


# A century of change: Reconstructing the biogeochemical history of Hubbard Brook

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## Abstract

Ecosystems constantly adjust to altered biogeochemical inputs, changes in vegetation and climate, and previous physical disturbances. Such disturbances create overlapping ‘biogeochemical legacies’ affecting modern nutrient mass balances. To understand how ‘legacies’ affected watershed-ecosystem (WEC) biogeochemistry during five decades of studies within the Hubbard Brook Experimental Forest (HBEF), we extended biogeochemical trends and hydrologic fluxes back to 1900 to provide an historical framework for our long-term studies. This reconstruction showed acid rain peaking at HBEF in the late 1960s-early 1970s near the beginning of the Hubbard Brook Ecosystem Study (HBES). The long-term, parabolic arc in acid inputs to HBEF generated a corresponding arc in the ionic strength of stream water, with acid inputs generating increased losses of  $H^+$  and soil base cations between 1963 and 1969 and then decreased losses after 1970. Nitrate release after disturbance is coupled with previous N-deposition and storage, biological uptake, and hydrology. Sulfur was stored in soils from decades of acid deposition but is now nearly depleted. Total exports of base cations from the soil exchange pool represent one of the largest disturbances to forest and associated aquatic ecosystems at the HBEF since the Pleistocene glaciation. Because precipitation inputs of base cations currently are extremely small, such losses can only be replaced through the slow process of mineral weathering. Thus, the chemistry of stream water is extremely dilute and likely to become even more dilute than pre-Industrial Revolution estimates. The importance of calculating chemical fluxes is clearly demonstrated in reconstruction of acid rain impacts during the pre-measurement period. The aggregate impact of acid rain on WEC exports is far larger than historical forest harvest effects, and even larger than the most severe deforestation experiment (Watershed 2) at HBEF. A century of acid rain had a calcium stripping impact equivalent to two W2 experiments involving complete deforestation and herbicide applications.

## KEYWORDS

legacies, acid deposition, watershed flux, watershed ecosystem

## 1 | INTRODUCTION

In 1963, when the Hubbard Brook Ecosystem Study (HBES) was initiated, the founders (Gene E. Likens, F. Herbert Bormann, Noye

M. Johnson, and Robert S. Pierce) were not focused on antecedent chemical conditions nor whether they had legacy effects on the ecosystems they were about to study. Their initial focus was on pioneering WEC, mass-balance relationships, although they did

recognize that landscape change and forest history were critical parts of WEC development and change (Bormann et al., 1970; Likens, 1972a; Likens & Davis, 1975; Siccama et al., 1970).

Indeed, they were struggling to start a massive research effort with limited funds and technical support, and they had little to go on regarding the biogeochemical history of the area where they were launching the study (see Likens & Davis, 1975). Nevertheless, they moved forward to develop the WEC concept in early 1960 (Bormann & Likens, 1967). The WEC allowed ecosystem scientists to take advantage of the difference between biogeochemical inputs and outputs for a well-defined catchment and to use these mass balances to make inferences about the ecosystem's inner workings (Bormann & Likens, 1967; Holmes & Likens, 2016; Likens et al., 1967; Likens et al., 1970; Likens et al., 1996; Likens et al., 1998). Ecosystems are always adjusting to altered biogeochemical inputs or changes in vegetation and climate, and recovering from one to many previous physical disturbances. It is extremely difficult to determine how these 'ecosystem memories' or 'biogeochemical legacies' affect modern, chemical input-output budgets. Today, there is increasing recognition of the impact of antecedent conditions on ecosystem dynamics, such as the degree of change from a given disturbance, as well as the lasting effects of the disturbance (e.g., Cullen, 2007; Franklin et al., 2000). Both existing and pre-existing conditions are critical determinants for understanding the current and future structure and function of ecosystems (e.g., Pickett et al., 1997).

Antecedent conditions, resulting largely from varied disturbances, provide important insights and suggest constraints, that is, what we understand today is largely the result of what occurred before. This core principle for understanding the structure and function of ecosystems holds for biogeochemical dynamics as well, although the importance has not commonly been quantified. Clearly, it is one thing to measure what *is*, and another to estimate what *was*. It is yet more difficult to estimate what *might be*.

A critical simplifying assumption of the WEC is that the ecosystem of interest is at, or near, dynamic equilibrium with internal stocks and processes equilibrated to the average fluxes of water, solutes and gases. Our discovery about the acidity of precipitation (acid rain) at Hubbard Brook Experimental Forest (HBEF) and our subsequent efforts to determine whether this acidity was anthropogenic in origin and whether sulfur and nitrogen oxide precursors to the acidity originated from fossil-fuel fired power plants in the Ohio Valley (Holmes & Likens, 2016; Likens, 1984; Likens, 2010; Likens et al., 1972; Likens & Bormann, 1974) began to make it clear that the forests of HBEF were, in fact, not at 'steady state'. We initiated long-term monitoring at the beginning of this very dynamic period (Holmes & Likens, 2016; Likens, 2010; Likens, 2013). Arguably, therefore, we may have started the HBES at a problematic time because the chemistry of precipitation and stream water was changing so markedly and rapidly. Conversely, these large changes gave clearer evidence of ecosystems responding to external drivers of many types. The success of acid rain science at HBEF in corroborating the implications of the Clean Air Act Amendments of 1970 and informing policy makers during the debate over the passage of the Clean Air Act Amendments of 1990 further

challenged steady state assumptions for our focal ecosystem. These federal policies led to substantial declines in acid inputs to HBEF (Likens, 2010; Likens, 2013; Likens et al., 2021). Ultimately, because of the implementation of these policies, the present-day precipitation chemistry in the northeastern U.S. is now approaching the presumed chemistry of pre-industrial revolution (PIR) times (Holmes & Likens, 2016; Likens, 2013; Likens & Buso, 2012).

This article is the result of our efforts to consider the aggregate impact of acid rain on the biogeochemistry at HBEF, from its onset in the 1950's to the point in the last decade at which  $H^+$  inputs returned to levels comparable to the PIR. We used statistical relationships within our measured, almost five-decades dataset, and between our data and historic time-series data from nearby monitoring locations to develop reasonable estimates of what precipitation and streamwater amount and chemistry at HBEF were likely to have been between 1900 and 1963, when our measurements began. We have good estimates of the precipitation chemistry in PIR times (Galloway et al., 1982; Likens et al., 1987). We have records of precipitation and river flow from nearby gauges that stretch back to the beginning of the 20th century. We have estimates of emissions from fossil-fuel-fired power plants upwind of the region since the early 1900's. Limited measurements of precipitation and streamwater chemistry prior to the HBES were available from the region, allowing us to examine how well our historical reconstruction fit real historic data. While we looked at whether our estimated trends were consistent with data collected prior to 1963, we made no effort to fit our estimates to these index points. Our goal in this reconstruction exercise was to use the relationships among sites and among solutes that we have observed at Hubbard Brook over multiple decades (Holmes & Likens, 2016; Likens, 2013; Likens, 2017) to make reasonable estimates of the pre-measurement biogeochemical history of this forest ecosystem. This reconstruction also allowed us to address multiple questions about the historical hydrologic and chemical concentration trends and fluxes that have occurred at the HBEF and more broadly in the northeastern U.S., and most importantly, to compare the total chemical fluxes associated with acid deposition with other disturbances at the HBEF.

## 2 | SCOPE OF THIS RECONSTRUCTION

The span of measured data included in this analysis is from 1963 through 2010. We do not include the most recent data for the following reasons:

- 1) It is not our intention here to provide an update of the most recent results from HBES. Those data are given elsewhere (e.g., Likens, 2017);
- 2) The long-term record we use (1963–2010) is robust and long enough to inspire multiple and important questions related to our reconstruction;
- 3) The 47-year period of measurement captures a time of remarkable change and reveals distinct patterns among many solutes; the recent extreme dilution in precipitation and streamwater chemistry

(Likens & Buso, 2012) may represent a new 'state change' where stoichiometric relationships are becoming much more indistinct;

4) The process by which hydrologic and chemical data are compiled and linked has changed since 2010; the potential impact of those changes has not been analysed and is beyond the scope of this effort;

5) We assume that our analysis will be used as the basis for testing past assumptions, asking new questions, and promoting the watershed ecosystem concept (WEC) approach with any new data moving forward.

### 3 | APPROACH TO RECONSTRUCTION

Building on the long biogeochemical database of measured values (1963–2010), we used statistical and stoichiometric relationships to extrapolate the hydrology and chemistry of precipitation and stream water back to 1900 (see below and Supplementary Information [SI] for details). All major ionic solutes were considered in the ion balances. The reconstructed annual chemical values were verified against historical index values and merged with the measured annual data. These reconstructed chemical concentrations were multiplied by estimated water values to provide historical deposition and export fluxes for the period from 1900 to 1963, that is, prior to the measured record.

Others have attempted to model the long-term biogeochemical dynamics at HBEF (e.g., Tominaga et al., 2010), but those approaches were significantly different, and our reconstruction includes for the first time long-term, biogeochemical fluxes (water flux times chemical concentration) via precipitation and stream water.

### 4 | METHODS AND PROCEDURES USED IN RECONSTRUCTION

The description of the Study Site and Standard Methods has been published many times and is detailed in SI 1 along with estimates of uncertainty; details and procedures for reconstruction are given in SI 2.

### 5 | GUIDELINES FOR RECONSTRUCTION

Our efforts to reconstruct historic precipitation and streamwater chemistry concentrations at HBEF for the period 1900–1963 had four critical assumptions that were used as guidelines:

1. That acid rain as a phenomenon and its ecological effects at the HBEF started in the mid-1950s (Butler et al., 1984; Cogbill et al., 1984; Cogbill & Likens, 1974; Holmes & Likens, 2016; Likens, 2010; Likens, 2013; Likens & Bormann, 1974);
2. That the relationships observed between fossil fuel emissions and precipitation chemistry during the measurement record held for the previous period;

3. That the stoichiometry and ion balances for ions in precipitation and stream solutions during the measured period were consistent with the pre-monitoring period and thus could be extrapolated to 1900;
4. That precipitation concentrations in 1900 at HBEF emulated conditions from areas of the world remote from human influences.

