MINERAL SOIL AND SOLUTION RESPONSES TO EXPERIMENTAL N AND S ENRICHMENT AT THE BEAR BROOK WATERSHED IN MAINE (BBWM)

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Abstract. Buried mineral soil-bags and natural solutions were studied as indicators of forest ecosystem response to elevated N and S inputs at the Bear Brook Watershed in Maine (BBWM). The BBWM is the site of a paired watershed manipulation experiment in a northern New England forested ecosystem. The study includes two small (~10 ha each) catchments dominated by northern hardwood forests with red spruce in the upper elevations. Treatments consist of $(NH_4)_2SO_4$ applied to the West Bear watershed six times per year, increasing N and S deposition 3x and 2x above ambient values, respectively. Buried mineral soil-bag changes over time reflected both the native soil environment and the treatments. Most of the treatment effects on mineral soils were evident as higher inorganic S found in the treated watershed soils. Adsorbed SO_4 in the buried mineral soil-bags increased by approximately 40% under softwood stands and 50% under hardwood stands over the study period. Hardwood soil solutions responded with significant increases in NO_3 and SO_4 concentrations that resulted in accelerated cation leaching, primarily Ca and Al. Few differences that could be attributed to treatments were evident in soil solutions under softwoods. No treatment effects were evident in throughfall and stemflow chemistry.

1. Introduction

Atmospheric deposition of nitrogen (N) and sulfur (S) has received a great deal of public and scientific attention over the past two decades in the United States and Europe. One approach to studying the effects of elevated atmospheric N and S deposition is to artificially increase N and S loading to whole ecosystems. Sullivan (1997) pointed out the value of ecosystem manipulation experiments, particularly when available computer models are based on imperfect knowledge of ecosystem processes. Rasmussen and Wright (1998) discussed the role of whole-ecosystem manipulation experiments in helping us understand the complexity of ecosystems, and the linkages between field and laboratory findings. They suggested that insights gained from several major European studies of this type provided unexpected results at times that could not have been predicted from smaller-scale experiments. This approach was taken at the Bear Brook Watershed in Maine (BBWM) where a study has been conducted on a pair of forested stream catchments in eastern Maine for the past decade (Norton *et al.*, 1994). One forested catchment has received experimental treatments of N and S, in the form of $(NH_4)_2SO_4$, beginning in the fall of 1989. These chronic amendments of $(NH_4)_2SO_4$ have resulted in elevated stream water NO_3 and SO_4 concentrations, accompanied by increased leaching losses of base cations and aluminum (Al) (Norton *et al.*, 1994; Kahl *et al.* 1993).

Understanding forest ecosystem response to elevated N and S inputs requires understanding changes and transformations that occur in the soil. We have conducted a series of studies

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designed to evaluate the chemical signal resulting from experimental acidification in forest soils using lysimetry for soil solution collections. Plot studies in coniferous forest stands (Fernandez and Rustad, 1990) and northern hardwood stands adjacent to the BBWM watershed (Rustad *et al.*, 1993) have shown similarities in the effects of increased strong acid anion loading as well as differences that reflect vegetation type, form and rate of N and S amendment, and length of time for treatments.

The high heterogeneity of forest soils and soil solutions makes field studies particularly challenging, yet critical for us to integrate laboratory and small-scale research with whole ecosystem processes. Soil solutions usually require as much replication in space and time as resources can support. For soils, one approach that was developed as part of the research at BBWM has been the use of homogenized forest soil materials incubated *in situ* so that soil chemical properties at the origin of the experiment are known, and soil response to treatments can occur under field conditions. Earlier findings published using this buried mineral soil-bag technique on plot-scale acidification irrigation experiments adjacent to the BBWM are described in David *et al.* (1990), Mitchell *et al.* (1994), and Rustad *et al.* (1996). This technique has proven useful in identifying responses of soil properties and processes to treatments. Coupled with soil solution chemical data, results of the buried mineral soil-bags provide insight into the manner in which N and S are accumulated, transformed, and released by this ecosystem. The objective of this paper is to describe the multiple-year responses of buried mineral soil-bags and natural solutions, primarily soil solutions, to the effects of elevated N and S inputs in both the treated and reference watersheds at BBWM.

2. Methods

2.1. STUDY SITE

The study site is located in eastern Maine (44°52' N lat., 68°6'W long.) approximately 50 km from the Atlantic Ocean. The site lies on the southeast slope of Lead Mountain, with total relief of 210 m and a maximum elevation of 475 m. Two nearly perennial, low DOC, low ANC streams (East and West Bear Brook) drain 10.2 and 10.7 ha contiguous watersheds. Vegetation at the site is dominated by northern hardwoods (*Fagus grandifolia* Ehrb., *Acer rubrum* L., *Acer saccharum* Marsh., *Betula alleghaniensis* Britt., *Betula papyrifera* Marsh., and *Acer pennsylvanicum* Marsh.) with stands of softwoods (*Picea rubens* Sarg., *Abies balsamea* Mill., and *Tsuga canadensis* (L.) Carr.) at higher elevations. Soils are coarse, loamy, mixed, frigid Typic Haplorthods developed on till. Bedrock consists of quartzites and meta-pelites intruded locally by granite.

2.2. WATERSHED MANIPULATION

Chemical additions of N and S, as $(NH_4)_2SO_4$, were delivered bimonthly via helicopter to the West Bear watershed beginning in November 1989 and continuing through the period of data reported. The adjacent untreated East Bear watershed serves as a reference. Total

experimental loadings were 1800 eq ha^{-1} yr^{-1}, which is 2x and 3x the ambient wet-plus-estimated dry deposition of S and N, respectively (Rustad *et al.*, 1994). These rates were chosen to make total S deposition to the West Bear watershed similar to that in the more heavily polluted regions in the U.S. (NADP, 1990). Total N deposition was approximately 1.5x that of the highest estimated wet-plus-dry deposition in the U.S. (NADP, 1990), but was less than 70% of the total N deposition in areas of central Europe (Dise and Wright, 1992).

2.3. Experimental Design

Three 15 x 15-m plots were located in portions of each watershed that were dominated by hardwood and mixed hardwood stands, referred to here collectively as "hardwoods". One 15 x 15-m plot was located in the portion of each watershed dominated by softwoods, for a total of four plots per catchment. Mineral soil response to the treatments was investigated using a buried mineral soil-bag approach (David *et al.*, 1990, Mitchell *et al.*, 1994). This method has the advantage of reducing the inherent variability of forest soils, thereby providing a more sensitive index of soil response to treatments. Briefly, bulk mineral soil (Tunbridge series; refer to David *et al.* (1990) and Mitchell *et al.* (1994) for initial chemistry data) was collected from a representative pedon near the East Bear watershed, thoroughly homogenized, and passed through a 6 mm sieve. Field-moist soil, equivalent to ~300 g air-dry soil, was placed in 15 x 15 x 2.5 cm nylon mesh (250 μm) bags, and sewn closed. During the fall of 1987, 25 soil-bags were installed in a corridor across each plot. The bags were installed by carefully opening a slit in the forest floor with a knife and inserting the mineral soil-bags at the top of the mineral soil, just below the O horizon. The forest floor was then replaced relatively intact. Three to four bags from each plot were collected annually in October from 1990 through 1993.

