Dilution and the Elusive Baseline

Gene E. Likens*[,†,‡,§] and Donald C. Buso[†,§]

[†]Cary Institute of Ecosystem Studies, Millbrook, New York 12545, United States
[‡]Department of Ecology and Evolutionary Biology, University of Connecticut, Storrs 06269

S *Supporting Information*

ABSTRACT: Knowledge of baseline conditions is critical for evaluating quantitatively the effect of human activities on environmental conditions, such as the impact of acid deposition. Efforts to restore ecosystems to prior, "pristine" condition require restoration targets, often based on some presumed or unknown baseline condition. Here, we show that rapid and relentless dilution of surface water chemistry is occurring in the White Mountains of New Hampshire, following decades of acid deposition. Extrapolating measured linear trends using a unique data set of up to 47 years, suggest that both precipitation and streamwater chemistry (r^2 >0.84 since 1985) in the Hubbard Brook Experimental Forest (HBEF) will approximate demineralized water within one to three decades. Because such dilute chemistry is unrealistic for surface waters, theoretical baseline compositions have been calculated for precipitation and streamwater: electrical conductivity of 3 and 5 μS/cm, base cation concentrations of 7 and 39 μeq/liter, acid-neutralizing capacity values of <1 and 14 μeq/liter, respectively; and pH 5.5 for both. Significantly large and rapid dilution of surface waters to values even more dilute than proposed for Pre-Industrial Revolution (PIR) conditions has important ecological, biogeochemical and water resource management implications, such as for the success of early reproductive stages of aquatic organisms.
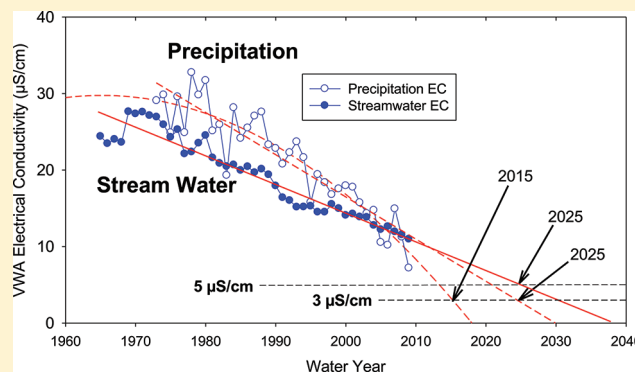
INTRODUCTION

Results from long-term research often provide ecological and biogeochemical insights not available from other types of studies, for example, refs 1–4. These rare measurements provide critical information about background or baseline chemical conditions, and give a framework for judging when changes are significant or extreme, for evaluating response to natural disturbance or the effect of an experimental manipulation or management intervention, and for documenting phenomena that have a prolonged time until expression, see refs 3 and 4. For example, the chemistry of bulk precipitation and streamwater in the Hubbard Brook Experimental Forest (HBEF) in the White Mountains of New Hampshire has been measured since 1963 (ref 2 and the Supporting Information (SI)).

In 1996, we published a linear relation between the long-term, changing sums of base cations ($\sum C_B$) and sums of two acid anions ($\sum AA$: SO_4^{2-} plus NO_3^-) in streamwater of Watershed 6 (W6) within the HBEF.[5] The trajectory of streamwater acidification (1963−1969), then recovery (1970−1993) of this headwater stream followed a statistically significant hysteresis. We predicted that the trend in recovery in this stream would indicate baseline values for pre-industrial revolution (PIR) conditions (∼1800) for these biogeochemically important solutes in surface waters common to the northeastern U.S. and southeastern Canada.[5] We also predicted that acid-neutralizing capacity (ANC) of W6 streamwater would become positive during the autumn of 1999.[5] Now, we have extended these relations, through continuous long-term

monitoring, by an additional 17 years. The results of these chemical trends, and extrapolations of these unique, long-term data, are both surprising and instructive relative to the establishment of biogeochemical baselines and management of such surface water resources in the future.

