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Introduction

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MtBE in Groundwater: The Maine Experiment

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The Persistence of MtBE in Groundwater in Windham, Maine, USA.

By: John M. Peckenham[1]

Abstract

A study was conducted on the occurrence and distribution of the fuel oxygenate MtBE (methyl *tert*-butyl ether) in a glacial sand and gravel aquifer in southern Maine. Ninety samples were collected from 31 different wells in the Windham aquifer, in North Windham, Maine, for analysis of MtBE between July 1998 and August 2001. MtBE was detected in 42 percent of the samples and 52 percent of the individual wells sampled. In addition, 92 percent of wells with detectable concentrations of MtBE were in an area of the aquifer designated as a "high-yielding" aquifer (Neil, 1998). Land uses were found to be associated with MtBE detection rates in the wells in the study area. The overall median concentration in wells with detectable MtBE was 1.85 μg/L. The mean concentration has risen from ~0.5 μg/L in April 1998 to 6.3 μg/L in August 2001. An analysis of the distribution and concentrations of MtBE that were detected in ground water indicates that recharge from precipitation containing MtBE is not a likely source. The strong association of MtBE with land use and aquifer transmissivity suggests a variety of potential land-based sources.

Introduction

The 1992 implementation of the 1990 Clean Air Act mandated oxygenated gasoline containing methyl *tert*-butyl ether (MtBE) in certain areas in the country to meet part of the Federal requirement of reducing VOC concentrations in Maine's air by 15 percent. The State of Maine elected to use reformulated gasoline (RFG) that contained at least 11 percent MtBE by volume (Maine Department of Human Services, 1995). In December 1994, RFG was introduced in southern Maine, in Kennebec, Sagadahoc, Androscoggin, Cumberland, York, Lincoln, and Waldo Counties and by 1995, oxygenated gasoline use was common in the northeast. Soon after the widespread use of gasoline containing MtBE began, water-quality surveys began detecting MtBE in ground water, often without the other sparingly soluble gasoline compounds—benzene, toluene, ethyl benzene, and xylenes (BTEX)—usually found in ground water near gasoline spills (Maine Department of Human Services, 1998).

MtBE has been detected in ground water in Maine as early as 1985. However, it was not until 1998 that evidence of widespread, low-concentration MtBE contamination in the ground water was documented, when several widely publicized instances of contamination in drinking-water wells prompted the State of Maine to conduct a random sampling of 951 private wells and nearly all the 830 non-transient public water supplies in the state of Maine. The sampling found

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MtBE in ground water in all parts of Maine, including areas not required to use RFG (Maine Department of Human Services, 1998). This study and additional studies by the U.S. Geological Survey (USGS) across the country documented low concentrations of MtBE in ground water, especially in urban areas (Zogorski et al., 1998) and in over 8 per cent of public drinking water supplies (Gullick and LeChevallier, 2000). The widespread occurrence of MtBE has prompted discussion about possible nonpoint sources of MtBE in ground water, especially precipitation and atmospheric deposition (Squillace, Pankow et al., 1996; Squillace, Zogorski, et al. 1996; Pankow at al., 1997; Lopes and Bender, 1998; Baehr at al., 1999; Moran et al., 1999). Few studies to date, however, have examined the persistence of MtBE, or how low MtBE concentrations in ground water respond to changes in gasoline formulations.

In 1998, the USGS in cooperation with Senator George J. Mitchell Center at The University of Maine, the Maine Department of Environmental Protection and the Town of Windham, Maine (Figure 1) began a study of MtBE in the Windham aquifer (Nielsen and Peckenham, 2000). The study was designed to collect information on the occurrence and distribution of low concentrations of MtBE (defined as less than 2 µg/L) in the aquifer, a shallow aquifer used for drinking water in an area in which RFG was used exclusively. In this report we evaluate the occurrence of MtBE in groundwater from 1998 during RFG use to 2001, two years after RFG use ceased. Additional sampling and analysis occurred in August 2001. Key objectives are to determine: (1) if MtBE is still detectable in groundwater post-RFG; (2) if the rates of detection and spatial patterns have changed over time; (3) if the spatial patterns relate to potential MtBE sources; and (4) if the concentrations of MtBE change uniformly over time.

Previous Investigations

In 1998, the State of Maine conducted a comprehensive survey of MtBE in ground water, which consisted of sampling 951 randomly selected domestic water wells and 793 of the 830 public supply wells (Maine Department of Human Services, 1998). MtBE was detected at concentrations greater than 0.1 µg/L in 15.8 percent of the residential wells and in 16.0 percent of the public supply wells. More than 90 percent of the detections of MtBE were below 1.0 µg/L. The data were interpreted with respect to well type, knowledge of a recent gasoline spill nearby, population density, and inclusion in the RFG area. No significant differences in MtBE occurrence were observed by well type (drilled bedrock wells compared to unconsolidated surficial wells) or among wells where there were known recent gasoline spills compared to those where there were no known spills (State of Maine, 1998). The State tested the risk of an MtBE occurrence associated with population density and whether or not the well was in a mandatory-RFG area. Both factors were statistically significant, when controlled for the other, in determining the risk of MtBE detections in domestic and public-supply wells. The reason for the smaller percentage of MtBE detections in higher density areas for public-supply wells where RFG was not required was not evident. MtBE detection rates for areas with more than 1,000 people/mi^2 were similar to those for the National Ambient Water Quality Assessment (NAWQA) studies (State of Maine, 1998).

Known and suspected sources of MtBE in ground water include point and non-point sources. Point sources include pipelines, storage tanks (above- and below-ground), accidental spillage, homeowner disposal, spillage during fueling, and waste motor oil. Heating-oil spills also have been identified as another source of some MtBE in ground water (Robbins et al., 1999). Suspected nonpoint sources include atmospheric deposition (recharge from precipitation or direct transport to ground water through gaseous diffusion), vehicle evaporative losses, and urban runoff (Moran et al., 1999; Baehr et al., 1999).

Point sources will cause locally elevated concentrations of MtBE and other related gasoline compounds. Point sources have the potential to generate very high concentrations of MtBE in water, up to 50,000 mg/L (Barker et al., 1991). The geochemical characteristics of point sources are: local effects with a limited area of contamination, steep concentration gradients with marked changes in concentrations away from source area, and consistent time-series changes in concentrations over time.

Non-point sources, most significantly direct precipitation and subsequent recharge of contaminated rainfall, and stormwater runoff primarily containing gasoline flushed from land surfaces, have been suggested as the source of some low levels of MtBE in ground water (Zogorski et al., 1998; Pankow et al., 1997). Concentrations of MtBE in ground water from non-point sources are limited to low levels, well below 20 µg/L (Moran et al., 1999).

Investigators in a small number of studies have attempted to use models to predict the behavior of aqueous phase MtBE once it starts to infiltrate the unsaturated zone (Johnson et al. 2000). Pankow et al. (1997) modeled various scenarios of recharge in a hypothetical aquifer to test the possibility that MtBE in precipitation could have traveled into shallow ground water during the time frame of its use as a gasoline additive. Assuming no attenuation, they found that it took just 14.3 in/yr of recharge to saturate ground water 6.5 feet below the water table with atmospheric levels of MtBE in 5 years. Baehr et al. (1999) developed a model to predict the concentration of MtBE at the water table, taking into account diffusion, recharge flux, thickness of the unsaturated zone, and several decay functions. They found that the concentration of MtBE at the water table is most sensitive to the thickness of the unsaturated zone and that the reason why MtBE is not universally detected in shallow ground water could be explained by variations in saturated thickness and recharge. Factors that may affect the degradation rate of MtBE, such as aquifer material composition, also would contribute to the heterogeneity of MtBE detection.

MtBE is also present at detectable levels in urban stormwater in areas where RFG was used (Delzer et al., 1996). MtBE was detected in more than 43 percent of stormwater samples collected for permitting requirements for urban stormwater runoff in areas with RFG use. The source of MtBE in the stormwater samples may be either gasoline washoff from paved surfaces or MtBE in the precipitation (Lopes and Bender, 1998). Modeling the behavior of MtBE and other BTEX compounds found in stormwater runoff, at concentrations of MtBE above 1.0 µg/L (the lower detection limit for samples in the study), showed that the source of MtBE was most likely dissolved gasoline entrained during the storm event and not precipitation. This was determined primarily by the co-occurrence of MtBE and other BTEX compounds in the storm-water runoff.

Windham Aquifer Hydrology

The Windham aquifer depicted in Figure 1 is a shallow, glacial sand and gravel aquifer in Cumberland County, southern Maine. It is mapped as a significant sand and gravel aquifer (Neil, 1998), with expected yields ranging from 10 to more than 50 gal/minute (38 to 189 L/m). The aquifer consists primarily of marine deltaic sand and gravel, interbedded in places with a marine silt/clay deposit. A buried esker lies in the northern part of the aquifer (Gerber, Inc., 1997). Thickness of the aquifer ranges from approximately 10 feet to more than 120 feet (3 to 37 m), and depth to water in the aquifer ranges from 5 feet to more than 50 feet (1.5 to 15 m). Hydraulic conductivities calculated from slug tests (Bouwer and Rice, 1976) range from less than 1 foot/day to more than 400 feet/day (0.7 to 122 m/d) (W.J. Nichols, U.S. Geological Survey, written commun., 1999). Average hydraulic conductivities used in a calibrated model of the aquifer (Gerber, Inc., 1997) are 250 feet/day (76 m/d) in the buried esker; 44 feet/day (13 m/d) in the sand and gravel; 1.5 feet/day (0.46) in the till surrounding the aquifer; and less than 0.1 feet/day (0.03 m/d) in the marine silt/clay. Flow paths based on observed and modeled heads indicate recharge areas in the western and southwestern areas of the aquifer and discharge areas at Outlet Brook and on the edges of the aquifer (Gerber, Inc., 1997; W.J. Nichols, written commun., 1999). Some recharge also may come from Little Sebago Lake, a heavily developed lake that borders the Windham aquifer on the northeast.

Temperature data are available for Portland, Maine, 14 miles (22.4 km) southeast of Windham and the average annual temperature at Portland is 45.4°F (7.4°C) (Northeast Climate Center, 2002). Temperatures were consistently greater than the mean for 1998 (48.3°F/9.0°C), 1999 (47.9°/8.8°C), and 2001 (47.0°F/8.3°C). Average annual precipitation near Windham is 44.34 inches (1.12 m). Precipitation varied markedly from the mean for the study years 1998 (54.77 inches/ 1.39 m), 1999 (40.70 inches/1.03 m), and 2001 (32.93 inches/0.84 m).

The potential for MtBE-bearing precipitation to recharge the Windham aquifer depends on the amount of precipitation, amount of ground-water recharge, and average yearly and monthly temperatures. An estimate of the maximum amount of yearly recharge to sand and gravel aquifers can be calculated using average annual temperature to estimate evapotranspiration and precipitation (Lyford and Cohen, 1988). The estimated average annual temperature of 43°F (6.1°C) translates into an annual evapotranspiration of 19.5 inches (0.49 m). This evapotranspiration combined with an annual average precipitation of 44 inches (1.12 m) for the Windham area, yields a maximum potential recharge to the Windham aquifer of 22 in/yr (0.56 m). In the Windham area, some runoff is collected in detention basins that route runoff from paved areas into ground-water recharge zones and some is surface runoff.

Methods

Ground-water samples

An existing network of shallow wells (Figure 1), installed by the USGS and distributed throughout the ground-water flow system in the Windham aquifer was used for this study (Nichols and Silverman, 1998). These wells are completed in different types of glacial sediments. Samples were collected in July and August 1998 in 31 wells; subsequent sampling rounds in November and December 1998, April and May 1999, and August 2001, included a smaller number of wells (Table 1). Well depths ranged from 19 to 132 feet (5.8 to 40 m), with screened interval depths ranging from 8 to 130 feet (2.4 to 39.6 m). Screened intervals were mostly 5 or 10 feet (1.5 to 3.0 m) long, with a few wells having longer screens, up to 30 feet (9.1 m). Depth to water in the wells at the time of sampling ranged from 4.5 to 61.1 feet (1.37 to 18.6

m). All the wells are completed in unconfined parts of the aquifer; the sampling points range from water-table position to more than 110 feet (33.5 m) below the water table. Seven pairs of nested wells were sampled to evaluate vertical distributions of MtBE. The dominant land cover (Table 1) near each well was determined from the NLCD land-cover classification: urban, undeveloped, or low-density residential**.**

USGS National Water Quality Assessment protocols for sampling ground-water wells (Koterba et al., 1995) were followed in sample handling, quality assurance/quality control (QA/QC), sampling equipment, and cleaning. The USGS protocols were modified, however, to follow the U.S. Environmental Protection Agency (USEPA) low-flow (minimal drawdown) sampling procedures (Puls and Barcelona, 1995). A small number of wells did not yield enough water to meet the minimum drawdown requirements. These wells were pumped dry and sampled the next day.

The sampling equipment setup was simplified from USGS protocols to reflect what was necessary for the small number of constituents sampled in this study. A submersible Fultz 300R pump with Teflon-lined tubing was used to collect samples. The Teflon outflow tube was connected to a Hydrolab flow-through cell for monitoring field parameters. Once field parameters stabilized as defined as a change of less than 5 percent for three consecutive measurements and drawdown was kept to within 20 percent of the standing head, the flow rate was measured and the sample collected. Flow rates were generally within the range of 0.026 to 0.11 gal/min (100 mL/min to 400 mL/min). Samples for analysis of VOCs (benzene, toluene, ethyl benzene, xylene, and methyl tert-butyl ether) were collected directly from the Teflon outflow tube into three 40-mL amber glass volatile organic analysis vials with septum tops and no air space. The collection method was modified in 2001 to minimize cross-contamination by using disposal polyethylene bailers following the purging of the wells. Samples were kept on ice and shipped within 24 hours to the USGS laboratory for analysis for the 1998 and 1999 samples and the Mitchell Center laboratory for the 2001 samples. After sampling, all the equipment was cleaned with a dilute Liquinox solution, rinsed with distilled water, rinsed with methanol, and rinsed again with distilled water. The pump and cleaned tubing were packed in plastic sheeting for transport between sites.

Quality assurance samples consisted of equipment blanks (15 percent of all samples), 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 shipped for analysis). In all, 26 percent of all the samples analyzed were QA/QC samples. During the initial round of sampling, deionized water created in the District laboratory was used for rinsing; this presented a problem, however, in that the water was later found to be contaminated with very low concentrations of VOCs. An additional round of samples was collected for all the environmental samples with VOC detections in the first round to eliminate the rinse water as a source of VOCs to the samples. Purchased distilled water was used for all additional sampling, and all sampling equipment and supplies were stored in a clean environment.

Detections of MtBE in the first round of samples (11 detections) were recoded as a “less than” value larger than the observed analytical result. For example, a detection in the first round of 0.42 µg/L would have been recoded to <0.5 µg/L, to make sure that the database did not contain detections of MtBE from potentially compromised samples. MtBE was also detected in subsequent sampling rounds in 9 of the 11 wells with in which it was detected in the first round. Statistical analyses were performed using SYSTAT ver. 9.

PERSISTENCE OF MTBE IN THE NORTH WINDHAM AREA

Analyses of the ground-water samples conclusively demonstrate that MtBE is widely distributed at low concentrations in the Windham aquifer. Additionally, time-series results indicate that MtBE is persistent and widespread throughout the aquifer.

MtBE in ground water

MtBE was detected in the majority of the water samples from the Windham aquifer. This result is based on analyses of 90 individual samples collected from 31 wells (Table 1). A cumulative total of one to four water samples were collected from each of the wells on different sampling dates in 1998, 1999, and 2001. Sixteen of the 31 wells sampled (52 percent) had at least one detection of MtBE (Table 1). MtBE was detected in 38 individual samples (42 percent of all samples), and the median concentration of MtBE was 1.85 µg/L (excluding the samples that were recoded as “less thans” from the first sampling round). MtBE was below the detection limit in 52 samples (58 percent); however, 13 of these samples had elevated detection limits at greater than 0.2 µg/L. Two of the three highest concentrations detected, 14.0 µg/L and 6.64 µg/L, were collected from the same well, CW 2012. This well is located in an urbanized area, close to a gasoline station. The single highest concentration, 38.7 µg/L, was detected in well CW 2004 located in a light-industrial and commercial area.

The detection of MtBE was accompanied by the detection of the other sparingly soluble BTEX compounds- benzene, or toluene in less than 10 percent of the samples. This observation is consistent with other findings of MtBE along with some BTEX in trace concentrations in Maine (State of Maine, 1998). Since 1998 the median concentration for detections has varied from 0.35 µg/L in 1998 to 2.17 µg/L in Winter 1998 to 0.50 µg/L in 2001 (Figure 2). Over the same period the mean MtBE concentration has increased consistently from 0.50 to 6.30 µg/L. This trend has been driven by a few high concentrations from the same group of three wells (CW 2004, CW 2005, and CW 2012).

To determine if there were any spatial patterns to the MtBE detections, the data were analyzed with respect to: depth of the sample within the aquifer; location of sample in either the high- or moderate-yielding parts of the aquifer as mapped by the Maine Geological Survey (Neil, 1998); and land cover. In addition, the association of MtBE with hydraulic conductivity (K) independent of aquifer yield zone was analyzed (Nielsen and Peckenham, 2000).

Fourteen of the wells sampled were paired wells screened in both the shallow and deep parts of the aquifer. Using the distribution of detections in the paired wells, a Chi-square test (Ott, 1993) failed to detect a significant difference between the concentrations of MtBE in shallow and deep parts of the aquifer. The probability of detecting MtBE is nearly equal in each well of a pair. An analysis of the entire sample population with respect to depth of sampling point shows a higher number of detections in the shallow parts of the aquifer as defined as <50 feet (15.2 m) deep, but there are still enough detections at depth to affect statistical significance.

To test the effect of aquifer transmissivity, the spatial distribution of MtBE detections was grouped according to location in the aquifer as either high-yield zone (i.e. wells are expected to produce more than 50 gal/min) or moderate-yield zone (i.e. wells are expected to produce between 10 and 50 gal/min), as mapped by the Maine Geological Survey (Neil, 1998). The high-yield zone had many more wells with detections (92 percent) compared to the moderate-yield zone (58 percent). These two subgroups are significantly different ($p = 0.05$). In this report, p-values less than 0.05 indicate that the null hypothesis of the test was rejected.

The wells in which MtBE was detected were grouped according to the land-cover classification defined as: undeveloped, urban, and low-density residential (Figure 2). Although the concentration of detected MtBE was not noticeably different among the groups, the frequency of MtBE detection was quite different. MtBE was detected in 83 percent of the samples collected from wells in the low-density residential area, in 50 percent of samples from the urban area, and in 60 percent of samples from the undeveloped areas. A Kruskall-Wallis test (Helsel and Hirsch, 1992) on the MtBE concentrations by land-cover classification showed that at least one group is significantly different from the others ($p = 0.013$) when compared by pairs. The significance level varied by collection date with the samples collected in the winter of 1998 exhibiting the greatest level of significance.

MtBE detections are more frequent in the areas of the aquifer with higher K values than in areas with lower K values. Hydraulic conductivity for each well, as determined by slug tests (W.J. Nichols, written commun., 1999) was compared to MtBE detections for wells having at least one detection per well. For this test, the wells were divided into two equal groups of K ranges: < 5 feet/day and > 5 feet/day. A 2x2 contingency table test (Chi-square test) shows a statistically significant difference ($p=0.049$) in the distribution of wells with detections in the two groups.

SUMMARY AND CONCLUSIONS

A study was conducted on the occurrence and distribution of the fuel oxygenate MtBE (methyl *tert*-butyl ether) in a glacial sand and gravel aquifer in southern Maine. Ninety samples were collected from 31 different wells in the Windham aquifer, in North Windham, Maine, for analysis of MtBE between July 1998 and August 2001. MtBE was detected in 42 percent of the samples and 52 percent of the individual wells sampled. In addition, 92 percent of wells with detectable concentrations of MtBE were in an area of the aquifer designated as a “high-yielding” aquifer (Neil, 1998). MtBE was much more commonly detected in wells with measured hydraulic conductivities more than 5 feet/d (1.5 m/d) than in wells with hydraulic conductivities less than 5 feet/d (1.5 m/d). Urban and low-density residential land uses were found to be associated with MtBE in the wells in the study area. The median concentration in wells with detectable MtBE was 1.85 μg/L.

Before Maine opted out of the RFG program in March 1999, median concentrations of MtBE in air at the North Windham site were 0.25 ppbv (Nielsen and Peckenham, 2000). According to this study, after Maine stopped using RFG, the median concentration in air dropped to 0.09 ppbv, but no MtBE was detected in the precipitation samples obtained after RFG phase-out. On the basis of the equilibrium partitioning of MtBE from the air into rain, the predicted average concentration of MtBE in rainfall during months when recharge typically takes place (October-December and March-April) is approximately 0.3 to 0.4 µg/L when Maine was using RFG and approximately 0.1 µg/L after the phaseout of RFG. The concentration before the phaseout would be detectable in ground water if the recharge reached the water table with no degradation of MtBE. After the phaseout, it is unlikely that MtBE from recharge would be detectable in ground water.

An analysis of the distribution and concentrations of MtBE that were detected in ground water indicates that recharge from precipitation containing MtBE is not a likely explanation for the occurrence of MtBE in the Windham aquifer. The mean concentration of MtBE detections in ground water has increased from ~0.5 µg/L in April 1998 to 6.3 µg/L in August 2001, while the median has been near 0.5 µg/L since Spring 1999. The strong association of MtBE with land use and aquifer transmissivity/hydraulic conductivity suggests land-based sources. The mechanisms by which MtBE enters the aquifer were not identified in this study. The Maine State study of MtBE tentatively identified very small spills of gasoline associated with filling of lawn-care equipment fuel tanks, recreational vehicle tanks, and automobile tanks as likely being responsible for the majority of the low levels of MtBE found. If true, MtBE should be detectable statewide in similar urban to suburban settings.

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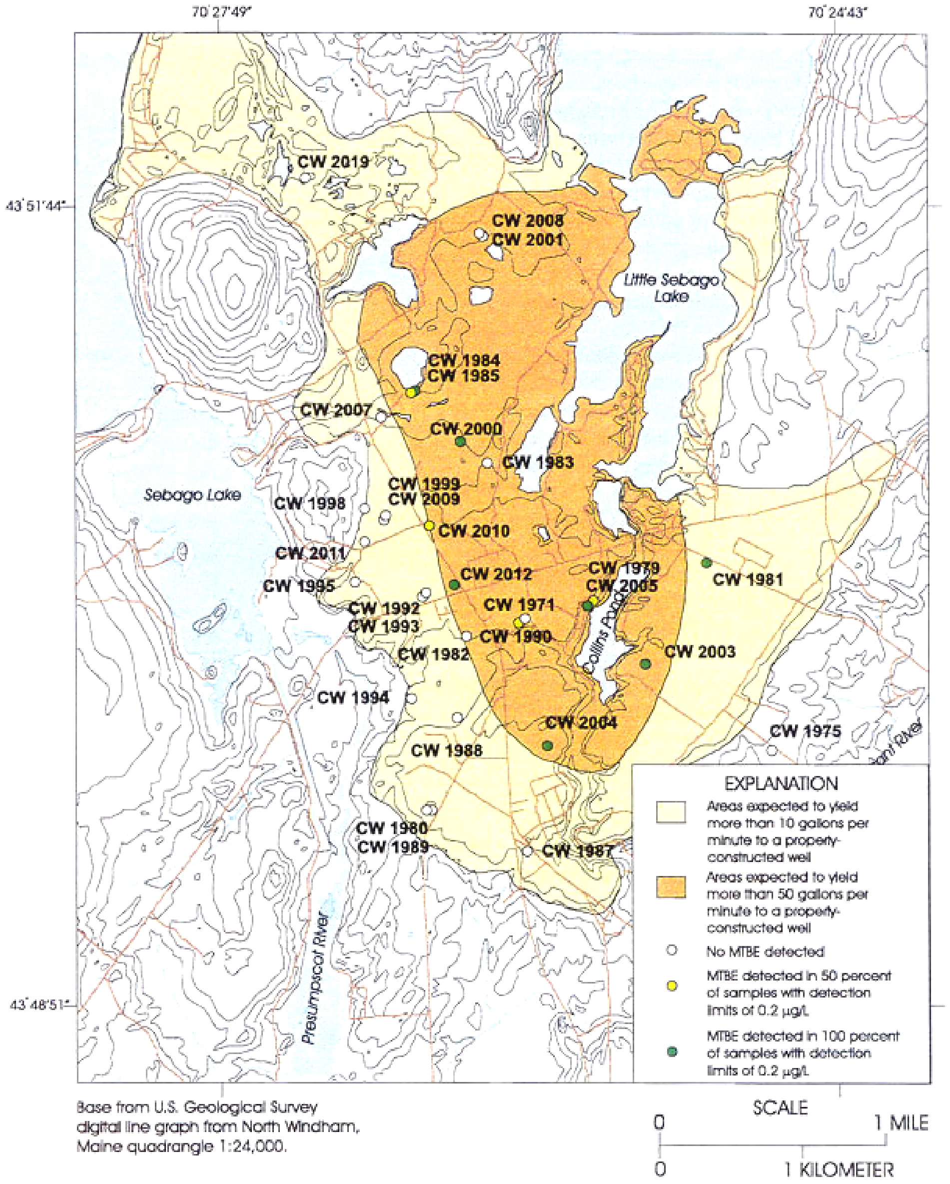
Figure 1. Location of Windham Aquifer and Groundwater Wells. Aquifer boundaries from Neil (1988), map based on Nielsen and Peckenham (2000).



Base from U.S. Geological Survey digital line graph from North Windham, Maine quadrangle 1:24,000.

Figure 2. MtBE Concentrations Summaries by Sample Date and Land Use Category.

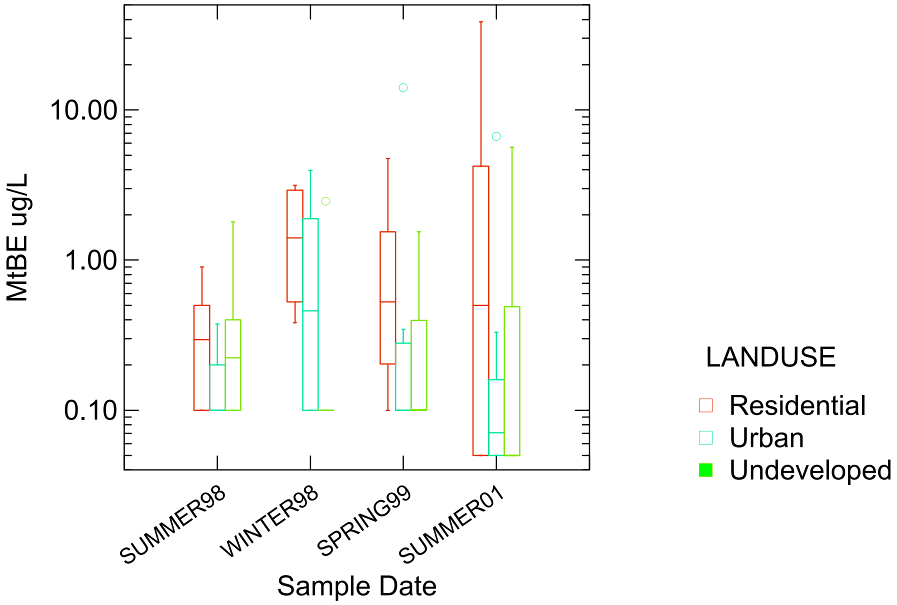


Table I. Summary of Sample Locations and Analytical Results.

Station Identification		**Land Use^1**	**Sample Date and MtBE Detections (ug/L)^2.**			
Station	**Couplet**		**Summer 98**	**Winter 98**	**Spring 99**	**Summer 01**
CW 1971	CW 1990	U	N		N	N
CW 1975		Z	N			
CW 1979	CW 2005	L	N		**0.20**	**0.50**
CW 1980	CW 1989	Z	N			**0.49**
CW 1981		L	**<0.25**	**0.30**	**0.47**	
CW 1982		L	N			
CW 1983		Z	N			
CW 1984	CW 1985	Z	**<1.80**	**2.46**	**1.54**	
CW 1985	CW 1984	Z	**<0.25**	N	**0.10**	N
CW 1987		L	N		N	N
CW 1988		L	**<0.30**			
CW 1989	CW 1980	Z	N			
CW 1990	CW 1971	U	N		**0.23**	N
CW 1992	CW 1993	U	N	N		N
CW 1993	CW 1992	U	N		N	N
CW 1994		Z	N			
CW 1995		Z	N	N		
CW 1998		Z	**<0.35**		N	**0.10**
CW 1999	CW 2009	U	N		N	N
CW 2000		U	**<0.20**	**0.46**	**0.35**	**0.16**
CW 2001	CW 2008	Z	**<0.40**	N	N	N
CW 2003		L	**<0.50**	**0.72**	**0.47**	N
CW 2004		L	**<0.50**	**3.14**	**0.6**	**38.7**
CW 2005	CW 1979	L	**<0.90**	**2.73**	**1.54**	**4.22**
CW 2007		L	N			
CW 2008	CW 2001	Z	N	N		**5.65**
CW 2009	CW 1999	U	N	N		N
CW 2010		U	N	**1.89**		**0.33**
CW 2011		Z	N	N	N	N
CW 2012		U	**0.37**	**3.96**	**14**	**6.64**
CW 2019		Z	N			
	n=	31	31	16	21	22

Note 1. Land Use Codes: L = Residential, U = Urban, and Z = Undeveloped.