Soil chemical analyses on air-dried soil included: pH in water and 0.01 M $CaCl_2$, unbuffered 1 N NH_4Cl exchangeable cations (Robarge and Fernandez, 1986), and exchangeable H and Al (Thomas, 1982). Effective cation exchange capacity (CEC) was determined as the sum of exchangeable base cations plus exchangeable acidity. Base saturation (BS) was expressed as the sum of exchangeable base cations as a percentage of the calculated CEC. Total C and N were determined using a Perkin-Elmer 2400 CHN analyzer. Sulfur constituents were determined on freeze-dried samples. Total S (S) was measured using a LECO SC-132 analyzer (David *et al.*, 1989), and then fractionated into hydroiodic-acid-reducible S (HI-S), Zn-HCl-reducible S (Zn-HCl-S) (Landers *et al.*, 1983), and phosphate-extractable SO_4 (SO_4-S) (Fuller *et al.*, 1985). Hydroiodic-acid-reducible S includes all non-carbon-bonded S; Zn-HCl-reducible S includes non-sulfate inorganic S such as sulfide, elemental S, and thiosulfate. Carbon-bonded S (CBS), which includes amino acids, sulfones, and sulfonates (Strickland and Fitzgerald, 1985), was calculated as the difference between total S and HI-S. Ester sulfate was calculated as the difference between HI-S and the sum of phosphate-extractable SO_4 plus Zn-HCl-reducible S.

Soil solutions were collected from two pairs of ceramic cup tension lysimeters per plot, and three zero-tension lysimeters per plot (Figure 1). One lysimeter from each pair of tension lysimeters was located in the upper Bhs horizon directly below the E horizon and the second

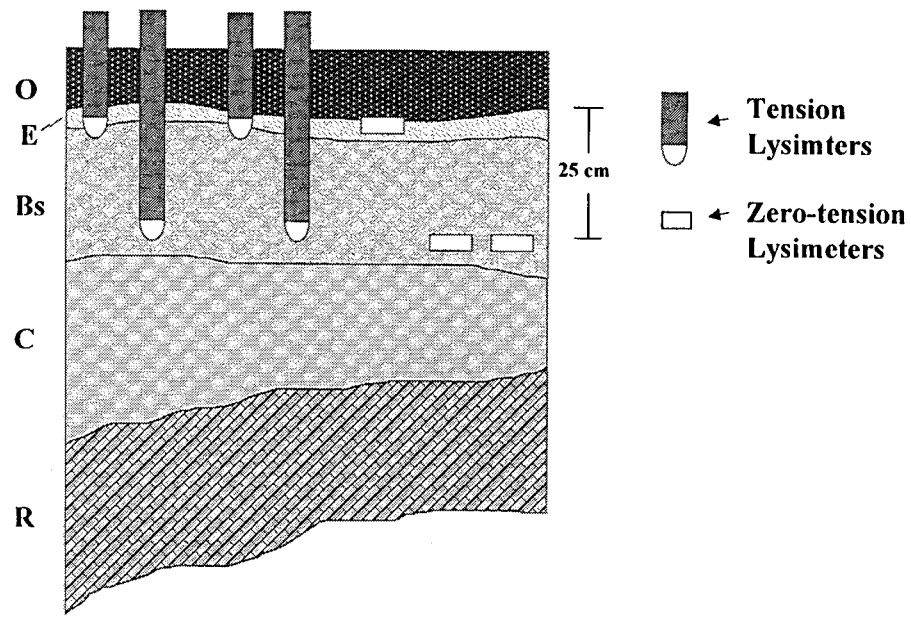

Fig. 1. Schematic diagram of lysimeter placement for an individual plot at BBWM. The soil morphology depicted is modal for the ecosystem with a range of depths at BBWM for solum material above bedrock (R).

was located at 25 cm below the mineral soil surface in what was typically the Bs horizon. In addition, one of the three zero-tension lysimeters was located directly below the O horizon and the other two were co-located 25 cm below the mineral soil surface. Two lower zero-tension lysimeters were employed to improve collection efficiency at the lower depth. This totaled seven soil solution collectors per plot. Soil solutions were collected tri-weekly during the initial two years of the study in order to characterize chemistry, and less frequently thereafter. Soil solution volumes were measured directly in the field, and samples were bulked by plot and depth for chemical analyses. Samples were stored at 4°C in polyethylene bottles until analyzed. Within seven days of collection, pH and acid neutralizing capacity (ANC) were measured and subsamples were filtered through a 0.4 μm filter before analysis of cations and anions, and through a 0.7 μm glass fiber filter for dissolved organic carbon (DOC). Solution pH was measured potentiometrically, ANC by automated titration with Gran Plot, base cations by flame atomic absorption spectroscopy, Al by furnace atomic absorption spectroscopy, and anions by ion chromatography (Hillman *et al.*, 1986). Sum of base cations (SBC) was calculated as the sum of calcium (Ca), magnesium (Mg), potassium (K), and sodium (Na). Sum of acid anions (SAA) was calculated as the sum of SO_4, NO_3, and Cl. Ammonium and Si were analyzed by automated colorimetry (Anonymous, 1986 a,b), and DOC by CO_2 liberation and infrared analysis (American Public Health Association, 1981).

In each plot, bulk throughfall was collected using three funnel-type (16.5 cm diam.) collectors (Eaton *et al.*, 1973) per plot during the snow-free months and a single polyethylene bucket (24 cm diam.) per plot during the snow season. Samples were collected every three weeks, bulked by plot, and processed by the same methods as described for soil solutions. Stemflow was collected from a 5 x 5 m area immediately downslope from each watershed plot.

All trees > 5 cm DBH within these areas were fitted with stemflow collars. Samples were collected every three weeks, bulked by plot, and processed by the same methods as described for soil solutions.

All solution collections were initiated in 1988. Throughfall and stemflow collections continued through 1992, and soil solutions through 1997 although with infrequent samples collected after 1992. Here, we report on throughfall + stemflow results from two years of pre-manipulation monitoring (1988 and 1989) and three years of treatment applications (1990 through 1992), and soil solution results from two years of pre-manipulation monitoring (1988 and 1989) and six years of treatment applications (1990 through 1995) for overall mean comparisons. Time series graphs were limited to the 1990 to 1992 treatment period because of the infrequent sample collections after 1992, with only one field season collection per year for certain sites.