SITE DESCRIPTION AND METHODS

The Hubbard Brook Experimental Forest (HBEF), a 3,160-ha area of northern hardwood forest (43° 56′N, 71° 45′W), contains nine experimental, instrumented watershed ecosystems. The amount and chemistry of bulk precipitation and streamwater have been measured in these gauged watershed ecosystems on a weekly basis since 1963 using strict and consistent protocols for sampling and QAQC.[6−8] Bulk precipitation is collected in continuously open collectors for chemical analysis.[7,8] Additional information about the HBEF is found in ref 7, www.hubbardbrook.org, and the SI. Sigma Plot was used for graphics and Sigma Stat for statistics. The key components of the model used to establish biogeochemical baseline values are given in the SI.
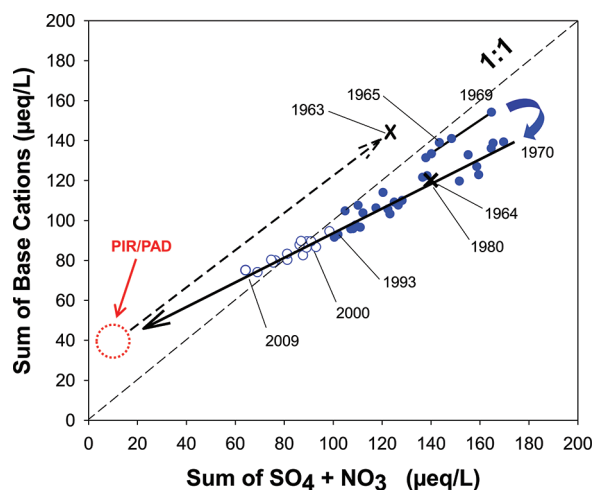
■ RESULTS

The extended acidification and recovery of base cation and acid anion concentrations from acid rain impacts is shown in Figure 1. The hysteresis pattern suggests the occurrence of extremely low values in the very near future.

Figure 1. Relation between volume-weighted, average annual concentrations of $\sum C_B$ and $\sum AA$ in streamwater (W6) of the HBEF from 1963−1964 through 2009−2010 (o-o are updated points after 1993, from ref 5). The linear regression equation for data from 1970−1971 through 2009−2010 is $\sum C_B = 0.613(\sum AA) -32.6$ ($r^2 = 0.96$, $p < 0.001$) in μeq/liter. The projected pre-industrial revolution/post acidic deposition (PIR/PAD) value is 39 μeq for $\sum C_B$ and 11 μeq for $\sum SO_4^{2-} + NO_3^-$. The line (- - -) from the PAD value to the 1963−1964 estimated value for W6 is a linear projection (see ref 5). $\sum C_B$ is sum of base cations and $\sum AA$ is sum of acid anions, SO_4^{2-} plus NO_3^-.
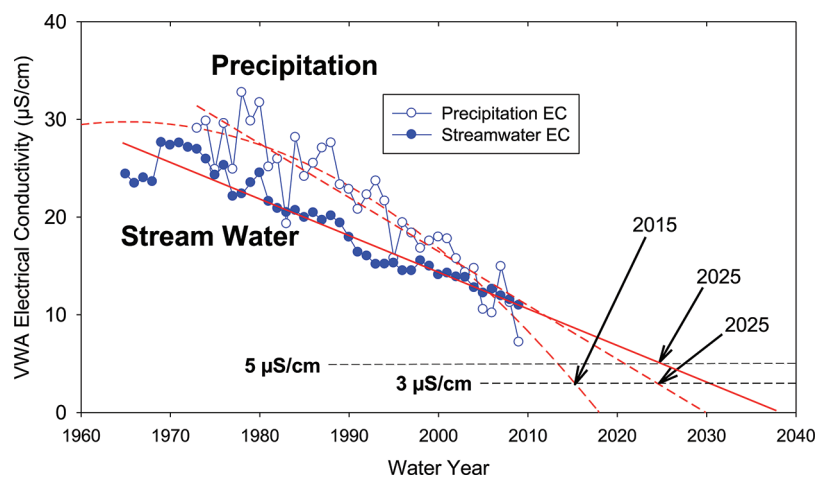
The volume-weighted, average annual concentrations of all ionic solutes, based on electrical conductivity (EC), in bulk precipitation and streamwater for W6 have been persistently declining since measurements began in 1963 (Figure 2). The average EC concentrations have declined by 20 μS/cm (66%) over 37 years for bulk precipitation, and by 17 μS/cm (61%) over 40 years for streamwater, and are trending toward even lower (more dilute) values (Figure 2). Remarkably, trend lines for EC will approach zero in only a few years (for bulk precipitation: in 2030 ($r^2 = 0.83$ for linear projection) or 2018 ($r^2 = 0.86$ for second-order polynomial projection); for stream-water: in 2038 ($r^2 = 0.92$ for linear projection). Surprisingly, since about 2005, average EC in ambient bulk precipitation has become ≤ than in streamwater (Figure 2). Higher EC values in precipitation resulted from the dominance of H^+, which has a significantly larger effect on EC values relative to other ions.

