

# Comparing decadal responses of whole-watershed manipulations at the Bear Brook and Fernow experiments

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**Abstract** The Bear Brook Watershed in Maine (BBWM), USA, and the Fernow Experimental Forest in West Virginia, USA, represent unique, long-term, paired, whole watershed, experimental manipulations focusing on the effects of nitrogen (N) and sulfur (S) deposition on temperate forests. Both watersheds began whole-ecosystem additions of N and S as  $(\text{NH}_4)_2\text{SO}_4$  in the fall of 1989, and both are entering their third decade of chronic enrichment of the treated watersheds, while the reference watersheds offer unique opportunities to evaluate forest watershed responses

to recovery. Differences between BBWM and Fernow in the history of atmospheric deposition, soil properties, and forest composition all contribute to different response trajectories in stream chemical exports over time. The four watersheds represent a spectrum of N enrichment and retention, ranging from  $\approx 98\%$  N retention in the reference watershed in Maine, to  $\approx 20\%$  N retention in the treated watershed in West Virginia. Despite these differences, there is evidence that mechanisms of response in base cation leaching and other processes are similar among all four watersheds. In both cases, the history to date of two decades of research and monitoring has provided new insights into ecosystem response not evident in more traditional short-term research.

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## Introduction

The Bear Brook Watershed in Maine (BBWM), USA, and the Fernow Experimental Forest (FEF) in West Virginia, USA, represent unique, long-term, paired, whole watershed, experimental manipulations focusing on the effects of nitrogen (N) and sulfur (S) deposition on temperate forests. The BBWM and FEF acidification experiments

were established as part of the National Acid Precipitation Assessment Program which called for a better understanding of the effects of acidic deposition on processes in forested ecosystems (Adams et al. 2006). The use of the small paired watershed approach provides a powerful experimental tool for studying the mechanisms of ecosystem change and comparing patterns of response across multiple watershed environments (Likens 2001). Experimental manipulations at both sites began in 1989 with additions of ammonium sulfate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>) and have continued to the present (Adams et al. 2006, 2008; Fernandez and Adams 2000; Norton and Fernandez 1999). These treatments make it possible to study the simultaneous response of these temperate forested ecosystems to acidification and N enrichment, as well as the response of the reference watersheds to changes in ambient deposition over two decades (Aber et al. 1989, 1998; Fernandez and Adams 2000).

Soil, soil solution, and stream data from these watershed research programs have provided critical insights on the underlying mechanisms governing ecosystem processes such as base cation depletion, N enrichment, and P mobilization in temperate forests (Adams et al. 2006; Fernandez and Adams 2000; Fernandez et al. 2003; Norton and Fernandez 1999; Roy et al. 1999; SanClements 2009). The studies at BBWM and FEF have allowed hypothesis testing to proceed over nearly identical time scales in two important forest regions in the eastern USA with different histories of atmospheric pollution. Both BBWM and FEF are also valuable whole-ecosystem research sites that represent an opportunity to study recovery processes in response to decreased ambient atmospheric S deposition over the past 20 years, due in part to the US 1990 Clean Air Act Amendments, and all four watersheds are simultaneously responding to a changing physical climate.

Both BBWM and FEF are among the few long-term chronic forest N addition experiments in the world that are able to address decadal-scale consequences of N enrichment in temperate forests, thereby providing unique insights on N dynamics and forest N enrichment (Campbell et al. 2004; Fernandez and Adams 2000). Mechanistic studies of N dynamics at BBWM and FEF have utilized

<sup>15</sup>N additions, inferential stream chemistry, foliar chemistry, soil fractionation, and N mineralization studies to understand the effects of N deposition on carbon (C) sequestration, litter decomposition, nutrient cycling, and tree regeneration and health (Adams and Angradi 1996; Bethers et al. 2009; Elvir et al. 2005; Jefts et al. 2004; Nadelhoffer et al. 1995; Parker et al. 2002). Research on N dynamics at BBWM and FEF has revealed, in one or both watersheds, evidence for increased rates of N mineralization, nitrification, stream N export, and increased foliar and root N concentrations in the manipulated watersheds.

Terrestrial phosphorus (P) limitations can be induced by chronically elevated N deposition (Elser et al. 2007; Gradowski and Thomas 2006) and associated acidification, highlighting the complex interactions evident in ecosystems. A body of research at BBWM and FEF has focused on the effects of elevated N and S deposition on soil, stream, and foliar P (Elvir et al. 2005; Laird 2006; SanClements 2009). This research has demonstrated the importance of Al in determining P dynamics and retention in the acidic soils of these forested watersheds. The research at BBWM and FEF has also provided evidence for the importance of soil acidity in controlling metal–nutrient ratios, which can have important implications for P bioavailability and cycling in soils.

The objectives of this study were to compare temporal patterns of whole-ecosystem response at BBWM and FEF after more than 20 years of research on atmospheric deposition and chemical manipulation effects. Here we focus on atmospheric inputs and their associated stream chemistries for N, S, calcium (Ca), and magnesium (Mg). This comparison includes both reference watershed responses to trends in ambient deposition, as well as responses in the paired watersheds subject to chronic chemical manipulations from both the northern New England and the Central Appalachian study sites.

