NITROGEN AND SULFUR INPUT-OUTPUT BUDGETS IN THE EXPERIMENTAL AND REFERENCE WATERSHEDS, BEAR BROOK WATERSHED IN MAINE (BBWM)

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Abstract. Dry $(NH_4)_2SO_4$ (1,800 eq^{-1} ha^{-1} yr^{-1}) has been applied to the western of two contiguous 10 ha catchments at the Bear Brook Watershed in Maine (BBWM) since November, 1989. The initial rapid and significant response in both S and N in West Bear, compared to the reference East Bear, slowed after three years. Annual S retention of the total experimental treatment decreased from 86 to 34%, with a seven year cumulative retention of 59%. Hydrology influences the export flux of S; S is retained more in dry seasons and dry years. The annual retention of N has decreased from 96 to 81%, with a cumulative retention of 82%. The export of N from the reference watershed has declined from 178 to 23 eq^{-1} ha^{-1} yr^{-1} during the treatment period. The treatment N (as NH_4) initially stimulated nitrification, and caused pre-existing N to be lost in runoff, rather than the treatment N. Retention of the treatment N has decreased to approximately 80%. The majority of the retained N is stored in the soil, but the reasons for the decreased flux from the reference watershed are not known.

1. Introduction

Scientific knowledge is incomplete concerning how terrestrial ecosystems influence the response of aquatic systems to acidic atmospheric deposition, especially for N (e.g., Stoddard, 1994; Aber *et al.*, 1989), and on the *recovery* of impacted systems. Understanding these processes is especially relevant. Implementation of the Clean Air Act Amendments of 1990 has resulted in a marked decrease in atmospheric deposition of SO_4 since 1995 (MacLean, 1998), accelerating the 30 year decline in S deposition. Nitrate in deposition is increasing relative to SO_4, at the same time that ecosystems in the northeastern U. S. are experiencing an overall decline in acidic deposition.

Sulfate has typically been considered the most important 'mobile anion' for soil processes in watersheds affected by acidic deposition, serving as a mobile counter-anion to base cations, Al, or H^+ in leaching to surface waters (Church *et al.*, 1989; Rochelle and Church, 1987; Johnson *et al.*, 1986; Reuss and Johnson, 1986; Galloway *et al.*, 1983; Cronan *et al.*, 1978). In the 1980s, acidification of surface waters was generally considered to be a function of the competing rates of cation supply from soils and acid anion supply (principally SO_4) from deposition (National Academy of Sciences, 1984).

Sulfate adsorption is an important control on short-term S retention (Fuller *et al.*, 1986; Johnson and Todd, 1984), and is positively correlated with soil acidity (Nodvin *et al.*, 1988), particularly below the forest floor. However, acidic northern Spodosols seem to retain the least amount of S of the major soil orders (Church *et al.*, 1989;

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Rochelle *et al.*, 1987). Rochelle *et al.* (1987) concluded that there was little retention of S by soils in glaciated terrain. They found that for many watersheds dominated by Spodosols, there was a greater output flux than deposition input, suggesting that there were missing sources of S input (dry deposition or weathering of bedrock S) or that S stored during periods of higher deposition was leaching from soils. At the Hubbard Brook Experimental Forest (HBEF), NH, export of S exceeded measured bulk deposition inputs by 40% for the 10 years of record summarized by Likens *et al.* (1977). Similar results have been inferred for other localities by Mitchell *et al.* (1996b), Farley and Werrity (1989), Calles (1983), and Lynch and Corbett (1989). Hultberg and Greenfelt (1992) and Rustad *et al.* (1994) suggested that underestimation of dry deposition is a common problem in these studies, and that SO_4 dry deposition may exceed wet deposition by more than 2-fold (Rustad *et al.*, 1994). Driscoll *et al.* (1998) concluded that dry deposition is an important source of S at HBEF.

The question in the late 1990s is why ANC in surface waters of the northeastern U.S. is not recovering concurrently with the substantial declines in SO_4 deposition. One of the possible explanations is continued chronic N deposition from the atmosphere. Nitrogen in deposition was not considered important until the late 1980s. Since then, N-saturation has received increasing attention on a hemispheric scale (Aber *et al.* 1998; Mitchell *et al.*, 1996a; Williams *et al.*, 1996; Nodvin *et al.*, 1995; Jeffries, 1995; Stoddard, 1994; Kahl *et al.*, 1993; Sullivan, 1993; Murdoch and Stoddard, 1992; Aber *et al.*, 1989; Schulze, 1989; Hauhs *et al.*, 1989; Henriksen and Brakke, 1988).

There is no apparent regional pattern in the U. S. for retention and output flux of N. During 1987-94, N flux in surface water from the Catskill Mountains, NY exceeded the export from the East Bear reference stream by about a factor of 2. The stream fluxes of N at HBEF and Huntington Forest, NY were similar to runoff N in East Bear (Mitchell *et al.*, 1996a). At HBEF, retention of NH_4 and NO_3 were estimated at 84% and 85%, respectively, although a substantial additional input component from N fixation was not quantified. Therefore, Likens *et al.* (1997) considered that N storage was underestimated. At Arbutus watershed in the Adirondack Mountains, NY, export flux of 90 eq N ha^{-1} represented a retention of 85% of N deposition (Mitchell *et al.*, 1996b). In Maryland, N export equaled N input for two upland watersheds (Katz *et al.*, 1985). Ninety percent N retention is typical of watersheds in many regions (Stottlemeyer and Troendle, 1987; Calles, 1983; Wright and Johannessen, 1980).