Note 2. Detections only are reported. N = None Detected, Blank = No Sample, < = see text for explanation.

EVALUATING CHANGES IN WATER CHEMISTRY AS RISK FACTORS FOR ATLANTIC SALMON IN DOWNEAST MAINE

Basic Information

Title:	EVALUATING CHANGES IN WATER CHEMISTRY AS RISK FACTORS FOR ATLANTIC SALMON IN DOWNEAST MAINE
Project Number:	2002ME3B
Start Date:	5/1/2002
End Date:	4/30/2004
Funding Source:	104B
Congressional District:	2
Research Category:	Not Applicable
Focus Category:	, Acid Deposition, Management and Planning
Descriptors:	
Principal Investigators:	Steve Kahl, Kenneth Johnson, John M. Peckenham

Publication

USGS Interim Report 2003
USGS Salmon and related research

The number of salmon returning to Maine rivers has declined annually for more than a decade. There are a number of chemical agents that have been suggested as potentially responsible, including endrocrine disruptors such as PCBs, herbicides such as arsenic and velpar, and natural aluminum from acid leaching of soils. We propose to evaluate recent changes in surface water chemistry that may *decrease the mitigation* of anthropogenic chemical agents, or *increase* the toxicity of these substances.

Pilot data from downeast Maine support the hypothesis that a general decline in ionic strength is underway in surface waters of the northeastern US. In particular, a decline in base cations may be removing some of the mitigation capacity of surface waters. Alternatively, an apparent increase in dissolved organic carbon may be increasing the chelation of some toxic substances and decreasing toxicity. The potential balance between these factors, and the uncertainties in the trends in acid-base status, lead to this proposal to address these uncertainties for downeast Maine. These data are directly relevant to the current debate over the Endangered Species Act listing for salmon.

Funding for this work is requested only for the first year, as seed money to attract funding from the Atlantic salmon stakeholders. These stakeholders have expressed their intention to fund this work and two projects have begun on Downeast Maine salmon rivers with funds from the Atlantic Salmon Commission.

The first project consisted of seventy-one samples from 62 sites collected on May 7, 2003, by 7 staff of ASC, NOAA, College of the Atlantic, and the UMaine Mitchell Center from 11 salmon rivers and streams in central and eastern Maine. The objective of the sampling was 1) to collect samples within a few hours on the same day on all rivers and all stations, and 2) measure pH and acid neutralizing capacity (ANC, or 'alkalinity') under identical conditions in the same laboratory. This was the first attempt to standardize the collection day for a snapshot under the same hydrologic conditions. This was also the first time that all samples were measured by the same laboratory under the same conditions. As a result, we have developed an excellent baseline for acidity under spring conditions. The survey will be repeated at least twice more, in summer and fall of 2003.

The second project will begin a sampling regime on the Union River tributaries originally included in the EPA INSTUD project of the mid 1980's and to continue the sampling on the Narraguagus tributaries and main stem that started in 2000. We proposed a two-year project period, which will yield three years of data on the Narraguagus due to the ongoing sampling. Episodic sampling will be handled by ISCO automated samplers, already installed, and base flow samples will be collected bi-weekly by hand. Sampling should continue for at least two years to minimize the effects of anomalous precipitation and weather patterns. Samples will be analyzed for base cations (Ca, Mg, Na, K), anions (NO_3, SO_4, Cl), ANC, air-equilibrated pH, closed-cell pH, DOC, conductance, total Al, exchangeable Al, and organic Al for the Union and Narraguagus River tributaries samples. Some samples may be analyzed for the major acidity-related variables to reduce costs: pH, ANC, conductance, and color. The data will be compared among watersheds to determine landscape characteristics that may influence water chemistry. These data will also be compared to data from 1985-87 to determine long-term patterns in water chemistry.

The funding from the USGS grant has allowed us to pre-purchase equipment (ISCO) to initiate sample collection while other funding agencies acquired funding for the projects, allowing us to begin sampling at the beginning of the all important spring melt instead of the beginning of the fiscal year. This funding has partially supported three researchers, allowing them to work with NOAA Fisheries and the Atlantic Salmon Commission to develop not only the two projects above, but to gain the opportunity to submit a proposal for a large-scale acid related chemistry study in Downeast Maine.

The functional role of forested seeps in maintaining hydrology, water qualityand biological diversity in a New England watershed

Project 2002ME13G was not funded for FY2002.

Research Proposal

Title

The functional role of forested seeps in maintaining hydrology, water quality and biological diversity in a New England watershed.

Statement of Critical Regional or State Water Problem:

Forested hillside seeps are widely distributed throughout the northeastern United States and adjacent Canada (Thompson, 2000); it is estimated that greater than 50,000 ha of forested seeps occur in northern Maine alone (A. Cutko, Maine Natural Heritage Program pers. comm.). Because oxic ground water feeds these seeps, seep soils often do not develop characteristic redoximorphic features required of a hydric soil (New England Hydric Soils Technical Committee, 1998). It is not clear if forested seeps perform water-quality functions associated with wetlands or upland forests (Reddy and Patrick, 1975). Most work to date has been conducted on more lotic systems including springs, karst seeps, or in landscapes characterized by development and/or agriculture (Zhu and Ehrenfeld, 2000). The northern Maine landscape affords us an opportunity to evaluate baseline hydrologic, biochemical, and ecological functions of hillside seeps in an environment removed from anthropogenic influences. From these data, baseline indices of biological or hydrologic integrity can be developed.

The quantity and quality of spring water may be impacted by a variety of human-induced and natural process including ground-water extraction, forestry practices, chemical deposition (e.g., N and S from fossil fuels), landscape development, and climate change (LaMoreaux and Tanner, 2001). Ground-water springs are currently an important economic resource (LaMoreaux and Tanner, 2001) that is actively developed in Maine (e.g., bottled water). Forestry practices may impact seeps by altering ground-water recharge pattern and biogeochemical cycling following forest harvesting. Local development may reduce recharge rates by covering the landscape with impermeable surfaces, increasing pollutant loading, and increased demand upon the aquifer. The hydrologic and geochemical impacts to a watershed from ground-water extraction, development, and other natural and human-induced factors is difficult to assess because the role of ground-water discharge through these seeps is not known. Changes in water quality or discharge will, in turn, influence the ecology within these watersheds.

West et al. (2001) suggests that springs are an important source for nitrogen loading to streams within the Catskill Mountains (New York). Nitrogen loading by seeps may be important in maintaining high nitrate concentrations in streams through the growing season by allowing N-rich water to bypass biological systems. However, the slow or 'lentic' water flow in seeps, as compared to springs, may favor denitrification and N loss to the atmosphere and this has important implications for water quality and nutrient dynamics in streams that receive seep drainage or recharge. Increased nitrogen loading to New England through atmospheric deposition may be reflected in seeps. Because seeps and springs integrate the water quality across large areas in a basin, they may provide a simple and inexpensive way to monitor the overall impacts of human and natural changes to ground water within a watershed (Manga, 2001). By monitoring changes over time in springs and seeps, a record of long term impacts to ground-water (both natural and human) may be developed and will be useful for watershed management.

We propose to study the biogeochemical, hydrologic, and biological functions of hillside seeps and to directly address landscape scale functions. Cirmo and McDonnall (1997) suggest that integrated biogeochemical and hydrologic studies assessing the role of nutrient dynamics in forested catchments are needed. Our research will focus on northern white cedar (NWC; *Thuja occidentalis*) seeps in a northern Maine watershed. NWC seeps are known to be hotspots for rare flora (and possibly fauna), thus reflecting unique edaphic and hydrologic features. Furthermore, NWC seeps tend to support older growth forests (and hence more intact functions) because cedar was not historically logged. As seeps are an abundant landscape feature in New England, our research will have broad application. Identifying connections among hydrology, nutrient dynamics, and the plants and animals they support will contribute substantially to seep management and conservation strategies. This information will also be used to improve wetland functional assessments which, to date, rate small forested wetlands as the lowest value wetland type.

Statement of Results or Benefits:

This research will provide hydrologic, biogeochemical, and ecological baseline data on seeps in a forested watershed. Information that will be collected includes:

- discharge rates of seeps to assess the relative importance of seeps in maintaining low streamflow conditions;
- geochemistry of seeps, including nutrients fluxes and alkalinity contribution to streams;
- evaluation of microbial communities to assess redox conditions and nutrient dynamics (production or consumption of nitrogen in seeps);
- evaluation of the ecological function of seeps (are they wetlands?).

Benefits include:

- baseline data on seasonal hydrology and geochemistry within seeps, providing an integrated view of ground-water chemistry for the watershed;
- quantifying the role of seeps as sources or sinks for nutrients in a watershed removed from anthropogenic influences;
- clarification of the role of saturated aerobic soils: should seep soils be considered *problem soils* or do they function biogeochemically as hydric soils;
- adding vegetation community data to the Maine Natural Areas database, providing information on within-community diversity;
- quantifying the relationships among soils, hydrology, and biogeochemistry as drivers for biological communities. It is possible that all NWC seeps do not perform the same functions; they may deserve further classification.

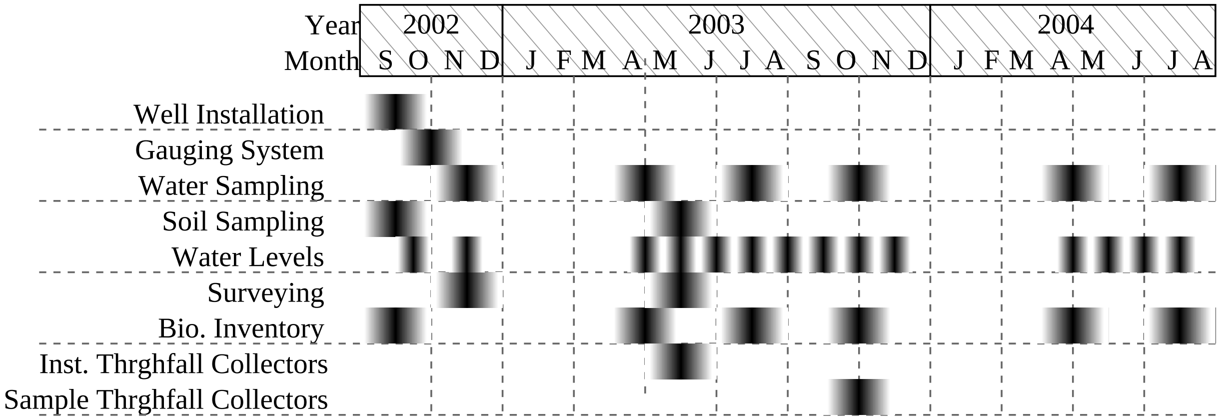


Figure 1: Anticipated schedule of work plan.

Nature, Scope and Objectives

This research will test three hypotheses:

- forested seeps have biogeochemical and ecologic functions distinct from upland forests and provide unique ecological and geochemical environments within watersheds,
- ground-water chemistry in the north woods of Maine has not been impacted by atmospheric deposition, and
- seeps sustain low flow conditions in associated streams and buffer stream geochemistry.

The biogeochemical processes within seeps will be evaluated and the hydrogeologic conditions associated with these seeps will be identified to assess why these seeps occur within a watershed. Activities for this project will be performed from the fall, 2002 through the summer, 2004 (figure 1)

Methods, Procedures, and Facilities

Installation of Monitoring Stations

Six monitoring well clusters will be installed using a Little Beaver Power Auger or bucket auger around three separate seeps (18 monitoring well clusters). One well cluster will be positioned in the seep, with the remaining wells positioned around this central well cluster (figure 2). Soil samples will be collected at 0.5 m increments at boring locations using a split spoon sampler and characterized in the field (soil color, grain size, structure, contacts, etc). Borings will stop at refusal or at a depth of 4 m. Additional borings will be advanced at each location to accommodate up to three wells spaced at depth increments of 0.5 to 1.5 m, to establish vertical hydraulic and chemical gradients. PVC pipe with 12 inch long machine-slotted screens will be installed in these openings. A sand pack will be placed around the screen and bentonite pellets will be placed on the sand pack to seal the hole and prevent fluids from migrating along the annulus of the well. The remainder of the opening will be backfilled with excavated sediment mixed with bentonite powder to ensure a

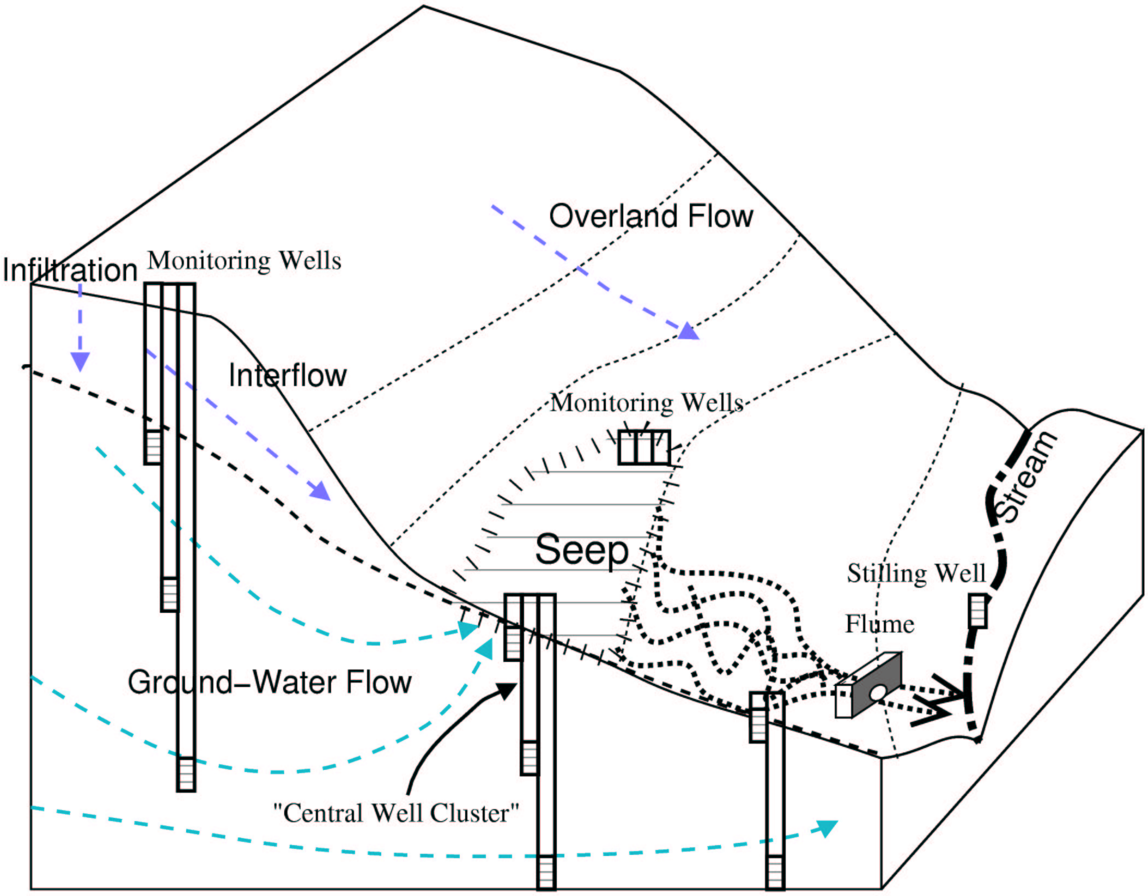


Figure 2: Conceptualized diagram of monitoring framework.

good seal. Larger diameter PVC pipe will be placed around each monitoring well for protection. Stilling wells will be constructed of slotted pipe driven into nearby streams or placed in holes created with a split spoon sampler. Seep surface flow will be diverted into a flume or closed pipe and discharge will be measured directly or with calibrated flume/culvert flow equations (Hager and DelGiudice, 1998).

All monitoring stations will be surveyed with two Ashtech duel frequency geographic positioning system (GPS) and laser level. Hydraulic head will be measured in the monitoring wells and used to calculate vertical and horizontal hydraulic gradients and establish ground-water flow directions.

Discharge through stream channels will be measured using a current meter or by injecting a tracer in the stream (Carter and Davidian, 1968; Kilpatrick and Cobb, 1985). The stream velocity will be measured in several equidistant stream segments by suspending the current meter at 0.6 of the stream depth and measuring the water velocity. The discharge across each section will then be summed to calculate the total discharge through the stream. In streams where a current meter cannot be used, a tracer will be injected as a slug into the stream and a response curve for the tracer will be measured and interpreted by the dilution-discharge method (Kilpatrick and Cobb, 1985). Discharge measurements will be made at several locations upstream and downstream of the seep to assess the impact of the seep on stream discharge and determine if the stream is gaining or loosing water to the ground-water system. Discharge measurements will be compared to stream stage and an empirical relationship will be developed between stage and discharge for the streams.

The hydraulic conductivity of the geologic materials will be determined by measuring the recovery rates in a well after a volume of water is removed from the well (Hvorslev, 1951; Bouwer and Rice, 1976). The porosity of sediment samples will be estimated by weight portion of the split spoon sample when wet and dry, and assuming the volume of water lost is equal to the porosity. Discharge rates and ground-water velocities will be calculated with Darcy's Law (Fetter, 1994) using hydraulic head and hydraulic conductivity data.

Hydrologic Monitoring

Water elevations in monitoring well clusters and stilling wells will be measured on at least a monthly basis from May through November. Stream discharge rates will be measured monthly at the same time water levels are measured. Three Telog 2100e data loggers (or equivalent) with 2.5 psi pressure transducers will be placed in stilling wells and wells positioned in seeps. Stream and seep discharge will be estimated from rating curves developed with monthly discharge and water-elevation data. Baseflow separation, as described by Szilagya and Parange (1998), will be used to interpret hydrographs generated from discharge and hydraulic head measurements (including pressure transducer data).

Water Quality

Water samples will be collected from the surface-water and ground-water monitoring stations four times during the growing season over two consecutive years. Water samples will be placed in acid leached amber HDPE bottles, stored in a cooler with ice packs and transported to the University of Maine's Senator George Mitchell Center for Environmental and Watershed Research (GMC). The GMC participates in regular laboratory audits, ensuring high quality chemical analysis. All water samples will be field filtered (0.2 μ m) and split into anion, cation, nutrient and field parameter samples. Anion (NO_3, SO_4 and Cl) and cation (Ca, Mg, Na, K, Si, Fe, Mn, As, Cu) samples will be analyzed at the GMC through ion chromatography and inductively coupled plasma spectrometry. Nutrient samples will be frozen in the field post filtration by placing samples on dry ice. Nutrient samples will be analyzed at the GMC for inorganic N (NO_2^-/NO_3^- and NH_4^+), total nitrogen (TDN) and reactive phosphorus. Probes will be used to measure pH, water temperature, and specific conductance in the field. Alkalinity will be measured in the field using a Hach digital titrator. Collection of this data set will allow data quality to then be assessed through charge-balance calculations.

Nutrient Dynamics

At the time of well installation, soil horizons will be subsampled from the removed profile for total N analysis using solid state Isotope Ratio Mass Spectroscopy (IRMS). Salt solution and water extractions of horizon material will also be performed to remove dissolved or soluble inorganic

(DIN) and organic (DON) nitrogen, respectively. These soluble fractions can then be concentrated via a modified diffusion (Sigman et al., 1997) procedure of Sorensen and Jensen (1991) for IRMS. The natural abundance isotope ratio (^{15}N:^{14}N) of nitrate in soil water will be used to analyze for isotope discrimination that is known to be in favor of the lighter N isotope in soils where denitrification occurs (e.g., nitrate remaining in soil water becomes comparatively enriched in ^{15}N as $^{14}NO_3^-$ is denitrified to N-gas; (Mariotti et al., 1981; Bauer et al., 2000) and high ^{15}N:^{14}N ratio is presumptive of ecosystems that are losing rather than gaining N (Hogberg, 1990; Hogberg and Johannisson, 1993).

Subsequently, we will determine the isotopic signature of N forms in gravitational water collected from the zero tension wells installed in seeps, upland areas and seep fed streams in spring, midsummer and fall. The timing of these sample periods reflects important changes in nutrient demand of seep plant communities and microbial N demand and will allow us to assess the form and fate of seep-N and potentially link internal N cycling of the seep to stream N-loading by way of isotopic signatures. This data will also be used to assess the redox conditions within the seeps.

Seep and upland plant communities and plant litter will be sampled in year 2 and subjected to natural abundance nitrogen IRMS. Dominant plant isotopic composition will be compared to potential sources in N in the seep and upland communities; e.g., precipitation throughfall collectors and litter collectors will be installed in year 2 in each of the three intensively sampled forested seeps. N isotopic composition of wet and dry precipitation (collected on a wet precipitation basis), soil organic matter-N (SOM-N) and seep waters will be compared to that of plant biomass to assess the source of plant community N resource(s) (Lajtha and Marshall, 1994).

Soil Characterization

Soils will be classified and described at each of the seep study sites. A minimum of three sample points will be described along the hydrologic gradient. In the three intensively studied seeps, soil profile descriptions, and an analysis of A and B horizons (texture, percent organic matter, CEC, and pH) will be characterized along the hydrologic gradient. The number of samples per elevational gradient will be dictated by the width of the seep. At least one sampling point will coincide with the piezometers at each site. Soil samples will be analyzed by the Maine Soil Testing Service and Analytical Lab.

Biological Inventory

Floristic inventories of all the study sites will be conducted in spring, mid-summer, and fall. Data will be collected following the protocol used by the Maine Natural Areas Program (nested plots for trees, saplings, shrubs, herbs/forbs, and bryophytes with cover classes recorded for each species) for inclusion in their database (Gawler, 2000). In addition, data will be collected on tree basal area (using 10 factor prism), vegetation in adjacent uplands (dominant species in each strata), and a volume measurement of standing and down deadwood (coarse woody debris) using a method adapted from the US Forest service.

Detrended correspondence analysis will be performed to evaluate floristic variability among seeps. The influence of edaphic factors and hydrology on species composition will be evaluated using Canonical Correspondence Analysis (direct gradient analysis) (Hall et al., 2001).

Amphibian use of hillside seeps will be investigated by area and time-constrained searches in all of the seeps with the same sampling strategy employed in the adjacent uplands. Searches under all cover objects (stones/coarse woody debris) will be completed in randomly located 5x5 meter plots; complete searches of substrate will be conducted in nested 1x1 meter plots. The number of plots will be dictated by seep size. Searches will be conducted in spring, mid-summer, and fall. Due to the fragile nature of seep soils, pitfall arrays will not be used.

Invertebrate sampling will be conducted in both years. Survey methods will vary depending on size of seep, whether there is some standing/flowing water, amount of saturated substrate, and whether the seep is a headwater stream system or diffuse. Very small seeps will be sampled with emergence traps to capture hatching adults. Trap placement will be dictated by seep size. Captured animals will be frozen and then preserved using the method for benthic animals. Larger spring-like seeps may be sampled using aquarium dip nets in a time-area constrained search. In addition, searches under cover objects will be conducted during the same time period and sampling plots as those for amphibians. Surveys will be conducted the same time of day to reduce variability in detectability (Hansen and Michael, 1982). Newly collected benthic samples and frozen emergents will be preserved in 85-95% ethyl alcohol. The preservative will be replaced with the same concentration within 24 hours if sorted specimens will be preserved in 75-80% ethyl alcohol (Pescador et al., 1995). Very small seeps will be sampled with emergence traps to capture hatching adults. Trap placement will be dictated by seep size. Traps will be constructed from fine mesh screening. The bottom of the trap will have a drawstring and be secured at the base on hoops; a stake through the center will hold the traps in place. Captured animals will be frozen and then preserved using the method for benthic animals. Invertebrate samples will be identified to genus at a minimum and to species when possible.

Related Research

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Training Potential

Calhoun and Dail are both tenure-track professors at the University of Maine. This project will be important in the development of their research programs and will facilitate interdisciplinary collaboration that combines Reeve's interests in hydrogeology with Calhoun's interest in wetland ecosystems and Dail's interest in microbiology. This project will also support one M.S. graduate student and two undergraduate students. Potential for other undergraduate involvement exists through PSE 423 (a wetland ecology and conservation course) and GES 580 (a hydrogeology course). Students from these courses participate in outside projects or field trips and this project would be incorporated into these courses. Work on this project will also be offered as an option for a Senior thesis. Students will be exposed to issues in wetland classification and soil classification, ground-water and watershed hydrology, geochemical and microbial sampling methods, and plant and animal inventory methods. We hope this will stimulate these students to pursue graduate studies in the environmental sciences. These students will have opportunities to interact directly with faculty and students from several disciplines, enhancing their educational experience.

Statement of Government Involvement

Robert Lent will oversee U.S. Geological Survey staff (e.g. Charles Culbertson) who will assist with stream gaging and seep discharge measurements. Dr. Lent (or his staff) will also provide guidance and training on stream gaging techniques that conform with U.S. Geological Survey methodologies and will assist with the development of stream discharge rating equations. Dr. Lent is currently overseeing a project involving stream gaging in northern Maine and will coordinate activities between his staff and Dr. Reeve.

Information Transfer Plan

The results of this research will be disseminated in peer-reviewed publications, as a database to the Maine Natural Areas Program for incorporation into their natural community descriptions, through presentation at the Maine Water Conference (sponsored by the George Mitchell Center at the University of Maine), and meetings of the Geological Society of America, Maine Association of Wetland Scientists and the Maine Association of Professional Soil Scientists.

Development of An Acoustic Wave Sensor for E. coli Bacteria in Drinking Water

Project 2002ME15G was not funded for FY2002.

13. Title: Development of An Acoustic Wave Sensor for *E. coli* Bacteria in Drinking Water

14. Statement of Critical Regional or State Water Problems

The presence of coliform bacteria specifically, Eschericha coli (*E. coli*), in drinking water sources is the cause for much of the treatment required before the water can be safely consumed. Failure to detect *E. coli* bacteria has led to numerous public health crises and the scale of this problem is global. The most notable recent examples in North America are Walkerton, Ontario, where there were several fatalities and Washington County, New York, where numerous people became very sick. The very young and very old are particularly vulnerable to the effects of *E. coli* bacteria with such symptoms as diarrhea and even kidney failure. According to the most recent summary of public drinking water systems compiled by the US EPA in 1998 there were 4,012 public water systems in violation of the SDWA (USEPA National Drinking Water Contaminant Occurrence Database, http://www.epa.gov/ncod/). Twenty-five states reported at least one violation related to *E. coli* bacteria in the categories of monitoring or control. Nearly 50% of the total number of violations reported by individual states was related to the *E. coli* monitoring rule. In Maine, there are 9 public water suppliers currently under active boil orders due to coliform detections (Andrews Tolman, personal communication, Maine Drinking Water Program, 2002). Increasing the speed and reliability of *E. coli* detection using sensor technology will improve protection of public health.

15. Statement of Results and Benefits

Results

Successful completion of the proposed project will result in a prototype microsensor for the detection of *E. coli* bacteria in drinking water.

Specifically, this prototype sensor will have the following properties:

(1) Small, portable, low cost and field deployable
(2) Highly sensitive, selective and reusable
(3) Real-time detection of *E. coli* bacteria
(4) Ability to assess raw water in distribution systems at multiple locations and minimize disinfectant by-product formation by managing dose rate requirements more accurately

The *E. coli* prototype sensor will allow industry to proceed with sensor commercialization.

Potential Benefits of Project

There are several benefits to developing a sensor for *E. coli* bacteria, all of which have direct positive benefits to human health. The first is that the sensor will operate in real-time and the 24 to 48 hour incubation period will no longer be needed. This will allow water systems operators to monitor and adjust the treatment distribution system efficiently. The basic sensor design should allow for production at a modest cost. This will let systems deploy numerous sensors throughout their supply and distribution system. The sensor system can be readily tied into an existing supervisory control and data acquisition (SCADA) system so that distributed points can be monitored at a central location. This benefit is expected to produce numerous efficiencies in the management of a drinking water system. The source of supply can be monitored in several points so that source problems can be identified, even before bacteria blooms reach the intake. Raw water can be monitored so that the water treatment process can be adjusted accordingly. The distribution system can be monitored so that the effectiveness of disinfection can be determined and managed to a finer degree. This in turn should help minimize formation of disinfection by-products (DBPs) caused by excess disinfectant.

Sensor technology will allow many locations in the supply and distribution system to be monitored in real-time. Presently the number of samples that can be tested is limited because traditional methods are constrained by laboratory space and incubation time. Multiple monitoring points will minimize the effects of false negative results by making it feasible to have a greater system-wide redundancy. The sensor system can be configured as a field probe and used to monitor for bacteria during water main construction and repair. Application of this technology will improve our ability to protect public health at a reasonable cost.

DBPs are potentially hazardous substances and their occurrence is directly related to pathogen control. Real-time sensors will allow the dosage of disinfectant to be managed more closely, since bacteria respond to changes in nutrients and growing conditions rapidly. In order to minimize the formation of DBPs, the dosage needs to be tailored to real demand. Traditional bacteria testing has a delay time that favors high disinfectant dose rates- exactly the conditions that favor DBP formation. Real-time sensing of bacteria will allow for a much more accurate control of disinfecting and minimize the potential for hazardous DBPs to form.

16. Nature, Scope and Objectives of the Project

Background

In order to comply with the Safe Drinking Water Act (SDWA) the US EPA requires all public water supplies to monitor for coliform bacteria. *E. coli* is found in the intestines of animals and humans and its presence is an indicator that the water has been contaminated with animal or human waste. Although some strains of *E. coli* can cause severe intestinal illness, more deadly strains and other pathogenic organisms may also occur in the contamination. Coliform bacteria are targeted for monitoring because they are relatively easy to detect compared to the other types of more dangerous bacteria.