## Materials and methods

BBWM and FEF comprise a unique pair of long-term, whole watershed acidification experiments

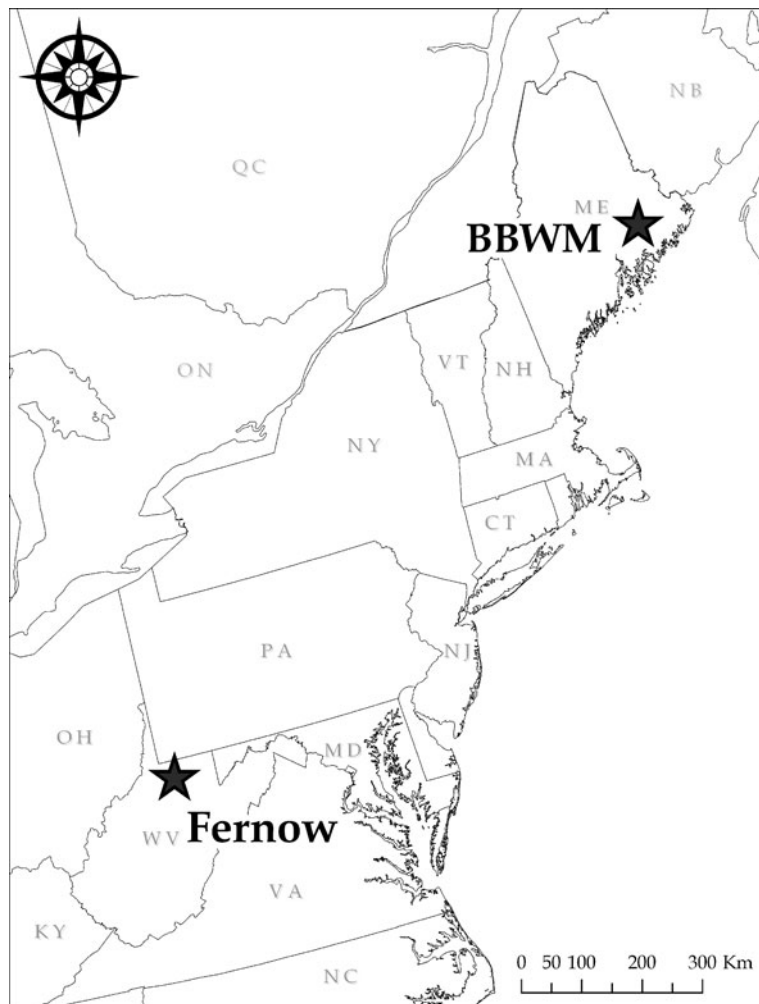
in temperate forest ecosystems of the eastern USA:

The Bear Brook Watershed in Maine

Located in eastern Maine, USA, approximately 50 km from the Gulf of Maine (Fig. 1), BBWM is comprised of the reference East Bear (EB) watershed and the manipulated West Bear (WB) watershed. Both watersheds are fully forested; EB is 11.0 ha while WB is 10.3 ha. Treatment of WB began in November 1989 and continues to the present with bimonthly applications of ammonium sulfate  $[(\text{NH}_4)_2\text{SO}_4]$  at the rate of  $28.8 \text{ kg S ha}^{-1} \text{ year}^{-1}$  and  $25.2 \text{ kg N ha}^{-1} \text{ year}^{-1}$ . The mean annual temperature has been  $4.9^\circ\text{C}$

and mean annual precipitation has been 140 cm. Soils in both watersheds are dominated by coarse-loamy, mixed, frigid Typic Haplorthods formed from Wisconsinan till (Fernandez et al. 2003). Soil sampling included the O horizons, the upper 10 cm increment of the B horizon referred to as “Upper-B” and 10 cm above the C-horizon called the “Lower B”. Further details regarding soil sampling and chemical analyses are in SanClements (2009). Vegetation was similar in both watersheds at BBWM with higher elevations dominated by red spruce (*Picea rubens* Sarg.) and less balsam fir (*Abies balsamea* L.); lower elevations were dominated by northern hardwoods, predominately American Beech (*Fagus grandifolia* Ehrh.), sugar maple (*Acer saccharum* Marsh.),

**Fig. 1** Location of the BBWM and FEF experimental forest watershed sites in the eastern USA (courtesy S. Nelson, UMaine Mitchell Center with data from the Maine Office of GIS)



and red maple (*Acer rubrum* L.; Norton and Fernandez 1999).

*Precipitation and streamflow sampling and analyses* Precipitation was collected using a wet-only Aerochem-Metrics™ precipitation collector located at the EB weir, following National Atmospheric Deposition Program protocols (Dosset and Bowersox 1999; Fernandez et al. 2003). Both watersheds were gauged with standard 120° V-notch weirs with redundant systems for recording discharge with 5-min resolution (Fernandez et al. 2003). Weekly stream samples for chemical measurements were collected on Tuesday mornings, just above the weir in each watershed. Additional samples were collected more frequently during high flow events ( $>0.028 \text{ m}^3 \text{ s}^{-1}$ ) with automated flow activated samplers (Model 3700, ISCO Inc., Columbus, OH, USA). Weekly stream and more frequent ISCO chemical data were coupled with concurrent discharge measurements for the calculation of chemical fluxes. Further details on stream flux measurements can be found in Norton et al. (2010). All chemical analyses were conducted at the Sawyer Environmental Research Chemistry Laboratory at the University of Maine. The algorithm used for supplying artificial data for missing water samples uses a yearly concentration–discharge relationship. Precipitation chemistry and amount, and stream chemistry and discharge, are non-stationary through the last 20 years and seasonally (Navrátil et al. 2010). These variations cause slight uncalculated errors in all chemical budgets. In this chapter, we discuss data lumped to annual volume-weighted means.