In the severely polluted Czech Republic, N outputs were negligible from some catchments, despite high deposition (Kram *et al.*, 1997; Paces, 1985). Of the eight control sites in the NITREX experiments in Europe, only the three receiving the highest N input (as throughfall) leaked significant percentages of N (Bredemeier *et al.*, 1998). At the Turkey Lakes Watershed, Ontario, N input ranged up to 2,500 eq^{-1} ha^{-1} yr^{-1}, and 35 to 60% was retained (Nicholson, 1988). In Great Britain, Farley and Werrity (1989) reported low retention of N in their experimental reforestation experiments. The differences among these data support the hypothesis that land use history may be important for N cycling and flux. Fire history may be especially important for control of N retention and flux (Riggan *et al.*, 1993; Buso *et al.*, 1985).

Results from the NITREX watershed manipulations in Europe (Wright and Rasmussen, 1998) suggest that the concept of 'N-saturation' and NO_3 export is valid.

When more N was added to such sites, the system leaked more NO_3; when N was reduced (even to below the previous ambient), the systems leaked less (Bredemeier *et al.*, 1998). However, the response to N additions was not linear; some manipulated sites had only minor increases in N export in response to treatment. During nine years of experimental HNO_3 loading of 7 kg N ha^{-1} yr^{-1} at Sogndal, Norway, 90% of the N was retained in a 1,900 m^2 mini-catchment (Wright and Tietema, 1995). This site had the lowest ambient deposition in NITREX (Dise and Wright, 1992; Bredemeier *et al.*, 1998). Sites with higher ambient deposition showed more linear response to N additions, but some of these sites were not calibrated stream watersheds.

The research described here is part of the whole ecosystem paired-watershed study at the Bear Brook Watershed, Maine (BBWM) (Church, this volume; Norton *et al.*, this volume). We have added N and S as dry $(NH_4)_2SO_4$ to the 10.2 ha West Bear catchment, with the adjacent 10.9 ha East Bear catchment remaining untreated as a reference system. During the 1990-1997 treatment of West Bear, the watershed export in streamwater has increased for NO_3, SO_4, base cations, Al, and H^+, while ANC has decreased. The chemical relationships among several analytes have changed during this period (Norton *et al.*, this volume). The focus of this paper is the comparison of watershed responses over time and an estimate of the input-output mass balances for N and S. Processes governing ecosystem function within the watershed are addressed more fully in accompanying articles in this volume.

2. Methods

2.1. STUDY SITE

The Bear Brook Watershed is in eastern Maine at 44°52' N and 68°06' W, 50 km from the Gulf of Maine. The watersheds cover the upper 210 m of the southeast slope of Lead Mtn (475m). Two nearly perennial, low DOC, low ANC streams drain the 10.2 and 10.9 ha contiguous watersheds. The forest is mixed northern hardwoods (*Fagus grandifolia, Acer rubrum, Acer saccharum, Betula alleghaniensis, Betula papyrifera, and Acer pensylvaticum*) with softwoods at higher elevations (*Picea rubens*, *Abies balsamea*, and *Tsuga canadensis*). Soils are coarse, loamy, mixed, frigid Typic Haplorthods on till averaging 0.9 m in depth. The bedrock is quartzite and metapelite, intruded by granite (Norton *et al.*, this volume).

2.2. EXPERIMENTAL DESIGN

The research at BBWM was designed to evaluate the assumptions and behavior of watershed acidification models using a whole-watershed response to artificial acidic deposition. The research design included a two year period of baseline data collection (1987-89) before treatment initiation. The remarkable similarities in chemical and hydrologic response of the two catchments (Norton *et al.*, this volume; Norton *et al.*, 1992), provided a solid foundation for later evaluation of the response of the treated versus reference catchment (Cosby *et al.*, 1996; Uddameri *et al.*, 1995; Sullivan and

Cosby, 1995; Norton *et al.*, 1994; Kahl *et al.*, 1993). The BBWM experimental design allowed us to test the response of West Bear Brook against its pre-treatment period, and against the reference response in East Bear Brook.

2.3. WATERSHED EXPERIMENTAL TREATMENT

Dry $(NH_4)_2SO_4$ has been applied every two months since November, 1989 to the 10.2 ha West Bear catchment. The adjacent 10.9 ha East Bear catchment serves as an untreated reference. The treatment loading is 1,800 eq^{-1} ha^{-1} yr^{-1} of N and S, compared to 600 eq^{-1} ha^{-1} yr^{-1} ambient (wet plus estimated dry) N deposition, and 900 eq^{-1} ha^{-1} yr^{-1} for (wet plus estimated dry) S at the start of the experiment in 1989. The experiment increases the annual loading of N (total of measured wet plus estimated dry) by 300%; S is increased 200%. The resulting dose to the landscape of the West Bear catchment, including the treatment, is now approximately 60% higher than in the highest deposition region of North America, about 30% lower than has recently occurred in some areas of central Europe, and similar to other experimental addition research experiments (Table I).

TABLE I

Examples of natural and treatment N and S deposition at watershed sites compared to BBWM. Data are from Dise and Wright (1995), Adams *et al.* (1995), Johnson and Lindberg, (1992), and Bredemeier et al. (1998).

Site	natural N	treatment	total N dep.
Gårdsjøn, Swe.	900 eq ha^{-1} yr^{-1}	3500 eq ha^{-1} yr^{-1}	4400 eq ha^{-1} yr^{-1}
Ysselsteyn, Neth.	4200		4200
Fernow, WV	1100	2500	3600
Solling, Ger.	2700		2700
BBWM	**650**	**1800**	**2450**
Great Smokey, NC	1900		1900
White Face, NY	1100		1100
Sogndal, Nor.	190	500	950
Howland, ME	550		550

Site	natural S	treatment	total S dep.
Solling, Ger.	4800 eq ha^{-1} yr^{-1}		4800 eq ha^{-1} yr^{-1}
Fernow, WV	1200	2500 eq ha^{-1} yr^{-1}	3700
BBWM	**800**	**1800**	**2600**
Ysselsteyn, Neth.	2300		2300
Great Smokey, NC	1900		1900
Gårdsjøn, Swe.	1300		1300
Sogndal, Nor.	500	500	1000
White Face, NY	1000		1000
Howland, ME	580		580

The treatment is chemically similar to actual deposition at the BBWM because precipitation chemistry in Maine, U.S., is dominated by H^+, NO_3, NH_4, and SO_4. As of

1995, S in wet deposition at the site had declined to slightly less than a 1:1 equivalent ratio of N:S in wet deposition. Over the course of the experiment, the 1:1 N:S equivalent ratio in the treatment approximated the ratio in deposition. The bimonthly schedule is a reasonable distribution of acidifying deposition at the site. Up to 80% of the annual precipitation loading of solutes has occurred in as few as the 10 largest storms in a year.

