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Episodic Stream Acidification Caused by Atmospheric Deposition of Sea Salts at Acadia National Park, Maine, United States

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Major episodic acidifications were observed on several occasions in first-order brooks at Acadia National Park, Mount Desert Island, Maine. Short-term declines of up to 2 pH units and $130 \mu\text{eq L}^{-1}$ acid-neutralizing capacity were caused by HCl from soil solutions, rather than by H_2SO_4 or HNO_3 from precipitation, because (1) SO_4 concentrations were constant or decreased during the pH depression, (2) Cl concentrations were greatest at the time of lowest pH, and (3) Na:Cl ratios decreased from values much greater than those in precipitation (a result of chemical weathering), to values equal to or less than those in precipitation. Dilution, increases in NO_3 concentrations, or increased export of organic acidity from soils were insufficient to cause the observed decreases in pH. These data represent surface water acidifications due primarily to an ion exchange "salt effect" of Na^+ for H^+ in soil solution, and secondarily to dilution, neither of which is a consequence of acidic deposition. The requisite conditions for a major episodic salt effect acidification include acidic soils, and either an especially salt-laden wet precipitation event, or a period of accumulation of marine salts from dry deposition, followed by wet inputs.

INTRODUCTION

Episodic changes in stream chemistry occur during storm or snowmelt runoff events. These changes are often characterized by short-term decreases in pH and acid-neutralizing capacity (ANC). The reduction of ANC is caused by "titration" by strong acids in precipitation, increased edaphic export of organic acids, dilution by lower ANC water, or exchange of a cation(s) in high concentrations for hydrogen ion. This latter process is the "salt effect" [Bache, 1984; Wiklander, 1975], the displacement of hydrogen ion from soil exchange sites by another cation in excess. The likely cations are Na and Mg from marine salts [Wright *et al.*, 1988; Norton *et al.*, 1987; Skartveit *et al.*, 1980], with Cl serving as the counterion with hydrogen. The "salt effect" decreases soil acidity, but necessarily increases the acidity of percolating solutions [Wiklander, 1975].

We report here on the salt effect mechanism of episodic acidifications in low-order streams in Acadia National Park (ANP), Maine. We believe data from this site provide the first evidence documenting this phenomenon in North America [Heath *et al.*, 1991; Kahl *et al.*, 1985]. We illustrate depressions of pH and ANC caused by the salt effect in a first-order stream in the Upper Hadlock Pond watershed.

The episodic salt effect phenomenon has been demonstrated by both laboratory soil column experiments and larger-scale field experiments. Soil column experiments done by Njos [1978] indicated that humus soils have a high capacity to exchange H for Na. Declines in soil solution pH from 4.10 to 3.80 occurred after equilibration with 6 pore volumes of 1 meq L^{-1} NaCl. Johnson *et al.* [1986] demonstrated that passage of 1 mmol L^{-1} NaCl solutions through either O or B horizons caused larger decreases in pH than

did distilled water controls. Wright *et al.* [1988] simulated salt effect episodic acidification by spraying a small catchment in western Norway with diluted seawater containing $605 \mu\text{eq Cl L}^{-1}$. The pH of stream runoff dropped from 6.1 to 5.1 and ANC declined from 20 to $-2 \mu\text{eq L}^{-1}$. Base cation exchange for H^+ in soils was identified as the most important process leading to the short-term acidification of runoff.

Although the salt effect is well known among soil scientists, actual documentation of the effect on the chemistry of surface waters is limited. Gorham [1957] first suggested that sea salts might be important in determining the acidity of Nova Scotian waters. Several natural episodic acidifications in Norway have been attributed to the salt effect [Skartveit, 1981; Skartveit *et al.*, 1980]. Chronic acidification in Great Britain appears to be aided by increased dry deposition of salts due to afforestation [Harriman and Morrison, 1982]. Thompson [1982] reported similar chemical relationships for coastal streams in Newfoundland to those we report here, but did not relate acidification to the input of neutral salts. On rare occasions, such acidifications were also reported in Maine in higher-order streams up to 40 km from the ocean [Kahl *et al.*, 1992]. There is no evidence of chronic acidification of coastal lakes in the United States resulting from the salt effect [Sullivan *et al.*, 1988].