Using these four rules, we created operationally defined starting points in 1900 for precipitation and streamwater chemistry and progressively changed concentrations with time up to the beginning of the measured record (1963/1964). These estimated concentration values were used in combination with estimated hydrologic values to calculate chemical fluxes for the reconstructed period of 1900–1963 (see SI 1 and 2 for details on statistical analyses and calculations).

### 6 | RESULTS AND DISCUSSION

We organized our evaluation and response to the results of the biogeochemical reconstruction into five major questions. This approach provided a useful framework for dealing with this complicated material. These questions do not stand alone, but interact and interconnect both temporally and spatially. We attempted to respond to this critical feature of the reconstruction by commenting on the legacies of disturbance in Question 5.

#### 6.1 | Question 1- what is the evidence that our reconstruction estimates are reasonable?

Our understanding of pre-European settlement history of the Hubbard Brook Valley is of a relatively pristine ecosystem undergoing gradual, 'natural' development driven by climate and forest species changes. The paleoecology and chemistry of sediments collected from nearby Mirror Lake do not suggest any abrupt, massive disturbances affecting the area within the past millennia (Davis et al., 1985; Likens, 1985; Likens & LaBaugh, 2009) until the last century or so. While modest natural disruptions to the forest, for example, insect eruptions, droughts, floods, wind damage and severe frost have occurred, we assume this was a highly resilient, nutrient-retentive ecosystem that recovered quickly from such disturbances (Holmes & Likens, 2016; Likens, 2013).

Given this fundamental assumption, we estimated precipitation chemistry for the PIR period based on data collected from regions of the planet remote from human activity (Likens et al., 1987; Likens & Buso, 2012). However, for our 1900 starting point, we increased the published, initial PIR concentration values by 10% to reflect enhanced atmospheric loading from local coal and wood burning and dust from agricultural activity (see, e.g., Likens, 1972b; Likens & Bormann, 1974; also, SI 1). We then assumed that ionic strength of precipitation, while still quite dilute, would approximately double from PIR to 1900 due to these inputs (Table 1). Otherwise, our estimate of the PIR solution

**TABLE 1** Composite solutions emulating yr-1900 conditions in HBEF biogeochemical reference W6. (uncertainty for individual ions estimated at  $\pm 50\%$ ; sensu Likens & Buso, 2012)

Bulk precipitation			Stream water		
Ion	Conc <sup>a</sup> (mg/L)	Conc <sup>a</sup> ( $\mu\text{eq/L}$ )	Ion	Conc <sup>a</sup> (mg/L)	Conc <sup>a</sup> ( $\mu\text{eq/L}$ )
Calcium	0.15	7.5	Calcium	0.53	26.3
Magnesium	0.04	3.5	Magnesium	0.14	11.9
Potassium	0.06	1.5	Potassium	0.12	3.0
Sodium	0.11	5.0	Sodium	0.42	18.2
Aluminium	0.000	0.0	Aluminium	0.001	0.1
Ammonium	0.060	3.3	Ammonium	0.002	0.1
pH ( $\text{H}^+$ )	5.22	6.0	pH ( $\text{H}^+$ )	6.00	1.0
sum $\text{C}_\text{B}$	n/a	17.5	sum $\text{C}_\text{B}$	n/a	59.4
CATION Sum	n/a	26.8	CATION Sum	n/a	60.6
Sulfate	1.01	21.0	Sulfate	0.87	18.0
Nitrate	0.15	2.5	Nitrate	0.06	1.0
Chloride	0.12	3.4	Chloride	0.14	4.0
Phosphate	0.001	0.1	Phosphate	0.001	0.1
ANC	0	0.0	ANC	n/a	30.0
DOC	0.50	0.0	DOC	1.45	8.0
sum AA	n/a	23.5	sum AA	n/a	19.0
ANION sum	n/a	27.0	ANION sum	n/a	61.1
IMBALANCE	n/a	-0.2	IMBALANCE	n/a	-0.5
Calculated Conductance (Theoretical)		5.4 $\mu\text{S/cm}$	Calculated Conductance (Theoretical)		6.8 $\mu\text{S/cm}$

<sup>a</sup>Conc = concentration.

chemistry would have ignored the rapid industrialization of the region prior to 1900.

Using data from remote locations (Likens & Buso, 2012), we established a pH of 5.2 for precipitation in 1900 and a balance of cations and anions that summed to  $\sim 54 \mu\text{eq/l}$  total ionic charge, which produced a theoretical electrical conductance of  $\sim 5 \mu\text{S cm}^{-1}$  (Table 1). In addition, we made four additional assumptions for precipitation chemistry in 1900, justified by our knowledge of 'clean' precipitation samples over the past 50+ years at HBEF: (1)  $\text{Al}^{n+}$  concentration was fixed at zero; (2) acid neutralizing capacity (ANC) was fixed at zero because the pH of precipitation was below the null point (pH 5.3) for positive ANC in a dilute solution; (3) the DOC charge was set at zero because DOC in precipitation is generally not a charged ionic species, as it can be in stream water; (4)  $\text{PO}_4^{3-}$  concentration was fixed at  $0.1 \mu\text{eq/l}$  to reflect samples not contaminated by bird droppings, insects, or plant debris and assumed not to have changed significantly from PIR to the measurement period (see Buso et al., 2000).

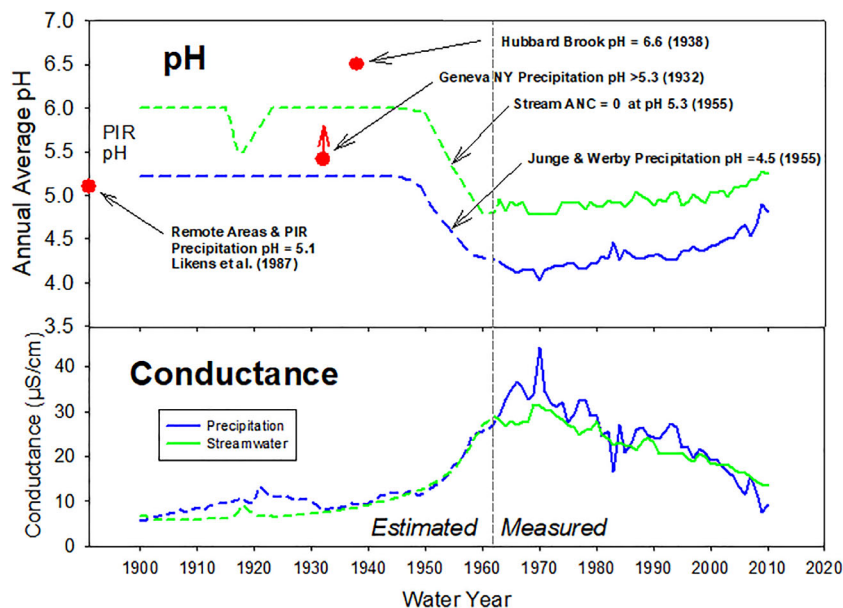
Extension of the time-series pH data for precipitation from pH 5.2 in 1900 was based on the assumption of a stable pH for several decades and then a curvilinear pH decline, starting about 1945, and reaching the lowest pH of 4.0 around 1960 (Figure 1). This synthetic equation (Table S5 in SI2) matches a typical acid titration curve for a dilute solution. Our reasoning for creating this pH trend, with a long delay and then a rapid decline, is based on three logical concepts: (1) gradually increasing atmospheric sulfur concentrations starting in

the late 1800s, primarily from coal burning; but (2) neutralized by concentrations of base cations ( $\text{C}_\text{B}$ ),  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ , and  $\text{Na}^+$  from fly ash and agricultural dust; followed by (3) simultaneous reduction of  $\text{C}_\text{B}$  and increasing strong acid anions ( $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ ) in precipitation by the middle of the 20th century. These are reasonable assumptions for how acid rain began in eastern N. America (Butler et al., 1984; Cogbill et al., 1984; Likens & Bormann, 1974).

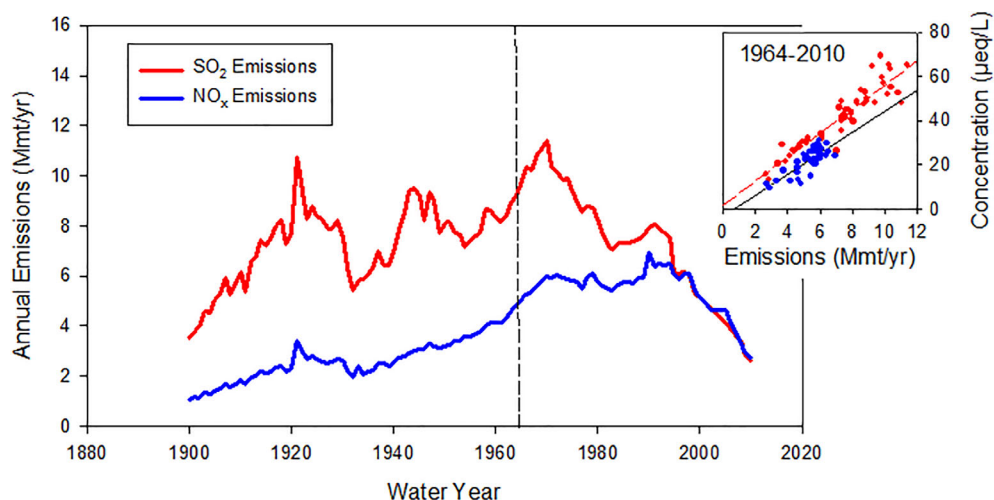
Once the critical trend in pH was established, the next step was to estimate the starting concentrations for other solutes in 1900. We employed the current measured relationships between the major solutes,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ , and emissions of sulfur dioxide ( $\text{SO}_2$ ) and nitrous oxides ( $\text{NO}_x$ ) from fossil-fuel fired power plants upwind of the region (Figure 2) to construct a long-term trend for precipitation  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  concentration (Figures 3 and 4). The remaining charge imbalance in precipitation was assumed to be provided from  $\text{C}_\text{B}$ . Starting with  $\text{Ca}^{2+}$  concentrations in 1900, and constrained by charge balance, theoretical conductance, and pH (Likens & Buso, 2012), the individual hindcasted  $\text{C}_\text{B}$  values were apportioned in accord with micro-equivalent ratios derived from the period 1964 to 1970 (see Methods). We assume that the  $\text{C}_\text{B}$  ratios have remained similar since 1900 because the stoichiometry of their main sources (weathering and precipitation) has not changed appreciatively.