The experimental addition of N is modest relative to total N soil pools and to annual vegetation requirements. The loading rate of 25 kg N ha^{-1} yr^{-1} is less than 25% of estimated vegetative requirements of 80 to 120 kg^{-1} ha^{-1} yr^{-1} (Aber *et al.*, 1991), and only about 10% of typical forest fertilization application rates of 200 kg^{-1} ha^{-1} yr^{-1} (Allen, 1987). The annual experimental loading is about 1% of the estimated total N pool of 2,500 kg N ha^{-1} in upper soil horizons at BBWM.

2.4. CALCULATION OF MASS BALANCES

Likens *et al.* (1977) pioneered the use of watershed mass balances at HBEF, NH. The relationship is simple.

$$\text{storage} = \text{input} - \text{output} \tag{1}$$

For N, we define input as wet deposition (measured) plus dry deposition (estimated) plus N fixation (not measured) plus treatment. N output is stream output of inorganic (measured) and organic N (estimated) plus denitrification (not measured). For S, we define input as wet deposition (measured) plus dry deposition (estimated) plus treatment. Output of S is through stream flow as inorganic S (measured). A negative value for storage in equation (1) is a net outflux and a positive value is retention within the watershed.

We have made the following assumptions:

1. Particulate flux is assumed to be neglible in these clearwater streams with low concentrations of suspended solids. Changes in particulate flux are not likely to be related to the experiment until there is physical disturbance in the forest.
2. Neither N nor S are derived from chemical weathering of the mineral soil or bedrock. The SO_4 source in streamwater at BBWM is atmospheric, with little or no bedrock source (Stam *et al.*, 1992). An apparent lack of S isotopic fractionation within the watersheds indicates that abiotic processes control S chemistry, rather than more complex biotic and redox factors.
3. Gaseous losses of N and S are low (e.g., we assume denitrification is low because most of the soils at BBWM are well-drained) and unchanged by the treatment. Gaseous gains (N-fixation) are assumed to be the same for both watersheds and unchanged by the treatment.
4. Substantial inputs of water and solutes occur as cloud water and fog, based on data collected by a fog collector operated at the summit of Lead Mountain for several years (Norton *et al.*, this volume). Quantification at the watershed-scale of this

input of water and solutes from this device has not occurred. However, inputs should be comparable for the two watersheds.

5. Substantial inputs of some solutes occur as dry deposition. Rustad *et al.* (1994) estimated dry deposition of S and Cl at BBWM is at least 2 times the wet input. The calculations in this paper use a dry deposition estimate of 2 times for both S and N. The values in Figures 4 and 6 are derived for each watershed as [wet plus estimated dry deposition](plus treatment for West Bear) minus [stream flux]. No direct measure is available for dry deposition to our sloping, irregularly surfaced, and heterogeneously forested mountainside. Although there are uncertainties in estimates of dry deposition of S and particularly N, dry deposition should be comparable for both watersheds. Thus differences between the two watershed budgets that evolve during the treatment are assumed unrelated to changes in dry deposition to either of the watersheds.
6. Organic S is low in the discharge. Organic N was measured for several years. It was a small percentage of the total N (dominantly NO_3) and was unchanged in absolute amount as a result of the treatment.
7. Concentrations of S and especially N increased in the treated watershed vegetation and forest floor (Wang 1993, and White *et al.* this volume) but the mass changes were small compared to the treatment and output values.

The application of equation (1) to the real world is not simple (Gorham *et al.*, 1979). Data requirements also include interpolation of stream chemistry during the period of the discharge record without samples. The methods used to estimate mass balances at Bear Brook are described below.

Calculation of wet deposition input

The input term at Bear Brook is the product of chemistry and water deposition volume from two NADP-style Aerochem-Metrics wet-only precipitation collectors with Belfort gauges for volume measurement. These stations are operated on a standard NADP Tuesday collection schedule (NADP, 1986). One is located at the East Bear Brook weir, and one is at a mid-elevation station (the 'Camp'). The Camp station was not operated in 1997. At the Camp station, we operated an independent Belfort gauge with a U.S. Weather Service shield to reduce turbulence around gauges and increase the accuracy of wet deposition measurement. During 1989-95, this gauge collected 5.8% more water than the companion Belfort gauge located 6 meters away. Therefore, the Belfort precipitation volume data are increased by +5.8% each year.

Aerochem™ or Belfort collectors may report only part of a precipitation event because of malfunction, wind patterns, or evaporation of the sample. These devices can not collect more sample than actually fell. Therefore, we used the higher total precipitation value at the Camp or the East Bear Belfort stations for each weekly value used to calculate deposition flux. This procedure yields total annual deposition estimates for Bear Brook that are higher than either gauge estimates individually (Table II). Precipitation and water yields from the nearest NADP station at Acadia National Park generally agree with these estimates of wet deposition (Table II). There are only minor differences in chemistry between Camp and East Bear precipitation, and no consistent seasonal pattern (Table III). We multiplied the weekly chemical concentrations from the Camp station (East Bear if Camp station data were unavailable) by the maximum weekly volume for the total input of chemical constituents from wet deposition. The annual deposition is the cumulative sum of the weekly deposition data.

