



PERGAMON

Atmospheric Environment 36 (2002) 1589–1598

ATMOSPHERIC
ENVIRONMENT

www.elsevier.com/locate/atmosenv

Persistent episodic acidification of streams linked to acid rain effects on soil

G.B. Lawrence

US Geological Survey, Troy, NY 12180, USA

Received 11 May 2001; accepted 13 October 2001

Abstract

Episodic acidification of streams, identified in the late 1980s as one of the most significant environmental problems caused by acidic deposition, had not been evaluated since the early 1990s despite decreasing levels of acidic deposition over the past decade. This analysis indicates that episodic acidification of streams in upland regions in the northeastern United States persists, and is likely to be much more widespread than chronic acidification. Depletion of exchangeable Ca in the mineral soil has decreased the neutralization capacity of soils and increased the role of the surface organic horizon in the neutralization of acidic soil water during episodes. Increased accumulation of N and S in the forest floor from decades of acidic deposition will delay the recovery of soil base status, and therefore, the elimination of acidic episodes, which is anticipated from decreasing emissions. Published by Elsevier Science Ltd.

Keywords: Acidic deposition; Episodic acidification; Aluminum; Acid neutralizing capacity; Calcium depletion

1. Introduction

Assessments of acid rain effects on the chemistry of lakes and streams have focused largely on baseflow conditions—periods between storms when stream flows tend to be low and chemical concentrations are stable. Surface waters that are acidic during baseflow are also likely to be acidic during high flow, and are therefore considered to be chronically acidified, whereas waters that are acidic only during high flow (which can last from a few hours to a few weeks) are considered to be episodically acidified. Episodic acidification can result naturally from the mobilization of organic acids, but decreases in pH associated with increases in SO_4^{2-} and NO_3^- are generally attributable to acidic deposition effects (Wigington et al., 1996), although disturbances such as severe canopy defoliation can also elevate NO_3^- concentrations in stream water (Eshleman et al., 1998). Episodic acidification is most common during seasons of high precipitation (and during spring snowmelt in regions where snow accumulates), and is least common

in summer, when evapotranspiration reduces soil moisture.

The transient nature of high flows makes episodic acidification difficult to measure. Therefore, assessments have generally estimated the number of lakes and streams prone to episodic acidification by combining episode information from a few sites with baseflow values of acid-neutralizing capacity (ANC) determined in surveys (Eshleman et al., 1995; Bulger et al., 2000; Driscoll et al., 2001). Inclusion of episodically acidified water bodies in regional assessments substantially increases estimates of the extent of surface water acidification. For example, baseflow samples collected from 1991 to 1994 through the US Environmental Protection Agency (USEPA) Environmental Monitoring and Assessment Program (EMAP) indicated that 10% of the 1812 lakes (>1 ha surface area) in the Adirondack region of New York could be considered chronically acidic on the basis of ANC values $<0 \mu\text{eq l}^{-1}$, but that an additional 31% of these lakes had baseflow ANC values $<50 \mu\text{eq l}^{-1}$ and could, therefore, be considered susceptible to episodic acidification (Driscoll et al., 2001).

E-mail address: glawrenc@usgs.gov (G.B. Lawrence).

The most thorough characterization of episodic stream chemistry was conducted through the USEPA Episodic Response Program (ERP), in which 13 low-order streams (watershed areas <24 km²) in the Adirondack and Catskill regions of New York, and the Appalachian Plateau in Pennsylvania were monitored from 1988 to 1990 (Wigington et al., 1996). Acid episodes with chemical concentrations within the 90th percentile involved decreases in ANC of up to 200 $\mu\text{eq l}^{-1}$, decreases in pH of up to one unit, and increases in concentrations of inorganic monomeric Al (Al_i) of up to 15 $\mu\text{mol l}^{-1}$ (Wigington et al., 1996). Results also showed that acid episodes reduced the size of fish populations and eliminated acid-sensitive species if median high-flow pH was <5.2 and Al_i concentrations exceeded 3.7 $\mu\text{mol l}^{-1}$, despite the relatively short duration of episodes (Baker et al., 1996). Largely on the basis of this study, the USEPA concluded that reversal of effects from episodic acidification could be used as a key ecological endpoint for an acid deposition standard for protection of the environment (USEPA, 1995).

The ERP study firmly established the ecological significance of episodic acidification, but efforts to detail the watershed flow-path mechanisms through which episodic acidification occurs have been largely unsuccessful (Sullivan, 2000). Information on the changes in watershed processes that would lead to recovery from episodic acidification, therefore, is limited. Furthermore, the most recent episode data published for the eastern United States were collected in 1993–1994 in three watersheds (areas of 11–13 km²) in Shenandoah National Park, VA (Hyer et al., 1995): data collection for the ERP ended in 1990 (Wigington et al., 1996). In the absence of recent data, the response of episodic acidification to the decreasing national trend in atmospheric deposition of SO₄²⁻ (40–45% from 1990 to 1999 in the Adirondack and Catskill regions; NADP, 2001) has not been determined. The need for information on the current status of episodic acidification and the potential for recovery from this impact takes on added significance as Congress debates whether modifications of the Clean Air Act Amendments of 1990 will be needed for the recovery for acidified surface waters (Driscoll et al., 2001).

Although research programs have not focused on episodic acidification since the early 1990s, relevant information has recently become available from related ongoing research conducted through several studies. The objectives of this paper is to integrate these results to provide (1) a report on the current status of episodic acidification in the northeastern US, (2) new information on the link between atmospheric deposition, soils and episodic acidification and (3) an evaluation of the spatial extent of chronic and episodic stream acidification within a watershed of 85 km².

