Supporting Information

Dilution and the Elusive Baseline

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GL conceived of the project and wrote the initial draft, but both authors contributed equally to the development of the final draft. Both authors analyzed these data. DB prepared the illustrations.

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Site Description

The HBEF climate is cool-temperate, humid-continental with mean July and January temperatures of 18.7°C and –8.3°C, respectively, at 450-m elevation. The long-term, mean annual precipitation in Watershed 6 (W6) is 1420 mm (SD=201), with 25-33% of the total occurring as snow; mean annual streamflow is 911 mm (SD=203) during 1963-2006.[1, 2] American beech (Fagus grandifolia Ehrh.), yellow birch (Betula alleghaniensis Britt.) and sugar maple (Acer saccharum Marsh.) dominate from 500 to 730-m elevation. Red spruce (Picea rubens Sarg.) balsam fir (Abies balsamea (L.) Mill) and white birch (Betula papyrifera Marsh.) largely dominate at elevations above 730 m and on north-facing slopes. The HBEF was logged intensively between 1909-1917, but there is no evidence of recent fire.[3, 4, 5, 6, 7] Some scattered damage occurred from a hurricane in 1938.[8, 9] Forest biomass has been measured at the HBEF in 1965 and 1977, and at 5-yr intervals, thereafter. Initially (1965-1977), the forest showed significant rates of aboveground plus belowground biomass accumulation and associated element uptake (4.85 Mg/ha-yr).[5, 10, 11, 12] However, between 1982 and 2002, forest biomass accumulation has been essentially zero[12, 13, 14, 15] and since 2002 has been negative as mortality exceeded growth.[15, 16, 17] Glacially-derived soils of the HBEF, like those underlying much of New England, are relatively young (ca 14,000 yr B.P.),[7, 18] highly acidic [19] and have low, clay content. They are well-drained, coarse-textured Spodosols (Haplorthods), with a well-developed surface-organic layer (3-15 cm). The mineral soil is characterized by low base saturation, ~12%. [20] Soils in the experimental watersheds are shallow (averaging about 0.5 m from surface to bedrock or till) and variably increase in depth with decreasing elevation.[3, 21] The eastern portion of the HBEF is underlain by a complex assemblage of metasedimentary schists and smaller igneous intrusions; the western portion is underlain by Devonian Kinsman Granodiorite. [22]

Methods

We applied a straightforward theoretic model, based on our long-term empirical observations, to calculate biogeochemical baseline values. Major components of this model are: *(i)* The hysteresis trajectory for stream water is rigorous and clearly trends toward a quantifiable endpoint. *(ii)* This endpoint is described by a central tendency of C_B and AA values with a confined range. *(iii)* The choices applied using points *(i)* and *(ii)* (above) are restricted by stoichiometric considerations, such as ion ratios and charge balance, and results must be consistent with all of these considerations (see Table S1).

Supporting Information Table S1. Key components used to develop theoretical PAD values.

1. Linear extrapolation of long-term data, particularly the hysteresis model (Fig. 1);
2. Long-term depletion of calcium from the ecosystem by acid rain;[13]
3. Minimum background weathering values for calcium, sodium and sulfur assuming all weathered products are lost in stream water; [13, 14, 23]
4. Extrapolation of our long-term precipitation chemistry data (Figs. 2, 3B, 4B);
5. Paleolimnological data in nearby Mirror Lake. [7, 24, 25]

A critical factor in developing the theoretical PAD values was consistency in the endpoints determined from each of the components given in Table S1, and internal consistency and stoichiometric validity of values presented in Table 1. It is difficult, if not impossible, to determine PIR conditions exactly because legacy effects in disturbed ecosystems have a direct and long-lasting impact on biogeochemical baselines.[26] Nonetheless, data from remote pristine watersheds (see text), and from the paleo sediments in nearby Mirror Lake, suggest that PIR water quality did not resemble demineralized water.

Supporting Information Table S2. Current chemistry of bulk precipitation and W6 stream water based on volume-weighted annual average concentrations from water-year 2009-2010.

CURRENT CHEMISTRY (2009-2010)

	Stream Water (W6)		Bulk Precipitation	
Ion	Conc (mg/L)	Charge (μeq/L)	Conc (mg/L)	Charge (μeq/L)
Calcium	0.57	28.6	0.06	3.2
Magnesium	0.18	15.1	0.02	1.5
Potassium	0.14	3.6	0.03	0.8
Sodium	0.63	27.5	0.07	3.0
Aluminum	0.05	6.0	0.000	<0.01
Ammonium	0.005	0.3	0.087	4.8
H^+ (pH)	(5.24)	5.8	(4.88)	13.3
Sum C_B =		74.8		8.5
CATION Sum =		86.9		26.6
Sulfate	3.07	63.8	0.64	13.3
Nitrate	0.04	0.6	0.58	9.3
Chloride	0.31	8.7	0.14	4.0
Phosphate	< 0.001	<0.01	0.001	<0.01
Bicarbonate	2	2	0	0
DOC	2.18	12.0	0.50	0.0
Sum AA (SO_4^{2-} + NO_3^-) =		64.4		22.6
ANION Sum =		87.1		26.6
BALANCE =		–0.2		0.0
Specific Electrical Conductivity (μS/cm)		11.0*		7.2*

* calculated [27]