TABLE II

Annual water yields for East and West Bear Brook. Data are in meters of precipitation or runoff. Precipitation at Acadia National Park, Maine (ANP) is the nearest NADP station and is included for reference.

year	ANP	BBWM	East Bear		West Bear	
	precipitation		runoff	yield	runoff	yield
1989	1.42	1.42	0.95	64.5 %	1.02	70.5 %
1990	1.53	1.41	0.90	61.7	0.93	64.6
1991	1.42	1.44	0.97	64.8	1.05	71.9
1992	1.21	1.17	0.76	62.4	0.80	67.6
1993	1.48	1.06	0.72	65.2	0.77	70.9
1994	1.44	1.38	0.92	66.5	1.05	77.0
1995	1.48	1.21	0.65	52.0	0.64	51.6
1996	1.53	1.78	1.19	66.8	1.02	57.3
1997	1.15	1.35	0.85	62.9	0.79	59.6
mean	1.40	1.36	0.88	64.8	0.89	65.6

TABLE III

Volume-weighted precipitation chemistry at the East Bear weir and the mid-elevation 'camp' station, 1990-1996. Units are μeq l^{-1} except for volume and pH

Variable	n	camp	n	weir
cm	305	113	312	110
pH	290	4.71	300	4.69
cond.	290	15.4	302	15.3
Ca	297	3.5	305	3.0
Mg	297	3.3	305	3.3
K	297	1.2	305	1.0
Na	297	11.7	305	12.9
NH_4	299	7.1	308	6.9
Cl	305	14.8	311	16.6
NO_3	305	14.0	312	13.9
SO_4	305	23.5	312	22.9

Calculation of N and S in stream output

Calculating fluxes of input and output are different. Atmospheric wet input of water and chemistry occurs in discrete precipitation events that are nearly completely sampled. In contrast, the output process operates continuously, but we sample it discontinuously.

For each year, we have up to 8,784 values of hourly discharge data, but typically fewer than 250 samples for chemistry. The challenge of calculating output fluxes is the interpolation of chemistry to provide a value for each discharge observation. The annual solute fluxes are the sum of (≤ 8,784 values of discharge)*(concentration for 21 chemical variables)*(n).

Scheider *et al.* (1978) and Dillon *et al.* (1982) provided a summary of the methods for calculating output budgets. The two methods involve different procedures for interpolating chemistry between samples, or for summing annual chemical flux using various assumptions. The simplest method for watersheds with continuous discharge and periodic chemistry is to calculate a volume-weighted mean concentration for each analyte, and multiply by the annual water flux. This method is biased by any tendency to collect at certain stages of flow, and underestimates the influence of the largest discharge episodes and the peak of most hydrographs.

A better method interpolates stream chemistry to provide a reasonable value for each value of hydrology, by using a concentration–discharge calculation for each analyte. Unfortunately, concentration–discharge relationships typically apply to only one storm or one season (Scheider *et al.*, 1978). Differences in antecedent conditions, flow paths, and biotic influences prevent consistent relationships among seasons or years. Scheider *et al.* (1978) suggest two alternatives for assigning chemistry to each value of discharge. For each interval of discharge data between chemistry samples, 1) assign the value for chemistry at the *beginning* of the interval to all values of hourly discharge until the next sample for chemistry is taken, or 2) assign the chemistry value as the *midpoint* of the discharge interval. Scheider *et al.* (1978) infer that method 2 is the better method because the value of chemistry assigned to each discharge is closer in time to the actual sample. For their nutrient budgets, they determined that method 2 was at least 4% more accurate than method 1.

At Bear Brook, we use an extension of method 2 of Scheider *et al.* (1978). Our method calculates a linear interpolation between adjacent stream chemistry data, and assigns the interpolated chemical concentration to each value of discharge between actual samples. During low flow when concentrations are not changing, our interpolation is accurate even when applied over a week or more (lower panel, Figure 1). In the example of Figure 1, 33 samples were collected from West Bear Brook in June, and the results approximate a concentration-discharge relationship for each hydrologic episode. In contrast, 11 samples were adequate in June (low flow) to represent the output of NO_3 during that month. This method is superior to method 2 because we have a large number of samples per year, and collect several samples during most of the significant hydrologic episodes. We approximate a concentration–discharge relationship by collecting several samples during a single storm hydrograph (upper panel, Figure 1). At high flow, our interpolations span shorter periods, so each interpolative segment between samples spans a relatively short, quasi-linear portion of the hydrograph (Figure 1). Because this relationship is based on data for each period, there is no seasonal bias in the relationship that would occur if we used a generalized concentration–discharge relationship. The relationship holds at both high (upper panel in Figure 1) and low flow (lower panel).