2. Methods

2.1. Assessment of episodic acidification status in Buck Creek watershed

To assess the recent status of episodic stream acidification, water sampling during non-winter (April–November) episodes was resumed in June 1998, in two tributaries of Buck Creek (referred to as the north and south tributary), an Adirondack stream studied in the ERP. Frequency of sampling is determined by the frequency of high-flow episodes. In this paper, results are reported for one storm in August 1998 and one storm September 1999. Automated samplers, triggered by rapidly increasing water levels (determined by pressure transducers), were used to collect samples at these sites. Sampling and chemical analysis procedures follow those described in Lawrence et al. (1995a, b).

Soils in the Buck Creek tributary watersheds are classified as Spodosols. The underlying bedrock is interlayered metasedimentary rocks and various forms of gneiss. The relationship between stream flow and precipitation in these watersheds suggests that the north tributary has little or no till, whereas, till deposits are likely to occur in the south tributary. The north tributary has sphagnum wetlands in the headwaters, but is otherwise well-drained. The south tributary is well drained throughout. Coniferous species (*Picea rubens*, *Tsuga canadensis*, *Abies balsamea*) comprise 43% of the basal area of trees in the north tributary, but are almost absent (1.5% of basal area) in the south tributary watershed, in which 68.4% of basal area is *Fagus grandifolia*.

2.2. Relationships between atmospheric deposition and soil S and N

To evaluate relationships between atmospheric wet deposition and soil chemistry, Oa horizon soil samples were collected in 12 red spruce stands in New York, Vermont, New Hampshire and Maine, in 1992 and 1993, for the analysis of total S and total N. Site characteristics and details of sampling and chemical analysis are given in David et al. (1996). Methods for estimating atmospheric wet deposition at each of these sites is given in Lawrence et al. (1997), except for the Hubbard Brook, N.H. site, where precipitation was estimated from elevational model (Dingman, 1981) and chemical concentrations of samples determined at the National Atmospheric Deposition Program station at Hubbard Brook, ~500 m below the red spruce stand. Atmospheric wet deposition estimates for the 12 red spruce sites are based on data collected during the period of 1986–1993. Soil samples from the Oa horizon in the north and south tributary watersheds of Buck Creek were also collected and analyzed for total N in 1997 and

1998. In this analysis, atmospheric wet deposition for the Buck Creek tributary watersheds is assumed to equal the average of water years 1998 and 1999 measured at a monitoring site ~ 15 km west. Collection and analysis of wet deposition at this site followed NADP protocols (NADP, 2001).

2.3. Relationships between stream chemistry and soil chemistry

To establish relationships between stream chemistry and soil chemistry, high-flow water samples were also collected with stage-activated automatic samplers at six small watersheds (in addition to the north and south tributaries of Buck Creek), in northern New York, New Hampshire and Maine (Table 1, Fig. 1), from 1992 to 2000. Because stream chemistry most reflects the chemical characteristics of soil during high flows (Chen et al., 1984), stream-water concentrations were reported as unweighted means, calculated from the concentrations of storm and snowmelt samples. Samples were included if they were collected during the highest 20% of the storm flows when samples were collected. This approach minimized the effects of flow paths beneath the soil that reflect geochemical reactions with till and bedrock. At an additional watershed (watershed 6 at the Hubbard Brook Experimental Forest), concentrations of stream water was represented by the average monthly concentrations (determined from flow-weighted weekly samples) for the 3 months with the highest average flows during 1990–1992. Flows for these 3 months were in the highest 10% of monthly flows measured from 1963 to 1992. Sampling and chemical analysis of stream chemistry for all sites were similar, as described in Likens et al. (1977), Norton et al. (1994) and Lawrence et al. (1995a, b). Methods of flow measurement are given in Lawrence et al. (1995a) and Likens et al. (1977).

Soil samples were collected from the Oa and B horizon of each of these watersheds, except in the case of the Hubbard Brook, where soil samples were collected in adjacent watershed 5 (Table 1). The Oa value for the Bear Brook site represents a combined Oe–Oa sample, and therefore may overestimate the exchangeable Ca concentration of the Oa horizon at this site. Exchangeable Ca concentrations in the B horizon were determined from samples collected in the upper 10 cm of this horizon, except at (1) the Winnisook site, where values were determined from a composite of equal-volume samples collected at 10 cm intervals through the B horizon profile (mean depth = 33 cm), and (2) the Hubbard Brook and Bear Brook sites, where the average of the Bh and Bs1 horizon was used (Johnson et al., 1991). Watershed concentrations of Ca for Oa and B horizons are reported as unweighted averages of all sites within the watershed, except at Cone Pond and Laurelly Fork, where distinct landscapes enabled chemical concentrations to be areally weighted to develop the watershed average. Methods of soil analysis are given in Johnson et al. (1991), David and Lawrence (1996) and Robarge and Fernandez (1986).

In this analysis, soil moisture at Buck Creek was also measured at a site adjacent to both north and south tributary watersheds with time-domain reflectometry (TDR) in the forest floor, at three locations 10 cm below the surface. The universal relationship between soil moisture and the dielectric constant was used to measure volumetric water content (Dasberg and Hopmans, 1992).

