Lakewater Chemistry at Acadia National Park, Maine, in Response to Declining Acidic Deposition

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Introduction

Title IV of the 1990 Clean Air Act Amendments (CAAA) sets target reductions in the United States for sulfur and nitrogen emissions from industrial sources to reduce the acidity in deposition. These reductions have continued the trend of reductions in emissions and deposition of sulfur during the past 30 years, with the rate of decline accelerated by Phase I of the 1990 CAAA that was implemented in 1995 (Lynch et al. 2000). Slight reductions in nitrogen emissions have occurred since 1996.

One of the intended effects of the CAAA reductions was to decrease the acidity of low-alkalinity waters and thereby improve their biological condition. The key science and policy questions related to the CAAA are whether (1) the declines in emissions yield reductions in acidic deposition; (2) changes in deposition cause changes in surface water chemistry; and; (3) biologically relevant water chemistry has improved in acid-sensitive regions as a result of changes in deposition.

Documentation of acidification of surface waters began in Scandinavia (e.g., Oden 1968), although reports of acidic lakes date back to the 1950s in North America (Gorham 1957). Recognition of the issue became common in the U.S. in the early 1970s (Likens et al. 1972), with identification of impacts on fish by the mid-1970s (e.g., Schofield 1976). Trend assessments for surface waters have been common in the literature for more than a decade, with the general conclusion that surface water recovery is slow to non-existent (Stoddard and Kellogg 1993; Webster et al. 1993; Kahl et al. 1993; Driscoll and van Dreason 1993; Dewalle and Swistock 1994; Driscoll et al. 1995; Likens et al. 1996; Mattson et al. 1997; Stoddard et al. 1998; Driscoll et al. 2001; Skjelkvåle et al. 2001; Evans and Monteith 2001; Stoddard et al. 2003).

This paper reports on lake chemistry data collected at Acadia National Park since 1982 (Kahl et al. 1985; Figure 1), and puts the response to acidic deposition in the context of the recent assessment of the response of surface waters in the northeastern United States to changes in atmospheric deposition (Stoddard et al. 2003).

Why do we care about lake and stream chemistry? Long-term chronic acidification and short-term temporary episodic acidification are of concern in regions receiving acidic deposition. Surface water chemistry is a direct indicator of the potential deleterious effects of acidification on biotic integrity. Because surface water chemistry integrates the sum of processes upstream in a watershed, it is also an indicator of the *indirect* effects of watershed-scale impacts, such as nitrogen saturation, forest decline, or soil acidification.

Biologically relevant surface water chemistry. The main cause for concern over the effects of surface water acidification in the U.S. and elsewhere is the potential for detrimental biological affects (Baker and