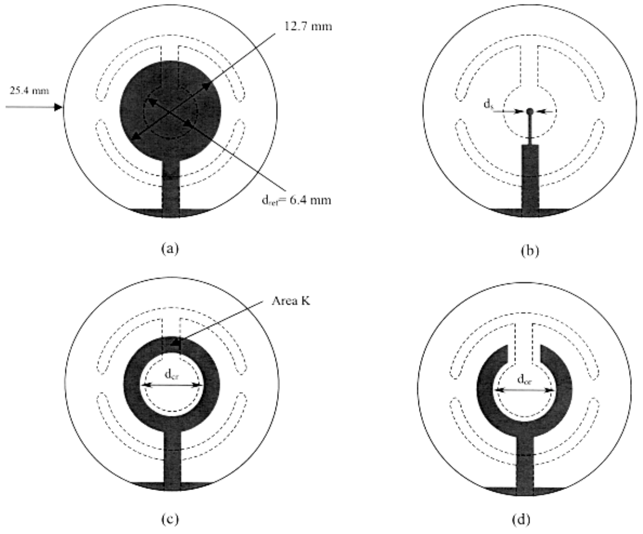

Figure 1. Electrode geometries of various BAW sensors. (a) Standard BAW sensor, (b) small electrode geometry, (c) closed ring geometry, (d) open ring geometry. The electrode pattern exposed to the liquid is shown darkened, dashed lines indicate the electrode pattern on the reverse side of the quartz crystal

In order to remove or control bacteria, systems add a disinfectant to the delivered water. Typical disinfectants are chlorine compounds such as chlorine gas, sodium hypochlorite, chlorine dioxide, and chloramine. If water contains dissolved organic matter the free chlorine can react to form disinfection by-products (DBP). DBPs include some hazardous substances such a chlorform and chloroacetic acid, which are regulated under the Disinfection By-Product Rule (40 CFR parts 141 and 142). Water utility operators must manage their systems along the fine line between controlling bacterial growth and minimizing formation of DBPs.

Traditional methods for detecting *E. coli* require a sample to be incubated for 24 to 48 hours so that colonies can be counted. This method requires time and laboratory space to make precise and repeatable measurements. In many cases laboratory space and personnel, or contract laboratory costs, limit the number of samples that can be processed. A fast and reliable sensor to detect coliform bacteria will allow water utilities to protect public health more effectively by limiting bacterial outbreaks and possibly minimizing the formation of DBPs.

The acoustic wave sensor research group at the University of Maine (UM) under the direction of Dr. John Vetelino has examined a wide range of acoustic sensors. Their work has been documented in over 50-refereed publications [1].

As a result of the work by the UM group and others [2], BAW sensors have emerged as being particularly attractive for fluid phase sensing. One of the most interesting properties of the BAW sensor (shown in Fig. 1) is its high sensitivity, which is in the parts per billion (ppb) range. The novel electrode configurations allow efficient acoustic wave excitation while allowing the associated electric field to penetrate into the adjacent fluid. As a result the new electrode geometries are capable of detecting both mechanical fluid property changes such as mass, density, elasticity and viscosity, and electrical fluid property changes such as ionic conductivity, electronic conductivity and dielectric constant.

These novel BAW sensors have been shown to respond to ppb levels of ammonium ions in aquaculture environments [3] and have also found applications in the liquid phase detection of the pesticide, phosmet [4]. Figure 2 shows the results of an experiment in which small quantities of a 3.2% phosmet in methanol solution were injected into the water bath containing the coated crystal. A 10 micro-liter injection of the phosmet/methanol solution into the water bath corresponded to a 4.7ppm phosmet concentration in bath. Changes in concentration of less than 1ppm are easily resolved in the data. The turnaround in frequency that occurred near 300 minutes is due to the concentration of phosmet in the water bath exceeding the solubility limit of phosmet in water (approx. 25 mg/liter). Control experiments verified that the sensor did not respond to injections of pure methanol.

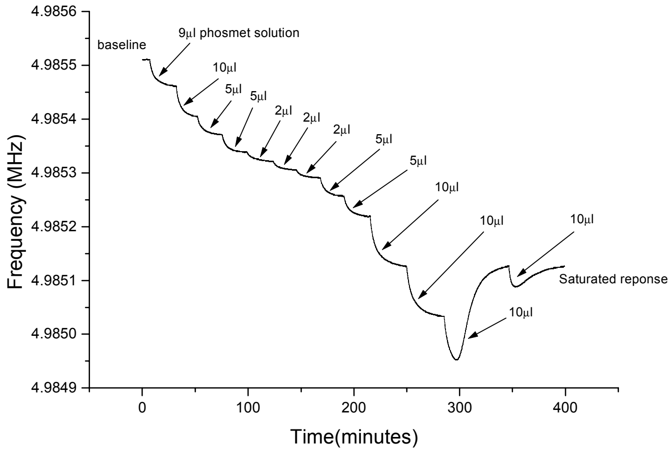

Figure 2. Resonant frequency changes of a PECH-coated BAW device during a series of phosmet injections to the water bath containing the sensor.

This work is significant because to our knowledge it is the first demonstration of the ability to detect organophosphate pesticides in the liquid phase by adsorption on a coated acoustic wave device. Since the liquid-phase sensor shows promise, we are proposing to further develop this technology for the detection of *E. coli* in drinking water.

Objectives

The major goal of the project is to develop the technology required for a compact low cost, real time portable sensor for the detection of *E. coli* bacteria in drinking water. Once developed, this technology could be transferred to companies for commercialization. This sensor will have immediate application to monitor water quality in real time in distribution systems at multiple locations. The sensor will also serve as a feedback element in a real time control system whose function is to minimize disinfectant by-product formation. In order to achieve this goal, three objectives must be achieved.

The first objective involves the development of a biochemical sensing film, which is capable of selectively sorbing the *E. coli* bacteria. This film must not only bind the *E. coli* bacteria but also be attached to the AT-cut quartz substrate. The film and the attachment chemistry should be capable of functioning in a water environment where variations in temperature may occur.

The <u>second objective</u> involves the design and fabrication of the electrode geometry for the acoustic wave sensor. This geometry must be capable of efficiently exciting the transverse shear mode (TSM) in the quartz crystal while allowing significant penetration of the electrical and mechanical fields of the TSM into the film. This will allow a very sensitive monitoring of the film's electrical and mechanical properties changes upon sorption of the *E. coli* bacteria.

The <u>third objective</u> is to perform an extensive experimental investigation on several prototype BAW sensor configurations. Important sensor properties such as sensitivity, selectivity, reproducibility and response and recovery times will be critically evaluated in order to identify prototype sensors which may be seriously considered for commercialization.

Timeline of Activities

YEAR 1 (9/01/9002 – 8/31/2003

Month	9	10	11	12	1	2	3	4	5	6	7	8	9
Design Electrodes	X	X	X	X									
Deposition of electrodes on quartz substrates			X	X	X	X	X						
Development of attachment Chemistry	X	X	X	X	X								
Biofilm Development		X	X	X	X	X	X						
Sensor Testing in air					X	X	X	X					
Sensor testing in water							X	X	X	X	X	X	X

YEAR 2 (9/01/9003 – 8/31/2004

Month	9	10	11	12	1	2	3	4	5	6	7	8	9
Sensor testing in water with *E coli*	X	X	X	X									
Identification of specific electrode configurations			X	X	X								
Determination of Sensor Properties				X	X	X	X	X	X	X	X	X	X
Sensitivity					X	X	X						
Selectivity							X	X	X				
Reproducibility										X	X	X	X
Identification of prototype *E. coli* Sensor												X	X

17. Methods, Procedures and Facilities

The project will determine the feasibility of an acoustic wave sensor to detect *E. coli* bacteria. The work will focus on the design, fabrication and testing of a sensor element that consists of an *E. coli* sensitive film deposited on a substrate which will consist of a variety of gold electrode configurations deposited on an AT-cut quartz crystal.

Overview of sensing film preparation

Immunoglobulin-based target recognition will be combined with acoustic wave-based sensors to permit detection of whole bacteria. The device will detect *E. coli* O157:H7, from potable water or environmental samples. The sensor will combine high sensitivity, selectivity and longevity, with exceptional ease-of-use.

Representative assays will initially be developed for the detection of non-enteropathogenic *E. coli*. Once we have defined a range of important physical characteristics of our new devices, and have developed appropriate procedures using this model system, we will apply identical strategies to the specific detection of enteropathogenic *E. coli*

Coupling of antibodies to acoustic wave sensors

Conditions initially will be defined for attachment of antibody molecules to the surface of quartz crystals. We will explore two methods for covalent attachment of antibodies to surfaces involving (1) direct coupling to gold electrode surfaces and (2) coupling to an SiO_2 layer deposited on the surface of the gold sensing electrode. Initial studies to develop an ideal acoustic wave platform will be carried out using IgG antibodies which are directed against the DNP hapten (αDNP-IgG), but are highly cross-reactive with trinitrophenyl moieties. Nonpathogenic *E. coli* bacteria will be derivatized with aqueous trinitrobenzene sulfonate, blocked with excess lysine and washed repeatedly by centrifugation to remove unbound reacted and unreacted reagent. This model system will be used to characterize antibody surface binding, target recognition and longevity of the sensing surface. Once parameters for creation of the sensor platform have been rigorously established and tested, *E. coli* serotype-specific antibodies will be substituted for αDNP-IgG.

Coupling antibodies directly to gold electrodes

The gold substrate and antibody molecules will be bridged with thiolated peptide [5] or polyethyleneglycol [6] linker molecules, which are spontaneously bound to the gold substrate and then covalently coupled to intact IgG or F_{ab} fragments via hetero- or homobifunctional crosslinking reagents. The hydrophilic polymer cushion between the gold substrate and the antibody layer formed by this tethering method will permit natural association of the antibodies with the surface of the target organisms by decoupling the these molecules from the substrate, consequently reducing steric hindrance and promoting multivalent binding to surface determinants of the *E. coli* cells [7, 8]. The association conditions for recognition layer formation will be fine-tuned using both fluorescence and acoustic wave measurements with the gold electrodes as sample platforms.

Coupling antibodies to SiO_2 surfaces overlain on sensor electrodes

Coating custom-etched Au/Cr crystals with SiO_2 may alter the sensitivity of the devices both to mass loading and to solution conductivity, whereas direct attachment to gold may be less stable than attachment to SiO_2. Since these effects depend on a range of parameters, only some of which are completely characterized and understood, empirical testing will be required to identify the optimum combination of electrode configuration, mode of attachment and coating parameters. A range of thickness of SiO_2, ranging between 250 Å and 1000 Å, will be applied in order to determine sensor response to both mass loading and to solution conductivity and composition.

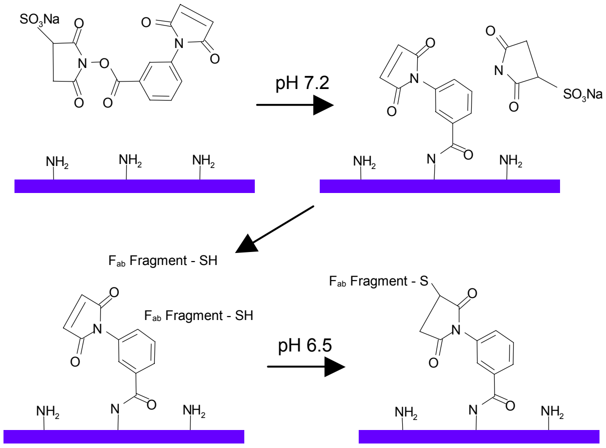

Figure 3. Coupling thiol-modified IgG Fab fragments with amine-derivatized SiO_2. The reaction between the surface amine groups and the NHS-ester of sulfo-MBS yields a maleimide-activated surface. A thiol-containing Fab fragment is then conjugated to the substrate via the maleimide moiety.

Preliminary experiments have been carried out to develop effective procedures for coupling proteins to SiO_2-overlain QCM crystals using glass microscope slides as model substrates. Thus far, the most stable and reproducible method for conjugation to the surface of glass slides has been found to involve thiol-based chemistry. Derivatization consists of three steps: (1) derivatization of the glass surface with amino-propyl*triethoxy*silane in dry acetone or a gas phase reaction mixture of 1:1 triethylamine: aminopropyl*monoethoxy*silane to functionalize the surface with amine moieties, (2) reaction of the amine-glass with the water soluble heterobifunctional crosslinker sulfo-MBS (Pierce Chemical

Company, Rockford, IL) to generate a maleimide-activated surface [9], and (3) addition of proteins containing a free thiol (steps 2 & 3; and see Figure 3).

Functional testing of sensor-immobilized immunoreagents

General measurement strategy

Ultimately, tests of antibody-conjugated sensors will be carried out using two crystals in tandem, a sensing crystal conjugated with a target-specific antibody and a reference crystal conjugated with an antibody directed against an irrelevant target molecule. Simultaneous exposure of both devices to the same analyte solution will permit direct correction for temperature, ionic strength, viscosity, and nonspecific target binding. Preliminary experiments have been carried out in which the resonant frequency and conductance of paired QCM devices was monitored using two identical phase-lock oscillators (model PLO-10, Maxtek, Santa Fe Springs, CA), each with shunt capacitance cancellation and low phase error.

Detection of model pathogens

Binding of wild-type *E. coli* to antibody-derivatized gold or SiO_2 surfaces will be measured in parallel using acoustic wave devices and using fluorescence-based methods. Live bacteria will be prelabeled with the cell-permeant nucleic acid stain SYTO-13 (Molecular Probes, Inc). The number of bacteria binding the sensor surface, or an equivalent substrate, will be measured *in situ* by direct observation of fluorescence in an upright fluorescence microscope (Olympus BX-51, Optical Analysis Corp) using optics for FITC fluorescence, and a cooled CCD camera (Spot-2, Diagnostic Instruments Corp) for digital imaging. Alternatively, bacteria will be physically stripped from the surface and the fluorescence signal measured in a fluorescence spectrophotometer (Quantamaster, Photon Technology Intl.).

Comparison of Performance of the Assay with Protocols Currently in Use

Comparisons with standard methods for detection of fecal coliforms, and specifically *E. coli*, will be performed as appropriate to evaluate the sensitivity, selectivity and robustness of the sensor. All tests with the acoustic wave-sensing device will be performed with cultured bacteria at appropriate cell densities. Actual comparison with standard methods will require pre-concentration of *E. coli*-containing samples by filtration with 0.45 um membrane filters.

Design and Fabrication of the Acoustic Wave Sensor Element

Previous work on BAW sensors for the detection of ammonia in an aquaculture environment and the pesticide, phosmet, in a liquid environment has yielded very promising results. In the proposed work this technology will be extended and improved upon in order to optimize the BAW sensor for the detection of *E. coli* bacteria. Each of the novel electrode geometries shown in figures 1b, 1c, and 1d will be explored. Critical electrode dimensions such as the small electrode diameter, ds, (figure 1b), the ring diameter, dcr (figure 1c) and the open ring diameter, dor, (figure 1d) will be varied. Photolithography and thin film deposition facilities in the Laboratory for Surface Science and Technology (LASST) cleanroom will be used to fabricate the electrode geometries on AT-cut quartz crystals. For different electrode dimensions the BAW sensor will be tested in air and a liquid environment with and without the analyte-selective film.

In order for the sensor to operate, efficient excitation of the TSM in the quartz crystal must occur. Two limiting cases occur for each of the geometries. If there were no metalization on the sensing surface the TSM electric field would have optimum penetration into the liquid. However, in this case one could not excite the TSM since there is no metalization on the sensing surface. The other limiting case would have the sensing surface completely metalized. However, in this case the electric field associated with the TSM could not penetrate into the liquid. Obviously the ideal situation would be a geometry which would efficiently excite the TSM while allowing penetration of the electric field associated into the liquid. Testing each of the three geometries for a range of critical electrode dimensions will determine specific configurations which will result in maximum sensitivity to different fluid properties.

Experimental Investigation of Several Prototype BAW Sensor Configurations

The experimental setup for sensor testing is shown in figure 4. The BAW quartz sensor is dipped into the liquid. A commercial oscillator will be used to drive the sensor and the resonant frequency will be measured with a high accuracy counter interfaced to a data acquisition PC . The impedance of the resonators will be measured with a network analyzer (HP 8751A).

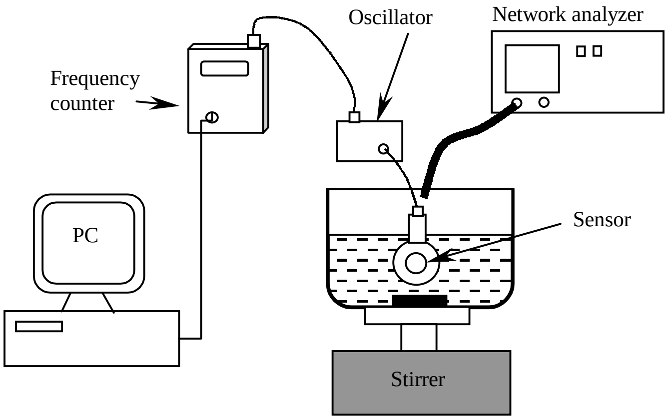

Figure 4. Experimental setup for liquid-phase sensing with a BAW device.

Experiments will be performed in order to obtain critical information on the selectivity of the BAW sensor by configuring more than one sensor in a differential setup. The separation of mechanical and electrical property changes caused by an analyte in the liquid can be performed by having one BAW sensor with a metalized surface while the other BAW sensor would have one of the novel electrode configurations shown in figure 1.

Several critical sensor parameters will be determined by examining the sensor at various stages of development. Initially the sensor without sensing film will be tested in air and water with different electrode configurations. The next step will involve the sensing film that is coupled to the sensor platform. Studies will be performed initially with the attachment film in water followed by similar experiments with the sensing film attached. Finally, experiments will be performed with *E. coli* bacteria introduced in the water. Important sensor parameters to be evaluated include the response and recovery times, sensitivity, reproducibility, short and long term stability and selectivity. Other interferents will be used so that the selectivity of the sensor can be determined.

Facilities

The facilities that will be used in this project are located in the Department of Chemical Engineering (ChE) and the Laboratory for Surface Science and Technology (LASST). Research relating to the biofilm and the appropriate attachment layer will be performed in Dr. Millard's laboratory in ChE while the fabrication and testing of the acoustic sensors will be performed in LASST.

Dr. Millard's laboratory has a scanning XYZ Olympus BX51 epifluorescence microscope, 10 mW frequency-doubled Nd:YAG laser, optical bench, megapixel cooled CCD camera, dual PMT microphotometer, fluorescence spectrophotometer, UV-VIS spectrophotometer, QCM oscillators, computers with PCI multifunction data acquisition boards, automated microinjection apparatus, linear scanning stages, PAGE gel apparatus, and centrifuges.

LASST has the capability of depositing and patterning a variety of metals and dielectrics to form acoustic wave devices. The device fabrication equipment is located in or adjacent to a class 1000 clean room. The equipment includes: an electron beam evaporation system, contact printer/mask aligner, spin coater, wet bench, RF sputter deposition system, reactive ion etch system, surface profilometer, ultrasonic bonder and high speed wafer dicing saw. Sensor test instrumentation which is available to characterize sensor platforms and devices includes a network analyzer, vector voltmeter, impedance analyzer, signal generators, frequency counters, pulse generators, electrometers, RF amplifiers, a device/wafer microwave probe station and oscilloscopes. Computer controlled data acquisition systems are available to interface with the sensor testing setups.

18. Related Research

E. coli has been a focus for the monitoring of indicators of potential enteric pathogens in water for many years [10]. It also serves as a microbiological indicator for fecal contamination in water [11, 12]. Currently several methods exist for *E. coli* cell detection in water. Most detection schemes, such as those involving membrane filter technology, use culture based methods that need long times (18 to 72 hours) to complete [13]. These schemes are based on selective growth and detection of gas or acid which is produced after fermentation of lactose [13]. Other detection techniques such as chemiluminescence, [14] amperometric methods, [15] and impedance technology [16] have also been proposed for *E. coli* detection. Although these techniques are faster, less than 18 hours, they utilize laboratory-based equipment and do not offer high sensitivity and selectivity.

To date, a small, cheap, portable real-time sensor for *E. coli* is not available. Acoustic wave technology employing bulk acoustic wave devices offers the possibility of realizing a real time sensor. This type of sensor has been studied in depth by UM researchers for the detection of analytes in air and aqueous environments [1]. In regard to the latter, the detection of pesticides in water [4] and ammonia in aquaculture environments [3] have shown the potential of this technology. It is anticipated that a BAW sensor designed with electrode configurations capable of measuring both mechanical (density, elasticity, viscosity) and electrical (conductivity and dielectric constant) changes induced by *E. coli* cells sorbed on a deposited sensing film will result in a prototype *E. coli* sensor.

References:

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19. Training Potential

One graduate student in biological engineering will be involved in the development of the sensing film and appropriate attachment chemistry to the quartz substrate. The other graduate student in electrical engineering will be involved in the design, fabrication and testing of the acoustic wave sensors. Several undergraduates, who will be supported by the National Science Foundation Research Experience for Undergraduates program and the GK-12 program, will participate in both the summer and academic year as project assistants.

20. Statement of Government Involvement

The proposed research is designed to both supplement and integrate with several state agencies with an interest in water quality and bio-monitoring (Department of Environmental Protection and Drinking Water Program) and the local USGS District.

21. Information Transfer Plan

The information transfer process will include electronic forms, meeting presentations, and professional publications, coordinated by PI Peckenham, who is Interim Director of the USGS Water Institute in Maine. Information transfer is a fundamental role of the Maine Institute. Electronic forms of the data and conclusions will be data summaries and project information postings on the George Mitchell Center's web page (http://www.umaine.edu/WaterResearch).

This will be the primary outlet for progress reports intended for general use. The results will also be provided to the general public via an ‘Information Digest’, one of our series of short publications that have been produced for nearly 15 years. It is the goal of the investigators to produce peer-reviewed publications resulting from this project sensor development and the detection of *E. coli* in water. The investigators intend to give at least two presentations at meetings of regional and national significance. The regional meeting may be the Maine Water Conference, held every spring. The investigators also are prepared to conduct briefing sessions for federal and state environmental regulators in the New England region.

22. Investigators’ Qualifications

The senior investigators in the proposed project form a highly qualified interdisciplinary team critical to the success of the project. Dr. John F. Vetelino is an electrical engineer who has been working in the area of microsensors for over 30 years. Dr. Mauricio Da Cunha is also an electrical engineer who has published extensively in the area of acoustic wave devices. Dr. Paul Millard is a microbiologist who has both industrial and university experience in the area of bio-detection. Dr. John Peckenham is the acting director of the Senator George J. Mitchell Center for Environmental & Watershed Research and has extensive background in the area of water quality. The vitae of the investigators provide more details on their qualifications.

Characteristics and provenance of litterfall control mobilization of mercury in forested watersheds

Project 2002ME16G was not funded for FY2002.

12. <u>Title</u> Characteristics and provenance of litterfall control mobilization of mercury in forested watersheds.

13. <u>Statement of Critical Regional Problems</u>

Mercury (Hg) in the environment is a national problem because its source is largely atmospheric. Mercury concentrations greater than 0.5 µg/g wet weight have been detected in many species of freshwater fish in waters unaffected by direct discharge throughout the U.S. As a result, as of 1999, 41 states had issued Hg-related human health advisories for fish consumption, up from 27 states in 1993 (*1*). Mercury concentrations in aquatic biota at Acadia National Park, Maine, are among the highest in the nation, with concentrations in some fish exceeding 3 ppm (*2*). The discovery of high Hg at Acadia eventually lead to Hg human health advisory for the entire state. The Maine Bureau of Health has already issued a blanket fish consumption advisory because of Hg for all fresh waters in the state.

Atmospheric deposition is believed to be the important source of Hg in the northern U.S., with deposition rates in the range of 5 to 10 $\mu g/m^2$-yr (*3*). Wet deposition of Hg at Acadia has averaged 7.9 $\mu g/m^2$-yr since 1995 (Mercury Deposition Network (MDN), National Atmospheric Deposition Program (NADP)). Accumulation rates of Hg to the sediment at two locations in Acadia were 100-200 $\mu g/m^2$-yr in the 1980s, suggesting a large amount of dry Hg input not measured by wet-only MDN collector. These rates are comparable to those reported from urban lakes (*4*) and presumably reflect deposition of Hg from upwind sources; e.g., the metropolitan Boston region and solid waste incinerators in southern and central Maine. These high deposition rates at Acadia are a major concern for the Park Service, considering the Class I air quality status of the Park, and the ecological implications of the Hg advisories. *This high deposition of Hg makes Acadia especially well suited as a natural field laboratory for the proposed study on Hg cycling and availability.*

Our field location is the pair of upland gauged watersheds at Acadia National Park, established by EPA/USGS/NPS funding under the PRIMENet program. One watershed was burned in 1947 and one is the unburned reference. Mercury concentrations in deposition, water and soils are well characterized. This proposal is especially cost-effective because complimentary mercury research and monitoring continues under *separate* funding, including streamwater under PRIMENet and wet deposition under the mercury deposition network.

14. <u>Statement of Results and Benefits</u>

One of the mysteries surrounding the bioaccumulation of Hg is that its concentration may differ greatly between lakes and streams in adjacent watersheds. Given proximity, the deposition of Hg to neighboring watersheds will be similar, so there must be watershed factors controlling bioavailability. Our upland watershed research at Acadia confirmed that the differing fire history be correlated to Hg accumulation and availability (fire reduces the amount of mercury present in watershed soils). <u>More specifically, we now propose that the different quality and characteristics of the leaf litter in the two watersheds may be the factor that controls Hg availability.</u> One of the PRIMENet watersheds is dominated by regenerating hardwoods after the 1947 fire, and has lower mercury in streamwater than that the unburned watershed with dominant softwoods.

15. Nature, Scope and Objectives of the Project

Acadia has been the site of integrated ecological research to study nitrogen and Hg cycling (PRIMENet) by several groups at the University of Maine. The objective of PRIMENet is to establish long-term sites that can serve to identify changes in environmental parameters in the ecosystem. The present PRIMENet focus is nitrogen cycling and saturation, and characterization of Hg input and output in two watersheds with different forest types. The information on atmospheric wet deposition is provided by MDN. Specifically, Hg and MeHg distribution in the throughfall, litterfall and streams are being studied as part of PRIMENet. Soil samples for mercury analysis have been collected and characterized by the PIs group (*5*). Recently, the PIs also studied the association of MeHg with humic substances and its bioavailability to algae and fish (*6*,*7*).

We have previously studied the mass balance and biogeochemistry of Hg in two adjacent burned and unburned watersheds at Acadia (*5*,*8*). Our field observations, and those of other groups (*9*,*10*), supported by experimental lab data indicate 1) a strong association between Hg and organic carbon concentrations in stream and soil, and 2) litterfall as one of the most important input Hg vectors into the watershed. In this research, we will investigate the role of leaf and litterfall organic matter in binding Hg and the implications for mobilization of Hg in forested watersheds under possible changes in deposition as a result of regulator controls.

Fire and its effect on Hg fate and transport in Acadia

In 1947, a severe wildfire burned nearly one third of the park. As part of PRIMENet, two gauged watersheds, one in the zone of the fire (Cadillac Brook) and one in an unburned area (Hadlock Brook) were chosen for study in 1998. The gauge stations at Cadillac and Hadlock Brook sites have elevations of 135 and 151 m. Watershed areas of 36 ha and 50 ha, respectively.

The contrasting site histories have caused significant differences in the properties of the two ecosystems. The burned Cadillac watershed has predominantly deciduous (hardwood) vegetation, less organic matter in the soil, in contrast to the unburned Hadlock coniferous (softwood) forest with older (thicker) soil organic horizons. The O horizon soil at Hadlock watershed has a lower average pH of 3.0±0.05 than that in Cadillac watershed with an average pH of 3.4±0.1 (*5*). Deciduous forests tend to have faster rates of nutrient cycling than coniferous types, as evidenced by higher rates of nitrogen mineralization under conifers (*11*). This further increases the pool of available nutrients in soils.

Throughfall and stream fluxes of Hg are shown in Fig. 1 (*8*). Mercury input due to wet deposition had an average of 4.1 μg/m^2/yr as determined by one MDN precipitation collector in the

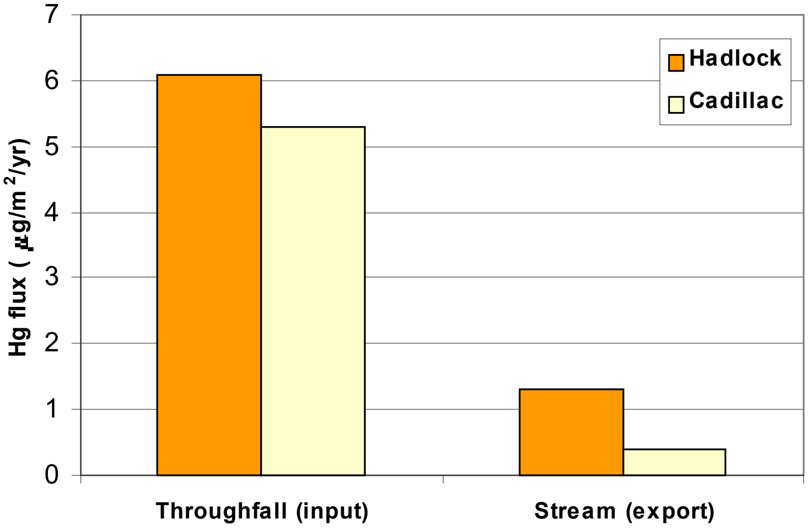

Fig.1. Throughfall and stream Hg fluxes in the two watersheds

Park. The stream export flux was higher in Hadlock Brook (1.3 μg/m^2/yr) than that in Cadillac Brook (0.4 μg/m^2/yr). The input flux due to throughfall was comparable in the two watersheds. Driscoll et al. (*12*), however, observed significantly higher Hg concentrations in the throughfall of coniferous stands than deciduous stands in a forested watershed in the Adirondack region.