STUDY AREA

Acadia National Park is located on Mount Desert Island, Maine (Figure 1). The island is underlain predominantly by biotite granites and hornblende-biotite granites [Gilman and Chapman, 1986; Chapman, 1970], which are spatially uniform in chemical composition [Carl *et al.*, 1984]. At higher elevation, soils are generally thin spodosols or histosols, or are absent. Below the Holocene marine limit (about 80 m), thicker glacial deposits and/or Pleistocene glaciomarine sediments occur discontinuously as precursors of inceptisols or

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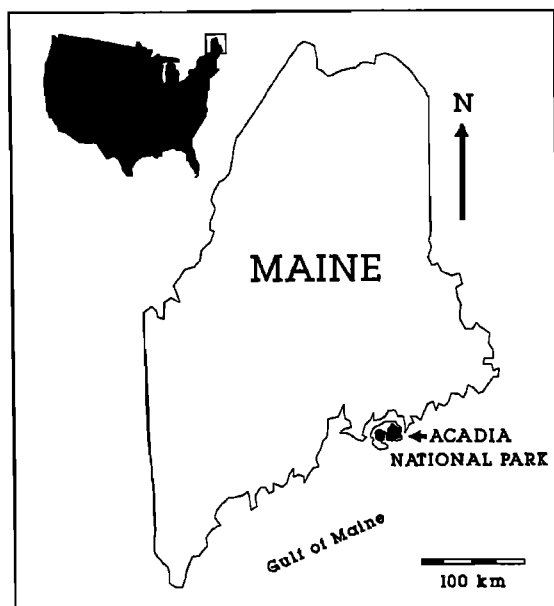


Fig. 1. Map of Maine, showing Acadia National Park located on Mount Desert Island. The Upper Hadlock Pond Watershed is in the south central portion of Acadia National Park.

spodosols. Streams in the two pedologic environments have somewhat different chemistries, and differ in their responses to episodic hydrologic events. The lower-elevation, higher-order streams have higher discharge, more stable base flow, and higher pH compared to the headwater brooks.

Surface waters within the Upper Hadlock Pond watershed are exceptionally clear (mean of 10 platinum-cobalt units) and oligotrophic. The 40-ha Penobscot Brook subcatchment which is the focus of this paper is on the southwest slope of Sargent Mountain about 3 km from the Gulf of Maine. The upper 15% part of the subcatchment is virtually treeless due to the lack of soil. The lower part is a mature coniferous forest made up predominantly of red spruce (*Picea rubens*) and balsam fir (*Abies balsamea*). The gradient of the bedrock and cobble streambed is approximately 14%.

Average annual rainfall measured at ANP was 139.3 cm (data from the National Atmospheric Deposition Program (NADP) for 1982–1989), with precipitation relatively uniformly distributed among months. Streamflow responds rapidly to rainfall with snowmelt alone unlikely to produce significant increases in discharge. Major spring hydrologic

events are often caused by rainfall on a snowpack, or rainfall on snowmelt-saturated soils. Large increases in acidity occur only with large increases in discharge.

Volume-weighted means for the chemistry of precipitation show distinct seasonal differences (Table 1). Sodium, Mg, and Cl concentrations are high during the fall and winter and low during the summer. Coastal frontal systems rich in marine aerosols generate much of the precipitation in the later part of the year, while summer precipitation is often derived from localized convective storms moving offshore.

METHODS

Surface water samples were collected periodically from streams between 1982 and 1984 as part of a survey of water chemistry in ANP [Kahl *et al.*, 1985]. Discharge measurements were made periodically only on Canon Brook during part of 1983. Surface water and bulk precipitation samples were collected in the Upper Hadlock Pond watershed weekly during 1988 and at least biweekly in 1989. In addition, stream sampling during high-discharge hydrologic events was done with ISCO Model 2900 automatic samplers on a frequency of 1 to 12 hours. Freezing of the precipitation collector prevented data collection within the watershed in the winter. Comparisons between the Acadia NADP site at McFarland Hill, and the Upper Hadlock Pond Watershed Study (HPWS) precipitation collection site for pH and weekly precipitation depth yield correlation coefficients of 0.91 and 0.97 respectively. Thus, we report here data from the NADP precipitation collection site. Discharge was measured with 90° V notch weirs in conjunction with Stevens model 68 Type F continuous water level recorders. An empirical linear relationship between the discharge of Penobscot Brook and a nearby brook gaged by an ice-free flume estimated discharge on Penobscot Brook during periods of missing record due to weir icing.

Samples were transported to the laboratory on ice and kept refrigerated except during processing. Separate aliquots for the determination of anions, base cations, and Si were vacuum-filtered through 0.4- μm Nucleopore filters. Aliquots for dissolved organic carbon (DOC) and true color were vacuum-filtered through 0.7 μm Whatman GF/F glass fiber filters. Analytical methods were protocols adapted from Hillman *et al.* [1986]). Cations were analyzed on a Perkin-Elmer model 703 atomic absorption spectrophotometer, anions by Dionex 2020i ion chromatography, ANC by radiometer ARAS[®] automated Gran plot method, DOC on an

TABLE 1. Volume-Weighted Seasonal Means of the Chemical Composition of Precipitation at Acadia National Park

Volume-Weighted Seasonal Means											
Season*	pH	Specific Conductance	NH ₄	Ca	Mg	K	Na	Na/Cl	Cl	NO ₃	SO ₄
Summer	4.55	21.9	7.8	4	2	1	6	0.86	7	16	45
Fall	4.81	15.6	4.6	3	8	1	39	0.85	46	10	22
Winter	4.50	24.3	5.7	6	10	1	43	0.86	50	23	36
Spring	4.59	20.4	9.6	4	5	1	19	0.83	23	15	40

NADP data reports (1982–1989) (available from Colorado State University). Concentrations are in microequivalents per liter; specific conductance is in microsiemens per centimeter.