### The Fernow Experimental Forest

The FEF is located in the Appalachian Mountains of north-central West Virginia, USA (Fig. 1). Watershed 4 (W4) is the reference watershed while Watershed 3 (W3) has been treated three times per year with  $(\text{NH}_4)_2\text{SO}_4$  at a rate of  $40.6 \text{ kg S ha}^{-1} \text{ year}^{-1}$  and  $35.4 \text{ kg N ha}^{-1} \text{ year}^{-1}$  since January 1989. Mean annual temperature has been  $8.8^\circ\text{C}$  and mean annual precipitation has been 147 cm (Adams et al. 2008). Soils in both watersheds are loamy-skeletal, mixed, active,

mesic Typic Dystrochrepts formed in colluvium and residuum overlying quartzose sandstone and shale (Kochenderfer et al. 2006). The B horizon was sampled for this study with the 0–10 cm increment of mineral soil below the O, E, or A being referred to as “Upper-B”, while the term “Lower-B” refers to the 40–50-cm increment. Additional details regarding soil sampling and chemical analyses are in SanClements (2009). The watersheds were not glaciated during the Wisconsinan ice age. The dominant overstory vegetation consisted of American beech (*F. grandifolia* Ehrh.), black cherry (*Prunus serotina* Ehrh.), red maple (*A. rubrum* L.), and red oak (*Quercus rubra* L.) (Edwards et al. 2006).

*Precipitation and streamflow sampling and analyses* Precipitation volume at Fernow was calculated for each watershed using a group of seven standard rain gauges and the Thiessen method for calculating precipitation averages over large areas (Thiessen 1911; Wood 2009 personal communication). An Aerochem-Metrics™ wet-only precipitation collector was located at the top of W4. Watershed inputs were calculated using precipitation chemistry from the wet-only collector (Adams et al. 2006; Wood 2009, personal communication). Both watersheds at Fernow were equipped with 120° V-notch weirs with FW-1 water level recorders that measure streamflow continuously on 7-day strip charts. Streamwater samples were collected weekly with more frequent sampling during high flow events. Details regarding calculations of stream chemical fluxes are in Adams et al. (1993). Chemical analyses were conducted at the Timber and Watershed Laboratory at Parsons, VA, using US Environmental Protection Agency Protocols (Adams et al. 2007).

## Results

Table 1 shows selected soil chemical properties for EB and W4, the reference watersheds at both sites. Both watersheds were dominated by acidic, base-poor soils with relatively low buffering capacities attributable to exchangeable base cations. Both sites have surface O-horizons that developed under closed canopy forest cover. The O horizons

**Table 1** Selected soil chemical parameters characterizing the reference watersheds at BBWM and FEF

Watershed and soil increment	pH <sub>Salt</sub>	LOI %	CEC cmol <sub>c</sub> kg <sup>-1</sup>	BS %	C %	N %
EB O horizon	3.13	87	22.9	49	46	1.72
W4 O horizon	3.02	84	20.2	41	na	na
W4 A horizon	3.63	22	9.3	32	9	0.56
EB Upper B horizon	3.77	17	9.5	11	8	0.39
W4 Upper B horizon	3.99	8	5.0	10	3	0.16
EB Lower B horizon	4.20	10	4.3	7	4	0.19
W4 Lower B horizon	4.02	7	4.8	8	1	0.06

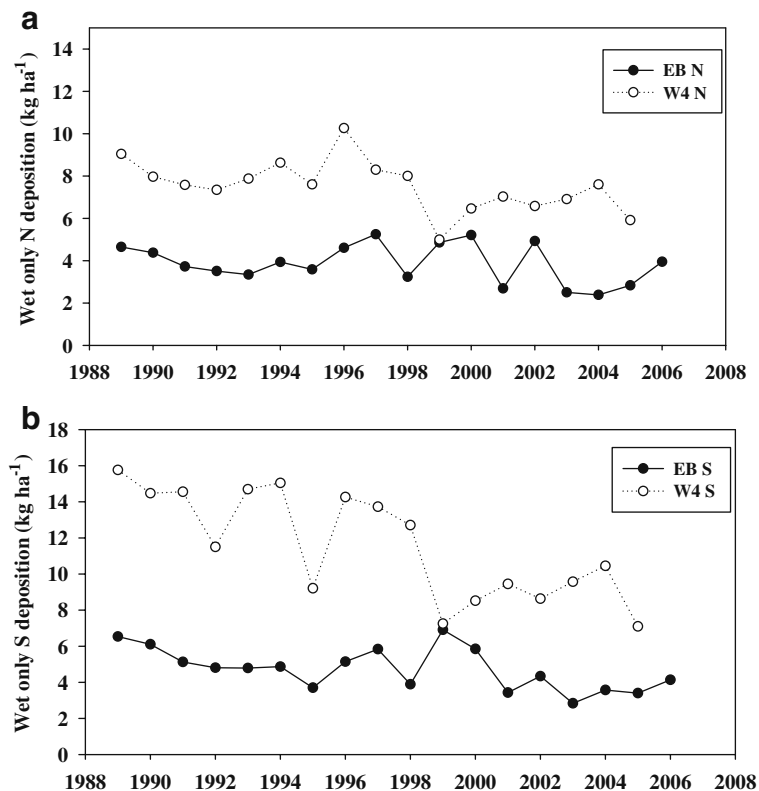
have a relatively high percent base saturation (BS %) compared to the underlying mineral soil, despite their lower pH, and are dominated by organic soil materials. The contrast with depth between the surface O horizon and the underlying mineral soils is dramatic, as BS % and C % decreased markedly in the upper mineral soil at EB and W4, as exchangeable Al becomes dominant. There was a notable decline in % loss-on-ignition (LOI %) in EB with depth between the upper and lower mineral B horizon, which was reflected in the other soil parameters. There were few differences between the upper and lower B horizons at W4. Additional details on soil prop-

erties for BBWM and Fernow are available in SanClements et al. (2010) and Adams et al. (2006).