2.4. Spatial comparison of chronic and episodic stream chemistry

To contrast the spatial extent of chronic and episodic stream chemistry, a reference site within the West Branch of the Neversink River Basin (labeled West

Table 1

Watershed areas, collection dates and number of samples collected to assess the relationship of soil chemistry to stream chemistry in small watersheds

Watershed	Area (ha)	Water samples		Soil samples		
		Collection period	No.	Oa horizon. no.	B horizon no.	Collection date
Bear Brook, ME	11	1995–1997	122	20	20	1997
Buck Creek, North, NY	37	1998–2000	19	30	30	1997
Buck Creek, South, NY	52	1998–2000	14	30	30	1998
Burnt Mill Brook, NH	355	1999–2000	14	12	12	1999
Cone Pond, NH	34	1992–1994	22	31	30	1988–1995
Dry Creek, NY	22	1993–1995	51	30	45	1995
Hubbard Brook, NH	13	1990–1992	3	53	23	1983
Laurelly Fork, PA	967	1998–2000	15	12	12	1999
Winnisook, NY	205	1991–1995	73	66	51	1993

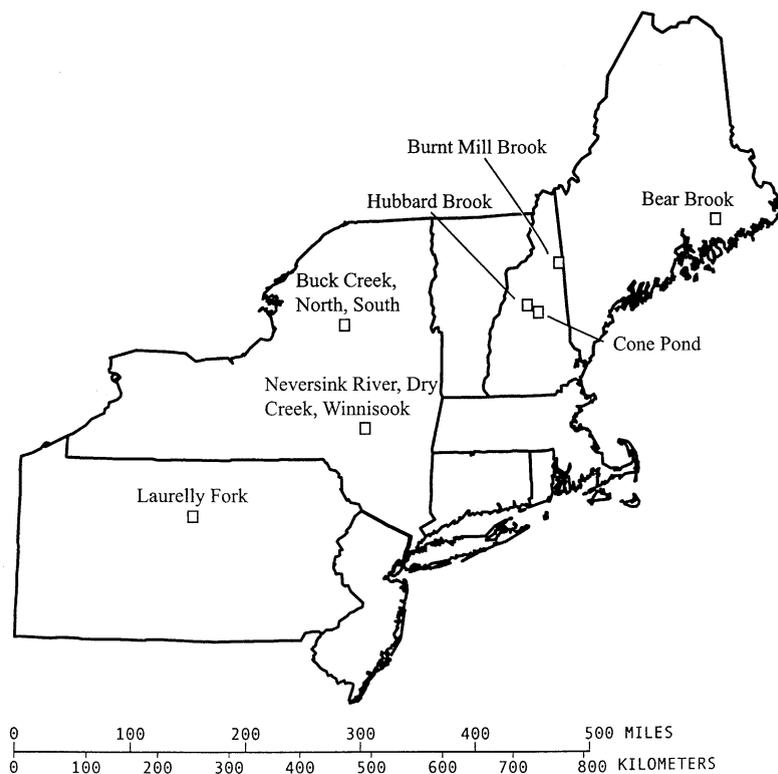


Fig. 1. Locations of small watersheds used to evaluate relationships between soil chemistry and stream chemistry.

Branch site; Fig. 4) at which ANC approached $0 \mu\text{eq l}^{-1}$ at high flow (ANC ranged from 8 to $146 \mu\text{eq l}^{-1}$, pH from 5.3 to 7.3, and Al_i from 0 to $1.2 \mu\text{mol l}^{-1}$) was selected to define the base of the watershed (area of 85 km^2). Automated sampling was conducted at the West Branch site and 3 upstream sites from 1991 to 1995 (Fig. 4), and at two additional upstream sites, where flow was monitored, manual samples were collected over a range of flows from 1991 to 1993. The number of samples collected at the six sites ranged from 66 to 491.

In this analysis, chronically acidified stream reaches were defined as those bracketed by sites with baseflow ANC values $< 10 \mu\text{eq l}^{-1}$. Because chronically acidic sites acidified further during high flows, the chronically acidic reaches were also considered to be episodically acidic. Comparison of ANC-discharge relations between the West Branch site and the 5 upstream sites (watershed areas from 0.22 to 64 km^2) indicated that if the ANC of a water sample collected at any of these upstream sites was less than the ANC at the West Branch site, on a specific date, at specific time, then the ANC at the upstream site would always be less than that at the West Branch site, regardless of flow. We observed no exceptions. Because, the West Branch site represented the highest minimum ANC necessary to be considered episodically acidic, it was assumed that sites with ANC

values less than those at the West Branch site (on the same date at the same time) were prone to episodic acidification. To identify the acidification status of stream reaches, baseflow water samples were collected at 108 locations on stream reaches upstream from the West Branch site from 1991 to 1994, and at 14 locations in 1999. Linear regression between ANC and $\log_{10}\text{flow}$ ($\text{ANC} = -51 \log_{10}\text{flow} + 168$; SE slope = 2.0; SE intercept = 4.36; $R^2 = 0.88$, $n = 94$) was used to estimate ANC at the West Branch site on dates for which both upstream samples and West Branch samples were not collected. Further description of the Neversink River Basin, field methods and laboratory analyses are given in Lawrence et al. (1995a, b, 2001).

3. Results and discussion

3.1. Episodic acidification at Buck Creek

The responses of stream chemistry to high flows can be characterized by results of storm sampling on 24 August 1998 and 16–23 September 1999. In the north tributary, the August 1998 storm resulted in a decrease in the sum of basic cations minus the sum of acid anions (BC–AA), of $15 \mu\text{eq l}^{-1}$, and small changes in pH and

Table 2

Stream chemistry in tributaries of Buck Creek, western Adirondack region of New York, during high-flow events in (a) August 1998, and (b) September 1999