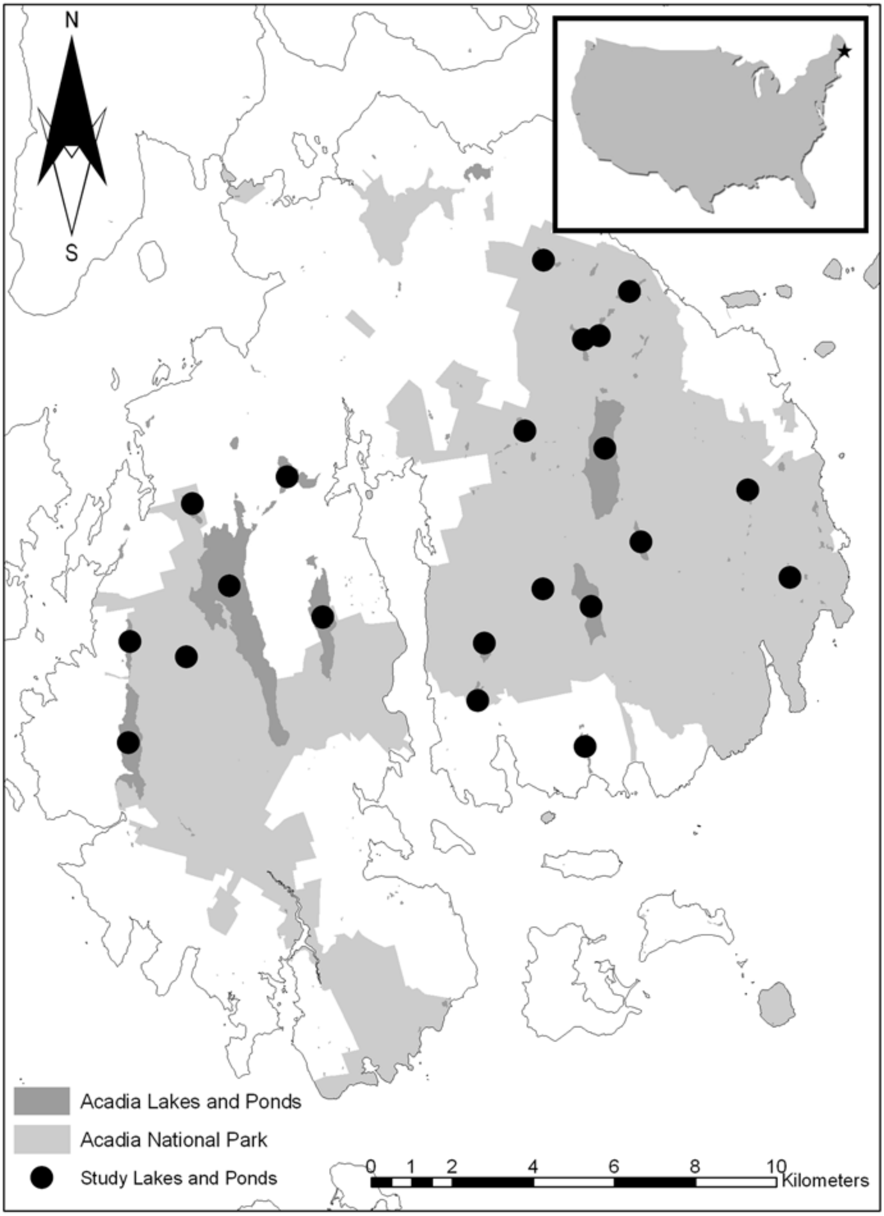

Figure 1. Location of Acadia National Park on Mount Desert Island in Maine, USA, with locations of study lakes and ponds.

Christensen 1991; NADP 1998). Typically, there is concern for biological impact if surface water pH is less than 6. At low pH values, aluminum may be present at concentrations that are toxic to biota, including sensitive life stages of fish and sensitive invertebrates. Aluminum is an abundant and normally harmless component of rocks and soils. However, it leaches from silicate minerals when they come in contact with low-pH waters. While much of the aluminum present in surface waters is organically bound and relatively non-toxic, certain inorganic species are highly toxic.

Nitrogen saturation. One of the key remaining research issues is the role of nitrogen in watershed responses to acidic deposition. The concept of *nitrogen saturation* (Aber et al. 1989; Stoddard 1994) received increasing attention in the 1990s (Mitchell et al. 1996; Williams et al. 1996; Aber et al. 1998). "Nitrogen saturation" is defined as deposition of nitrogen to a watershed in excess of the assimilative capacity of soils and vegetation, resulting in the export of nitrate (NO_3). Nitrate export can contribute to acidification (especially episodic acidification), mobilization of aluminum, and leaching of cations from soils (Aber et al. 1998).

Methods

This paper uses long-term records of wet deposition from the NADP (http://nadp.sws.uiuc.edu/), repeat surveys of lake chemistry at Acadia National Park dating back to 1982 (Kahl et al. 1985; Kahl 1996), data collected by the park's resource management division, and long-term records of lake chemistry from research conducted in New England (Kahl et al. 1991; Stoddard et al. 2003). The lake data from Acadia cover the period from 1982 to either 1998 or 2000, depending on the availability of data at each site. Accepted Environmental Protection Agency (EPA) methods and quality assurance are documented in various publications (Nelson and Kahl 2003; Morrison 1989; Newall et al. 1987; Hillman et al. 1986).

Results and Discussion

Declines in sulfate deposition. Sulfate concentrations declined substantially in the northeastern U.S. at a median rate of between –1.0 and –1.5 µeq/L/year for the period 1990 to 2000 (Table 1). At Acadia's NADP site, the rate of change in sulfate was –0.53 µeq/L. Changes in sulfate emissions correspond directly to changes in sulfate deposition.

Declines in nitrate emissions and deposition. Decreases in NO_x emissions were more modest than those of sulfur (Table 1). There was a slight increase in nitrogen deposition at the park. Since 1990, total utility NO_x emissions (Phase I and II sources) were reduced an average of 23% nationally, following implementation of Phase I of the Acid Rain Program. However, electric utilities contribute only about one-third of total NO_x emissions. Total NO_x emissions from other sources have remained relatively constant (motor vehicles and other industrial sources also contribute significantly), and therefore the reductions achieved under the Acid Rain Program have not resulted in a significant change in total NO_x emissions and deposition.