Similarly, $\sum C_B$ concentration declined by 60 μeq/liter (46%) and $\sum AA$ by 96 μeq/liter (60%), respectively, in W6 stream-water since the beginning of the recovery period in 1970 (Figure 3A). From 1996 through 2007, the volume-weighted concentrations of $\sum C_B$ and $\sum AA$ in W6 streamwater were (i) not significantly different in value, (ii) not significantly different in slope (linear regression), and (iii) much less variable than previously, suggesting a more stable stoichiometry. However, since 2007 $\sum AA$ has declined faster than $\sum C_B$ in streamwater. Streamwater $\sum AA$ concentrations continue to be coupled to precipitation inputs, while $\sum C_B$ concentrations now result primarily from terrestrial sources (Figure 3A, B).

Concentrations of $\sum C_B$ in precipitation were higher in the past than currently, but have been consistently low for 3 decades. In contrast, concentrations of $\sum AA$ in precipitation have declined markedly since 1970 in response to Federally mandated reductions in emissions of SO_2 and NO_X (Figure 3B). Bulk precipitation trends for $\sum C_B$ and $\sum AA$ are projected to PAD values of 7 μeq/liter and 10 μeq/liter in 2020, respectively (Figure 3B, Table 1). Rapid declines for $\sum AA$ are better fit by a second-order polynomial ($r^2 = 0.77$).

Because surface waters with zero EC are unrealistic, we have calculated theoretical baseline concentrations for streamwater and precipitation (Table 1; SI Table S1). Current chemistry for bulk precipitation and streamwater (W6) are given in Figure 4 and SI Table S2. Baseline values for streamwater (Table 1) were constructed to agree with the "end point" we generated from the extended hysteresis recovery in Figure 1, for example, $\sum C_B = 39$ μeq/liter and $\sum AA = 11$ μeq/liter. These proposed baseline values are lower, and appreciably more dilute than the Pre-Industrial Revolution (PIR) conditions projected in 1996,[5]

Figure 2. Long-term trends in volume-weighted, average annual electrical conductivity (EC) for bulk precipitation and W6 streamwater of the HBEF. The linear regressions for bulk precipitation and streamwater have r^2 values of 0.83 and 0.92, respectively. Extrapolation of trend lines for bulk precipitation and streamwater cross the proposed baseline (3 and 5 μS/cm, see text and Table 1) in 2025. A 2nd-order polynomial regression increases the precipitation r^2 to 0.86, crossing the 3 μS/cm baseline in 2015. Prior to ~1971, EC was not measured consistently in precipitation and data not shown here. Annual averages are calculated from ~30 annual measurements.
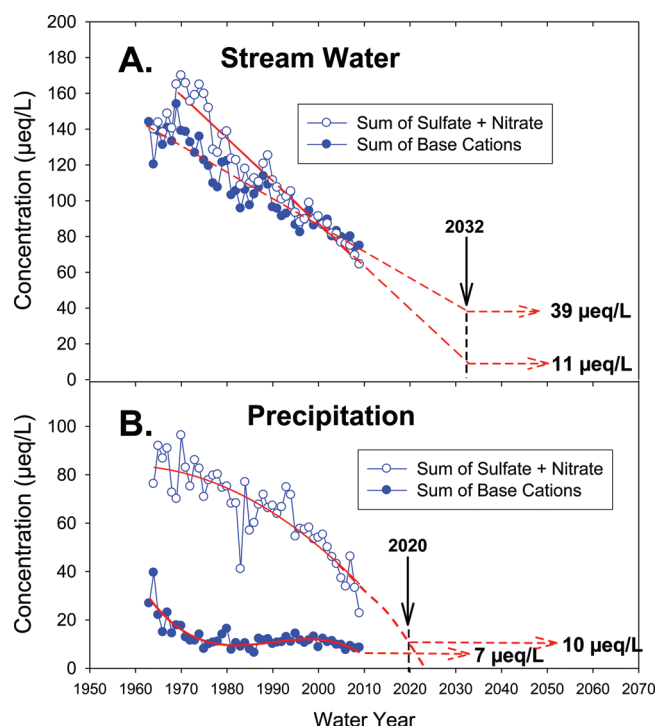
Figure 3. Long-term trends in volume-weighted, average annual $\sum C_B$ and $\sum AA$ in W6 streamwater (A) and bulk precipitation (B) at the HBEF. Streamwater linear trends for $\sum C_B$ ($r^2 = 0.88$) and $\sum AA$ ($r^2 = 0.83$) are projected to post acidic deposition (PAD) values of 39 μeq/L and 11 μeq/L in 2032, respectively. Bulk precipitation trends for $\sum C_B$ and $\sum AA$ are projected to PAD values of 7 μeq/liter and 10 μeq/liter in 2020, respectively (Table 1). Rapid declines for $\sum AA$ are better fit by a 2nd-order polynomial ($r^2 = 0.77$).

