Stream water and soil solution responses to 5 years of nitrogen and sulfur additions at the Fernow Experimental Forest, West Virginia

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Abstract

To examine the effects of elevated N and S inputs on a central hardwood forest, a whole-watershed acidification experiment was initiated in 1989 on the Fernow Experimental Forest, West Virginia. Annual experimental additions of 40 kg S ha^{-1} year^{-1} and 35 kg N ha^{-1} year^{-1} as ammonium sulfate fertilizer were applied to a 34 ha watershed with a 25-year-old stand of central Appalachian hardwoods. An adjacent watershed served as the control. After 5 years of treatment (total additions of 275 kg S ha^{-1} and 220 kg N ha^{-1}), stream water NO_3^-, Ca^{2+}, Mg^{2+} concentrations and export increased. Soil solution concentrations provide evidence that the treatment watershed is nitrogen-saturated, which was unexpected for such a young stand. No statistically significant changes in annual SO_4^{2-} export were observed, but peak stream water concentrations of SO_4^{2-} did increase during the treatment period. Changes in soil solution chemistry suggest that the treated watershed also may be approaching SO_4^{2-} saturation. © 1997 Published by Elsevier Science B.V.

Keywords: N saturation; Air pollution; Calcium; Nitrate; Sulfate

1. Introduction

Nitrogen (N) deposition over much of the northeastern United States is expected to increase 25% over the next 25 years (Aber et al., 1993). Effects of these increasing inputs on forest ecosystems are not well understood, but are of interest because of concerns about N saturation. N saturation has been defined in several ways: N exports equal to or in excess of inputs (Ågren and Bosatta, 1988), N inputs

in excess of biological demand of an ecosystem (Aber et al., 1991), and elevated nitrate (NO_3^-) concentrations in drainage waters (Booltink et al., 1988; van Breemen and Verstraten, 1990). Christ et al. (1995) distinguished between N saturation (defined by the authors as N outputs equal to N inputs), N leakiness (NO_3^- losses above normal), and N overload (N inputs so high as to cause ecosystem damage). These definitions of N saturation imply fundamental changes in N cycling within an ecosystem. Possible consequences of these changes include increased or decreased vegetative growth, altered carbon cycling due to changes in soil and litter chemistry, increased base cation leaching, and

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changes in water quality. Atmospheric influxes of N can alter the N chemistry of streams draining forested watersheds, but the magnitude depends on the season, source and form of N (Nuckols and Moore, 1982), soil type (Norton et al., 1994) and forest type (Aber et al., 1993; Stoddard, 1994).

In this paper, we present the results of a study designed to evaluate the effects of elevated atmospheric deposition on element cycling within a central Appalachian forest ecosystem. We have experimentally increased the N and sulfur (S) deposition on a small watershed on the Fernow Experimental Forest, WV, USA. Our objectives were to determine: (1) changes in chemical characteristics of streamflow; 2) flow paths and residence times of soil water and groundwater within the study watersheds; and (3) chemical changes of water as it filters through a forested watershed. This paper addresses Objectives 1 and 3, and focuses on N, S, calcium (Ca), and magnesium (Mg).

2. Methods

2.1. Description of watersheds

The two watersheds (treatment, control) used in this study are located on the Fernow Experimental Forest near Parsons, WV, USA (39°3'15"N, 79°42'15"W). The Fernow is situated on the

Fig. 1. Input of N and S to WS3, water years 1984–1993. Does not include dry deposition.

Table 1
Characteristics of WS3 and WS4, Fernow Experimental Forest. Soil chemical values are means ± SE, $n = 30$ (Gilliam et al., 1994)

Characteristic	WS3	WS4
Area (ha)	34	39
Aspect	S	ESE
Minimum watershed elevation (m)	735	750
Maximum watershed elevation (m)	860	870
Mean annual precipitation (mm)	1480	1450
Mean annual streamflow (mm)	670	640
Slope (%)	27	20
Soil pH$_{water}$ (0–10 cm)	4.3 ± 0.1	4.2 ± 0.1
Soil CEC (0–10 cm, meq per 100 g)	5.1 ± 0.9	4.1 ± 0.1
Soil organic matter (0–10 cm, %)	14.2 ± 1.2	13.8 ± 0.5
Soil Ca (ueq g^{-1})	15.6 ± 9.4	4.7 ± 0.4
Soil Mg (ueq g^{-1})	2.5 ± 0.8	1.6 ± 0.1
Soil NO$_3$-N (ueq g^{-1})	2.4 ± 0.4	1.9 ± 0.3
Soil NH$_4$-N (ueq g^{-1})	0.9 ± 0.1	0.7 ± 0.1

unglaciated Allegheny plateau in the Allegheny Mountain Section, within the Central Appalachian Broadleaf Forest Province (Bailey et al., 1994). Precipitation is distributed evenly between dormant and growing seasons (average annual precipitation: 145 cm). Average annual precipitation pH is 4.2 but lower values are common in summer (Adams et al., 1994); S and N atmospheric wet deposition are among the highest in the United States ($\sim$ 15 kg S ha^{-1} and 13 kg N ha^{-1} [Edgerton et al., 1992]). On both watersheds, the predominant soil type is Calvin channery silt loam (loamy-skeletal, mixed, mesic Typic Dystrochrepts) underlain with fractured sandstone and shale of the Hampshire formation (Losche and Beverage, 1967). Both watersheds are drained by second-order streams. Because of shallow soils ($\leq$ 1 m), steep slopes and little near-surface groundwater storage (DeWalle et al., 1997), streamflow is high during periods of high precipitation and soil moisture, and recedes quickly (Reinhart et al., 1963). Other watershed characteristics are given in Table 1.