Increases in pH and base cations in deposition. Lynch et al. (2000) found significant declines in hydrogen ion at many NADP stations during 1990–2000, at rates that were less than the decrease in sulfate. Wet deposition of hydrogen ion decreased in every region (Table 1). Base cation deposition increased non-significantly in the northeastern U.S., continuing the pattern of flat-to-increasing base cation deposition at most stations in the

Table 1. Regional trend results (1990–2000) for atmospheric deposition (wet-only annual concentration data from NADP/NTN network) in acid-sensitive regions (from Stoddard et al. 2003). All units are µeq/L/yr. Values are the median slopes for each region, with significance determined by calculating confidence intervals around each regional median. Data for Acadia are the NADP results for the station at McFarland Hill (NADP 2002). Base cations are defined here as the sum of Ca + Mg (^{ns} regional trend not significant, $p > 0.05$; * $p < 0.05$; ** $p < 0.01$).

Region	SO_4	Nitrogen	NO_3	Base Cations	Hydrogen Ion
New England	-0.96**	-0.26*	-0.20**	+0.02^{ns}	-0.81**
Adirondacks	-1.47**	-0.37**	-0.38**	+0.01^{ns}	-1.48**
Acadia NP	-0.53**	+0.04^{ns}	+0.05^{ns}	+0.17**	-0.29*

region during the past 20 years. Deposition of base cations increased significantly at Acadia, driven by decadal increases in deposition of marine salts from the Gulf of Maine (Figure 1).

Status of surface waters. The National Surface Water Survey (NSWS) documented the status and extent of chronic acidification during probability surveys conducted from 1984 through 1988 in acid-sensitive regions throughout the U.S. (Linthurst et al. 1986; Landers et al. 1988; Kaufman et al. 1988). The NSWS concluded that 4.2% of lakes in the northeastern U.S. were acidic. The Adirondack Mountain region had the greatest proportion of acidic surface waters (14%) for lakes larger than 4 ha. Counting smaller lakes, the Adirondack Lake Survey Corporation estimated that 26% of lakes larger than 0.5 ha were acidic (Driscoll et al. 1991). The large numbers of lakes in these regions translate to several hundred acidic waters in each region. At Acadia, Sargent Mountain Pond and Duck Pond are acidic, representing 9% of the 21 lakes sampled. This is a higher percentage than in the rest of Maine, reflecting the granitic bedrock and thin soils common at Acadia.

Changes in surface water chemistry. Our analysis of surface water response to changing deposition focuses on the key variables that play major roles in acidification and recovery: sulfate and nitrate, base cations, pH and ANC (acid neutralizing capacity), and DOC (dissolved organic carbon), a possible indicator of changes in natural organic acidity.

Sulfate (SO_4) declined in surface waters in the glaciated regions of the northeastern U.S. by median values of between –2 and –4 μeq/L/year (–0.4 μeq/L at Acadia; Table 2). The declines in SO_4 concentrations are almost certainly direct responses to declining emissions and SO_4 deposition in the 1990s, and represent the most dramatic effects of Title IV of the CAAA and previous emissions regulations. These changes in emissions and deposition continue the trend in declining SO_4 that has been occurring for three decades (Stoddard et al. 2003).

Stoddard et al. (2003) concluded that surface waters in glaciated terrain have, on average, responded relatively rapidly to the decline in sulfate deposition. Additional reductions in deposition will result in additional declines in surface water concentrations of sulfate in glaciated terrain.

Changes in NO_3 were much smaller than changes in SO_4, with the only significant changes occurring in the two regions with the highest ambient NO_3 concentrations. Most waters at Acadia have low NO_3 concentrations. However, sites such as the PRIMENet sample site at Hadlock Brook have significant leakage of NO_3, and there is no indication in the data that NO_3 concentrations have declined at Hadlock Brook as they have in many other areas during the 1990s. These

Table 2. Regional trend results for long-term monitoring sites for the period 1990 through 2000 (Stoddard et al. 2003). Values are median slopes for set of sites in each region. Units for sulfate, nitrate, base cations [Ca + Mg], Gran ANC and hydrogen are μeq/L/year. Units for DOC are mg/L/year (insufficient historical data at Acadia). Units for aluminum are μg/L/year (^{ns} regional trend not significant, $p > 0.05$; $*p < 0.05$; $** p < 0.01$, NA insufficient data).

Region	SO_4	NO_3	Base Cations	Gran ANC	Hydrogen	DOC	Aluminum
New England Lakes	-1.77**	+0.01^{ns}	-1.48**	+0.11^{ns}	-0.01^{ns}	+0.03*	+0.09^{ns}
Adirondack Lakes	-2.26**	-0.47**	-2.29**	+1.03**	-0.19**	+0.06**	-1.12**
Acadia lakes	-0.39*	-0.06^{ns}	-0.43*	+0.33^{ns}	+0.02^{ns}	NA	+0.05^{ns}

unexplained changes in NO_3 in many surface water concentrations at a time of stable nitrogen deposition underscore the complexities of nitrogen biogeochemistry. We expect that that a decline in nitrogen deposition will lead to general declines in surface waters, but the timing and the correlation cannot be predicted at this time.

