and West Virginia), the Ridge and Blue Ridge provinces of Virginia, and the Upper Midwest (Wisconsin and Michigan). The data covered in this report are from 1990 through 2000, the period since the last major science review by the National Acidic Precipitation Assessment Program (NAPAP).

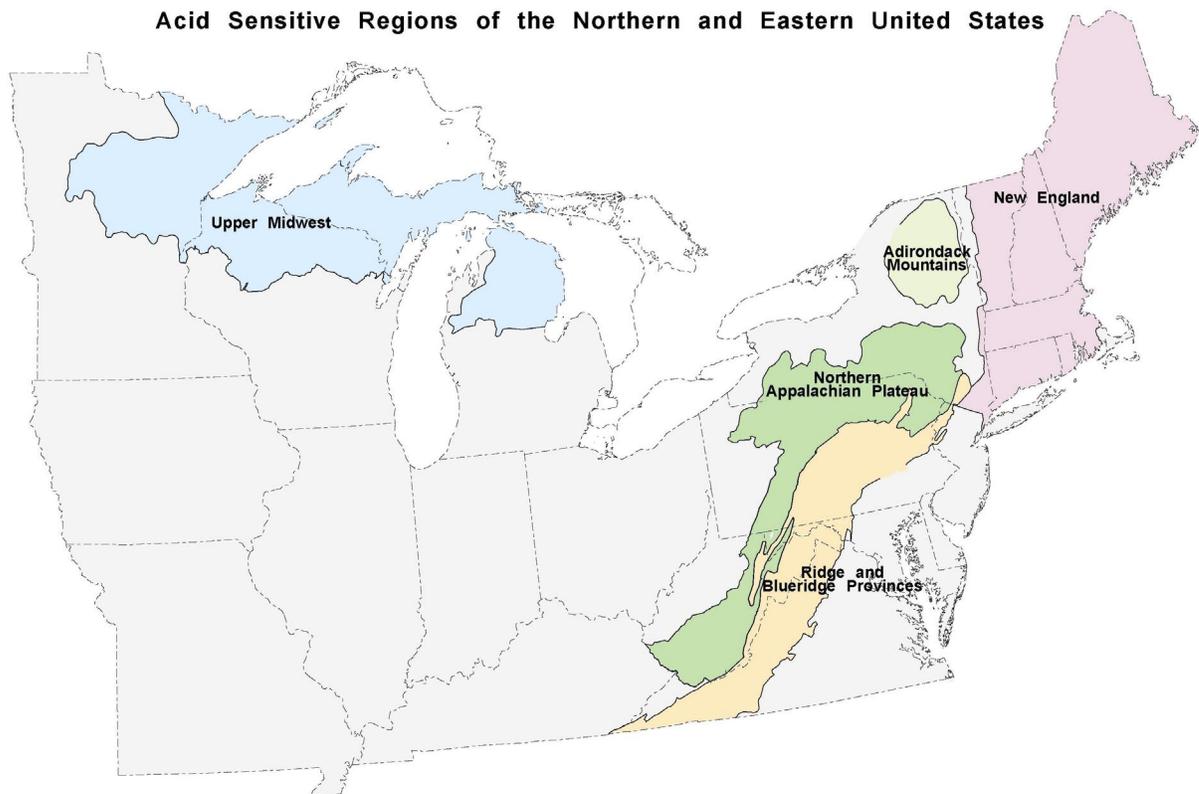


Figure A. Acid sensitive regions of the northern and eastern United States; this report assesses trends in surface waters in each of these regions.



Substantial reductions in emissions of sulfur have occurred in the past 30 years, with the rate of decline accelerated by Phase I of the 1990 CAAA, implemented in 1995. Modest reductions in nitrogen emissions have occurred since 1996. The key questions are a) whether the declines in emissions translate into reductions in acidic deposition; and b) whether biologically-relevant water chemistry has improved in acid sensitive regions. The measures of expected 'recovery' include decreased acidity, sulfate, and toxic dissolved aluminum concentrations.