Date	Time	Flow ($l s^{-1}$)	pH	BC-AA ($\mu eq l^{-1}$)	Al _i ($\mu mol l^{-1}$)	DOC ($\mu mol l^{-1}$)
<i>(a) North tributary^a</i>						
August 24	2:23	9.4	4.26	0.2	5.3	534
August 24	4:24	153	4.21	-14.8	5.9	605
August 24	7:43	420	4.18	-2.8	5.4	692
August 24	11:09	177	4.12	-5.2	5.4	805
August 24	14:59	15.5	4.15	-3.02	6.0	774
<i>South tributary^a</i>						
August 24	0:33	7.2	5.72	35.2	1.6	192
August 24	3:26	38.2	5.15	23.0	3.4	183
August 24	7:02	958	4.66	3.3	7.3	278
August 24	9:51	448	4.64	-8.5	7.3	320
August 25	1:30	55.8	4.61	-8.5	7.3	245
<i>(b) North tributary^b</i>						
September 16	16:48	3.2	6.34	164	1.1	1141
September 16	19:45	18.9	4.14	-53.1	10.5	1275
September 16	23:21	76.2	4.17	-50.0	10.2	1433
September 19	14:00	8.6	4.09	-94.2	15.2	1167
September 20	23:50	44.4	4.14	-60.3	10.1	1333
September 26	15:14	1.6	6.49	116.5	0.7	1241
<i>South tributary^b</i>						
September 16	14:58	6.0	6.1	136	0.5	875
September 16	18:09	10.3	5.78	68.5	1.0	625
September 17	1:05	31.2	5.15	27	3.7	675
September 20	18:32	4.0	6.01	69.2	0.8	450
September 23	9:47	11.5	4.84	-2	6.1	492
September 24	8:31	5.5	5.94	44.6	1.4	400

^aTotal precipitation during previous 6 weeks: 15.3 cm. Soil moisture at onset of storm: 22% (26, 27). Total precipitation during the storm: 9.0 cm. Storm duration: 13 h, 45 min.

^bTotal precipitation during previous 6 weeks: 3.7 cm. Soil moisture at onset of storm: 6.2% (26, 27). Total precipitation during the storm: 13.8 cm. Storm duration: 158 h, 15 min.

Al_i concentrations (Table 2a). The value of BC-AA (calculated as $Ca^{2+} + Mg^{2+} + Na^{+} + K^{+} - SO_4^{2-} - NO_3^{-} - Cl^{-}$), provides an index of the capability of a watershed to neutralize acidic deposition; values near or less than $0 \mu eq l^{-1}$ indicate a low capacity to neutralize inputs of acidic deposition through the release of base cations into solution (Driscoll and Newton, 1985). The low value of BC-AA at the onset of the storm suggests chronic acidification as a result of acid deposition, although the low baseflow pH was due at least in part to organic acidity derived from the decomposition of litter from coniferous vegetation, and from the sphagnum wetlands in the upper reach. The response of the south tributary—a pH decrease of more than 1 unit, a decrease in the BC-AA value of more than $40 \mu eq l^{-1}$, and an increase in Al_i concentration of $5.7 \mu mol l^{-1}$ (Table 2a), strongly reflected episodic acidification induced by acid

rain. The decrease in pH in the south tributary exceeded the 90th percentile for the pH decreases of the 13 streams studied in the ERP, and the increase in inorganic Al concentrations exceeded the median for all but one of the ERP streams studied.

The storm in September 1999, resulted in acidification responses in the Buck Creek watersheds that were distinctly different than those of the 1998 storm. Early in the 1999 storm, the pH in the north tributary decreased by more than 2 units, the BC-AA value decreased by more than $200 \mu eq l^{-1}$, and the Al_i concentration increased by a factor of 10 (Table 2b). Additional precipitation, 3 days later resulted in further acidification of this stream to a pH of 4.09, a BC-AA value of $-94.2 \mu eq l^{-1}$, and an Al_i concentration of $15.2 \mu eq l^{-1}$. The response to this storm differed from that of the 1998 storm both in the high pH and high value of BC-AA at

the onset, and the extremely low minimum values of BC–AA and peak concentration of Al_i . This acidification episode resulted from large increases in inorganic acidity— NO_3^- concentrations reached $149 \mu\text{mol l}^{-1}$, and SO_4^{2-} concentrations reached $148 \mu\text{mol l}^{-1}$, whereas in the 1998 storm, NO_3^- concentrations peaked at $16.4 \mu\text{mol l}^{-1}$ and SO_4^{2-} concentrations peaked at $45 \mu\text{mol l}^{-1}$. Despite the severe acidification in the 1999 storm, the peak flow was only 18% of the peak flow of the 1998 storm. The difference in responses of the south tributary to these two storms was less pronounced (Table 2b), although in the 1999 storm, NO_3^- concentrations reached $43 \mu\text{mol l}^{-1}$ (compared to $18 \mu\text{mol l}^{-1}$ in 1998), SO_4^{2-} concentrations reached $60 \mu\text{mol l}^{-1}$ (compared to $49 \mu\text{mol l}^{-1}$ in 1998), and peak flow of the 1999 storm was 3.2% of the peak flow measured in the 1998 storm.

3.2. The role of antecedent soil moisture conditions

The stronger acidification response in 1999 than in 1998 was likely related to dry conditions that preceded the 1999 storm (Table 2). Acidification associated with high levels of SO_4^{2-} export from wetlands following droughts was previously documented for lakes in Ontario, Canada, between 1983 and 1993 (Dillon et al., 1997). Through a similar process, drying of wetlands in the headwaters of the north tributary probably led to an accumulation of SO_4^{2-} , NO_3^- , and acidity from mineralization of organic matter that was then flushed out by the storm (Lazerte, 1993). Acidification in the well-drained south tributary was probably caused by mineralization of organic S and N, and possibly the destruction of microbial cells within the soil. Nitrogen incorporated in microbial biomass was previously found to represent 3.4% of total organic N in the Oa horizon of an Adirondack hardwood stand (Christ et al., 1997). On the basis of this percentage, and the maximum NO_3^- concentration measured in the south tributary during the September 1999 storm, export of N over the 24 h of maximum flow was ~ 3 orders of magnitude less than the microbial N pool of the Oa horizon in the hardwood-forested south tributary watershed. The mechanisms of S retention and release in these watersheds are probably similar to those of N. Because much of the total S content of forest soils is in organic forms (David et al., 1987).