2.4. Statistical Analysis

All data were tested for normality using a Kolomogorov test (Conover, 1980). Data that did not fit a normal distribution were transformed logarithmically and retested for normality. This transformation proved adequate in all cases. Differences between catchments, horizons, vegetation types, and pre-treatment versus treatment periods were determined using a t-test. Analysis of variance and mean separations were performed using the GLM procedure. All statistical analyses were performed on the Statistical Analysis System (SAS, 1985) at a significance level of 0.05, unless otherwise noted.

3. Results and Discussion

3.1. The Buried Mineral Soil-Bags

Data from 1990 through 1993 from the buried mineral soil-bag experiment were pooled by watershed and vegetation type (Table I). All homogenized soil samples started with a nearly identical chemical composition and were installed beneath the O horizon at the surface of the mineral soil. David *et al.* (1990) showed that variation among individual soil-bags prior to installation was exceedingly small. These mineral soil-bags have the advantage of detecting relatively subtle treatment effects in the mineral soil, but results will also be influenced by local site conditions (*i.e.*, soil and vegetation). The buried mineral soil bag technique has previously proven to be a valuable tool in BBWM research (Mitchell *et al.*, 1994, David *et al.*, 1990, Rustad *et al.*, 1996).

Even though the buried mineral soil-bags had been exposed to these environments for only a few years, significant differences were evident, reflecting the influence of soil types, forest cover and treatment. The most consistent difference in buried mineral soil-bag chemistry between watersheds was that of higher concentrations of S in West Bear. Total S, SO_4-S, and HI-S were primarily responsible for the sequestration of added S in the treatments. The increase in HI-S was due to extractable SO_4-S and not ester-SO_4, which did not change, similar to results reported in an adjacent plot experiment using wet chemical manipulations

TABLE I
Mean buried soil bag chemistry by catchment and vegetation type for 1990-1993

	Hardwood				Softwood			
	East Bear		West Bear		Esat Bear		West Bear	
Ca	0.21	a	0.25	a	0.13	b	0.14	b
Mg	0.04	a	0.04	a	0.03	b	0.03	b
K	0.06	A	0.05	aB	0.06	A	0.03	bB
Na	0.03		0.03		0.03		0.03	
SBC	0.34	a	0.37	a	0.24	b	0.23	b
pH (H_2O)	4.84	aA	4.76	aB	4.69	bA	4.44	bB
pH ($CaCl_2$)	4.22	a	4.20	a	4.13	bA	3.96	bB
CEC	5.47		5.56	a	5.67	A	6.51	bB
BS	4.26		4.27	a	2.90		2.52	b
Al	3.63	a	3.87	a	4.09	bA	5.49	bB
TC	38.4		38.5		37.3		39.0	
TN	1.8		1.8		1.7		1.7	
C/N	21.5		21.7		21.7	A	22.5	B
TS	268	aA	301	B	285	bA	319	B
SO_4-S	43.7	aA	67.4	B	51.8	bA	72.9	B
HI-S	110	A	135	B	115	A	141	B
Zn-S	8.76		8.52		8.72		8.76	
Ester-S	57.5		59.4		54.5		59.0	
CBS	158		165		170		178	
n	38-40		38-39		13-14		13	

Units are $cmol_c\ kg^{-1}$ for base cations, Al, and CEC; % for TC, TN, and BS; and $mg\ kg^{-1}$ for S constituents. SBC is the sum of base cations. Lower case letters indicate significant differences between vegetation types within a catchment. Upper case letters indicate significant differences between catchments within a vegetation type. Differences between vegetation types and catchments were determined using a t-test.

(David *et al.*, 1990; Mitchell *et al.*,1994). Mitchell *et al.* (1998) summarized results for forest soil S from several chemical manipulation studies in the Adirondack Mountains of New York. They showed that chemical manipulations with S of forest soils in this region consistently showed a response in extractable SO_4 and not organic S, despite organic S accounting for >71% of total soil S. Results reported here for BBWM are comparable, with BBWM mineral soil-bags having >77% of total S as organic S. Figure 2 shows the annual mineral soil-bag results for extractable SO_4-S. Most of the increase in adsorbed SO_4-S over the treatment period occurred in the first year for softwoods and within two years for the hardwood sites. Relatively small changes occurred in the buried mineral soil-bag extractable SO_4-S concentrations in 1992 and 1993. This suggests that after the first two years the sorption process, which is concentration and pH dependent, was in steady state for these buried mineral soil bags. In soil-bags from the plot-scale chemical manipulation study adjacent to the watershed, extractable SO_4-S increased with each year of treatment in that

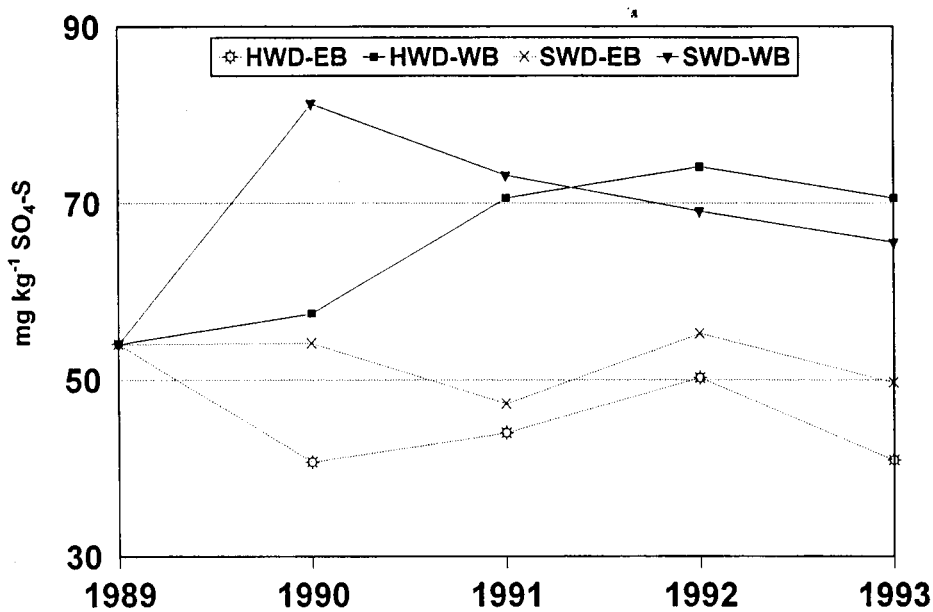

Fig. 2. Soil extractable inorganic SO_4-S from the buried mineral soil-bags over the four years of the experimental treatments at BBWM. The 1989 data represent the initial bulk soil characteristics according to David *et al.* (1990) and the 1990 data represent mineral soil-bag concentrations one year after installation. (EB=East Bear, WB=West Bear, HWD=Hardwood, SWD=Softwood)

study, reaching concentrations of 31 mg kg^{-1} SO_4-S in the low S treatments compared to the controls (Mitchell *et al.*, 1994). This is similar to the concentration of extractable SO_4-S in the treatment watershed soil-bags reported here, which increased by 24 mg kg^{-1} SO_4-S under hardwoods, and 21 mg kg^{-1} SO_4-S under softwoods. Both the whole watershed and the adjacent plot study had similar loadings of S, but the method of application differed (liquid versus dry salt), and this probably contributed to the differences in accumulation patterns. Fernandez and Rustad (1990) showed that in a Maine coniferous forest the form of S treatment used influenced soil response in experimental acidification studies.