**Anthropogenic acidity in atmospheric deposition.**  $\text{NO}_x$  and  $\text{SO}_x$  from the combustion of fossil fuels react with water in the atmosphere to produce 'acid rain', a dilute solution of nitric and sulfuric acids. This acidity (and the acid anions sulfate and nitrate) may travel hundreds of miles before being deposited on the landscape. The northern and eastern U.S. receives precipitation with mean pH that ranges from 4.3 in Pennsylvania and New York, to 4.8 in Maine and the Upper Midwest. The acidity (hydrogen ion concentration) in precipitation in the eastern U.S. is at least twice as high as in pre-industrial times. Atmospheric deposition is one of the most ubiquitous non-point sources of chemicals to ecosystems.

**Acid-base status of surface waters.** The 1984-86 EPA National Surface Water Survey (NSWS) estimated the number of acidic waters at 4.2% of lakes and 2.7% of stream segments in acid-sensitive regions of the North and East. 'Acidic' waters are defined as having acid neutralizing capacity (ANC) less than zero (i.e. no acid buffering capacity in the water), corresponding to a pH of about 5.2.

This report addresses the recent chemical responses in the surface waters in five regions of the North and East that are considered sensitive to acidic deposition. The data in this report are largely from the EPA Long Term Monitoring (LTM) and the EPA Temporally Integrated Monitoring of Ecosystems (TIME) projects, part of EMAP (Environmental Monitoring and Assessment Program). The regions include lakes in the Adirondacks, central and northern New England, and the upper Midwest. Sensitive regions with small streams are found in the mid-Atlantic region, including the northern and central Appalachian Plateau and the Ridge and Blue Ridge provinces. Surface waters in most other regions are not sensitive to the impacts of acidification due to the nature of the local geology.

**Recent changes in atmospheric deposition.** We evaluated the changes in atmospheric deposition from the five regions during 1990-2000, using National Atmospheric Deposition Program (NADP) data. Sulfate declined significantly at a rate between -0.75 and -1.5  $\mu\text{eq/L/year}$ . There was a sharp drop in sulfate concentrations in 1995 and 1996, followed by a modest increase in 1997-2000, in parallel with emissions. Nitrogen (nitrate + ammonium) declined slightly in the Northeast, and increased slightly in the Upper Midwest; most of these changes can be attributed to changes in nitrate deposition. Base cations in deposition, which are important for the neutralization of acidity in precipitation and in watersheds, showed no significant changes during the decade in the East, and increased slightly in the Upper Midwest. These changes in deposition are a continuation of trends that pre-date the 1995 implementation of Phase I of the CAAA,

and are consistent with other recent published analyses of changes in regional deposition patterns.

**Recent changes in acid base status in surface waters.** All regions except the Ridge/Blue Ridge province in the mid-Atlantic showed significant declines in sulfate concentrations in surface waters, with rates ranging from -1.5 to -3  $\mu\text{eq/L/year}$  (Figure B). These declines were consistent with the decline in sulfate in precipitation. Nitrate concentrations decreased in two regions with the highest ambient nitrate concentration (Adirondacks, Northern Appalachian Plateau), but were relatively unchanged in regions with low concentrations. Dissolved Organic Carbon (DOC) increased in each region, potentially contributing natural organic acidity to offset the recovery from decreased acidity and sulfate in deposition.

Acid neutralizing capacity is a key indicator of recovery, as it reflects the capacity of watersheds to buffer inputs of acidity. We expect increasing values of either ANC, pH, or both, in response to decreasing deposition of sulfur and nitrogen from the atmosphere. ANC increased in three of the regions (Adirondacks, Northern Appalachian Plateau and Upper Midwest) at a rate of +1 to +2  $\mu\text{eq/L/year}$ , despite a decline in base cations (calcium + magnesium) in each region (Figure B). The decline in base cations offsets some of the decline in sulfate, and thus limits the increase in ANC or pH. In the Adirondacks, surface water ANC and pH both increased significantly in the 1990s, and toxic aluminum concentrations declined slightly. Regional surface water ANC did not change significantly in New England or in the Ridge/Blue Ridge.