Watershed 3 (WS3), the treatment watershed, contains a young stand that originated in 1969 from natural regeneration following clear-cutting. Dominant tree species include *Prunus serotina* Ehrh., *Acer rubrum* L., *Betula lenta* L., and *Fagus grandifolia* Ehrh. Watershed 4 (WS4), the control water-

Table 2
Nutrient input (ambient) and total export from two forested watersheds, Fernow Experimental Forest

Water Year	Ppt (cm)	Total flow (cm)	Storm flow (%)	Precipitation loadings (input) kg ha⁻¹							Flow loadings (output) kg ha⁻¹						
				N	NO$_3$	NH$_4$	S	SO$_4$	Ca	Mg	N	NO$_3$	NH$_4$	S	SO$_4$	Ca	Mg
WATERSHED 3																	
1984	152.1	71.0	33.2	15.05	31.33	10.34	18.70	55.96	8.82	0.76	3.93[a]	17.40	–[b]	7.76	23.25	7.98	4.62
1985	175.2	91.5	49.3	19.27	45.73	11.56	22.08	66.05	4.91	0.70	5.01[a]	22.18	–[b]	11.23	33.66	10.41	5.84
1986	140.3	59.8	24.4	15.02	29.19	10.81	17.40	52.20	4.35	0.42	3.83[a]	16.95	–[b]	7.01	20.99	6.66	3.84
1987	121.1	43.5	22.0	11.98	25.18	8.35	12.83	38.37	4.72	0.48	2.79[a]	12.35	–[b]	4.86	14.57	4.77	2.63
1988	145.7	62.2	33.0	8.16	23.02	3.93	14.57	43.71	4.66	0.73	3.50	15.49	0.00	7.71	23.09	7.26	3.75
Mean	146.9	65.6	32.4	13.90	30.89	9.00	17.12	51.26	5.49	0.62	3.81	16.87	–[b]	7.71	23.11	7.42	4.14
Total	734.4	327.9		69.49	154.45	45.00	85.58	256.30	27.46	3.09	19.06[a]	84.37	–[b]	38.57	115.56	37.08	20.68
1989	160.4	77.9	26.1	10.11	27.91	4.97	16.84	50.21	3.85	0.48	6.10	26.92	0.02	9.43	28.24	10.96	5.49
1990	163.6	72.8	30.7	9.49	25.51	4.58	15.86	47.76	6.21	0.98	10.27	45.46	0.00	8.04	24.08	12.32	6.43
1991	125.3	43.0	24.7	8.65	24.44	4.01	14.16	42.49	3.51	0.50	6.61	29.22	0.01	5.67	16.99	8.08	4.06
1992	129.2	51.3	29.6	8.27	24.55	3.62	13.57	40.84	2.84	0.39	8.76	38.65	0.04	7.15	21.41	10.15	5.13
1993	168.1	78.2	40.8	9.06	26.21	4.05	16.18	48.49	3.68	0.47	13.72	60.07	0.19	12.93	38.74	16.62	8.03
Mean	149.3	64.6	30.4	9.11	25.73	4.25	15.32	45.96	4.02	0.56	9.09	40.06	0.05	8.64	25.89	11.63	5.83
Total	746.7	323.1		45.57	128.64	21.23	76.62	229.79	20.10	2.82	45.46	200.32	0.26	43.21	129.46	58.13	29.14
WATERSHED 4																	
1984	147.1	69.0	31.7	14.56	30.31	10.00	18.10	54.14	8.53	0.74	5.63[a]	24.92	–[b]	10.16	30.45	10.33	5.40
1985	175.7	88.5	48.3	19.33	45.86	11.60	22.14	66.25	4.92	0.70	5.74[a]	25.41	–[b]	11.65	34.91	13.37	6.84
1986	137.7	56.5	22.3	14.73	28.63	10.60	17.07	51.21	4.27	0.41	4.30[a]	19.04	–[b]	8.45	25.31	8.06	4.25
1987	117.5	41.5	22.5	11.63	24.43	8.11	12.45	37.24	4.58	0.47	3.10[a]	13.72	–[b]	5.92	17.75	5.77	2.96
1988	142.6	62.6	34.4	7.99	22.54	3.85	14.26	42.79	4.56	0.71	4.24	18.73	0.01	9.90	29.66	9.37	4.64
Mean	144.1	63.6	31.8	13.65	30.36	8.83	16.80	50.33	5.37	0.61	4.60[a]	20.36	–[b]	9.22	27.62	9.38	4.82
Total	720.6	318.1		68.24	151.78	44.16	84.02	251.63	26.87	3.03	23.01[a]	101.82	–[b]	46.09	138.08	46.90	24.09
1989	158.8	78.8	28.1	10.00	27.63	4.92	16.67	49.70	3.81	0.48	6.30	27.80	0.02	12.19	36.52	13.56	6.09
1990	160.8	76.9	31.5	9.33	25.09	4.50	15.60	46.96	6.11	0.96	8.58	37.98	0.00	11.01	32.99	13.82	6.56
1991	120.7	43.7	25.0	8.33	23.54	3.86	13.64	40.93	3.38	0.48	3.84	17.00	0.00	6.77	20.27	7.51	3.53
1992	125.9	53.9	30.7	8.05	23.91	3.52	13.21	39.77	2.77	0.38	4.25	18.81	0.00	8.96	26.83	8.59	4.15
1993	164.5	81.0	40.6	8.86	25.64	3.96	15.82	47.43	3.60	0.46	6.26	27.62	0.02	13.64	40.87	12.78	6.15
Mean	146.1	66.9	31.1	8.92	25.16	4.16	14.99	44.96	3.93	0.55	5.85	25.84	0.01	10.51	31.50	11.25	5.30
Total	730.7	334.4		44.58	125.81	20.78	74.95	224.79	19.67	2.76	29.23	129.21	0.04	52.56	157.48	56.26	26.48

