Chapter 4

SOIL WATER AND STREAM WATER CHEMICAL RESPONSES

Pamela J. Edwards[1], Karl W. J. Williard[2], Frederica Wood[1], and William E. Sharpe[3]
[1]*USDA Forest Service, Northeastern Research Station, Timber and Watershed Lab, Parsons, West Virginia 26287;* [2]*Southern Illinois University Carbondale, Department of Forestry, Mailcode 4411, Carbondale, Illinois 62901;* [3]*The Pennsylvania State University, School of Forest Resources and Institutes of the Environment, University Park, Pennsylvania 16802.*

1. INTRODUCTION

Acidification of forested watersheds by anthropogenic inputs of nitrogen (N) and sulfur (S) compounds has been a concern for many decades in North America. While it has been difficult to show changes to vegetative health or species diversity (Hendershot and Belanger 1999, Hendershot and Jones 1989), changes to stream water and soil water chemistry and acid/base status have been easier to document (DeWalle et al. 1988, Wigington et al. 1996, Herlihy et al. 1993). Many of the first studies in which both chemical and biological effects of acidification were observed were in surface waters (Corbett and Lynch 1982, Schofield 1976, Haines 1981). Changes to or complete elimination of fish and other aquatic populations due to changes in lake and stream chemistries drove much of the research and political interest in acidic deposition in the United States during the 1970s-80s (Cowling 1982). Since that time, interest in stream water and soil water chemistry has shifted to trying to make connections between solution chemistry and the buffering capacity of watershed soils and forest health (Sverdrup and Warfvinge 1993, Cronan and Grigal 1995), and defining critical loads to predict future forest condition (Arp et al. 1996, Ouimet et al. 2001, Holmberg et al. 2001).

M. B. Adams et al. (eds.), The Fernow Watershed Acidification Study, 71–136.

2. METHODS

2.1 Soil Water Sampling

Soil leachate was collected from WS3, WS4, and WS9 (Fig. 4-1) with zero-tension pan lysimeters (see DeWalle et al. 1988 for lysimeter construction details). Lysimeters were installed at the base of the A and B horizons, and when possible, the C horizon at 15 locations on WS3 and WS4 (Fig. 4-2). Average depth of the A, B, and C horizon lysimeters was 13, 79, and 119 cm, respectively. On WS9, lysimeters were installed in 12 plots (Fig. 4-3) at 45.7-cm depth, which approximates the lowest rooting depth in the catchment. Six of the lysimeter plots on WS9 were untreated controls and six served as adjacent treated pairs (Fig. 4-3).

Soil water samples were collected approximately monthly from the lysimeters. Overflow that exceeded sample bottle capacity was collected in a bucket and its volume and the volume in the bottle were determined gravimetrically, but chemical analyses were determined only on the sample collected in the bottles. On WS3, the soil was allowed to equilibrate for approximately 5 months before the first sample was collected. On WS9, 2 months of equilibration were allowed after lysimeter installation. The first gravity-drained samples were collected 1 October 1986 on WS9 and in January 1989 on WS3 and WS4. Sample collection continued until October 2002 on WS9, and it continues today on WS3 and WS4. Lysimeter samples were not collected from October 1994 through January 1996 on WS9 and from June 1993 through December 1995 on WS3 and WS4 due to budget constraints.

2.2 Stream Water Sampling

Stream water was grab-sampled from WS3, WS4, and WS9 weekly from a fixed location near the mouth of each watershed (Figs. 4-2 and 4-3). This set of routinely collected samples (i.e., routines) includes chemistries influenced by baseflow as well as various stages of stormflow. From the routine data set from each watershed, the chemistries of all of the samples that were not from any portion of a storm hydrograph were placed into a separate data set for analysis (i.e., baseflow).

Stormflow samples from discrete runoff events also were collected from 1988-1995 for WS3 and from 1987-1997 in WS4 and WS9 using automatic pumping samplers on pre-set time intervals; however, there were no storms sampled in 1996 and only one in 1997. Storms that were sampled tended to be moderate to large in size, with a few smaller ones included when possible.

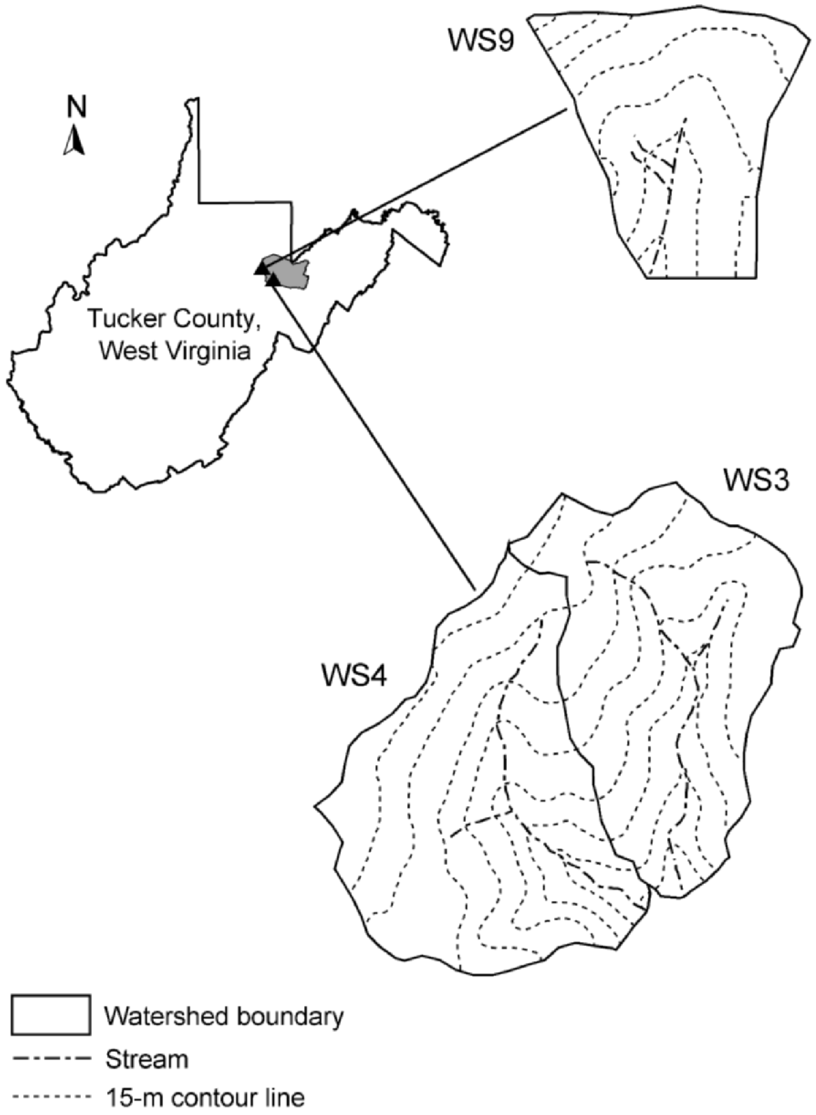

Figure 4-1. Locations and topographic conditions of WS3, WS4, and WS9.

Larger storms were focused on because smaller events often did not result in measurable flow or chemical changes. The overall average peakflows for the sampled events for each watershed were in the largest 10 percent of the storms for the years sampled, but the minimum peakflows sampled were as low as the 1 percent quantile for those years (Edwards et al. 2002).

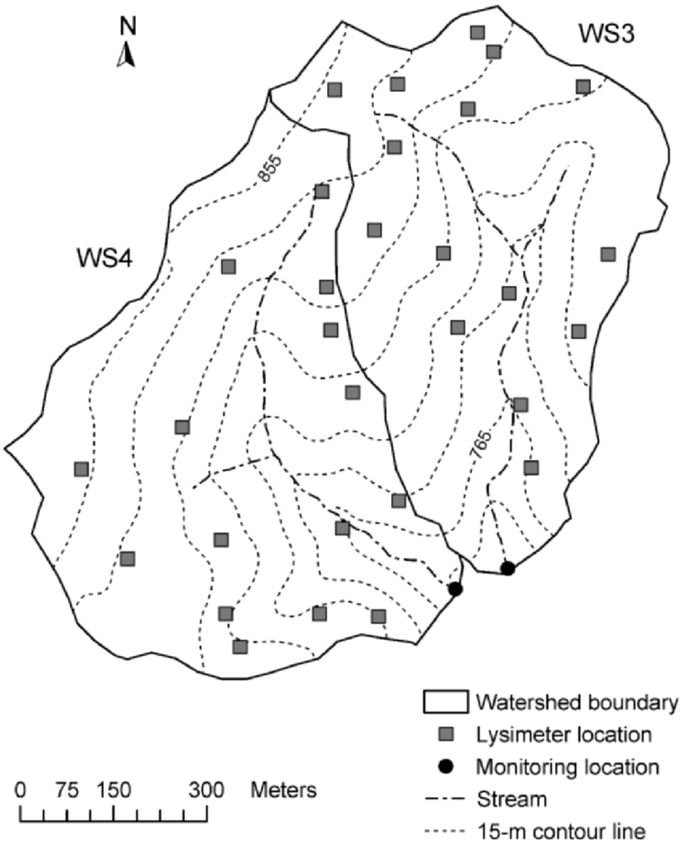

Figure 4-2. Lysimeter locations on WS3 (treatment) and WS4 (control).

Samplers typically were actuated manually because manual actuation provides more reliable sampling along the entire hydrograph than stage actuation in these flashy headwater streams. Growing season samples (May-October) were collected at approximately 15-minute intervals on the rising limb of the hydrograph and for at least several samples after peakflow. Dormant season samples were collected on 30- or 60-minute intervals on the hydrograph rising limb and for several samples after peakflow. Longer time intervals were used in the dormant season because the hydrologic responses are longer because soil moisture deficits are negligible or absent.

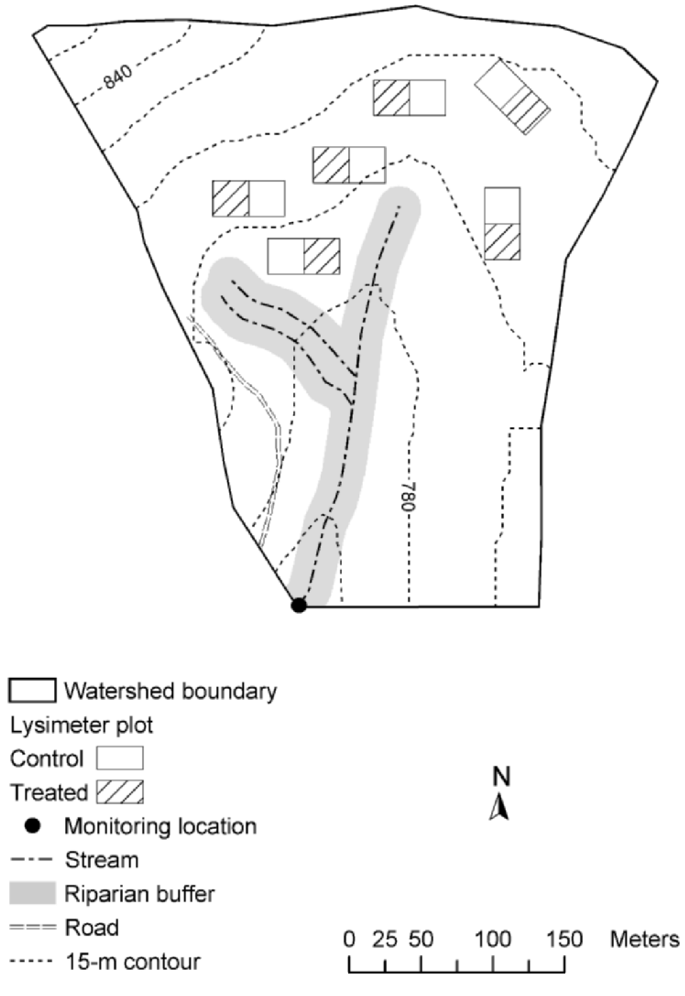

Figure 4-3. Treatment and control plot lysimeter locations in WS9.

From the stormflow data set, the chemistries of the sample collected nearest to the peakflow for each storm in each watershed was extracted and placed in a third data set (i.e., peakflow). These data represent samples that are generally the most chemically different from baseflow, as observation and analysis by Edwards et al. (2001) show. The greatest concentrations of all analytes except nitrate (NO_3) and pH occur near the time of peakflow. Nitrate is less consistent and can occur slightly before peakflow, but usually tends to occur several hours after peakflow, presumably because, to some degree, its behavior is controlled by biological reactions (Edwards et al. 2001). However, the differences in NO_3 concentrations between the actual maximum of NO_3 and those at peakflow are small. By contrast, pH reaches its minimum in-storm value near peakflow.

2.3 Chemical Analyses

Chemistry for the routine, baseflow, and peakflow stream water samples, and soil leachate samples was determined at the USDA Forest Service, Northeastern Research Station's Timber and Watershed Laboratory in Parsons, West Virginia using EPA-approved protocols. Samples were analyzed for calcium (Ca), magnesium (Mg), potassium (K), sodium (Na), sulfate (SO_4), NO_3, chloride (Cl), and pH. Sample handling, processing, and analytical techniques are detailed in Edwards and Wood (1993). Due to budget constraints, analyses for total dissolved aluminum (Al) were performed only rarely for soil water samples collected from WS9; Al was not analyzed for any water samples collected from WS3 or WS4. Pretreatment samples were collected on 30 October, 14 November, and 10 December 1986 from the zero-tension pan lysimeters and analyzed at a water quality laboratory formerly operated by the USDA Forest Service, Northeastern Forest Experiment Station in Berea, Kentucky. Samples also were collected from the pan lysimeters on 13 August 1992, 4 January 1993, and 18 February 1993 to examine Al responses after a number of years of treatment. These samples were analyzed at The Pennsylvania State University's Environmental Resources Research Institute water quality laboratory. As part of another small study done in conjunction with the acidification study on WS9, a limited number of Al analyses were made for soil water samples collected in tension lysimeters located at 10-cm depth during 1992-1994. Foliar samples also were collected from WS9 as part of that smaller study and analyzed for total Al (Pickens 1995). These samples were analyzed at The Pennsylvania State University Agricultural Analytical Services Laboratory (Dahlquist and Knoll 1978).

Acid neutralizing capacity (ANC) was calculated as the difference in concentrations ($\mu eq\ L^{-1}$) between the sum of the mineral bases (Ca, Mg, Na, and K) and the sum of the mineral acids (SO_4, NO_3, and Cl). If ANC is negative the solution has a strong acid acidity (Reuss and Johnson 1986) and these mineral acids are supporting or counterbalancing hydrogen (H^+) ions or Al species (Baker et al. 1990). If the ANC is positive, the solution has net mineral base or alkalinity, and all or some of the H^+ ions are being countered by other anions, such as bicarbonate and organic anions (Rustad et al. 1993).