Similar to what we reported in the external plot study (Rustad *et al.*, 1996), no changes were observed in buried mineral soil bag organic S constituents or in total N at BBWM due to treatments. Although organic forms of both N and S dominate soil pools, the four year treatment period did not affect concentrations of either in the soil-bags. Nitrogen is also primarily in the organic form in these soils, and small changes in labile phases of N would be difficult to detect from total N measurements in these soil-bag experiments. Over longer time periods it is possible that changes in organic N and S pools could be detected. Wang and Fernandez (this issue) showed that differences exist between East and West Bear in measures of forest floor N dynamics. White *et al.* (this issue) showed evidence of greater foliar N concentrations in West Bear compared to East Bear, although no growth responses were detected. These results, coupled with soil solution and stream water responses, indicate differences exist between watersheds in N dynamics, despite the lack of response of total N in the buried mineral soil-bags.

Softwood stands, compared to hardwoods, produced mineral soil-bag chemistries that were significantly lower in Ca, Mg, pH, and base saturation. Mineral soil bags installed under

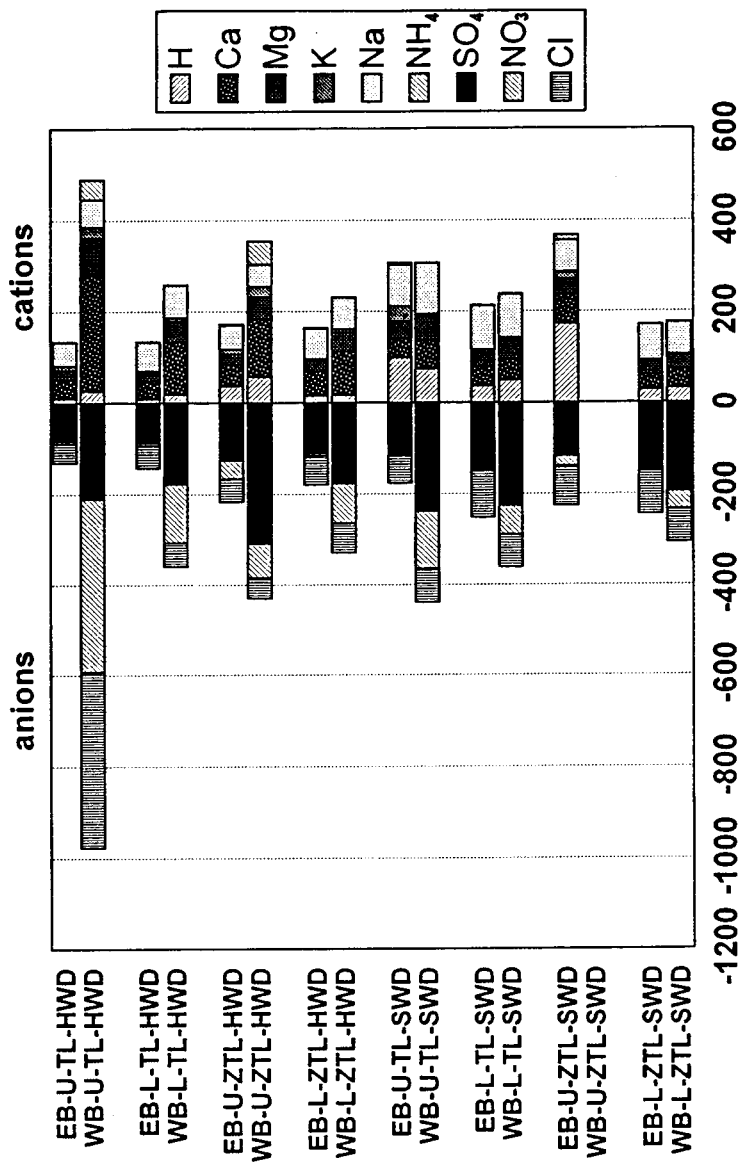

Fig. 3. Ion balances for tension and zero-tension lysimeter soil solutions by vegetation type, watershed, and soil depth and mean stream chemical composition for 1992. (EB=East Bear, WB=West Bear, U=Upper Lysimeters, L=Lower Lysimeters, TL=Tension Lysimeter, ZTL=Zero-tension Lysimeter, HWD=Hardwood, SWD=Softwood)

TABLE II
Soil solution chemistry for combined treated and reference watershed by horizon, catchment and vegetation type for the pre-manipulation period 1988-1989

	Hardwood				Softwood			
	East Bear		West Bear		East Bear		West Bear	
UPPER								
H	10		8	a	20		35	b
Ca	59	Aa	91	a	88	b	65	b
Mg	24	a	28	a	37	Ab	48	Bb
K	10	a	14		22	b	18	
Na	47	a	55	a	85	Ab	132	Bb
SBC	140	Aa	189	a	232	Bb	263	b
NH_4	1.5		1.9		1.3		2.2	
Al	17	a	16	a	34	Ab	90	Bb
Si	84		92	a	73	A	108	Bb
SO_4	87	a	86	a	146	Ab	219	Bb
NO_3	16	a	59	a	4	Ab	170	Bb
Cl	40	a	37	a	76	b	102	b
SAA	142	Aa	181	a	226	Aa	491	Bb
ANC	2		11	a	4		-30	b
DOC	524	a	490		915	Ab	533	B
n	21-29		28-32		9-10		9-11	
LOWER								
H	4	a	6	a	26	b	44	b
Ca	69	A	87	Ba	71		56	b
Mg	22	a	25	a	32	Ab	46	Bb
K	14	a	9		16	Ab	7	B
Na	66	a	62	a	96	Ab	127	Bb
SBC	171	a	183	a	215	b	235	b
NH_4	1.2		0.9		0.7		2.8	
Al	10	a	12	a	31	Ab	65	Bb
Si	81		77	a	86	A	123	Bb
SO_4	99	a	96	a	155	b	193	b
NO_3	9	A	37	Ba	3	A	105	Bb
Cl	45	a	48	a	83	b	108	b
SAA	153	Aa	181	Ba*	242	Ab	406	Bb
ANC	23	a	14	a	-18	b	-43	b
DOC	229	a	268	a	747	b	786	Bb
n	20-29		33-35		10-11		10-12	

Upper case letters indicate significant differences between the catchments within vegetation type. Lower case letters indicate significant differences between vegetation types within a catchment. Upper = upper tension lysimeter data; Lower = lower tension lysimeter data. Units are umol/L for Al and Si, umol C/L for DOC, and ueq/L for all others.