[a] Estimated.
[b] Data not available.

shed, contains a relatively undisturbed stand. This watershed was heavily cut in 1905; in the 1940s, dead American chestnut (*Castanea dentata* Marsh.) were removed. The current stand is approximately 85 years old, but some residual trees may be up to 200 years old (J.N. Kochenderfer, unpublished data). Dominant tree species include *Acer saccharum* Marsh., *Acer rubrum* L., *Fagus grandifolia* Ehrh., and *Quercus rubra* L.

2.2. Description of treatments

Granular ammonium sulfate fertilizer (21-0-0-24, relative proportions of N, P [phosphorus], K [potassium] and S) was used to accelerate N and S inputs to WS3. The proportional N and S composition of this fertilizer mimics N and S in throughfall on these watersheds. Fertilizer was applied at a rate double

Table 3

Results of time series analyses, WS3 and WS4 stream chemistry loadings. Asterisks indicate statistically significant differences ($P < 0.05$)

Analyte	Pretreatment			Treatment		
	Intercept	Slope	R^2	Intercept	Slope	R^2
NO_3	0.170	0.733	0.86	−0.159 *	1.619 *	0.88
SO_4	0.129	0.783	0.74	−0.101	−0.859	0.95
Ca	0.000	0.789	0.99	−0.065	1.088 *	0.91
Mg	0.004	0.850	0.98	−0.036 *	1.166 *	0.94

the ambient N and S throughfall inputs, which was considered to approximate the combined N and S inputs of wet and dry deposition. Because ambient deposition varies seasonally, with approximately half of the annual S deposition occurring from May to August, three applications were made each year, in March, July, and November. The March applications (33 kg ha^{-1}) were twice the average historical deposition rates for the January–April period, July applications (101 kg ha^{-1}) were twice the May–August rates, and November applications (33 kg ha^{-1}) were twice the September–December rates. These rates correspond to 7.9 kg S ha^{-1} and 6.9 kg N ha^{-1} for the March and November applications, and 24.2 kg S ha^{-1} and 21.3 kg N ha^{-1} for the July applications. The first application was made in January 1989 (Fig. 1). Ambient deposition is shown in Table 2.

2.3. Measurements

Precipitation was estimated from a network of standard rain gages on the Fernow Experimental Forest. Precipitation chemistry samples were also collected on the Fernow (Helvey and Kunkle, 1986). Streamflow and stream chemistry sampling and analyses are described in Adams et al. (1993). Weekly stream water grab samples were collected just upstream from each weir pond. All water samples were analyzed at the USDA Forest Service's Timber and Watershed Laboratory in Parsons, WV, using EPA-approved protocols, holding times, and quality assurance/quality control procedures (Edwards and Wood, 1993).

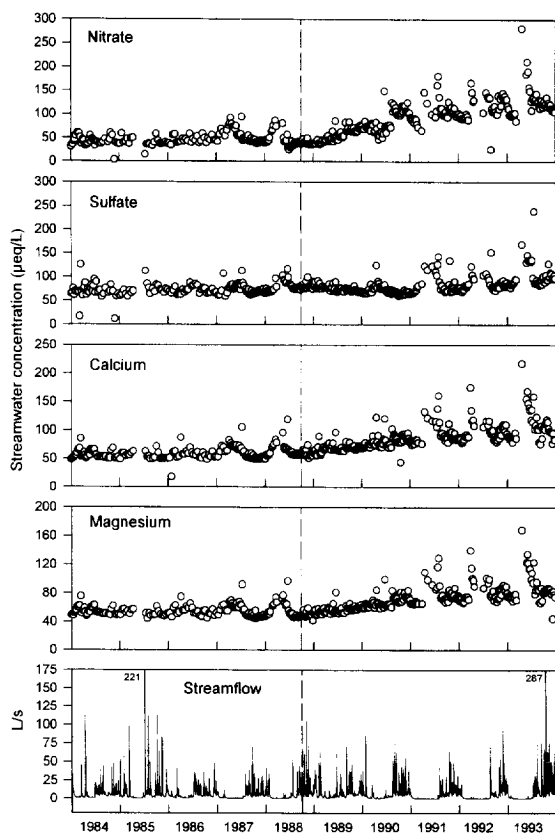Stream chemistry exports (kg ha^{-1} month^{-1}) were calculated as mean weekly concentration × streamflow rate × watershed area^{-1}. Total monthly

Fig. 2. Daily streamflow, and weekly concentrations of NO_3^-, SO_4^{2-}, Ca^{2+}, Mg^{2+} in stream water from WS3, water years 1984–1993. Vertical line indicates initiation of treatment.

exports were used in data analysis to reduce the influence of unequal sample sizes or missing data. Data were summarized by water years (WY). Our water years begin on 1 May and continue through April 30; for example, WY 1989 began 1 May 1989 and ended 30 April 1990. Data were split into two sets—a 5-year pretreatment or calibration set (WY 1984–1988) and a 5-year treatment set (WY 1989–1993)—and were analyzed using either linear regression or, in the presence of serial correlation in the error terms, time series analysis (Littell et al., 1991). Separate regression equations with WS3 loadings as the dependent variables and WS4 loadings as the independent variables were developed for each 5-year period. Slopes and intercepts were then tested to determine if they were statistically different ($P < 0.05$).