2.4 Data Analyses

To account for differences in dilution or concentration of soil water chemistry that could be caused simply by different catch volumes, volume-weighted mean concentrations by horizon were determined for WS3 and WS4, and for the control plot lysimeters and treatment plot lysimeters on WS9. These were calculated by multiplying the concentration for each sample by its corresponding volume. The volume was the sum of the lysimeter sample plus any overflow, if overflow existed in the bucket. Overflow was recorded as 16,148 ml if the bucket volume was overflowing, which was the maximum volume the buckets could hold with bottle displacement. Then for each date and by horizon, the concentration x volume results were summed and divided by the sum of the volumes, which yielded volume-weighted mean concentrations. Because pH is logarithmic and averages should not be calculated directly, H^+ concentration was determined from each pH, and mean volume-weighted concentrations were determined from the H^+ values. These values then were converted back to average pH values.

No flow-adjusting (i.e., to account for concentration or dilution effects) was performed for stream water samples collected. There were several reasons for not flow-adjusting. The typical way to adjust for flows for stream water is to do volume-weighted averaging. However, because only one sample was available per watershed per sampling date (vs. 15 per horizon per watershed for soil leachate) determining volume-weighted averages would result in reducing display of the data and the sample sizes for statistical analyses by at least 75 percent (e.g., four samples per week for routines reduced to one volume-weighted average per month). Furthermore, there was no real way to determine volume-weighted averages on just the peakflow chemistries; volume-weighted averages would have required considering every point collected during the storm and the result would not have been representative of the most episodic response during each storm. Flow-adjusting for stream water samples could have been done by plotting the concentrations against streamflow at the time the sample was collected and then using the time series of the residuals to display treatment responses (Helsel and Hirsch 2000, Hipel and McLeod 1994). However, by this method, there is no way to ascertain quantitatively how much the chemistry changed over time because the units of the residuals are not meaningful. But analysis of the relationships between the concentrations and flows indicated that no or only very weak relationships existed for most analytes. And even for the analytes that had the strongest relationships, predominantly pH, as well as SO_4 and NO_3 to a much lesser extent, there was little need to flow-adjust because the trend lines applied to flow-adjusted and unadjusted data showed essentially the same patterns and timing of responses. Consequently, to preserve the ability to consider the responses in concentration units we are using the original data without adjusting for streamflow.

The volume-weighted mean soil water concentrations and the stream water (routines, baseflow, and peakflow) concentrations of each ion were graphed against time, and a locally weighted regression line (Cleveland and Devlin 1988) was fitted through the data using Locfit software (Loader 1998) to aid in showing trends (Hipel and McLeod 1994). Locally weighted regression does not provide regression coefficients, but it does display data trends (especially non-monotonic trends) very effectively without the assumptions or limitations of predefined equation forms (i.e., linear, quadratic, cubic, etc.) that accompany least squares regression. Locally weighted regression also is appropriate for irregularly spaced nonparametric time-series data, which describe many of the data in this study.

To avoid oversmoothing the trend lines, various combinations of fitting degrees and smoothing values were applied to each ion vs. time data set. Then residuals were determined for each data point and were plotted against time. A locally weighted regression line developed using the same fitted degrees and smoothing values as for the original data was overlaid on the plotted residuals data. The degree of fit and smoothing values were considered appropriate when the latter locally weighted regression line was essentially flat using the lowest possible smoothing value (Cleveland 1994).

Mann-Kendall tests (Mann 1945) were used to determine whether the volume-weighted mean soil water concentrations or the stream water concentrations increased or decreased significantly over time (probability ≤ 0.05). These tests were performed on the concentrations and not the trend lines since locally weighted regression does not provide estimates of regression coefficients to test for significance. Because Mann-Kendall tests can determine the significance of only monotonic data trends, where the trend lines changed direction (indicating a change in the direction of the concentrations) a separate Mann-Kendall test statistic was calculated for the data on both sides of that change as recommended by Hipel and McLeod (1994). Sen-slope estimates (Sen 1968) were calculated to identify the direction (i.e., positive or negative) of the data trends, since these were not always obvious where the data were quite variable or where the change was small.

3. SOIL WATER

3.1 WS4 and WS3 Responses

The concentrations of many ions in soil water on WS4 changed significantly during at least some portion of the period of record, and the concentration of most ions decreased over the entire 15 year period (Table 4-1). Nitrate and the major base cations, Ca, Mg, and K, experienced the most consistent decreases in soil water concentrations in terms of both time and horizon (Fig. 4-4a and 4-4b). Sodium decreased during the initial half of the period of record and then increased resulting in little net change in concentrations over time. Sulfate decreased significantly in the A horizon, did not change in the B horizon and increased significantly through 1996 in the C horizon then did not change through 2003. The only constituent to increase significantly throughout the entire 15 years was pH in the A horizon (Table 4-1, Fig. 4-4b). ANC on WS4 was negative at the start of the study (Fig. 4-5), but it remained fairly constant in all horizons throughout the study, though in the C horizon there was a borderline, but significant decrease in ANC ($\alpha = 0.05$), probably resulting from the combination of increasing SO_4 and decreasing base cations.

While WS4 was not treated with ammonium sulfate fertilizer, it has received high levels of ambient acidic deposition over at least the last several decades (Council on Environmental Quality 1989, National Atmospheric Deposition Program 2000). But, because of implementation of the Clean Air Act Amendments, emissions and resulting deposition of NO_3, SO_4, and base cations have decreased slightly (Hedin et al. 1994, and see Chapter 7). Some of the decrease in NO_3 observed in soil water on WS4 is believed to be attributable to the NO_3 decreases in deposition. The base cation decreases could be from decreases in base cations in atmospheric deposition from new scrubber technologies (Hedin et al. 1994), or they could indicate base cation depletion over the long-term in ambient acidic deposition. The different responses to SO_4 with depth may have occurred simply because there was a lag in the time required for it to move deep into the soil; initially decreased deposition is showing only in A horizon soil water and will not occur for sometime in the lower soil horizons. The increasing concentrations in the C horizon reflect the accumulation of SO_4 ions leached from above under periods of higher deposition.

The ammonium sulfate treatments on WS3 had significant effects on many of the soil water ions (Table 4-1). Of the four base cations, Ca was affected the most. Calcium concentrations in A horizon soil water of WS3 increased steadily and significantly (Table 4-1) for approximately 3.5 years after the initiation of acidification (Fig. 4-4a) in response to increasing anion

Table 4-1. Mann-Kendall and Sen slope results for soil water from WS4 and WS3, by horizon.

		WS4			WS3		
Ion	Horizon	Period	Mann-Kendall probability	Sen slope	Period	Mann-Kendall probability	Sen slope
Ca	A	1989-2003	0.000	-2.88	1989-10/1992	0.032	29.98
					11/1992-5/1998	0.006	-20.71
					6/1998-2003	0.252	-4.78
	B	1989-2003	0.000	-7.57	1989-10/1992	0.039	17.63
					11/1992-2003	0.032	-5.41
	C	1989-2003	0.000	-5.23	1989-7/1996	0.000	22.30
					8/1996-2003	0.000	-17.46
Mg	A	1989-2003	0.000	-1.28	1989-2003	0.000	-1.28
	B	1989-2003	0.000	-2.30	1989-10/1992	0.234	1.90
					11/1992-2003	0.061	-1.23
	C	1989-2003	0.000	-2.74	1989-7/1996	0.000	8.17
					8/1996-2003	0.003	-6.86
Na	A	1989-7/1996	0.909	-0.01	1989-2003	0.500	-0.03
		8/1996-2003	0.000	0.38			
	B	1989-7/1996	0.000	-0.50	1989-2003	0.002	0.13
		8/1996-2003	0.000	0.39			
	C	1989-7/1996	0.000	-0.34	1989-2003	0.648	-0.03
		8/1996-2003	0.000	0.42			
K	A	1989-2003	0.000	-1.10	1989-8/1994	0.472	-1.59
					9/1994-3/2000	0.002	7.66
					4/2000-2003	0.023	-12.12
	B	1989-2003	0.000	-0.33	1989-5/1998	0.005	-0.76
					6/1998-2003	0.086	-1.12
	C	1989-8/1994	0.042	-3.47	1989-7/1996	0.650	-0.20
		9/1994-2003	0.756	-0.17	8/1996-2003	0.001	-2.58
SO_4	A	1989-2003	0.000	-4.65	1989-10/1992	0.000	88.39
					11/1992-2003	0.599	-2.78
	B	1989-2003	0.077	-0.96	1989-7/1996	0.000	31.65
					8/1996-2003	0.685	-2.08
	C	1989-7/1996	0.001	8.33	1989-7/1996	0.000	35.83
		8/1996-2003	0.077	-8.29	8/1996-2003	0.002	-8.82
NO_3	A	1989-2003	0.015	-2.96	1989-3/2000	0.000	17.50
					4/2000-2003	0.149	-33.34
	B	1989-2003	0.000	-7.77	1989-3/2000	0.000	28.47
					4/2000-2003	0.537	-21.76
	C	1989-2003	0.000	-5.96	1989-3/2000	0.000	31.94
					4/2000-2003	0.115	18.73
Cl	A	1989-2003	0.063	-0.16	1989-2003	0.005	0.47
	B	1989-2003	0.001	-0.29	1989-7/1996	0.000	0.91
					8/1996-2003	0.001	-1.71
	C	1989-7/1996	0.058	-0.43	1989-7/1996	0.088	0.76
		8/1996-2003	0.120	-0.99	8/1996-2003	0.000	-1.28
pH	A	1989-2003	0.010	0.01	1989-2003	0.000	-0.01
	B	1989-2003	0.227	0.00	1989-2003	0.000	-0.01
	C	1989-12/1992	0.001	-0.08	1989-2003	0.000	-0.01
		1/1993-2003	0.054	0.01			
ANC	A	1989-2003	0.311	0.77	1989-1994	0.000	-74.78
					1995-2003	0.080	-13.21
	B	1989-2003	1.000	-0.00	1989-1997	0.000	-48.14
					1998-2003	0.455	10.19
	C	1989-2003	0.043	-1.63	1989-1997	0.000	-30.51
					1998-2003	0.037	20.16

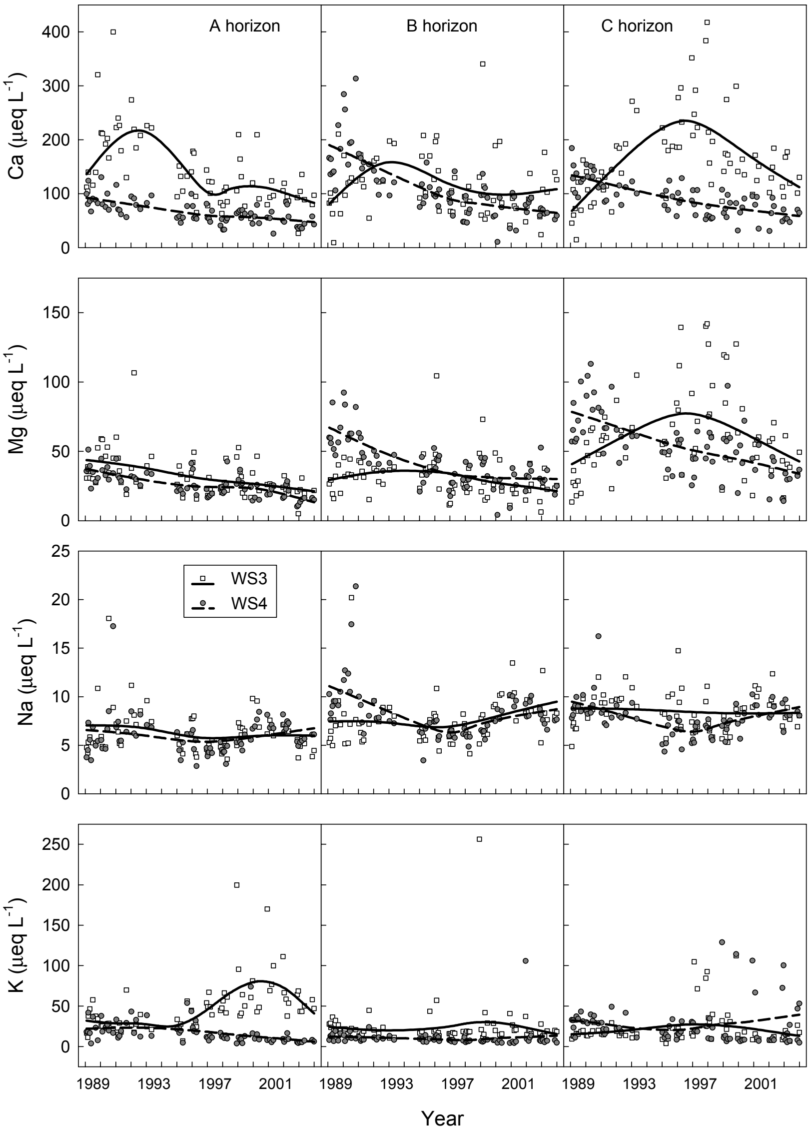

Figure 4-4a. Volume-weighted average chemical concentrations for soil water from WS3 and WS4 with trend lines overlaid, by horizon.

concentrations (Fig. 4-4b). The trend line for the A horizon peaked in approximately 1992, at a concentration slightly greater than 200 μeq L^{-1}, though a few individual concentrations increased to much greater

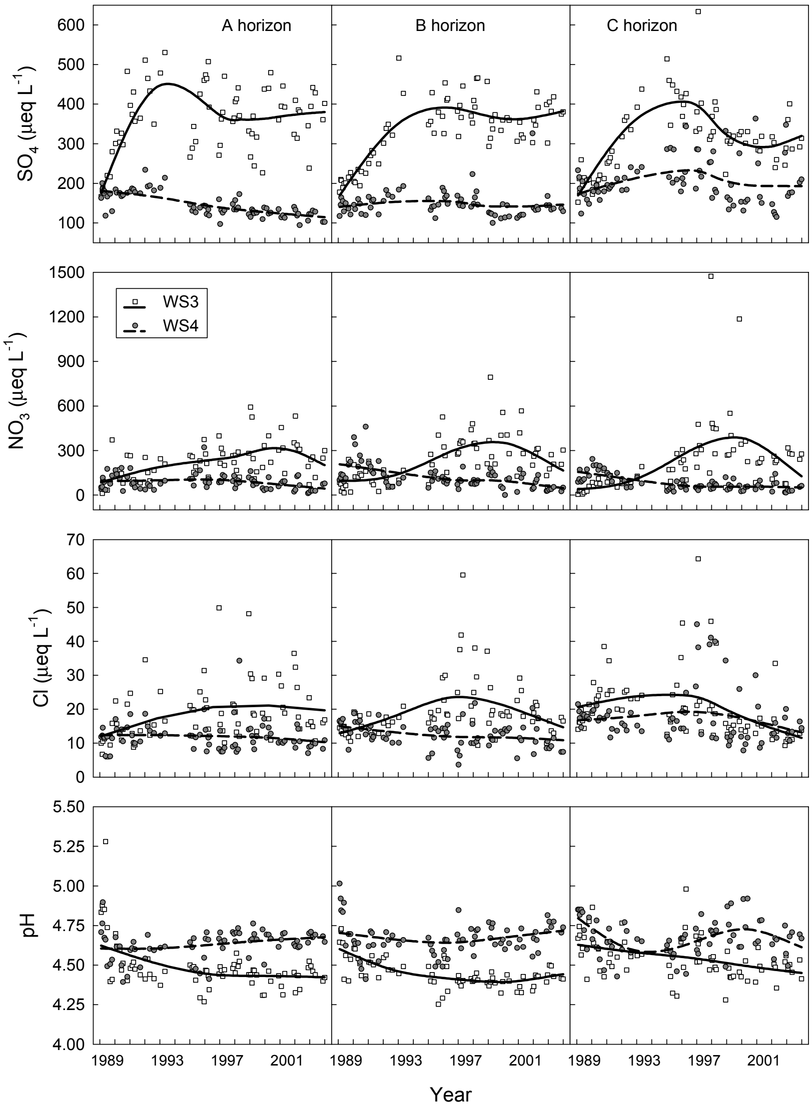

Figure 4-4b. Volume-weighted average chemical concentrations for soil water from WS3 and WS4 with trend lines overlaid, by horizon.

concentrations than 200 µeq L^{-1}. The trend line then decreased significantly through about 1996 and then leveled off (Table 4-1, Fig. 4-4a) and concentrations have returned to approximately those observed just at the initiation of treatment (~100 µeq L^{-1}) in 1989 (Fig. 4-4a).