## Regional Trends, 1990-2000 (in lakes and streams)

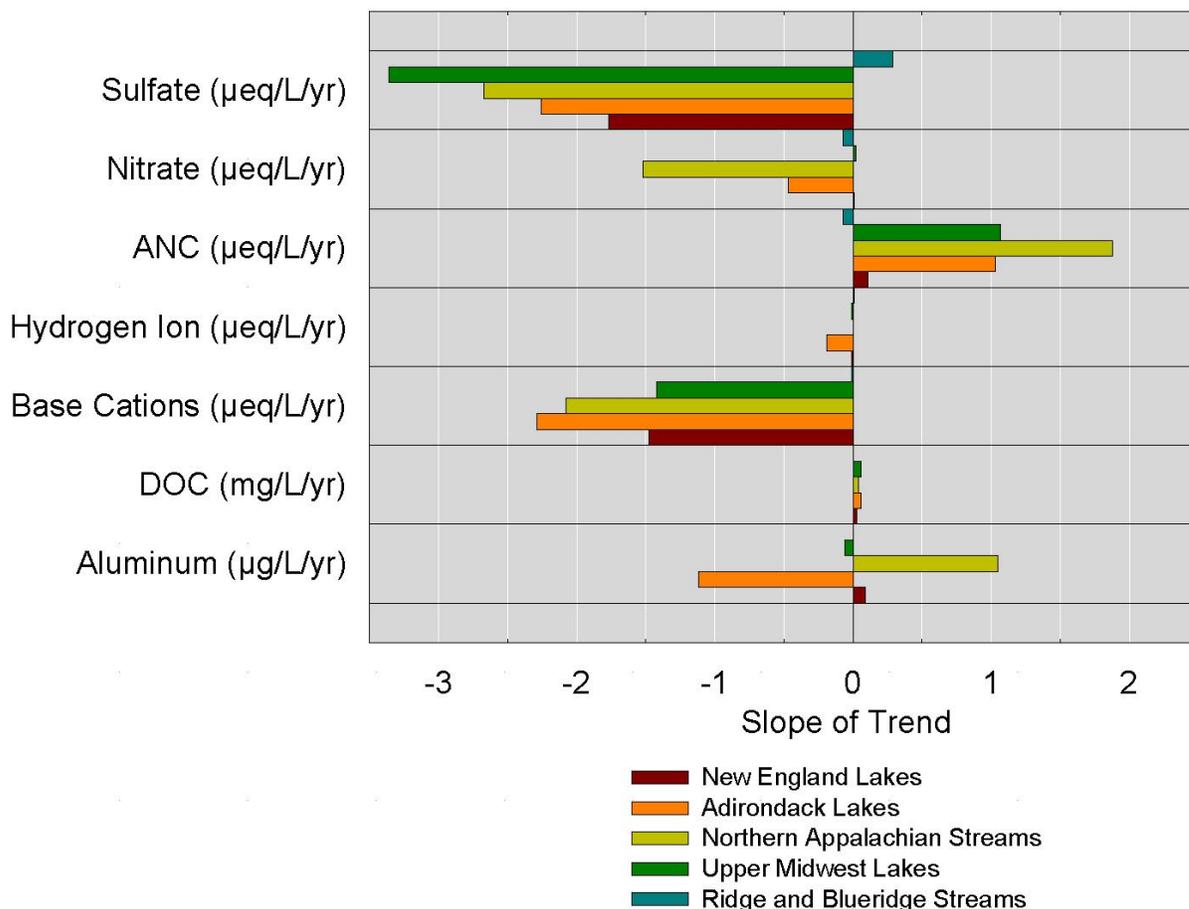


Figure B. Summary of regional trends in surface water chemistry in regions covered by this report.