*Here, spring is March, April, and May; summer is June, July, and August; fall is September, October, and November; winter is December, January, and February.

OI model 700 carbon analyzer, and pH with Orion Ross glass electrodes on samples equilibrated with 304 ppm CO₂ standard air. Soil exchangeable cations were extracted with unbuffered neutral salt solutions according to *Robarge and Fernandez* [1986]. Nonmarine concentrations of Na (indicated as Na*) were calculated assuming that Na was in the same proportion to Cl in atmospheric deposition as in seawater. Ionic charge contributions for Al assumed that total Al in micrograms per liter had a +2 charge, a reasonable assumption in hyperoligotrophic, relatively particulate free waters. DOC was assumed to have a charge density of 5 $\mu\text{eq mg}^{-1}$. Full sampling and analytical techniques and a complete listing of data are given by *Heath et al.* [1991] and *Kahl et al.* [1985].

RESULTS

Primary empirical evidence for the salt effect is the depression of the Na:Cl ratio in surface waters [*Wright et al.*, 1988; *Kahl et al.*, 1985]. The ratio in precipitation (Table 1) averaged 0.85 at ANP (seawater is 0.86). During base flow, the ratio is 1.1–1.4, due to Na from weathering of plagioclase feldspar, and from secondary weathering processes. Depressions in the Na:Cl ratio during salt effect acidifications at ANP have been as low as 0.71. Equivalent evidence for identifying the salt effect is a depression in the calculated nonmarine concentration of Na (Na*). Na* will be a negative value if the Na:Cl ratio is less than 0.86.

Other contributors to acidification were inadequate to explain the degree of acidification observed. The magnitude of dilution is not sufficient to explain observed declines in ANC, nor the depressions in the Na:Cl ratio. While discharge is increasing by a factor of 10,000, potential indicators of dilution such as specific conductance or Si concentrations change by percent, rather than by orders of magnitude. Similarly, SO₄ concentrations are typically constant or declined during episodic acidifications in Maine [*Kahl et al.*, 1992], including those resulting from the salt effect at ANP. Nitrate was generally only a small contributor to total anionic charge. DOC generally contributes less than 20 $\mu\text{eq L}^{-1}$ of anion charge at ANP.

Although we focus on one stream for brevity, salt effect acidifications have been documented on several occasions in all 12 first-order streams sampled at ANP since 1982 (Figure 2). Episodes in March and November 1984 especially exhibited characteristics of salt effect acidification. The March 1984 episode was a salt-laden precipitation event. Preceding the March event, 4.4 cm of wet deposition with Cl concentration of 125 $\mu\text{eq L}^{-1}$ fell on a deteriorating snowpack. The salts in wet deposition were augmented by salts from dry deposition during the winter period of low flow.

The concentration of marine salts in the precipitation of the November 1984 episode was not unusual; dry deposition deposited salts prior to the event. Total precipitation in the previous 4 months was 15 cm, compared to normal precipitation of about 38 cm. Headwater streams were nearly dry from early August until early November. Salts from dry deposition and low rainfall were mobilized by heavy November rains, causing the acidification. Sulfate concentrations declined during the period of lowest pH. Chloride concentrations peaked approximately concurrently. Sodium to Cl ratios declined from a norm of 1.1 in Penobscot Brook, to values less than 0.88, the ratio in precipitation during that