TABLE III

Soil solution chemistry by horizon, catchment and vegetation type for the treatment period 1990-1995

	Hardwood				Softwood			
	East Bear		West Bear		East Bear		West Bear	
UPPER								
H	11	a	21		56	b*	57	*
Ca	41	Aa*	152	Ba*	51	*	53	b
Mg	20	Aa*	58	Ba*	34	Ab	62	Bb*
K	8	Aa	17	Ba	16	Ab	7	Bb*
Na	51	a	58	a	88	Ab	96	Bb*
SBC	120	Aa*	286	B*	190	Ab*	219	B*
NH_4	0.7	A	13.5	B	1.4	A	1.8	B
Al	19	Aa	48	Ba*	46	Ab*	103	Bb
Si	77	A	91	Ba	91	A	107	Bb
SO_4	81	Aa	195	Ba*	140	Ab	246	Bb
NO_3	8	Aa*	151	Ba*	1	Ab	157	Bb
Cl	46	a	43	a	74	Ab	85	Bb
SAA	135	Aa	390	Ba*	216	Ab	488	Bb
ANC	-4	a*	-15	a*	-67	b*	-66	b*
DOC	396	a	525	a	1582	Ab	699	Bb*
n	68-85		63-80		21-25		22-25	
LOWER								
H	8	Aa*	14	Ba*	36	Ab	55	Bb
Ca	43	*	90	Ba	43	*	50	b
Mg	19	Aa*	37	Ba*	30	Ab	46	Bb
K	5	Aa*	7	B*	10	Ab*	7	B
Na	58	a*	65	a	88	b	88	b
SBC	124	Aa*	199	B	171	b*	190	
NH_4	0.6	a	1.4		0.2	Ab	1.6	B
Al	16	Aa*	34	Ba*	36	Ab	79	Bb
Si	69	a	72	a	77	Ab	99	Bb*
SO_4	88	Aa	162	Ba*	154	Ab	224	Bb*
NO_3	5	Aa	65	Ba*	1	Ab	74	Bb
Cl	47	a	51	a	87	b	70	b*
SAA	140	Aa*	279	Ba*	241	Ab	369	Bb
ANC	-2	Aa*	-10	Ba*	-40	Ab*	-63	Bb*
DOC	266	a	220	a	520	Ab*	754	Bb
n	76-84		83-94		21-24		24-30	

Upper case letters indicate significant differences between the catchments within vegetation type. Lower case letters indicate significant differences between vegetation types within a catchment. '*' indicates a significant difference between the pre-treatment and treatment period chemistry using a standard t-test. Upper = upper tension lysimeter data; Lower = lower tension lysimeter data. Units are umol/L for Al and Si, umol C/L for DOC, and ueq/L for all others.

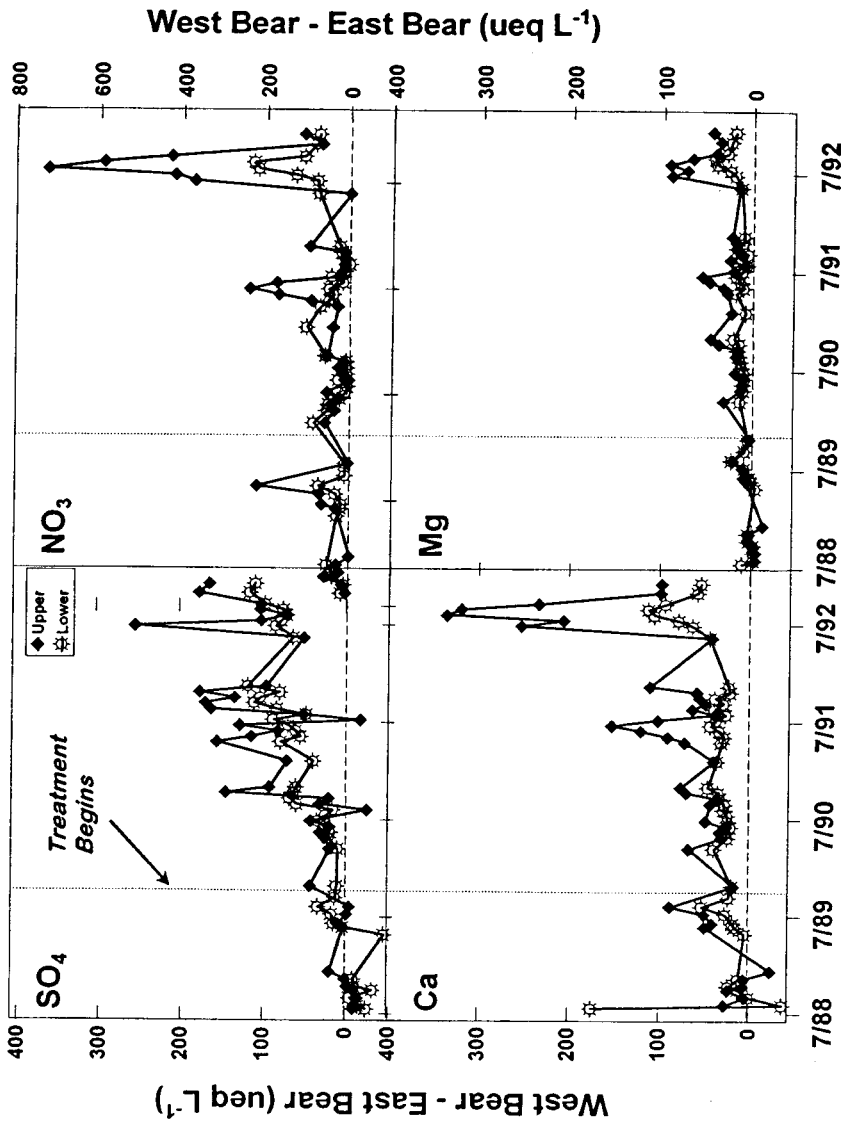

Fig. 4. Difference diagrams for soil solution time series concentrations at BBWM. Data are the differences between West Bear (the treatment watershed) minus East Bear (the reference watershed) expressed as ueq L^{-1}.

TABLE IV
Volume-weighted mean throughfall and stemflow chemistry by for combined treated and reference by vegetation type for the period 1988 through 1992

	Throughfall				Stemflow			
	Hardwood		Softwood		Hardwood		Softwood	
H	22	a	72	b	1	a	154	b
Ca	22	a	39	b	42	a	105	b
Mg	15	a	24	b	20	a	41	b
K	41	a	43	a	419	a	71	b
Na	24	a	52	b	30	a	80	b
SBC	103	a	185	b	509	a	297	a
NH_4	11	ab	10	a	5	a	10	a
Al	0.3	a	0.8	b	0.3	a	1.6	b
Si	2.6	a	1.2	b	46	a	2.3	b
SO_4	56	a	109	b	97	a	236	b
NO_3	20	a	43	b	12	a	48	b
Cl	31	a	65	b	40	a	93	b
SAA	108	a	218	b	149	a	377	b
ANC	-8	a	-78	b	294	a	-122	b
DOC	475	a	886	b	1152	a	2421	b
n	455-466		143-151		146		82-90	

Lower case letters indicate significant differences between vegetation types. Units are umol/L for Al and Si, umol C/L for DOC, and ueq/L for all others.

softwood stands also had higher concentrations of Al. Because differences between forest types were evident in both East and West Bear watersheds, we attribute these differences to the acidifying influences of coniferous litter on chemical cycling, and higher dry deposition inputs under coniferous canopies (Rustad *et al.*, 1994).