From this initial framework of chemical relationships, the full array of estimated ions was arranged in an interactive spreadsheet format (see SI2). This array was designed to be adjusted to balance the charge

**FIGURE 1** Annual average precipitation and streamwater pH and electrical conductance values for Watershed 6 of the Hubbard Brook Experimental Forest for water years from 1900 to 2010. Data from 1900 to 1963 were estimated; data from 1964 to 2010 were measured. Some historical pH values are shown for reference. PIR = preindustrial revolution



**FIGURE 2** Annual emissions from 1900 to 2010 of sulfur dioxide ( $\text{SO}_2$ ) and nitrogen oxides ( $\text{NO}_x$ ) for the HBEF, 24-h, back trajectory source area. Inset: The relation between annual  $\text{SO}_2$  emissions and  $\text{SO}_4^{2-}$  concentration ( $r^2 = 0.85$ ) and annual  $\text{NO}_x$  emissions and  $\text{NO}_3^-$  concentration ( $r^2 = 0.57$ ) in bulk precipitation during 1964–2010 for HBEF



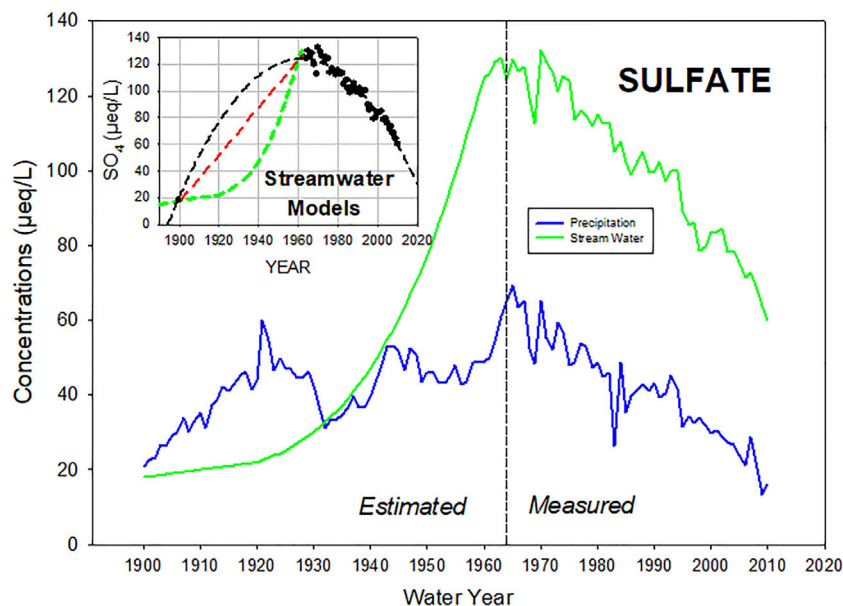
on an annual basis starting in 1901 and ending in 1962 (or 1963 for  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{Cl}^-$ ) using current stoichiometry from our measured, long-term precipitation chemistry record. The estimated concentration trends were joined to the period of record. In practice, the logical assumptions made to provide starting points and the correlative relationships among solutes made this process relatively straightforward and eliminated unexplained extreme values. As a result, the reconstructed trends resembled the gradual pattern we have observed in our 50+ years of ion-balance measurements (Figure S1 in SI 2).

As a validation of the above processes, a limited number of independent data points from precipitation collections in the region were used to evaluate the robustness of our estimated trends. We are fortunate to have a few historical index points with which to anchor such an exercise. Our trends were not ‘tuned’ to fit these index data; instead, they are presented to test the plausibility of our hindcasted estimates. For example, pH measurements of precipitation made in the region in 1932 (Likens, 1972b) and 1955 (Junge & Werby, 1958)

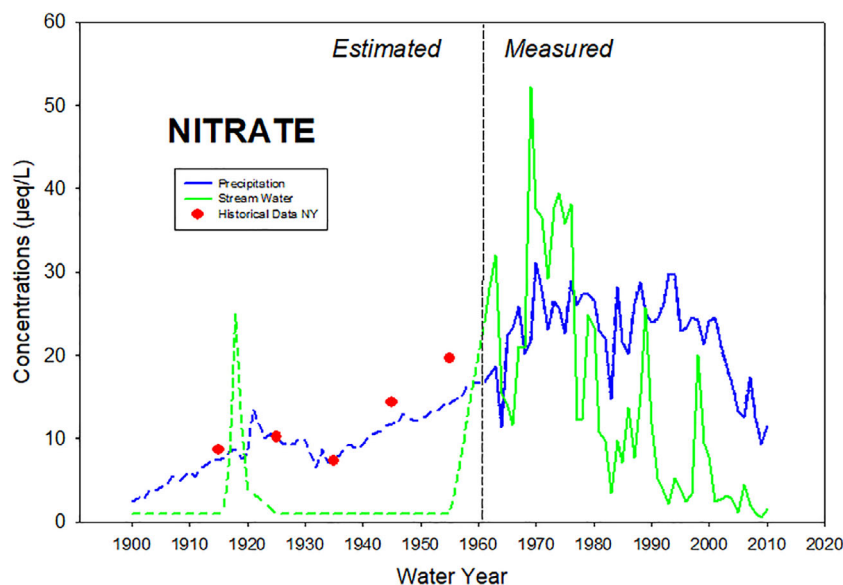
were used as benchmarks to corroborate the reconstructed pattern in pH (Figure 1). Also, the hypothesized pattern in calculated concentrations for  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  (data not shown on graph) compared favourably with those measured in precipitation by Collison and Mensching in central NY in 1929 (Likens, 1972a) (Figure 4).

Estimating streamwater chemistry for the year 1900 and projecting it forward in time required more assumptions than for precipitation. We started with a pH of 6.0, and a correspondingly minimal ANC value ( $\sim 30 \mu\text{eq/l}$ ) and created a balanced solute mixture for biogeochemical reference W6, a 2nd order stream (Table 1). The trajectory of measured pH increase and relentless solute dilution currently found in W6 point toward a return to a pH value of  $\sim 6.0$ , an ANC of  $< 30 \mu\text{eq/l}$  and an EC below  $\sim 7 \mu\text{S cm}^{-1}$  in the future (Likens & Buso, 2012). We constructed the remaining cation and anion starting arrays for stream water within these constraints.

Streamwater  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  concentrations approximately matched values for estimated precipitation concentrations in 1900,



**FIGURE 3** Annual sulfate ( $\text{SO}_4^{2-}$ ) concentrations in precipitation and stream water for Watershed 6 of the Hubbard Brook Experimental Forest for water years from 1900 to 2010. The inset shows three possible models to characterize trends in stream water during the period 1900–1963. Precipitation hindcasts were based on current concentration and emissions data (see text and Supplementary information)



**FIGURE 4** Annual nitrate concentrations in precipitation and stream water for Watershed 6 of the Hubbard Brook Experimental Forest for the water years from 1900 to 2010. The peak in streamwater concentrations during 1915–1920 is related to forest harvest during this period; peaks in stream water in 1990 and 1999 are related to soil frost and an ice storm, respectively. Precipitation hindcasts were based on current concentration and emissions data (see text and Supplementary information). Some historical precipitation values (red dots) are shown for reference, but were not used to develop the hindcast model: 1915, Ithaca, NY (from Wilson, 1926); 1925, average for Ithaca and Geneva, NY (from Collison & Mensching, 1932, Wilson, 1926); 1935 and 1945, Ithaca, NY (from Leland, 1952); 1955, average for Ithaca and Aurora, NY (from Junge & Werby, 1958)

rather than being more concentrated by evapotranspiration (ET) water losses. The sulfate values are justified by competing processes: (1) atmospheric sulfate inputs were retained initially by organic soils, but (2) balanced by minor geologic release (weathering of sulfides in local till) at the same time, resulting in similar concentrations between input and output (Likens, 2013; Likens et al., 2002; Mitchell et al., 2001). Chloride sources are rare in local geologic substrate, but atmospheric chloride was retained initially by organic soils, so that input and output concentrations were also similar despite the influence of ET (Lovett et al., 2005). These lags in solute throughput are detected later in the long-term mass balances for sulfate and chloride.

Nitrate,  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$ , on the other hand were assumed to be highly retained within the ecosystem and thus minimized in stream water. At pH 6 the aluminium contribution was also minimized. A

DOC charge of 8  $\mu\text{eq/l}$  was used to balance the remaining charge discrepancy in the array. This charge corresponds to 1.45 mg/L on a mass basis (6  $\mu\text{eq/mg C}$ ; see Buso et al., 2000), which is a typical DOC concentration in clear-water, mildly acidic W6 under most flow conditions (Buso et al., 2000).

The extension of streamwater chemistry from 1900 to 1963 was similar to the projection of precipitation chemistry. We assumed no consistent decline in streamwater pH until the 1950s. In this reconstruction, the pH of stream water was decreased to 5.5 in the years 1917 and 1918 to reflect minor amounts of nitrification due to forest cutting in 1910–1919, but this excursion was brief (see Question 5 below). In 1950, the ‘titration’ of streamwater pH began, starting at pH 6 and reaching the lowest pH of  $\sim 4.3$  about 1969–1970 (Figure 1). The slow decline in estimated ANC started earlier than the plunge in pH, because it was tied to the gradual rise in the imbalance

between the sum of  $C_B$  and  $SO_4^{2-}$  plus  $NO_3^-$ . By 1950, the ANC declined quickly following the synthetic pH data curve we created. These scenarios are supported by investigations of surface water pH and ANC decline in the northeastern U.S. (Likens et al., 1972).

Next, streamwater  $SO_4^{2-}$  concentrations were estimated in accord with the following assumption: while the deposition of S from fossil fuel combustion and gradual regional air pollution ramped up after 1900 (Figure 2); a lagged response occurred in streamwater  $SO_4^{2-}$  concentrations. Given that declines in streamwater pH and ANC were not generally detected prior to the 1950s, a delay in the presence of appreciable streamwater  $SO_4^{2-}$  concentrations is reasonable. A 2nd-order polynomial curve was created to emulate the lagged stream response for  $SO_4^{2-}$  concentrations using a curve-fitting program (Equation (S16) in SI 2), which connected the starting  $SO_4^{2-}$  concentration in 1900 (Table 1) to the first measured values in 1964 (Figure 3).