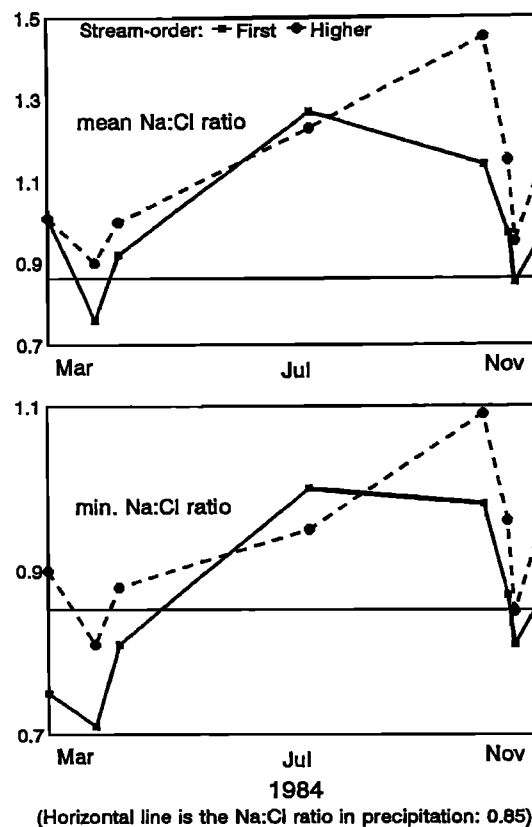


Fig. 2. Mean (top) and minimum (bottom) Na:Cl ratios in 12 first-order and nine second-order streams at Acadia National Park during 1984.

storm. Ratios less than 0.90 (mean, 0.85) occurred in all 12 of the first-order brooks. In contrast, only six of the 11 higher-order streams exhibited Na:Cl ratios less than 0.90 during March, and only two were less than 0.90 in November. A portion of the ANC decline is attributed to dilution by increased flow during higher runoff. However, we interpret a major portion of the acidification in the headwater brooks to be from HCl export from soil solutions to surface waters.

We recorded nine acidic episodes (ANC < 0 $\mu\text{eq L}^{-1}$) in Penobscot Brook during the 1988–1989 study period (Figure 3). The lowest pH (4.59) recorded was a rain/snowmelt event on February 21, 1989. The episode of October 22, 1988, displays the general chemical characteristics of salt effect acidification on Penobscot Brook (Figure 4). Between 1200 and 1500 hours, concentrations of Cl, H and Al increased, and total base cations, SO₄, ANC, and pH decreased. Minor increases in DOC probably contributed in small part to the acidification. Declines in ANC and pH were 44 to $-2 \mu\text{eq L}^{-1}$, and 6.5 to 4.9, respectively. Na* declined substantially more than concentrations of other nonmarine base cations, from 43 to $-2 \mu\text{eq L}^{-1}$. The decline in the Na:Cl ratio to 0.85 also indicated the ion exchange removal of Na from solution.

DISCUSSION

Neither SO₄ nor dilution fully explain the pH and ANC depressions observed in the first-order brooks as typified by Penobscot Brook. The relationships between pH, ANC, Cl,