**Has the number of acidic waters changed?** Modest increases in ANC have reduced the number of acidic lakes and stream segments in some regions. We estimate that there are currently 150 Adirondack lakes with ANC less than 0, or 8.1% of the population, compared to 13% (240 lakes) in the early 1990s. In the Upper Midwest, an estimated 80 of 250 lakes that were acidic in mid-1980s are no longer acidic. TIME surveys of streams in the northern Appalachian Plateau region estimated that 5,014 kilometers of streams (ca. 12%) were acidic in 1993-94. We estimate that 3,393 kilometers of streams, or 7.9%, remain acidic in this region at the present time. *In these three regions, approximately one-third of formerly acidic surface waters are no longer acidic, although still with very low ANC.* We find little evidence of a regional change in the acidity status of New England or the Ridge/Blue Ridge regions, and infer that the numbers of acidic waters remain relatively unchanged. There is no evidence that the number of acidic waters has increased in any region, despite a general decline in base cations and a possible increase in natural organic acidity.

**Do changes in deposition translate into changes in surface waters?** A major goal of this assessment is to evaluate the effectiveness of emission reductions in changing surface water chemistry. We only make this assessment for sulfate, because changes in the deposition of nitrogen have been minor. In New England, the Adirondacks and the Northern Appalachians, the percent declines in sulfate concentrations in precipitation were generally steeper than in surface waters. This is largely as expected, and suggests that, for a majority of aquatic systems, sulfate recovery exhibits a somewhat lagged response. However, the lakes and streams with the steepest declines in sulfate had very similar rates to those in deposition, indicating that the *most responsive* watersheds responded directly and rapidly to the sulfate decrease in deposition. As expected, there was little correspondence between rates of sulfate decline in streams and deposition in the Ridge and Blue Ridge provinces, due to the adsorptive capacity of the soils in the region. In the upper Midwest, the rate of decline in lakes was *greater than* the decline in deposition, probably reflecting the residual effects of the drought of the late 1980s. Longer term, we expect the chemistry of seepage lakes in the Upper Midwest to mirror the decline in deposition, similar to the pattern seen in seepage lakes in New England that did not experience the 1980s drought.

**Complications for assessing ‘recovery’.** Declines in atmospheric deposition of sulfate have led to nearly universal declines in sulfate concentrations in surface waters. This response is one simple measure of the intended recovery in surface waters, and marks a success of the CAAA and efforts by industry in reducing SO<sub>2</sub> emissions. However, the anticipated decrease in acidity corresponding to the decline in sulfate has been modest.

It is important to recognize that *recovery will not be a linear process*. Moreover, the changes in surface water chemistry reported here have occurred over very short periods relative to the implementation of the CAAA emission reductions in 1995. The decline in sulfate is without question due to the decline in emissions and deposition, but mechanisms producing other changes are much less clear. Other responses in surface waters may be partially attributable to factors other than atmospheric deposition, such as climate change and forest maturation. In particular, some of the observed increase in ANC may result from decreases in nitrate concentrations (e.g., in the Adirondacks and Northern Appalachian Plateau); changes in nitrate are unrelated to changes in nitrogen deposition, and are not expected to continue. If the trend toward lower nitrate in surface water reverses, some of the gains in ANC may be lost.

We can identify at least five factors that are important in determining the recovery, or lack of recovery, in surface waters of the northern and eastern U.S. Continued long-term research and monitoring will be necessary to understand the causes, effects, and trends in these processes.

- 1) Base cations. We report declining surface water concentrations of base cations (e.g. calcium, magnesium) in all of the glaciated regions in this report (the Ridge and Blue Ridge region is the only non-glaciated region). At some individual sites, further acidification has occurred because base cations are declining more steeply than sulfate. While decreases in base cation loss from watersheds probably indicates slower rates of soil acidification, they none-the-less limit the

magnitude of surface water recovery. Continued long-term research at acid-sensitive sites is needed to determine the cause and effect of the relationship between base cations and sulfate, and the effects of cation loss on soil and surface water recovery.