In 1988, 15 soil pits were excavated on each watershed, representing the range of topographic position, vegetation, and soil characteristics present. In each pit, zero-tension lysimeters were installed at the bases of the A and B horizons, and, in some cases, at the base of the C horizon. Thirty-nine lysimeters

Fig. 4. Delta values (WS3 concentrations – WS4 concentrations) of NO_3^-, SO_4^{2-}, Ca^{2+} and Mg^{2+}, water years 1984–1993. Units are ueq L^{-1}. Vertical line indicates initiation of treatment.

were installed in each watershed. Leachate samples (up to 4L) were collected approximately monthly or whenever sufficient sample volume existed for analysis. Each sample was analyzed using the same methods and protocols as for stream water chemistry. Although lysimeters were installed approximately 6 months before treatments began, no pretreatment samples were collected. This was done to avoid any possible effects of soil disturbance due to lysimeter installation on soil solution chemistry. All soil solution treatment responses were assessed by comparing the control and treated watersheds, using a seasonal Kendall's test (Hirch et al., 1982).

3. Results

3.1. Pretreatment

Annual precipitation inputs of N and S exceeded outputs in stream water (Table 2) during the five
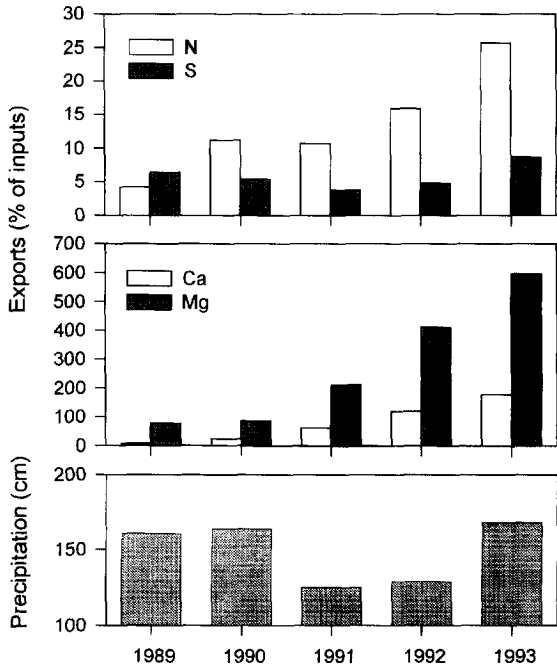

Fig. 3. Annual exports of N, S, Ca, and Mg, expressed as a percentage of inputs for water years 1989–1993. Bottom graph shows total annual precipitation for the same time period.
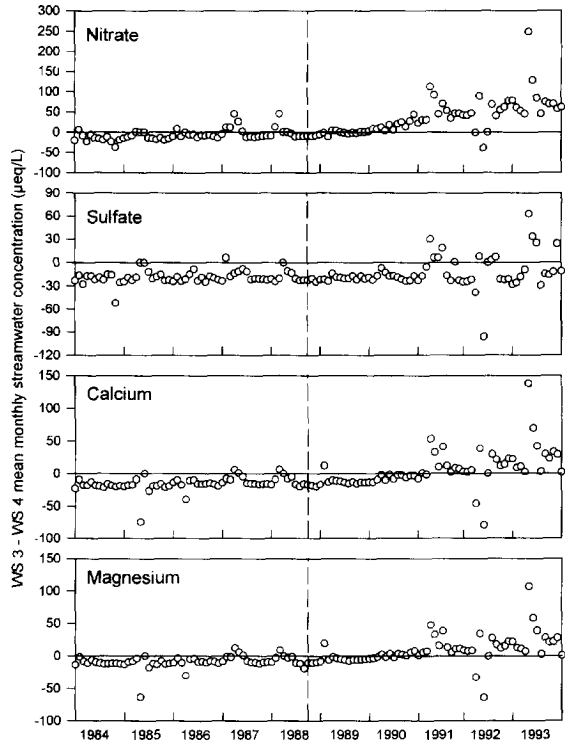
Table 4
Ion balances for two experimental watersheds, Fernow Experimental Forest. Units are ueq L^{-1}. Measurement of NH_4^+ and Cl^- did not begin until WY1988