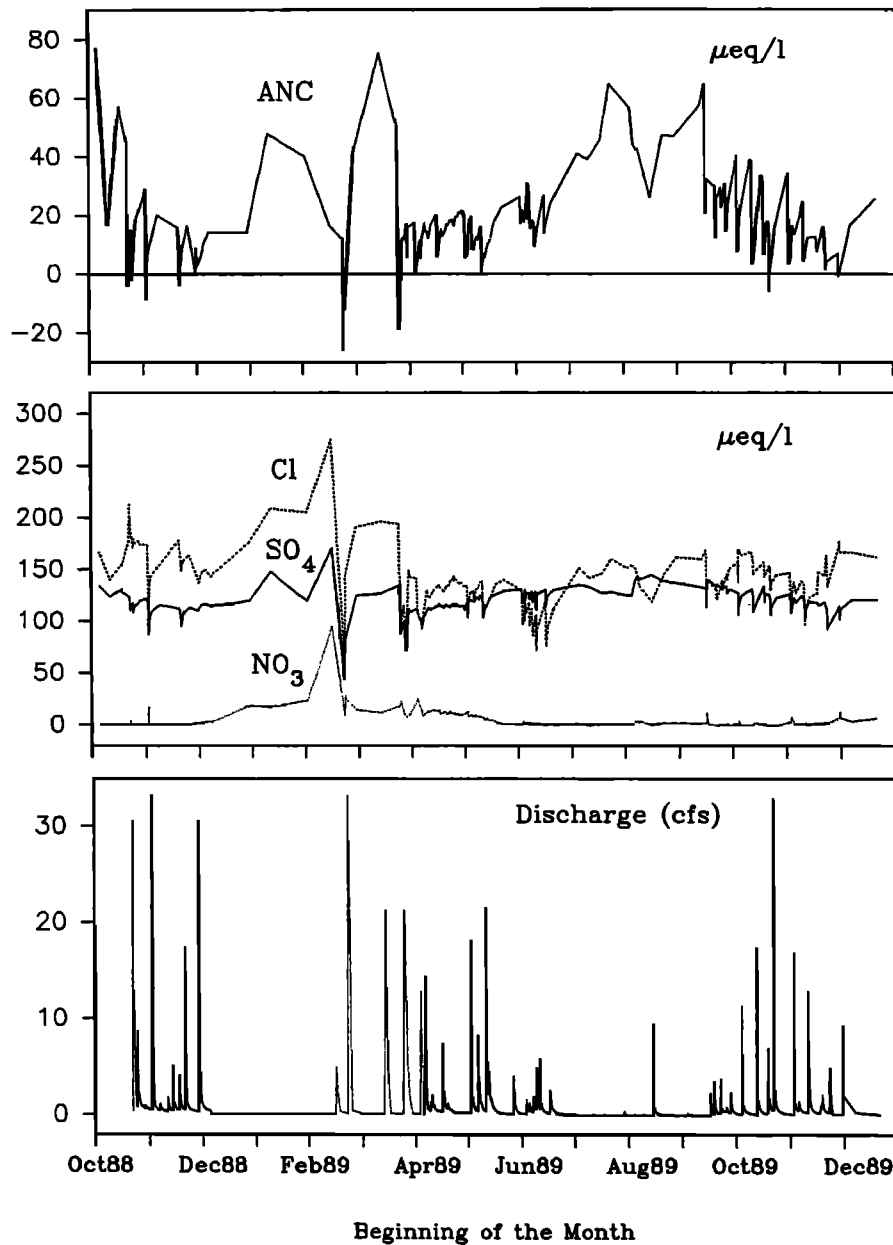


Fig. 3. Chemistry and discharge in Penobscot Brook for the period October 1988 to December 1989. Dotted discharge line indicates freezing weir conditions during which some portion of the record is estimated from an ice-free flume on an adjacent stream.

and SO_4 indicate that HCl is responsible for the pH and ANC declines. Na:Cl ratios in streams normally are greater than those in seawater or precipitation due to release of Na by chemical weathering. During the events discussed here, the Na:Cl ratios declined to values approaching those in incident precipitation. Dilution depresses the Na:Cl ratio somewhat, but removal of Na relative to Cl is necessary to depress the ratio to values well below 1.0. The major ion ratios also reflect a shift from an Na-Cl- HCO_3 or Na-Cl- SO_4 (as in Penobscot Brook) system to an Na-H-Cl-Al system. Sulfate declines further in relative importance during the events. Similarly, additional H^+ was added to the positive ions, and additional Cl more than replaced HCO_3 . Calcium increases in concentration (decreases less than the amount predicted from dilution) as a result of Na for H and Ca exchange reactions in the soil. Cation

exchange thermodynamic data suggest that similar relationships would exist for both Ca and K. However, the very low concentrations of K make detection of patterns in K concentrations difficult to detect.

The probable "salt effect" mechanism causing these acidifications is as follows. Neutral salts move into soil solution by one of two mechanisms: (1) deposition by a significant wet precipitation event, or (2) accumulation in and on soils from dry deposition or light rainfall, with subsequent flushing into the soil system by a later significant precipitation event. In the soil, neutral salts in the percolating solution displace hydrogen ions and Ca. Chloride becomes the dominant mobile counterion. If the pH is sufficiently low, Al is also mobilized. High concentrations of neutral salts are necessary to displace H^+ , in order to offset the unfavorable

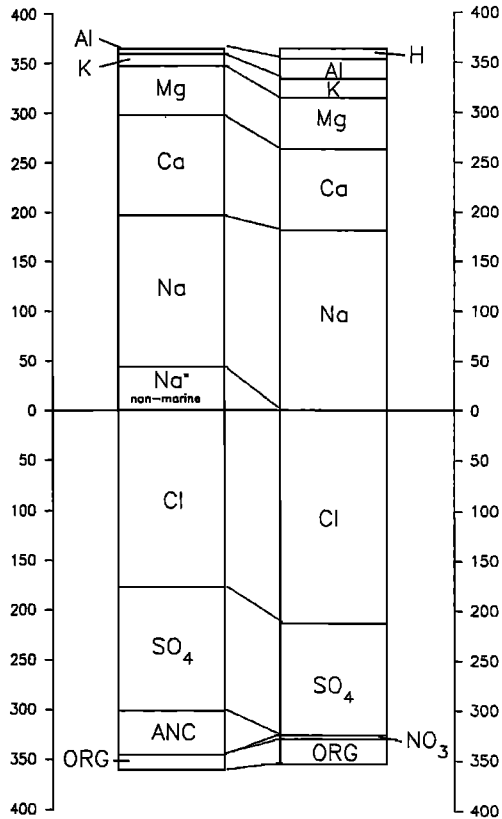
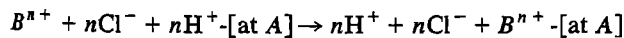


Fig. 4. Changes in chemistry in Penobscot Brook at 1200 and 1500 LT on October 22, 1988. Concentrations are in microequivalents per liter.

thermodynamics of the exchange of Na^+ for H^+ and Al^{3+} . Some SO_4 may also adsorb temporarily on acidic (positively charged) soil exchange sites [Johnson et al., 1986].