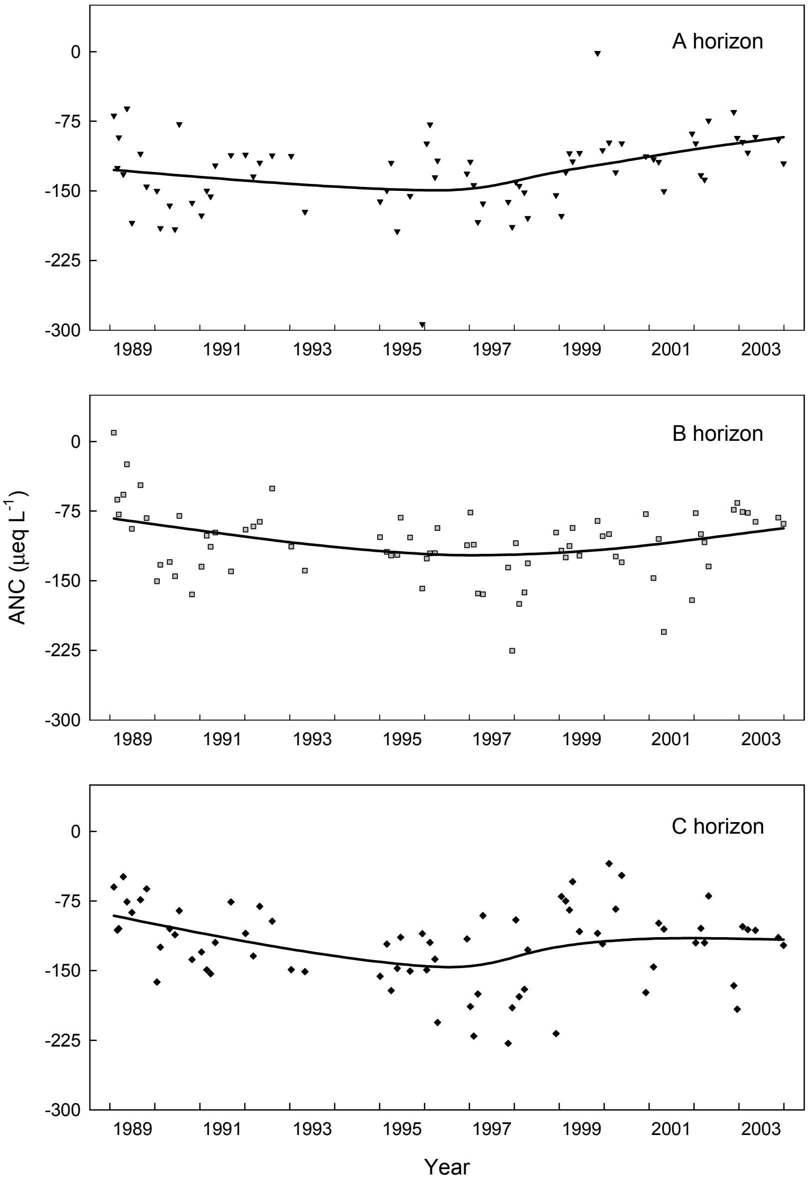

Figure 4-5. ANC for soil water by horizon for WS4.

Calcium concentrations in soil water from the B and C horizons of WS3 increased significantly in response to treatment (Table 4-1, Fig. 4-4a). In the

B horizon the increases lasted only about 3.5 years – the same duration as in the A horizon – compared to 7 years in the C horizon. Calcium concentrations in B horizon soil water essentially returned to pretreatment levels by 1996-97, whereas in the C horizon by 2003 they still were above the 1989 Ca concentrations (Fig. 4-4a).

Magnesium concentrations in A horizon soil water were only about 50 µeq L^{-1} at the beginning of the study (Fig. 4-4a), and they decreased steadily and significantly (Table 4-1) throughout the entire study period, ending at approximately 25 µeq L^{-1}. Throughout the 15 years of record, Mg concentrations in WS3 soil water were very similar to those in untreated WS4 (Fig. 4-4a). The inability of Mg to increase with increasing anion concentrations (Fig. 4-4b) indicates that reserves of exchangeable Mg were not present in WS3, even before the acidification treatments were initiated. Soil chemistry data from WS3 indicate substantially lower Mg concentrations than Ca or K from 0-10 cm depth (Adams and Kochenderfer 1999).

The trend line for Mg soil water concentrations in the B horizon suggests a slight increase in concentrations through 1992 followed by a slight decrease after 1992 (Fig. 4-4a). However, statistical analyses do not indicate a significant change during either of these two periods (Table 4-1).

Changes to Mg in the C horizon were much greater than in the A or B horizons (Fig. 4-4a), and there was a significant increase from 1989-1996 (Table 4-1) in response to the increasing availability of acid anions in soil solution during that time period (Fig. 4-4b). From 1996-2003 there was a significant decrease in Mg concentrations (Table 4-1, Fig. 4-4a), but concentrations did not return to pretreatment levels by 2003. The trend line indicates that Mg concentrations generally increased about 80 µeq L^{-1} above 1989 levels. However, several of the volume-weighted means increased much more than that and had values between 100 and 150 µeq L^{-1} (Fig. 4-4a).

Sodium concentrations in A horizon soil solution did not respond to the treatment (Table 4-1). Sodium concentrations were quite low compared to any of the other base cations, with most of the sample concentrations below 10 µeq L^{-1} (Fig. 4-4a). The lack of or very small responses by Na in any of the lysimeters on WS3 is not surprising given that it is present in low concentrations in these soils (Chapter 3). The area receives negligible inputs of Na from sea salt because of its distance from the Atlantic Ocean and the predominant westerly and northwesterly wind current, and it receives only low concentrations and small loads annually from atmospheric sources (National Atmospheric Deposition Program 2000).

There was no significant response in K concentrations in A horizon soil water for approximately 6 years (Table 4-1), but by the end of 1994, the trend line increased in response to treatment (Fig. 4-4a) and K concentrations increased significantly through 2000 (Table 4-1). The trend line shows concentrations generally increased from approximately 30 μeq L^{-1} to 80 μeq L^{-1}. From the end of 2000 through the period of record, K concentrations again declined significantly (Table 4-1) to levels approximately equal to those at the beginning of the study (Fig. 4-4a).

Normally, monovalent cations, such as K, are exchanged into soil solution more easily than divalent cations, such as Ca, which would suggest that K should have become mobilized in A horizon soil solution at least as early as Ca. While K exchange can be delayed by strong adsorption on certain types of 2:1 layer silicates (Bohn et al. 1985), the soils on all of the study watersheds contain 1:1 not 2:1 layer silicates. Thus, the cause of the 6-year delay in exchange of K in the A horizon is not known.

Potassium concentrations changed much less over time in B and C horizon soil water than in A horizon soil water (Fig. 4-4a). Even though the trend line from 1989-1998 suggests a slight increase in B horizon soil water concentrations (Fig. 4-4a), the Mann-Kendall results indicate that the concentrations actually decreased significantly during that period (Table 4-1). This discrepancy is primarily due to the large number of clustered concentrations that were just slightly greater than other subsequent values at the very beginning of data collection. Because these values were clustered over such a short period of time, the number of observations had a much greater effect on the Mann-Kendall results than they had on the locally weighted regression line. There were no significant changes after 1998 (Table 4-1). In the C horizon, K concentrations did not change significantly from 1989-1996, but they decreased after 1996 (Table 4-1, Fig. 4-4a). However, the net change in K concentrations in soil water in the B and C horizons between 1989 and 2003 was very small (Fig. 4-4a).

The base cation concentrations observed for WS3 can be interpreted in terms of a conceptual model described by Fernandez et al. (2003) for soil water and stream water. In this model, seven states of base cation availability or depletion are described in terms of elevated or declining levels of N and S inputs to soils. Stage I describes concentrations of base cations in equilibrium with existing conditions, so concentrations are essentially constant over time. During Stage II, N and S inputs increase and are accompanied by increases in exchangeable base cations in solution to counterbalance the negative charges of increasing acid anion concentrations (i.e., NO_3 and SO_4). Base cation concentrations continue to increase until soil exchangeable base cations begin to become depleted, and they can no longer counterbalance the levels of acid anions they once could. At that point Stage III is entered, and base cation concentrations begin declining until they return to approximately the same concentrations that were present before N and S loads were elevated (i.e., in Stage I). In Stage IV, base cation concentrations remain approximately constant at that initial equilibrium concentration, during which base cation exchange to soil solution is in equilibrium with mineral weathering. Because base cations no longer provide the dominant source of buffering, in Stage IV, Al predominantly replaces base cations in counterbalancing the negative charges of mobile acid anions. Stage V is entered at the time where excess N and S loadings decline or cease, and is marked by decreasing concentrations of base cations below levels that were observed in Stage I. During this time, soil exchangeable pools of base cations are recovering, which causes the concentrations to decrease. In Stage VI cation soil exchange pools become replenished to the level at which base cations can now be exchanged and enter soil solution at an increasing level; thus, base cation concentrations in soil water increase in Stage VI. Eventually, concentrations return to equilibrium, where mineralization inputs control exchange of base cations. At this point, the system is in Stage VII until another alteration to acid inputs occurs. It is clear from the different responses and timing of responses of base cations in Figure 4-4a that the base cations were in different states of cation availability or deficiency through time as well as across horizons.

The inputs of N and S at known elevated levels on WS3 make the evaluation of the base cation responses fairly easy to interpret in terms of the base cation model. Available Ca was present on exchange sites in all horizons so Stage II was entered immediately in response to the acidification treatments in all three soil horizons (Fig. 4-4a). Initial signs of increasing depletion of Ca, or the start of Stage III occurred in the A and B horizons about 4 years after the start of increased N and S inputs. In the C horizon, Stage II lasted about 8 years for Ca. In the A and B horizons, Stage III lasted about 4-5 years. Mineralization has controlled exchangeable Ca (Stage IV) since about 1997 in the A horizon and since about 1998 in the B horizon. The C horizon is still in Stage III, but concentrations in soil solution are approaching those prior to treatment. At its current rate of decline (Fig. 4-4a), Stage IV will be reached in approximately 2007.

Since Mg concentrations in soil water from the A horizon decreased significantly through the entire period of N and S applications, the supply of exchangeable Mg already was largely depleted before the study began meaning the A horizon was in Stage III at the beginning of the study (Fig. 4-4a). Given that A horizon concentrations of Mg have continued to decrease, it appears that the A horizon remained in Stage III through 2003. This region has received some of the highest levels of pollutant inputs of N and S for decades (Council on Environmental Quality 1989, National Atmospheric Deposition Program 2000), which accelerated depletion of Mg reserves on soil exchange sites, particularly since Mg concentrations in these soils are very low compared to Ca (Chapter 3) and Mg is removed more easily than Ca from soil colloids (Bohn et al. 1985). The general lack of change in WS3 Mg concentrations in the B horizon (Table 4-1), suggests that Mg depletion already had occurred, and the B horizon was in Stage IV, where mineralization is controlling exchangeable Mg concentrations.

The greatest Mg response to the acidification occurred in the C horizon (Fig. 4-4a). Mg was not deficient at the beginning of the study in the C horizon presumably because the C horizon acted as a receptor for some of the Mg ions that had been leached from the overlaying A and B horizons. The fertilizer applications induced an increase in Mg exchange and charge pairing (Stage II) through approximately the end of 1995, at which time Stage III was entered and continued through 2003.

The base cation depletion model includes a lag in base cation exchange (Stage II) in relation to the timing of elevated N and S loadings; thus, K follows the graphical depiction of the model as it is presented in Fernandez et al. (2003). Average K concentrations in the 0-10 cm soil depth, which corresponds approximately to the A horizon, were about double the Mg concentrations in 1994 (Adams and Kochenderfer 1999), which explains the substantial differences in responses over time between K and Mg (Fig. 4-4a). By 2003, the A horizon was in Stage III with respect to K concentrations. In the B and C horizons, the very small changes in K trend lines in WS3 (Fig. 4-4a) and the very small Sen slopes that were present even when the concentration changes were significant (Table 4-1), make it difficult to determine whether these horizons are nearing the very end of Stage III or have entered Stage IV. Either way, the level of neutralization of acid anions by K in either the B or the C horizon was small throughout the study.

In all three horizons, SO_4 concentrations increased immediately and significantly in response to treatment on WS3 (Table 4-1, Fig. 4-4b). The increase was expected since SO_4 is the principal ion in the applied fertilizer, and SO_4 is not normally limiting in forest soils (Reuss and Johnson 1986). However, within 5 to 7 years after the initiation of ammonium sulfate applications (depending on the horizon), SO_4 concentrations essentially leveled off (Table 4-1, Fig. 4-4b), indicating that SO_4 was being retained in all of the soil horizons. Interestingly, the change in SO_4 responses occurred when the concentrations reached similar values in all three horizons and when the absolute maximum concentration reached approximately 500 μeq L^{-1} (Fig. 4-4b).

It is unlikely that increased biotic assimilation of SO_4 was important in controlling SO_4 mobilization, as S rarely is limiting to plant growth, particularly in this region that receives high levels of atmospheric S deposition (National Atmospheric Deposition Program 2000). More likely, adsorption and/or precipitation of SO_4 minerals would explain the retention of SO_4. Adsorption would be enhanced if soils in WS3 had pH-dependent charge. Anion adsorption on pH-dependent exchange sites increases as pH decreases and occurs predominantly in kaolinitic (1:1) soils (Bohn et al. 1985). The pH in WS3 soil solution decreased significantly over time in all the soil horizons, reaching between 4.25 and 4.5 during the time that SO_4 retention occurred (Fig. 4-4b), and the soils are kaolinitic, making it highly likely that some pH-dependent adsorption occurred. Whether precipitation of SO_4 minerals was a factor in SO_4 retention is unknown, as there is disagreement as to how low soil pH has to be before precipitation becomes important (e.g., Neary et al. 1987, Plumlee et al. 1995, Reuss and Johnson 1986).