Inputs of N and S at BBWM and FEF

Mean annual ambient wet-only N deposition for the reference watersheds (i.e., EB and W4) are presented in Fig. 2a. Mean annual wet-only N deposition was 3.0 kg ha<sup>-1</sup> at BBWM, ranging from 2.3 to 5.2 kg ha<sup>-1</sup> over the period 1989–2006. The temporal trend for wet-only N deposition at BBWM was not significant (*p* = 0.40, *r* = -0.20). At FEF, mean annual wet-only N input

**Fig. 2** Annual wet-only (a) N and (b) S deposition for BBWM and FEF



was 6.0 kg ha<sup>-1</sup> over the period 1988–2005 and ranged from 4.9 to 10.2 kg ha<sup>-1</sup>, approximately twice the N deposition of BBWM. There was a significant negative correlation between year and N inputs at FEF ( $p = 0.02$ ,  $r = -0.53$ ; Fig. 2a).

Figure 2b illustrates mean annual ambient wet-only S deposition for BBWM and FEF. At BBWM, mean annual wet-only input of S was 3.7 kg ha<sup>-1</sup>, ranging from 2.8 to 6.9 kg ha<sup>-1</sup> year<sup>-1</sup>. Mean annual wet-only S input for FEF was 9.4 kg ha<sup>-1</sup> and ranged from 7.0 to 15.7 kg ha<sup>-1</sup> year<sup>-1</sup>. There was a significant negative correlation between S inputs and time at both BBWM and FEF, ( $p = 0.01$ ,  $r = -0.57$ ) and ( $p = <0.01$ ,  $r = -0.53$ ), respectively. Deposition of both N and S are much lower at BBWM compared to Fernow because Maine is farther downwind of the major power plants and metropolitan centers of the eastern USA compared to Fernow.

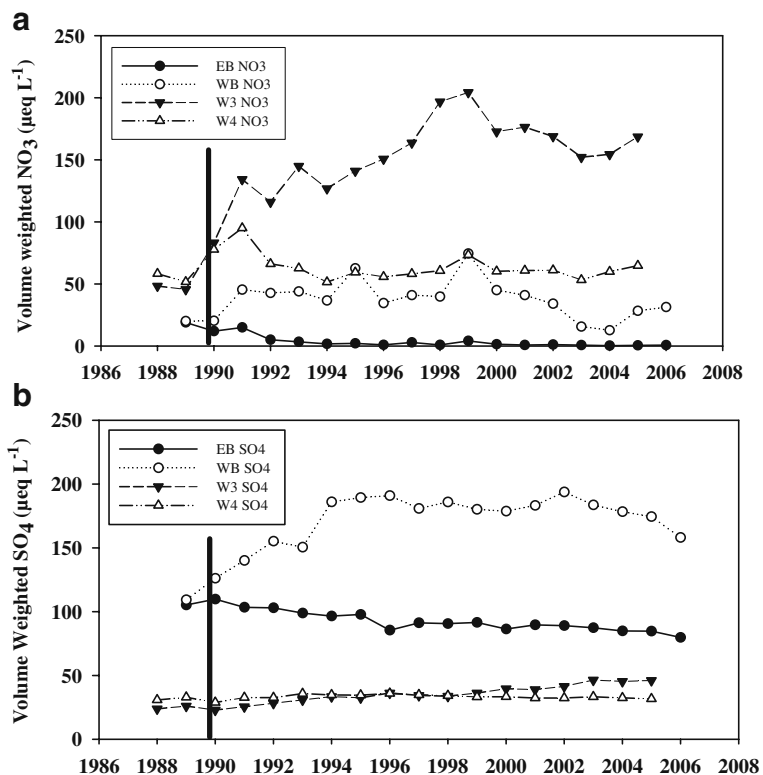
We emphasize that these inputs are wet-only. Rustad et al. (1994) suggested that dry deposition of SO<sub>4</sub>, NO<sub>3</sub>, Ca, and Mg was at least equivalent to wet deposition. This conclusion is equivocal for these non-conservative elements, being involved

significantly in biological cycling in proportion to their concentration (SO<sub>4</sub>, NO<sub>3</sub>, and Mg) and ion exchange. However, if Cl is considered conservative and is derived entirely from marine aerosols, then the atmospheric input of SO<sub>4</sub> and Mg is clearly increased by dry deposition by at least 10% and 100% of wet-only, respectively. Our discussion ignores this contribution, assuming that it is steady state over the study period and part of the soil contribution to runoff. We do not have direct dry deposition measurements to calibrate dry deposition trends over time during the study period. Results from research at Fernow have shown that dry deposition is about half of wet for S, and slightly less than half of wet for N (Adams et al. 2006).

### Stream chemistries

*Nitrate and sulfate* The FEF watersheds had higher stream N concentrations than BBWM watersheds, and these differences were enhanced in the treated watersheds during the treatment period. Prior to the onset of treatments, export of N

**Fig. 3** Stream volume weighted (a) NO<sub>3</sub> and (b) SO<sub>4</sub> concentrations for BBWM and FEF over the time periods 1989–2006 and 1988–2005, respectively. The thick black bar designates the onset of treatment in WB and W3