Nitrate was assumed to be near detection limit in stream water starting in 1900 (Table 1), aside from a small spike after extensive forest cutting in the Hubbard Brook Valley during 1910–1920 (see above and Questions 2 and 5 below). Nitrate concentrations were increased linearly from near detection in about 1955 to the first-measured data in 1964 in parallel with a rapid decline in streamwater pH.

Annual  $Cl^-$  concentrations were hindcast using a linear regression equation derived from measured streamwater  $SO_4^{2-}$  and  $Cl^-$  concentrations in W6 (Equation (S17) in SI 2).

Streamwater  $NH_4^+$  and  $PO_4^{3-}$  were set at near detection limit and held invariant since 1900 (Table 1), assuming biological uptake has always strongly controlled these solute concentrations, as it does today (Bernhardt et al., 2003; Likens, 2013). Total  $C_B$  in stream water from 1900 to 1963 were calculated from the extraordinarily strong stoichiometric relationship of  $C_B$  with the sum of  $SO_4^{2-}$  and  $NO_3^-$  (acid anions: AA) in W6 for the period of watershed ‘recovery’ from acidification spanning the years 1970 to 2010. Unlike  $C_B$ , aluminium was not a major contributor to the ion balance of stream water until pH declined in the 1950s. Streamwater total aluminium was fixed at 0.1  $\mu eq/L$  from 1900 to 1950 based on streamwater pH being greater than 5.8 for that period. After 1950, the  $Al^{n+}$  concentration was estimated using a linear extension from 0.1  $\mu eq/L$  to the first measured  $Al^{n+}$  values in 1964 at pH 4.9. In this approach, the  $Al^{n+}$  concentration parallels the streamwater titration curve for declining pH and rising  $NO_3^-$  values during the same time. Aluminium was not measured from 1969 to 1976, so  $Al^{n+}$  values were inserted to match the missing cation in the ion balance (Buso et al., 2000). Measured total aluminium values in mg/L were converted to  $\mu eq/L$  assuming a +3 valence state (Buso et al., 2000). This is a simplifying assumption given that much of the measured Al is complexed with DOC and may have led us to underestimate total Al, or to over-attribute positive charges to Al during this decade. While this represents an important caveat to any conclusions about Al toxicity during this period, the small mass and charge of Al relative to major solutes means this assumption has very limited effects on our conclusions about major ion concentration and mass balance. Despite widespread reports linking declining freshwater DOC concentrations to acidification and rising DOC concentrations in

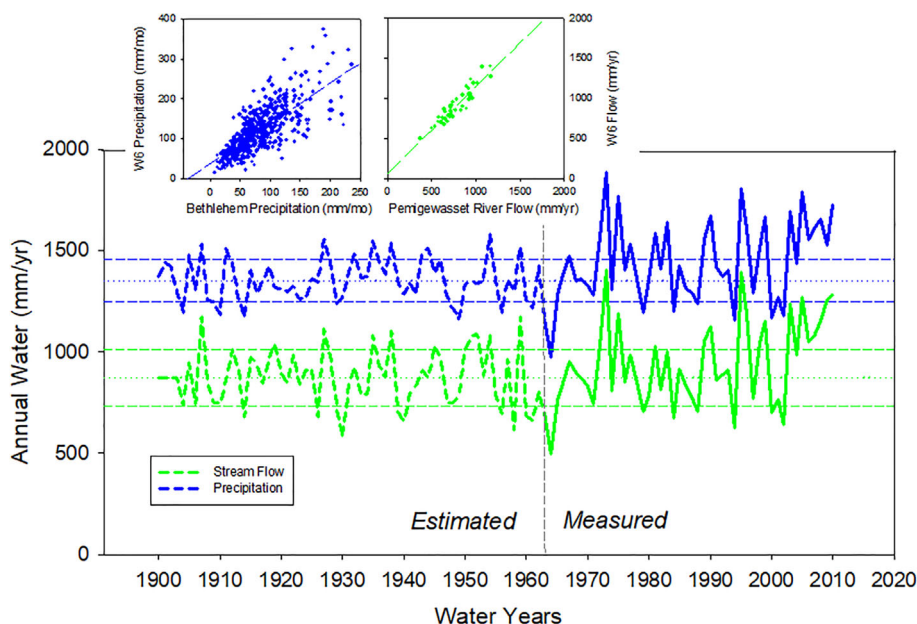
regions recovering from acid rain (de Wit et al., 2016; SanClements et al., 2018), we were unable to detect any systematic change in DOC concentrations in stream water over the 47 year record at HBEF (Likens, 2013). Thus, we left the DOC concentration at 8  $\mu eq/L$  for the period 1900 to 1964 (see above).

Using the above approach, an interactive spreadsheet, mirroring that for precipitation chemistry (see SI 2), was constructed to extend the annual streamwater chemical array from 1900 to 1964 (Figure S1 in SI). Similar to the annual precipitation array, the multiple assumptions, processes, relationships and starting conditions made the results simple and straightforward, essentially eliminating extreme values in the estimated annual streamwater data.

Unfortunately, benchmark corroborative data for streams in NH are scarce. Hoover (1938) measured a pH of 6.6 in Hubbard Brook near the eastern opening of the Valley on 27 August 1938 (Figure 1). Currently, headwater streams have a pH of 1.0 to 0.5 pH units lower than the mouth of Hubbard Brook, so the choice to use pH 6.0 for W6 prior to acidification appears reasonable.

The last step in creating the database for this reconstruction was to calculate annual export and import values for 1900–1964 from our estimated annual concentrations in precipitation and stream water. Because mass balances are critical in the WEC approach, we reconstructed them as well. Much of the unique value of the HBES has been in the development of mass balances for the major solutes derived from the measurement of both water and chemical concentrations leading to calculation of flux based on those data (e.g., Likens, 2013). For example, acid rain, as a serious environmental problem, was not clearly identified until acidic inputs, both cations and anions, could be quantified and compared against the base-poor mass available to neutralize it (e.g., Likens, 2013). In fact, our work at HBEF demonstrates that ecosystem processes leading to mass balances include temporal lags, in which internal cycling and storage, and external hydrologic functions, de-synchronize the inputs and outputs depending on the element (Likens, 2013). For example, major research efforts at HBEF on chloride (Lovett et al., 2005) and sulfur (Likens et al., 2002) demonstrated the need to quantify inputs well in advance of the measured chemical outputs to explain the mass balance of these elements (see Question 2).

There are no historic records of nutrient flux for HBEF or surrounding areas. However, we are fortunate that nearby hydrologic stations provided long-term historic precipitation and streamwater data that could be used to estimate the HBEF precipitation and streamflow volumes prior to 1963 (Figure 5). By application of the reconstructed concentrations, these reconstructed hydrologic data were used to extend the watershed mass balances (see SI 1). The NOAA site chosen in Bethlehem NH was drier than HBEF, but the other New England sites had more impact from large, coastal storms. The estimated annual precipitation volumes exhibited patterns in wet and dry years, that corresponded to documented droughts and hurricanes (Ludlum, 1976), and no unexplained extreme values were created (Figure 5). In the same way, the estimated flow data for W6 were strikingly similar in pattern to the estimated precipitation data, with corresponding, and historically documented, wet and dry years and no values that could not be supported by the independently



**FIGURE 5** Annual estimated and measured precipitation and streamflow for Watershed 6 of the Hubbard Brook Experimental Forest for water years from 1900 to 2010. Values from 1900 to 1963 were estimated from nearby locations with long-term records (see text and Supplementary information) and values after 1963 were measured. Monthly precipitation regression with Bethlehem, NH has  $r^2$  of 0.55 and annual flow regression with Pemigewasset River has  $r^2$  of 0.86. Dashed horizontal lines show  $\pm 1$  SD of the mean dotted line)

derived precipitation data (Figure 5). On an annual, water year basis, the wettest (1973–74) and driest (1964–65) years both occurred during the HBES measurement period. It is generally wetter now than it was in the past at the HBEF - a long-term climate change signal - and interannual variability in both precipitation and streamflow appears to have increased (Figure 5). As long as the statistically strong relationship between the Pemigewasset River and the HBEF watersheds (see SI 2) did not fundamentally shift at the point our record was initiated, this conclusion is robust. This increased flux of water further exacerbates the developing dilution problem at HBEF (Likens & Buso, 2012 and below).

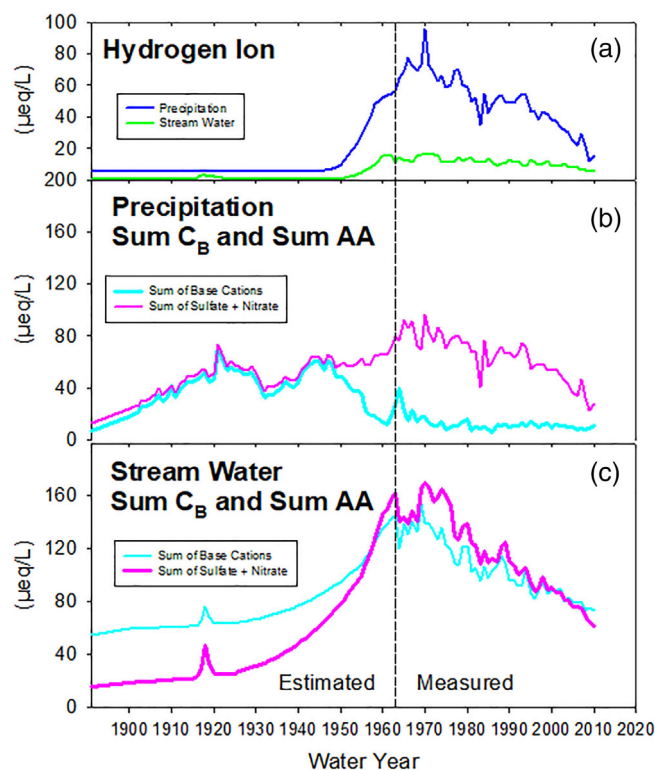
To estimate total, annual (water year) precipitation input and streamwater output fluxes for all solutes from 1900 to 1963 (or 1964 depending on the solute), we multiplied our estimated pre-monitoring annual chemical concentrations by estimated annual precipitation and streamflow amounts to create annual estimates of net hydrologic flux. This is a simplified version of the standard procedure for calculating flux at HBEF because measured annual (water year) input and export fluxes at HBEF are calculated on volume-weighted, weekly samples (see SI 1 and Likens, 2013).