WY	Ca^{2+}	Mg^{2+}	No_3^-	SO_4^{2-}	K^+	Na^+	NH_4^+	Cl^-	H^+	Cations	Anions	All ions
WATERSHED 3												
1984	55.42	52.97	38.71	66.96	18.35	21.65			0.62	149.00	105.66	254.67
1985	55.83	51.69	35.73	78.59	21.56	21.58			0.92	151.58	114.32	265.90
1986	54.59	52.02	44.99	72.18	17.99	23.05			0.81	148.46	117.17	265.63
1987	54.03	49.09	45.18	68.66	19.37	20.10			1.14	143.73	113.85	257.57
1988	54.49	49.80	40.57	77.89	17.52	19.07	0.045	10.52	0.95	145.87	128.98	274.85
1989	68.66	57.17	55.72	75.30	20.05	20.05	0.121	14.08	0.91	166.95	145.10	312.05
1990	83.99	71.54	100.67	67.45	21.60	22.98	0.022	19.97	1.17	201.30	188.09	389.39
1991	92.77	77.07	109.02	80.34	22.53	22.67	0.096	19.95	1.43	216.57	209.30	425.88
1992	99.06	82.20	122.27	87.22	21.45	21.84	0.001	20.23	1.81	228.08	231.56	459.64
1993	101.17	80.36	119.71	94.94	21.68	19.21	0.257	20.14	3.00	236.99	242.87	479.86
WATERSHED 4												
1984	74.94	64.58	59.81	91.94	17.15	23.21			0.94	180.81	151.74	332.55
1985	75.97	63.77	50.77	97.26	19.23	23.41			1.49	183.87	148.03	331.90
1986	70.68	61.72	54.85	92.89	16.32	23.61			1.16	173.50	147.74	321.24
1987	69.38	58.43	53.71	88.78	17.56	21.17			1.33	167.88	142.48	310.36
1988	75.56	61.44	49.44	99.47	15.95	19.71	0.077	12.42	1.36	174.09	161.32	335.41
1989	78.89	59.35	57.18	95.50	17.85	20.33	0.118	15.83	1.16	177.69	168.51	346.20
1990	89.56	69.48	79.35	87.70	18.24	22.39	0.018	18.81	1.249	200.94	185.85	386.79
1991	86.01	66.71	63.91	97.45	17.90	21.46	0.00	16.92	1.24	193.32	178.28	371.60
1992	80.52	63.94	57.10	105.13	16.30	19.32	0.03	15.10	1.36	181.47	177.33	358.80
1993	78.88	61.67	55.06	101.14	14.48	18.03	0.297	14.79	1.69	175.04	170.99	346.03

pretreatment years of this study, with no obvious temporal trends. On WS4, approximately 65% of the N and 45% of the S that was deposited via precipitation was retained; on WS3, about 73% of the N and 55% of the S was retained. Dry deposition added an estimated 2–5 kg ha^{-1} of NO_3-N and an estimated 4–8 kg ha^{-1} year^{-1} of SO_4 – S (Edgerton et al., 1992). Although ammonium (NH_4^+) inputs contributed 30–50% of the incoming N, stream water NH_4^+ export was very low. For both watersheds, inputs of Ca^{2+} and Mg^{2+} were less than the amounts exported during the pretreatment period.

Mean monthly stream water NO_3^- concentrations for WS3 generally ranged from 25–110 ueq L^{-1} during the pretreatment period, with most values < 50 ueq L^{-1} (Fig. 2). Stream water SO_4^{2-} concentrations were generally in the range of 50–100 ueq L^{-1}, but with several outliers. Stream water Ca^{2+} and Mg^{2+} concentrations varied from 50–100 ueq L^{-1}, and 40–80 ueq L^{-1}, respectively. Peak concentrations generally occurred during low flow, but concentrations appeared fairly constant during the pretreatment period.

3.2. Treatment effects

Stream water Annual total and mean annual export of NO_3^- from WS3 increased during the 5-year treatment period relative to the 5-year pretreatment period (Table 2). Analyses revealed statistically significant differences in the slope and intercept of the regression of WS3 vs. WS4 (Table 3) for N, suggesting a change in total amount of N available in WS3 due to treatment. Calcium and Mg^{2+} exports also increased significantly during the treatment period, despite no significant change in inputs. Sulfate exports increased only slightly during the 5-year treatment period, and regression slopes and intercepts were not significantly different.

Using the pretreatment regressions in Table 3, we estimated the fraction of WS4 export that was represented by WS3 export. We then computed the 'extra' export during the treatment period. Export of N, expressed as the percentage of added N, increased gradually during the 5-year treatment period and was not directly related to total annual precipitation (Fig. 3). In WY 1993, 25% of the added N was exported

Table 5

Results of seasonal Kendall analyses for soil solution chemistry by horizon for two watersheds on the Fernow Experimental Forest. * *: Significant at $\alpha = 0.05$ level

	WS	Season	Season * WS	Seasonal Kendall slope estimate	
				WS3	WS4
A horizon					
NO_3^-	* *	NS	NS	No trend	−9.78
SO_4^{2-}	* *	NS	NS	63.85	4.21
Ca^{2+}	* *	NS	* *	16.69	No trend
Mg^{2+}	* *	NS	NS	No trend	−2.14
B horizon					
NO_3^-	* *	NS	NS	No trend	−35.79
SO_4^{2-}	NS	NS	NS	48.15	12.42
Ca^{2+}	* *	NS	NS	22.94	No trend
Mg^{2+}	* *	NS	NS	1.12	−6.58
C horizon					
NO_3^-	* *	NS	NS	13.55	−22.78
SO_4^{2-}	NS	NS	NS	42.64	13.98
Ca^{2+}	* *	NS	NS	34.02	−6.30
Mg^{2+}	* *	NS	NS	12.39	No trend

(as inorganic N) in stream water. Note that we do not include organic N in these estimates. Sulfur did not exhibit a consistent trend. Calcium and Mg export increased dramatically, expressed as a percentage of ambient inputs, since none was added via fertilizer.