The very similar shapes and timing of upturns and downturns of the trend lines for Ca and SO_4 (Fig. 4-4a and 4-4b) suggest that the mobility of Ca was controlled by SO_4 mobility. And indeed, cooperative adsorption or co-adsorption of SO_4 and base cations has been reported in the literature (Marcano-Martinez and McBride 1989, Mitchell et al. 1992, Sumner 1990). However, an analysis of the relationship between concentrations of Ca and SO_4 show little stoichiometric dependency of Ca on SO_4 (Fig. 4-6), with the exception of the C horizon. Thus, the similarities between the two are mostly coincidental, and Ca is controlled predominantly by the exchange processes described earlier. These processes obviously involve SO_4 since it is an acid anion, but Ca responses, particularly during Stages III and IV were clearly controlled by the availability of Ca on exchange sites and its progressive depletion, not by the cessation of increasing SO_4 concentrations.

The other major anion that increased in soil water from the acidification treatments was NO_3. Nitrogen inputs from the fertilizer were as ammonium (NH_4), but Gilliam et al. (1996) reported the vast majority of applied NH_4 on WS3 is nitrified rapidly to NO_3 so that soil water NH_4 concentrations were very small and typically below detection limits throughout most of the study in all soil horizons (Fig. 4-7).

Nitrate concentrations in soil water of all three horizons increased significantly for 11-12 years (Table 4-1). Following that period, the trend line suggests a decrease in NO_3 (Fig. 4-4b), but the Mann-Kendall tests indicate no statistical change from 2000-2003 (Table 4-1). The discontinuation of rising NO_3 concentrations was unexpected, particularly at this late point in the study, because ammonium sulfate was applied during every year of the study. As with SO_4, some type of NO_3 retention or conversion to another chemical species must have occurred.

Retention of NO_3 (though likely as some other form of N) may have occurred but none of the reported processes as currently understood can fully explain the retention of NO_3. An onset of nonspecific adsorption of NO_3 is improbable because SO_4 was readily available and would have been preferentially adsorbed over NO_3. Inducement of biotic NO_3 assimilation by vegetation or microorganisms would have been unlikely at this late time in the stand's age. Additionally, if the watershed soils were N deficient, NO_3 retention by tree assimilation or microorganisms would have occurred and been evident when the fertilizer applications were begun (Aber et al. 1998).

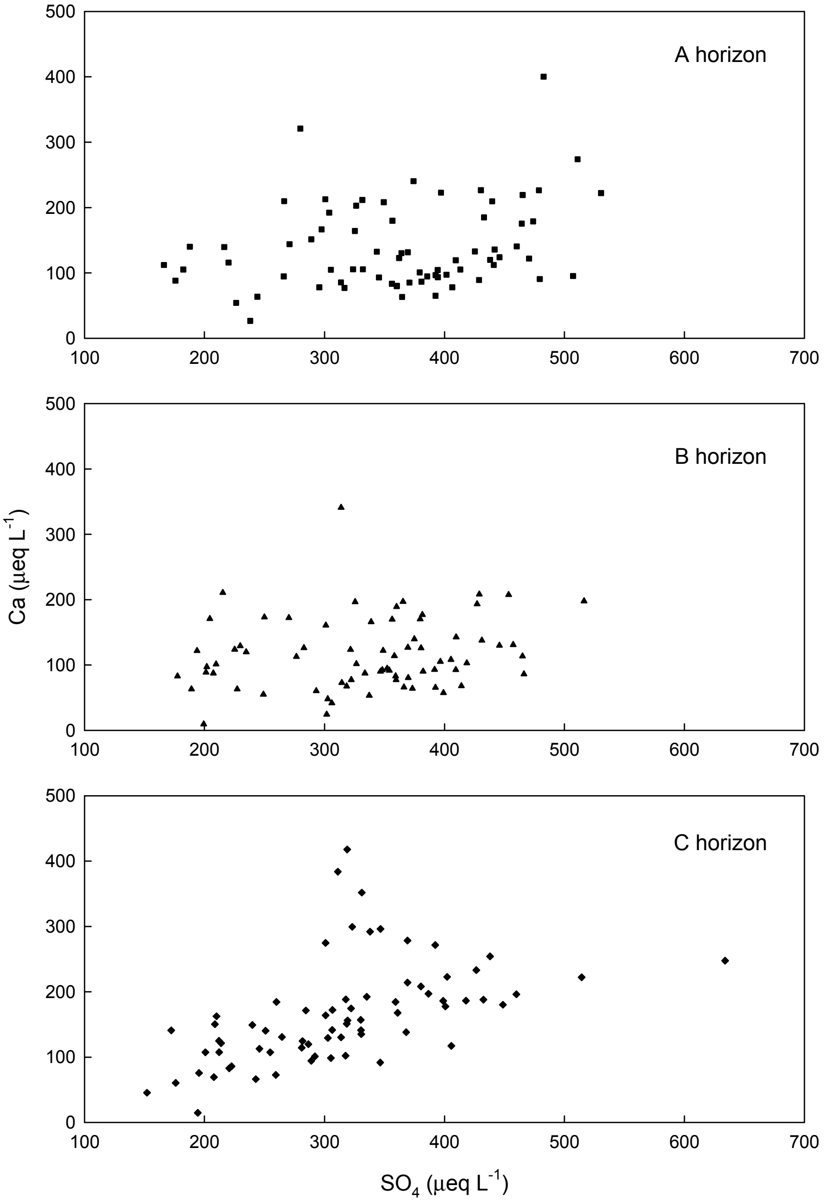

Figure 4-6. Relationships between Ca and SO_4 concentrations in soil water from WS3, by horizon.

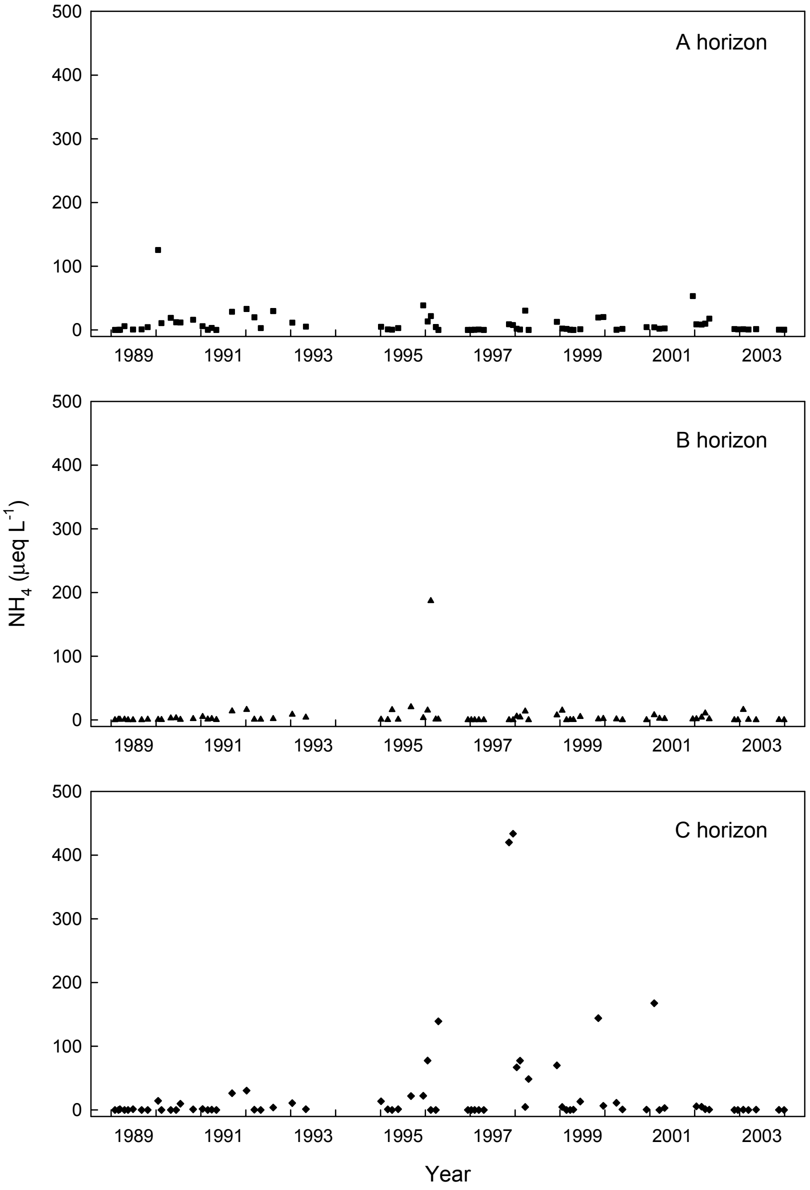

Figure 4-7. Volume-weighted average NH_4 concentrations in WS3 soil leachate, by horizon.

The delayed inducement of large levels of biotic immobilization simply by providing more NO_3 to the soil is contrary to current understanding of nutrient demands. Likewise, N retention through biotic immobilization by mycorrhizae (Aber 1998) also should have been demonstrated earlier rather than later in this study and not below the A horizon. Abiotic immobilization of NH_4 and nitrite (NO_2) in soil organic matter (Fitzhugh et al. 2003, Berntson and Aber 2000, Dail et al. 2001) would have been unlikely in the deeper B and C horizons where organic matter composed <6 percent of the soil (see Chapter 3). Soil conditions, such as high concentrations of organic matter, reducing conditions, or basic soil pH to support some of the more contemporary proposals or theories of abiotic NO_3 retention as green rusts (Hansen et al. 1996, 2001), or by iron (Fe) and possibly manganese (Mn) catalysts (Davidson et al. 2003, Kaiser et al. 1996, Currie et al. 1996) also are not believed to be present broadly or with depth across WS3. It also is possible that abiotic transformations of NO_3 to dissolved organic nitrogen (DON) occurred, but DON was not measured in this study. However, because a large percentage of available DON tends to be retained rather than exported from forested watersheds on an annual basis (Davidson et al. 2003), DON retention may have been an important N-controlling mechanism on WS3. Clearly, the N-retention mechanisms that developed over time on WS3 are not understood, and they do not fit into the current understanding of N saturation theory as presented by Aber et al. (1998).

Chloride is an acid anion, but was present in soil water in significantly lower concentrations than NO_3 or SO_4. Like Na, atmospheric inputs of Cl by sea salts are not high in this region. However, the dissimilar Cl responses on WS3 and WS4 suggest that the Cl increases in the A horizon and in the B horizon through 1996 in WS3 (Table 4-1) were attributable to treatment. It is possible that some of the Cl response was due to contamination in the fertilizer, but Cl was not one of the constituents analyzed during fertilizer assays. The changes to Cl concentrations were not large (Fig. 4-4b) and Cl represents on average only 3.7 percent of the acid anion concentration in soil water.

Through the additions of excess NO_3 and SO_4 and the corresponding movement toward base cation depletion in all horizons, soil water in WS3 became significantly more acidic. At the start of the study, the total concentration of acid anions in WS3 always exceeded the total concentrations of the base cations (Fig. 4-8), resulting in soil solution with a net acidity, or negative ANC, in all soil horizons (Fig. 4-8). At that time, the base cations could counterbalance about 80 percent of the negative charge of the soil water in the A horizon of WS3, and about 60 percent in the B horizon. While there was more sample to sample variation in the C horizon, on average about 60 percent of the acidity could be neutralized in 1989 (Fig. 4-9). The ratio of base cations to acid anions leveled off by about 1996 in all horizons and has stayed approximately level since then. Thus, whether a horizon is nearing the end of Stage III or already within Stage IV of base cation depletion, under current N and S input rates and levels of S and N mobilization in the soil, weathering is able to fulfill only about 20-30 percent of the buffering capacities in WS3 soil water (Fig. 4-9).

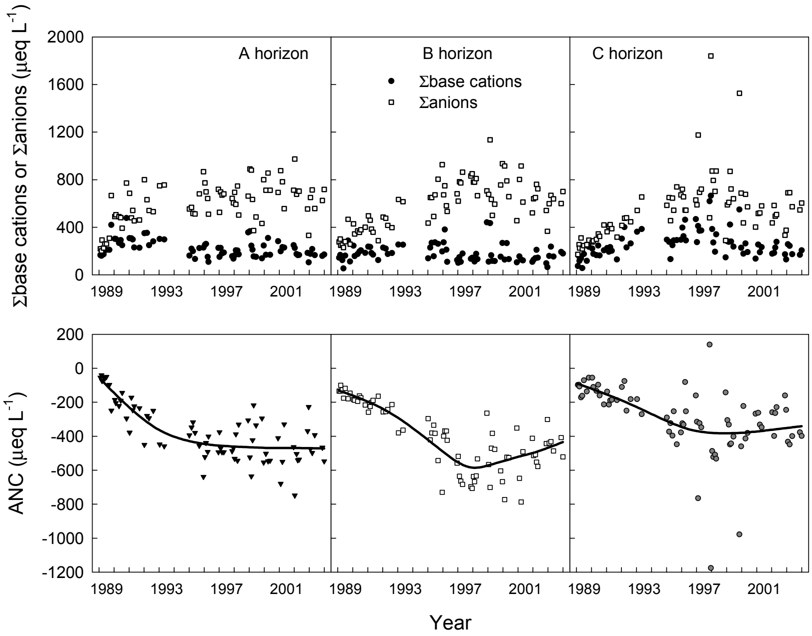

Figure 4-8. The sums of the base cations and acid anions in soil water for WS3 by horizon (top), and ANC for soil water by horizon for WS3 (bottom).

The deficits in charge neutralization throughout the study presumably have been filled by Al since the pH values of soil water were generally <4.75, soil water pH declined significantly through 2003 in all soil horizons (Table 4-1, Fig. 4-4b), and soil pH values throughout the mineral soil were below 4.55 in 1994 and 1997 (Adams and Kochenderfer 1999). Aluminum solubility increases substantially below pH 5.0, with Al^{3+} being the dominant form in acidic forest soils. Thus, Al fulfilled approximately 20 or 40 percent (depending on horizon) of the positive charge in soil solution in 1989, but by 1996 the contribution of Al had risen to approximately 70 percent in the A horizon, approximately 80 percent in the B horizon, and about 60-65 percent in the C horizon. The lower percentage of charge counterbalancing by Al in the C horizon reflects the fact that the C horizon is in Stage III with respect to Ca, Mg, and perhaps K.