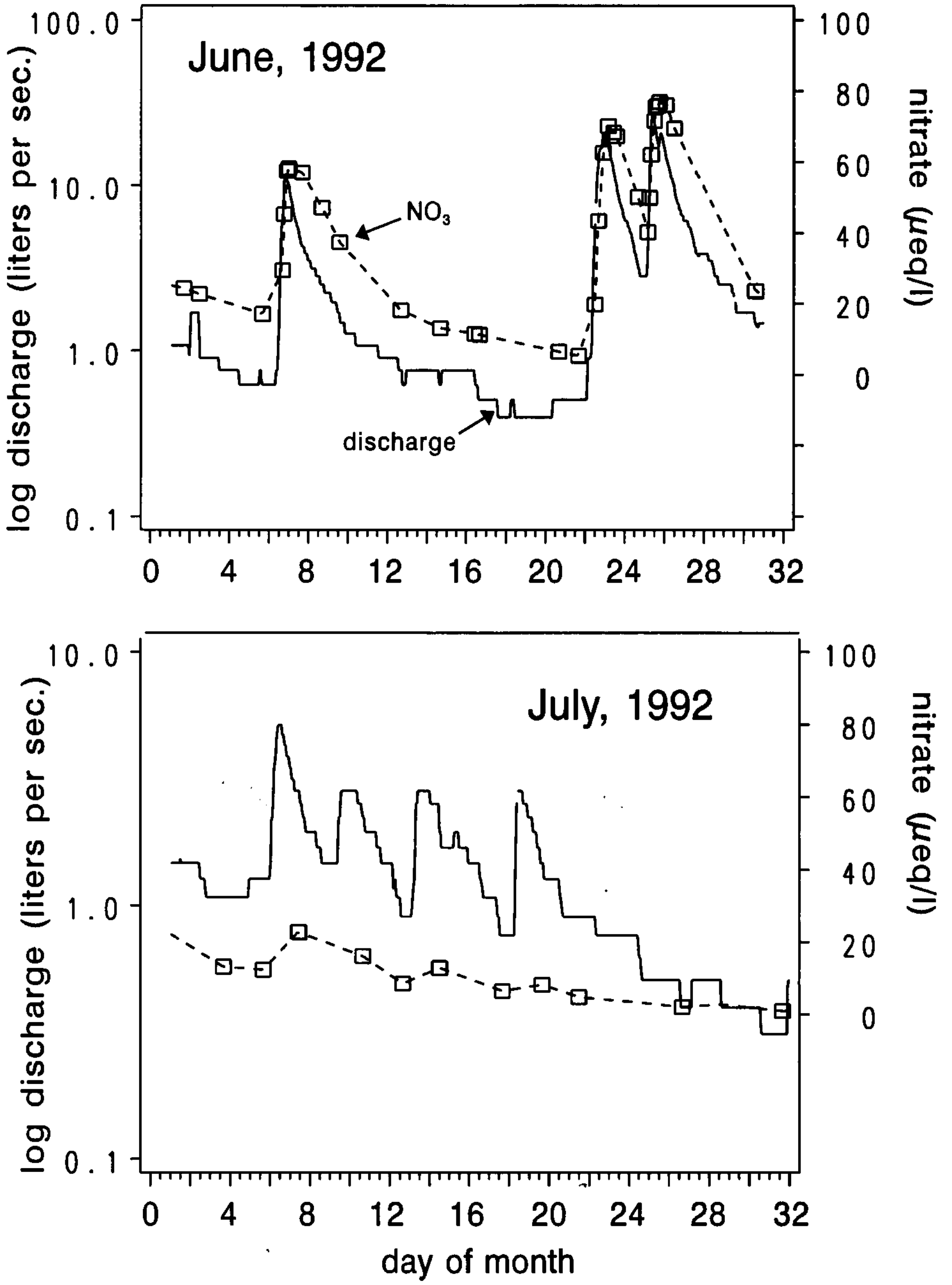

Fig. 1. Results from the interpolation routine used to calculate output fluxes. Interpolated chemistry is shown by dashed lines and discharge by solid lines. Squares indicate actual samples.

The most likely error in calculating output flux results from automated sampling equipment failure. Missed samples during periods of changing discharge may cause the interpolation model to assign incorrect values for chemistry. However, this problem exists only until the next chemistry sample occurs in the data record, after which reasonable interpolated values will be generated based on actual data. Thus, any error will be propagated in the data for no more than a few days, and will be a small percentage of the yearly record. Such errors can be identified easily by graphical inspection, and estimated values for chemistry at critical points on the hydrograph can solve this calculation problem.

3. Results and Discussion

3.1 CHANGES IN THE CHEMISTRY OF AMBIENT DEPOSITION

The period of record at BBWM (1987-1997) reveals the partial success of the 1990 Clean Air Act Amendments (CAAA) in decreasing the concentration of S in precipitation (Norton et al., this volume). From 1988 to 1994, S deposition exceeded N deposition (Figure 2). Beginning in 1995, the pattern reversed, with N deposition becoming greater by a small amount. This reversal coincided with the implementation of Phase I controls in the CAAA, which reduced S much more than N. Both ambient deposition and the experimental treatment have an equivalent N:S ratio of approximately 1:1. These results are typical of recent data from the eastern U.S. (Lynch *et al.*, 1995).

3.2. WATERSHED FLUX OF N

Experimental treatment began in November 1989. The response of West Bear relative to East Bear was rapid and statistically significant (Uddamari *et al.*, 1993). The N response of West Bear relative to East Bear has been relatively consistent since 1991 (Figure 3). The relatively constant higher (than east Bear) fluxes of N after 1990 may be related to regional climatic factors that have changed in the 1990s. Beginning in 1991, NO_3 concentrations and flux in EB have declined to near zero (NH_4 has always been near zero in both streams). At the same time West Bear has retained a relatively constant proportion of the sum of precipitation and treatment N (Figure 4). The yearly pattern of N retention in West Bear is proportional to that of East Bear (Figure 4). Mitchell *et al.* (1996a) suggested that a climatic factor has driven the N response in the northeastern U. S .during this period.

Prior to treatment, N retention at BBWM was 96%. For the experimental period, we have calculated the retention of the experimental $(NH_4)_2SO_4$ by assuming that the flux of N from EB and WB would have been the same if the experiment had not occurred. Therefore, the fractional loss of treatment N from West Bear is:

$$\text{loss (eq ha}^{-1}\text{ yr}^{-1}) = [(\text{output}_{WB}\text{-output}_{EB})/(\text{input}_{\text{treatment}})] \qquad (2)$$