Our preliminary data show that Hg input due to litterfall is significantly greater than throughfall. Mercury flux in litterfall is greater in Cadillac (57 μg/m^2/yr) than in Hadlock (29 μg/m^2/yr), primarily due to higher amount of litterfall in the deciduous forest, as also observed by Schwesig and Matzner (*9*). However, preliminary data indicate the Hg content in the litterfall in Hadlock and Cadillac watersheds were 52.9±5.6 and 39.7±3.1 ng/g, respectively (*8*). These concentrations are comparable to those reported by other groups studying Hg in forested watersheds (*13*). These studies point to the importance of litterfall as a major input vector for Hg in forested watersheds.

Figure 2 shows a strong correlation between the dissolved organic carbon (DOC) and Hg concentrations in the streams of both watersheds (*8*). This is expected given the strong binding of Hg to dissolved organic matter (*14*).

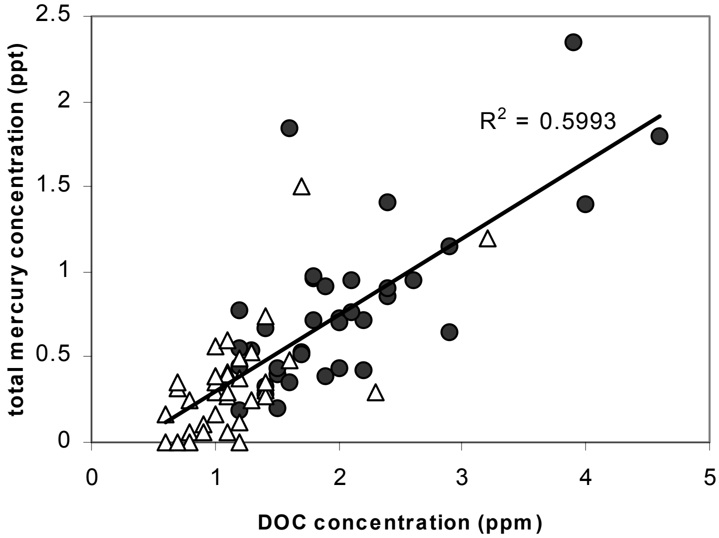

Fig. 2, DOC vs. total mercury concentration in Acadia streams. Unburned Hadlock Brook (circles) and burned Cadillac Brook (triangles).

The unburned Hadlock Brook possesses higher concentrations of both DOC and Hg than the burned Cadillac Brook (Fig. 2). Our field and preliminary laboratory data suggest that the organic matter in the O horizon of Hadlock watershed is a) more labile (and therefore more soluble), and b) has a higher affinity for binding Hg than that in Cadillac watershed (*5*). We propose that the difference in the Hg release rates between the two watersheds is due to the quality of soil organic matter, which is in turn controlled by factors such as pH and vegetation type.

Hypotheses

1. Mercury is bound to different fractions of the organic matter with a wide spectrum of binding energies. The variations in the binding energy are due to the source, age and history of organic matter. In a forested watershed, the type of vegetation largely influences the solubility and reactivity of organic matter.
2. The watershed Hg mobilization rate, and therefore its bioavailability, are controlled by the lability of the watershed soil organic matter.

Our rationale for the hypotheses is based on several studies on the role of organic mater in mobilization and transport of Hg. These studies suggest a) a strong association between Hg and selective fractions of organic matter, b) the significant contribution of litterfall to the total

Hg budget, and c) the differences in organic matter lability from different litterfall sources with implications on the enhanced mobility and availability of Hg:

1. Shanley et al. (*1*) observed strong correlations between the dissolved and particulate Hg and the dissolved and particulate organic carbon fractions for 10 Vermont streams of diverse watershed size and land cover during the snowmelt. They mentioned that even though Hg behaves similarly to DOC, the Hg source appears to be even more enduring than DOC and the Hg/DOC ratio in stream water tends to increase as snowmelt progresses. They concluded that Hg is associated with a particular fraction of DOC that may behave differently than total DOC.
2. Norton et al. (*15*) observed differences in background and maximum Hg (and Pb) accumulation rates, and the timing of the maximum in an ombrotrophic bog in Maine compared to lake sediments from the Adirondack Mountains, Minnesota and Wisconsin. They concluded that the differences among lake sediment Hg content may be partly due to transport from the watershed to the lake, suggesting the influence of organic matter in different watersheds in mobilizing Hg.
3. Schwesig and Matzner (*9*) reported the contribution of litterfall to the total Hg input as 55% in a deciduous catchment, and 29% in a coniferous catchment. Rea et al. (*10*) reported that approximately 40% of total Hg input into the forest sites surrounding lakes Champlain and Huron was due to litterfall. Our preliminary estimates for Acadia are that litterfall contributes as much as 80% of the total Hg input (*8*). These studies point to the significance of litterfall as an Hg input vector.
4. Johnson (*8*) observed that in Acadia, 3% of total Hg input was released from Hadlock Brook and 0.6% of total Hg input was released from Cadillac Brook. Schwesig and Matzner (*9*) observed that in two Bavarian forested watersheds the coniferous forest released 13% and 15% of Hg and MeHg, and the deciduous forest released 4.5% and 5% of their total input of Hg and MeHg, respectively. These studies perhaps suggest the presence of more labile organic matter fractions in coniferous litterfall than in deciduous litterfall.
5. Preliminary laboratory Hg leaching, adsorption and spectroscopic studies of Acadia soils indicate that the organic matter in Hadlock O-horizon is more soluble and the dissolved organic matter (DOM) from Hadlock O-horizon binds Hg more strongly than the DOM from Cadillac O-horizon (*5*). As a result, Hg is more mobile in the coniferous Hadlock watershed than in the deciduous Cadillac watershed (*5*,*8*).
6. In a study of Hg concentration in salamanders (*Eurycea bislineata*) from 6 headwater streams in Acadia (3 in the burned deciduous and 3 in the unburned coniferous watersheds; $n = 45$), Bank et al. (*16*) observed significantly higher total Hg concentrations in salamanders from the unburned watershed streams (73.47±9.4 ng/g wet weight) than in those from the burned streams (53.4±4.7). This suggests a higher bioavailability of Hg in the unburned streams compared to the burned streams. We believe that the higher Hg bioavailability is brought about by the higher degree of lability of DOM and the enhanced mobility of Hg in the unburned coniferous watershed.

The **long-term objective** of this study is to address the response of a watershed in terms of Hg release to changes in the atmospheric deposition of Hg. We propose that the Hg release rate is determined by the lability of the organic matter in the soil and litter.

The **specific objectives** of this study are:

1) To determine mobilization of Hg from fresh and senescent leaves at different times.

   The Hg and DOM in leaves from several dominant trees in the two watersheds will be extracted using simulated rainwater at different times from spring bud break to autumn litterfall. The rainwater extraction releases loosely bound and more labile Hg. The DOM will be characterized using spectroscopic techniques. Total Hg in the leaves will also be measured.

2) To quantify the litter input of Hg to the two gauged watersheds.

   This project component will provide the missing input vector for Hg, completing the input equation for our ongoing gauged watershed research in the PRIMENet watersheds at Acadia.

3) To determine binding characteristics of Hg and organic matter extracted from senescent leaves.

   Fulvic and humic acid fractions of senescent leaves from four different tree species will be isolated. These are the dominant species in the two watersheds that include red spruce (*Picea rubens*) and balsam fir (*Abies balsamea*) in Hadlock, and American beech (*Fagus grandifolia*) and paper birch (*Betula papyrifera*) in Cadillac. The extractable organics will be characterized using wet chemistry and spectroscopic techniques. Partitioning experiments using membrane dialysis technique will be conducted to determine the relevant thermodynamic parameters for the stability of Hg-leaf DOM complexes, with the use of chemical equilibrium modeling.

16. Methods, Procedures and Facilities

Successful completion of the above objectives depends on careful characterization of different organic matter samples, and evaluation of the thermodynamic parameters that govern the interaction between Hg and leaf DOM for varying concentrations and sources of DOM and at different pH values. Only after this thorough analysis can the factors that control mobilization of Hg in forested watersheds be understood. To this end, we propose the following tasks:

Task 1: Mobilization of Hg from foliage and senescent leaves.

Depending on its source and age, natural organic matter exists in different degrees of humification. Older materials are more humified than the freshly introduced materials (e.g., from rhizoexudation, cell lysis, fresh leaf litter), which are less humified (*17*). As humification of natural organic matter increases, chemical properties such as total exchangeable acidity increase. This increase in functional group content enhances DOM interaction with ionic species in solution and mineral surfaces, and its solubility.

We will conduct batch experiments to examine Hg release from fresh and senescent leaves by simulated rainwater in the two watersheds. The basic hypothesis here is that water-soluble extracellular organic material in fresh leaves binds less Hg than the humified material in senescent leaves. Given our observations regarding the higher DOM solubility and Hg binding strength in the unburned Hadlock soils than the burned Cadillac soils (*5*), we also expect a greater extent of Hg binding and mobilization potential by the DOM from coniferous leaves than the deciduous leaves.

Sampling and extraction procedures:

Mercury will be extracted from foliage and senescent leaves collected at different times throughout the growing season using simulated rainwater in batch experiments. These experiments will show the extent of water solubility of leaf Hg content, and the potential for mobilization of Hg from foliage and litterfall as a function of species and time in the two watersheds. For a limited set of experiments, 0.1 M NaOH will be used to mobilize Hg and organic matter. Base extraction releases Hg associated with humic and fulvic acid fractions.

Foliage will be collected from dominant tree species at each watershed. These will include red spruce, balsam fir and white spruce at Hadlock, and American beech, paper birch and white birch at Cadillac. Sampling will be conducted on a monthly basis from spring bud break in May to end of September following the method of Rea et al. (*18*).

Characterization of the extent of humification:

We will use fluorescence spectroscopy to characterize the extent of humification in the extracts of the foliage and senescent leaves. This is a simple and fast technique that has been previously used to determine the extent of humification of DOM, which is characterized by quantifying the shift in the emission spectra toward longer wavelengths with increasing humification (*19*). We expect the red-shifting of the emission spectra from the extracts of fresh leaves to the extracts of the senescent leaves. The humification index (HIX) of each DOM sample will be measured by dividing the emission intensity in the 300–345 nm by the sum of intensity in the 300–345 nm and 435–480 nm regions (*19*,*20*). This allows quantitative comparisons among DOM samples of different origin, treatment and age, with fresh DOM exhibiting low and humified DOM exhibiting high HIX values (*20*).

Tasks 2: Litterfall contribution to the mass balance input of Hg.

Litterfall will be collected in early and late fall from several locations in each watershed. Samples for a given species from each watershed will be composited. Polyethylene collectors will be placed at the center of each of 12 PRIMENet soil plots in the two watersheds previously sampled by our group (*5*,*8*). Foliage and litterfall samples will be air-dried to minimize changes in organic matter (*19*). Total Hg concentrations in grinded foliage and litterfall will be measured using microwave digestion as described by Rea and Keeler (*21*). Concentrations of DOC, major cations and other trace metals of relevance will also be measured in the extracts.

Task 3: Binding of Hg to the humic and fulvic acid fractions of senescent leaves.

Field studies comparing Hg cycling in forested watersheds indicate a higher flux of Hg export in the streams of coniferous than deciduous watersheds (*8*,*9*). Based on laboratory Hg adsorption studies of Acadia soils, the organic matter in the coniferous Hadlock O-horizon is more labile and binds Hg more strongly than the organic matter in the deciduous Cadillac O-horizon (*5*). Fourier Transform Infra Red (FTIR) spectroscopic analysis of Hadlock and Cadillac O horizons also indicates a higher distribution of carbonyl carbon moieties including carboxylic acid group (at 1720 cm^{-1}) in the unburned soil (*5*). These observations suggest the presence of more reactive organic matter with respect to Hg in coniferous litterfall than in deciduous litterfall. To test this hypothesis, we will isolate fulvic and humic fractions from several senescent leaf species in both watersheds, and will determine the thermodynamic stability of Hg-leaf DOM complexes.

Isolation and characterization of the DOM from senescent leaves:

Fulvic and humic acid fractions of senescent leaves from red spruce, balsam fir, American beech and paper birch will be isolated. The leaves and needles will be collected from the litterfall at the end of fall. We will follow the procedures of Thurman and Malcom (*22*) and Wershaw et al. (*17*) for isolation of humic and fulvic acids from the leaves. The procedure involves extraction of DOM in 0.1 M NaOH followed by separation at pH 1 and adsorption onto

XAD-8 resin. The PI has a great deal of experience in isolation of humic substances from soils and natural waters (*7*,*23*).

The organic matter characterization will involve wet chemistry and spectroscopic techniques to determine elemental composition, acid-base properties, and the functional group distribution of the humic and fulvic fractions. Potentiometric titration will be conducted to characterize the acid-base properties of the humic samples in constant temperature batch reactors using an autoburette for a fixed ionic strength adjusted by $NaNO_3$ (*23*). Elemental analysis will be performed on a small portion of the freeze-dried samples to determine the C, N, H, O, S and ash contents. FTIR spectroscopy will be used to characterize the functional group distribution of the freeze-dried humics (*17*).

Association of Hg with litterfall DOM – Equilibrium dialysis experiments:

Partitioning experiments using membrane dialysis technique will be conducted to determine the stability of Hg-litterfall DOM complexes and to obtain relevant thermodynamic parameters for this interaction. Mercury binding to DOM extracted from soil and peat has been studied previously by several researchers (*24-26*). These studies indicate a very strong interaction between Hg and DOM involving the reduced sulfur (thiol) group of DOM. The significant presence of Hg-thiol interaction has been directly observed using spectroscopic techniques (*27*).

Equilibrium dialysis technique will be used to study the extent of association of Hg with litterfall DOM. The procedure will be similar to the previous study by our group on the association of MeHg with humic acids (*7*). Experiments will be performed in dialysis cells with two 15 ml glass chambers, one containing Hg and the other DOM, separated by an asymmetric cellulose ester dialysis membrane sheet with a molecular size cutoff of 500 Da. The Hg contents of the two cells will be measured by the EPA method 1631 that involves cold vapor atomic fluorescence spectrometry (CVAFS).

Typical Hg adsorption experiments will be conducted at a concentration range of 0.05 to 100 nM (10 ppt to 20 ppb), a pH between 4 and 5, an ionic strength of 1 mM ($NaNO_3$), and a DOM concentration range of 1 to 10 ppm (*7*). For a subset of experiments, pH dependence (3 to 9) relationship will be developed. The pH dependent interaction between Hg and DOM has not been rigorously studied previously. Based on MeHg-humic interactions, we expect maximum adsorption at a circumneutral pH range (*7*). The role of chloride in competing with DOM for binding Hg will be investigated for a subset of experiments.

The experimental data for equilibrium sorption of Hg will be modeled using a discrete log K spectrum approach (*28*), and the corresponding unconditional equilibrium stability constants for the Hg–DOM complex will be determined. The interaction between Hg and the humic functional group $\mathrm{RS}_{(i)}^{-}$ may be written as

$$\mathrm{Hg}^{2+} + \mathrm{RS}_{(i)}^{-} \Leftrightarrow \mathrm{RS}_{(i)}\mathrm{Hg}^{+}; \qquad K_{s(i)}$$

where $\mathrm{RS}_{(i)}^{-}$ is the deprotonated form of the i^{th} thiol functional group, and $K_{s(i)}$ is the equilibrium stability constant. We previously used this approach to represent MeHg sorption to humics for a wide range of pH and humic concentrations (*7*).

Knowledge of Hg-litterfall DOM binding is essential to understanding the mobilization potential of Hg in litterfall. Process-level research on Hg-DOM interaction allows us to methodically compare and quantify the effect of vegetation type and solution chemistry (i.e., pH, DOM and chloride concentration, ionic strength, etc.) on mobilization and bioavailability of Hg in forested watersheds.

Facilities:

The proposed experiments will be conducted at the laboratories of the George J. Mitchell Center for Environmental and Watershed Research, and the Civil and Environmental Engineering Department. Low-level Hg measurements will be performed at the Mitchell Center laboratory, in two clean rooms constructed specifically for the research program at Acadia. The Mitchell Center has Brooks-Rand cold-vapor atomic fluorescence spectrometer (model 2), two TOC analyzers (OI), a furnace AA spectrometer (Perkin-Elmer), and an IC system (Dionex). A Hitachi F-4500 spectrofluorimeter and a Perkin-Elmer FTIR exist on campus.

17. Related Research

Soil plays a significant role in determining the fate and transport of Hg within a watershed (*29,30*). Cycling and speciation of Hg are largely dependent on watershed characteristics, namely percentage of wetland areas, slope, soil thickness, vegetation type, and carbon content (*31*). These characteristics help define the fate and transport of atmospherically deposited Hg within the watershed, thus influencing output concentrations into lakes and rivers. Mercury retention can be affected by the characteristics of different watersheds having similar precipitation and discharge rates (*32*).

Litterfall and throughfall have been shown to have a more significant contribution to the total Hg input than wet deposition (*8*,*10*). The source of Hg in litterfall is primarily atmospheric and is not due to uptake from soil (*33*). Vegetation type plays an important role in Hg content and lability in litterfall (*9*,*13*,*18*,*34*). In a comparative watershed study in Germany, soils of a coniferous forest catchment contained approximately four times more Hg than a deciduous forest catchment over similar soil depths (*9*). The relatively high Hg levels found in throughfall and litterfall of coniferous watersheds may be attributed to the high needle specific surface area (*34*). There are major variations in the Hg contents within tissues of the same species (*33*,*35*). Rea et al. (*10*) observed Hg litterfall concentrations of 52.3±25.9 ng/g for deciduous species, and 20 to 65.5 ng/g for coniferous species in the watersheds around lakes Champlain and Huron. They reported that Hg concentrations in foliage increased ten-fold from spring bud break to autumn litterfall. In the decomposing litterfall, however, total Hg concentration decreases with time (*36*). Grigal et al. (*13*) studied Hg cycling in a hardwood upland surrounding a softwood bog. The litterfall Hg contents were 34.3±6.9 and 126±19 ng/g in the upland and in the bog, respectively. The Hg content in the leaf litterfall only, however, was considerably lower.

During intense fires, much of the forest floor organic matter can be mineralized. The carbon pool in the burned watershed is reduced due to the fire, and therefore, has an impact on the speciation and transport of Hg and MeHg. The effect of fire on DOC mobilization, and hence on Hg and MeHg mobilization, has been studied previously (*37*). Results indicate that DOC mobilization rate, especially immediately after the fire, may be increased in burned watersheds due to erosion, compared to undisturbed watersheds. However, these findings were based on a 1995 fire, where significant erosion of the watershed is expected due to lack of vegetation. Our past and ongoing studies at Acadia examine Hg cycling in the burned watershed more than half century after the fire, where vegetation has largely been reestablished, and therefore, extensive erosion of the top forest soil is not expected.

Project Timeline:

	Year 1				*Year 2*			
Objective/task | Month	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
Task 1 – Hg in leaf and litter								
- sample collection and measurements	X	X	X	X	X	X	X	
- Hg leaching experiments	X	X		X	X	X		
Task 2 – Hg Binding								
- humic extraction	X				X			
- Hg binding experiments	X	X	X	X	X	X	X	
Organic Characterization	X	X	X	X	X			
Reporting				X				X

18. Training Potential

The graduate student employed for this project will be involved in the extraction and characterization of humics from the senescent leaves, and the Hg binding studies. The undergraduate student will be involved in sample collection from Acadia National Park and leaching studies. The technician will conduct Hg measurements in the leaf and litter. Staff paid by other funding sources will assist in the field sample collections as part of the larger research program at Acadia PRIMENet watersheds, enhancing the cost-effectiveness of this research.

19. Statement of Government Involvement:

This research is a collaborative effort with several key partners including, 1) the USGS WRRI at UMaine (Kahl), and their long history of policy-relevant watershed research in acid rain and mercury, 2) the USGS BRD field station at UMaine (Haines), a leader in mercury research for more than a decade, and 3) Acadia National Park, Department of the Interior, the sponsor and home of the long-term PRIMENet research program originally funded by EPA, NPS, and USGS.

20. Information Transfer Plan:

The results of this study will be of major importance to policy makers. The USGS WRRI information transfer role of the Mitchell Center provides a mechanism to put this information into layperson language. Our IT mission includes working with our sister research unit (the UMaine Smith Center for Public Policy) to transfer this information to policy makers. A second opportunity for IT is offered by Acadia National Park, the location of the research. The Park is developing a new Learning Center specifically to integrate research and education. There will be staff at Acadia whose jobs include providing the relevance of research to the public.

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21. Investigator's Qualification

Amirbahman is an environmental chemist and engineer with expertise in energetics and kinetics of environmental reactions. Kahl is a geologist and an environmental chemist with extensive experience in watershed and lake processes. He led the development of the watershed research program at Acadia. Haines is a national expert on Hg biogeochemistry. This group has previously studied the cycling of Hg, MeHg and other trace elements in forested watersheds.

Do Microorganisms Control Arsenic Mobility in Groundwater?

Basic Information

Title:	Do Microorganisms Control Arsenic Mobility in Groundwater?
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Focus Category:	, Groundwater, Toxic Substances
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Principal Investigators:	Jean D. MacRae, Charles Culbertson, John M. Peckenham

Publication

1. 1. McCaffery, K., and MacRae, J.D. 2002. Microbial arsenate reduction in anaerobic groundwater. Poster presentation at the Maine Water Conference, May, 2002.
2. 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
3. 1. Lavine, I., McCaffery, K., and MacRae, J.D. 2003. Characterization of an arsenate-reducing bacterium from Maine groundwater. Poster presentation at the 103rd General Meeting of the American Society for Microbiology, May, 2003.
4. 2. McCormick, E., and MacRae, J.D. 2003. An investigation into factors affecting arsenic release into grounwater. Poster presentation at the Maine Water Conference, April, 2003.
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Role of microorganisms in arsenic contamination of groundwater

Jean MacRae, John Peckenham, Charles Culbertson

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 may 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.

An isolate that can directly reduce As(V) to As(III) was obtained from a well water sample from Northport, Maine. The isolate, called NP4, has been tested for its ability to use a variety of electron acceptors and electron donors, and the 16S rDNA has been amplified and sequenced. The isolate is unique in the GENBANK database, indicating that it is a new environmental isolate. Incubation of ground bedrock from the Northport well with groundwater decreased the arsenic concentration in the water phase, indicating that the surface chemistry of the cracks is different from the bulk rock.

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 μg/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 was to identify the ways in which microorganisms participate in arsenic transformations and mobility in groundwater.

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). The control had no inoculum, total arsenic in the media (water phase) remained constant throughout the experiment, and the eluent from the ion exchange resin, which is As(III), for control and inoculated samples are shown.

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 to lactate consumed. Presumably this is due to the production of biomass and other end-products that were not measured in the HPLC assay. The lactate and arsenate levels in the controls did not significantly change with time.

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

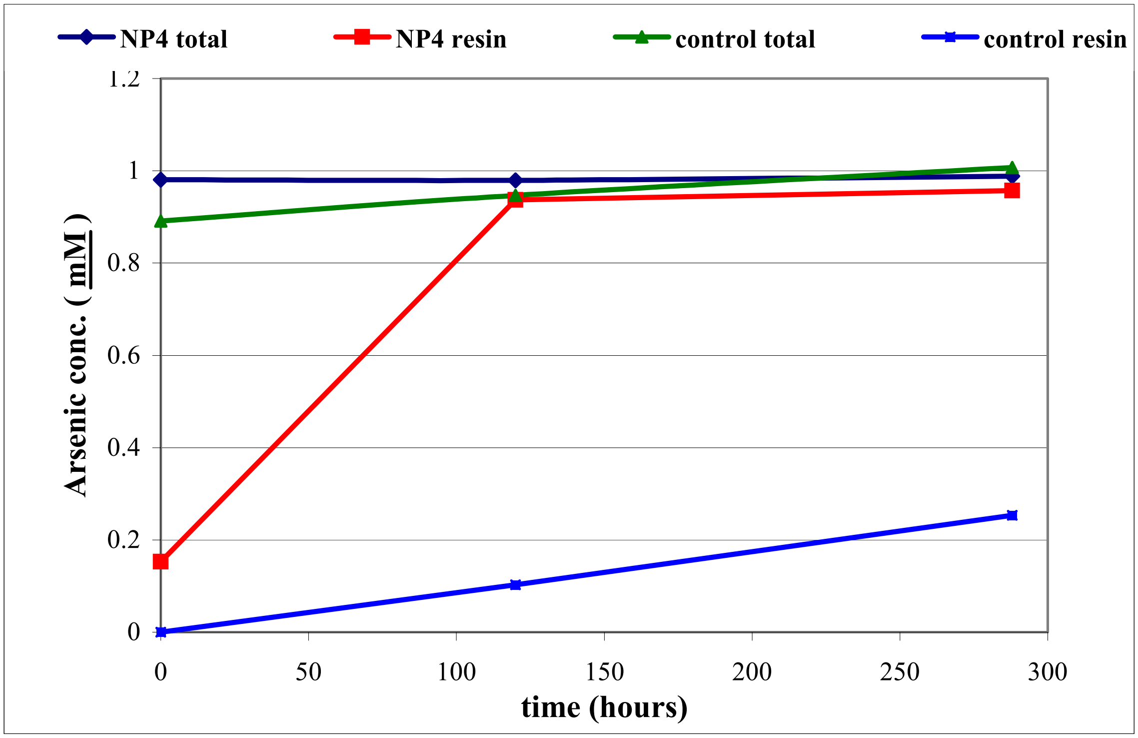
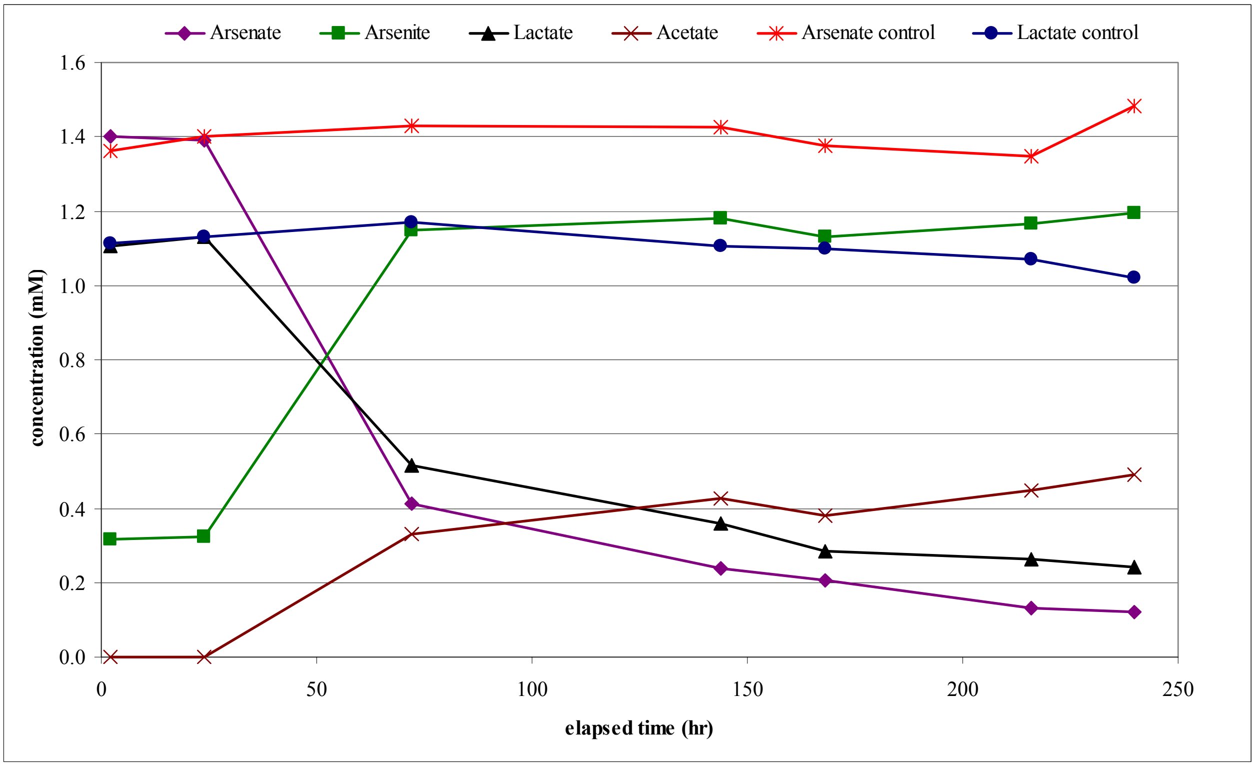


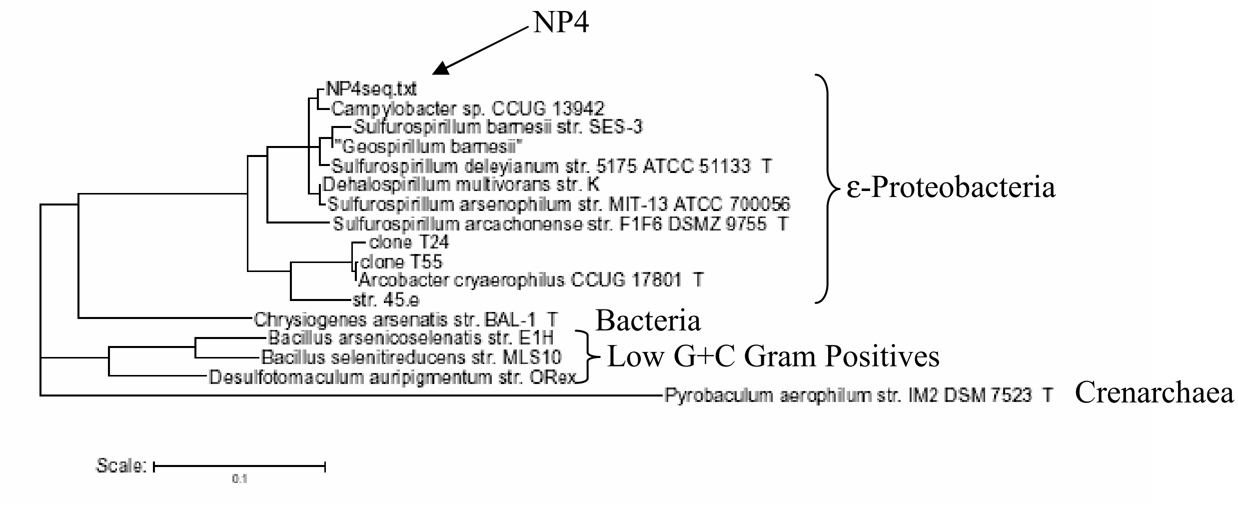
Figure 2: Growth of NP4



The 16S rDNA of the isolate was amplified by PCR analysis using bacterial primers and the fragment was sequenced. Comparison of the sequence to the entire GenBank database revealed that NP4 is a new isolate and a member of the ε-Proteobacteria.