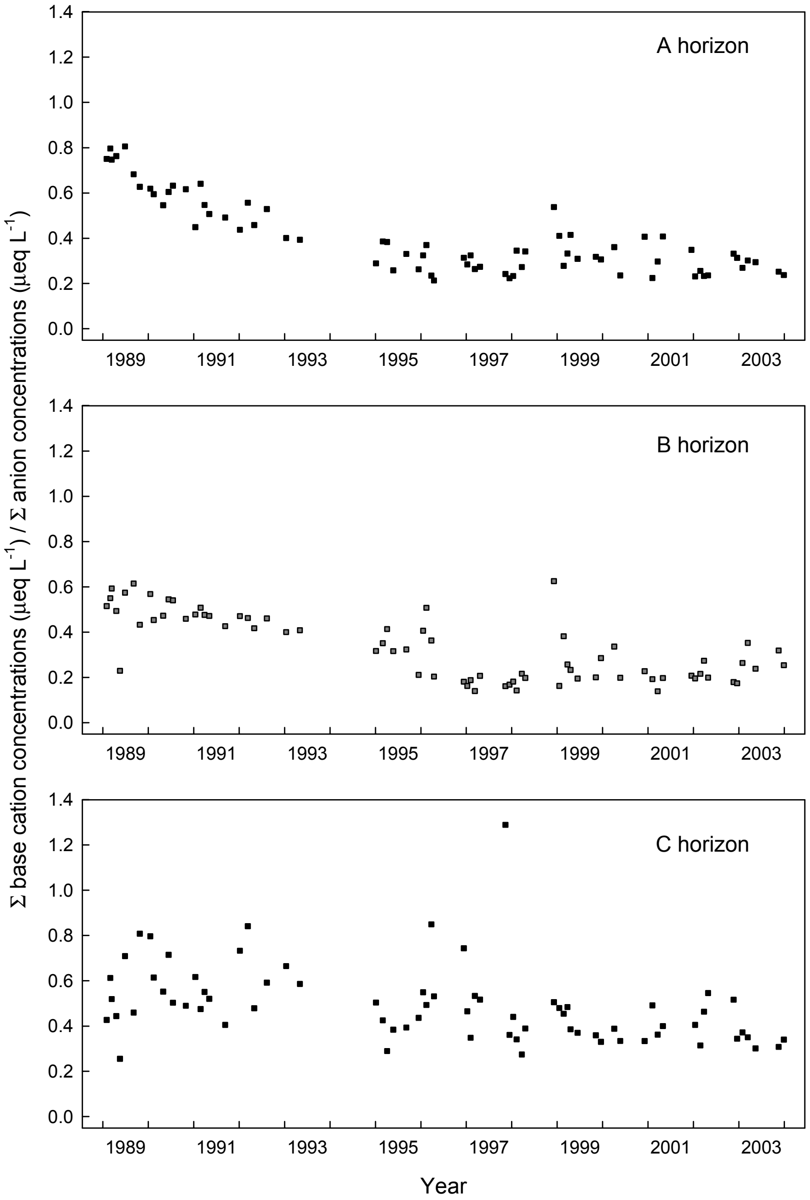

Figure 4-9. The proportion of acid anion charge counterbalanced by base cations in soil water from WS3, by horizon.

There was a noticeable shift over time in the relationships between SO_4 and NO_3, and ANC levels in all three horizons (Figs. 4-10 and 4-11, respectively) During the time that ANC was declining, ANC responses were strongly correlated stoichiometrically to SO_4 but not to NO_3. After ANC leveled off, which also corresponded to the periods that SO_4 retention was

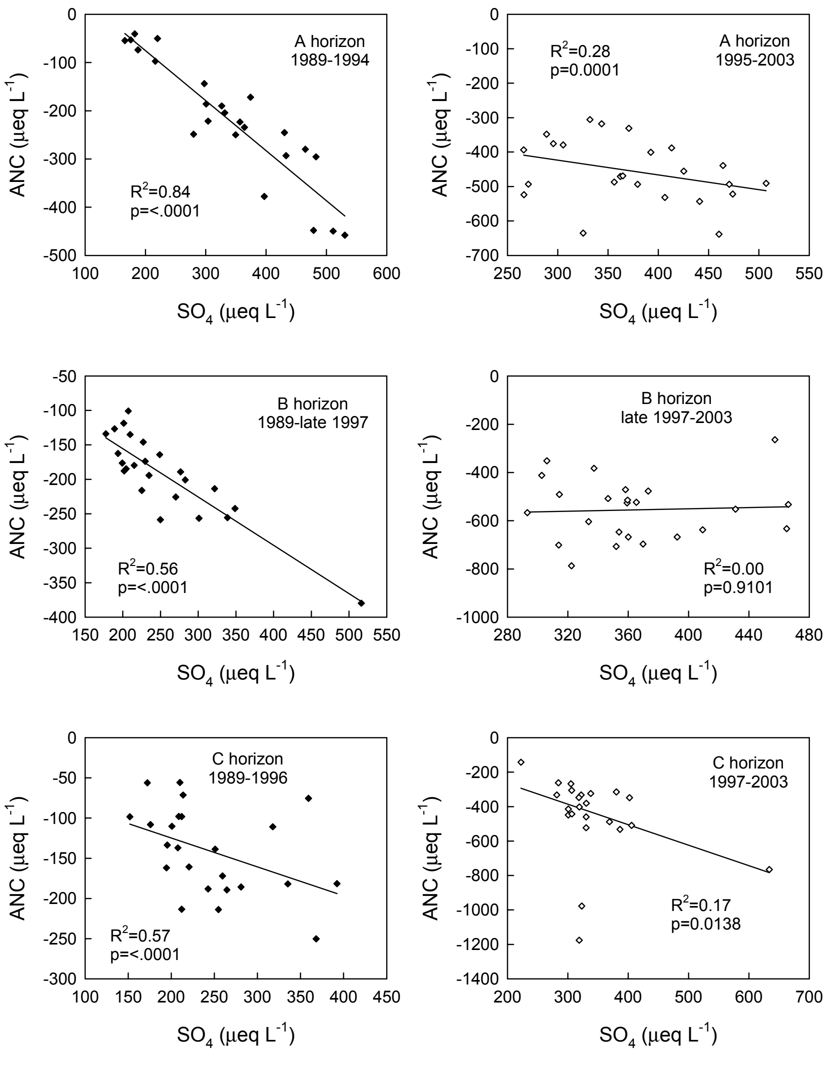

Figure 4-10. Stoichiometric relationships between SO_4 and ANC for WS3 soil leachate before and after the ANC trend lines stopped decreasing (refer to Figure 4-8).

occurring, there was no strong relationship between ANC and SO_4; NO_3 then became correlated strongly with ANC. This relationship shows how the importance of SO_4 and NO_3 in affecting ANC could change in the future under predicted conditions of decreasing SO_4 and increasing NO_3 deposition.

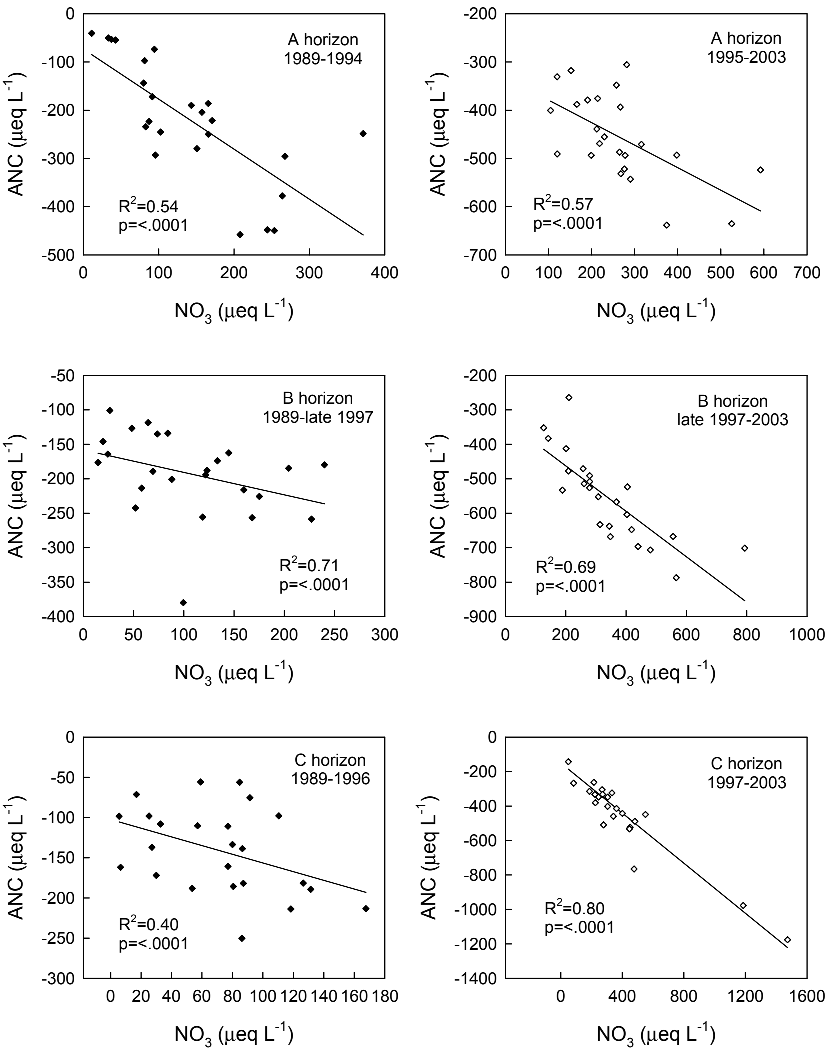

Figure 4-11. Stoichiometric relationships between NO_3 and ANC for WS3 soil water before and after the ANC trend lines stopped decreasing (refer to Figure 4-8).

3.2 WS9 Responses

Calcium and Mg concentrations collected from the control lysimeters in WS9 declined significantly throughout the entire 16 years of record (Table 4-2), suggesting that the unfertilized plots are in Stage III with respect to Ca and Mg levels. However, these trends are difficult to see from the data and the trend lines (Fig. 4-12). Thus, it is difficult to say with great certainty that the watershed soils were in Stage III. Sodium and K concentrations decreased through 1994, but then increased from 1996 through 2002 (Fig. 4-12, Table 4-2). Nitrate and Cl concentration trend lines for the control lysimeters followed the K and Na concentration patterns (Fig. 4-12). However, there was no meaningful correlative relationship between these anion:cation pairs. Thus, rather than either NO_3 or Cl driving the K and Na responses, all four ions simply responded similarly (i.e., the trend lines) to some event that apparently has affected availability/exchange of these ions. Whatever the process that resulted in the K and Na increases since 1995, the data suggest that there is still some K and Na on the exchange sites to provide enhanced levels of buffering, or Stage II, as the concentrations of Ca and Mg decrease. But because the K and Na concentrations are both very low (Fig. 4-12), the actual amount of buffering that they provide is small.

Table 4-2. Mann-Kendall and Sen slope results for soil water from WS9 control and treated lysimeters.

	Control			Treated		
Ion	Period	Mann-Kendall probability	Sen slope	Period	Mann-Kendall probability	Sen slope
Ca	1986-2002	0.005	-1.58	1986-10/1990	0.000	29.33
				11/1990-1998	0.000	-15.25
				1999-2002	0.778	-0.97
Mg	1986-2002	0.000	-0.25	1986-10/1990	0.000	5.87
				11/1990-1998	0.000	-3.30
				1999-2002	0.310	-0.87
Na	1986-2002	0.078	-0.06	1986-10/1990	0.002	1.17
	1986-1994	0.041	-0.17	11/1990-1994	0.029	-0.55
	1995-2002	0.001	0.52	1995-2002	0.000	0.89
K	1986-12/1995	0.000	-0.44	1986-1994	0.000	0.78
	1/1996-2002	0.000	1.95	1995-2002	0.105	0.94
SO_4	1986-2002	0.000	-2.51	1986-10/1992	0.000	32.27
	1986-1994	0.000	2.11	11/1992-2002	0.000	-17.56
	1995-2002	0.000	-6.21			
NO_3	1986-2002	0.000	2.61	1986-10/1990	0.000	12.44
				11/1990-1994	0.005	-7.01
				1995-2002	0.524	0.35
Cl	1986-12/1995	0.018	-0.12	1986-2002	0.000	-0.35
	1/1996-2002	0.012	1.25			
pH	1986-2002	0.000	-0.01	1986-2002	0.000	-0.01

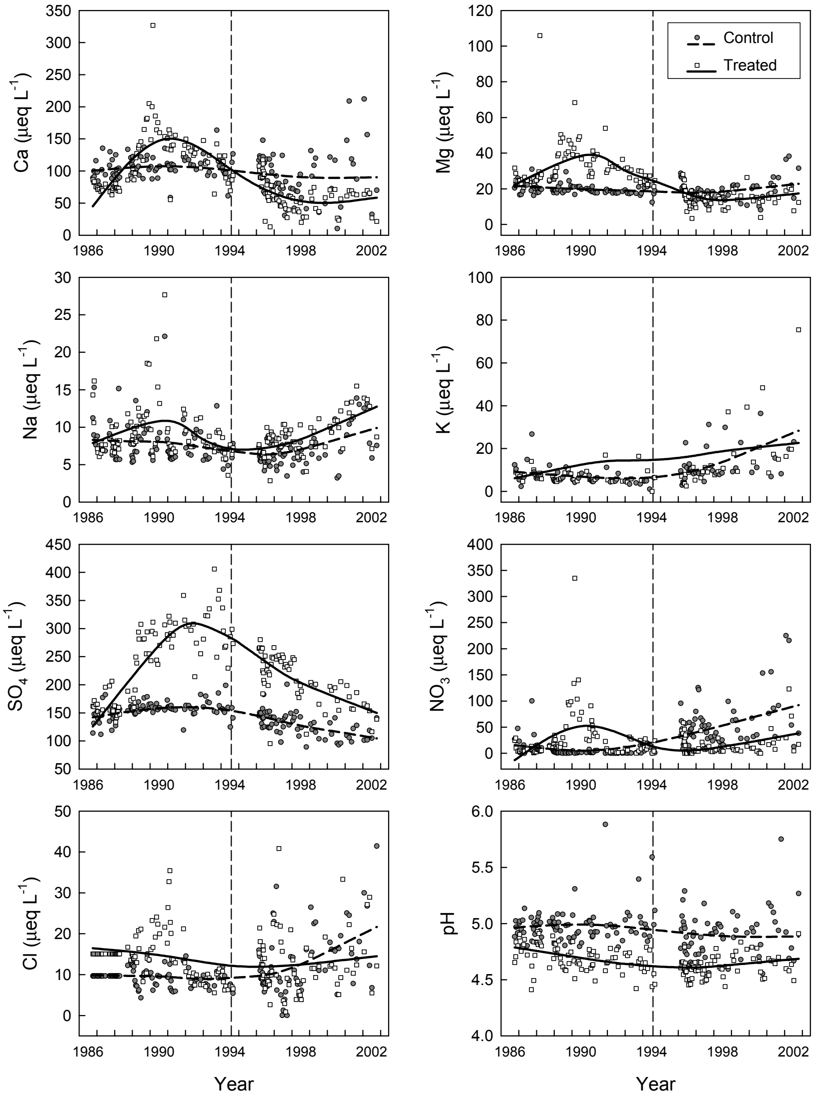

Figure 4-12. Volume-weighted average chemical concentrations for soil water from WS9 control and treatment lysimeters with trend lines overlaid. Dashed vertical line marks end of treatment.