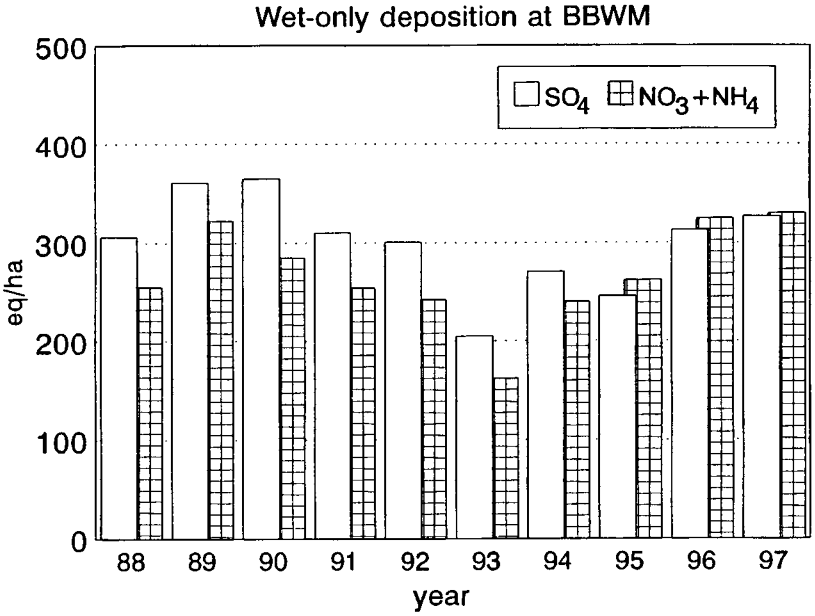

Fig. 2. S and N wet-only deposition at BBWM, 1988 -1997.

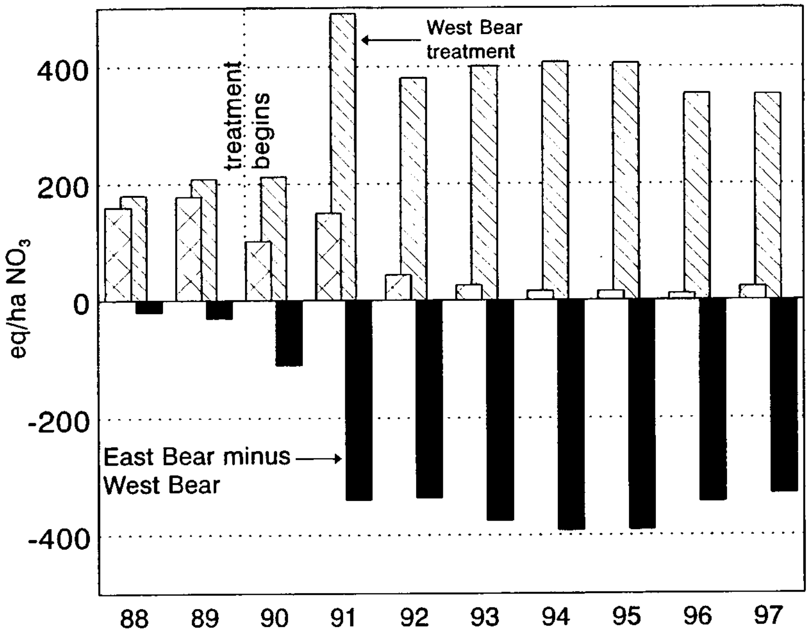

Fig. 3. N flux from East and West Bear watersheds.

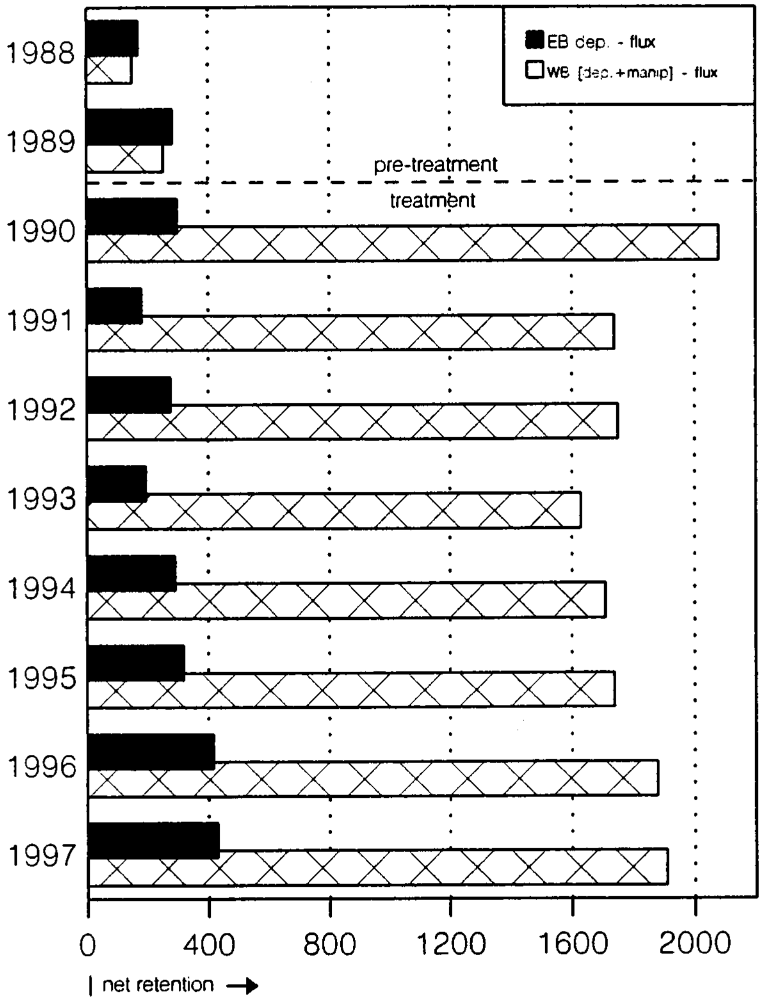

Fig. 4. Input-output budget for N in East and West Bear watersheds.

and the retention is:

$$\text{retention (\%)} = [1 - [(\text{output}_{WB} - \text{output}_{EB})/\text{input}_{\text{treatment}}] \times 100] \qquad (3)$$

West Bear retained 94% of the treatment in the first year of treatment (1990), and this retention has slowly declined to 81% of the experimental treatment added in each year (Table IV). The yearly retention and the cumulative retention are approaching the same value (82%). The annual retention values decreased until 1995. The annual retention of N in 1997 was equivalent to adding approximately 1% to the total soil N, and supplying approximately 20% of the annual vegetation requirements. At the NITREX N research sites in Europe (Wright and Rasmussen, 1998), different forms of N, including NH_4NO_3 and $NaNO_3$, were added to a variety of watersheds ranging from low N input (<3 kg ha^{-1} yr^{-1}) (Sogndal, Norway) to >18 kg N ha^{-1} yr^{-1} (Klosterhede, Denmark). Retention was very variable and not directly comparable to that at BBWM because of the different chemical forms of N. Retention of NH_4 at all the NITREX sites is >90% whereas retention of NO_3 is typically much lower.