- 2) Nitrogen. Continued atmospheric loading of nitrogen may be influencing the acid-base status of watersheds in yet undetermined ways. Unlike sulfate, concentrations of nitrogen in deposition have not changed substantially in 20 years. Also unlike sulfate, most nitrogen deposited from the atmosphere is retained in watershed soils and vegetation; nitrogen sequestration is not expected to continue *ad infinitum* (Stoddard 1994, Aber et al. in press). We report that surface water nitrate concentrations are largely unchanged, except in two regions characterized by high nitrate concentrations a decade ago (Adirondacks, Northern Appalachian Plateau). The mechanisms behind these decreases in nitrate are not understood, and could include climate change, forest maturation, and the effects of land-use history. Future increases in nitrate concentrations in all regions are not improbable, and would retard recovery if other factors remain constant.
- 3) Natural organic acidity. Increases in dissolved organic carbon in acid-sensitive waters may have contributed additional natural organic acidity to surface waters, complicating our interpretation of the response in acidity. This factor is an important long-term research question that is probably linked to complex issues including climate change and forest maturation.
- 4) Climate. Climatic fluctuations induce variability in surface water chemistry, and thus obscure changes that we expect to result from declining acidic deposition. Climate or climate-related processes may counteract recovery by producing declines in base cations to offset a decline in sulfate, or by inducing an increase in natural organic acidity. These interactions of factors underscore the need to continue monitoring a subset of sensitive systems so as to understand the full suite of drivers and responses in ecosystems.
- 5) Lag in response. Documentation of the response of watersheds to changes in atmospheric deposition may take longer than the timeframe of available data. Recovery itself may have an inherent lag time, beyond the time scale of currently available monitoring data. Moreover, the changes observed are not unidirectional. Uncertainty with respect to timeframes can only be resolved with continued long-term data.

**Indicators of recovery.** A main goal of the Title IV of the CAAA is to decrease the acidity of affected surface waters. Although decreases in acidity have occurred in several regions, additional factors appear to point toward recovery, *forecasting* an improvement in biologically-relevant surface water chemistry. It is not yet clear if further reductions in emissions and deposition will be necessary for widespread recovery to occur. These factors forecast the onset of recovery:

- a) Sulfate is an increasingly smaller percentage of total ion concentration in surface waters.

- b) ANC has increased modestly in three of the five regions.
- c) Dissolved Organic Carbon has increased regionally, perhaps toward a more natural pre-industrial concentration as acidity decreases in surface waters.
- d) Toxic aluminum concentrations appear to have decreased slightly in some sensitive systems.

**Expectations for recovery.** An important consideration for measuring the success of the CAAA is to have appropriate expectations for the *magnitude* of potential recovery. Lakes inferred to have been measurably acidified by atmospheric deposition were already marginally acidic, typically with pH less than 6, before anthropogenic atmospheric pollution began more than 100 years ago. Therefore, full recovery of acidic lakes will not yield neutral pH. However, there is evidence that DOC will increase during recovery, and both increasing DOC and increasing pH values will lower the toxicity of aluminum. This change may allow recovery of fish populations to historical conditions even if pH remains low.

**Recommendations.** In the North and East, there is evidence of recovery from the effects of acidic deposition. The complexities of ecosystem response – effects of forest health, soil status, natural organic acidity, the relative importance of sulfur vs. nitrogen deposition, future emission/deposition scenarios – make predictions of the magnitude and timing of further recovery uncertain. The results of this trend analysis suggest two recommendations for environmental monitoring:

- 1) Deposition monitoring: The analyses in this report depended heavily on the long-term NADP/NTN program for monitoring the chemistry of precipitation. The future assessment of deposition and aquatic trends will depend heavily on these data, and therefore our recommendation is to maintain a national precipitation chemistry network.
- 2) Surface water monitoring: The effectiveness of current or future amendments to the Clean Air Act can best be determined by monitoring the response of subpopulations of sensitive surface waters through time. Long-term records provide the benchmark for understanding trends in ecological responses. The reviewers of early drafts of this report strongly urged the authors to recommend the continuation of the long-term research programs upon which this report is based, and the addition of biological monitoring to begin documenting potential biotic recovery.