In summary, we contend that the chemistry of precipitation and streamwater in 1900 was comparatively free of pollution impacts and local forest disturbances. Recent measurements of increasingly dilute conditions in precipitation and stream water (Likens & Buso, 2012) provide strong evidence for this argument. The correlation between current concentrations of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  in precipitation and regional  $\text{SO}_2$  and  $\text{NO}_x$  emissions provided convincing evidence that our hindcasts of concentrations of these key solutes are justified (Figure 2). No major solute was ignored in this reconstruction. As a final check on this empirical approach, concentration data were used in conjunction with the historical water data to calculate annual fluxes. These annual flux values were consistent within the range in our measured hydrologic fluxes and estimates of element pools at HBEF (Likens, 2013, and see below).

## 6.2 | Question 2- how do the measured and historical biogeochemical trends at HBEF relate to and support each other?

Based on long-term measurements, the peak of acid rain at HBEF occurred between 1965 and 1970 (Figure 6). This pattern effectively constrains the scenarios we invoke for our reconstructed, long-term chemical trends. First, atmospheric deposition was certainly not *more* acidic prior to our research initiative. Second, there is no justification for an abrupt increase in acidic deposition or the acidity of streams in our region just prior to the measurement period. Finally, there is no evidence for a drawn-out, decades-long period of acutely low pH in precipitation and stream water prior to about 1950.

The most logical scenario, based on our measured data and the few benchmark data, is a gradually rising arc of acidity and overall solute increases that culminated in the measured record in the mid-1960s (Figure 6). The close correlation between pH and EC throughout our measurement record support our conclusion (Figure 1) that pre-measurement trends in EC in precipitation and stream water should also be closely correlated with pH. The neutralization and dilution of precipitation and stream water measured since 1970 were gradual (Likens, 2013; Likens & Buso, 2012) reflecting the reductions in acidic deposition since about 1970. If the ecosystem stoichiometry were reasonably consistent, the incremental increase in estimated acidity and EC prior to 1970 should mirror the measured pattern (Figure 3). Concentrations of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  in precipitation prior to the measurement period were derived from estimated emissions of  $\text{SO}_2$  and  $\text{NO}_x$  and the relationship of those emissions to measured concentrations today (Figure 2, see Table S5 SI 2). The  $\text{SO}_2$  emissions peaked and began declining around 1970 (Figure 2), in correspondence with the decline in precipitation  $\text{SO}_4^{2-}$  at HBEF (Figure 3). It remains unanswered as to why the measured  $\text{SO}_4^{2-}$  concentration maximum occurred from 1965 to 1970, prior to the 1970 peak in



**FIGURE 6** Estimated and measured  $H^+$  in precipitation and stream water, sum of base cations ( $C_B$ ) and sum of acid anions (sulfate + nitrate, AA) in precipitation or stream water for Watershed 6 of the Hubbard Brook Experimental Forest for water years from 1900 to 2010 (see text and Supplementary information)

emissions and the 1970 CAA (Figure 2). One answer may simply lie in extreme precipitation variability, driven by the severe drought of the mid-1960s, affecting the deposition rate (Figure 5).

The decision to use a concave logarithmic curve to describe streamwater  $SO_4^{2-}$  concentrations prior to the period of measurement is a critical interpretation (Figure 3). A linear or convex expression of streamwater  $SO_4^{2-}$  trends would have required either (1) much higher  $H^+$  concentrations (lower pH), or (2) the release of more  $C_B$  to balance the  $SO_4^{2-}$  over time. Neither of these patterns is supported by the history of gradually increasing acid rain in our reconstruction. First, lower streamwater pHs at an earlier date, say shortly after 1900, are not supported by observations in the region. Second, because the difference between the  $C_B$  and AA at a pH 5.2 or above is essentially equal to ANC; maintaining a positive ANC under higher  $SO_4^{2-}$  concentrations would have required unjustifiably higher  $C_B$  concentrations.

Estimated  $NO_3^-$  concentrations in precipitation increased gradually in the 1950s in accord with emissions, and then  $NO_x$  emissions levelled off from 1970 until about 1990 after which emissions have declined quickly and steadily for the past 20 years (Figure 2). The measured precipitation  $NO_3^-$  concentrations, though quite variable from year to year, do not drop systematically until about 1993 (Figure 4). By 2010, precipitation  $NO_3^-$  concentrations were reduced to 1940s levels (Figure 4), but the source of the  $NO_3^-$  today may not be the same as it was in the 1940s (see Likens et al., 2021 for brief

review of legislation affecting emissions). Nitrate in precipitation has grown to about 42% of the charge for AA in precipitation by 2010, versus 58% for  $SO_4^{2-}$ . This is a radical change from the 1940s, when  $NO_3^-$  was only 10–15% of the AA charge, and  $SO_4^{2-}$  dominated atmospheric deposition (Likens, 2013).

Our reconstruction suggests that streamwater  $NO_3^-$  rose very rapidly after the stream pH began declining in the mid-1950s (Figure 4), in conjunction with dissolved aluminium, which also should have responded to plummeting pH at that time (Figure S1 in SI). Nitrate was not a dominant ion in stream water until the pH was lowered by acid rain in the 1950s. It was at this time that measurements of forest biomass accumulation at HBEF revealed an unexpected slowing in forest growth - a phenomenon that has been attributed to a combination of acidified soils, aluminium inhibition, and nitrogen ‘saturation’ (Aber et al., 2002; Whittaker et al., 1974). Measured streamwater  $NO_3^-$  was high and quite variable during 1965 through 1980. The inability of the ecosystem to retain  $NO_3^-$  may have come after the initial loss of available  $C_B$  from the soil exchange pool bathed in sulfuric acid from the atmosphere (Likens et al., 2002). The extreme variability in  $NO_3^-$  concentrations also may have been driven by periods of drought and re-wetting (Bernal et al., 2012). Nitrate declined to a low point in 1983, but a sequence of disturbances followed: severe soil frost in 1990 and an ice storm (extensive forest canopy damage) in 1998 (Figure 4; Figure S5 in SI) (Houlton et al., 2003). Both reactions demonstrate the sensitivity of these watersheds to natural disturbance.

Finally, in our reconstruction, a brief peak in streamwater  $NO_3^-$  of about 25  $\mu\text{eq/l}$  was inserted in 1918 to account for the increased nitrification (Figure 4) we would expect to have occurred during the period of extensive forest harvest between 1910 and 1920. In this case, the  $NO_3^-$  was largely balanced by a decrease in ANC, and small increase in  $H^+$ , as the pH was still above 5.5. This cutting disturbance was more ‘gentle’ than current harvests, as it was selective, occurred over several years and was done with horses and sleds during the winter (Bormann & Likens, 1979). Further, the harvest was conducted prior to the presence of acidic deposition, when stream ANC was still positive (See Question 5).

Putting all these estimated and measured trends together and combining the solutes to sum of  $C_B$  and AA for precipitation and stream water, provides a composite view of the ‘history’ of acid rain impacts at HBEF (Figure 6). The sum of  $C_B$  and AA essentially were balanced in precipitation until the 1940s (Figure S1 in SI). The  $C_B$  input was increased via agricultural dust and soot particles emitted to the atmosphere from 1900 through the 1960s (Likens et al., 2021; Likens & Bormann, 1974). The  $C_B$  concentrations in precipitation were reduced by ‘cleaner’ air after the 1970s due to smokestack scrubbing of particles (e.g., Likens, 1984). Then  $H^+$  ion soared in precipitation as the  $C_B$  declined and AA increased (Figure 6).

The  $H^+$  increase in stream water lagged a few years behind that in precipitation, due to neutralization in watershed soils. The difference between streamwater  $C_B$  and AA concentrations, viewed operationally as +ANC, slowly diminished as streamwater ANC was titrated, essentially by sulfuric acid, until the AA exceeded the sum of

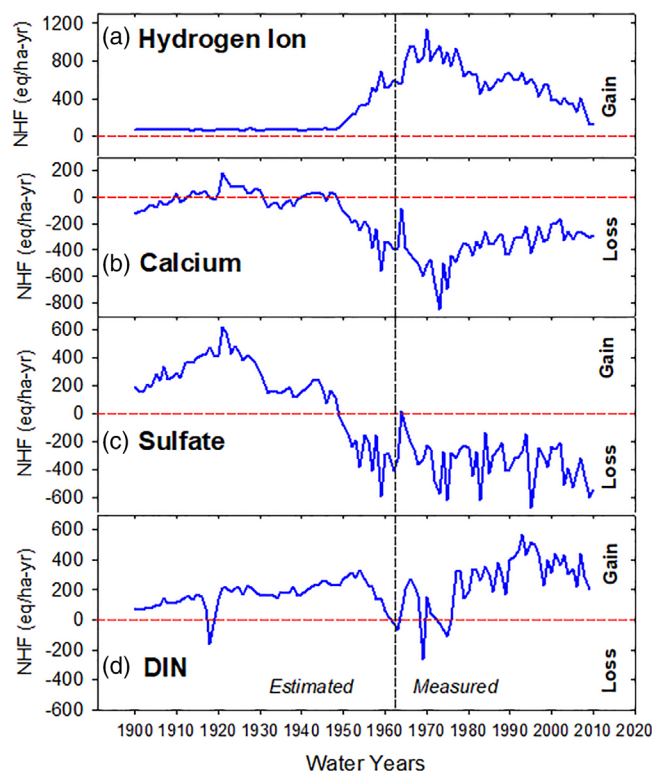
$C_B$  around 1955, and the ANC declined to zero. The brief up-tick in  $C_B$  around 1964 is likely because of dust collected during the severe drought of 1963–64.

Between 1964 and 1970, the precipitation  $C_B$  declined further and concentrations have since remained low and largely invariant (Figure 6(b)). This decline in  $C_B$  has been accompanied by a more gradual decline in  $H^+$  and AA (Figure 6), collectively resulting in increasingly dilute precipitation over time. By 2010, the specific conductance of precipitation had declined to less than  $10 \mu S \text{ cm}^{-1}$  (Figure 1). Other than elevated  $\text{NO}_3^-$ , the composition of precipitation in the last decade of monitoring is now very similar to our estimate of precipitation solution chemistry for 1900 (Likens & Buso, 2012). Streamwater  $C_B$  began to exceed the AA around 2000, providing positive acid neutralizing capacity (ANC) for the first time in the HBES record. Our historical reconstruction estimates that streamwater ANC had been positive until  $\sim 1955$  (see Question 4).