Interestingly, it is fairly closely related to two other arsenate respiring organisms, *Sulfurospirillum barnesii* (SES-3) and *Sulfurospirillum arsenophilus* (MIT-13). Figure 3 shows the closest relatives in the database as well as some other arsenate respiring microorganisms.

Figure 3: NP4 Phylogenetic Tree



Experiments were also conducted to determine carbon utilization and electron acceptor usage. The carbon substrate usage results are shown in Table 1, which compares NP4 data to its close relatives. NP4 can also use nitrate and selenate as electron acceptors in the absence of arsenate. NP4 grows to higher cell densities on nitrate than when it is grown on arsenate. Higher arsenate concentrations (>1 mM) also appear to be inhibitory to NP4, perhaps indicating As(III) toxicity.

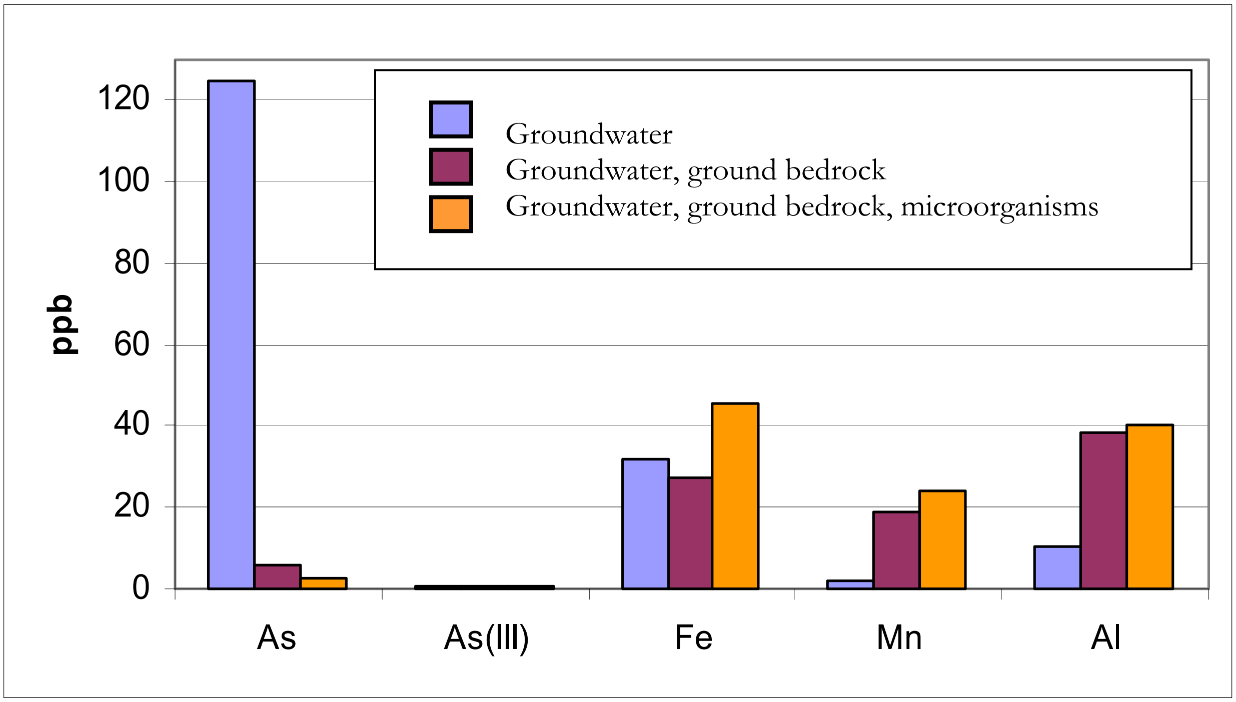
Table 1: Carbon Substrate Utilization by NP4 and Related Species

Carbon Source	***S. barnesii*** **SES–3**	***S. arsenophilum*** **MIT-13**	**NP4**
acetate	-	-	-
benzoate	0	0	-
butyrate	0	$+^c$	+
citrate	+	0	+
ethanol	0	0	+
formate	$+^c$	$+^c$	+
fumarate	+	+	+
glucose	0	0	+
glycerol	0	0	+
H_2	-	-	-
H_2 & acetate	+	+	+
methanol	0	0	-

^{c} growth only in presence of acetate

In incubations containing ground bedrock from the Northport site and high As groundwater, As was actually bound by the ground bedrock, indicating that grinding had exposed additional As binding sites that could scavenge As from solution, while Fe, Mn and Al were leached (*Figure 4*). This was somewhat contrary to expectation, and indicates that the surface chemistry of the cracks through which the groundwater passes is different from the bulk rock. It may also indicate that the heterogeneity of the aquifer bedrock material was inadequately represented in the samples that were tested.

Figure 4: As concentration in water after 1 month incubation with ground bedrock



Funding has been awarded to Jean MacRae through an **NSF-Career** grant 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.

Earlier Presentations:

1. 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.
2. McCaffery, K., and MacRae, J.D. 2002. Microbial arsenate reduction in anaerobic groundwater. Poster presentation at the Maine Water Conference, May, 2002.

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

Basic Information

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Principal Investigators:	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.
4. 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 2003, Augusta, Maine. (Award for Best Student Poster)

Problem and Research Objectives:

Climate changes predicted for North America over the next century include warming temperatures, long periods of drought, and increased levels of precipitation, all of which pose serious risks to freshwater ecosystems (Poff et al., 2002). Global Climate Models have been used to predict the type and magnitude of physical climate changes. Several scenarios have been suggested and more than one may be accurate, causing great uncertainty in the future of lakes and streams (New England Regional Assessment, 2001).

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 the transport of water and solutes to a lake, affecting its water budget and generating strong chemical responses. 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). Because surface water inlets and outlets are lacking, the hydrologic budgets of high-order, precipitation-dominated, seepage lakes are dominated by precipitation, some groundwater input, evaporation, and inflow from adjacent wetlands. Thus, during climate change, the magnitude of shifts in ionic strength for these water bodies becomes a function of the relative importance of wetland connections, 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 that potentially reflect climate-induced shifts in hydrologic connections between lakes and (1) wetlands and (2) groundwater inputs. We expect to find that these precipitation-dominated seepage lakes located higher in the landscape, with weaker connections to groundwater flow systems are responsive to climate and thus provide more sensitive indicators of climate change. In addition, we have access to long-term data on the chemistry of seepage lakes in Wisconsin for comparison with lakes in Maine.

We have three general objectives for this research project:

- Determine if changes in the chemistry of sensitive seepage lakes in Maine reflect climatic shifts over the past two decades.
    - ~ Determine if there is a strong signal of chemical response to climate-induced shifts in a lake's hydrologic connections to wetlands and local groundwater systems.
    - ~ 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 potential for using seepage lakes in Maine as sensitive sentinels of climate change.
- 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 future.

In addition to the main objective in this proposal to evaluate the use of Maine lakes as sentinels of climate change, we cannot ignore the value of basic data for increasing 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. In addition, 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 ~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 µeq/L, our operational definition of lakes with low groundwater influence. Lakes were then allocated to classes defined by strength of connection to surrounding wetlands (low, mid, high) using National Wetland Inventory (or Wisconsin Wetland Inventory) and USGS 7.5 Minute Topographical maps, and watershed boundaries (Figure 1 and Table 1). As these lakes have low values of ANC, they all are considered to have transient connections to local groundwater systems.

Graduate research assistant Emily Seger sampled the subset of 66 Maine lakes in fall 2001 and fall 2002. Chemical variables measured from the lakes include 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. The lake chemistry in both Maine and Wisconsin were collected as part of the same EPA program (Long Term Monitoring), so the data are comparable in field and analytical methods. Precipitation data for both Maine and Wisconsin were compiled from National Climate Data Center monitoring stations near locations of seepage lakes (Augusta Airport, Portland Jetport, and Grand Lake Stream for Maine; Minocqua Dam for Wisconsin). Statistical analysis was performed using ANOVA tests with Systat 10.2 software package.

Principal Findings and Significance:

The field sampling data for the Maine lakes corresponded to periods of (1) normal precipitation in 1986-87; (2) above average in 1998; (3) the lowest precipitation year on record in 2001; and (4) recovery from severe drought in 2002 (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 between 1987-1990, followed by a recovery period (Figure 3).

Analyses have focused on the four chemical constituents we proposed as indicators of flowpath shifts due to climate change. We assume that (1) dissolved organic carbon (DOC) and true color levels reflect changes in wetland-lake connections (higher the DOC and true color, the more connected lakes are to wetlands) and (2) changes in silica and calcium concentration reflect shifts in groundwater-lake interactions (higher the silica and calcium, the more connected lakes are to groundwater flowpaths). 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.

Lakes in Maine with stronger connections to wetlands had the largest chemical response to precipitation shifts for all constituents analyzed (using ANOVA and a p-value of 0.1). We had expected lakes in the low and mid wetland classes to be more responsive. For both Wisconsin and Maine lakes, true color appeared more responsive to precipitation changes than DOC, and both analytes decreased during dry periods (see Figure 4 for example of Maine results).

Calcium concentrations appeared more susceptible to evapoconcentration and dilution effects than silica. Figure 5 shows this response for Maine. Decreases in silica concentrations occurred during a short period of severe drought in Maine, while in Wisconsin decreases in both silica and calcium were seen during long-term drought.

We conclude that water chemistry does reflect drought-induced shifts in wetland and groundwater hydrologic connections. Thus, water chemistry of precipitation-dominated seepage lakes has potential as an indicator of climate change, and its corresponding effects upon the landscape. Due to their isolated landscape position and precipitation-dominated water budget, the chemistry of higher order seepage lakes is more sensitive to changes in climate-induced groundwater input, evaporative losses, and connection to shoreline wetlands than drainage lakes, in which significant chemical variations occur from noise of large catchment inputs and faster flushing rates. Climate-induced alteration of lake hydrologic connections to the landscape will affect lake DOC, true color, and solute concentrations such as calcium and silica. Climate may also confound recovery of acid-sensitive waters like these seepage lakes through drought-induced re-oxidation of sulfate and decline of base cation inputs. Consequently, precipitation-dominated seepage lakes are a sensitive indicator of climate change and its translation onto the landscape and freshwater systems.

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.

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Wetland Classification

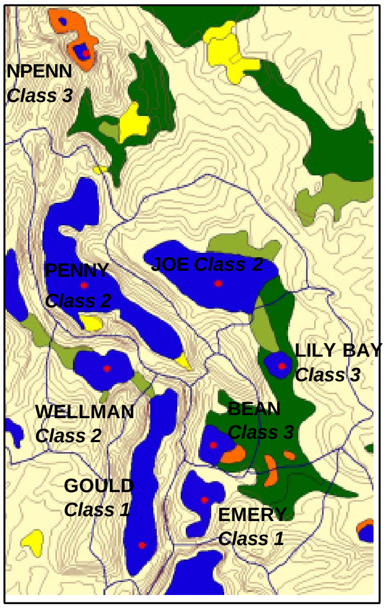

Table 1. Classes based on degree of connection to adjacent wetlands

Class	Description
1 *n = 26*	• No connections to wetlands, or • 1 narrow connection to small wetland (relative to lake size)
2 *n = 23*	• 1 - 4 connections to small/medium size wetland (relative to lake size), or • One half to three quarters of the pond's perimeter is adjacent to small/medium size wetland (relative to lake size)
3 *n = 14*	• Over half of shore perimeter shares interface with large wetland, or • Whole pond is surrounded by medium/large size wetland (relative to lake size)

Numbers of lakes (n) in each class refer to those in the Maine wetland classes.

Figure 1. Lakes were classified qualitatively by using digital National Wetland Inventory maps, topographic contours, and watershed boundaries to determine strength of connection to adjacent wetlands. This map shows several seepage lakes and their surrounding wetlands near Augusta, Maine.

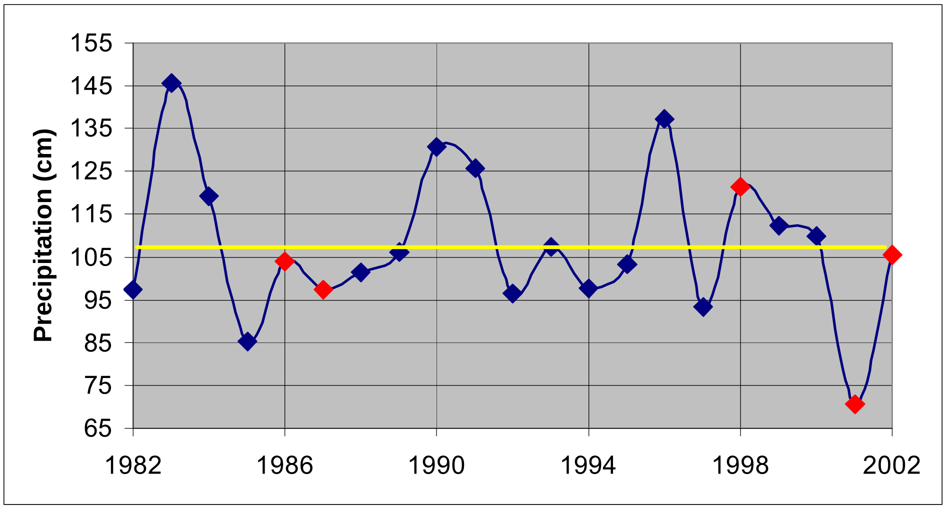

Figure 2. Maine total annual precipitation averaged over three Maine NCDC Stations. NCDC thirty year normal precipitation mean = 105.84 cm (indicated by yellow line). A pattern of normal, to above average, to severely low precipitation, to recovery from drought occurred during years with data.

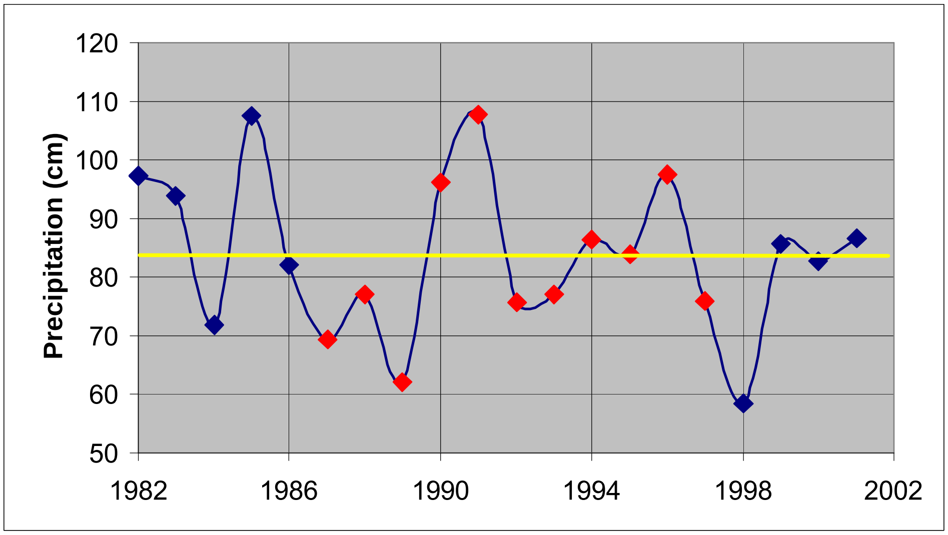

Figure 3. Wisconsin total annual precipitation at Minocqua Dam NCDC station in northern Wisconsin. Shaded areas indicate years with lake data. NCDC thirty year normal precipitation mean = 83.24 cm (indicated by yellow line). A severe drought from 1987 to 1990 occurred, followed by a transition to above/normal precipitation.

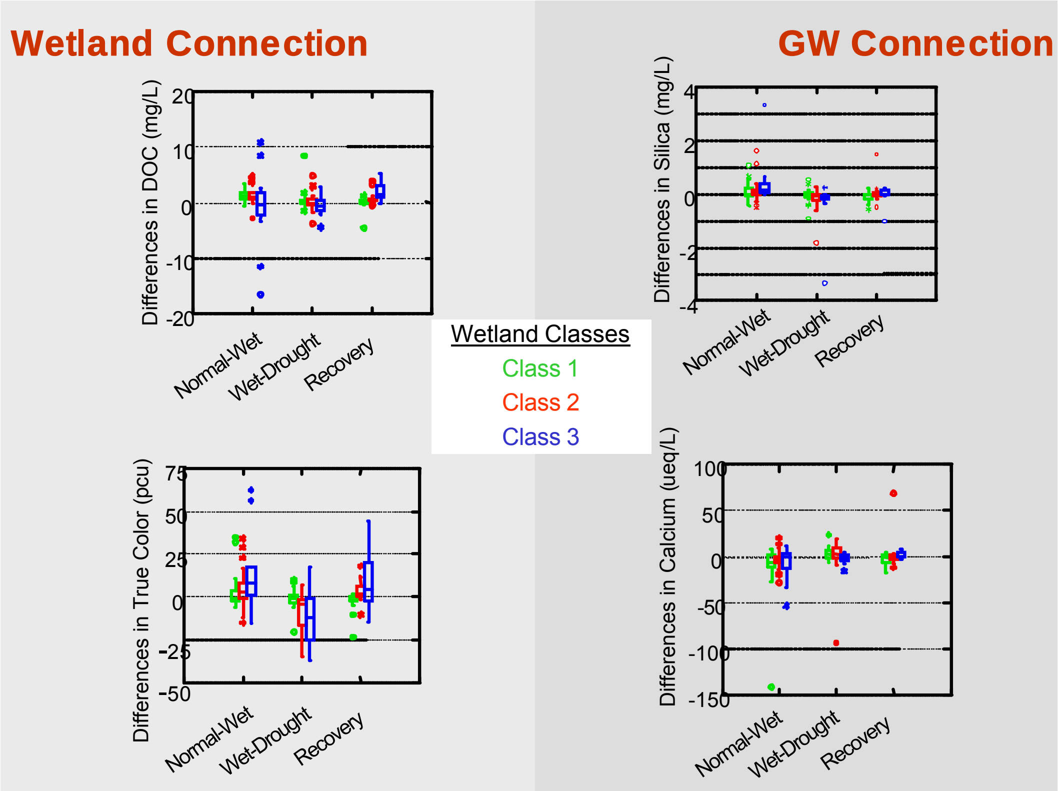

Figure 4. **Maine Results:** Boxplot graphs show *differences* in concentrations from each year with available data, grouped by lake class (the strength of connection with wetlands increases from class 1 to 2 to 3). The Normal-Wet period represents changes in chemistry from 1986/87 to those samples gathered in 1998. The Wet-Drought period represents changes in data from 1998 to 2001, and Recovery represents 2001 to 2002. The starting points for comparison are data from 1986/87 (the first years of the dataset and normal precipitation conditions) and represents zero on the y-axis of these graphs.

Class 3 lakes, with the strongest connection to wetlands, had the largest response to changes in DOC and true color. DOC and true color decreased during drought, and increased with increased precipitation. Silica concentrations slightly decreased during drought, and increased during wet or recovery years. Calcium had an opposite pattern, with some increases during drought, possibly due to evaporation and dilution effects.

Does aluminum geochemistry control the trophic status of oligotrophic lakes?

Basic Information

Title:	Does aluminum geochemistry control the trophic status of oligotrophic lakes?
Project Number:	2001ME1481G
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Focus Category:	, Water Quality, Non Point Pollution
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Publication

1. Norton,S. A., Fernandez, I. J., Kahl, J. S., and Reinhardt, R., 2002, Acidification trends and the evolution of neutralization mechanisms through time at the Bear Brook Watershed in Maine (BBWM), USA: 4th International Symposium on Ecosystem Behavior (BIOGEOMON), Reading, England.
2. Reinhardt,R. L., Norton, S. A., Handley, M., and Amirbahman, A. 2002, Mobilization and linkages among P, Al, and Fe during high discharge events at the Bear Brook Watershed in Maine, USA: 4th International Symposium on Ecosystem Behavior (BIOGEOMON), Reading, England.
3. Vesely, J., Majer, V., Kopacek, J., and Norton, S. A., 2002, Climate warming accelerates decreased aluminum concentrations in lakes recovering from acidification: 4th International Symposium on Ecosystem Behavior (BIOGEOMON), Reading, England.
4. Norton, S. A., Fernandez, I. J., and Kahl, J. S., 2002, Intersections of monitoring, manipulation, and modeling: 4th International Symposium on Ecosystem Behavior (BIOGEOMON), Reading, England.

Acidification trends and the evolution of neutralization mechanisms through time at the Bear Brook Watershed in Maine (BBWM), USA

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Abstract

The paired catchment study at the forested Bear Brook Watershed in Maine (BBWM) USA documents interactions among short- to long-term processes of acidification. In 1987-1989, the runoff from the two catchments was nearly identical in quality and quantity. Ammonium sulfate has been added bi-monthly since 1989 to the West Bear catchment at 1,800 eq ha^{-1} yr^{-1}; the East Bear reference catchment is responding to ambient conditions. Initially, the two catchments had nearly identical chemistry (e.g., Ca^{2+}, Mg^{2+}, SO_4^{2-} , and Alk □ 82, 32, 100, and 5 μeq L^{-1}, respectively). The manipulated catchment responded initially with increased export of base cations, lower pH and alkalinity, and increased dissolved aluminum, nitrate, and sulfate. Dissolved organic carbon and silica have remained relatively constant. After seven years of treatment, the chemical response of runoff switched to declining base cations, with the other analytes continuing their trends. Additionally, the exports of dissolved and particulate aluminum, iron, and phosphorus increased substantially as base cations declined.

The reference catchment has slowly acidified under ambient condition, caused by the base cation supply decreasing faster than the decrease of sulfate, as pollution abates. Export of aluminum, iron, and phosphorus is mimicking that of the manipulated watershed but lower in magnitude and lagging in time.

Probable increasing sulfate adsorption caused by acidification has moderated the longer-term trends of acidification in the reference and manipulated watersheds. The trends were interrupted by the effects of several short-term events including severe ice storm damage to the canopy, unusual snow pack conditions, snow melt and rain storms, and episodic input of marine aerosols. These episodic events alter alkalinity by 5 to 15 μeq L^{-1} and make it more difficult to determine recovery from pollution abatement.

Key Words: acid rain, acidification, episodic acidification, aluminum, iron, phosphorus, models, soil, stream water

1.Introduction

Acidification in ecosystems results in chemical changes to soil and to surface and groundwater as a consequence of depletion of base cations in soils and a decrease of base cations relative to strong acid anions in runoff. The most fundamental changes during naturally occurring chronic acidification are an increase in exchangeable H^+ or Al^{3+} ions in soils, an increase in H^+ activity in soil water, and a decrease in alkalinity in waters draining from the catchment. As systems acidify, the biotic community changes composition. Poorly drained terrestrial systems acidify and develop into ombrotrophic bogs or blanket peat systems – where atmospheric inputs of water and nutrients and mineralization of organic matter control water chemistry and vegetation. Acidified systems may include dystrophic to clear-water oligotrophic streams and lakes.

There is no rigorous definition of when a system has become “acidic”, nor is there sharp definition between chronic and episodic acidification. Acidification processes operate at different time scales (Figure 1). Natural chronic acidification occurs over time frames of 10^3 to 10^6 years as base cation-rich soluble minerals are depleted from the soil profile. During the process, concentrations of base cations decrease in runoff and, with no change in the supply of acidity from any source, the pH and bicarbonate alkalinity decline. Even sulfate concentrations, if derived from the weathering of sulfide minerals, may decline. Such acidification trajectories have been demonstrated by inference using fossil diatom and chrysophyte assemblages in sediments (Whitehead et al., 1989) and soil chronosequences, and using contemporaneous water chemistry from spatially distributed lakes of varying age (Engstrom et al., 2000). The pH in lakes in glaciated terrane typically declines about 1.5 to 2 pH units over periods ranging from a few hundred to a few thousand years after deglaciation. With no change in other processes that may cause acidification, runoff chemistry approaches a steady state value. If paludification of the catchment occurs, base cation supply may be decreased through hydrologic isolation of mineral soil, production and export of organic acidity (dissolved organic carbon) may increase, and alkalinity and pH decline further. Paludification may occur over hundreds to thousands of years and result in new steady state chemistry for runoff.

Acidification processes operating at intermediate time frames (10^1 to 10^3 years) include acidic deposition and biomass variation. Biomass increases in an aggrading forest, resulting in a sink for base cations (Nilsson, 1982). The effect of net accumulation of biomass is acidification. Decreasing net biomass may be gradual, driven by climate or soil evolution. The result, not well documented and hidden in the noise of other processes, would be an increase in mineralization and release of base cations, thereby reducing or reversing acidification, causing alkalization. Loss of biomass may be catastrophic (short-time disturbance) due to fire, wind-throw, insect invasion, or ice storms thereby producing unpredictable consequences for pH and alkalinity. Effects on acid-base status in the range of 10^1 to 10^{-1} years include afforestation, climate, and deforestation. These processes affect acid-base status through variations in input of aerosols, production of organic acidity, storage of base cations in biomass, and mineralization. Lastly, a number of processes operate on a time scale of <1 year: nutrient cycling, snowmelt, marine aerosol incidents, and rain storms. As each of these vary in strength from year to year, their impact on the acid-base status of a watershed will vary. Isolating their individual effects requires high frequency data over relatively long periods of time.

We report here on the “natural” acidification and artificially induced acidification of two adjacent low alkalinity systems, as well as several natural short-term acidification mechanisms at Bear Brook Watershed in Maine, USA (BBWM) during the period 1987-2002.

2. Methods

The Bear Brook Watershed in Maine, USA (BBWM) is a paired watershed study designed to test models of surface water acidification caused by atmospheric deposition of acidic or acidifying substances (Norton and Fernandez, 1999). The two contiguous, forested watersheds are drained by low alkalinity headwater streams. The watersheds have very similar aspect, topography, vegetation (Eckhoff and Wiersma, 2002), soils (Fernandez et al., 1999; Swoboda-Colberg and Drever, 1993), bedrock lithology (Norton et al., 1999), and stream hydrology (Chen and Beschta, 1999). Continuous monitoring of precipitation quantity and quality (weekly), discharge volume (5 minute intervals), and stream chemistry (weekly or more frequently at high flow) from the watersheds started in 1987 (Norton et al., 1999). The West Bear catchment has been treated bi-minthly since November 1989 with 1,800 eq ha-1 yr-1 of $(NH_4)_2SO_4$. Additional details about the watersheds and analytical methods are in Norton and Fernandez (1999). Analytical methods have changed for cations and trace metals since 2000. They are determined by ICP analysis on single solutions. Phosphorus is determined by both standard colorimetric procedures and ICP. The two methods give comparable results.