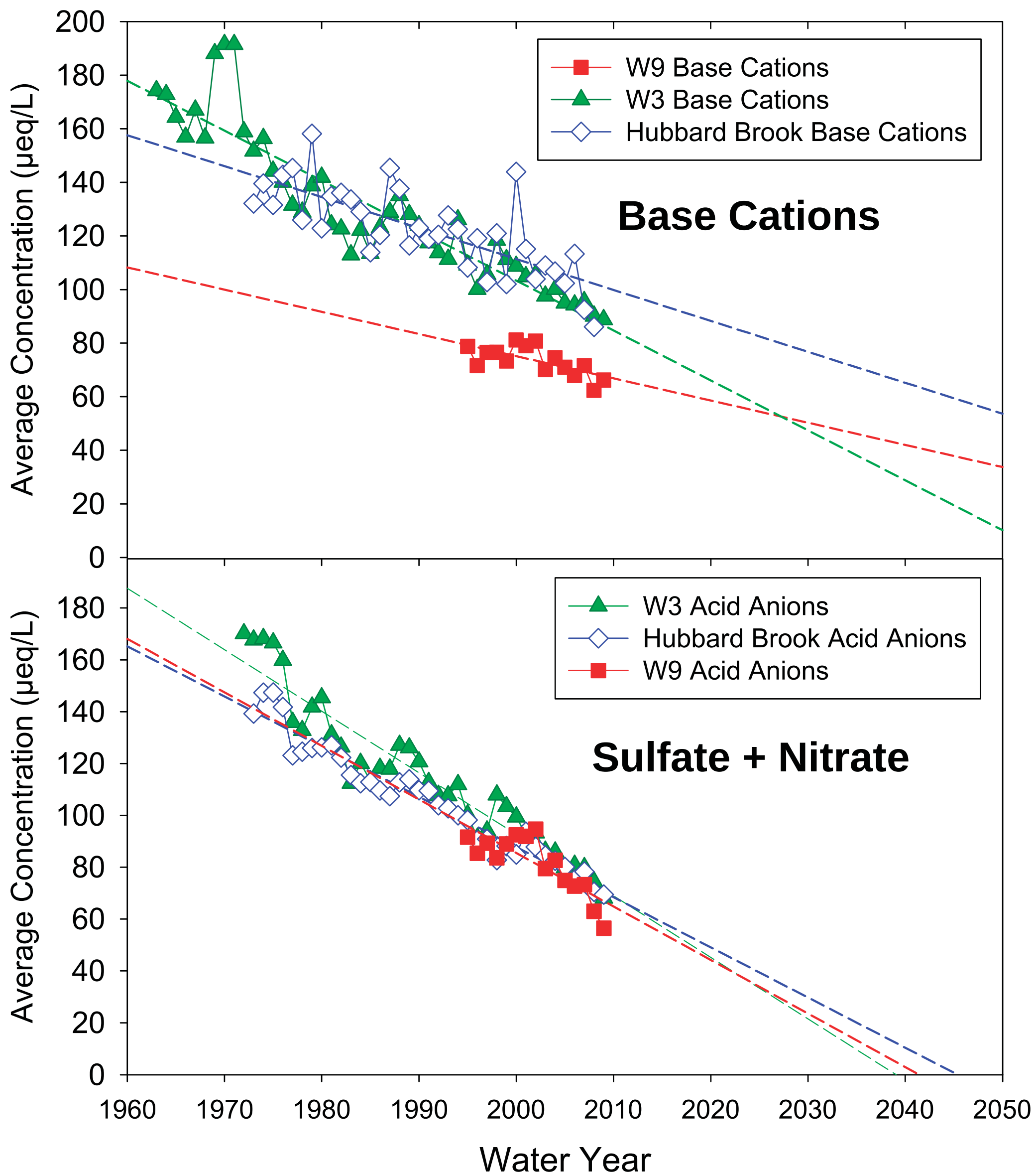
Supporting Information Table S3. Some Characteristics of Hubbard Brook Experimental Forest Watersheds (2005-2009)

Characteristic	Watershed			
	W3	W6	W9	Hbk
Area (ha)	42.4	13.2	76.1	~2900
Aspect	SSE	SE	NNE	N & S
Vegetation	NH	NH	NH/MC	NH/MC
pH	5.41	5.17	4.49	6.14
Ca*	35.7	29.4	25.2	53.4
Na*	37.3	28.8	24.1	43.1
ΣCB*	92.7	77.4	67.8	102
ΣAA*	76.6	72.2	68.1	75
DOC	2.0	2.2	8.9	3.4
ANC*	+8.4	+2.5	-32.7	+30.3

*Units in µeq/liter, ex. for pH and DOC (mg/liter)
W3, W6, W9 concentrations are annual vol-wt average values for water-years 2005-2009 (n=5)
Hbk is the main Hubbard Brook (arithmetic averages for 2005-2009; n=251)
Area is above sampling location
Dominant forest types are Northern Hardwood (NH = American Beech, Yellow Birch, Sugar Maple) and Mixed Conifer (MC = Red Spruce, Balsam Fir, Paper Birch)

Supporting Information Figure Legend

SI Figure S1. Long-term trends for (A) base cations (ΣCB); and (B) acid anions (sulfate plus nitrate, ΣAA) in stream water of Watersheds 3 and 9 and the main stem of Hubbard Brook of the Hubbard Brook Experimental Forest (all linear regressions significant to $p < 0.001$) with correlation coefficients as follows: for ΣCB in W3, $r^2 = 0.84$; in W9, $r^2 = 0.45$; and in Hubbard Brook, $r^2 = 0.57$; for ΣAA in W3 $r^2 = 0.91$; in W9, $r^2 = 0.66$; and in Hubbard Brook, $r^2 = 0.95$.



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