In addition to reconstructing and comparing concentrations, we developed an historical solute flux database for HBEF. The balance between hydrologic inputs (precipitation) and outputs (streamflow) is referred to as Net Hydrologic Flux (NHF, Likens, 2013). The total NHF for  $H^+$ ,  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$ , and dissolved inorganic nitrogen (DIN) was compiled for each period of reconstruction and measurement (Table 2), and expressed as annual rates for the entire 110 years (Figure 7). The annual NHF trends quantify changes in ecosystem mass balances over time and show the impact of temporal lags on the export of solutes during the measured period, 1963–2010. The long lag times between changing inputs and changing outputs effectively demonstrate the difficulty of interpreting mass balances based on only short periods of measurement.

For example, our historical estimate of a logarithmic curve for streamwater  $\text{SO}_4^{2-}$  concentrations before 1963 (Figure 3) accounts for the temporal delay between sulfur deposition and acidic stream water. It also assumes that fossil fuel-derived  $\text{SO}_4^{2-}$  was progressively accumulated in soils for about 60 years and has been slowly released from adsorption sites associated with soil organic matter throughout subsequent decades (Alewell et al., 1999; Likens et al., 2002; Mitchell

et al., 2001). Between 2005 and 2010 average annual inputs of S in wet deposition were less than  $4 \text{ kg ha yr}^{-1}$  while exports were  $> 30 \text{ kg ha yr}^{-1}$ . Dry deposition of S may add 0.5–2.5 additional  $\text{kg S ha yr}^{-1}$  (Likens et al., 2002; Mitchell & Likens, 2011). This difference in inputs vs. exports can only be explained by a temporal subsidy, with S deposited in an earlier era and accumulated in soil pools (most recently estimated at  $\sim 1700 \text{ kg ha}^{-1}$ ; Likens, 2013) being



**FIGURE 7** Net hydrologic flux (NHF = precipitation input minus streamwater output in  $\text{eq/ha yr}^{-1}$ ) for hydrogen ion (a), calcium (b), sulfate (c) and dissolved inorganic nitrogen (d) for Watershed 6 of the Hubbard Brook Experimental Forest during 1900–2010 (see Supplementary information). Gain or loss in the NHF is shown

	$H^+$	Ca	Na	$\text{SO}_4$	Cl	DIN
1900–1962 (K $\text{eq/ha}$ ) <sup>a</sup>						
Precipitation Inputs	9.9	14.9	9.9	42.4	6.8	15.8
Streamwater Outputs	1.3	19.0	13.2	26.6	3.9	2.2
Net Hydrologic Flux <sup>a</sup>	8.6	−4.1	−3.3	15.8	2.9	13.6
1963–2010 (K $\text{eq/ha}$ )						
Precipitation inputs	34.4	3.2	2.9	34.3	5.5	27.0
Streamwater Outputs	5.1	21.0	13.9	43.8	5.6	6.5
Net Hydrologic Flux <sup>a</sup>	29.3	−17.8	−11.1	−9.5	0.0	20.5
1900–2010 (K $\text{eq/ha}$ )						
Precipitation inputs	44.3	18.1	12.8	76.7	12.4	42.9
Streamwater Outputs	6.4	40.1	27.1	70.5	9.5	8.7
Net Hydrologic Flux <sup>a</sup>	37.9	−21.9	−14.3	6.3	2.9	34.2

<sup>a</sup> $\text{SO}_4$ , Cl and DIN precipitation totals increased by 20% to account for dry deposition (see Likens, 2013).

**TABLE 2** Cumulative precipitation inputs and streamwater outputs for reference Watershed 6 of the Hubbard Brook Experimental Forest during 1900–1962, 1963–2010 and 1900–2010

exported in modern stream water. Since 1963, annual  $\text{SO}_4^{2-}$  exports in stream water have been higher than annual  $\text{SO}_4^{2-}$  inputs via precipitation (NHF is negative: Table 2). The overall sum of NHF for  $\text{SO}_4^{2-}$  was essentially the same during both periods, resulting in near balance over the entire 110-year period (Figure 7 and Table 2). Had we chosen to describe streamwater  $\text{SO}_4^{2-}$  concentrations with a linear or convex-parabolic function, there would not be enough previous NHF gains to balance the current NHF losses. Essentially, such a solution would require an additional source of sulfur at HBEF. A similar trend has been documented for chloride ( $\text{Cl}^-$ ) in HBEF ecosystems (data not shown). Stream exports of  $\text{Cl}^-$  exceeding atmospheric inputs throughout much of the HBES record, a finding which led Lovett et al. (2005) to conclude that previous, adsorbed  $\text{Cl}^-$  inputs had to be supporting current, measured outputs.

The long-term NHF pattern for other critical solutes also makes sense in this context. As expected, the NHF shows neutralization (NHF gain) of  $\text{H}^+$  throughout the entire record, but the rate of neutralization must have increased rapidly as acid rain ramped up in the 1950s (Figure 7(a)). When precipitation  $\text{Ca}^{2+}$  declined and could no longer buffer the incoming  $\text{H}^+$ , the  $\text{Ca}^{2+}$  NHF swung from near balance to high on-going losses to match the acidity (Figure 7(b)). The rate of expected NHF gains for DIN was interrupted in the late 1960s, when the watershed released DIN (primarily  $\text{NO}_3^-$ ) in 'pulses' corresponding to variations in  $\text{Ca}^{2+}$  and  $\text{H}^+$  NHF, and perhaps aluminum (Figure 7(d)). The impact of logging around 1920 can be visualized in the brief excursion of NHF of DIN from gains to losses. Note that in our reconstruction, this DIN loss is not accompanied by a large pH decline -the estimated  $\text{H}^+$  increase at pH 6 was simply too small to alter the NHF of  $\text{H}^+$ , and the abundant ANC buffered the  $\text{H}^+$  produced by nitrification. In the measured period of NHF, 1963–2010, the continued losses of  $\text{Ca}^{2+}$  are to greater degree balanced by continued losses of  $\text{SO}_4^{2-}$ , rather than to the necessary neutralization of  $\text{H}^+$  (Figure 7). This conclusion is further supported by the recovery of pH to PIR levels in these streams (Figure 1).

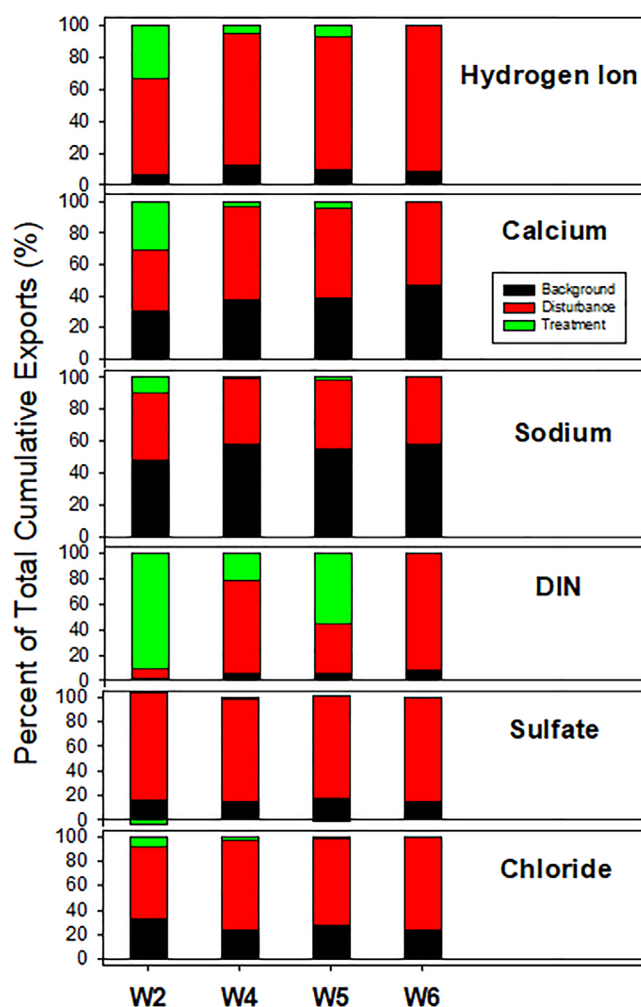
Each step of this reconstruction, from the estimate of annual concentration trends based on chemical stoichiometry and the balancing of cations against anions in both precipitation and stream water, makes sense when ultimately applied to mass balances within the WEC. While the NHF approach is less instructive in situations where gaseous transfers and biological uptake and/or fixation are factors (as in a net ecosystem flux of DIN), the use of NHF provides confirmation that the reconstructed data are valid and insightful when compared with the measured data.

### 6.3 | Question 3: What is the aggregate impact of acid rain on the watershed ecosystems and how is it different from the background response and effects of experimental watershed treatment?

Fully estimating the long-term biogeochemical impacts of decades of acid rain requires distinguishing acid rain impacts from the important impacts of forest disturbance, including experimental manipulations.

We attempted to partition solute exports into three categories: (1) baseline chemistry (normal background); (2) treatment chemistry (resulting from experimental WEC manipulations); and (3) disturbance chemistry (resulting from acid rain or natural disturbance events, such as soil freezing). Data and approaches for evaluating these categories were based on defined criteria given in SI 2. The partitioned exports can be compared among watersheds as a percent of total exports of each solute for each watershed during the measured period 1963–2010 (Figure 8) and over the 110-yr reconstruction (Table 3).