TABLE IV

Yearly and cumulative retention of S and N resulting from the treatment of the West Bear Brook watershed at BBWM. The calculations use the reference stream as the natural experimental control, assuming that the flux from West Bear without treatment would have equaled those from East Bear. The differences between West and East Bear are inferred to be the response to treatment from which the annual and cumulative retentions are calculated.

Year	Cumulative N or S (eq ha^{-1}) from treatment	Annual N retention %	Cumulative N retention %	Annual S retention %	Cumulative S retention %
1989	0	0	0	0	0
1990	1886	94.0	94.0	86.3	86.3
1991	3791	81.7	87.8	72.8	79.5
1992	5603	80.9	85.6	73.6	77.6
1993	7415	77.9	83.7	66.0	74.7
1994	9227	78.4	82.7	41.4	68.2
1995	11039	78.0	81.9	63.0	67.3
1996	12851	80.8	81.7	36.8	63.0
1997	14663	81.3	81.7	33.7	59.4

The retention of N in West Bear is higher than expected based on watershed characteristics. McNulty *et al.* (1991) found that BBWM had forest floor properties such as higher % N, and lower lignin:N and C:N ratios compared to other New England sites, suggesting BBWM would be less retentive for added N. The relatively slow rates of N mineralization in coniferous forest soils of northern New England due to acidic soil conditions and high C:N properties may have been offset by relatively high foliar N concentrations. Wang *et al.* (this volume) report significantly greater N potential mineralization in the treated forest floor under hardwoods (the dominant forest type at BBWM) after three years of treatment, but no significant effect under softwoods. Because soil solutions from the treated watershed showed a gradual increase in NO_3 concentrations (Fernandez *et al.*, this volume), N cycling in the lower mineral soil may play a key role in the ecosystem-level processing of added N and subsequent N mineralization and nitrification.

A plot study adjacent to West Bear utilized HNO_3 treatments (Nadelhoffer et al., 1995). When added as dilute ^{15}N-enriched HNO_3, 14% of the added ^{15}N was sequestered in green leaves and wood, 15% of the N was sequestered in litter, forest floor, and top of the mineral soil, and 65% of the experimental NO_3-N was presumably retained in the lower mineral soil. More than 75% of the dry treatment NH_4-N was retained in the soil and forest floor in the West Bear treated watershed (Nadelhoffer *et al.*,1993, 1994, 1995). The increased NO_3 export in stream water (Kahl *et al.*, 1993; Norton *et al.*, this volume) was primarily from 'old' N, not N derived from the NH_4 treatments. Our $(NH_4)_2SO_4$ experiment appears to have initially stimulated nitrification of old N, rather than leaching of the new N, which was applied as NH_4.

3.3. WATERSHED FLUX OF S

The initial response for S after the beginning of treatment was also rapid and significant (Uddamari *et al.*, 1993). The increase of SO_4 (eq ha^{-1}) in West Bear was double the initial response for NO_3 and increased to almost 3-fold the N response by 1997 (Figure 5). With the exception of the dry year in 1995, the export of SO_4 has continued to increase relative to East Bear (Figure 5).

In contrast to the clear retention of N in both watersheds (Figure 4), the consistent net loss of SO_4 from East Bear (Figure 6) indicates that our estimate of dry S deposition as 2-fold wet may be too low. An adjustment for this factor would decrease the values of the response for East and West Bear individually, but would not change the experimental response (the difference between East and West Bear) shown by the black bars in Figure 5. The 'missing' input term for S may be S desorbed from soils, stored during prior years of higher S deposition. This possibility may be tested as we collect additional mass balance estimates, because 1995-97 have the lowest residual S in the mass balance term in East Bear. The period of this study has seen substantial declines in S concentrations in precipitation due to the implementation in the mid-1990s of Phase I of the 1990 Clean Air Act Amendments. The decline of SO_4 in East Bear over the last decade is concurrent with the decline in concentration of SO_4 in atmospheric deposition. This observation suggests close linkages between changes in atmospheric deposition and SO_4 concentrations in East Bear. Even though the amount of S stored in soils is large compared to the annual atmospheric flux, the labile S pool is comparatively small.

Retention of the treatment S was 86% in the first year, and has declined to 34% in 1997 (Table IV). Almost 60% of the treatment S has been retained from 1989 to 1997. Data from other watershed studies suggest that the loss of SO_4 may slow as soils are acidified from the added N (producing NO_3) coupled with the mobile anion SO_4. The acidification would increase the SO_4 adsorption capacity (Nodvin *et al.*, 1986). While the pHs of the O, E, and upper B horizons were likely too low to have been acidified appreciably by the treatment, acidification further along flow paths is clear from the stream chemistry (Norton *et al.*, this volume). Sulfur retention in soils is as inorganic S under both softwood and hardwood soils (Fernandez *et al.*, this volume). Previous work on plots adjacent to BBWM also showed that H_2SO_4 treatments increased SO_4 adsorption largely in the inorganic SO_4 fraction rather than ester or carbon-bonded SO_4 (Mitchell *et al.* 1994). This inorganic fraction was presumably adsorbed as a result of increased soil solution SO_4 concentrations and decreased pH. David *et al.* (1991a, 1991b) using laboratory column experiments, showed that a BBWM Spodosol adsorbed