Sulfate concentrations in the control lysimeters declined significantly over time (Table 4-2), but the majority of that decline occurred after 1995 (Fig. 4-12). If the data set is analyzed in two parts (pre and post 1995), SO_4

concentrations decreased only after 1995, and the slope of that change was larger than the slope for the single analysis of the entire period of record (Table 4-2). Sulfate concentrations and loadings in atmospheric deposition have been declining significantly in this area since 1978 (see Chapter 7) and the declining SO_4 concentrations in soil water from control plots may be reflecting lower atmospheric inputs.

The pH of soil water collected from the control lysimeters in WS9 has declined slightly but significantly over time (Table 4-2). The pH of soil water in the WS9 control lysimeters is and has been much higher than WS4 since 1989 (Figs. 4-12 and 4-4b, respectively). The greater pH of soil water from the control lysimeters on WS9 is surprising; this watershed has been reported to have undergone abusive farming in the past and was abandoned because of poor soil productivity, and it was thought to have had low nutrient supplies at the start of this study. Furthermore, the planting of Japanese larch on the watershed was expected to reduce soil pH as this tree is a deciduous conifer, so a large supply of acidic needles is dropped onto the soil annually. However, Japanese larch has low rates of Ca uptake and high rates of Ca leaching (Eriksson and Jönsson 1994), thus contributing to the relatively high pH levels in soil water on WS9. In 1983 when the previously existing low-quality hardwood stand was harvested, a substantial amount of tops and woody debris were left on the site. So while there was a net loss of base cations, especially Ca, to the site from bole removal, there was a sustained elevated return of Ca and other cations to the soils during the time those materials mineralized. This also potentially could explain some of the high pH and base cation concentrations, at least why they were greater than those expected from earlier reports. However, the logging slash was windrowed after harvesting (Kochenderfer and Helvey 1989), which would have tended to concentrate those base cations along the contoured areas but not across the whole watershed, so harvesting may not be a factor in the explanation.

Soil water from the treated lysimeters clearly showed responses to the acidification treatment (Fig. 4-12). In many respects, during the applications of ammonium sulfate (1987-1994), the responses from WS9 were similar to those from WS3. But examination of WS9 also provides the opportunity to examine the recovery phase of base cations in response to the termination of the artificially elevated loadings of S and N.

Calcium and Mg concentrations in soil water became mobilized immediately (Stage II) and increased significantly (Table 4-2) with the initiation of fertilization. Stage II lasted about 3 years for both cations (Fig. 4-12). Progressive depletion of Ca and Mg (Stage III) began sometime just before or during 1990 and for Ca it continued until perhaps 1996, though the timing is impossible to define well with no data from the second half of 1994-1995. However, the high initial Ca concentrations present in 1996 (Fig. 4-12), suggest that Stage III still existed in 1996. The very rapid decline in concentrations in 1996 indicates a short period of equilibrium with weathering (Stage IV) with respect to Ca concentrations. Magnesium appears to have experienced Stage IV from 1994 to 1996, as the final concentrations in 1994 and the initial concentrations in 1996 were approximately equal to those in 1986 and early 1987 before treatment began (Fig. 4-12). Recovery of Ca and Mg and replacement on soil exchange sites (Stage V) appears to have begun in about 1996.

Calcium recovery was more obvious; the data visibly illustrate (Fig. 4-12) a significant decrease in soil water concentrations (Table 4-2) through 1998 (Stage V), followed by increased exchange into soil water (Stage VI) through 2002. The number of data points available from 2002 are insufficient to determine if Ca had returned to equilibrium, or Stage VII by that time; the majority of the Ca concentration values in 2002 are above the trend line and approximate the lowest concentrations in 1986, but there are two points below the trend line that suggest recovery was still occurring. Either way, it is likely that by now equilibrium (Stage VII) has been reached since two additional years have passed since the last sample shown was collected.

Magnesium concentrations did not drop as much as Ca concentrations, resulting in a more muted recovery period and greater difficulty in distinguishing between Stages V and VI. However, since 2000 the concentrations in soil water do appear to have increased slightly (Stage VI) but not signifycantly (Table 4-2). Magnesium concentrations had not returned to Stage VII by 2002, and the slow rate of increase shown for Mg concentrations (Fig. 4-12, Table 4-2), makes it difficult to estimate whether equilibrium has been reached in the subsequent two years.

The behavior of K was very unusual compared to any of the other base cations on either watershed. The trend line and Mann-Kendall tests show increasing concentrations throughout the entire period of record (Fig. 4-12, Table 4-2), though the actual concentrations are small. This pattern suggests an immediate increase of K in response to the acidification treatment (Stage II), but at a very slow rate. The slow rate of exchange may reflect the unknown soil conditions that also were responsible for the slow release of K in the A horizon of WS3. Potassium concentrations became more variable beginning in about 1999, which coincided with the timing of some substantially higher values from 1999-2002 (Fig. 4-12). By 1999, the pH values of soil water had dropped about 0.2 pH units and were just above pH 4.5 (Fig. 4-12), so that the progression of soil acidification may have spurred the elevated exchange of K. Thus, with respect to K the soil was in Stage II throughout the entire treatment and post-treatment period.

Nitrate concentrations increased significantly (Table 4-2) through 1990 (for about 2.5 to 3 years after the initiation of fertilization) and then decreased significantly until the end of 1995 (Fig. 4-12, Table 4-2) in a manner similar to but more distinct than what occurred on WS3 (Fig. 4-4b). Consequently, the NO_3 retention phenomenon observed on WS3 was not an isolated anomaly. The concentrations present during the period of retention were generally quite low, almost always <40 μeq L^{-1} and typically ≤25 μeq L^{-1} (Fig. 4-12). After 1995, NO_3 concentration responses did not change significantly (Table 4-2), even though the watershed transitioned from a period of treatment to non-treatment.

Edwards et al. (1999) originally reported this decline in NO_3 concentrations for WS9 soil water but attributed it to a vegetative uptake by the Japanese larch planted on the site. They suggested that the planted larch did not fully utilize the N applied to the site because the tree roots had not become established sufficiently during the first years of the study to fully occupy the soil and exploit available nutrients. However, there are several pieces of evidence and reasoning that indicate this original interpretation was incorrect: the similar response in WS3, the fact that Japanese larch do not require or even thrive in high N-available environments (VanGoor 1953), the lack of other, more gradual changes in concentrations that would be expected as N uptake increased with root establishment, and that biotic assimilation cannot be induced simply by adding N if the site is not initially N deficient. These factors all indicate that the NO_3 decline on WS9 was due to something other than biotic immobilization.

DeWalle et al. (1985) reported that WS9 had lower soil nutrient pools than WS3 and suggested that WS9's past farming history created N-limited conditions in the soil, but in such an environment, immobilization of NO_3 by microorganisms and vegetation would have been expected to occur immediately upon fertilization, not several years after treatment began. Sudden and substantial increases in ammonification rates at the expense of nitrification processes also are not suggested by the NH_4 concentrations in soil water on WS9 (Fig. 4-13). Thus, as on WS3, some type of abiotic immobilization again seems to be a reasonable explanation for the decreases in mobile NO_3.

Soil water concentrations of SO_4 increased significantly at a rate of about 32 μeq L^{-1} yr^{-1} until 1992 (Fig. 4-12, Table 4-2). Concentrations leveled off until treatment stopped in 1994, presumably due to adsorption. Once the ammonium sulfate applications were terminated, SO_4 concentrations in soil water decreased at a fairly constant rate annually (11 μeq L^{-1} yr^{-1}) indicating the adsorption was at least partially reversible (Reuss and Johnson 1986).

Soil water from the control lysimeters in WS9 had nearly equivalent amounts of base cations and acid anions until 1996 so that the ANC values remained just below 0 μeq L^{-1} (Fig. 4-14). But beginning in 1996, the ANC trend line dropped slightly and then stayed constant at that lower level through the end of the data collection period. The variability in the base cations and acid anions also increased after 1995. This may signal a slight degree of contamination from fertilizer leaching into the control plots from the surrounding treated area. The individual ion concentrations do not suggest this to have been a problem, but because ANC involves summing the base cations and acid anions, the accumulation of small undetectable leaching of individual constituents may become more visible or measurable. It is doubtful that the change in 1996 was due to ambient deposition changes of acid anions and base cations because these latter changes occurred over time. ANC changes from decreasing ambient deposition would have occurred gradually over time rather than during one year.

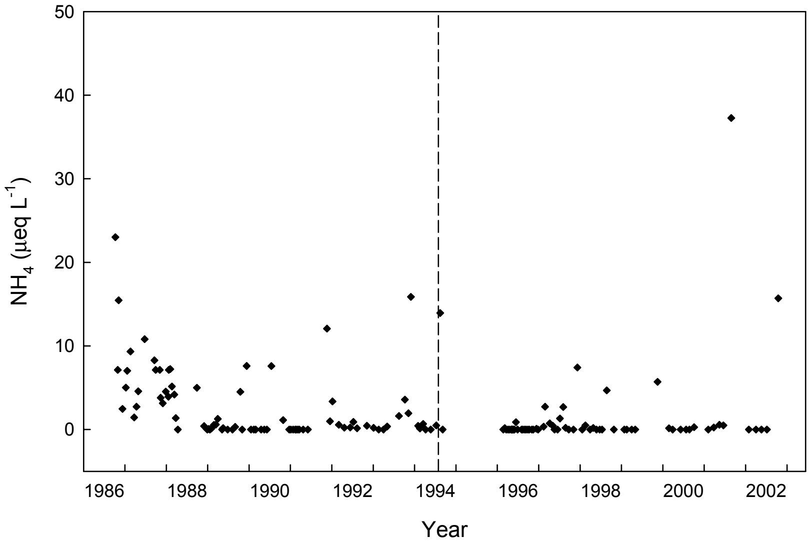

Figure 4-13. Volume-weighted average NH_4 concentrations in soil water for WS9 (treatment lysimeters). Dashed vertical line marks end of treatment.

Average Al concentrations in soil water samples collected monthly from October through December 1986 from the control and treatment zero-tension lysimeters were similar prior to treatment (control = 0.24 mg L^{-1}, treatment = 0.31 mg L^{-1}). Samples from three dates in late 1992 to early 1993 showed the concentrations from the control lysimeters remained at similar levels (Table 4-3) with an overall mean of 0.33 mg L^{-1}. By contrast, Al concentrations in the treatment lysimeters increased significantly to an overall mean of 1.13 mg L^{-1}. Sample results from the shallower 10-cm tension lysimeters (Pickens 1995) suggest the Al concentrations were not altered by the acidification as much near the soil surface, as mean Al values at 10 cm were substantially less than those from the deeper pan lysimeters.

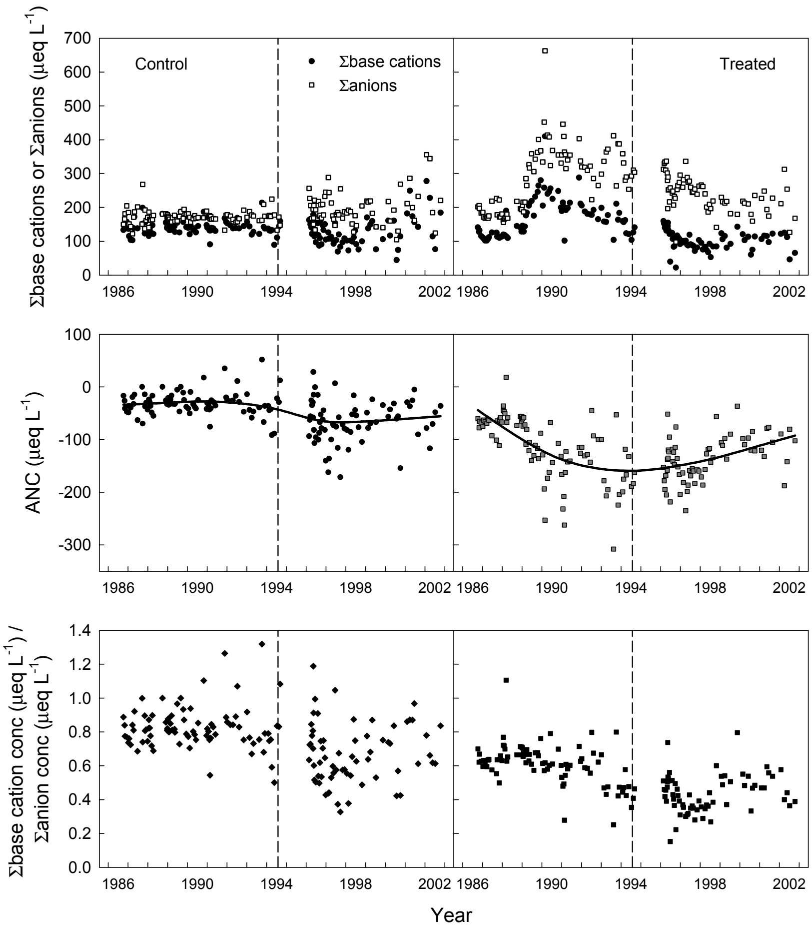

Figure 4-14. Sum of base cations or sum of acid anions in soil water from control and treated lysimeters in WS9 (top), ANC of soil water from control and treated lysimeters in WS9 (middle), and the proportion of acid anion charge counterbalanced by base cations in soil water from control and treated lysimeters in WS9 (bottom). Dashed vertical lines mark end of treatment.

Table 4-3. Al concentrations for pan lysimeters on WS9.

	13 August 1992		4 January 1993		18 February 1993	
Pair	Treated	Control	Treated	Control	Treated	Control
	mg L^{-1}					
1	0.914	0.100	0.393	0.020	0.776	0.013
2	2.450	0.826	2.578	0.780	2.608	0.743
3	2.154	0.498	2.177	0.314	2.618	0.305
4	0.176	0.769	0.079	0.576	0.122	0.726
5	0.114	0.044	0.067	0.018	0.052	0.013
6	1.095	0.082	0.915	0.041	1.059	0.031

The Al concentrations increased significantly over time in the treated lysimeters and were significantly ($p = 0.0003$) greater than the control concentrations (Fig. 4-15). The mean Al concentration in the tension lysimeters in treated areas was 0.25 mg L^{-1} for samples collected between October 1992 and July 1994, compared to 0.11 mg L^{-1} for tension lysimeters in the control plots. Foliage of blackberry, red maple, and Japanese larch growing in the treatment plots also had significantly greater Al concentrations than that growing in the control plots (Pickens 1995). Thus, these data support the assumption that Al became an increasingly more important component of soil water and increasingly important to charge pairing with acid anions.