One unique aspect of the induced stream water chemistry in West Bear Brook is the extremely high concentrations of dissolved Al and particulate Al and Fe. Our protocol for analysis of various analytes consisted of removal of aliquots from field samples within 48 hours for anions (ion chromatography), dissolved organic carbon (DOC) (IR detection), alkalinity (Gran titration), pH (ISE), and P (colorimetric and ICP) and processing appropriately for each of the respective analytical methods. For ISCO™ samples that remain in the field for as long as one week, we decanted and filtered 60 ml of sample for determination of "dissolved Al" and we removed 45 ml of sample and acidified it to pH = 0 to 1 for the determination of "total laboratory Al". We then acidified the remaining contents of the sample in the field bottle to 0.5% acid. The Al in this sample is termed "total field Al". Repeated samples, repeated speciation steps, and repeated reanalysis of the various solutions reveal that "total field Al" > "total laboratory Al" >> "dissolved Al" (Table 1). Table 1 shows the partial chemistry of a sequence of samples taken during a two-day snowmelt event in February of 2002 that affected West Bear Brook. Samples were collected into polypropylene bottles in an automated ISCO™ collector. The samples were retrieved after several days and then processed as described above. Dissolved Al shows a typical pattern for an acidic episode, with concentrations of Al increasing as pH decreases. The "laboratory total Al" also increases. The difference between them is in particulate form. The "field total Al" is substantially greater than the "laboratory total Al" and follows the same trend of increasing as pH declines. We interpret these data to indicate that Al had precipitated within the field sample bottle as a continuous process during warming and as excess CO_2 degassed from them (Norton and Henriksen, 1983). The existence of an overpressure of CO_2 is indicated by the increase in pH induced during the measurement of the air-equilibrated pH compared to the pH at the beginning of the Gran titration, even after several days of shelf time. Apparently the precipitated Al (and Fe) must plate out on the container wall as well as some of it remaining in suspension, the latter to be determined as part of the "laboratory total Al". As a consequence, the concentration reported as "laboratory total Al" underestimates the true Al in the original sample, some Al having been lost to the container surface. The "field total Al" overestimates the true Al in the original sample, some Al having been added to the residual field sample in the ISCO bottle (because of removal of aliquots) by acidifying it and dissolving any particulate Al left on the container wall. The true total Al lies between the "field" and "laboratory" totals. In summary, dissolved Al and particulate acid-soluble Al are operationally defined and may not be reproducible or comparable among studies.

ID	Date	Time	ANC pH	Equil. pH	Total P, ug L^{-1}	Diss. P, ug L^{-1}	Lab. Total Al, ug L^{-1}	Field Total Al, ug L^{-1}	Diss. Al, ug L^{-1}	Lab. Total Fe, ug L^{-1}	Field Total Fe, ug L^{-1}	Diss. Fe, ug L^{-1}
WB-1	2/26/02	1600	4.72	5	5.1	0.6	609	997	545	440	1,480	12
WB-4	2/27/02	800	4.64	4.9	6	0.4	1,720	2,080	730	200	1,020	4.27
WB-7	2/27/02	1400	4.53	4.8	34.2	0.7	2,630	4,600	1,060	585	2,870	5.07
WB-10	2/27/02	2000	4.49	4.7	93.4	1.2	3,400	13,900	1,080	1,130	11,900	6.10
WB-12	2/28/02	0	4.48	4.7	18.4	1.5	1,420	8,910	1,130	248	5,620	2.39
WB-14	2/28/02	400	4.52	4.7	9.8	0.7	1,060	7,590	1,100	135	6,000	3.68
WB-18	2/28/02	1200	4.55	4.8	4.6	0.3	1,020	4,290	1,080	161	4,050	2.65
WB-24	3/1/02	0	4.60	4.8	1.8	0.7	1,090	1,360	1,000	86	679	0.93

Table 1: Partial chemistry of sequential samples from West Bear Brook, Maine during a snow melt event in February 2002.

To test this hypothesis we collected daily ISCO® samples from East Bear (reference) for five days during a period of low and relatively constant flow. Stream pH remained near 6. Each 1-liter sample was decanted into a clean container and acidified. The resulting solution was analyzed for major analytes, total Al (Table 2), and trace metals. The field ISCO® container was refilled with deionized water and acidified, and the resulting solution was analyzed to determine the amount of Al and other elements on the wall of the collection bottle. The decanted solution typically had between 177 and 135 µg total Al L^{-1} while the acidified container plus deionized water had between 12 and 32 µg Al L^{-1}. These data from relatively non-acidic and severely acidified surface waters suggest that it is extremely difficult to determine dissolved Al in waters where Al concentrations are elevated because of the input of groundwater charged with CO_2. The concentration of dissolved Al is probably decreasing with time, and the precipitated Al is partitioning between the container and the solution. If our data are representative of low alkalinity streams undergoing episodic or chronic acidification, it is likely that the flux of both dissolved Al and particulate acid-soluble Al has not been well characterized in many studies. The results for Fe are parallel with respect to the particulate matter. Dissolved Fe was relatively low in both the acidic and non-acidic conditions in both streams with a small increase during periods of depressed pH. The partitioning of Fe to the container walls is equally as dramatic as for Al, and apparently faster. The numerical value of the concentration of dissolved Al and Fe may be a moving target, changing rapidly as a result of degassing of CO_2 from, and introduction of oxygen to, emerging groundwater.

The dramatic amount of P associated with the particulate Al and Fe (Table 1) indicates that the concentration of total and dissolved P in acidic solutions may be equally difficult to characterize.

Collection bottle filled with DI and acidified

ISCO ID	Al	Ca	Fe
	μg L^{-1}	mg L^{-1}	μg L^{-1}
E2	21.8	0	0
E5	20.9	0.001	0
E6	14.6	0.006	0
E7	24.3	0.001	4.68
E8	31.8	0.008	0
E10	11.8	0.005	0

Decanted solution, acidified

ISCO ID	Al	Ca	Fe
E2	135	0.989	0
E5	120	1.05	2.03
E6	117	1.07	0
E7	119	1.09	12.7
E8	123	1.07	0

Table 2: Concentrations of Al, Ca and Fe in solution decanted from sampling bottle and acidified, and from the field collection bottle filled with distilled water and then acidified.

In November of 1989, bi-monthly applications (1,800 eq ha^{-1} yr^{-1}) of pelletized $(NH_4)_2SO_4$ to West Bear (10.2 ha) were initiated and continue to the present. These applications were designed to be a realistic way of accelerating the processes related to acid rain-driven acidification. In 1989, the dose represented a 200% increase in the flux of S to the watershed and an increase of 300% for N. East Bear (10.7 ha) serves as a reference watershed. During the period of study (1987-2002) we assume that the long-term chemical weathering acidification trajectory was essentially at steady state, paludification is nearly absent and at steady state, living biomass is relatively constant in quality and quantity, and climate (T and moisture) has not changed systematically or appreciably. However, there was one defoliation episode (both catchments) in the mid-1990s that preferentially attacked the beech component of the forest (and the beech is in decline), and a major ice storm in January of 1998 destroyed approximately 1/3 of the hardwood canopies. Canopy closure was essentially complete after four years. The paired catchment design allows us to isolate the effects of the chemical manipulation from these other variable processes.

3. Results

Prior to the start of the chemical manipulation (November 1989), the chemistry of both streams were highly variable as a consequence of the seasonality of nutrient uptake and mineralization, variable discharge due to rain storms and snowmelt, and variable input of marine aerosols (Figures 2a and b). However, volume-weighted means of major analytes were nearly identical. The volume-weighted means for Ca and Mg in the two streams for 1989 and subsequent years are shown on Figure 3. The temporal variability of the chemistry of the two catchments during the period 1987-1989 was virtually identical with respect to all major analytes, pH and ANC. The similarity of behavior for the pre-manipulation period is emphasized by inspection of a “difference” diagram (Figure 4) on which the differences between concentrations of simultaneous samples from both streams are plotted. Even compounds with seasonally highly variable values (e.g., NO_3) or elements that may be considerably diluted during high discharge events (e.g., Ca and Mg) behave very similarly in the two watersheds, prior to the manipulation

3.1 East Bear

Runoff from East Bear Brook, the reference catchment, has slowly acidified from 1989 to 2001, as SO_4 and NO_3 declined, and base cations declined even more on an equivalent basis (Figures 2 and 3). The mean annual volume-weighted concentrations of Ca and Mg decreased irregularly from 1989 (78 and 30 μeq L^{-1}, respectively) to 1998. Starting in 1998; the mean values increased slightly for two years and then declined again in 2000 to 52 and 21 μeq L^{-1}, respectively. The DOC (ca. 2 mg L^{-1}) and Si (ca. 2 mg L^{-1}) have remained nearly unchanged. The concentration of SO_4 in stream water declined from about 105 to 85 μeq L^{-1}, as SO_4 declined in precipitation. The concentration of NO_3 was strongly seasonal with minimum values during the growing season, and spikes of high concentration during periods of high flow in the spring and fall. Annual export of NO_3 from East Bear, the reference watershed, has declined since the early 1990s, a pattern repeated at many localities in the eastern United States. Mitchell et al. (1996) attributed the period of high NO_3 export in the late 1980s and early 1990s to short term climate fluctuations, particularly cold and dry winters. The acidification of East Bear, in the context of declining NO_3 and SO_4 in stream water is enigmatic. It is clearly driven by base cations declining more rapidly than the acid anions but the cause of the decline in base cations is unclear. Such a declining pH and alkalinity in spite of decreased SO_4 is common in the northeastern U.S. (Stoddard et al., 1998, 2003). The declines are not caused at BBWM by changes in atmospheric deposition of non-marine base cations (Norton et al., 1999). The decline of stream concentrations of base cations may relate in part to recovery of base saturation by the soils as SO_4 declined. Such a decline in response to decreased SO_4 is predicted by ion exchange theory. However, the decline in stream base cations should not exceed that of the strong acid anions, as it did. It may be that watershed soils have not yet reached equilibrium even with reduced SO_4 loading from the atmosphere.

A short-term de-acidification climate-related event not caused by atmospheric pollution occurred in the period 1989-1991. Then, we had concurrent measurement of soil PCO_2 and stream chemistry. High soil PCO_2 during one winter exceeded summer values (Fernandez et al., 1993) and coincided with elevated export of base cations (and thus alkalinity). The high PCO_2 was coincident with a substantial and continuous snow pack. The tendency for pH of soil solutions to be depressed by the high PCO_2 was apparently offset by desorption of more base cations in the soil, producing extra bicarbonate alkalinity of 10 to 15 μeq/L. Lower than normal PCO_2 resulted in slightly lower pH and alkalinity in runoff. Modeling with MAGIC (Cosby et al., 1985) indicated that the variations of soil PCO_2 were sufficient to explain the variation in alkalinity from winter to winter (Norton et al., 2001). Nearly half of the runoff in any year at BBWM is associated with the melting of the snowpack, making this mechanism important in the alkalinity budget. Systematic variations in alkalinity production are not sustainable over long periods of time. The variability make it more difficult to statistically identify the acidification due to the chemical treatment in West Bear, and the longer term decline in pH in East Bear that is possibly driven by base cation depletion.

A second meteorological event appears to have caused a two-year (1998-1999) reversal of the decline of base cation concentrations in stream water. In January of 1998, both Bear Brook watersheds were subjected to a freezing rainstorm that lasted nearly one week. The storm deposited up to 10 cm of ice on horizontal surfaces and destroyed as much as one third of the hardwood canopy. Subsequently, base cation concentrations and annual volume-weighted means increased for two years (Figures 2a and 3), after which the decline in base cations continued. Nitrate was also higher in both watersheds than in the bracketing years (Figure 2b).

Periods of higher discharge during snowmelt or rainstorms are accompanied by slightly lower concentrations for base cations, reflecting dilution. The concentrations of cations, particularly Ca and Mg (Figure 5), are statistically highly related. This relationship is most likely caused by ion exchange equilibria. These periods of higher discharge also have slightly higher concentrations of DOC (□ = +1 to 2 mg DOC L^{-1} = 5 to 10 □eq organic acidic anion L^{-1}) and NO_3 (□ = +10 to 20 □eq L^{-1}), and relatively unchanged SO_4. Consequently pH and alkalinity decline during higher discharge episodes. Only rarely is precipitation rich enough in marine aerosols to cause measurable episodic acidification at BBWM (e.g., winter 1995/1996), driven by ion exchange of Na and Mg for H, although the effects are persistent (Norton and Kahl, 2000). The increasing Cl in runoff in 1998-2000 lags behind the sharp increase in Ca and Mg, suggesting that marine aerosols are not the dominant process involved in the sharply increased concentrations and fluxes of base cations starting early in 1998.

The annual mean volume-weighted concentration of dissolved Al varied between 4 and 8 □moles L^{-1} from 1989 to 2002. Higher concentrations occurred during higher discharge and lower pH. The increases in Al were all in the inorganic form (Postek et al., 1996). In high discharge events in 1995, dissolved Al reached 10 □moles L^{-1} and acid-soluble particulate Al increased slightly to as much as 5 or 6 □moles L^{-1} (Roy et al.,1999). The increased particulate Al was dissolved at pH = 0 in H_2SO_4, but there were no comparable increases in base cations, indicating that the particulate Al was not associated with alumino-silicate minerals. In snowmelt episodes in the winter of 2001/2002, dissolved Al reached as high as 11 umoles L^{-1} (Reinhardt et al., this volume) and particulate Al reached 185 □moles L^{-1}. Dissolved and particulate Fe both were below 0.5 □moles L^{-1} in the 1995 high discharge episodes. In 2001/2002 episodes, dissolved Fe remained <0.5 □moles L^{-1} while particulate, acid-soluble Fe increased to as much as 275 □moles L^{-1}, a five hundred-fold increase over 1995. As indicated above, these concentrations may slightly overestimate the original concentration of particulate Al and Fe but it is clear that enormous amounts of Al and Fe hydroxide are leaving the catchment as a consequence of acidification. The dissolved P typically remains below 2 □g L^{-1}, regardless of pH. However, particulate acid-soluble P has increased from a maximum of about 50 □g L^{-1} in 1995 to nearly 100 □g L^{-1} in 2002. Particulate P is about 50 times dissolved P.

3.2 West Bear

In the first 12 years of treatment (1989-2001), West Bear acidified more than East Bear as a result of the $(NH_4)_2SO_4$ addition. The response by most major analytes (Figure 4) was statistically significant within a few years (Uddameri et al., 1995). Alkalinity decreased about 20 □eq/L and and pH declined from ca. 5.5 to 4.7.

Concentrations of dissolved base cations increased by up to 75 µeq/L by 1995 (Figures 2a, 3, and 4). West Bear has responded to the $(NH_4)_2SO_4$ addition by exporting more base cations at higher flow, the reverse of East Bear. The excess export is Ca>Mg>Na>K. Consequently, the volume-weighted annual means for Ca and Mg generally increased for the first six years and then started to decline, apparently as base cations were depleted in the exchangeable soil pool (Fernandez et al., 2003). During the decline, runoff was depleted in Mg relative to Ca, suggesting that the soils had been preferentially depleted of Mg. The decline was interrupted in 1998, concurrent with the ice storm and for two years, Ca and Mg *increased* in runoff. This brief period of accelerated loss of base cations in both catchments was most likely caused by a combination of:

(1) mineralization of destroyed biomass lying on the forest floor,

(2) increased mineralization rates caused by higher moisture and temperature in the forest floor, and

(3) reduced base cation uptake due to the reduction in canopy area, and

(4) increased marine aerosols displacing some base cations from soil.

By 2001, the decrease of Ca and Mg resumed, with the mean volume-weighted value approaching that prior to the chemical manipulation, but at a substantially lower stream pH. The synchronicity of base cation trends in both watersheds from 1998 to 2000 indicates that the ice storm was the cause, rather than the chemical manipulation.

Mean annual volume-weighted dissolved Al has increased irregularly from about 5 µmole L^{-1} in 1989 to annual means greater than 20 µmole L^{-1}, with concentrations commonly well over 40 µmole L^{-1} (>1 mg L^{-1}). In 2000, the increase of dissolved Al exceeded the sum of all the excess base cations. The concentration of acid-soluble particulate Al in the 2001/2002 winter increased episodically up to as high as 520 µmoles L^{-1} (14 mg L^{-1}) (Figure 6) with associated particulate P (□ = up to nearly 100 µg L^{-1}) (see Reinhardt et al., this volume). The particulate Al is likely to have been derived from the B-horizon of mineral soil by either a one or two stage process. As soil waters have become progressively more acidic, more Al is mobilized in dissolved form and transported to the stream in shallow flow. Upon emergence into the stream and mixing of soil water with stream water with higher pH, combined with degassing of excess CO_2, much of the dissolved Al in the water column is precipitated (Norton and Henriksen, 1983). At low flow, some Al hydroxide may adhere to the stream substrate and some dissolved Al may adsorb on exchange surfaces. Subsequent higher stream flow with lower pH may physically and chemically mobilize the Al from the stream channel (Tipping and Hopwood, 1988; Norton et al., 1992) and add to the Al transported directly from the soil. Mobilization of Al from the soil consumes H^+ in the soil; precipitation of Al in the stream produces H^+. Effectively there is a translocation of Al due largely to carbonate equilibria with no net change in alkalinity of the system. However, the long-term effect is to mobilize the more labile $Al(OH)_3$ from the soil, with the consequence that more lower pH water will be translated to the stream. We caution that collection of samples and preserving their integrity to distinguish between dissolved and particulate Al is extremely difficult, due to changes in T, PCO_2, and other reactions (see section 2. Methods).

In 1995 high discharge episodes in West Bear Brook, dissolved Fe never exceeded 0.5 µmoles L^{-1} while particulate Fe reached 11 µmoles L^{-1}. In the winter of 2001/2002, concentrations of dissolved Fe reached 0.5 µmole L^{-1}; Mn reached 0.1 µmole L^{-1}. Concurrently, high concentrations of particulate acid-soluble Fe (up to 255 µmoles L^{-1}) occurred during periods of high discharge caused by rain and snowmelt (Figure 6). High concentrations of particulate P (up to 100 µg L^{-1}) accompanied the high Fe (Table 1). We have too few samples to assess whether the P is more strongly associated with Al or Fe in samples when both Al and Fe are high. The origin of Fe and Mn is also most likely from the Fe-, Mn-, and P-rich B-horizon of the forest spodosols (Fernandez, unpub.). The mechanism of mobilization should be the same as for Al. As soil solutions have become progressively more acidic, particularly along high flow paths, more Fe, Mn, and P are mobilized and transported toward the stream. Precipitation of mobilized Fe in the stream should be caused by increased pH in the stream related to mixing, degassing of excess CO_2, and exposure to higher PO_2. Historically, Fe and Mn were low in concentration in East and West Bear. Increases of dissolved and particulate Fe were documented for West Bear by Roy et al. (1999) in 1995 for high discharge events. However, in 1995 both dissolved and particulate Fe remained lower than dissolved and particulate Al. In 2002, particulate Fe is higher than particulate Al. Fe is emerging as an important indicator of lowering pH.

The pre-manipulation concentration of SO_4 was approximately 100 µeq L^{-1} with only slight variation during periods of variable discharge (Figure 2b and 4). Soils apparently buffered the value quite well. The chemical amendment of $(NH_4)_2SO_4$ corresponds to 1800 eq ha^{-1} yr^{-1} and in the absence of other influences should cause the runoff SO_4 to increase to approximately 300 µeq L^{-1} when steady state has been reached. However, by 2001 the volume-weighted annual mean SO_4 concentration was approximately 200 µeq L^{-1}. Retention of added SO_4 in 2001 was about 50% and over the time of manipulation averages about 75%. The rate of increase in retention is decreasing, even as anion adsorption capacity may be increasing as the soil pH decreases (Nodvin et al., 1988) or possibly Al-SO_4 phases may be forming in the soil.

Although NO_3 has increased up to 100 μeq L^{-1} during high discharge, there is still strong apparent retention of added N and a strong seasonal signal. (Figures 2b and 4). We do not know if N retention has resulted in increased biomass production. Uptake of NO_3 offsets acidification but uptake and storage of base cations in biomass would be an additional source of acidification. The extra N might stimulate mineralization of dead biomass, with the reverse effects. Nitrate was higher in 1998 than in the year before or after suggesting an effect from the ice storm.

4. Discussion

Both East and West Bear Brooks have acidified during the period 1987-2001. East Bear has acidified more slowly than West Bear and under ambient atmospheric deposition of excess SO_4, NO_3, and NH_4. The East Bear acidification was caused by decreasing export of base cations, apparently because of continued (but reduced) loading of excess SO_4 in excess of the rate of supply of base cations from weathering and other less significant sources. Superimposed on this slow acidification are variations linked with more episodic processes including:

1. ice damage to the canopy (base cation mineralization and reduced uptake),
2. unusual snow cover conditions (elevated soil PCO_2 producing more alkalinity),
3. episodic inputs of marine aerosols (ion exchange of Na and Mg for H and the reversal of this exchange),
4. highly variable hydrology (dilution at high discharge for East Bear and the increased desorption for West Bear), and
5. climate-driven variation in nitrogen retention (released as NO_3).

Initially, resistance to the acidification (short- and long-term) was provided by a combination of titration of bicarbonate alkalinity, cation desorption, Al desorption and dissolution, and possibly protonation of dissolved organic carbon. As acidification of the East Bear watershed has progressed, base cation concentrations, pH, and alkalinity in runoff have decreased and dissolved Al has increased. Progressively more Al and Fe are leaving the watershed in particulate form, probably as amorphous hydroxide. This particulate material does not represent a loss of alkalinity to the system. The translocation of Al and Fe requires H^+ to mobilize the metals from the soil and releases H^+ in the stream, with no net change in the acid-base status of the water. However, as the sources of labile Al and Fe become depleted in the soil, flow paths will progressively have lower pH, dissolved Al and Fe will increase further along in soil hydrologic pathways, and the acidification of stream water (particularly as measured by pH) will accelerate.

The addition of $(NH_4)_2SO_4$ to West Bear has accelerated the acidification processes documented for the East Bear catchment. Because of the additional strong acid anions SO_4 and NO_3, added and derived from increased nitrification, respectively, base cation desorption accelerated for about 6 to 7 years until both of the dominant base cations (Ca and Mg) became depleted on the soil exchange complex. Base cation depletion at BBWM (Fernandez et al. 2003) has the potential (under current investigation) to impact the chemistry of vegetation as well as disrupting normal forest processes, including regeneration and seedling growth. Despite increasing SO_4, NO_3, and H^+ in soil water and runoff, desorption of base cations from soils has decreased since 1996. The dominant processes for neutralization of acidity shifted to desorption and/or dissolution of Al after about 6 to 7 years of treatment. A similar switch from Ca release to Al release was demonstrated experimentally by Carnol et al. (1997) using undisturbed soil cores also treated with $(NH_4)_2SO_4$. A shift in the Ca/Al ratio in soils has the potential for direct impact on root physiology and tree health (Cronan and Grigal, 1995). Most recently, Fe has started to mobilize as pH has declined, providing yet another line of defense against acidification. Mn, in short supply in these soils, is being mobilized but is insignificant in its capacity to neutralize.

The expectation for chemical behavior of West Bear Brook is shown on the schematic plot of chemistry through time (Figure 7). Galloway et al. (1983) proposed a 7-stage conceptual model for base cation behavior during acidification and recovery. Prior to acidification (stage I), base cation concentrations in runoff are in steady state with chemical weathering and input from marine aerosols. Under an imposed stress of elevated acid input, there is a period of increased export of base cations during which base saturation of soils is reduced. This period (stage II) corresponds to years 1990 to 1995 in Figure 3 for West Bear. Stage III corresponds to a period of declining base cations and is the model for East Bear for the entire study period of 1987 to 2001 and in the context of ambient acid rain. It is also the model for West Bear since 1996 with its increased acid deposition due to the manipulation. Stage

IV corresponds to a new steady state where base cation export is essentially controlled again by the rate of chemical weathering and input from marine aerosols. Stage V corresponds to decreased base cation concentrations in runoff, after the acid stress is removed from the system and while soils are resorbing base cations. Stage VI corresponds to the period of increasing concentrations of base cations in runoff, as soils approach chemical equilibrium (Stage VII) with inputs from weathering and the atmosphere. This simple trajectory of recovery can be confounded by many of the short-lived transient effects noted in Figure 1.

We suggest that a more complete conceptual model of watershed acidification should include the dynamics of Al and Fe. Based on the dynamics of West Bear, manipulated over the last 13 years, it is clear that as desorption of base cations declines as the major acid neutralization mechanism, it is replaced by Al. This has been the impetus for research on the effects of acidic deposition on surface waters - acid rain lowered the pH of soil and surface waters. Lowered pH mobilized Al. Inorganic (unbound) Al is toxic to fish. These acidification relationships and recovery have been demonstrated empirically, using spatial studies (e.g. Henriksen et al., 1998) and elegantly in experiments (e.g., Wright et al., 1993). In turn, it appears that Fe may replace Al, either at lower pH and after much acidification, or in Al-deficient soils (e.g., Borg, 1986). The runoff event in February of 2002 was sampled every 4 hours. The concurrent sampling of the two streams found that export of particulate Fe was greater from East Bear at pH = 5 than from West Bear at pH = 4.6. It is possible that we missed a brief period when the more acidic stream exported more Fe. It is also possible that the threshold for increased mobilization of particulate Fe from these forest soils is reached at about 5.0 (stream pH) and that the most labile soil Fe is quickly depleted. The moblized labile Fe may be precipitated as groundwater emerges into streams and lakes and be subsequently deposited downstream as sediment. Many studies indicate that many currently acidic lakes have a period during their recent acidification when deposition of Fe in lake sediment was substantially increased (Norton, 1989). Not surprisingly, these catchment-scale responses to acidification are parallel to the buffer soil classes (base cations followed by Al followed by Fe) defined by Ulrich (1981).

There are many studies of watersheds at various stages of acidification, including stages I-IV, but it is extremely difficult to establish in which stage a system lies because very long-term data are necessary to determine this. We are fortunate to have created a long-term paired watershed study where one system (East Bear) was acidifying through a critical stage under ambient acidic deposition conditions, and we were able to force the other system

(West Bear) to accelerate the process of acidification. The volume-weighted chemistry of West Bear Brook has evolved through at least three stage of acidification (the end of I, II, III, and into IV). However, shallow rapid flow paths heavily bias the volume-weighted chemistry. Base flow at West Bear has chemical characteristics of stage III, while some high flow paths may be dominated by Fe mobilization.

Lastly, the increased movement of particulate Al and Fe through the groundwater system and into surface waters may have profound implications for the availability of dissolved P in systems that are acidifying. At the Bear Brooks, P export is 25 to 50 times greater in acid-soluble particulate form than dissolved. The presence of the two Al- and Fe-hydroxide phases in suspension may effectively decrease the dissolved P in streams and lakes through adsorption, causing oligotrophication (Dickson, 1978), thereby altering the trophic status of receiving waters (Kopá_ek et al., 2000). The release of P from sediments even during development of anoxia in the hypolimnia of lakes may be prevented if Al $(OH)_3$ is present in the sediment.

5. Summary

Acidification of the paired watersheds at Bear Brook Watershed in Maine over a 14 year period has occurred as a consequence of depletion of several acid-neutralizing processes. The East Bear watershed has served as a reference and is acidifying largely as a consequence of decreased base cation export exceeding the decline in strong acid anions (NO_3 and SO_4). The West Bear watershed has been treated with $(NH_4)_2SO_4$ to accelerate acidification. The treatment accelerated the export of dissolved base cations and Al with a concurrent depression of alkalinity and pH. Base cation export then decreased, especially Mg, even as pH and alkalinity continued to decline.

Short-term acidification processes include:

(1) *decrease* of base cations in runoff at higher discharge because of shallow flow paths in the soil being dominated by soils with low base saturation (East Bear)

(2) *increase* of base cations in runoff at higher discharge because of a substantially increased flux of SO_4 and NO_3 from the treatment (West Bear)

(3) increased dissolved organic acids during higher discharge (both catchments),

(4) episodic input of marine aerosols producing a salt effect (ion exchange for H^+, both catchments).

The consequences of these episodic events of varying duration is a decrease in alkalinity, pH, and base cations (East Bear only) and an increase in dissolved Al, DOC, and NO_3.

Short-term alkalization has been caused by:

(1) increased export of base cations caused by mineralization of biomass provided by a severe ice storm and reduced photosynthesis (biomass production) and

(2) higher-than-normal soil PCO_2 in the winter that causes excess desorption of base cations into spring runoff.

In both catchments, substantial loss of Al, Fe, and P occurs because of acidification of soil flow paths and elevated soil PCO_2. The Al and Fe, occurring dominantly as amorphous hydroxide in the soil, are transported from the soil in solution to the streams where lower PCO_2 and higher pH and PO_2 cause precipitation. The P, probably adsorbed and occluded in soil phases, is mobilized with the Al and Fe, and then resorbed by the Al and Fe particulate material in the stream. Primary productivity of downstream systems may be reduced by the sequestration of P by Al, in particular.

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Figure Captions

Figure 1: Conceptual model of time scales for mechanisms of surface water acidification.

Figure 2: Concentrations of cations (a) and anions (b) at East and West Bear Brooks, Maine for 1989-2000. The vertical line on both graphs at November 1989 is the onset of the chemical manipulation. All data are in μeq L^{-1}. West Bear is shown by the dotted line, East Bear by the solid line.