Although the amount of N and S exported in the September 1999 storm differed between the north and south tributary watersheds, each are likely to have experienced enhanced accumulation of these elements from decades of atmospheric deposition. Total N and total S contents in Oa horizons at varying elevations of red spruce stands throughout the northeast were found to be positively correlated with the atmospheric deposition rates (Fig. 2). A similar relation for N was

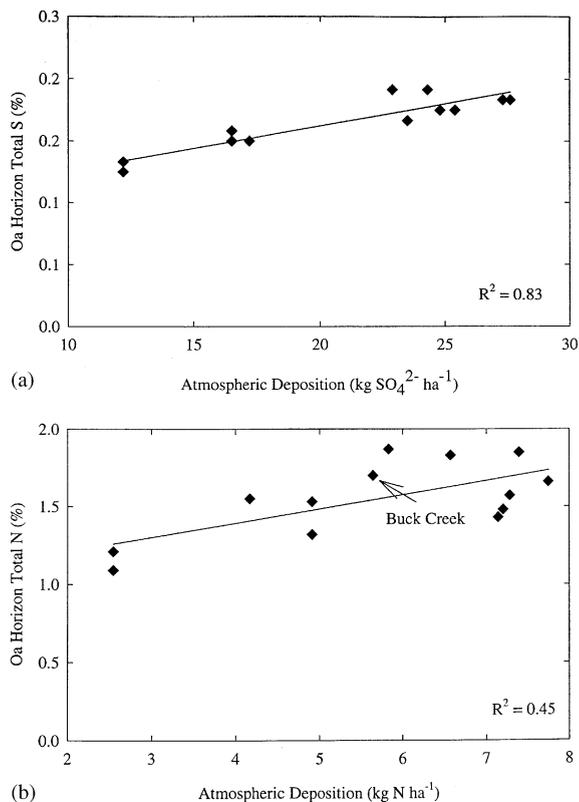


Fig. 2. Concentrations of (a) total S as a function of atmospheric wet deposition of SO_4^{2-} and (b) total N as a function of atmospheric wet deposition of N, in Oa horizons of red spruce stands in New York, Vermont, New Hampshire, and Maine.

documented in an earlier study of mostly high-elevation northeastern conifer stands (McNulty et al., 1990). Accumulation of N has been linked to increased leaching of HNO_3 into surface waters (Aber et al., 1998), and long-term accumulation of S in soils has been identified as a possible factor that may delay recovery from surface-water acidification (Driscoll et al., 1998).

3.3. Relationships between stream chemistry and soil chemistry

Results of episode monitoring in Buck Creek indicate a link between soil processes and episodic acidification. Because much of the water that causes high-flow episodes passes through the soil quickly en route to the stream channel (Chen et al., 1984; Wigington et al., 1996), neutralization of acidity is dependent upon rapid cation-exchange reactions that buffer decreases in the pH of soil solution through the release of bases (mostly Ca) adsorbed to particle surfaces. Recent evidence indicates, however, that concentrations of exchangeable

Ca in mineral soils have decreased as a result of acidic deposition (Likens et al., 1996; Markewitz et al., 1998; Lawrence et al., 1999). This decrease may have reached the level in some watersheds at which little neutralization of soil water is occurring within the mineral soil. No relation between exchangeable Ca concentrations in the mineral soil and high-flow stream chemistry was found among nine small watersheds in New York and northern New England (Fig. 3a). In contrast, exchangeable Ca concentrations in the Oa horizon of these watersheds were strongly correlated with high-flow stream chemistry (Fig. 3b), which implies that acid neutralization during episodes is more dependent on the availability of Ca in the forest floor than in the mineral soil.

The relations of soil Ca to high-flow stream chemistry are consistent with results of a previous study (Lawrence et al., 1997), which showed that the potential of parent material to release Ca through weathering in soils of 12 northeastern conifer stands was weakly related ($R^2 = 0.44$) to exchangeable Ca concentrations

(expressed as a percentage of cation-exchange capacity) in the mineral soil, where most release of Ca through weathering occurs, but was strongly related ($R^2 = 0.92$) to the exchangeable Ca concentrations in the Oa horizon, which is formed by the decomposition of leaves and wood. These relations were attributed to depletion of exchangeable Ca in the mineral soil to the level at which further depletion is buffered by the release of Al, thereby obscuring the relation with parent material. In the Oa horizon, the relation with parent material has been maintained despite decades of acidic deposition by (1) a high root activity that has limited Ca leaching through vegetative recycling, and (2) the relatively high cation-exchange capacity of this horizon. In soil samples collected in a previous study, 120 sites in northeastern red spruce stands in New York, Vermont, New Hampshire and Maine, CEC averaged 31.3 and 7.8 cmol kg⁻¹ in the Oa and upper 10 cm of the B horizon, respectively (David and Lawrence, 1996).

3.4. Contrasting the spatial extent of chronic and episodic acidification

Relations between Ca availability in soils and acidification of surface waters provide evidence that depletion of soil Ca is a key factor that has led to acidic episodes in streams. Streams in watersheds with a sufficient supply of bases within the soil profile, such as Laurelly Fork (Fig. 3), will not become acidic during high-flow episodes, whereas watersheds with base-depleted soils (receiving sufficient levels of acidic deposition) will experience either chronic or episodic acidification of stream water. Chronic acidification will occur in the absence of discharging ground water that is generally neutralized by passing through till or bedrock before entering the stream channel. A stream that does receive a significant amount of discharging ground water will tend to be well neutralized during baseflow, but will become acidic as the contribution of poorly buffered soil water increases with increasing flow (Wigington et al., 1996). Episodic acidification, therefore has the potential to extend further downstream than chronic acidification, because the likelihood of discharging ground water increases from headwaters to downstream reaches.