Differences in buried mineral soil-bag properties that existed between watersheds in the same forest type reflected experimental enrichment with N and S, as well as possible differences in native soil characteristics between these two watersheds that pre-date the treatments. Differences attributable to watershed or treatment effects were few. Both forest types had significantly lower exchangeable K and pH, and higher inorganic SO_4-S, in West Bear compared with East Bear. Softwood buried mineral soil-bags also had significantly higher exchangeable Al in West Bear, which resulted in a significantly higher CEC because CEC was calculated by summation. Softwood mineral soil-bags had significantly higher C/N ratios in West Bear compared to East Bear, but differences were small and likely not important to soil processes.

3.2. TENSION, ZERO-TENSION, AND STREAM COMPARISONS

Tension and zero-tension lysimeters responded to treatments similarly in this study. Figure 3 shows mean concentrations for both hardwood and softwood stands, upper and lower lysimeter depths, and includes both zero-tension and tension lysimeters for 1992. Data for 1992 were used for this comparison because it was the last year of a full schedule of collections, and should best reflect any differences due to treatment. Concentrations of NO_3 and SO_4 were greater in tension and zero-tension soil solutions in West Bear than in East Bear. Under hardwood cover, increased Ca concentrations were the most prevalent changes in cation concentrations as a result of the increased strong acid anions, which is consistent with higher exchangeable Ca found in buried mineral soil-bags under hardwood stands as compared with softwoods. Concentrations of all base cations increased in softwood stand soil solution. Sodium increased as much as other cations, much more so than under hardwoods. Higher Na in softwood soil solutions likely reflected a higher marine aerosol capture efficiency by softwood canopies compared with hardwood stands (Table I). Soil solutions collected by tension lysimeters in the upper soil profile under hardwoods in West Bear had uniquely high concentrations of NO_3 and Cl that reflect some combination of treatment response and natural variability. This was only evident at the end of the study period reported here.

Stream water had lower H concentrations than soil solutions, but was otherwise relatively similar to soil solutions in ionic composition (Figure 3). No charge was assigned to dissolved Al and therefore its contribution to charge balance is not shown in Figure 3 but is discussed elsewhere. Further evaluations of stream response are in Norton *et al.* (this issue). Nitrate concentrations East Bear Brook were near detection limits, similar to the lack of NO_3 in soil solutions throughout East Bear. However, West Bear stream water NO_3 concentrations were higher than East Bear, consistent with higher NO_3 concentrations evident in soil solutions throughout this watershed. The similarities in stream and soil solution chemistries reflect linkages between stream water and soil chemical response within the watershed. Soil solutions, particularly from hardwood sites, were chemically different in West Bear as was stream water, with higher concentrations of NO_3, SO_4 and other solutes. Hardwood soil

solutions in 1992 had notably higher Ca concentrations in West Bear but softwoods did not. These differences, if sustained, suggest a closer linkage between the hardwood components of the West Bear watershed and stream response to treatments, because Ca also dominated increased cation concentrations in West Bear stream water chemistry. In the following sections, only tension lysimetry will be used to define responses because of a higher collection efficiency, particularly during dry periods.

3.3. PRE-TREATMENT SOIL SOLUTIONS

Soil solutions were evaluated for two years prior to the initiation of treatments to characterize their chemistry and identify pre-existing differences between catchments. In pre-treatment soil solutions, Ca and Na were the dominant cations (on a charge equivalent basis) and SO_4 and Cl were the dominant anions (Table II). Sulfate dominated the inorganic anions in all solutions with low NO_3 concentrations attributable to biological immobilization. The strong contribution of Na and Cl to the chemistry of these solutions is attributable to the significant influence of marine aerosols, discussed below.

Soil solutions collected from under softwood versus hardwood forest types differed markedly. Softwood soil solutions had consistently higher concentrations of most solutes and a lower ANC, except for ANC in East Bear hardwoods where there was no significant difference. These results are consistent with other studies and reflect the increased efficiency in aerosol capture by softwood canopies (Freedman and Prager, 1986; Shibata and Sakuma, 1996) and the greater leaching losses of base-poor organic acids and DOC from coniferous litter (Berg and Staaf, 1987; Blair, 1988; Blair *et al.*, 1990; Bockheim *et al.*, 1991). Nitrate concentrations were more variable. In East Bear, soil solution NO_3 concentrations were typically higher in the hardwood forest type (Table II), reflecting a better litter quality from hardwoods that could support more rapid N mineralization and subsequent nitrification (Blair, 1988: Bockheim *et al.*, 1991; Berg and Staaf, 1987). Conversely in West Bear, soil solution NO_3 concentrations were significantly higher in the softwood forest type than in hardwoods. This may reflect greater inputs of wet and dry deposition to the West Bear softwood plot compared with all other plots, or lower rates of biological immobilization of N in the soil. Higher rates of N deposition would be an explanation consistent with the evidence for higher values of Na, Cl, and SO_4 in West Bear softwood soil solutions compared to all other plots.

Several years of pre-treatment stream chemistry and hydrology for West and East Bear streams indicated that these watersheds were well paired for a watershed manipulation experiment (Norton *et al.*, 1994). In addition, Wang and Fernandez (this issue) reported a relatively comparable distribution of both soil and forest types between West and East Bear watersheds. Nevertheless, soil solution data suggest that some differences in N status may have existed between these two watersheds prior to the onset of treatments, although the pre-treatment record is relatively short. West Bear softwood stands had significantly higher soil solution NO_3 concentrations than East Bear prior to treatments, and both forest types in West Bear had significantly higher soil solution SO_4 and Cl concentrations compared to East Bear. These differences may reflect differences in dry deposition not evident in our throughfall data discussed below, or other undefined factors. Higher anion concentrations in West Bear compared to East Bear appeared to be balanced by greater Ca concentrations in hardwoods.

Given the high inherent variability of soil solution chemistries, particularly in forests, and the limited sampling sites in this study, caution is urged in drawing conclusions from these results. This is particularly true for softwood stands represented by only one plot in each watershed. The characteristics of the softwood plot data are consistent with our understanding of forest type effects on ecosystem processes from the literature, and we believe these data are useful if interpreted with caution. Identifying differences between watersheds that pre-date the beginning of whole ecosystem manipulations is critical for making informed interpretations of ecosystem response, and determining the magnitude of that response.