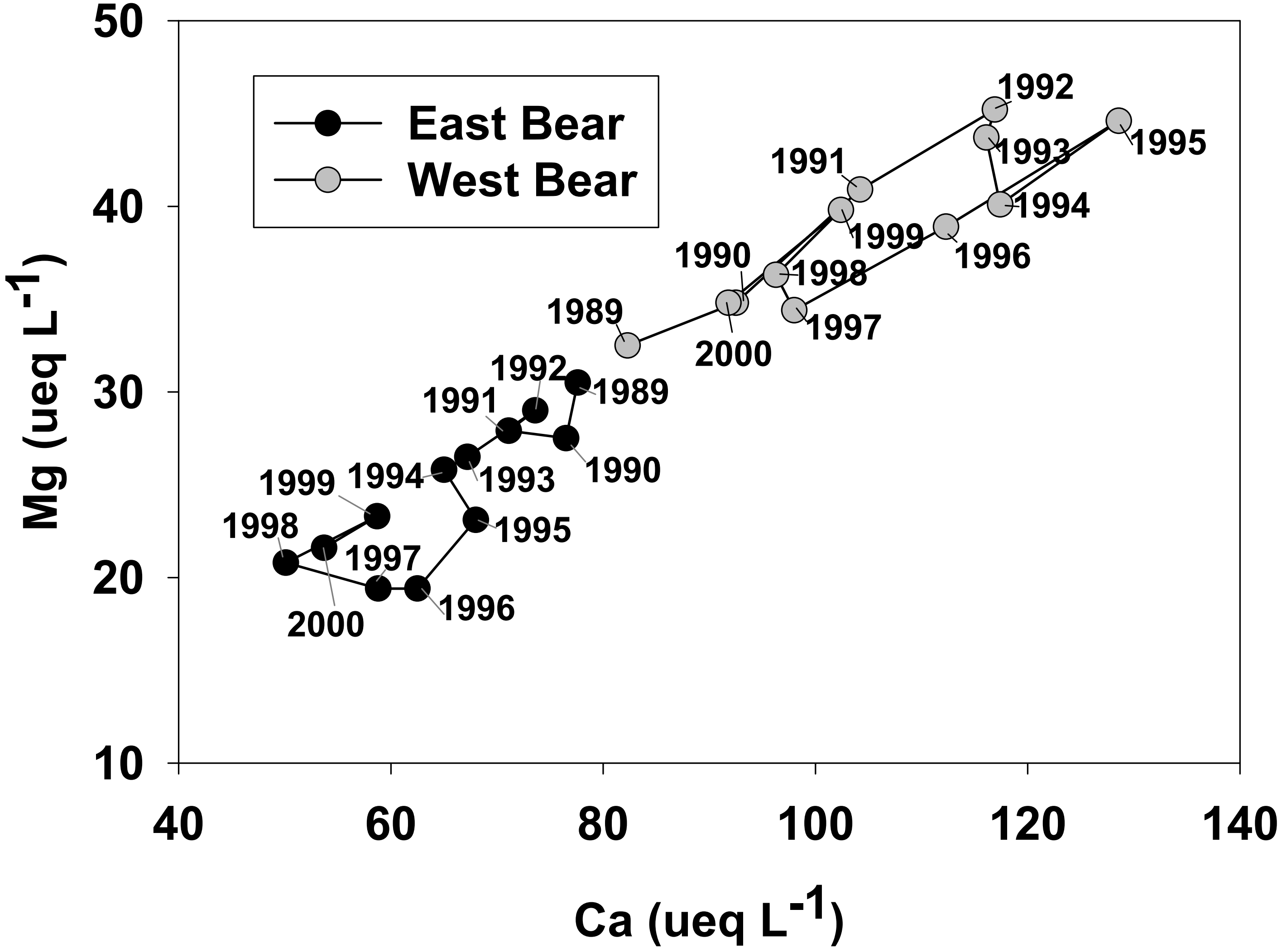
Figure 3: Mean annual volume-weighted concentrations of Ca and Mg for West (grey dots) and East Bear (black dots) Brooks, Maine for 1989 to 2000. All data are in μeq L^{-1}.

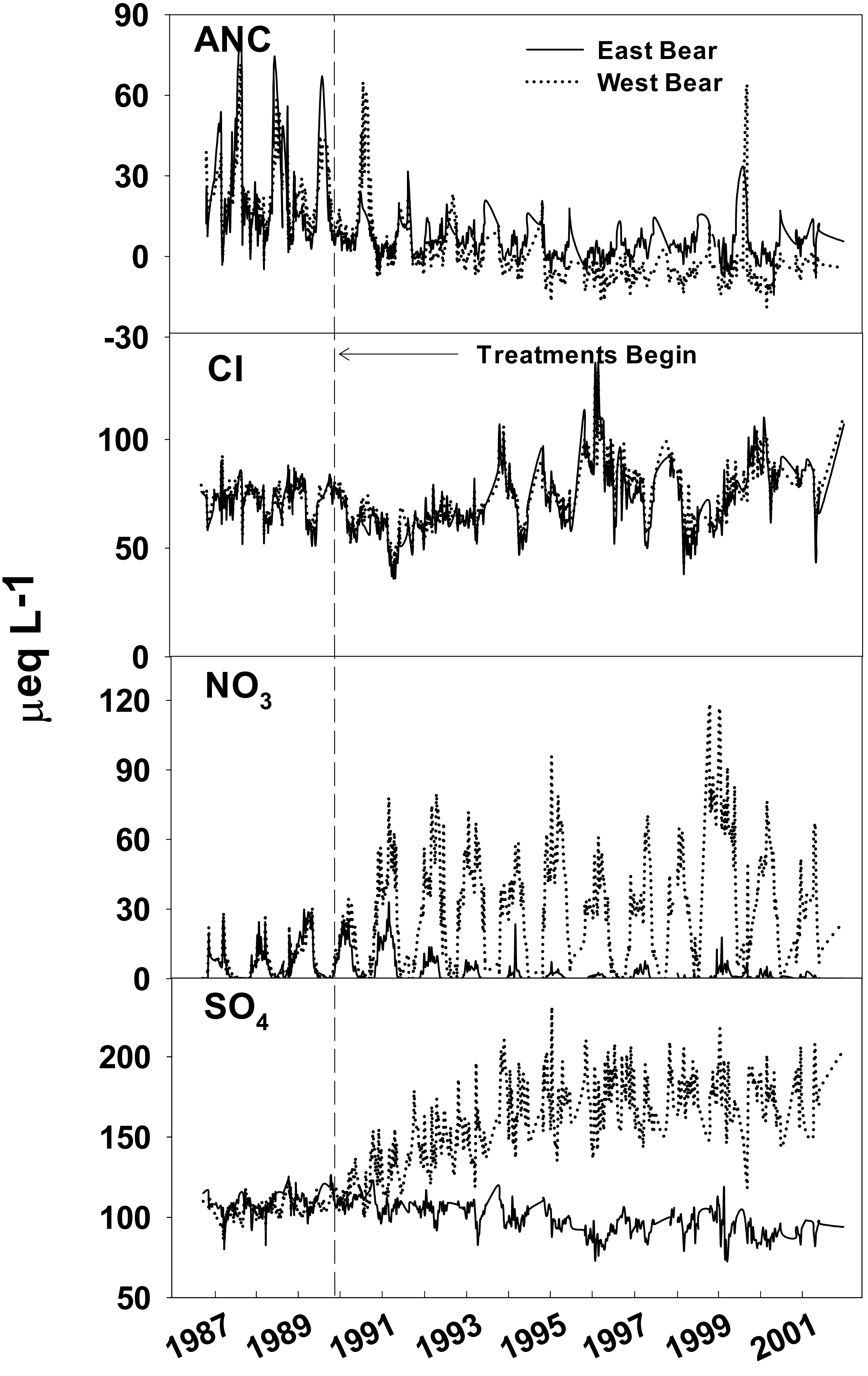
Figure 4: (Concentration of analytes in West Bear Brook, Maine) minus (concentration of analytes in East Bear Brook, Maine) for 1987-2000. All data are in μeq L^{-1}. The vertical dashed line indicates the beginning of chemical manipulation. Dashed line = SO_4. Solid line = Ca. Dotted line = Mg.

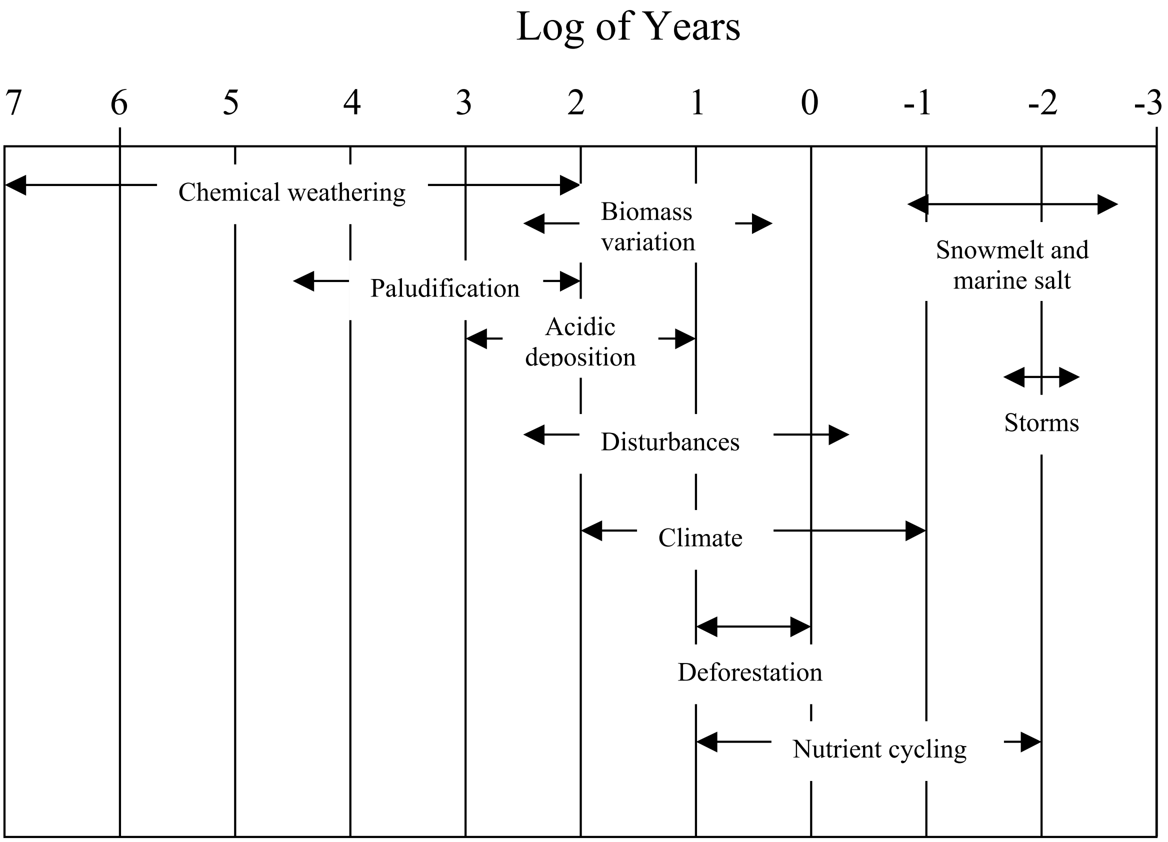
Figure 5: Variation of Ca and Mg for East Bear Brook, Maine for all samples in 1990. The volume-weighted annual mean is indicated by the filled symbol. All data are in μeq $^{-1}$L.

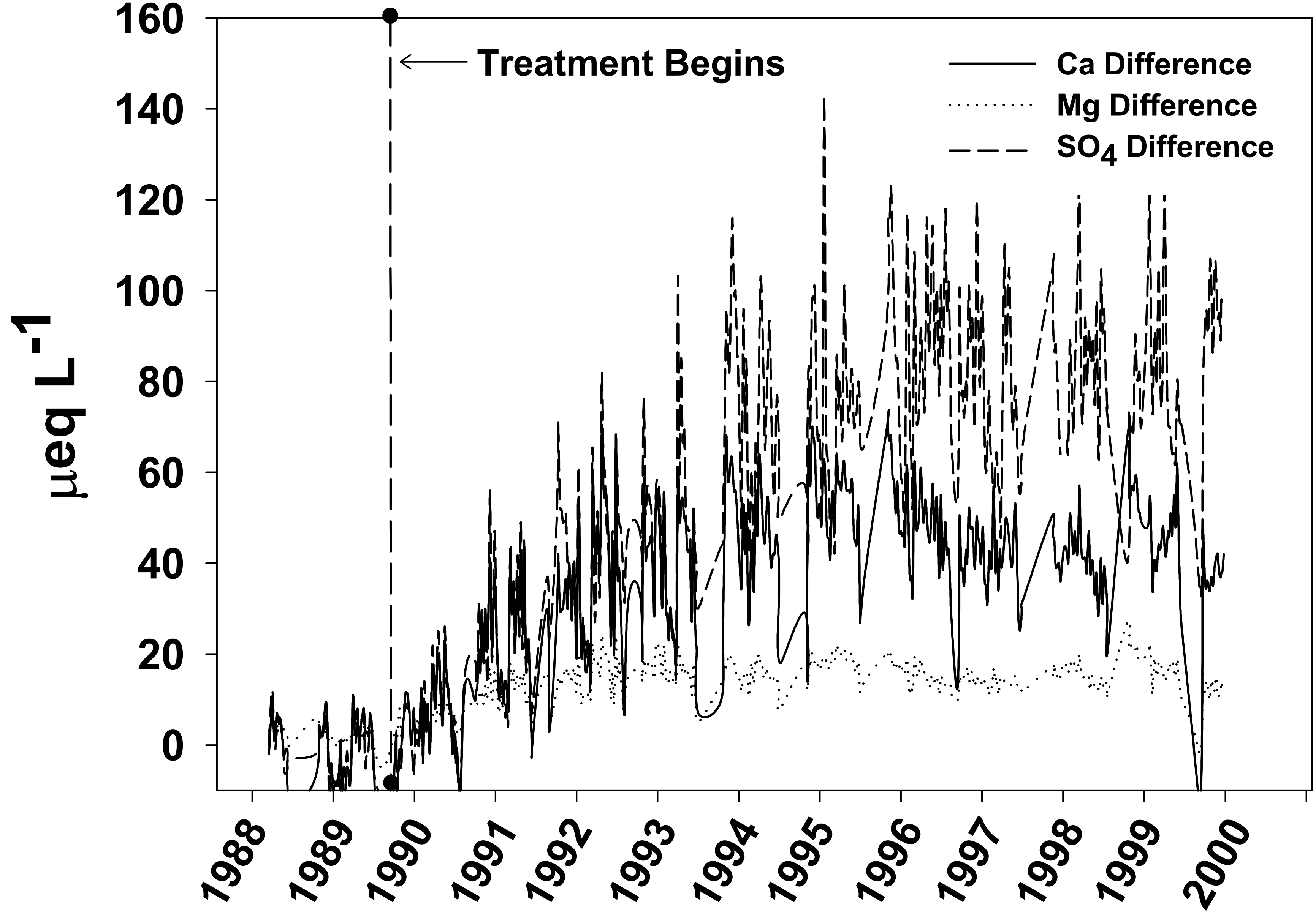
Figure 6: Variation of Al and Fe during an acidic episode at West Bear Brook, Maine in February 2002. All data are in μmoles L^{-1}. Diamonds = Al. Open squares = Fe. Solid lines = acid soluble particulate. Dotted line = dissolved. Filled circles with dashed line = discharge.

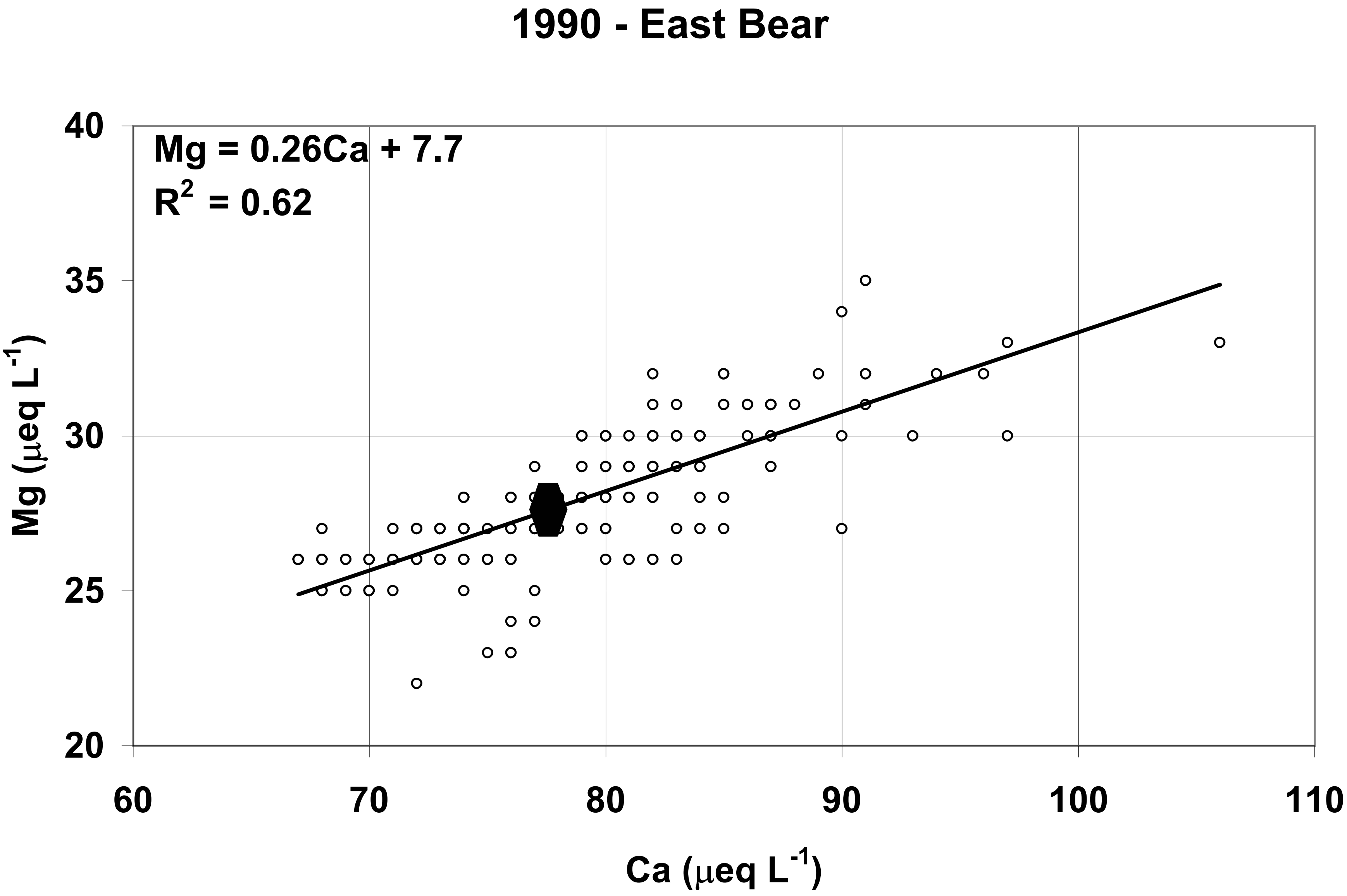
Figure 7: Conceptual model of mechanisms of neutralization through time, based partly on the behavior of West Bear Brook, Maine.

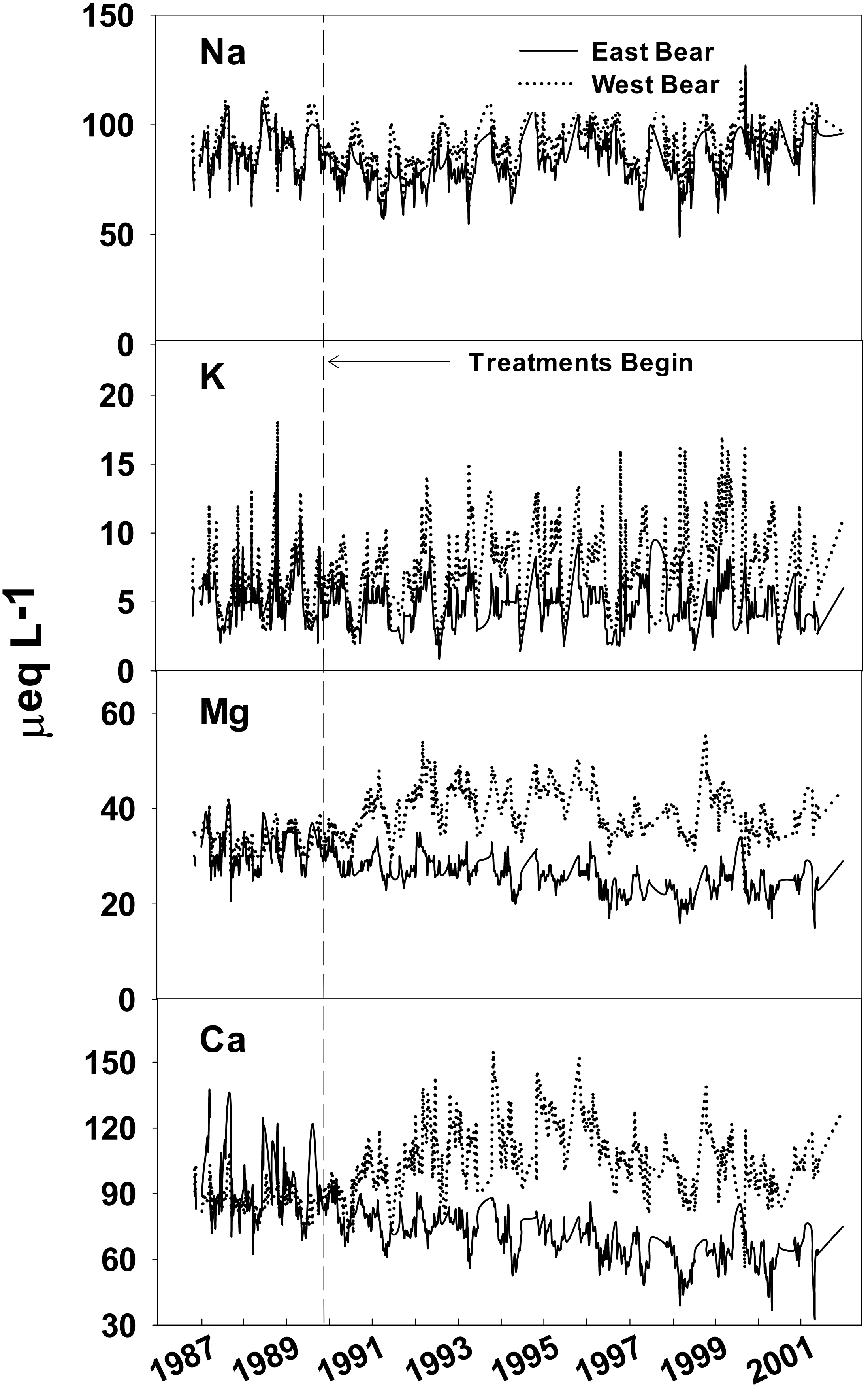

East Bear
West Bear
1992
1995
1993
1991
1994
1999
1996
1990
1998
1989
1997
2000
1992
1989
1991
1990
1994
1993
1999
1995
1998
1997
2000
1996
50
40
30
20
10
40
60
80
100
120
140
Mg (ueq L-1)
Ca (ueq L-1)

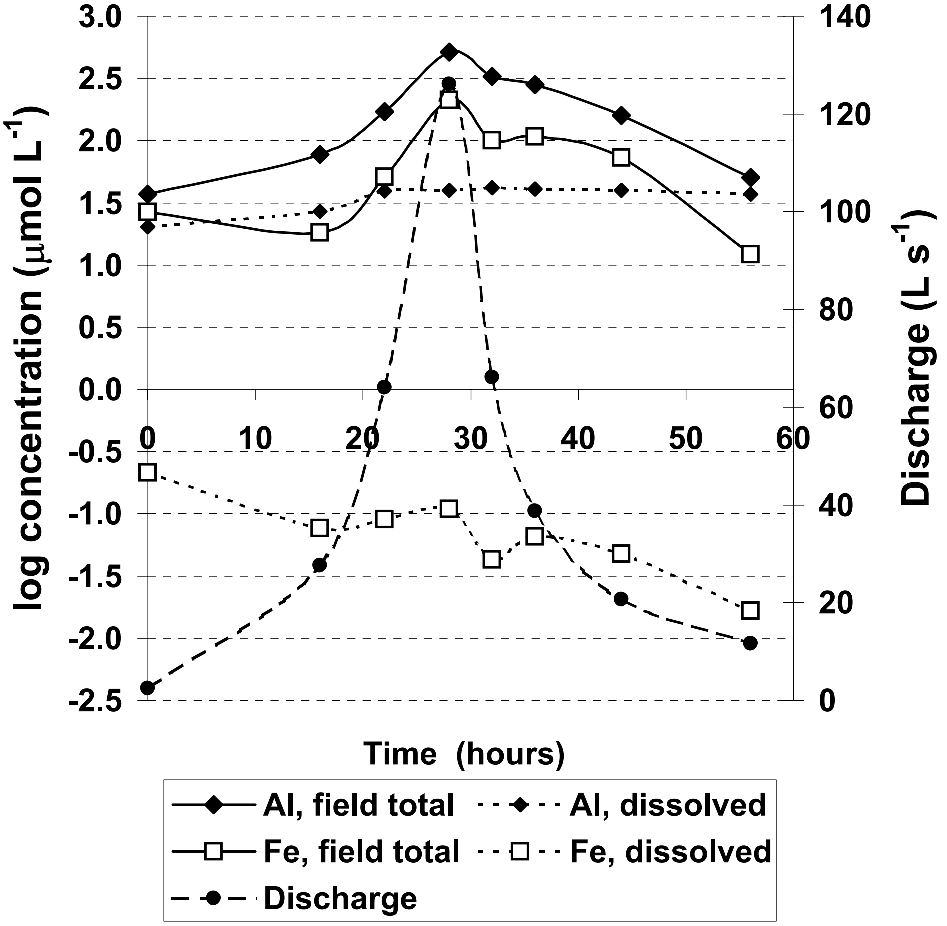

ANC
East Bear
West Bear
Treatments Begin
Cl
NO3
SO4
μeq L-1
90
60
30
0
-30
100
50
0
120
90
60
30
0
200
150
100
50
1987
1989
1991
1993
1995
1997
1999
2001


Log of Years
7
6
5
4
3
2
1
0
-1
-2
-3
Chemical weathering
Biomass variation
Snowmelt and marine salt
Paludification
Acidic deposition
Storms
Disturbances
Climate
Deforestation
Nutrient cycling

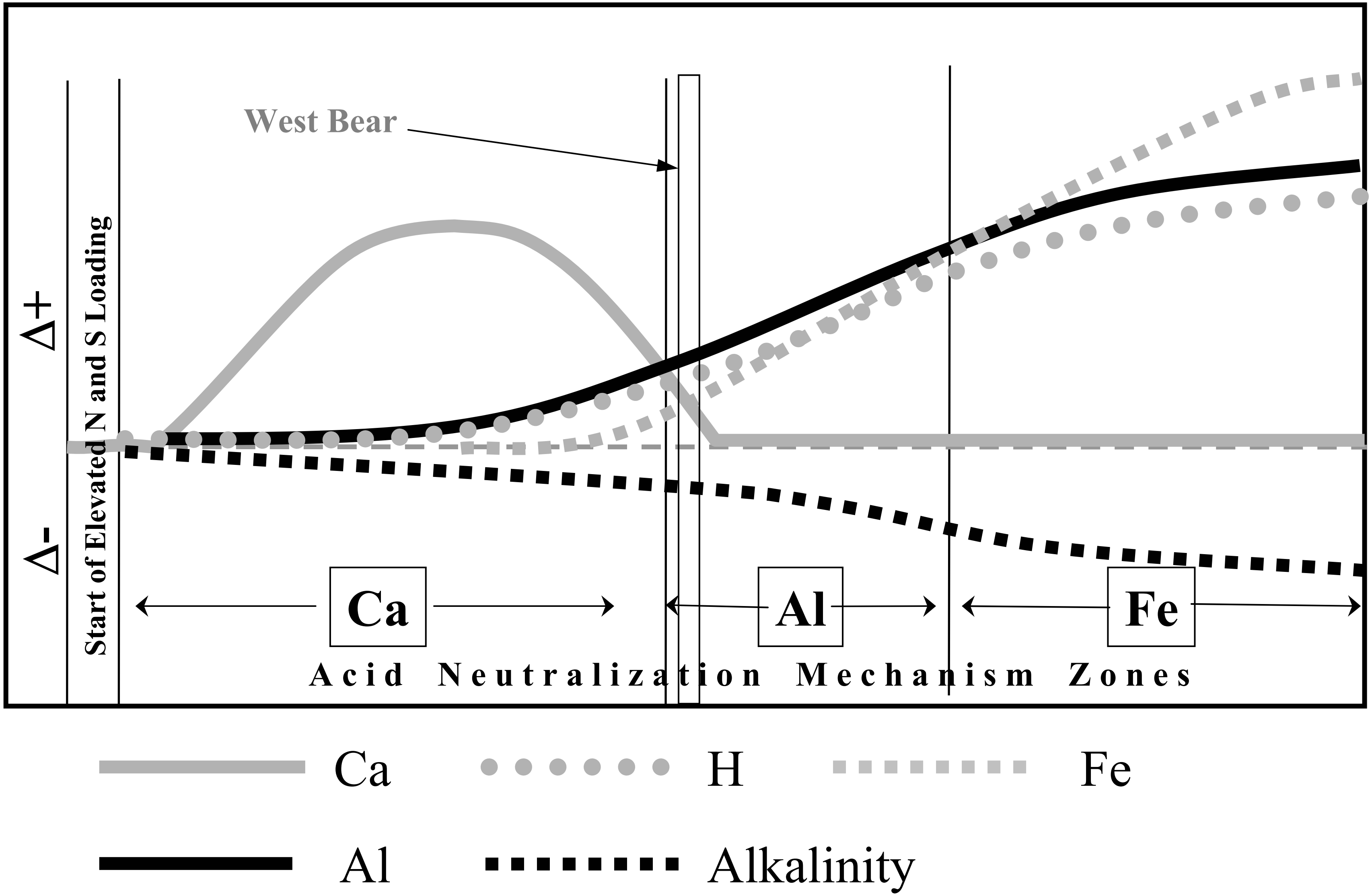

Treatment Begins
Ca Difference
Mg Difference
SO_4 Difference
μeq L⁻¹
160
140
120
100
80
60
40
20
0
1988
1989
1990
1991
1992
1993
1994
1995
1996
1997
1998
1999
2000


1990 - East Bear
Mg = 0.26Ca + 7.7
R^2 = 0.62
Mg (μeq L^{-1})
40
35
30
25
20
60
70
80
90
100
110
Ca (μeq L^{-1})


Na
K
Mg
Ca
East Bear
West Bear
Treatments Begin
µeq L-1
150
100
50
0
20
15
10
5
0
60
40
20
0
150
120
90
60
30
1987
1989
1991
1993
1995
1997
1999
2001



West Bear (2/26/02)


West Bear
Δ+
Δ-
Start of Elevated N and S Loading
Ca
Al
Fe
Acid Neutralization Mechanism Zones
Ca
H
Fe
Al
Alkalinity

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

Basic Information

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

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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).