The spatial relationship between chronic and episodic acidification can be demonstrated in the Neversink River Basin, of the Catskill region of southeastern New York, where soils are Ca depleted from acidic deposition (Lawrence et al., 1999), and ground water significantly affects stream chemistry during baseflow (Burns et al., 1998). A reference site (labeled West Branch site; Fig. 4) at which ANC approached 0 $\mu\text{eq l}^{-1}$ at high flow (ANC ranged from 7.9 to 146 $\mu\text{eq l}^{-1}$, pH from 5.3 to 7.3, and Al_i from 0 to 1.2 $\mu\text{mol l}^{-1}$) was selected to define the base of the watershed (area of 85 km²). Flow monitoring and water sampling at this site and 5 upstream sites,

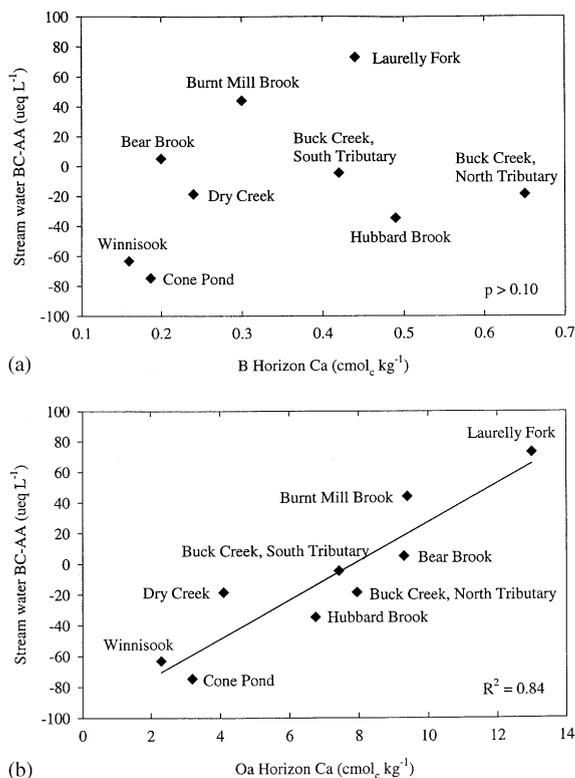


Fig. 3. The difference between the summed concentration of base cations (Ca^{2+} , Mg^{2+} , Na^+ , and K^+) and acid anions (SO_4^{2-} , NO_3^- , Cl^-), abbreviated as BC-AA, plotted as a function of exchangeable Ca concentrations in (a) the B horizon, and (b) the Oa horizon in small watersheds in Pennsylvania, New York, Vermont, New Hampshire and Maine.