3.4. Soil solution response to treatments

West Bear hardwood soil solution concentrations of H, Ca, Mg, SBC, Al, SO_4, NO_3, SAA, and ANC were all greater, most significantly, than those from East Bear and than the pre-manipulation values from West Bear. Large relative concentration increases occurred in hardwood upper soil solutions for Ca (67%), Mg (107%), Al (200%), SO_4 (126%), and NO_3 (156%) (Tables II and III). Calcium in hardwood soil solutions was 53% of the increase in upper lysimeter base cation concentrations; Mg was 20%. Similar but smaller changes occurred in the lower soil solutions. Thus, applications of NH_4 induced an increase in soil solution NO_3 export, and SO_4 applications induced increased concentrations of SO_4. An interesting conclusion that can be drawn is that although NO_3 export can be attributed to both hydrological properties of soil macropore flow and the signature N saturation excess over biological demand, NH_4 was still retained. This can be partly attributed to simple cation exchange, but implies that even as N saturation conditions in this soil develop, this acid forest soil may not yet be saturated with respect to NH_4. Similar results were reported by Fernandez and Rustad (1990), and more recently by Emmet *et al.* (1998) in European spruce forests.

Increased cation concentrations in hardwood soil solutions were dominated by Ca and Al. Increased soil solution concentrations of base cations would be expected because NH_4 most readily exchanges for base cations in forest soils (Matschonat and Matzner, 1996). East Bear hardwood soil solution concentrations of Ca, Mg, NO_3, SBC and SAA were significantly lower than West Bear during the treatment period (Table III), and compared to East Bear hardwood soil solution data during the pre-treatment period (Table II). ANC behaved similarly but differences were not statistically significant from West Bear. Concentrations of most solutes were relatively constant with depth in the hardwood sites with the notable exception of inorganic N. Decreasing N with depth in the soil was attributed to biological immobilization, with decreasing DOC reflecting illuvial processes and mineralization.

Increased leaching of NO_3, SO_4, and base cations was also reported in Rustad *et al.* (1993, 1996) from the plot-scale experimental acidification study adjacent to the hardwood stands of the paired watersheds at BBWM. Wet treatments were H_2SO_4 and HNO_3 solutions. That study, using H_2SO_4 and HNO_3 additions, showed a similar pattern of NO_3 and SO_4 attenuation with depth in soil solutions as reported here for the whole watershed manipulations with $(NH_4)_2SO_4$, despite differences in the form of the treatment. Most soil solution chemical responses to the H_2SO_4 and HNO_3 additions fully recovered within two years after treatments ceased (Rustad *et al.*, 1996).

West Bear softwood soil solution data had an inconsistent response in cations compared with

hardwood data. No significant differences were found in Ca concentrations in West Bear soil solutions when compared with either the pre-manipulation data, or with East Bear softwood soil solutions during the treatment period. Magnesium and Na concentrations were significantly greater, and K concentrations were significantly less, in West Bear compared to East Bear during the treatment period. This resulted in no significant differences in SBC for lower lysimeters, and a small increase in SBC in the upper lysimeters attributable mostly to Mg. Magnesium also significantly increased compared to pre-treatment means, while both K and Na significantly declined. The lack of response in softwood soil solution Ca could reflect lower soil exchangeable Ca concentrations under softwoods. Lower exchangeable soil Ca supply could be due to long-term exposure to canopy induced higher rates of acidic deposition, and slower rates of Ca resupply from organic matter mineralization under softwoods, both resulting in limited labile Ca and no additional Ca depletion due to treatments. Evidence for a depletion of Ca has been mostly reported for coniferous sites in the northeastern U.S. (Shortle and Smith, 1988; Lawrence *et al.*, 1995, 1997). Our data suggests continued Ca depletion in the BBWM coniferous forest soils may be unlikely and that continued acidification would result in increased Al and Mg leaching. Indeed, longer term data from West Bear Brook indicates a depletion of Mg relative to Ca as acidification has proceeded (Norton *et al.*, this issue). Magnesium deficiency due to acidic deposition has been demonstrated to be a major concern in coniferous forests in central Europe that also have been exposed to longer histories of higher deposition (Ulrich, 1989), but we are not aware of evidence for widespread Mg deficiencies evident in eastern North America. For both NO_3 and SO_4, softwood soil solutions during the treatment period were surprisingly similar to pre-treatment soil solution values, except for a significant increase in lower soil solution SO_4 concentrations.

In East Bear, softwood soil solutions had higher concentrations than hardwoods for most solutes except for NO_3, NH_4 and Ca in the lower soil (Table III). Dissolved organic carbon concentrations were particularly high in the upper soil solutions (1582 μmol L^{-1}), and dramatically less in lower soil horizons (520 μmol L^{-1}), as expected in illuvial Spodosol B horizons. East Bear softwood soil solutions during the treatment period had lower Ca, Mg, and K concentrations but only Ca was significantly lower, and this appeared to be coupled with significantly greater concentrations of Al and a lower ANC.

3.5. Soil solution response time series

Soil solution responses to treatments were most evident in hardwood stands as already described above. Figure 4 illustrates the characteristics of hardwood soil solution response over time for selected solutes in tension lysimeters. These time series are presented as difference diagrams calculated by subtracting East Bear (reference watershed) concentrations from West Bear (treated watershed) concentrations for each collection. Therefore, values increasingly different from 0 μeq L^{-1} indicate changing concentrations in West Bear soil solutions in response to the treatment relative to East Bear, because both watershed soil solution chemistries were comparable prior to treatments. No trends were evident for either forest type in soil solutions over time for NH_4, Cl, Na, and H. This further illustrates a continuing NH_4 uptake in the soil despite increasing NO_3 mobilization. Figure 4 shows the trends over time for those solutes with clear responses to treatments, all illustrating increasing

concentrations under hardwoods in response to the $(NH_4)_2SO_4$ additions. These trends were particularly evident for SO_4 and Ca, and all solutes that responded to the treatment had greater concentration increases in upper lysimeters (*i.e.*, shallow depths) and in the last year of data shown here (*i.e.*, 1992). Hardwood soil solution NO_3 concentrations were particularly high in 1992 which appeared to result in greater 1992 concentrations of Ca, Mg, and Al (not shown). Tables II and III showed that although differences existed between East and West Bear prior to the treatment period, only Ca showed a large increase in response to treatments that was greatest in soil solutions under hardwoods.