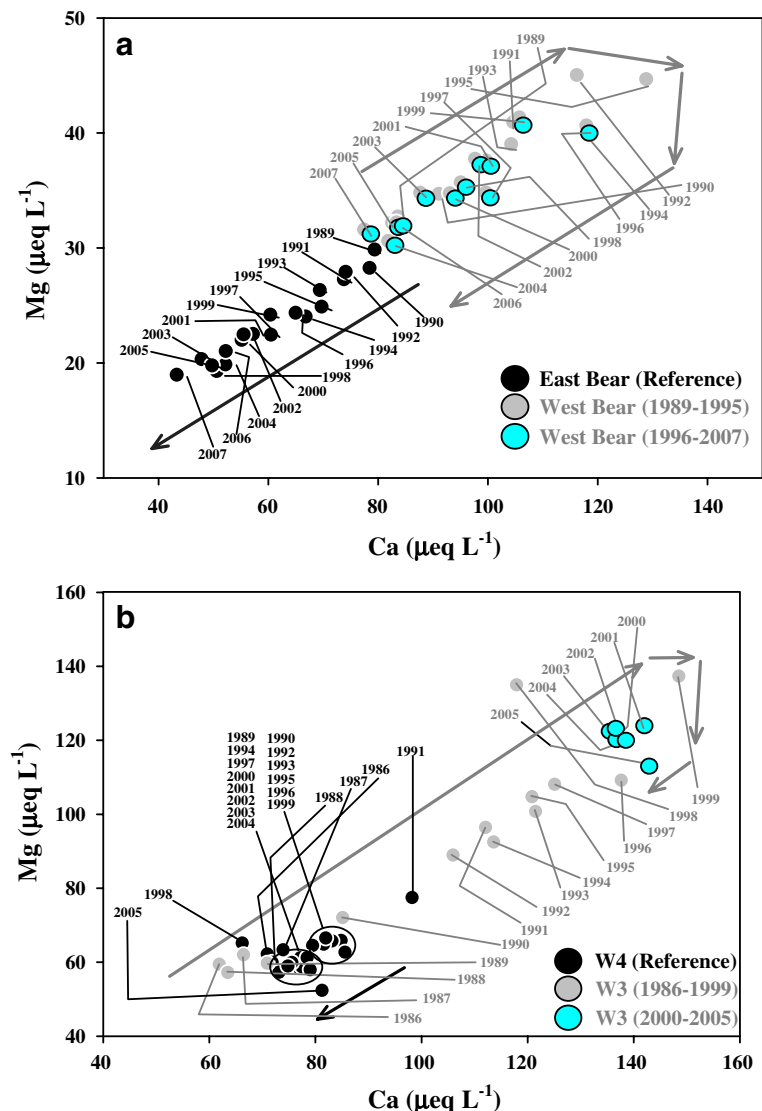


and S at BBWM and FEF were nearly identical in the treated and reference watersheds at each site (Fig. 2a and b; Adams et al. 2006; Norton and Fernandez 1999). Experimental additions of  $(\text{NH}_4)_2\text{SO}_4$  resulted in increased stream concentrations of N and S at both WB (treated watershed at BBWM) and W3 (treated watershed at FEF) within the first year of treatments (Fig. 2a and b). Nitrate ( $\text{NO}_3$ ) concentrations in both WB and W3 have exceeded concentrations from the reference watersheds to the present. WB  $\text{NO}_3$  concentrations became increasingly similar to W4 (the FEF reference stream)  $\text{NO}_3$  concentrations over time, while W3 stream  $\text{NO}_3$  concentrations

increased to the highest of all the study sites. The reference watersheds (i.e., EB and W4) displayed no apparent temporal trends with respect to  $\text{NO}_3$  (Fig. 3a).

Unlike  $\text{NO}_3$  concentrations, sulfate ( $\text{SO}_4$ ) concentrations had markedly different responses at BBWM and FEF. One year after the onset of treatment, volume-weighted  $\text{SO}_4$  concentration in WB had risen above EB and remained elevated throughout the study period (Fig. 3b). Mean annual volume-weighted concentrations of  $\text{SO}_4$  were  $4.0 \mu\text{eq L}^{-1}$  in EB and  $37.2 \mu\text{eq L}^{-1}$  in WB over the time period 1989–2006. EB stream  $\text{SO}_4$  export declined significantly during the study period

**Fig. 4** Chronology of EB and WB (a) and W4 and W3 (b) Ca and Mg volume-weighted stream concentrations



( $p < 0.01$ ,  $r = -0.92$ ). At FEF,  $\text{SO}_4$  concentrations were slightly higher in W4 (reference) at  $48.3 \mu\text{eq L}^{-1}$  versus W3 (treated) at  $58.2 \mu\text{eq L}^{-1}$ , prior to the onset of manipulation. Sulfate concentrations in FEF responded slowly to treatment with W4 remaining greater than W3 until 1999, 10 years after the onset of the experiment. Since 1999, concentrations in W3 have remained greater than W4 (Fig. 3b). Nevertheless, mean annual concentrations for both W3 and W4 over the period 1989–2005 are very similar at  $34.9$  and  $33.1 \mu\text{eq SO}_4 \text{L}^{-1}$ , respectively.

**Calcium and magnesium** The evolution of stream Ca and Mg volume-weighted concentrations at BBWM and FEF are shown in Fig. 4a and b. In 1989, Ca and Mg concentrations in WB and EB, and in W3 and W4, were similar, supporting the comparability of the paired streams for study at BBWM and FEF (Fig. 3a and b). Figure 4a and b show that responses at BBWM and FEF have evolved along similar trajectories over the study period, yet there have been important differences in the magnitude of response between watersheds.