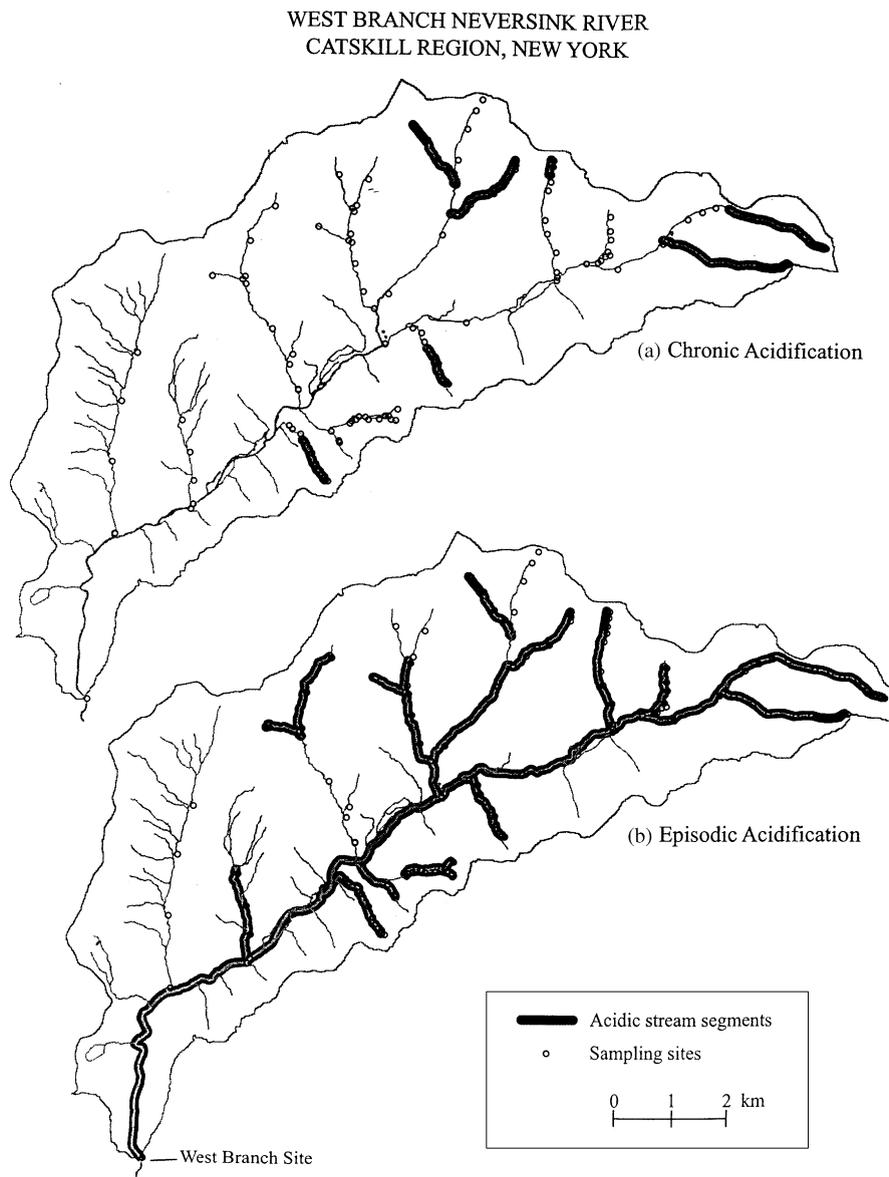


Fig. 4. Stream reaches of the West Branch Neversink River that were (a) acidic at all flows (chronically acidic), and (b) acidic only at high flows plus those acidic at all flows (episodically acidic). Chronically acidified stream reaches were defined as reaches bracketed by sites with baseflow ANC values less than $10 \mu\text{eq l}^{-1}$. Because chronically acidic sites tended to acidify further during high flows, the chronically acidic reaches were included as episodically acidic reaches in this figure.

indicated that any upstream site with a lower baseflow ANC than the reference site, at the same time, on the same date, would have a high likelihood of be subjected to acidic episodes (we observed no exceptions). On this basis, 122 baseflow samples collected throughout the watershed indicated that 16% of the stream reaches were acidic at baseflow ($\text{ANC} < 10 \mu\text{eq l}^{-1}$), and that an additional 66% of the reaches had a high likelihood of

becoming acidic at high flow. The high percentage of reaches that became acidified at high flow suggests that the soils throughout much of this basin are largely ineffective at neutralizing acidity. The results also indicated that sites in this basin with baseflow ANC values as high as $146 \mu\text{eq l}^{-1}$ could approach the threshold of toxic chemical conditions at high flow.

4. Conclusion

Atmospheric deposition of S has decreased ~40% in the 10 years since completion of ERP data collection, yet acidic episodes in streams of upland regions in the northeastern United States persist and are likely to be much more widespread than chronic acidification. Acidic episodes developed as a result of the depletion of exchangeable Ca in mineral soil horizons, which has increased the role of the Oa horizon in the neutralization of soil water during episodes. Neutralization of soil water in the Oa horizon is dependant upon a sufficient supply of available Ca and other base cations from within this horizon, which ultimately must come from either the mineral soil or atmospheric deposition. Mineralization of accumulated N and S in the forest floor (enhanced by acidic deposition), provides a source of acidity in addition to current atmospheric deposition loads that will continue to elevate leaching losses of Ca, as will transport of reactive Al from acidified mineral soil to the forest floor, a process previously identified (Lawrence et al., 1995c) in northeastern forest soils. These factors indicate that acid episodes will continue until the availability of S and N is further reduced and the base status of the mineral soil is improved.

Acknowledgements

This paper was developed through support from the USDA Forest Service Northern Global Change Program, The New York City Department of Environmental Protection, the USEPA Adirondack Effects Assessment Program, the US Geological Survey Acid Rain Program, and the US Geological Survey Hydrologic Benchmark Program. Data was also contributed by the Hubbard Brook Ecosystem Study, the Bear Brook Watershed Manipulation Study, and the Cone Pond Watershed Study. The author expresses their great appreciation to all the people involved in this support. The authors also thank R. P. Hooper, M.B. David, P. S. Murdoch, S.W. Bailey, and M. A. Nilles, for helpful manuscript reviews. This paper has not received USDA Forest Service peer review and should not be construed to represent the policies of this agency.

References

- Aber, J., McDowell, W., Nadelhoffer, K., Magill, A., Bernston, G., Kamakea, M., McNulty, S., Currie, W., Rustad, L., Fernandez, I., 1998. Nitrogen saturation in temperate forest ecosystems: hypotheses revisited. *Bioscience* 48, 921–934.
- Baker, J.P., et al., 1996. Episodic acidification of small streams in the northeastern United States: effects on fish populations. *Ecological Applications* 6, 422–437.
- Bulger, A.J., Cosby, B.J., Webb, J.R., 2000. Current, reconstructed past, and projected future status of brook trout (*Salvelinus fontinalis*) streams in Virginia. *Canadian Journal of Fisheries and Aquatic Sciences* 57, 1515–1523.
- Burns, D.A., Murdoch, P.S., Lawrence, G.B., 1998. The effect of ground water springs on NO₃⁻ concentrations during summer in Catskill Mountain streams. *Water Resources Research* 34, 1987–1996.
- Chen, C.W., Gherini, S.A., Peters, N.E., Murdoch, P.S., Newton, R.M., Goldstein, R.A., 1984. Hydrologic analyses of acidic and alkaline lakes. *Water Resources Research* 20, 1875–1882.
- Christ, M., David, M.B., McHale, P.J., McLaughlin, J.W., Mitchell, M.J., Rustad, L.E., Fernandez, I.J., 1997. Microclimatic control of microbial C, N, and P pools in Spodosol Oa horizons. *Canadian Journal of Forest Research* 27, 1914–1921.
- Dasberg, S., Hopmans, J.W., 1992. Time domain reflectometry calibration for uniformly and nonuniformly wetted sandy and clayey loam soils. *Soil Science Society of America Journal* 56, 134–13451.
- David, M.B., Lawrence, G.B., 1996. Soil and soil solution chemistry under red spruce stands across the northeastern United States. *Soil Science* 161, 314–328.
- David, M.B., Mitchell, M.J., Scott, T.J., 1987. Importance of biological processes in the sulfur budget of a northern hardwood ecosystem. *Biology and Fertility of Soils* 5, 258–264.
- Dillon, P.J., Molot, L.A., Futter, M., 1997. The effect of El Niño-related drought on the recovery of acidified lakes. *Environmental Monitoring and Assessment* 46, 105–111.
- Dingman, S.L., 1981. Elevation: A major influence on the hydrology of New Hampshire and Vermont, USA. *Hydrological Sciences Bulletin* 26, 399–413.
- Driscoll, C.T., Newton, R.M., 1985. Chemical characteristics of Adirondack Lakes. *Environmental Science and Technology* 19, 1018–1024.
- Driscoll, C.T., Likens, G.E., Church, M.R., 1998. Recovery of surface waters in the northeastern US from decreases in atmospheric sulfate. *Water, Air, and Soil Pollution* 105, 319–329.
- Driscoll, C.T., Lawrence, G.B., Bulger, A.J., Butler, T.J., Cronan, C.S., Eager, C., Fallon-Lambert, K., Likens, G.E., Stoddard, J.L., Weathers, K.W., 2001. Acidic deposition in the northeastern United States: sources and inputs, ecosystem effects, and management strategies. *Bioscience* 51, 180–198.
- Eshleman, K.N., Davies, T.D., Tranter, M., Wigginton, P.J., 1995. A two-component mixing model for predicting regional episodic acidification of surface waters during spring snowmelt periods. *Water Resources Research* 31, 1011–1021.
- Eshleman, K.N., Deviney, F.A., Galloway, J.N., 1998. Temporal Patterns of nitrogen leakage from mid-Appalachian forested watersheds: role of insect defoliation. *Water Resources Research* 34, 2005–2116.
- Hyer, K.E., Webb, J.R., Eshleman, K.N., 1995. Episodic acidification of three streams in Shenandoah National Park, Virginia, USA. *Water, Air, and Soil Pollution* 85, 523–528.
- Johnson, C.E., Johnson, A.H., Huntington, T.G., Siccama, T.G., 1991. Whole-tree clear-cutting effects on exchangeable