Mg exports by the end of the 5th year of treatment (WY 1993) were nearly 600% of inputs and Ca exports were approximately double the ambient inputs.
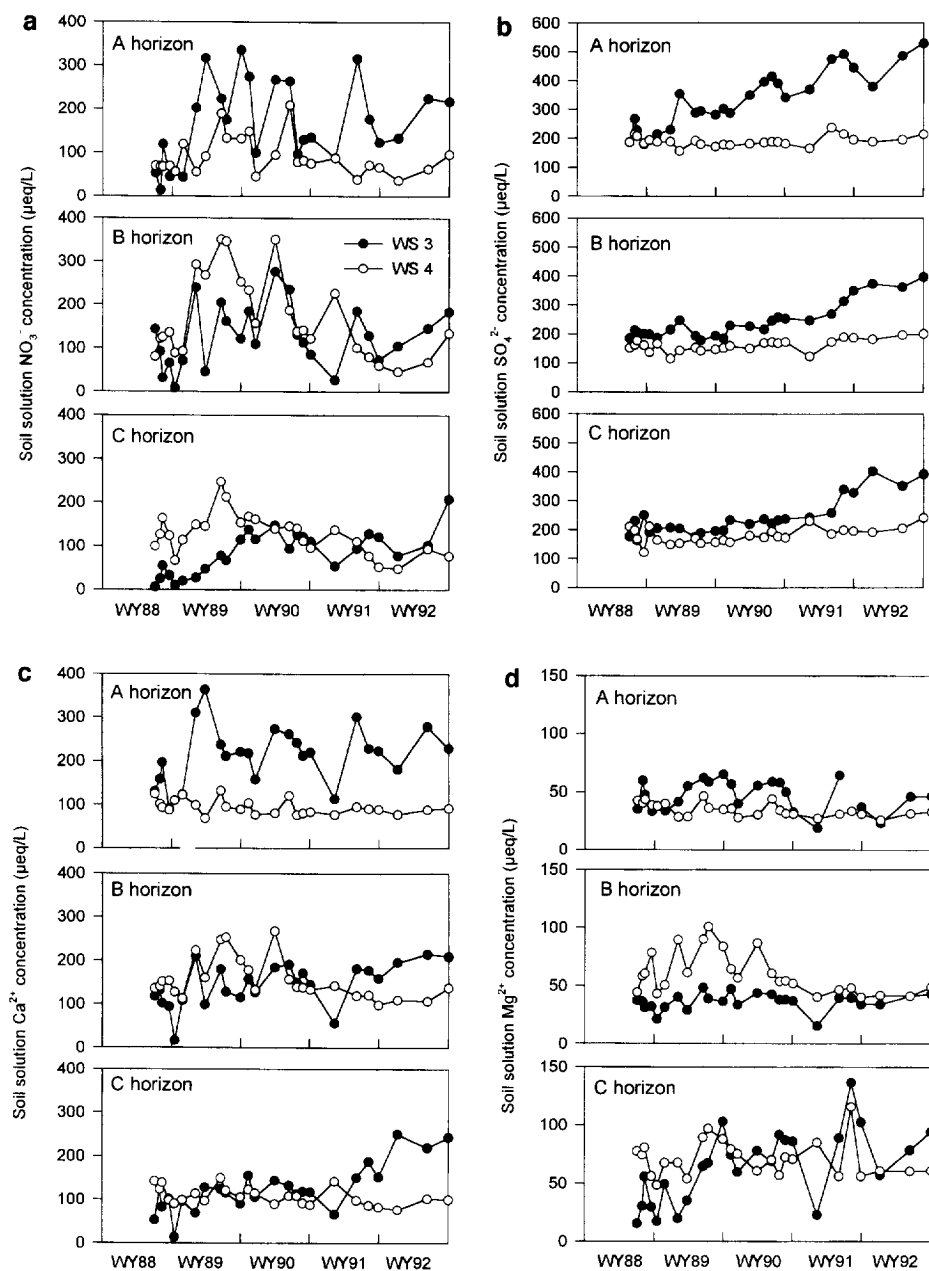
Stream water concentrations of all analytes in-

Fig. 5. Mean monthly soil solution concentrations of NO_3^-, SO_4^{2-}, Ca^{2+} and Mg^{2+} First application of ammonium sulfate was made 31 January 1989, first samples collected 11 February 1989. Soil solution samples were collected from lysimeters approximately monthly. Each point is the mean of 2–15 samples.

creased on WS3 during the treatment period (Fig. 2), and the range of concentrations also increased. The treatment vs. control regressions for monthly concentrations were so poor (R^2 values ranging from 0.001 to 0.16) that comparisons of concentrations between the two periods could not be made. Instead, we examined relative changes in concentration by subtracting volume-weighted mean monthly concentrations for WS4 from corresponding values for WS3 and plotting the differences (delta values; Fig. 4).

Initially, NO_3^- concentrations of WS3 stream water were less than WS4 stream water (delta values < 0). Delta values consistently greater than zero appeared for the first time in WY 1990, suggesting that a change had occurred in NO_3^- concentrations of the stream draining one of the watersheds. These changes can be seen in WS3 (Fig. 2). NO_3^- concentrations remained nearly constant on WS4, but varied seasonally. Positive delta values for SO_4^{2-} coincided with peak SO_4^{2-} concentrations on WS3, but no overall trend in delta values is apparent. Positive delta values for Ca^{2+} and Mg^{2+} occurred consistently beginning in WY 1991. All analytes displayed greater delta values late in the growing season (August through October), coincident with greater atmospheric inputs and low flow (Fig. 4).