Table 1. Derived Charge Balance for Stream Water and Bulk Precipitation in Watershed 6 of the HBEF for Post Acidic Deposition (PAD) Conditions Based on a Theoretical Electrical Conductivity of 5 and 3 μS/cm, Respectively[a]

| ion	W6 stream water charge μeq/liter	bulk precipitation charge (μeq/liter)
calcium	11	2
magnesium	6	1
potassium	3	1
sodium	19	3
aluminum	<0.1	0
ammonium	<0.1	3
hydrogen ion	3	4
$\sum C_B$	39	7
cation sum	42.2	13
sulfate	10	8
nitrate	1	2
chloride	8	3
phosphate	<0.1	<0.1
bicarbonate (from ANC)	15	<0.1
DOC	8	0
$\sum AA$ ($SO_4^{2-} + NO_3^-$)	11	10
anion sum	42.1	13.2
balance	+0.1	−0.2
theoretical electrical conductivity	5.4	2.7

[a]The $\sum C_B$ and $\sum AA$ ($SO_4^{2-} + NO_3^-$) values for stream water are taken from the intersection of the linear extrapolation phase in Figure 1. Bicarbonate was estimated from acid-neutralizing capacity measurements (see the SI). Uncertainty for individual ions is estimated at ±50%.

and represent our estimates of *minimum* $\sum AA$ values for this system in a post acidic deposition (PAD) period.

The composite result of projected streamwater concentrations for baseline PAD conditions (Table 1) give a theoretical EC of 5 μS/cm, pH of 5.5, sodium as the dominant cation and bicarbonate as the dominant anion. Sodium has been ≥ calcium concentrations in W6 streamwater since ~2002, because sodium concentrations changed very little during the last 47 yr, whereas calcium concentrations declined significantly (Figure 4). The 5.0 μS/cm value is projected to occur for W6 streamwater in 2025 ($r^2 = 0.92$ for linear projection; Figure 2). For bulk precipitation at theoretical baseline, EC would be 3 μS/cm in 2025 (Figure 2), with a pH 5.5; hydrogen ion, ammonium, and sodium are the dominant cations and sulfate as the dominant anion in PAD (Table 1).

Data and discussion here are focused on Watershed 6 (W6), the long-term biogeochemical reference watershed of the HBEF, but patterns were similar in other nonmanipulated experimental watersheds (W3, W9) of the HBEF, and for the main stem of Hubbard Brook, all of which are larger, with different topographic aspects and somewhat different forest cover types than W6 (see Figure 5, SI Figure S1; SI Table S3). The key components used to develop theoretical PAD values in streamwater are given in SI Table S1.

■ DISCUSSION

Long-term biogeochemical records from the HBEF provide a remarkable opportunity to gain insight into what may have been the chemical characteristics of precipitation and streamwater in

base-poor substrates of northeastern North America prior to the industrial revolution, and how major drivers have changed these conditions. Perhaps more important, these data offer insight into future biogeochemical conditions following abatement of acid rain impacts. Clearly, the chemistry of precipitation has been altered in recent decades by human activities, such as by emissions of SO_2, NO_X, NH_4 and dust to the atmosphere, for example, refs 9−12. Some estimates of baseline conditions have been derived from data collected from areas remote from human activity (e.g., refs 13−16) and from models of acidic deposition impact on soil and surface water chemistry, for example, ref 17. Further, models of biological recovery from acidic conditions have assumed a stepwise return to previous baselines, while overlooking hysteresis effects or stochastic factors (see ref 18). Bulk precipitation at HBEF has much different composition than precipitation collected remote from human activity (e.g., refs 13 and 14). These results beg the question whether streamwater changes, which have been induced by atmospheric deposition, are permanent?