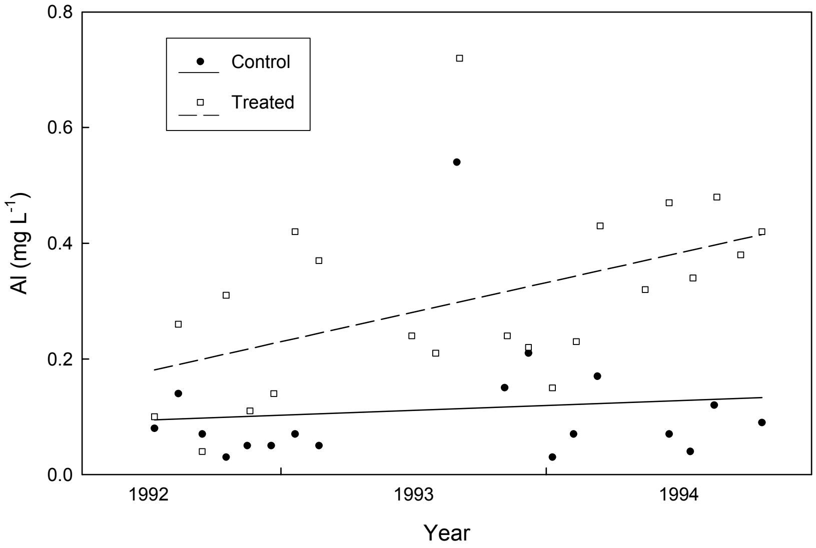

Figure 4-15. Al concentrations from control and treated 10-cm-deep tension lysimeters on WS9 (adapted from Pickens 1995).

4. STREAM WATER

As described in section 2.2, the baseflow data sets were extracted from the routine data set. Baseflow periods dominate annual streamflow in these small Appalachian watersheds; storm discharges generally constitute only about 30 percent of the annual streamflow (unpublished data). Storm runoff in this area responds very quickly to rain or snowmelt events when soil moisture is not highly depleted. More than 50 percent of precipitation events in this area typically begin between midnight and 7:00 AM and are less than

7 hours in duration (Patric and Studenmund 1975), so that by the time the weekly routine samples from WS3, WS4, and WS9 are taken during the workday the influence of many storms has passed. Even when a storm runoff event is in progress at the time routine samples are taken, there is only a small probability that the associated streamflow will be at or near peakflow. As a result, the chemistry data sets for routine and baseflow stream chemistry are almost identical for all three watersheds (Fig. 4-16). This information is important in understanding that nutrient exports calculated using

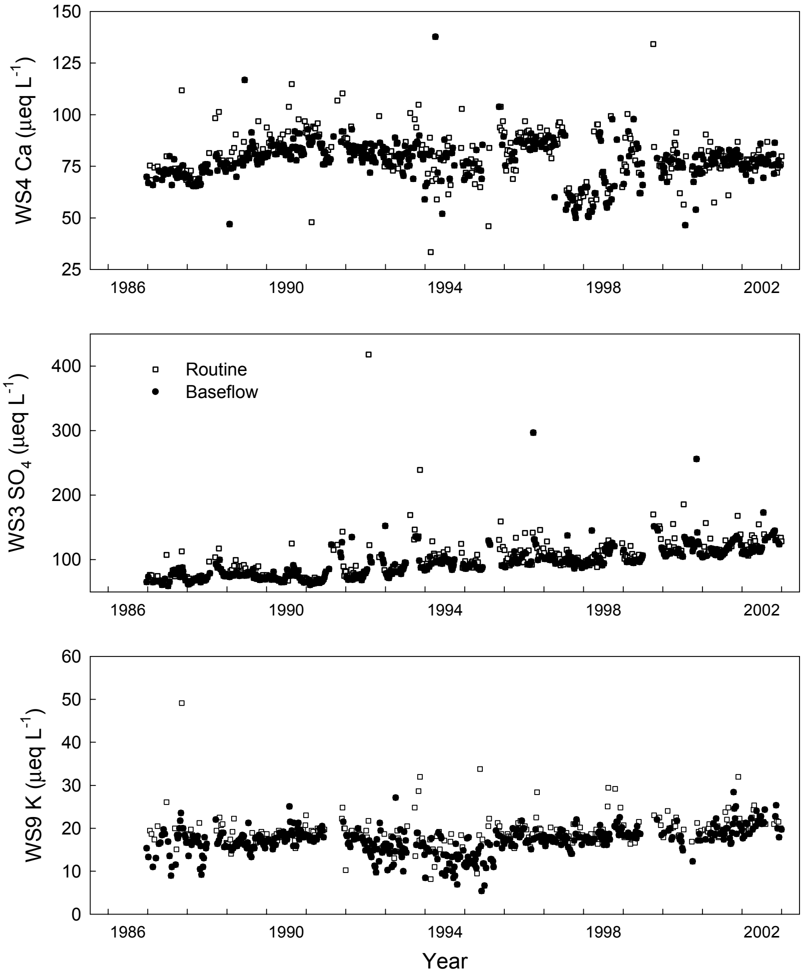

Figure 4-16. Representative examples showing the similarity between ionic concentrations in baseflow samples and weekly routine grab samples. The data for all of the ions for all three watersheds were almost identical.

concentrations from routine weekly samples (e.g., Chapter 7) will underestimate actual annual exports at least slightly since most chemical concentrations on WS3, WS4, and WS9 exhibit maximum concentrations near the period of peakflows (e.g., Edwards et al. 2001). The lack of chemical data along the hydrograph during stormflow may not result in highly significant differences in annual export estimates for some nutrients for watersheds that receive only ambient deposition (Edwards et al. 2004), but it may result in significant underestimates of nutrient exports on watersheds that are anthropogenically manipulated, since the manipulation may cause substantially elevated chemical responses during episodes.

Due to the similarities in the baseflow and routine concentrations (Fig. 4-16), their virtually identical fitted trend lines (not shown), and that conclusions drawn from both data sets are the same, only baseflow chemistries are described. However, the results approximate those of the routine sample chemistries. Baseflow was chosen so that concentrations from this flow regime could be contrasted to concentrations associated with peakflow.

4.1 Concentrations in Baseflow

4.1.1 WS4 Responses

Baseflow chemistry from WS4 showed significant changes over time for the major constituents (Table 4-4). However, most of the ions went through cycles of increases and decreases (Fig. 4-17), so that in most cases the actual net change in concentrations between the beginning and end of data collection were small – typically less than 10 μeq L^{-1} for any ion. It is

Table 4-4. Mann-Kendall and Sen slope results for baseflow from WS4.

Analyte	Period	Mann-Kendall probability	Sen slope
Ca	1986-9/1991	0.000	4.07
	10/1991-6/1998	0.057	-0.99
	7/1998-2002	0.008	1.44
Mg	1986-9/1991	0.000	1.73
	10/1991-2002	0.000	-0.62
Na	1986-2002	0.275	0.00
	1986-11/1995	0.072	-0.14
	12/1995-2002	0.000	0.86
K	1986-1/1995	0.038	-0.13
	2/1995-2002	0.000	0.52
SO_4	1986-11/1995	0.000	1.77
	12/1995-2002	0.000	-1.35
NO_3	1986-2002	0.093	-0.14
Cl	1986-2002	0.000	-0.18
pH	1986-2002	0.005	0.004
ANC	1986-2002	0.092	-0.25

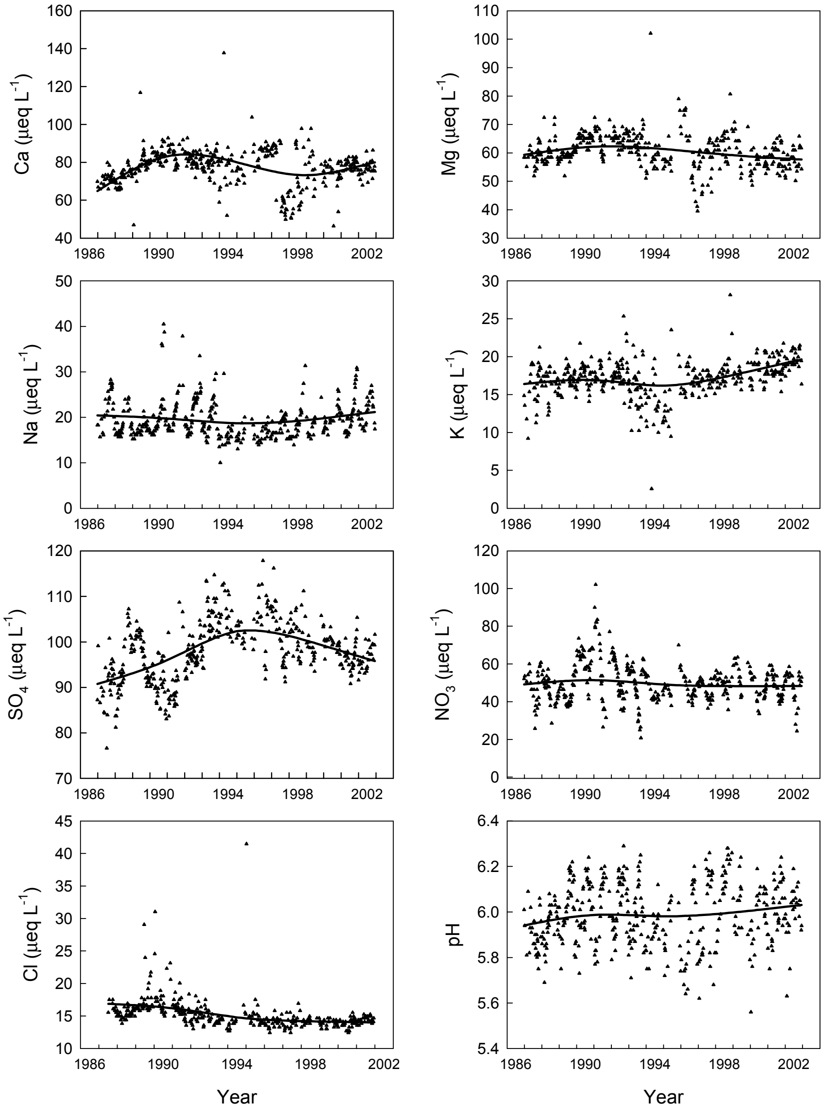

Figure 4-17. Chemical concentrations in baseflow from WS4 with trend lines overlaid.

impossible to know if these changes are simply fluctuations in the normal long-term variation of baseflow concentrations (i.e., Stage I), or if they occurred in response to changes in ambient deposition. We believe they are due to the latter, particularly based on SO_4 responses. The first phase of sulfur dioxide (SO_2) emissions reductions resulting from the Acid Rain Program (one of the 1990 Clean Air Act Amendments) began in 1995 and targeted power plants with the highest SO_2 emissions. Sulfur dioxide emissions at the Harrison power plant, which is upwind of the experimental watersheds, were reduced by 95-98 percent in 1996 compared to 1990. The downturn in SO_4 trend line for WS4 baseflow began in 1995 (Fig. 4-17), coincident with the first phase of SO_2 reductions (http://www.epa.gov/airmarkets/arp/overview.html). Improvements in visibility for nearby wildernesses also became evident in 1995-1996, further supporting the idea that lower acidic deposition caused a change in SO_4 in baseflow on WS4.

Thus, the initial mobilization of Ca and Mg would have been due to ambient inputs of acid anions from wet and dry deposition. Declines in Ca and Mg concentrations occurred before the 1995 improvements to scrubbers, suggesting the downturns signaled the onset of Ca and Mg depletion. Even though deposition of base cations would have decreased with the improved scrubber technology, the decrease in SO_4 deposition may have been so substantial that Ca concentrations could have shown some symptoms of recovery. The increase in K concentrations beginning in about 1995-1996 also may be from recovery following the large reduction in SO_4 emissions; however, the concentration patterns are not consistent with recovery in the base cation depletion model.

The pH concentrations of WS4 baseflow increased very slightly over time (Table 4-4). In 1987, the pH value at the trend line position was approximately 5.95; in 2002, it had risen to about 6.0 (Fig. 4-17). There was substantial variation in the pH values within years, which probably reflects the seasonality of pH.

The ANC of WS4 baseflow did not change significantly from 1987-2002 (Table 4-4) and typically was between 0 and 40 $\mu eq\ L^{-1}$, though several samples had negative ANC values (Fig. 4-18). The negative values primarily occurred in 1994, 1997, and 1998 though they were all $>-40\ \mu eq\ L^{-1}$. These years were associated with decreased levels of base cations (K in 1994, Mg in 1997, and Ca in 1997-1998) rather than increases in acid anions (Fig. 4-17). Similarly, the earlier increases in ANC (Fig. 4-18) corresponded to periods of increasing base cations. ANC did increase after 1996, which coincides with the decreases in SO_2 emissions and SO_4 concentrations in baseflow. The pH of baseflow on WS4 was always greater then 5.5 (Fig. 4-17), so when the ANC was <0 (Fig. 4-18), the amount of Al that would have been available to leach into the stream would have been present in fairly low concentrations and would have had trivalent Al as a minimal component.

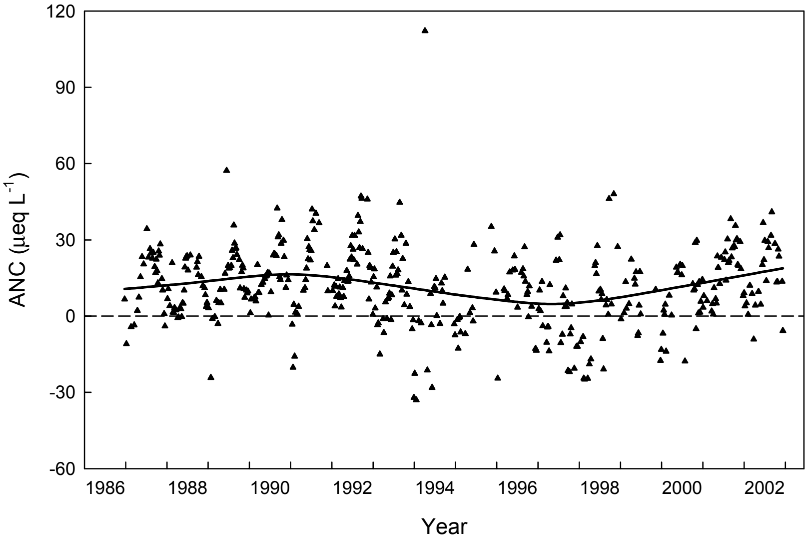

Figure 4-18. ANC concentrations of baseflow from WS4.

4.1.2 WS3 Responses

For the first 2 years of fertilizer treatments, concentrations in baseflow experienced some intra-year variation, but generally did not start showing consistent increases in concentrations for approximately 1.5-2 years (Fig. 4-19). This delay corresponds to the approximate 1.6-year mean transit time required for precipitation to become expressed as baseflow in WS3 (DeWalle et al. 1997).