Analysis of the ionic concentrations of stream water (Table 4) revealed that average annual ion output from WS3 increased by 55% during the 5-year treatment period relative to the pretreatment period, with a 147% increase in mean annual NO_3^- export. During the same period, average annual total ion export from WS4 increased by 11%, (16% increase in NO_3^-). The largest relative increase was in NO_3^- as a proportion of total ion output from WS3. The proportion of SO_4^{2-} in WS3 export declined, while the proportions of Ca^{2+} and Mg^{2+} decreased slightly during the treatment period.

Soil water Divergence in soil leachate concentrations was evident first in the A horizon (Table 5). Nitrate trends varied significantly between the two watersheds for all three horizons (Table 5). There was either no trend (A and B horizon) or an increase in NO_3^- concentrations for WS3 over time, and a negative trend for WS4.

Soil solution SO_4^{2-} concentrations in the A horizon of WS3 increased significantly relative to those of WS4 (Table 5, Fig. 5). This divergence between

the two watersheds was only significant for the A horizon, however. For B and C-horizon leachate, slopes of concentration vs. time since initiation of treatment were greater for WS3 than WS4, but the trends were not statistically different (Table 5).

Soil solution Ca^{2+} concentrations in the A horizon of WS3 exhibited a pattern similar to those for NO_3^-—a rapid increase, but with large seasonal variability (Fig. 5). WS4 A-horizon Ca^{2+} concentrations were much less variable than those in WS3 and showed no significant trend over time, while WS3 concentrations increased over time (Table 5). This pattern was repeated for the B-horizon soil solution. In the C horizon, WS3 concentrations increased over time, while for WS4, the trend was toward a slight decrease.

Soil solution Mg^{2+} concentrations from the A horizon were lower on WS4 than WS3, but for the B horizon, WS4 solution concentrations were greater (Fig. 5). Kendall's tests for trends revealed that for all horizons, the trends differed between the watersheds. For the A horizon, there was no trend in WS3 concentrations and a negative trend in WS4 concentrations. In the B and C horizons, soil solution Mg^{2+} concentrations increased slightly on WS3 over time and either decreased slightly or showed no trend on WS4.

4. Discussion

Ambient N inputs to these watersheds are greater than those for many areas in the United States (National Atmospheric Deposition Program, 1994), and treatment additions increased N loadings to values reported for some of the most severely impacted European sites (Dise and Wright, 1995). Likewise, pretreatment NO_3^- concentrations in stream water draining both watersheds were relatively high. These values could be explained for the untreated WS4 as N 'leakiness' due to stand maturity (Vitousek and Reiners, 1975, Emmett et al., 1993): older, non-aggrading forest stands have diminished N demand and slower N uptake rates. However, such high NO_3^- concentrations were somewhat unexpected for a stream draining a young, actively growing stand (WS3) because young forests are generally N-demanding and use most of the available N. Nitrate

concentrations reported here are higher than those for most streams in the region, but are comparable to values from streams draining forested watersheds in West Virginia, western Maryland, and western Pennsylvania (Hicks et al., 1992; DeWalle and Pionke, 1994).

Ammonium was a significant proportion of incoming N, both in precipitation and the fertilizer application, but stream water NH_4^+ levels were always low. This difference suggests that the incoming NH_4^+ was rapidly nitrified, assimilated or adsorbed onto soil particles. Gilliam et al. (1996) reported that rates of net nitrification were > 90% of net mineralizable N on an annual basis for these watersheds (7.0 g N m^{-2} year^{-1}). Boerner and Sutherland (1995) also reported high N mineralization potential and soil solution N levels for WS4 soils. The nitrification rates for the Fernow watersheds are high but within the range reported for temperate forests (Federer, 1983; Aber et al., 1993), and we conclude that nitrification is probably not limiting N availability in these stands, unlike those described by Christ et al. (1995).

Because of the lack of pretreatment data, we cannot attribute change in soil solution chemistry directly to the treatment. However, we have demonstrated significantly different trends in soil solution concentrations between the watersheds for all analytes for all horizons, with the exception of SO_4^{2-}. In most instances, the trend in concentrations of NO_3^-, Ca^{2+} and Mg^{2+} was positive for WS3 and either negative or not detectable for WS4. We hypothesize that the applied NH_4^+ was rapidly nitrified, creating more available N than could be assimilated by plants or microorganisms, resulting in leaching from the upper horizon. Very high nitrification rates in the mineral soils of these watersheds provide support for this hypothesis, as well as data that show that net mineralization rates roughly equalled net nitrification rates (Boerner and Sutherland, 1995; Gilliam et al., 1996). As NO_3^- was leached, Ca^{2+} and Mg^{2+} were also leached, stripped from the soil exchange sites to maintain charge neutrality. Similar patterns were observed by Hicks et al. (1992) and Helvey and Kunkle (1986). The similarity in patterns of soil solution concentrations suggests NO_3^- may be the more important anion in regards to removing Ca^{2+}. Other researchers also have reported Ca^{2+} and Mg^{2+} as

the dominant counter-ions for experimental additions of SO_4^{2-} and NO_3^- (David et al., 1991; Fernandez and Rustad, 1990). The results that we have described here, along with relatively low aluminum concentrations (0–1.5 mg L^{-1}), suggest that cation exchange processes are the main processes involved in neutralizing the mineral acidity in these soils.