The chemistry of surface waters at HBEF reached high concentrations in the early 1970s (Figure 1) because of high inputs of sulfate and nitrate from atmospheric deposition, and subsequent acid leaching of base cations from soils, for example, refs 19 and 20. As emissions of SO_2, NO_X and atmospheric particles were curtailed by Federal legislation, atmospheric deposition of S, N, and even Ca and Mg declined concomitantly, for example, refs 12,21, and 22, as did concentrations in streamwater (Figures 1, 3, 4A; SI Figure S1). For bulk precipitation, the H-ion and sulfate concentrations have declined by some 83% and 79%, respectively, since 1964. The rate of decline has been steady since ~1970 (Figure 4B); even the impact of the 1990 Clean Air Act Amendments did not change
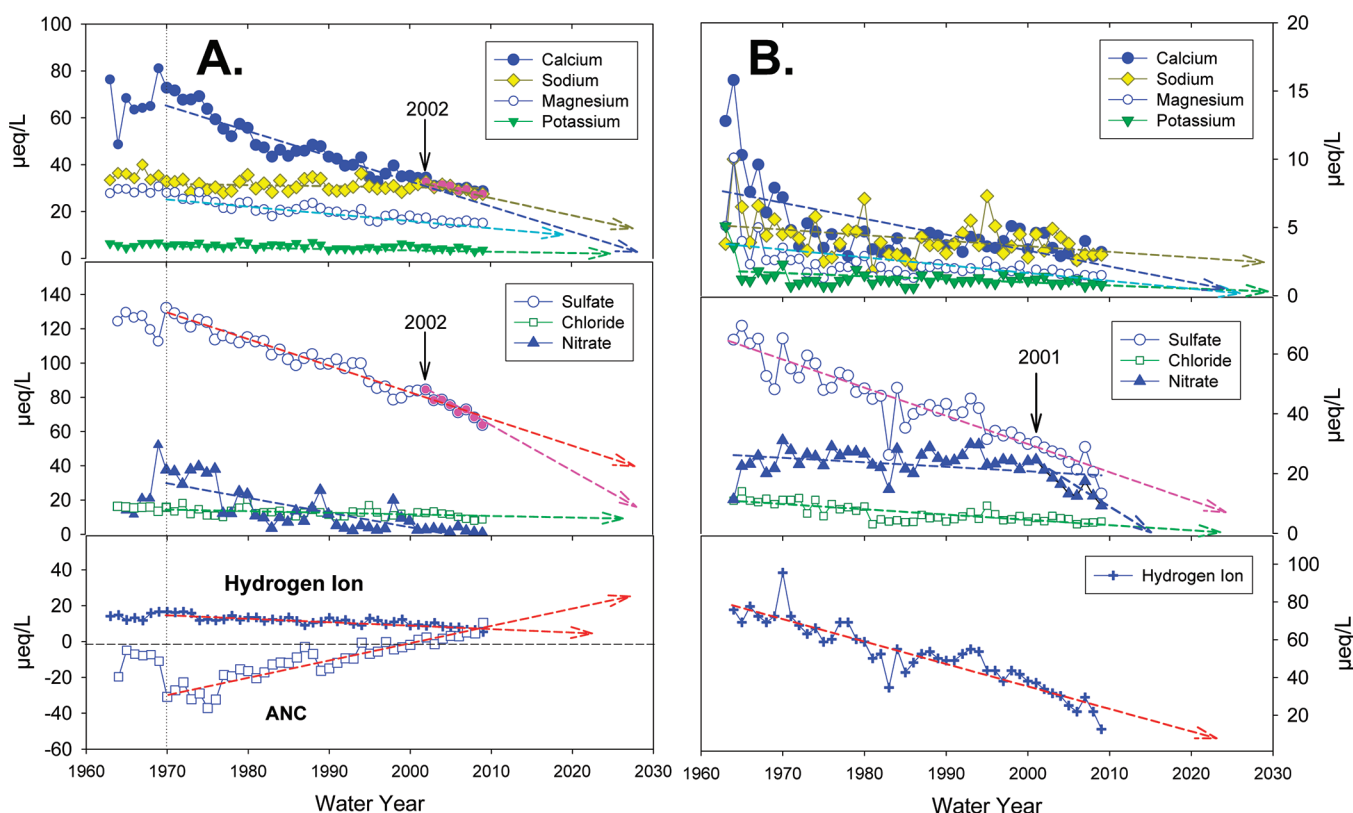
Figure 4. Long-term trends for volume-weighted average annual concentrations for calcium, sodium, magnesium, potassium, sulfate, chloride, nitrate, hydrogen ion, and acid-neutralizing capacity (ANC) (μeq/liter) in streamwater (A) of Watershed 6 of the HBEF for the period 1970 through 2009. Linear regression slopes are significant at $p < 0.001$ for all solutes except sodium, which is not significant at $p = 0.13$. Correlation coefficients are calcium: $r^2 = 0.90$; magnesium: $r^2 = 0.82$; potassium: $r^2 = 0.38$; sodium: $r^2 = 0.06$; sulfate: $r^2 = 