Treatment category exports from W2 (experimentally deforested in 1965–66), W4 (experimentally strip cut in 1974–1978 and W5



**FIGURE 8** Percent of total cumulative streamwater exports for hydrogen ion, calcium, sodium, dissolved inorganic nitrogen (DIN), sulfate and chloride for Watersheds 2, 4, 5 and 6 of the Hubbard Brook Experimental Forest during 1963 or 1964 to 2010. Disturbance impacts are due to acid rain and several natural disturbances, such as soil freezing; this category is defined as the residual of subtracting background and treatment estimates from the total measured exports. Treatment impacts are due to the following experimental manipulations: Watershed 2 was deforested in 1965–66; Watershed 4 was strip cut during 1970–74; Watershed 5 was whole-tree harvested in 1983 and Watershed 6 is the untreated, reference watershed

**TABLE 3** Cumulative net hydrologic fluxes compared. Note that  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ , and DIN precipitation totals increased by 20% to account for dry deposition (\*)

Precipitation inputs: Totals for 1900–2010 (estimated plus measured data)							
		$\Sigma\text{H}^+$ Keq/ha	$\Sigma\text{Ca}$ Keq/ha	$\Sigma\text{Na}$ Keq/ha	$\Sigma\text{SO}_4^*$ Keq/ha	$\Sigma\text{Cl}^*$ Keq/ha	$\Sigma\text{DIN}^*$ Keq/ha
All Watersheds 110 Years							
	Background Inputs =	9.3	3.1	3.1	15.4	3.1	4.6
	Disturbance Inputs =	35.1	15.0	9.7	61.3	9.3	38.2
	Sum 1900–2010 =	44.3	18.1	12.8	76.7	12.4	42.9
Streamwater exports: Totals for 1900–2010 (Estimated plus Measured Data)							
		$\Sigma\text{H}^+$ Keq/ha	$\Sigma\text{Ca}$ Keq/ha	$\Sigma\text{Na}$ Keq/ha	$\Sigma\text{SO}_4$ Keq/ha	$\Sigma\text{Cl}$ Keq/ha	$\Sigma\text{DIN}$ Keq/ha
<b>W2</b>	Background Exports	0.6	29.5	16.2	16.3	3.1	1.5
	Treatment Exports	1.4	13.4	1.5	−1.4	0.4	34.9
	Disturbance Exports	2.9	28.0	10.3	61.6	5.1	3.6
	Total Exports	4.9	70.9	28.0	76.5	8.6	39.9
	Net Hydrologic Flux	39.5	−52.8	−15.2	0.2	3.8	2.9
<b>W4</b>	Background Exports	0.3	31.2	24.1	15.1	3.1	1.3
	Treatment Exports	0.1	1.1	0.2	0.5	0.2	2.4
	Disturbance Exports	1.0	35.7	12.0	56.7	6.3	10.2
	Total Exports	1.4	68.0	36.2	72.4	9.5	13.8
	Net Hydrologic Flux	43.0	−49.9	−23.5	4.4	2.8	29.0
<b>W5</b>	Background Exports	0.8	24.8	17.4	14.8	2.9	1.1
	Treatment Exports	0.2	1.2	0.2	−0.4	0.4	4.5
	Disturbance Exports	3.4	25.2	9.4	47.5	4.9	4.1
	Total Exports	4.4	51.2	27.1	61.9	8.2	9.7
	Net Hydrologic Flux	39.9	−33.1	−14.3	14.8	4.2	33.2
<b>W6</b>	Background Exports	1.0	22.0	18.0	15.0	3.0	1.1
	No Treatment	0.0	0.0	0.0	0.0	0.0	0.0
	Disturbance Exports	5.4	18.1	9.1	55.5	6.5	7.6
	Total Exports	6.4	40.1	27.1	70.5	9.5	8.7
	Net Hydrologic Flux	37.9	−21.9	−14.3	6.3	2.9	34.2

(experimentally whole-tree harvested in 1985) are clearly evident for  $\text{H}^+$ ,  $\text{Ca}^{2+}$  and DIN, but only DIN represents a majority of the cumulative export during the entire 47-yr period in W2 and W5. The portion due to acid rain (disturbance category) predominates for  $\text{SO}_4^{2-}$ ,  $\text{H}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Cl}^-$ . The experimental deforestation in W2 caused minor retention of  $\text{SO}_4^{2-}$  for several years (negative % export: e.g., Likens et al., 1970; Nodvin et al., 1988) but the acid rain effect on total exports of  $\text{SO}_4^{2-}$  in W2 clearly was the dominant driver throughout the HBES record (Figure 8).

The effects of experimental deforestation on solute exports from W2 is obvious during the 6 years following deforestation in 1965–66, (Figures S2, S3, and S4 in SI 2). We estimate that the experimental deforestation was responsible for 30% of  $\text{Ca}^{2+}$  exports and 90% of DIN exports from W2 during the measured 47 years of record. In contrast, acid rain and natural disturbances were responsible for >80% of the  $\text{SO}_4^{2-}$  exports from all watersheds over this same time (Figure 8;

Table 3). We estimate that acid rain and natural disturbance were responsible for more than 50% of the exports of all measured solutes in untreated, reference W6 (Table 3), with the single exception of  $\text{Na}^+$ , where we estimate that background exports accounted for 60% of cumulative exports. The total experimental treatment effects on exports for  $\text{Na}^+$  and  $\text{Cl}^-$  were relatively small, as expected (Figure 8).

We speculate that if acid rain were to have started in say 1920 or if there were no acid rain in 1965, the dramatic  $\text{NO}_3^-$  exports in response to experimental deforestation in 1965 would have been different than observed. Since there are no N-bearing rocks in the HBEF, arguably N in the WECs at HBEF has accumulated with time, primarily from atmospheric deposition. In the absence of acid rain ('background'), we estimate that DIN exports would have been ~25% of the inputs from precipitation under PIR conditions. Our estimate assumes strong retention of DIN in these ecosystems, which is likely given the low total influx of N that would result during these

110 years (4.6 eq/ha). It is entirely reasonable to assume that this amount of DIN could be retained and sequestered in vegetation. However, the estimated DIN total export from deforested W2 from 1900 to 2010 ( $39.9 \pm 4.0$  keq/ha) was about 93% of DIN total deposition inputs for that same period ( $42.9 \pm 4.3$  keq/ha; Table 3). These treatment-driven values are  $\sim 10$ – $25\times$  higher than background fluxes. Thus, without a large reservoir of available nitrogen, major forest cutting in 1910–1920 could not have caused the same  $\text{NO}_3^-$  release as today. Our reconstruction estimates indicate that the predicted DIN annual exports from W6 did increase almost 25 times above background during 1910–1920. However, the total DIN export for that 10-year period of major cutting ( $\sim 0.5$  keq/ha) was estimated at only 1%, 21% and 11% in comparison to the total treatment exports for W2 (34.9 keq/ha), W4 (2.4 keq/ha), and W5 (4.5 keq/ha), respectively, four or more decades later (Table 3). The earlier cutting disturbance probably had a long-lasting legacy, however, because of organic matter left on the forest floor and within the soil (tops, branches and roots) during the logging operation, and because living biomass was aggrading during the initiation of acid rain in the region, with both soil organic matter and living biomass providing a strong sink for nitrogen inputs associated with acid deposition (Likens, 2013).

Fluxes of  $\text{SO}_4^{2-}$  follow a rather different pattern from DIN even though that anion is also retained, albeit temporarily (Table 3). Background (natural) inputs over 110 years are approximately equal to background exports (15.4 vs. 15.0) in W6 over the same period, but the disturbance inputs and outputs are not symmetrical over that period due to the temporary retention. Once the  $\text{SO}_4^{2-}$  deposition declined and streamwater pH began to increase in the 1970's, the desorption of  $\text{SO}_4^{2-}$  accelerated, such that  $\sim 90\%$  of the  $\text{SO}_4^{2-}$  that was input in precipitation during 110 years was lost by 2010 (Table 3).

Obviously, 'normal' watershed exports of solutes also add up over time in an unrelenting manner, and these outputs can be substantial over 110 years on a mass-balance basis. Early geochemical work at HBEF labelled such 'background' exports as 'cation denudation' in the case of  $\text{C}_B$  (Likens, 2013) – a natural process through which hydrologic exports of weathering derived solutes are balanced largely by mineral weathering. It is instructive to reconstruct these ongoing losses to compare with losses from both experimental manipulations and impacts from major exogenous disturbances, such as acid rain. If the background losses expressed in the hindcasted data were realistic, they might give some boundaries on the estimation of primary and secondary weathering necessary to sustain these losses – values that are very difficult to obtain under conditions of heavy acid anion deposition.

Clearly, the impacts of acid rain on these landscapes, when differentiated as part of the long-term fluxes, dramatically enhanced the cumulative export of most dissolved solutes. The only exception is for  $\text{NO}_3^-$  in W2, where exports of  $\text{NO}_3^-$  in the 6 years following a severe and acute experimental deforestation exceed those we can attribute to acid rain throughout the entire record (Figure 8). The acid rain impact is most extreme in the case of  $\text{Ca}^{2+}$ , where soil cation exchange and hydrologic flushing of  $\text{Ca}^{2+}$  neutralized incoming  $\text{H}^+$  in precipitation. We estimate that acid rain doubled the export of  $\text{Ca}^{2+}$

from the untreated reference W6 during 1900–2010 above estimated 'background' exports (see below).

The reconstructed data to 1900 also allow us to observe how the ecosystems might have been 'set-up' prior to the advent of acid rain, both in terms of surprisingly large  $\text{C}_B$  inputs from 'dirty' precipitation (Hedin & Likens, 1996) and subsequent acidification as the amounts of these buffering materials were reduced in precipitation (Figure 6). Some 82% of  $\text{Ca}^{2+}$  inputs over 110 years came during the period 1900–1962, but streamwater losses during this period were less than half of that lost in stream water during 1900–2010 (Table 3).