- cations and soil acidity. *Soil Science Society of America Journal* 55, 502–507.
- Lawrence, G.B., Burns, D.A., Murdoch, P.S., Baldigo, B.P., Baevsky, Y.H., 1995a. Workplan of the Neversink watershed study in the Catskill Mountains of southeastern New York. US Geological Survey Open-File Report 94-368, Troy, New York.
- Lawrence, G.B., Lincoln, T.A., Horan-Ross, D., Olson, M.L., Waldron, L.A., 1995b. Analytical methods of the US Geological Survey's New York District Water Analysis Laboratory. US Geological Survey Open-File Report 95-416, Troy, New York.
- Lawrence, G.B., David, M.B., Shortle, W.C., 1995c. Aluminum mobilization as a mechanism for calcium depletion in organic forest soil horizons. *Nature* 378, 162–165.
- Lawrence, G.B., David, M.B., Bailey, S.W., Shortle, W.C., 1997. Assessment of calcium status in soils of red spruce forests in the northeastern United States. *Biogeochemistry* 38, 19–39.
- Lawrence, G.B., David, M.B., Lovett, G.M., Murdoch, P.S., Burns, D.A., Stoddard, J.L., Baldigo, B.P., Porter, J.H., Thompson, A.W., 1999. Soil calcium status and the response of stream chemistry to changing acidic deposition rates. *Ecological Applications* 9, 1059–1072.
- Lawrence, G.B., Burns, D.A., Baldigo, B.P., Murdoch, P.S., Lovett, G.M., 2001. Controls of stream chemistry and fish populations in the Neversink River Watershed, Catskill Mountains, New York. US Geological Survey Open-File Report 00-4040, Troy, New York.
- Lazerte, B.D., 1993. The impact of drought and acidification on the chemical exports from a minerotrophic conifer swamp. *Biogeochemistry* 18, 153–175.
- Likens, G.E., Bormann, F.H., Pierce, R.S., Eaton, J.S., Johnson, N.M., 1977. *Biogeochemistry of a Forested Ecosystem*. Springer, New York. (Chapter 2–3).
- Likens, G.E., Driscoll, C.T., Buso, D.C., 1996. Long-term effects of acid rain: response and recovery of a forest ecosystem. *Science* 272, 244–246.
- Markewitz, D., Richter, D.D., Allen, H.L., Urrego, J.B., 1998. Three decades of observed soil acidification in the Calhoun Experimental Forest: has acid rain made a difference? *Soil Science Society of America Journal* 62, 1428–1439.
- McNulty, S.G., Aber, J.D., McLellan, Katt, S.M., 1990. Nitrogen cycling in high elevation forests of the northeastern US in relation to nitrogen deposition. *Ambio* 19, 38–40.
- NADP, 2000. National Atmospheric Deposition Program WEB page. <http://nadp.sws.uiuc.edu/>, data accessed October.
- Norton, S.A., Kahl, J.S., Fernandez, I.J., Rustad, L.E., Scofield, J.P., Haines, T.A., 1994. Response of the West Bear Brook Watershed, Maine, USA, to the addition of $(\text{NH}_4)_2\text{SO}_4$: 3-year results. *Forest Ecology and Management* 68, 61–73.
- Robarge, W.P., Fernandez, I.J., 1986. Quality assurance methods manual for laboratory analytical techniques, US EPA/USDA Forest Response Program, US EPA, Corvallis, OR.
- Sullivan, T.J., 2000. *Aquatic Effects of Acidic Deposition*. Lewis Publishers, Boca Raton, FL. (Chapter 6.1)
- USEPA, 1995. US Environmental Protection Agency, Acid Deposition Standard Feasibility Study Report to Congress EPA 430-R-001a.
- Wigington, P.J., Baker, J.P., DeWalle, D.R., Kretser, W.A., Murdoch, P.S., Simonin, H.A., Van Sickle, J., McDowell, M.K., Peck, D.V., Barchet, W.R., 1996. Episodic acidification of small streams in the northeastern United States: ionic controls of episodes. *Ecological Applications* 6, 389–407.