**Future research.** The data from these long-term sites will be invaluable for the evaluation of the response of forested watersheds and surface waters to a host of research and regulatory issues related to acidic deposition, including soil and surface water recovery, controls on nitrogen retention, mechanisms of base cation depletion, forest health, sinks for sulfur in watersheds, changes in DOC and speciation of aluminum, and various factors related to climate change. As one reviewer of this report noted, *“these sites have irreplaceable long-term data that should constitute a ‘research infrastructure’ akin to an EPA laboratory. These sites will help address many basic science issues in which EPA ORD has a continuing interest.”* Moreover, as several of the reviewers

observed, long-term data serve as the foundation for ecological research and modeling. Without such data, our ability to ask the right questions is reduced, and our ability to base the answers to these questions on actual data is likewise compromised

# **Information Transfer Program**

# Information Transfer

## Basic Information

<b>Title:</b>	Information Transfer
<b>Project Number:</b>	2001ME2921B
<b>Start Date:</b>	3/1/2001
<b>End Date:</b>	2/28/2002
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	2nd
<b>Research Category:</b>	Not Applicable
<b>Focus Category:</b>	Education, None, None
<b>Descriptors:</b>	Information Transfer, Education
<b>Principal Investigators:</b>	Jeffrey S Kahl, John M. Peckenham

## Publication

We have organized our Information Transfer efforts into three sections: Publications, Conferences, and Public Service.

### **Publications**

Kahl, J.S., C. Gray, J. Grimalt, K. Tonnessen, and J. Wiener, 2002. NPS Western Airborne Contaminants Assessment Project; report of the review panel. 14 p.

Stoddard, J., J.S. Kahl, and others, 2002. Response of surface water chemistry to the Clean Air Act Amendments of 1990; Report to Congress. US EPA, Washington DC. 74 p.

Amirbahman, A., A. Reid, T. Haines, J.S. Kahl, and C. Arnold, 2002. Association of Methylmercury with Dissolved Humic Acids. *Environ. Sci. Technol.* 36:690-695.

Pellerin, B., I Fernandez, S. Norton, and J.S. Kahl, 2002. Soil aluminum distribution in the near-stream zone at the Bear Brook Watershed. *Water Air Soil Pollut* 134:189-204.

Peckenham, J. M., S. Nelson, and S. Kahl (2002). Water Chemistry Trends in New England Lakes, report to the New England Governors and Eastern Canadian Premiers' Acid Rain Steering Committee, 10 p.

Peckenham, J.M. (2002) The occurrence and persistence of MtBE in groundwater in Windham, Maine, NE FOCUS Conf. On Groundwater Issues, October 3, 2002.

Schmitt, C. and J.M. Peckenham (2002) Drought and drinking water: How sensitive are Maine's surface water supplies?, NE FOCUS Conf. On Groundwater Issues, October 3, 2002.

C. Schmitt and J.M. Peckenham (2002) Public Law 761: Protecting Maine's Drinking Water, *Maine Geograph. Digest Ser.*, 4 p.

Kahl, J. S., 2002. 'How Maine lakes work'. Invited talk in special session on lakes, Maine Water Conference, May, 2002.

Kahl, J.S., 2001. Indicators of recovery from acidification (or not) in surface waters of the northeastern US. Gordon Research Conference on Biogeochemistry of Forested Watersheds, July, 2001 (invited plenary talk).

Kahl, J. S., 2002. 'How Maine lakes work'. Invited talk in special session on lakes, Maine Water Conference, May, 2002.

Kahl, J.S., 2001. Indicators of recovery from acidification (or not) in surface waters of the northeastern US. Gordon Research Conference on Biogeochemistry of Forested Watersheds, July, 2001 (invited plenary talk).

Kahl, J. S., 2002. 'How Maine lakes work'. Invited talk in special session on lakes, Maine Water Conference, May, 2002.

Kahl, J.S., 2001. Indicators of recovery from acidification (or not) in surface waters of the northeastern US. Gordon Research Conference on Biogeochemistry of Forested Watersheds, July, 2001 (invited plenary talk).

Peckenham, J. M. and G. Zielinski (2002). 'Climate and the Future of Water Use/Availability' invited talk in special session on extreme hydrologic events, Maine Water Conference, May 9, 2002.