Schematically, the reversible reaction in acidic soils would be



where A is a negatively charged exchange site, and B^+ represents a cation such as Na^+ or Mg^{2+} . Concentrations of salts in excess of normal are necessary. Acidic precipitation is not required for surface water acidification by this mechanism. Chronic acidification by episodic "salt effect" events is not likely, due to the reversible nature of the H^+ - Na^+ exchange reaction. With chronically elevated neutral salt deposition, soil exchange acidity would become diminished, and pH values in surface waters would rise. However, elevated chronic atmospheric deposition of base cations should lead to higher base saturation of soils. If the soils are naturally acidic, soil solutions (and perhaps surface waters) could have a chronically lower pH than similar soils that did not receive the base cations from the atmosphere.

We used a reduction of the $\text{Na}:\text{Cl}$ ratio in the surface water as an indicator of possible salt effect acidifications between October 1988 and December 1989 (Figure 5). Input of marine salts by wet deposition is seasonally variable (Table 1). The $\text{Na}:\text{Cl}$ equivalent ratio in wet deposition is similar to that in seawater (0.86) and relatively constant throughout the year (Table 1). The $\text{Na}:\text{Cl}$ ratios in Penobscot Brook vary between 0.86 and 1.80. The lowest ratios occurred when the marine salt concentration in precipitation was the highest (Figure 5). High $\text{Na}:\text{Cl}$ ratios during June 1989 are a result of low inputs of marine aerosols relative to nonmarine Na derived from the soil (Figure 5). Reduction of the $\text{Na}:\text{Cl}$ ratio in Penobscot Brook in the absence of wet precipitation inputs of marine salts suggests mobilization of dry deposited salts.

Streamflow at high discharge is a mixture of new water directly derived from rain or snowmelt and old water existing in the watershed prior to the hydrologic event [Hooper and Shoemaker, 1986]. Streamflow is sustained between events by relatively alkaline base flow from the lower mineral soil [Anderson and Bowser, 1986; Winter, 1984]. During high discharge, the upper mineral soil and overlying organic layers become active conduits for water delivered laterally to streams and lakes [Bache, 1984]. Based on chemical characteristics of base flow and precipitation we calculated dilution and the extent of marine salt cation exchange for the October 22 salt effect episode.

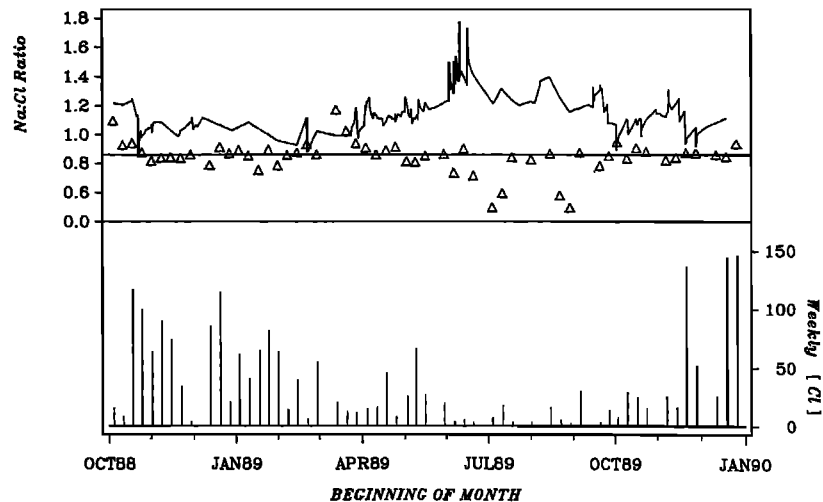


Fig. 5. (Top) Comparison of the $\text{Na}:\text{Cl}$ ratio in Penobscot Brook (solid line) versus the $\text{Na}:\text{Cl}$ ratio in weekly wet precipitation at the NADP collector (triangles) at Acadia National Park during the 1988–1989 study period. (Bottom) Concentration of Cl in wet precipitation.

TABLE 2. Concentrations of Solutes Just Prior to and at the Peak of the October 22, 1988 Episode on Penobscot Brook

	X_{old} Preevent Concentration	X_{peak} Event Concentration	X_{new} Marine Input	$(X_{old})(0.84)$ Proportion Preevent (Solute)	$(X_{new})(0.16)$ Proportion Marine (Solute)	X_{ss} /Sink/ Source
Si	94	79
Cl	177	213	402	149	64	...
Na	195	181	344	164	55	-38
Mg	49	51	74	41	12	-2
Ca	101	82	14	85	2	-5
K	12	19	7	10	1	8
SO ₄	124	112	40	104	6	1

Calculations of marine inputs and proportions of ions in event and preevent water are used to determine loss or gain of ions through cation exchange or other processes. Preevent concentrations are at 1200 LT and peak event concentrations are at 1500 LT.