Increasing ANC is the main indicator of recovery from acidification. In the northeastern U.S., there were modest increases in the Adirondack region and at Acadia (Table 2). Hydrogen ion (acidity) followed ANC with small declines in each region.

The largest recovery should be possible at sites that have undergone the most severe acidification. Stoddard et al. (2003) analyzed Gran ANC trends by ANC class and determined that the most impacted sites recovered faster in the 1990s. Sites with ANC less than zero gained ANC four times faster than sites with ANC greater than 25 µeq/L. The average increase in ANC was 12% for acidic lakes, 7% for low-ANC lakes, and less than 1% for lakes with ANC greater than 25 (Figure 2), suggesting that ANC values are converging during the recovery process toward an ANC that may be in the range of 25 to 30 µeq/L ANC (Stoddard et al. 2003).

One of the most universal watershed responses to acidic deposition is the mobilization of base cations from soils. As rates of acidic deposition decline, and the supply of acid anions to watershed soils decreases, the rates of cation mobilization are also expected to decrease. Lowered rates of cation mobilization translate to declines in surface water base cation concentrations, a change widely observed in the northern hemisphere for more than a decade. All of the glaciated regions in the northern and eastern U.S. exhibited significant declines in base cation [Ca + Mg] concentrations in the range of –1.5 to –2.5 µeq/L/year. This decline in base cations offsets some of the decline in sulfate concentrations, and limits the extent of recovery.

Conclusions

The rate of change in surface water ANC appears to largely be the result of changes in acid anions versus base cations, as represented by:

> Change in ANC = change in [Ca + Mg + Na + K] minus change in [SO_4 + NO_3 + Cl]

Regionally, SO_4 has decreased at a rate of approximately –2.5 µeq/L/year (the mean of regional median slopes), and NO_3 at a rate of

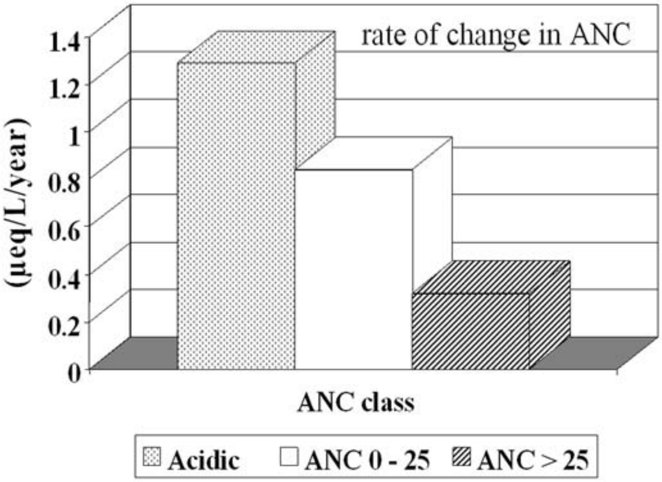

Figure 2. The lowest ANC (highest-acidity) lakes in the Northeast are responding fastest to declining acidic deposition.

–0.5 μeq/L/year, in surface waters of glaciated terrain. These rates of change set an upper limit to our expectation of ANC recovery of +3 μeq/L/yr (i.e., the sum of declines in SO_4 and NO_3). The actual increase in Gran ANC is about +1 μeq/L/year, because the decline in SO_4 and NO_3 (acid anions) has been offset by a decline of 1.8 μeq/L/year in base cations. At some sites, the decline in base cations has exceeded the decline in acid anions, and these sites have acidified.

This general pattern occurs in the lakes at Acadia. For example, Ca + Mg in Bubble Pond declined at a rate of 0.6 μeq/L per year, while sulfate was declining faster, at 1.2 μeq/L per year. The difference is a 0.6 μeq/L-per year increase in ANC, exactly the rate of increase in the data. Conversely, The Bowl has acidified slightly because base cations decreased faster (–0.6 μeq/L per year) than the acid anions (–0.3 μeq/L per year).

Regionally, there has been some recovery in ANC, especially in the lowest-ANC waters. Stoddard et al. (2003) estimated that there are about one-third fewer acidic lakes (ANC < 0) in the Northeast during the past 15 years, although these lakes still have very low ANC. At Acadia, Sargent Mountain Pond and Duck Pond both have higher ANC (less acidity) in 2000 compared with 20 years ago, but both are still acidic (i.e., negative ANC).

We do not know if the rates of increase in ANC will continue without further reductions in deposition. This is the major uncertainty for rates of recovery: to what extent is recovery resulting from recent changes in deposition already reflected in current surface water chemistry, or are further reductions in deposition necessary to continue the present trends? The only way to answer this question is to maintain the commitment to long-term assessments of surface water chemistry in regions such as Acadia that have waters that are sensitive to the effects of acidic deposition.

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