No similar trends over time in soil solution chemical responses were evident in the softwood soil solutions. The lack of response in softwood soil solutions over time due to treatments leads us to conclude that the hardwood-dominated portions of West Bear may have been more responsible through1992 for changes in stream chemistry in response to treatments as described by Norton *et al.* (this issue). Although this suggests that softwood soils were less responsive in these initial years of treatment, they also are apparently demonstrating a greater retention of added N. The lack of base cation responses to treatments in softwood soil solutions could be attributable to lower supplies of the more labile mono- and divalent base cations, and perhaps a history of greater base cation depletion due to greater softwood canopy capture of dry deposition. It is important to note that the soil solution responses presented here represent the initial three years of treatments, and largely reflect the more rapid response mechanisms such as adsorption/desorption phenomena. Chronic treatments over years or decades might be expected to reveal notably different mechanisms of response, particularly as the biologically immobilized N accumulates in the West Bear ecosystem. Available N in these forest soils can be expected to be preferentially taken up by the biota (Driscoll and Schaefer, 1989), so NO_3 leaching is interpreted to suggest excess N beyond biological demand. No data are presented here to clarify the role of hydrologic flow paths in determining contributing sources to stream chemistry in these watersheds, although it is clear that hardwood components of the watershed are contributing to stream response.

The absence of clear trends in softwood soil solutions for NO_3 and SO_4 concentrations over time suggests that adsorption by soil of NH_4 and SO_4, and biological immobilization of any NO_3 produced, adequately buffers against accelerated leaching from the soil due to elevated inputs of N and S during the initial years of these treatments. The data (Table II) suggest that West Bear had higher concentrations of NO_3 than East Bear prior to the onset of treatments in the fall of 1989. The reason for these differences is unknown, and could relate to prevailing wind influences on deposition, consequences of topography for leaching and organic matter accumulation, or differences in plant community distributions and structure. However, that these differences in N status appear to pre-date the manipulation suggests that West Bear may have been more susceptible to accelerating leaching losses of NO_3 due to higher soil N capital. While these pre-existing differences are important in our interpretations of response, the record of change between West Bear and East Bear over time, and the record of their divergence for selected parameters such as in stream chemistry, remain a compelling tool to investigate mechanisms of ecosystem response to elevated N and S inputs.

3.6. THROUGHFALL AND STEMFLOW

Soil solutions reflect the characteristics of the input solutions, and the changes subsequently taking place within soil systems. In closed canopy forests such as BBWM, throughfall and stemflow, not open precipitation, represent solution inputs to soils. There were no clear, significant effects of treatments on throughfall or stemflow chemistry at the BBWM, and therefore volume-weighted means of combined treated and control catchments for the entire period of collection were calculated (Table IV). All collectors were covered during watershed treatments, and therefore no direct effects of treatment application would be expected. Precipitation characteristics for the site can be found in Norton *et al.* (this issue). Evaluations at this site have shown that stemflow represents less than 5% of the chemical and hydrologic flux to these soils, with the exception of K deposition, which ranged between 20 and 30%. Therefore, stemflow is considered a minor contributor to ecosystem-level biogeochemical budgets with the exception of K. Stemflow has a potentially important influence on microsite chemical variability given its higher concentrations in most constituents, and spatial concentration at the boles of trees (Norden, 1994; Riha *et al.*, 1986; Skeffington, 1986). For most solutes, concentrations were higher in softwoods compared to hardwoods, and higher in

stemflow compared to throughfall. Higher softwood throughfall and stemflow concentrations for many solutes, compared to hardwoods, reflects the greater foliage surface area and efficient canopy architecture that results in increased capture of both marine aerosols and other materials in dry deposition (Rustad *et al.*, 1994). There was clear evidence of marine aerosols from the nearby Atlantic Ocean (~50 km), as indicated by the relatively high Na and Cl concentrations in stemflow and throughfall. If we assume that all the Na and Cl are marine-derived, then we can calculate the contributions of marine salts to throughfall deposition. Using proportional ratios, we found that less than 5% of the SO_4 under both forest types, approximately 35% of the Mg under hardwoods, and 40 to 50% of the Mg under softwoods, is marine derived. There was no significant difference in the marine contribution to throughfall inputs between the two watersheds. In addition, most constituents were more concentrated in softwood throughfall, particularly SO_4, due to dry deposition capture efficiencies. This canopy influence translated into differences in soil solution composition as can be seen in the higher Na and Cl concentrations under softwoods (Tables II and III). Rustad *et al.* (1994) reported dry deposition estimates of SO_4 and Cl at BBWM and found from one to greater than two times the incident wet deposition was attributable to dry deposition capture in these forest canopies, depending on the method used to estimate dry deposition. Concentrations are even greater in stemflow due to the wash-off from both foliar and bark surfaces. The notable exception was again K, which is more readily leached from hardwood foliage where it is found in higher concentrations compared to softwoods as shown at BBWM by White *et al.* (this issue), and because of more permeable leaf surfaces. No clear explanation is evident for the greater Si concentrations in hardwoods versus softwoods.

McLaughlin *et al.* (1996) showed a net uptake of NO_3, H, and NH_4, and a net enrichment of base cations, in throughfall for a spruce-fir site in eastern Maine. They also reported net canopy exchange calculations indicating almost twice the enrichment of K when compared to Ca at their site. Year-round foliage and higher leaf area indices for softwoods also explain the higher DOC reported in softwood stands. Lower ANC in softwood throughfall and stemflow compared to hardwoods at BBWM is a product of higher strong acid anion and DOC contributions in softwood forest types. This forest type effect is important in evaluating ecosystem responses to atmospheric deposition.

4. Conclusions

Buried mineral soil-bags installed under the forest floor showed relatively rapid changes in response to the *in situ* soil environment and treatments. The changes were primarily manifest as increased SO_4-S, with a decline in pH, but no other major differences between watersheds were evident. Soil solution chemistries showed that differences existed between East and West Bear watersheds, between hardwoods and softwoods, and with depth in the soil. Responses of soil solutions to chronic additions of $(NH_4)_2SO_4$ were similar to the changes in stream chemistry noted for this whole-watershed manipulation. Soil solution responses to treatment included increasing concentrations of SO_4, NO_3, Ca, and Al with more modest increases in Mg and declines in ANC and pH. These differences were most evident in the

upper soil lysimeters under hardwoods, with less evident changes in soil solution chemistry deeper in the soil. In contrast, soil solutions under softwood stands showed almost no response to treatments, although limited sampling locations precludes a rigorous evaluation of these stand differences. The parallels in chemical changes for both soil solutions and stream chemistry indicate that these systems are linked, and that certain soil compartments, such as shallow soil depths and hardwood components of the watershed, played a greater role during the initial four years of treatments in governing stream chemical response. Research is needed to better define the contributions of different ecosystem components to stream water chemistry that include contrasting soil and forest types, as well as upland versus riparian processes. We believe that the buried mineral soil-bag technique and soil lysimetry have continued utility in environmental monitoring and assessment research, as does whole-ecosystem manipulations. These tools remain important for evaluating *in situ* processes in the context of ecosystem-level research. Because most excess N is biologically immobilized in soil microbial biomass and in higher plants, longer treatment periods and comprehensive assessments of ecosystem responses are clearly needed to adequately evaluate the consequences of long-term air pollutants on forested landscapes.

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