We assume that Si is chemically conservative once released by primary weathering. Dilution of base flow was estimated by the ratio Si_{peak}/Si_{pre} , where Si_{pre} is the initial preevent Si concentration, and Si_{peak} is the Si concentration at the peak of the high-discharge episode. The concentration of Si_{peak} results from a mixture of Si-rich, preevent water, and new water with less dissolved Si. During the October 22 episode, $Si_{peak}/Si_{old} = 0.84$. Based on these assumptions, runoff was a maximum 84% old water and minimum 16% new water. Assuming that Cl is conservative, the Cl concentration at the time of the Si_{peak} (i.e., Cl_{peak}), is a function of the proportion of old water Cl concentrations (Cl_{pre}) mixed with new water Cl concentrations (Cl_{new}). In addition to the event precipitation chemistry, new water concentrations would include any solute dissolved from dry or occult deposition occurring prior to an episode, as well as chemical interactions with exposed mineral materials and organic soils.

With the percentage of new water and old water estimated by Si_{peak}/Si_{pre} , the concentration of Cl in new water (Cl_{new}) can be evaluated using Cl_{peak} and Cl_{pre} . Using old and new water percentages from the October 22 episode,

$$Cl_{peak} = (Cl_{pre}(0.84)) + (Cl_{new}(0.16)) \quad (1)$$

$$Cl_{new} = (Cl_{peak} - (Cl_{pre})(0.84))/0.16 \quad (2)$$

Solving for Cl_{new} yields a maximum value of $402 \mu\text{eq L}^{-1}$ for the concentration of Cl introduced during the episode, assuming conservative mixing of the two water sources. This calculated concentration of Cl is well above the $99 \mu\text{eq L}^{-1}$ in the wet precipitation for that event. The difference is residual Cl in the soil, plus Cl from dry deposition.

Inputs of Na, Mg, Ca, K, and SO₄ were calculated based on seawater ratios relative to Cl_{new} (Table 2). The difference between the calculated and actual concentrations became a sink/source component (X_{ss}) in (2), yielding

$$Na_{peak} = (Na_{pre}(0.84)) + (Na_{new}(0.16)) \pm Na_{ss} \quad (3)$$

The sink/source term represents the addition or removal of ions by processes other than dilution or marine salt additions. The sink/source term (X_{ss} in Table 2) indicates a loss of $-38 \mu\text{eq L}^{-1}$ Na to soil exchange sites, in part releasing H^+ to soil solution. The $38 \mu\text{eq L}^{-1}$ of acidity accounts for much of the loss of $46 \mu\text{eq L}^{-1}$ ANC (44 to $-2 \mu\text{eq L}^{-1}$). Dilution and marine input additions (both wet and dry)

account for most of the episodic variation in concentrations of Mg, Ca, K, and SO₄. Release of Ca has been observed during salt effect acidifications [Wright et al., 1988], but appears not to be important at ANP due to the low exchangeable Ca in the watershed soils (Figure 6).

Either Si or Cl may not be conservative during increasing stream discharge in certain situations [Kennedy, 1971]. The addition of Si to new water from rapid dissolution or desorption would produce an underestimation of the proportion of new water as defined by the ratio Si_{peak}/Si_{pre} . Underestimation of new water causes an overestimation of marine inputs with the new water.

The contribution of 16% new water may seem intuitively too low in an upland watershed of this character. An independent estimate of old and new water can be made from changes in base cation concentrations during the event. The sum of base cations was $357 \mu\text{eq L}^{-1}$ at 1200 local time, and 333 at 1500, a "dilution" of only 7%. However, there is probably a component of piston displacement of solutes from soils after only 3 hours. At midnight, the sum of base cations was $301 \mu\text{eq L}^{-1}$, or 84% of the original, the same value as estimated from changes in Si concentrations. This correspondence is fortuitous, but suggests to us that the estimate of 16% new water is not seriously in error. Even if we assume new water made up 25% rather than 16% of peak discharge during the October 22 episode, the resulting Cl_{new} would decrease from $402 \mu\text{eq L}^{-1}$ to 321. Recalculation of Na_{ss} results in a loss of $34 \mu\text{eq L}^{-1}$ rather than $38 \mu\text{eq L}^{-1}$ Na through ion exchange. Even with this substantial change in assumptions, loss of Na through cation exchange on soils is still the major consequence of this event for solution chemistry.