0.94$; nitrate: $r^2 = 0.64$; chloride: $r^2 = 0.36$; hydrogen ion: $r^2 = 0.71$; and ANC: $r^2 = 0.87$. Separate linear regressions (both significant at $p < 0.001$) are shown for annual average sodium and sulfate based on the last 8 years of data: sodium: slope $= -0.721$, $r^2 = 0.82$; sulfate: slope $= -2.580$, $r^2 = 0.94$; and bulk precipitation (B) for the Hubbard Brook Experimental Forest for the entire period of record. Linear regression statistics are: calcium: $r^2 = 0.39$, $p < 0.001$; magnesium: $r^2 = 0.31$, $p < 0.001$; potassium: $r^2 = 0.16$, $p < 0.005$; sodium: $r^2 = 0.12$, $p < 0.015$; sulfate: $r^2 = 0.86$, $p < 0.001$; nitrate: $r^2 = 0.15$, $p < 0.008$; chloride: $r^2 = 0.59$, $p < 0.001$; and hydrogen ion: $r^2 = 0.84$, $p < 0.001$. Trends projected beyond 2009 are shown.
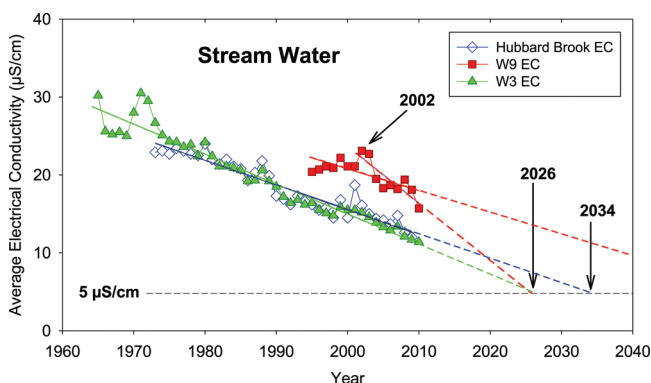
Figure 5. Long-term trends for annual, average electrical conductivity (EC) in streamwater of the main stem of Hubbard Brook (Hbk), Watersheds 3 and 9 (and 8 most recent years for W9). Slopes of all linear regressions are significant at $p < 0.001$: Hbk data: slope $= -0.314$, $r^2 = 0.94$; W3 data: slope $= -0.384$, $r^2 = 0.89$; W9 data: slope $= -0.281$, $r^2 = 0.47$; W9 2002−2009 data: slope $= -0.728$, $r^2 = 0.73$. Regression lines are projected from 2009 to calculated post acidic deposition (PAD) baseline of 5 μS/cm.