Stream Ca and Mg concentrations from the reference watersheds EB and W4 decreased over time, with this pattern of change more evident in EB than W4 (Fig. 4a and b). In the treated watersheds (WB and W3), Ca and Mg mean annual volume-weighted concentrations first increased, then reversed and declined to the present. In WB, mean annual volume-weighted concentrations of Ca and Mg increased from  $83.6$  and  $32.7 \mu\text{eq L}^{-1}$  in 1989 to  $128.8$  and  $44.7 \mu\text{eq L}^{-1}$  in 1995, respectively. After 1995, Ca and Mg concentrations in WB declined, overall, with the exception of increases in Ca and Mg concentrations from 1998 until 2003, followed by a return to declining values. By 2007, concentrations in WB had decreased to  $77.4$  and  $31.6 \mu\text{eq L}^{-1}$  for Ca and Mg, respectively (Fig. 4a). Stream concentrations of Ca and Mg at W3 also first increased, peaked, and then declined. Ca and Mg concentrations from W3 increased from  $70.9 \mu\text{eq L}^{-1}$  in 1989 to  $148.5 \mu\text{eq L}^{-1}$  in 1999 (Fig. 4b). After 1999, there is some indication of the beginning of a decline in W3 Ca and Mg concentrations, but decreases

in concentrations to 2007 have been relatively less consistent than those in EB (Fig. 4a and b).

A recent comparison of BBWM and FEF

Table 2 shows recent 3-year means for wet deposition and treatment, and stream exports, for both BBWM and FEF after nearly two decades of experimental manipulations. Atmospheric inputs of N and S are far greater than Ca and Mg at both sites. FEF continues to receive significantly more ambient N and S wet deposition than BBWM, despite the declines in S deposition over the study period. Exports of S as  $\text{SO}_4$  are greater at BBWM than at FEF, while the opposite is true for N as  $\text{NO}_3$ , with these differences reflecting differences in internal biogeochemical processes between the Maine and West Virginia watersheds.

**Table 2** Comparison of selected fluxes for the recent characteristics of the long-term, paired, whole-watershed experiments at BBWM and FEF

Parameter	EB	WB	W4	W3
Precipitation				
Mean annual precipitation	1,563	1,563	1,484	1,519
Wet-only deposition				
Mean deposition S	3.7	32.5	9.0	49.8
Mean deposition N	3.1	28.0	6.8	42.5
Mean deposition Ca	0.8	0.8	2.5	2.6
Mean deposition Mg	0.6	0.6	0.4	0.4
Stream exports				
Mean stream $\text{SO}_4\text{-S}$	15.3	33.9	11.6	17.0
Mean stream $\text{NO}_3\text{-N}$	0.1	4.4	5.6	15.6
Mean stream Ca	12.2	21.3	11.6	18.7
Mean stream Mg	3.4	9.2	5.1	9.6
Net				
Net watershed retention S	-11.6	-1.4	-2.5	32.8
Net watershed retention N	3.0	23.9	1.2	26.9
Net watershed retention Ca	-11.4	-20.5	-9.1	-16.1
Net watershed retention Mg	-2.8	-8.6	-4.7	-9.3

Three year means are shown for BBWM (2004–2006) and FEF (2003–2005). All units are as kilograms per hectare per year, except precipitation which is in millimeters. Net numbers do not include weathering. Deposition in EB and W4 are wet-only values while WB and W3 are wet-only + treatment



Both EB and WB showed a net export of 11.6 and 1.4 kg SO<sub>4</sub>-S ha<sup>-1</sup>, respectively (Table 2). At FEF there was a similar net export of 2.5 kg ha<sup>-1</sup> in the reference W4 watershed but a net retention of 32.8 kg ha<sup>-1</sup> SO<sub>4</sub>-S in the treated W3 watershed. All four watersheds show net retention of N, with the reference watersheds EB and W4 retaining 3.0 and 1.2 kg ha<sup>-1</sup>, while WB and W3 retained 23.9 and 26.9 kg ha<sup>-1</sup>, respectively (Table 2). None of these mass balances consider other input fluxes such as dry deposition (which would increase retention numbers) or denitrification (which would decrease retention numbers). Denitrification is thought to contribute little to ecosystem N mass balance in either of these watersheds (Peterjohn et al. 1998; Venterea et al. 2004). There is also a net export of Ca and Mg from all of the BBWM and FEF watersheds (Table 2). The treated watersheds at both sites are exporting more Ca and Mg than the reference watersheds (Table 2, Fig. 4a and b).

## Discussion

### N and S mass balance

The significant trends for declining wet-only S deposition at both BBWM (≈30% decline) and FEF (≈50% decline) since 1988 (Fig. 2a) result from S emissions reductions legislated by the US Clean Air Act of 1970 and its amendments in 1990. At BBWM, decreasing S deposition was reflected in decreasing EB stream volume-weighted SO<sub>4</sub>-S concentrations over time (Fig. 3b) of a magnitude similar to the S deposition decline. This rapid and near-stoichiometric response likely reflects a low SO<sub>4</sub> retention capacity in watershed soils that relatively quickly achieve a dynamic equilibrium with changing SO<sub>4</sub> concentration in deposition (Norton and Fernandez 1999). Exports of SO<sub>4</sub> from W4 at FEF differed from BBWM in that stream SO<sub>4</sub> concentrations responded little to changing ambient SO<sub>4</sub> deposition (Fig. 3b). The limited response in stream SO<sub>4</sub>-S exports from FEF is attributed to the high SO<sub>4</sub> adsorption capacity of soils in W4 and W3 (Adams et al. 2007), compared to the low SO<sub>4</sub> adsorption capacity at

BBWM. Most of the differences in SO<sub>4</sub> adsorption capacity in the soils of these watersheds are due to differences in the degree of secondary accumulations of Al and Fe in subsoils as a result of pedogenesis.