Peckenham, J. M. (2001). 'Planning for Future Water Use and Availability', Our Future Water Supply- Is There Cause For Concern, St. Lawrence River Inst., May, 2001

### **Conferences, Workshops, Annual Meetings**

All Research In Acadia Meeting, University of Maine, Orono, Maine. February 28, 2001. Organized by the Water Research Institute and Acadia National Park, this meeting was a platform for all researchers conducting projects at Acadia National Park. The goal of this meeting was to share research information and to foster cooperative studies.

Maine Water Conference 2001. Augusta Civic Center, Augusta, ME. May 3, 2001. The Maine Water Conference was founded in 1994 by the University of Maine Water Research Institute as an annual forum for water resource professionals, researchers, consultants, citizens, students, regulators, and planners to exchange information and present new findings on water resources issues in Maine. This years conference featured five afternoon sessions including: Atmospheric Deposition, Drinking Water and Health, Stream and River Water Quality, How Wetlands Work, Invasive Aquatic Plants, and Juried Student Posters.

Protecting Maine's Drinking Water, Six regional workshops on Source Water Protection for small public drinking water systems. This educational series was organized with the US EPA-Region I, New England Interstate Water, Pollution Control Commission, Maine Drinking Water Program, and Maine Department of Environmental Protection, and sponsored by the New England Water Works Association.

### **Public Service.**

Expanding Your Horizons, March 2001. The Mitchell Center participated in the EYH program giving laboratory tours to groups of 7th and 8th grade girls from Maine school systems. This program encourages participation in Science and Math disciplines by introducing them to career opportunities in these fields.

Boston Globe, March 2001. Article on acid rain research conducted at the Center.

Maine Times, October and November 2001. Articles about the Mitchell Center.

Testimonial: Mercury Products Advisory Council. Kahl, S. Mercury in Water in Maine various meetings.

#### Committees and Service:

##### Kahl

Gubernatorial appointment: *Mercury Products Advisory Commission*  
Gubernatorial appointment: *River Flow Advisory Commission*  
Gubernatorial appointment: *co-chair, Council on Environ. Monitoring and assessment*  
Board of Advisors, *Maine Lakes Conservancy Institute*  
Board of Directors, *Maine Lake Volunteer Monitoring Program*  
Board of Directors, *Friends of Acadia National Park*  
New England Governors & Eastern Canadian Premiers 'acid rain' working group  
Downeast research-enhancement planning committee (*Eastern ME Development Corp*)  
*Eco-reserves monitoring advisory committee*, Maine DEP  
*Policy Advisory Committee*, gubernatorial candidate John Baldacci  
*Global Program of Action Coalition, Watershed Forum committee* (regional coalition)  
*Union River Watershed Coalition* (local agencies)  
*Atlantic Salmon Research and Information Management Committee* (multi-agency)  
*Headwater Streams Research Advisory Committee* (Forest Products Industry)  
Organizer, fourth third annual '*Aquatic Research in Acadia*' Symposium, Acadia NP.

##### Peckenham

Gubernatorial appointment (alternate): *Mercury Products Advisory Commission*  
Gubernatorial appointment (alternate): *River Flow Advisory Commission*  
Board of Directors, *Penobscot River and Bay Institute*  
*Maine DEP-Consulting Engineers of Maine Task Force*  
*Water Resources Committee*, Maine Water Utilities Association  
*Watershed Committee*, Maine DEP and USEPA Region I  
*Union River Watershed Coalition* (local agencies)  
*Project S.H.A.R.E.* (multi-agency)  
*Northern Maine Children's Water Festival Committee*  
*Maine Water Conference Organizing Committee and Meeting Co-Chair 2000, 2001, 2002.*

Lakes resources online database, PEARL- continue improvement and new data added.

## Student Support

Student Support					
Category	Section 104 Base Grant	Section 104 RCGP Award	NIWR-USGS Internship	Supplemental Awards	Total
Undergraduate	2	0	0	0	2
Masters	10	1	1	0	12
Ph.D.	5	1	0	0	5
Post-Doc.	0	0	0	0	0
Total	17	2	1	0	19

## Notable Awards and Achievements

Bjorn Lake received a grant from the Maine Department of Environmental Protection to continue studies of dioxins in rivers in Maine.

## Publications from Prior Projects