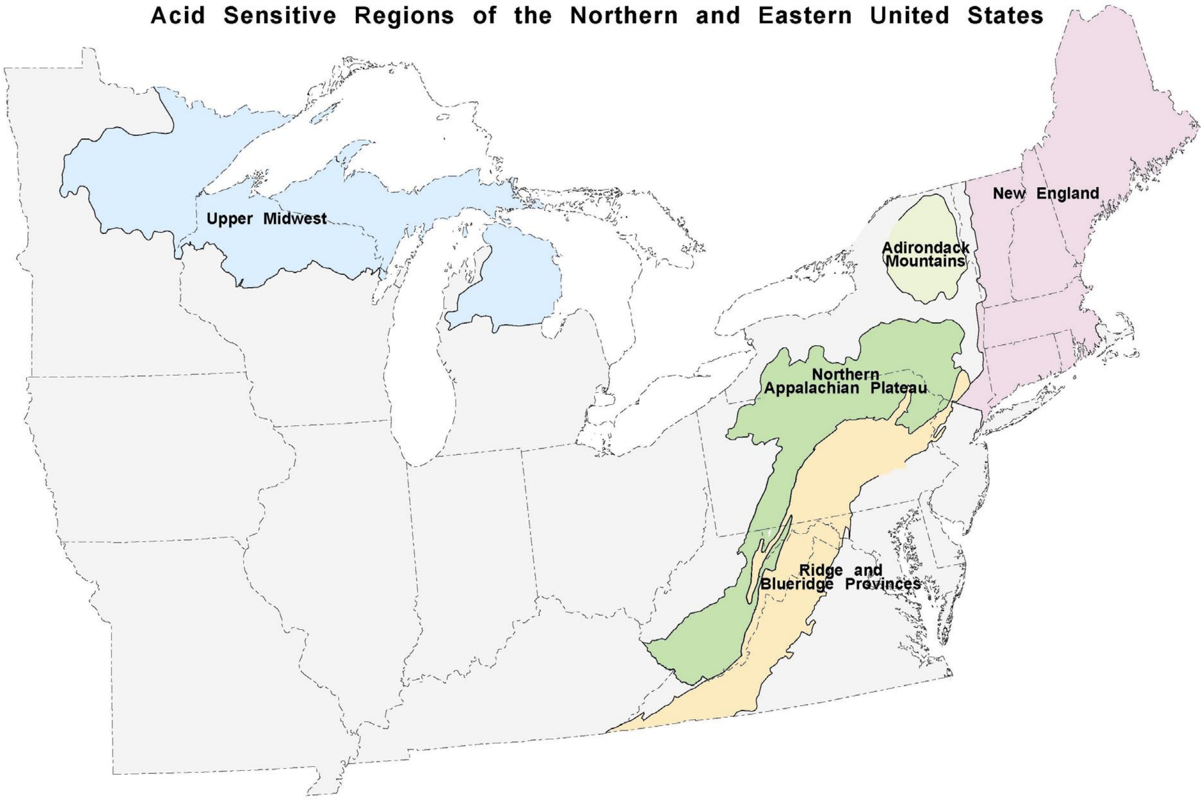

Figure A. Acid sensitive regions of the northern and eastern United States; this report assesses trends in surface waters in each of these regions.

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. NO_x and 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 μeq/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 µeq/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 µeq/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.

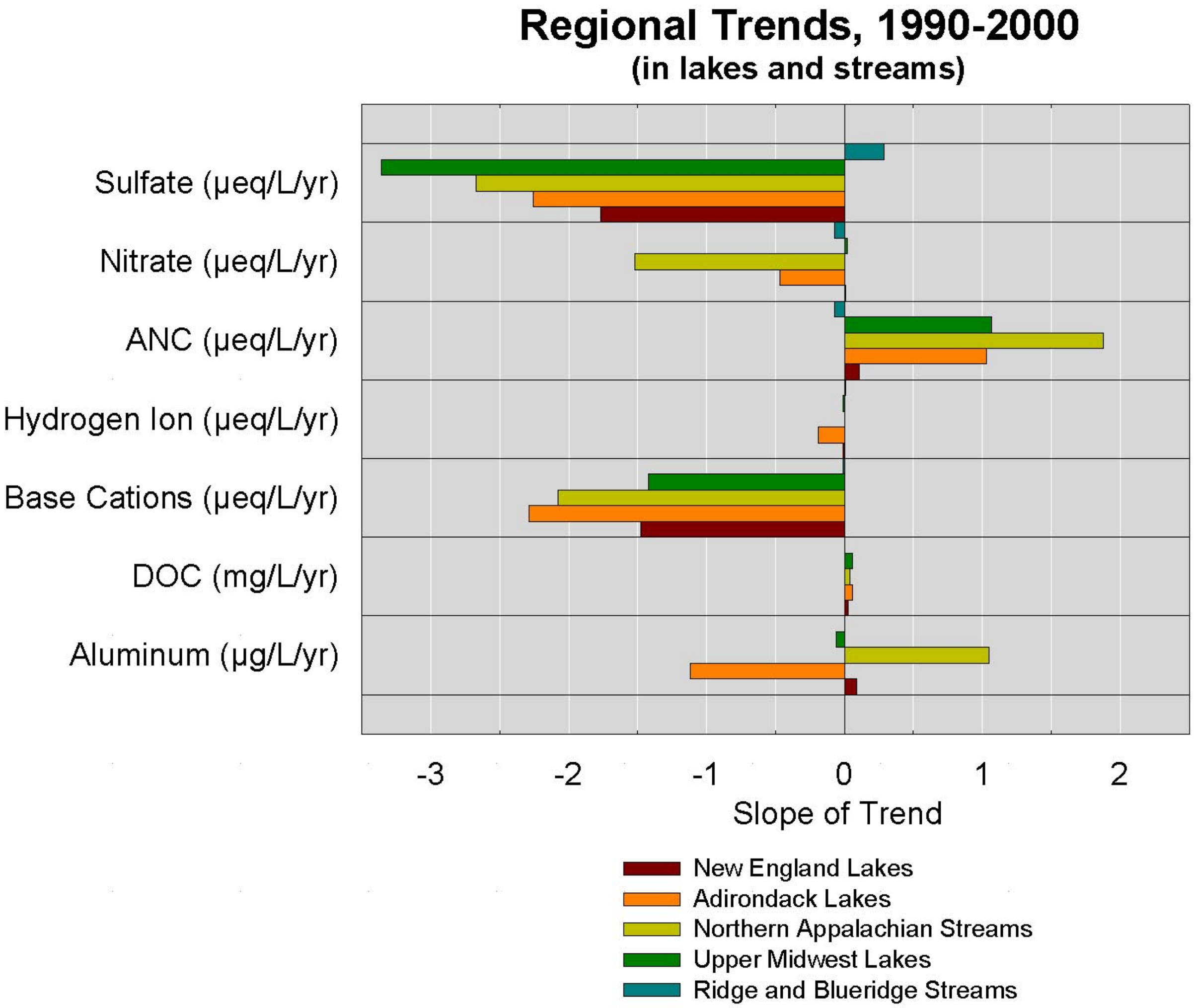

Figure B. Summary of regional trends in surface water chemistry in regions covered by this report.

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_2 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) <u>Base cations</u>. 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

The mission of the Maine Water Resources Research Center includes education, research, and outreach. Staff at the Mitchell Center are active on numerous boards and committees that deal with water resources issues. In addition, we have continued our efforts to support scholarly publications and publications for the general public.

FY 2002 MAINE WATER RESOURCES RESEARCH INSTITUTE Information Transfer

Basic Information

Title:	FY 2002 MAINE WATER RESOURCES RESEARCH INSTITUTE Information Transfer
Project Number:	2002ME4B
Start Date:	3/1/2002
End Date:	2/28/2003
Funding Source:	104B
Congressional District:	2
Research Category:	Not Applicable
Focus Category:	, None, None
Descriptors:	
Principal Investigators:	John M. Peckenham, Steve Kahl

Publication

1. Campbell, J. L., J.W. Hornbeck, M.J. Mitchell, M.B. Adams, M.S. Castro, C.T. Driscoll, J.S. Kahl, J.N. Kochenderfer, G.E. Likens, J.A. Lynch, P.S. Murdoch, S.J. Nelson, and J.B. Shanley, 2002. A Synthesis of Nitrogen Budgets from Forested Watersheds in the Northeastern United States. In review, Water, Air, and Soil Pollution.
2. Changes in Water Quality in New England and Eastern Canada, 2002. Dupont, J. T. Clair, S. Couture, R. Estabrook, P. Godfrey, D. Jeffries, J.S. Kahl, S. Nelson, J. Peckenham, W. Pilgrim, P. Stacey, D. Taylor, A. Van Arsdale. Report of the New England Governors and Eastern Canadian Premiers. 5p. NEG-ECP, Quebec Ministry of the Environment, Quebec City, PQ, CA.
3. Schmitt, C. and J.M. Peckenham (2002) Source Water Protection: Linking Surface Water Quality to the Watershed. Handbook, Univ. of Maine 85 p.
4. Schmitt, C. and J.M. Peckenham (2002) Public Law 761: Protecting Maines Dinking Water, Univ. Maine Geograph. Digest Ser., 4 p.
5. Pellerin, B., I Fernandez, S. Norton, and J.S. Kahl, 2002. Soil aluminum distribution in the near-stream zone at the Bear Brook Watershed in Maine. Water Air Soil Pollution 134:189-204.
6. Norton, S., B.J. Cosby, I. Fernandez, J.S. Kahl, and R. Church, 2002. Inter-annual and seasonal variations in soil-air CO2 cause variable watershed alkalinity generation. Hydrol. Earth Science Systems, in press.

7. Norton, S.A. and J.S. Kahl, 2001. Impacts of marine aerosols on surface water chemistry at Bear Brook Watershed, Maine. Verh. Internat. Verein. Limnol. (SIL) 27:1280-1284.
8. Peckenham, J.M., J. McNelly, A. Tolman, and J. Ziegra (2002). Moving from SWAP to source protection. Jour. New Eng. Water Works. Assoc., June 2002.
9. Changes in Water Quality in New England and Eastern Canada, 2002. Dupont, J. T. Clair, S. Couture, R. Estabrook, P. Godfrey, D. Jeffries, J.S. Kahl, S. Nelson, J. Peckenham, W. Pilgrim, P. Stacey, D. Taylor, A. Van Arsdale. Report of the New England Governors and Eastern Canadian Premiers. 5p. NEG-ECP, Quebec Ministry of the Environment, Quebec City, PQ, CA.
10. Kahl, J.S., C. Gray, J. Grimalt, K. Tonnessen, and J. Wiener, 2002. Western Airborne Contaminants Assessment Project; report of the review panel. 14 p.
11. Peckenham, J., J.S. Kahl, and S.J. Nelson, 2002. Lake Water Chemistry Trends in New England. Report to the New England Governors-Eastern Canadian Premiers, Water Quality Workgroup.
12. Kahl, J.S., J. Rubin, I. Fernandez, S. Norton, L. Rustad, J. Lawlor, D. Mageean, J. Cosby, and P. Ludwig, 2002. Linking watershed-scale indicators of changes in atmospheric deposition to regional response patterns. Final report, EPA/NSF Water and Watersheds program. 36 p., plus attachments.
13. Schauffler, M., S. Nelson, K. Johnson, J.S. Kahl, G. Jacobson, and I. Fernandez, 2002. Paleoecological assessment of forest-disturbance in upper Hadlock Brook and upper Cadillac Brook watersheds. Final report to NPS, Acadia National Park, Bar Harbor, ME. 30p.
14. Nelson, S.J., 2002. Determining Atmospheric Deposition inputs to two small watersheds at Acadia National Park. M. S. Thesis, University of Maine, Orono, ME. 163 pp.
15. Nelson, S.J., K. B. Johnson, eds., 2002. Maine Water Conference: Abstract Guide and Conference Program.

Publications

Peer-reviewed articles.

Campbell, J. L., J.W. Hornbeck, M.J. Mitchell, M.B. Adams, M.S. Castro, C.T. Driscoll, **J.S. Kahl**, J.N. Kochenderfer, G.E. Likens, J.A. Lynch, P.S. Murdoch, **S.J. Nelson**, and J.B. Shanley, 2002. A Synthesis of Nitrogen Budgets from Forested Watersheds in the Northeastern United States. In review, Water, Air, and Soil Pollution.

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 in Maine. Water Air Soil Pollution 134:189-204.

Norton, S., B.J. Cosby, I. Fernandez, **J.S. Kahl**, and R. Church, 2002. Inter-annual and seasonal variations in soil-air CO_2 cause variable watershed alkalinity generation. Hydrol. Earth Science Systems, in press.

Norton, S.A. and **J.S. Kahl**, 2001. Impacts of marine aerosols on surface water chemistry at Bear Brook Watershed, Maine. Verh. Internat. Verein. Limnol. (SIL) 27:1280-1284.

Peckenham, J.M., J. McNelly, A. Tolman, and J. Ziegra (2002). Moving from SWAP to source protection. Jour. New Eng. Water Works. Assoc., June 2002.

Reports and Miscellaneous Publications

Changes in Water Quality in New England and Eastern Canada, 2002. Dupont, J. T. Clair, S. Couture, R. Estabrook, P. Godfrey, D. Jeffries, **J.S. Kahl**, **S. Nelson**, **J. Peckenham**, W. Pilgrim, P. Stacey, D. Taylor, A. Van Arsdale. Report of the New England Governors and Eastern Canadian Premiers. 5p. NEG-ECP, Quebec Ministry of the Environment, Quebec City, PQ, CA.

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

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

Nelson, S.J., 2002. Determining Atmospheric Deposition inputs to two small watersheds at Acadia National Park. M. S. Thesis, University of Maine, Orono, ME. 163 pp.

Nelson, S.J., K. B. Johnson, eds., 2002. Maine Water Conference: Abstract Guide and Conference Program.

Professional Presentations

Kahl, J.S., 2002. Priority land-based environmental issues facing the Gulf of Maine Watershed. The Gulf of Maine Summit and Watershed Forum (invited), Blue Hill, Maine. November, 2002.

Kahl, J.S., J. Stoddard, K. Webster, and R. Haeuber, 2002. The 2002 Assessment of the Clean Air Act: surface water trends from the northeast US and upper midwest US. North American Lake Management Society annual meeting, Anchorage Alaska. October, 2002.

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

Nelson, S.J., 2002. National Park Service Air Quality Summit, October 21-24, 2002, Estes Park, CO. Poster Presentations (by proxy): *Sulfate and mercury deposition at Acadia National Park: integrating enhancement ratios, wet deposition, and landcover data; Modification of atmospheric inputs at Acadia National Park, Maine: the relative influence of landscape factors*

Nelson, S.J., 2002. Seminar for Water Resources Graduate Students, September 20, 2002. Powerpoint Presentation: *The Dos and Don'ts of Scientific Presentations*

Nelson, S.J., 2002. NERAQC (Northeast Regional Air Quality Committee) Annual Meeting, June 4-5, 2002, Hubbard Brook Experimental Forest Station, NH. Powerpoint Presentation: *Patterns in N and Hg processing in Lakes and streams across Maine*

Nelson, S.J., 2002. Maine Water Conference, May 9, 2002, Augusta, ME. Poster Presentation: Sulfate and mercury deposition at Acadia National Park: integrating enhancement ratios, wet deposition, and landcover data

Peckenham, J.M.., 2003. Water Quality and Monitoring, Invited Presentation to "Healthy Water, Healthy People' program, January 24, 2003

Peckenham, J.M. and C. Schmitt (2003) Moving from Source Assessment to Source Protection in Maine, Amer. Water Works Assoc. Symposium on Source Water Protection, January 19-22, 2003.

Peckenham, J., Schmitt, C., 2003. Presentations on source water protection efforts - assisting drinking water systems move from assessing threats to drinking water quality to actual protection efforts. Maine Water Utilities Association, annual meeting, February 2003.

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.

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.

Conferences, Workshops, Annual Meetings

Maine Water Conference 2002. Augusta Civic Center, Augusta, ME. May 9, 2002. 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: Drinking Water / Watershed Protection; Extreme Hydrologic Events; Perspectives on Sustainable Water Use; GIS Applications to Water Resources; How Lakes Work; and a juried student poster competition.

Public Service

Media/Press

University of Maine press release (Bangor Daily News 1/30/03)
Clean Air Act Reduces Acid Rain; UMaine Research Indicates that Recovery in New England Remains Elusive

Mitchell Center editorial (Bangor Daily News 2/13/03)
Federal budget threatens water research, education, outreach at UMaine Mitchell Center

University of Maine press release (UMaine Science 1/20/03 and MSTF newsletter 1/20/03)
UMaine Scientist on National Research Council Panel

Maine Sunday Telegram article (12/1/2002 – quotes from Steve Kahl)
Acidity levels in Maine lakes fail to improve by Meredith Goad

Workshops and Other Activities

Northern Maine Children's Water Festival - We helped to organize and run the festival that was attended by about 800 students. This program is designed for 5th and 6th grade students and their teachers to learn about the value of clean water in its many forms. Participants came from fields related to water- biologists, geologists, paper company engineers, water suppliers, foresters, and people from conservation groups. The goal of the festival is to show the role of water in ecosystem health, as habitat, and its function in other earth processes.

Maine Project WET Workshop - Maine Project WET (Water Education for Teachers) coordinator, MaryAnn McGarry hosted a "Healthy Water, Healthy People" workshop for middle level and high school science teachers, on Jaunuary 24, 2003. The workshop was conducted by John Etgen of Project WET. Participants received a copy of the newly published Healthy Water, Healthy People Water Quality Educators Guide. The new publication contains various grade level activities to help students learn fundamental principles such as accuracy and precision and connect both concepts to a broader view of water quality measurement. McGarry helped create the Educator's Guide.

Cove Brook Watershed Council Management Plan - Mitchell Center graduate student Heather Caron became involved with the Cove Brook Watershed Council through Laura Wilson, another graduate of the Mitchell Center who now works with the University's Cooperative Extension. Heather acted as a consultant to the Council in creating a management plan for the watershed. The plan is due out this summer (03) and will serve as a management model for other small, healthy, coastal watersheds in the New England region. Heather has provided an important connection between the Mitchell Center and the Cove Brook Watershed Council.

PEARL – Improvements continue to be made to PEARL: Public Educational Access to Environmental Education. This includes the addition of new data. Work on PEARL is scheduled to continue through summer 2003.

Penobscot River and Bay Institute- May-June 2002: Penobscot River Keepers Expeditions. These were day-long canoe expeditions on the Penobscot River with students in grades 7 to 12. In 2002 we provided about 450 students with an opportunity to learn about rivers, watersheds, history, and ecology.

Resource Acadia Seminar - Presentation for residents of the Acadia area, June 22, 2002, Acadia National Park Resource Management, Bar Harbor, ME. Powerpoint Presentation by Sarah J. Nelson: *PRIMENet Research – Paired Watersheds at Acadia*

Source Water Protection Cookbook - a guidance manual for operators of small public water systems, was published in May 2002. The "cookbook" was written by graduate student Catherine Schmitt as a part of her research project. The document is a reference on watershed protection techniques and resources and was distributed to water managers throughout the state.

Committees and Service:
Kahl

- Eco-reserves classification advisory committee, Nature Conservancy
- March Island Wildlife Management Committee
- Environmental Policy Advisory Committee, gubernatorial candidate John Baldacci
- Global Program of Action Coalition, Gulf of Maine Forum committee
- Chair, Boat launch and invasive species committee, Hopkins Pond
- Union River Watershed Coalition
- Atlantic Salmon Research and Information Management Committee
- Headwater Streams Research Advisory Committee
- Maine Watershed Management Advisory Committee
- Mercury Products Advisory Commission (Gubernatorial appt)
- River Flow Management Commission (Gubernatorial appt)
- Co-chair, Council on Environmental Monitoring & Assessment (Gubernatorial appt)
- Friends of Acadia National Park (Board member)
- Maine Lakes Conservancy Institute (Board member)
- ME Lake Volunteer Monitoring Program (Board member)
- Chair, peer-review panel, Western Airborne Contaminants Assessment Project (NPS/EPA, '02)
- Participant, AAAS panel on enhancing research competitiveness in downeast Maine (2002)
- New England Governors & Eastern Canadian Premiers 'acid rain' working group (1998-02)
- Downeast research-enhancement planning committee *(Eastern ME Development Corp*; 2002*)*
- Journal reviewer:
    - *Biogeochemistry*
    - *Environmental Science & Technology*
    - *Environmental Monitoring & Assessment*
    - *Water Air and Soil Pollution*
    - *Water Resources Research*

Peckenham

- River Flow Advisory Commission- Drought Task Force
- Maine Water Conference Organizing Committee
- Maine Water Utilities Association- Water Resources Committee
- Maine Watershed Management Advisory Committee
- Sustainable Water Withdrawal- Land and Water Resources Council
- Penobscot River and Bay Institute- Board of Directors
- Co-Chair Maine Water Conference- 1998, 2000, 2001, 2002, 2003
- Northern Maine Children's Water Festival Organizing Committee
- DEP-Consulting Engineers of Maine Task Force
- *Ad Hoc* Committee on Antimony in Drinking Water
- Planning Consortium- Environmental Health Tracking System, Maine DHS

Nelson

- Field Office, Congressman John Baldacci, Intern
- Ecological Society of America
- American Geophysical Union, Biogeosciences Section
- Associate of Graduate Students, Vice President
- UMaine Professional Employees Advisory Council
- Association of Graduate Students Grant Review Committee

Student Support

Notable Awards and Achievements

A paper by Mitchell Center graduate student Catherine Schmitt was selected as an Outstanding Student Presentation at the 2002 annual meeting of the American Water Resources Association in Philadelphia, Pennsylvania. Schmitt's paper, Drought and Drinking Water: How Sensitive Are Maine's Surface Water Supplies? discusses the potential impacts of low water levels on both the quantity and quality of public water supplies.

Mitchell Center graduate student Emily Seger was awarded first place in the juried poster competition at the 2002 Maine Water Conference. Seger's poster entitled, "Chemical Responses to Drought: A Comparison of Acid-Sensitive Seepage Lakes in Maine and Wisconsin" compared chemical trends in 66 Maine seepage lakes and 30 Wisconsin seepage lakes from the mid-1980s through 2001 including data from several droughts in both regions.

Graduate student Sarah Nelson placed second in the 2002 University of Maine's Association of Graduate Students Research Expo for her poster "Sulfate and mercury deposition at Acadia National Park: integrating enhancement ratios, wet deposition, and landcover data". Sarah Nelson received an Association of Graduate Students Degree-Related Grant, towards purchase of software and equipment for searchable database of water resources information to be used by Mitchell Center graduate students. She also received an award from UMaine's Professional Employees Advisory Council Professional Development Fund to support travel to the Eastern Snow Conference.

Funds were awarded to the Mitchell Center by the Margaret E. Burnham Charitable Trust toward the purchase of GIS software for presentation of water research maps on the Web. Graduate student Sarah Nelson was instrumental in the proposal writing process.

Graduate student Catherine Schmitt has had a number of articles published in local Maine publications related to the environment and water resources. 2002 articles include: *Deadline: Dioxin*, published in Northern Sky News; *Election '02 and the Environment* and *Cold War Residue in Glenburn* published in The Maine Commons; and *Affirmation: Acadia*, published in the Friends of Acadia Journal.

The USGS base grant provided a basis for the Senator George J. Mitchell center to secure other research funding. In addition to support from the US EPA to continue acid-rain related research, the following projects were funded in 2002:
Title: Quantification of nutrient loss from sludge stockpiles.
Investigator: Peckenham.
Agency: Maine Department of Environmental Protection.

Title: Correlating deposition of atmospheric pollutants in Acadia National Park.
Investigators: Kahl, Nelson, and others.
Agency: National Park Service.

Title: Promoting conservation using PEARL (internet environmental database).
Investigators: Kahl, Nelson, and others.
Agency: Maine Outdoor Heritage Fund.

Title: The effect of traffic on surface water quality in Acadia National Park.
Investigator: Peckenham and Kahl.
Agency: National Park Service.

Title: Boothbay Water Company- A national model for source protection.
Investigators: Peckenham and others.
Agency: US EPA.

Publications from Prior Projects

FY02 annual report for JS Kahl

	agency	title	PIs	$	grad. stud.
		PROPOSALS SUBMITTED DURING FY02			
1	USGS	Maine Water Resources Research Institutes Program	Kahl	84,785	4
2	DOI NPS	Correlating predictive contaminant deposition maps with stre	Kahl, Nelson, Fernandez	331,000	2
3	MOHF	PEARL: the Maine lakes database, III	Kahl and McGarry	23,000	1
4	DOI NPS	The impact of auto traffic on Mount Desert Island	Peckenham, Kahl	47,000	1
5	DOI NPS	Assessment of historic deposition at Acadia NP	Norton, Kahl	49,000	1
6	NSF	A web-based GIS searchable database for the Gulf of Maine	Beard, Kahl, Pettigrew	99,000	1
7	USGS	Does Al geochemistry control lake trophic condition?	Norton, Amirbahman, Kah	98,900	2
8	EPA	Evaluating the effect of the Clean Air Act on lakes	Kahl and Norton	206,707	1
9	EPA	2002 assessment report for the Clean Air Act	Kahl	89,000	0
10	USGS	Seepage lakes as indicators of climate change	Webster and Kahl	57,000	1
11	EPA	Protecting drinking water resources relative to changing clim	Kahl and Peckenham	52,000	1
12	NSF	Bridges for improving engineering content of curricula	Amirbahman, Johnson, Ka	86,200	1
13	USGS	Evaluating water chemistry risk factors for Atlantic Salmon	Kahl, Peckenham, Lent	39,200	1
14	EPA	Are the unrecognized risks from iron cyanides in road salt?	Kahl and Peckenham	192,000	1
				1,454,792	**18**
		PROPOSALS FUNDED DURING FY02			
1	EPA	Evaluating the effect of the Clean Air Act on lakes…	Kahl and Norton	189,198	1
2	USGS	Using calibrated watersheds…. atmospheric deposition	Kahl and Fernandez	64,993	1
3	USGS	Maine Water Resources Research Institutes Program	Kahl	84,785	4
4	EPA	Protection of small system surface drinking water supplies	Kahl and Peckenham	69,000	1
5	USGS	Does Al geochemistry control lake trophic condition?	Norton, Amirbahman, Kah	98,900	2
6	MOHF/DE	PEARL: the Maine lakes database, III	Kahl and McGarry	23,000	1
7	NSF	A web-based GIS searchable database for the Gulf of Maine	Beard, Kahl, Pettigrew	99,000	2
8	EPA	2002 assessment report for the Clearn Air Act	Kahl	89,000	0
9	USGS	Seepage lakes as indicators of climate change	Webster and Kahl	57,000	1
10	EPA	Protecting drinking water resources relative to changing clim	Kahl and Peckenham	52,000	1
11	USGS	Evaluating water chemistry risk factors for Atlantic Salmon	Kahl, Peckenham, Lent, Jo	39,200	1
				866,076	15

USGS Summer Intern Program

Student Support

Student Support					
Category	**Section 104 Base Grant**	**Section 104 RCGP Award**	**NIWR-USGS Internship**	**Supplemental Awards**	**Total**
Undergraduate	3	2	0	0	5
Masters	10	2	1	0	13
Ph.D.	4	0	0	0	4
Post-Doc.	0	0	0	0	0
Total	17	4	1	0	22

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Funds were awarded to the Mitchell Center by the Margaret E. Burnham Charitable Trust toward the purchase of GIS software for presentation of water research maps on the Web. Graduate student Sarah Nelson was instrumental in the proposal writing process.

Graduate student Catherine Schmitt has had a number of articles published in local Maine publications related to the environment and water resources. 2002 articles include: Deadline: Dioxin, published in Northern Sky News; Election 02 and the Environment and Cold War Residue in Glenburn published in The Maine Commons; and Affirmation: Acadia, published in the Friends of Acadia Journal.

The USGS base grant provided a basis for the Senator George J. Mitchell center to secure other research funding. In addition to support from the US EPA to continue acid-rain related research, the following projects were funded in 2002: Title: Quantification of nutrient loss from sludge stockpiles. Investigator: Peckenham. Agency: Maine Department of Environmental Protection.

Title: Correlating deposition of atmospheric pollutants in Acadia National Park. Investigators: Kahl, Nelson, and others. Agency: National Park Service.

Title: Promoting conservation using PEARL (internet environmental database). Investigators: Kahl, Nelson, and others. Agency: Maine Outdoor Heritage Fund.

Title: The effect of traffic on surface water quality in Acadia National Park. Investigator: Peckenham and Kahl. Agency: National Park Service.

Title: Boothbay Water Company- A national model for source protection. Investigators: Peckenham and others. Agency: US EPA.

Publications from Prior Projects

None