Unlike the marked decreases in S deposition that have occurred over the study period, wet-only N deposition has remained relatively consistent at BBWM. At FEF there was evidence for ≈20% decrease in wet-only N deposition. Despite the trend for decreasing wet-only N deposition at FEF, wet-only N deposition remains approximately twice that at BBWM (Fig. 2a). Stream NO<sub>3</sub> concentration responses to treatment are partly governed by the history of N deposition at BBWM (relatively low N deposition) and FEF (relatively high N deposition). Very little NO<sub>3</sub> export occurs at EB due to a low historical accumulation of atmospheric N deposition, and because of high soil C/N ratios resulting in biological immobilization of N in the watershed. The history of higher atmospheric N deposition at FEF has resulted in W4 being a less retentive watershed than EB (Fig. 3; Table 2). Experimental additions of N in these watersheds (i.e., WB and W3), therefore, resulted in dramatic increases in stream NO<sub>3</sub> concentrations, with the greatest increases in W3 where a history of higher N deposition appears to have reduced remaining N retention capacity in the soil. The only watershed that remains in what Aber et al. (1989, 1998) defined as Stage 0 in the development of N saturation is EB, where there are no N amendments and the watershed remains N-limited with little stream export of NO<sub>3</sub>. At FEF, W4 has been and remains in Stage 2 reflecting the relatively high rates of historical N deposition and evidenced by elevated NO<sub>3</sub> export in stream water. During the course of the study, experimental additions of N have increased WB stream NO<sub>3</sub> concentrations to values similar to those in W4. Similarly, treatments have shifted W3 to Stage 3 with relatively high rates of stream NO<sub>3</sub> export and chronically elevated NO<sub>3</sub> concentrations in stream base flow. On average, W4 is retaining less than ≈20% of N wet-only deposition while W3 is retaining ≈63%; EB is retaining ≈98% while WB is retaining ≈85%.

Elevated concentrations of foliar N have been detected in both WB and W3 consistent with the N saturation paradigm. Elvir et al. (2005) found

that in most foliage from BBWM, N concentrations were significantly greater in WB than in EB for all species (i.e., red spruce, American beech, sugar maple). Foliar N concentration increases also occurred in the treated W3 watershed at FEF, yet they have been less consistent than those at BBWM (Adams et al. 2006). Despite increases in stream NO<sub>3</sub> concentrations in the treated watersheds, all but the W4 watersheds are still retaining the majority of N inputs (Table 2), as is common in forested watersheds subject to high N loading (Aber et al. 1998; Campbell et al. 2004; Fernandez and Adams 2000; Jefts et al. 2004; Magill et al. 1997).

### Ca and Mg mass balance

Wet-only atmospheric deposition of base cations to both BBWM and FEF is low (Table 2) and net watershed retention of Ca and Mg in Table 2 was negative. If we include estimates of Ca and Mg inputs from mineral weathering, net watershed retentions would remain negative. At BBWM, Ca and Mg average inputs from weathering, based on the period (1988 to 2000) were estimated to be 1.5 and 0.8 kg ha<sup>-1</sup> year<sup>-1</sup>, respectively (Watmough et al. 2005). However, based on Fig. 4, the flux of Ca and Mg from EB is declining, and has been for at least 20 years, during a period of declining SO<sub>4</sub> deposition. Estimates of weathering rates for Ca at FEF ranged from 2–5 kg ha<sup>-1</sup> year<sup>-1</sup>; estimates of Mg weathering rates at FEF were not available (Bailey et al. 2003; Laudelot and Robert 1994). A low base cation rate of weathering supply results in rapid responses to acidification in WB and W3 in the form of increased stream Ca and Mg concentrations due to base cation exchange buffering; depletion of this mechanism occurs after only a few years of treatment as stream Ca and Mg concentrations decline and aluminum (Al) buffering becomes more prevalent for acid neutralization (Norton et al. 2004).

Three-year recent mass balance estimates at BBWM and FEF (Table 2) suggest that even in the reference EB and W4 watersheds, stream exports of Ca and Mg exceed wet deposition and mineral weathering on an annual basis. Apparently, the reference watersheds are acidifying under ambient levels of nearly constant N and

declining S atmospheric deposition. The treated WB and W3 show clear evidence of base cation depletion because treatments resulted in ≈50% increase in Ca and Mg stream export at both sites in the recent past (Table 2). The evolution of stream Ca and Mg concentrations over time (Fig. 4a and b) suggest that all four watersheds have elevated Ca and Mg stream export due to ambient or ambient plus treatment N and S deposition compared to non-polluted conditions. In the EB reference watershed concentrations of SO<sub>4</sub> have declined, whereas a similar trend is not yet evident in W3 that we attribute to soil buffering. The decrease in the strong acid anion concentrations (SO<sub>4</sub> + NO<sub>3</sub> + Cl) evident at BBWM, mostly SO<sub>4</sub>, of soil solutions and streams has been greater than the decrease in base cations (Ca + Mg + Na + K), mostly Ca, with a consequent decrease in pH and alkalinity (Navrátil et al. 2010). Thus, EB, at least, is continuing to acidify because the soils cannot provide sufficient base cations through weathering and desorption to electrically neutralize the SO<sub>4</sub> anion concentration, even with reduced SO<sub>4</sub> deposition. Reductions in EB Ca and Mg concentrations are larger and more uniform than at W4 (Fig. 4a). The smaller reductions in stream Ca and Mg concentrations at W4 compared to EB are likely linked to the higher SO<sub>4</sub> adsorption capacity of FEF soils, which has buffered evidence in stream chemistry of changes in deposition and possible differences in parent material mineralogy.