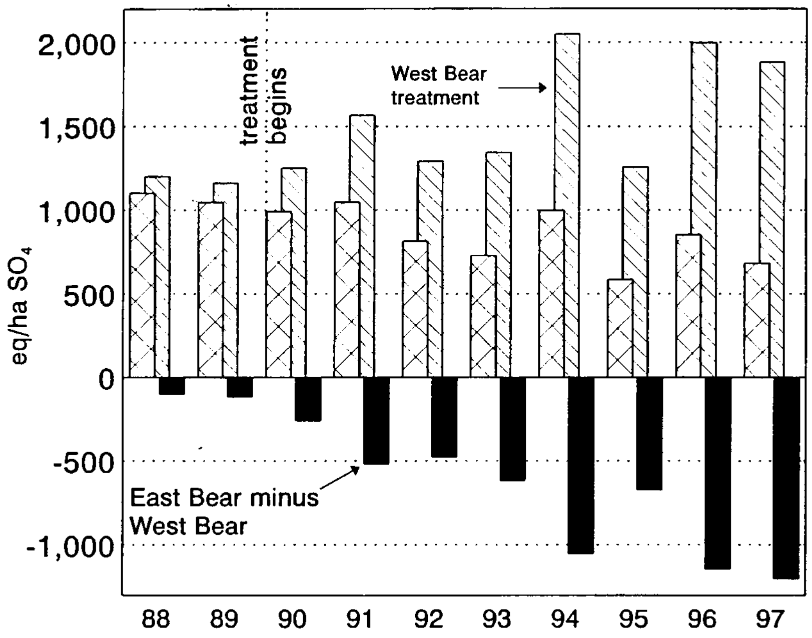

Fig. 5. S flux from East and West Bear watersheds.

SO_4 in the sesquioxide-rich B horizon. The majority of S at BBWM is in organic fractions, but the inorganic S pool is the most active pool, and apparently governs solution S flux (Dhamala and Mitchell, 1995).

4. Conclusions

Mass balance calculations for a treated and untreated watershed at the Bear Brook Watershed in Maine show that annual and cumulative retention of experimental N amendments has leveled off at about 80% after nine years of treatment. The export of N from the reference watershed has declined to near zero in just seven years, for unknown reasons. Retention of NH_4 is nearly 100%. Despite chronic additions of N and a relatively rapid response to treatments by NO_3 concentrations and export in West Bear, the majority of the N treatment is retained.

The annual retention of treatment S has declined to less than 34% after nine years, with the cumulative retention below 60% over the course of the experiment. Yearly flux is strongly influenced by hydrology, with greater retention of S in dryer seasons and years. The mass balance for S indicates that West Bear has lost increasingly greater percentages of S relative to East Bear, unlike the response for N. These responses are occurring in an environment of declining S emissions and deposition. Beginning in

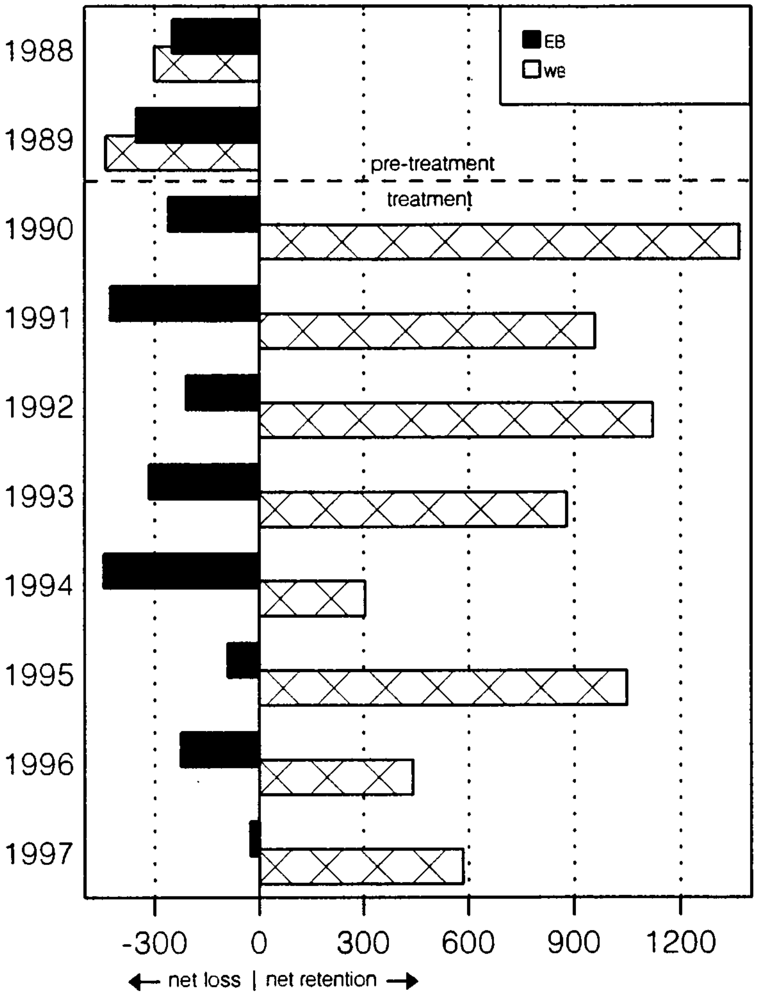

Fig. 6. Input-output budget for S in East and West Bear watersheds.

1995, N deposition became greater than S deposition for the first time. Despite this trend in deposition, both SO_4 and NO_3 concentrations in surface waters are declining in East Bear (Norton *et al.*, this volume) and region-wide (Mitchell *et al.*, 1996a; Stoddard *et al.*, 1998).

The contrasts between N and S input-output budgets reflect both the level of inputs and the different roles of biology in the response of these two elements. Increasingly smaller proportions of S are retained, and retention is largely abiotic. The majority of the N is retained in the watershed, presumably reflecting biological retention in the soil and the growing forest. Because of the character of the N retention, we expect recovery from elevated N deposition to be significantly longer than for S.

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