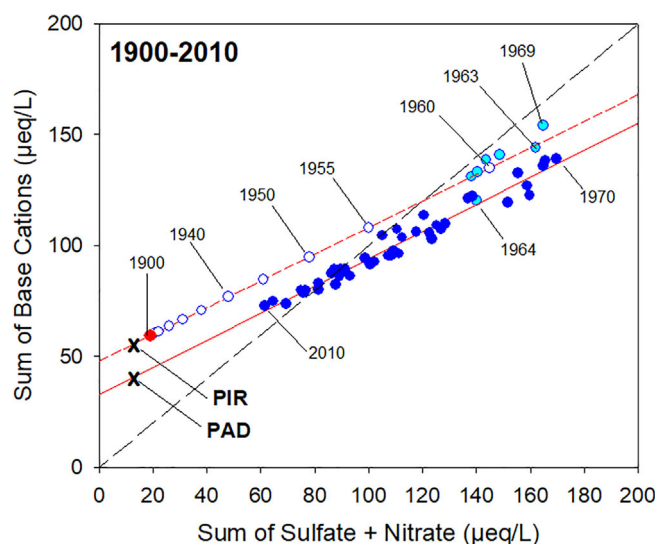
Acid rain had much greater and longer lasting impact on the biogeochemistry of the HBEF than deforestation/harvesting for most solutes, primarily through leaching of  $\text{C}_B$  from acidification. More than 85% of  $\text{H}^+$  input (on an equivalence basis) in acid deposition during 1900–2010 in W6 was neutralized by pre-existing exchangeable  $\text{C}_B$  in the soil as the water passed through the WEC. Consequently, losses of  $\text{Ca}^{2+}$  in W6 (equivalence basis) from the disturbance category (acid rain) amounted to about 85% of the total export of calcium during the same time. Even in the most intense experimental manipulation (W2), treatment losses of calcium were just 50% of the losses that occurred from disturbance (acid rain) during 1900–2010 (Table 3). Thus, a century of acid rain had a  $\text{Ca}^{2+}$  stripping impact equivalent to two deforestation experiments involving complete deforestation and herbicide applications. For the other treated watersheds, W4 and W5, the loss of  $\text{Ca}^{2+}$  due to acid rain over 110 years was  $21\times$  and  $32\times$  greater than the strip cutting or the whole-tree harvest, respectively. These results show that typical forest harvesting practices, and especially experimental deforestation, do not impact the critical ecosystem mass balance for  $\text{Ca}^{2+}$  as much as acid rain does over a long period.

#### 6.4 | Question 4: Has the ecosystem 'recovered' to a previous state following the effects of acid rain, or is there a new state and what is it?

We now suspect that our monitoring of precipitation chemistry at Hubbard Brook commenced just as the ionic strength and acidity of precipitation reached their most extreme values (Figure 1). Following implementation of Federal Clean Air Act legislation of 1970 and 1990 (the 1990 Amendments for the first time specifically focused on reducing acid rain in the U.S.), emissions of  $\text{SO}_2$ , and to a lesser extent  $\text{NO}_x$ , were reduced from the source area for HBEF (Figure 2, Likens et al., 2005). As a consequence,  $\text{SO}_4^{2-}$  was markedly reduced in bulk precipitation and stream water at HBEF during this period in direct relation to the reductions in  $\text{SO}_2$  emissions (Figure 3, Likens, 2013; Likens et al., 2005; Likens et al., 2001; Likens et al., 2021; Likens et al., 2002). As a further result of this large reduction in precipitation  $\text{SO}_4^{2-}$ , the pH of stream water in the various headwater WECs began to increase after 1970 (Likens et al., 1996; Likens et al., 2002) (Figure 1). Nevertheless, the pattern and rate of recovery differed in the individual WECs in large part because of the timing of other major disturbances, such as forest cutting. The pH of stream water in the non-manipulated W6 has been increasing since  $\sim 1973$  ( $r^2 = 0.82$  for

2nd-order regression) and much more rapidly in the last 5 years (Figure 1); the overall pattern somewhat resembles the “hockey-stick” pattern in rise of global air temperatures (Mann, 2001). In sharp contrast, the decline in  $C_B$  and  $SO_4^{2-}$  concentrations ( $r^2 = 0.89$  and  $0.94$ , respectively, for linear regression of trend) in stream water has been remarkably linear since 1963 even with the occurrence of soil frost and ice-storm disturbances (Figure 3, Figure 6(c)).

Starting with the estimates for PIR values, the plot of  $C_B$  against AA shows gradual loss of ANC and constant pH (the balance line between  $C_B$  and AA) from 1900 through 1940 and then rapid acidification as it crossed the ANC line between 1950 and 1960 (Figure 9). Then an abrupt drop in  $C_B$  occurred in 1969 and starting in 1970 a systematic recovery from acidification until 2010 was observed during the measurement period (Figure 9). Appreciable fluctuation in this relation occurred, again during the measurement period, between  $\sim 1960$  and 1965, as the ecosystem seemed to fluctuate in response to this major acidification disturbance and during and after the period of severe drought (1963–1964). Following this inflection point, the hysteresis is complete, when we reconstruct a historic trajectory constrained by charge balance and stoichiometry. For simplicity, we assume an identical slope for the pre-measurement period, which must result in a  $\sim 15 \mu\text{eq/L}$  drop in the y-intercept between the PIR and the present day. Put plainly, our analysis suggests that Hubbard Brook streams are more dilute and substantially depleted in  $C_B$



**FIGURE 9** Long-term acidification and recovery in Watershed 6 as shown by the relation between annual concentrations of the sum of base cations and the sum of acid anions (sulfate + nitrate) in stream water during 1900 to 2010. The solid red linear regression line ( $r^2 = 0.96$ ) applies to measured data (dark blue circles) from 1970 to 2010 and extended to PAD. The red symbol is the starting point in 1900; the open circles are estimated data from 1900 to 1960; the light blue symbols are the measured data from 1963 to 1969. The dashed linear regression line is for estimated data based on the measured data (same slope), but offset to start at PIR and extended to 1960. PIR = preindustrial revolution; PAD = post acid deposition (see Supplementary information)

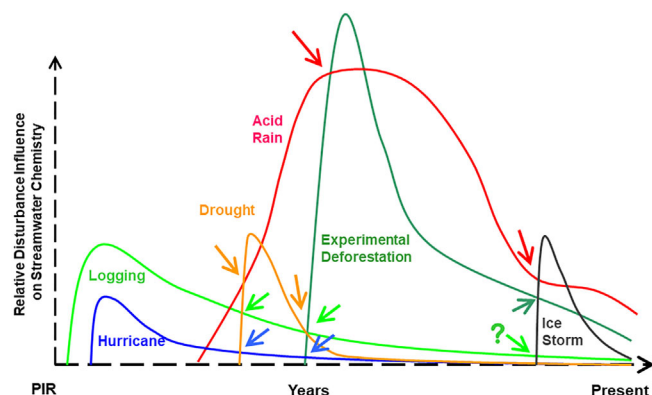
relative to PIR conditions (Figure 9). The recovery trajectory crossed the positive ANC line in about 2005 and is headed toward a historic low value in the  $C_B/AA$  ratio. We call this value Post Acid Deposition (PAD; Likens & Buso, 2012) because it is projected to be lower than the PIR value (Figure 9; Table 1). It is reasonable to expect the  $C_B/AA$  ratio to decline through time because of cation depletion (Kirchner, 1992). Thus, our analysis likely generates a conservative estimate of the extent of acid rain induced streamwater dilution between PIR and PAD, as the trajectories might be neither parallel nor straight.

## 6.5 | Question 5: How does historical reconstruction of watershed mass balances inform or enlighten future management decisions or suggest new experimental WEC manipulations?

The over-arching disturbance of acid rain not only provided  $H^+$  and acid anions, it removed far more of the critical  $C_B$  (via stream water) than did our deforestation experiments despite those experiments appearing *at the time* to cause ‘catastrophic’ solute losses. Arguably, acid rain will be affecting the forest ecosystem long after the public has forgotten that precipitation was ever acidic. Importantly, the patterns of watershed export observed in each of our whole-watershed forest harvest experiments were influenced by their timing with respect to the long-term ecosystem acidification caused by acid rain. Our hindcasting exercise suggests that until about 1945 the input of  $C_B$  via precipitation would have approximately balanced the  $C_B$  export via net soil release (*sensu*, Likens, 2013, p. 134) in the mass balance. As acid deposition inputs increased, this source of buffering was overwhelmed. The period of acidic deposition and enhanced  $Ca^{2+}$  export ended around 1970 as AA inputs declined and precipitation pH increased. The combination of reduced acid inputs and a depleted soil pool of exchangeable cations led to the observed reduction in the total ionic strength of stream water. Based on our analysis, natural soil release once again became the dominant source of  $C_B$  in stream water in about 1995 for W6 and about 2000 for W2, when Background flux > Disturbance flux for  $Ca^{2+}$  (Figure S3 in SI).

At the peak of acid rain in 1965–1970 the decidedly non-steady state conditions caused by long-term acid rain may have predisposed these ecosystems to be highly susceptible to nutrient loss following cutting disturbance. As soil pH declined over time, rates of organic mineralization should have slowed, perhaps protecting soil organic matter and preventing the same level of nutrient export in later clearcutting experiments. These modern insights raise the question of whether differences in the patterns of nutrient export observed among deforestation/clear-cutting experiments performed in 1965 (W2) versus 1974 (W4) versus 1985 (W5) differed because of the type of clearcutting practiced (Likens & Buso, 2010) or because of the declining trends in soil pH, in calcium availability or in climate variability.

Until our most recent whole watershed experiment (W1) demonstrated that calcium enrichment might lead to high exports of nitrogen without acidification (Rosi-Marshall et al., 2016), we had not considered



**FIGURE 10** Theoretical impacts of disturbance on streamwater chemistry concentrations. Decadal, residual influences (legacies) from early logging, hurricane, drought and ice storm are relatively minimal. Experimental treatments may be temporarily acute, but acid rain has a long-term legacy. Concurrence of different disturbances (coloured arrows) may have unexpected impacts on short-term and long-term streamwater chemistry

the additive or synergistic effects of these pulse and press disturbances on both  $C_B$  and nutrient cycles. If the experimentally calcium-enriched watershed (W1) (where soil pH has risen by about one unit) were to be cut today, we hypothesize a far more dramatic level of nutrient export might be seen than was observed for the most recent whole-tree harvest (W5). Moreover, we hypothesize that these exports would not be accompanied by the acid pulse that accompanied previous experimental clearcutting. We further hypothesize that the results would differ if we were to experimentally cut a non-calcium enriched watershed. In such a scenario, we would predict much more limited nutrient export. Future watershed-scale experiments should be viewed through the lens of the multiple interacting legacies that influence watershed condition (Figure 10). This reconstruction approach sheds light on the interactions of these legacies and strongly suggests that previous results from watershed experiments likely were impacted by the times when these experiments were conducted with respect to long-term trajectories in acid deposition.

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## DATA AVAILABILITY STATEMENT

The data that supports the findings of this study are available in Likens et al. 2017 and in the supplementary material of this article.

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