Sulfate data tell a conflicting story. Based on input/output budgets, these watersheds are still retaining SO_4^{2-}. Helvey and Kunkle (1986) also reported annual SO_4^{2-} inputs in excess of annual streamflow exports for WS4. Stream water SO_4^{2-} concentrations seem to be increasing on WS3, but no statistically significant differences in SO_4^{2-} export were detected between the two watersheds. Soil solution SO_4^{2-} concentrations below the A horizon increased quickly on the treated watershed, but increases below the B and C horizons were observed much later in the treatment period. Thus, SO_4^{2-} was leached rapidly from the A horizon, but was adsorbed by the B horizon for much of the treatment period. This progression of SO_4^{2-} through the soil profile suggests that soils on WS3 may be approaching their SO_4^{2-} adsorption capacity. The lack of treatment effects may be partly due to concurrent (but not equivalent) increases in soil solution SO_4^{2-} concentrations for WS4 (Table 5). Soils on these watersheds are sandy loam in texture, with only low to moderate SO_4^{2-} adsorption capacity, so it was not expected that they would have such a large capacity to adsorb SO_4^{2-}. This net retention of SO_4^{2-} is unusual for watersheds within the Appalachian Plateau (Herlihy et al., 1993).

We conclude that N cycling, and to a lesser extent S cycling, were altered on WS3 during the treatment period. Elevated N (~ 220 kg N ha^{-1}), in conjunction with a very high rate of nitrification, has resulted in increased availability of N, increased N concentration in some vegetation (Adams et al., 1995; Gilliam et al., 1996), elevated N in soil solution, and increased export in stream water, but no detectable changes in soil N (M.B. Adams, unpublished data, 1996). Inputs of ~ 275 kg S ha^{-1} have resulted in increases in soil solution SO_4^{2-} levels, but have not significantly affected total annual exports.

Five years of application of ammonium sulfate has altered not only the N and S cycling on WS3, but also the movement of Ca^{2+} and Mg^{2+}. Losses of

Ca^{2+} and Mg^{2+} exceed precipitation inputs (Table 2), and even with enrichment via throughfall (estimated 5–7 kg ha^{-1} $year^{-1}$ for Ca^{2+} [Helvey and Kunkle, 1986]), it is apparent that WS3 is a net exporter of Ca^{2+} and Mg^{2+}. Bedrock samples from WS4 contained 3.2% Ca and 0.24% Mg, relatively low values (DeWalle et al., 1988). Although weathering rates are not known for this parent material, Zabowski (1990) reported Ca inputs from weathering of similar parent materials to range from below detection limits to 8.7 kg ha^{-1} $year^{-1}$, and from below detection limits to 3.6 kg ha^{-1} $year^{-1}$ for Mg. These rates are not sufficient to replace losses observed in this study.

The results of this study raise concerns about the sustainability of forests that receive high N inputs, as many forests in the central Appalachian hardwood species (e.g. *Quercus* spp. and *Liriodendron tulipifera*) sequester large amounts of Ca^{2+} in wood (Raynal et al., 1992). Harvesting trees that contain large amounts of Ca^{2+} would further exacerbate low levels in the soil, potentially resulting in deficiencies or limitations to growth. Following the calculations of Federer et al. (1989), a single commercial clear cut (removal of all stems > 12.5 cm d.b.h.) during an 80-year rotation would decrease the total Ca pool in the soil by approximately 13% and Mg by 3%. Whole-tree harvesting (removal of all boles, tops, and branches) would remove an estimated 16% of Ca and 3% of Mg. Four diameter-limit cuts during an 80-year rotation (removal of all trees > 43 cm d.b.h. every 20 years) would remove 18% Ca and 3% Mg. Note that changes in Mg pools are relatively consistent across different cutting treatments, a reflection of low concentrations of Mg in aboveground biomass, but Ca removals increase with the intensity of harvesting. Additional losses of Ca and Mg from accelerated leaching by acidic deposition would further decrease the pools of these nutrients in the ecosystem. Expected increases in N deposition may further exacerbate base cation losses from sensitive soils.

In addition to concerns about sustainability of terrestrial systems, effects on sustainability of aquatic systems also must be evaluated. Acidification effects have been documented in experimental and lake and headwater systems (see Herrmann et al. (1993) for a thorough review). However, a better understanding of effects of changes in other chemical constituents and of downstream cumulative effects is needed. An effective riparian buffer strip was found to protect aquatic ecosystems from elevated NO_3^- in agricultural runoff (Peterjohn and Correll, 1984; Vought et al., 1994), but effectiveness for other nutrients is not as well known.

Although we conclude that N saturation is possible even in young, vigorously growing stands, we cannot estimate rates and time frames from these data. Further work is needed to develop and test predictive tools. Also, since N deposition is expected to continue increasing, we should begin to consider amelioration or mitigation techniques. Aber et al. (1991) evaluated the potential of forest harvesting as a means of delaying N saturation or for off-setting elevated N inputs. Their model suggested that harvesting would only change the timing of the occurrence of saturation, in addition to creating problems with removal of nutrient cations, as described above. Our data suggest that in some systems, available N may exceed uptake capacity even in young stands, supporting the conclusions of Aber et al. (1991). Soils with high C:N ratios have substantial capacity to immobilize added N (Johnson, 1995), so preservation of organic matter may be critically important in areas where N inputs are high. Soil amendments with high C:N ratios, such as wood ash or pulp residues also may provide for immobilization of N, and slow release of N to an ecosystem. Other tree species with higher demands for N also may help sequester, at least temporarily, some of the incoming N. Finally, additions of base cations via liming may become necessary to mitigate effects of decreasing Ca^{2+} levels.

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