We estimated a concentration of $402 \mu\text{eq L}^{-1}$ Cl introduced to soil solution during the episode. This value is a maximum value. As is the case for Si, release of micropore water and possibly desorption of adsorbed Cl [Loise, 1988] by watershed soils can be a mechanism for introducing Cl to streamwater. Alternatively, the loss of Cl to adsorption during an episode would underestimate both Cl_{new} in (2) and the marine ion concentrations based on Cl_{new} . The loss of Na relative to Cl at peak flow is based on observed concentrations in the surface water suggesting that adsorption of Na is in excess of any possible adsorption of Cl. This pattern is to be expected in soil materials generally considered to be

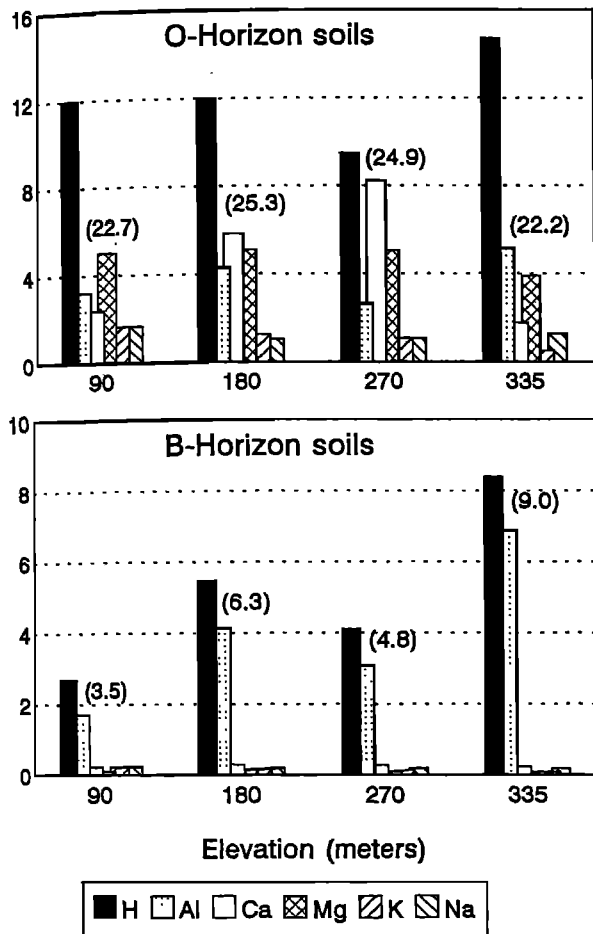


Fig. 6. Exchangeable cations (milliequivalents per 100 g) in O horizon and B horizon soils at the indicated elevations within the Upper Hadlock Watershed. Penobscot Brook was sampled at 130 m elevation. Numbers in parentheses are cation exchange capacity (milliequivalents per 100 g).

cation exchangers with little or no true anion exchange capacity.

There are significant differences between organic and mineral soils at HPWS (Figure 6). Organic horizons have a much higher concentration of exchangeable base (Ca, K, Mg, Na) and acid (H, Al) cations than mineral soils. The B horizons typically have a much lower cation exchange capacity with low base saturation. Exchangeable acidity is attributable largely to Al [Fernandez and Struchtemeyer, 1985; Fernandez, 1992]. This difference suggests that flow through O horizons will result in the exchange of Na for both H and Al, as seen in solution changes represented in Figure 4. Flow through the B horizon will result largely in Al release from the soil. When rates of percolation are slow, cation release from weathering will contribute base cations to these B horizon soil solutions. Therefore, time for equilibration and extent of soil contact are critical in determining the soil contribution to episodic solution chemical changes. There is an indication in the soil exchange data that acidity and Al are greater at higher elevations (Figure 6). Thus, the more sensitive upper reaches of stream watersheds are most prone to episodic acidifications from atmospheric deposition of marine salts.

The headwater streams receive a larger proportion of their

water from O horizon soils than the valley streams in thicker overburden. Water from headwater systems will be more acidic, as data for these streams illustrate. In addition, water introduced to streams from these soils will be relatively enriched in Na during base flow, as the internal production of H^+ exchanges for Na^+ . Thus, Na:Cl ratios in headwater streams were greater than in the lowland streams during base flow in both 1984 (Figure 2) and 1983.

CONCLUSIONS

Excess neutral salts in precipitation may cause significant episodic acidifications of surface waters due to an ion exchange of marine salts. At Acadia National Park, the phenomenon was observed principally in first-order, upland sites with thin soils. Higher-order sites at lower elevation are too well buffered to readily acidify, although the salt effect was evident in some of these streams. Soluble salts are deposited from wet precipitation, or accumulate from dry deposition. They are mobilized by rainfall or snowmelt. High concentrations of salt relative to normal levels are necessary for the effect to be apparent. When this occurs, temporary partial retention of Na, Mg, and/or SO_4 in soils, is the result. The process requires acidic soils, but acidic precipitation is not necessary for episodic acidifications to occur.

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