the long-term trajectory of sulfate decline in bulk precipitation at HBEF.[23]

What is most surprising, however, is the strikingly rapid rate of dilution of both precipitation and streamwater chemistry in

W6 since 1963, especially during the last two decades (Figures 2 and 3). Data presented here portend EC values approaching demineralized water (~2 μS/cm) by 2030. While extrapolation of these trends implies unrealistically low EC values in precipitation and streamwater, long-term trends have been robust and relentless ($r^2 > 0.84$). In fact, recent inputs to New England watersheds from TS Irene, provide a glimpse of a future not very different from the scenario presented here; precipitation at HBEF had an EC of 2.9 μS/cm, and W6 streamwater declined to an EC of 10.3 μS/cm during this catastrophic flooding event on 28−29 August 2011.

We assume that streamwater during PIR conditions was dominated by $Ca(HCO_3)_2$. This assumption is supported by the sediment history in nearby Mirror Lake.[24] In recent decades $CaSO_4$ has dominated W6 streamwater chemistry because of the large inputs of sulfate in acid deposition, but during the last 7 years or so, sodium has become (roughly equivalent to − on an equivalence basis − or exceeds calcium on a mass basis) the dominant cation (Figure 5; SI Table S2). The projected PAD baseline composition suggests that streamwater chemistry is now moving toward domination by $NaHCO_3$ (Figure 4A; Table 1; SI Table S2). Apparently calcium has been so depleted in soil of the HBEF from 55 years of acid deposition,[5,25] and is being replaced so slowly by weathering that it no longer has the potential to dominate, even in these dilute conditions.

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Surprisingly, these surface water systems are moving toward PAD concentrations, which are more dilute than PIR conditions were.

The long-term trends observed in W6 are not unique to this rather small watershed. Despite different drainage areas (the Hubbard Brook Valley is >3 orders of magnitude larger than W6), different chemistry, different topographic aspects and different dominant vegetation (SI Table S3), the EC, $\sum C_B$ and $\sum AA$ trends for Watersheds 3 and 9 (W3, W9), and the main Hubbard Brook in the HBEF during the last 10 years are all negative, with similar slopes and all declining toward an EC baseline of 5 μS/cm between 2026 and 2034 (Figure 5; SI Figure S1). Because the dominant driver of streamwater sulfate and nitrate is primarily inputs from the atmosphere at the HBEF,[20] temporal trends for $\sum AA$ in streamwater for W3, W9 and Hubbard Brook are not significantly different (SI Figure S1). Shorter records from elsewhere in New England, New York and Canada, for example,[26−28] also show recent, temporal declines in surface water concentrations. In contrast and as expected, surface waters from nearby, base-rich Sleepers River Watershed in Danville, VT[29] do not show the dilution response[30] measured in base-poor streamwater at the HBEF.

Redevelopment of dilute, surface waters represents a success story for Federal legislation, but presents new problems for managers. For example, if the stoichiometry of these waters were to change dramatically in the next decades, as suggested by our long-term data, it would raise serious questions about how the biota and hydrogeology of this ecosystem will function in the future, for example, ref 31. Much as highly dilute, purified water (low electrolyte concentrations) for human consumption has been associated with health problems, for example,[32] the potential impact of extreme dilution and stoichiometric changes in natural waters also cannot be ignored. Several examples are pertinent: extremely dilute surface water chemistry has been observed in areas remote from human influence, for example, ref 31. Enge and Kroglund[31] found such dilute waters in Norway to be "...detrimental to early life stages of brown trout (*Salmo trutta fario*)...". Marked decline in Ca^{2+} and ANC levels can impact the ecology of both aquatic and terrestrial ecosystems, for example, refs 17,33, and 34. Highly dilute water in alpine and subalpine lakes of the Sierra Nevada range in California are known to be sensitive to anthropogenic disturbances, such as acid rain.[35,36] Acidification or reacidification in such dilute systems and other sensitive ecosystems could be significant if controls on emissions were lessened. Extreme melting of sea ice in the Canadian Basin of the Arctic Sea can dilute surface water to the extent that food web dynamics are disrupted.[37] Finally, dilute waters require special wastewater treatment systems, for example, ref 38.

Although the effort, cost and sustained leadership required are daunting, the degree to which these aquatic ecosystems will continue to move toward such low baselines can only be ascertained by well-established, and carefully maintained long-term monitoring, for example, refs 3,39, and 40. Furthermore, monitoring chemical changes in such dilute waters without developing new technologies, including more sensitive, automated sensors will be challenging.[41]

ASSOCIATED CONTENT

S **Supporting Information**
Additional methods, tables and a figure are included. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author
*E-mail: LikensG@ecostudies.org.
Author Contributions
§Both authors contributed equally to this work.
Notes
The authors declare no competing financial interest.

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