The treated watersheds (i.e., WB and W3) have largely followed the evolution of acidification as depicted by Galloway et al. (1983) and Norton et al. (2004), and as modified to include a soil component by Fernandez et al. (2003). In this model of acidification as it relates to base cations, Stage 1 represents the system prior to the onset of acidification; or in this case the WB and W3 watersheds prior to acidic deposition, probably pre-1900. Stage 2 is defined by increased stream export of base cations as soil base saturation is depleted due to the leaching of strong acid anions. Stage 3 is a period of declining base cation export, yet still elevated above values that would result only from chemical weathering. EB and WB, and W3 and W4 were all in Stage 3 at the beginning of the treatments. Both WB and W3

(re-)entered Stage 2 at the onset of treatments (Fig. 4a and b). The ecosystem remains in Stage 2 until soil exchangeable base cations (e.g., Ca and Mg) are depleted to a point where they can no longer balance the leaching of excess strong acid anions. The depletion of base cations from the soil exchange complex leads to acidification and a switch from increasing to decreasing stream Ca and Mg concentrations as Al buffering becomes the dominant acid buffering mechanism. The shift in buffering from base cations to Al denotes the shift to Stage 3 and was evident in both WB and W3 (Fig. 3a and b), although less obviously so in W3.

In WB stream, peak concentrations of Ca and Mg occurred in 1995, while the same transition appears to have occurred in 1999 in W3. Although differing by several years, these transitions were remarkably similar, having taken place within a decade of the onset of treatments, and reflecting the relatively low base cation buffering capacity of these acidic forest soils. Measurements of soil base cation pools at BBWM in 1998 showed evidence that soil exchangeable Ca and Mg depletion inferred from stream chemistry was nearly identical in value to base cation depletion measured in WB as excess Ca and Mg, compared to EB (Fernandez et al. 2003). At BBWM base cation depletion was driven by the increases in both  $\text{SO}_4$  and  $\text{NO}_3$ , given their significant responses to treatments as evidence in stream concentrations (Fig. 2a and b). At FEF, stream  $\text{SO}_4$  responses were highly buffered by higher soil  $\text{SO}_4$  adsorption capacity; increased  $\text{NO}_3$  concentrations in soil solutions and streams dominated the increased strong acid anion effect (Edwards et al. 2006). Despite the muted stream  $\text{SO}_4$  response at W3, there was a rapid increase in stream Ca and Mg concentrations reaching concentrations two to three times greater than in WB, and only beginning to show signs of reversal to a declining trend. The greater concentration response in W3 is attributed to capacity factors such as deeper soils at FEF compared to BBWM, resulting in a larger exchangeable base cation pool for response. Despite the evidence for accelerated Ca and Mg leaching in W3, to date there have been no reported differences in soil exchangeable Ca and Mg concentrations between W4 and W3, attributable to

high spatial variability and higher base pools in these soils (Adams et al. 2006, 2007).

In both watersheds at BBWM, the general trends for decreasing stream Ca and Mg are interrupted by brief reversals following a major ice storm in January of 1998. The ice storm affected roughly 11 million acres in Maine, including BBWM (Miller-Weeks and Eager 1999); annual litterfall for 1998 increased by 10–20 times in nearby Quebec, predominantly as a consequence of this 1-week event (Hooper et al. 2001). Canopy damage due to this ice storm was obvious at BBWM, most notably in hardwoods. Although ice storm litterfall inputs were not measured at BBWM, we hypothesize that litter inputs increased, short-term increases in light penetration to the forest floor, accelerated litter and organic matter decomposition, and reduced biological uptake contributed to increased stream Ca and Mg concentrations, briefly disrupting the declining concentrations between 1999 and 2002 in EB and WB stream (Fig. 4a). This was also evident in the increased  $\text{NO}_3$  export in 1999 in EB and WB, the temporary increases in foliar nutrient concentrations following 1998 (Elvir et al. 2005), and significant declines in forest floor mass between 1998 and 2006 (SanClements 2009). A resampling of soils from EB and WB in 2006 revealed few trends in base cation chemistry over the 8 years since the 1998 sampling (SanClements 2009). It is possible that the contribution of base cations due to mineralization of ice storm litter inputs have obscured some temporal trends in soil chemistry, as well as streams, at BBWM.

## Conclusions

During this study, the BBWM and FEF whole watershed manipulations have revealed both similarities and differences with respect to the effects of elevated inputs of N and S. The response mechanisms of watersheds includes anion adsorption ( $\text{SO}_4$ , primarily), base cation desorption, and Al desorption and dissolution. BBWM has soils low in  $\text{SO}_4$  adsorption capacity and thus they have responded to acidification pressure largely by release of base cations, followed by Al. FEF has soils with high  $\text{SO}_4$  adsorption capacity and thus

FEF soils responded to acidification pressure by a combination of sorbing excess  $\text{SO}_4$  and desorbing base cations as defense mechanisms. EB is still acidifying under ambient  $\text{SO}_4$  loading, while W4 appears to be nearly at equilibrium with ambient deposition. The differences in response between BBWM and FEF are useful for interpreting mechanisms of integrated watershed responses with varying deposition legacies, climates, vegetation, and soils. However, perhaps the most notable finding from this site comparison is the similarity in response by both ecosystems to the conceptual models of the progression of ecosystem N enrichment and acidification. These long-term study sites enable multi-decadal tests of ecosystem function not possible with short-term studies. This highlights the importance of long-term ecosystem studies in hypothesis testing and in understanding the evolution of ecosystem processes relevant to landscape change. The reference watersheds in these studies are equally valuable as baseline comparisons for the manipulated watersheds, and as ecological observatories to monitor the effects of ambient changes in our chemical and physical climate on decadal time scales.

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