Baseflow originates from two sources: groundwater in the water table that has percolated vertically through the soil column and the slow seepage of water through the soil to the stream (Hewlett and Nutter 1969). The latter is more important in mountainous terrain than in flatter landscapes. Thus, the chemistry of baseflow ultimately is controlled by the biogeochemical processes in the soil source areas that contribute soil water and bedrock through which groundwater is transmitted. The deep soil sources that contribute directly to baseflow can have different biogeochemical characteristics than deep upland soils because the source areas are near the stream and act as long-term receptors of chemical leachates from the uplands. Source-area soils typically have different chemical characteristics because they are colluvium and they are thicker because organic and mineral material accumulates at the base of slopes along stream channels.

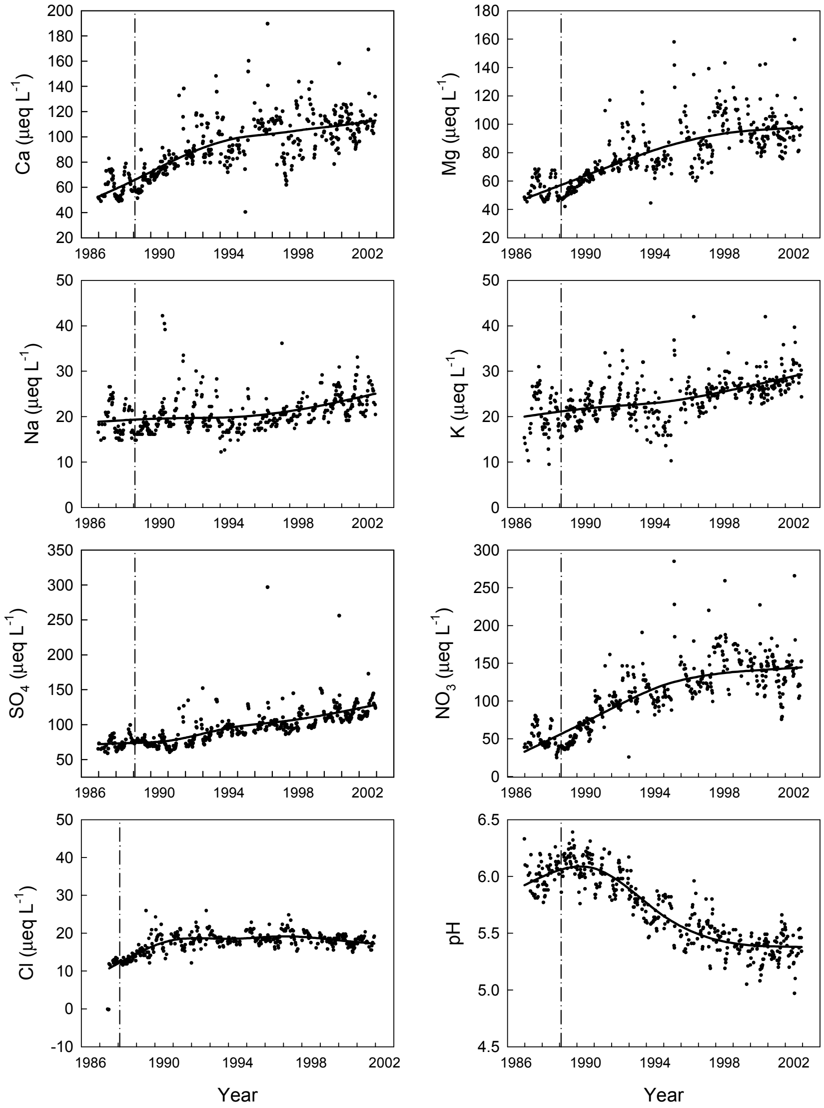

Figure 4-19. Chemical concentrations in baseflow from WS3 with trend lines overlaid. Dashed vertical line marks beginning of treatment.

Examination of the baseflow concentrations from WS3 compared to soil water (Figs. 4-19 and 4-4, respectively) show that the biogeochemistry of the uplands is very different from that which controls baseflow chemistry. Calcium, Mg, K, and Na cation concentrations on WS3 all increased in baseflow throughout the period of treatment in response to increasing acid anion concentrations (Fig. 4-19, Table 4-5). Therefore, the portion of the watershed controlling baseflow has at least some reserves of available base cations for neutralizing acidic inputs (Stage II). The influence of the source areas and bedrock on Mg was substantial, as Mg concentrations in baseflow were present in higher concentrations than Mg in soil (Chapter 3) and soil water (Fig. 4-4a). In fact, Mg concentrations in baseflow almost approximated those of Ca. A lag in K availability was not evident in baseflow (Fig. 4-19) compared to soil water (Fig. 4-4a), but the rate of increase in K concentrations in baseflow did become greater in about 1995 (Fig. 4-19), seemingly reflecting the lagged increases of K to stream water from soil water.

Table 4-5. Mann-Kendall and Sen slope results for baseflow from WS3.

Analyte	Period	Mann-Kendall probability	Sen slope
Ca	1986-2002	0.000	3.73
Mg	1986-2002	0.000	3.27
Na	1986-2002	0.000	0.37
K	1986-2002	0.000	0.55
SO_4	1986-2002	0.000	3.52
NO_3	1986-2002	0.000	7.45
Cl	1986-1990	0.000	1.73
	1991-2002	0.014	-0.06
pH	1986-1/1989	0.017	0.08
	2/1989-2002	0.000	-0.07
ANC	1986-2002	0.000	-3.30

Chloride concentrations in baseflow increased a small amount during the first four years of treatment but then decreased slightly but significantly through 2002 (Fig. 4-19, Table 4-5). Overall, however, Cl concentrations only increased by approximately 10 μeq L^{-1}, which was only one-tenth or less of the increases in SO_4 or NO_3 over the 15 years of fertilization (Fig. 4-19).

Nitrate concentrations in baseflow increased throughout the study, but the rate of increase declined (based on the trend line) from about 11 μeq L^{-1} yr^{-1} through 1995 to 1.5 μeq L^{-1} yr^{-1} after 1995 (Fig. 4-19). The reduction in the rate of increase may suggest an increase in NO_3 retention, similar to that, but not as far advanced as in soil water on WS3 (Fig. 4-4b).

There was no evidence of SO_4 retention in the soil source areas or bedrock. Instead, SO_4 concentrations in baseflow increased at an almost constant rate through the study (Fig. 4-19, Table 4-5). If the deep soil source areas that contribute to baseflow have acted as receptors for SO_4 over the long-term, it would not be surprising to have essentially no capacity for anion adsorption remaining, assuming any ever existed.

The pH of baseflow has decreased significantly since the initiation of the acidification treatment (Fig. 4-19, Table 4-5). Before treatment began in 1987, pH of baseflow generally was about 5.9 (based on the trend line) and then it increased for the next 2 years of pretreatment to above pH 6.0, with some values as high as 6.3-6.4. pH responded almost immediately to fertilization and by 2002 the pH on the trend line was about 5.4, though there were pH values in 2001-2002 as high as ~5.6 and as low as ~5.0. The reduction from pH 6.0 to 5.4 is quite substantial and equivalent to an increase of 2.9 μeq $H^+ L^{-1}$.

ANC in baseflow on WS3 decreased significantly throughout the study (Fig. 4-20, Table 4-5). WS3 ANC transitioned from being predominantly positive, generally between 0-40 μeq L^{-1} (similar to WS4) to predominantly negative during the last half of 1992 and the first half of 1993. During the transition period, there were approximately as many positive as negative ANC values and they ranged from about 10 μeq L^{-1} to about -20 μeq L^{-1}. After mid 1993, 90 percent of the ANC values associated with baseflow samples were negative. Thus, even though the concentrations of base cations in baseflow increased through time, the deep soil source areas and bedrock, through which baseflow is transmitted, buffer increasingly smaller percent-tages of acid anions (Fig. 4-21). As a consequence, baseflow has shifted from being only episodically acidic to being chronically acidic.

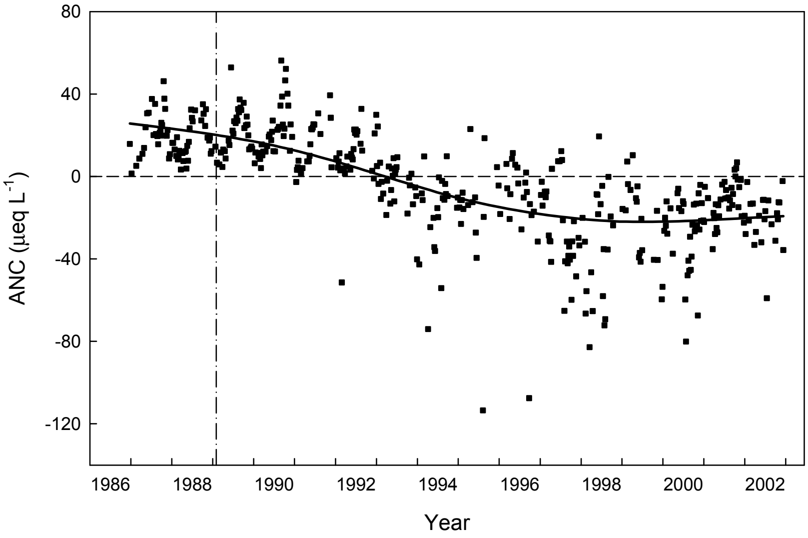

Figure 4-20. ANC concentrations of baseflow from WS3. Dashed vertical line marks beginning of treatment.

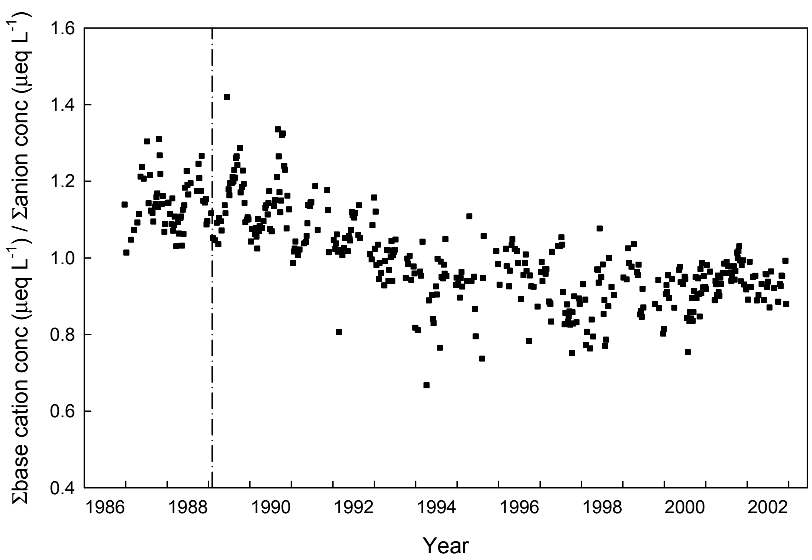

Figure 4-21. The proportion of acid anion charge counterbalanced by base cations in baseflow from WS3. Dashed vertical line marks beginning of treatment.

The acidification treatment clearly had a substantial effect on the buffering status of baseflow, but even the most negative ANC values in WS3 baseflow (Fig. 4-20) were greater than those present at the beginning of the study for upland soil water from WS3 (Fig. 4-8). As with soil water, Al probably has made up most of the deficit in positive charge as baseflow has become more acidic, but because the pH of baseflow is still above 5.0 (Fig. 4-19), the Al ions in baseflow are probably dominated by those of a +2 valence rather than trivalent aluminum since Al^{3+} is not common until the pH is ≤5.0.

4.1.3 WS9 Responses

While the chemical concentrations of WS3 and WS4 became widely divergent as the acidification treatment progressed, WS9 baseflow concentrations changed little. Indeed, WS9 and WS4 concentrations followed very similar patterns over time (Fig. 4-22), including during the treatment period from 1987-1994. There is a reasonably strong stoichiometric relationship for all constituents between the two watersheds, except Cl and pH (Fig. 4-23). Sulfate, NO_3, and K have nearly 1:1 slopes illustrating the nearly identical baseflow responses of the two watersheds for these ions. The two watersheds seemed to be responding very similarly to very dissimilar inputs of N and S.

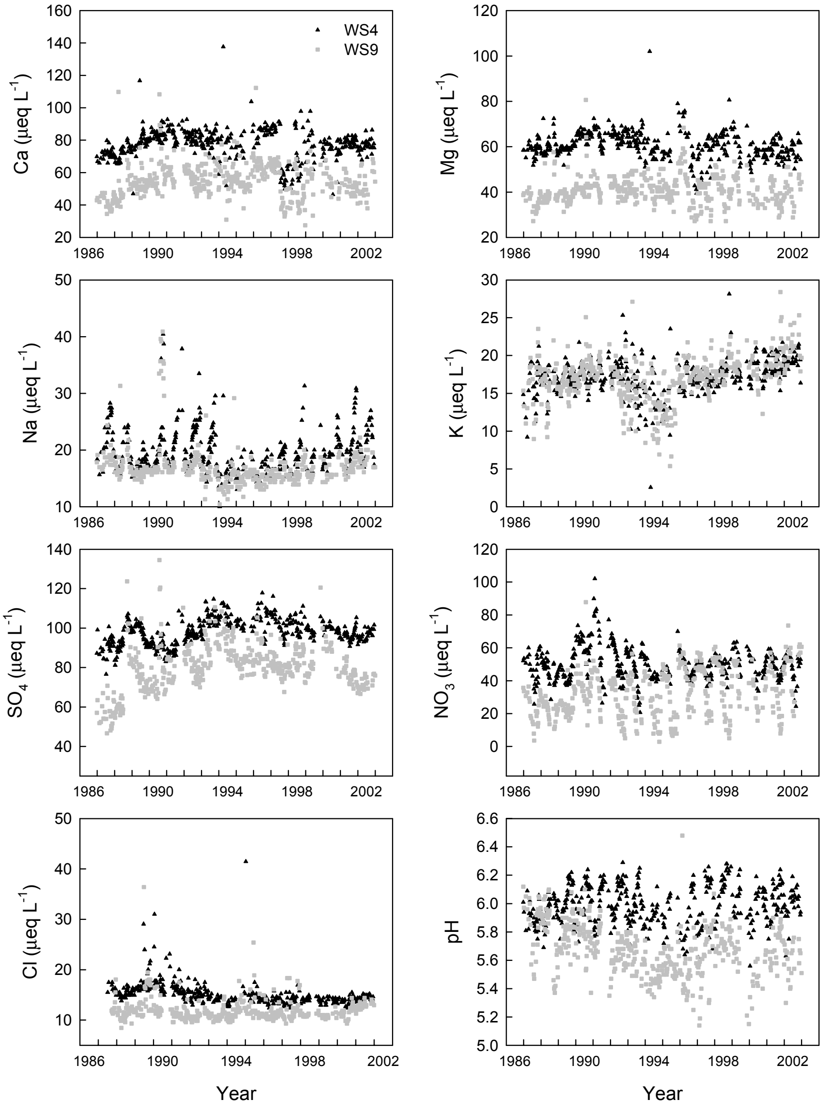

Figure 4-22. The chemical concentrations for baseflow in WS4 (reference) and WS9 (treated) displayed similar temporal patterns.

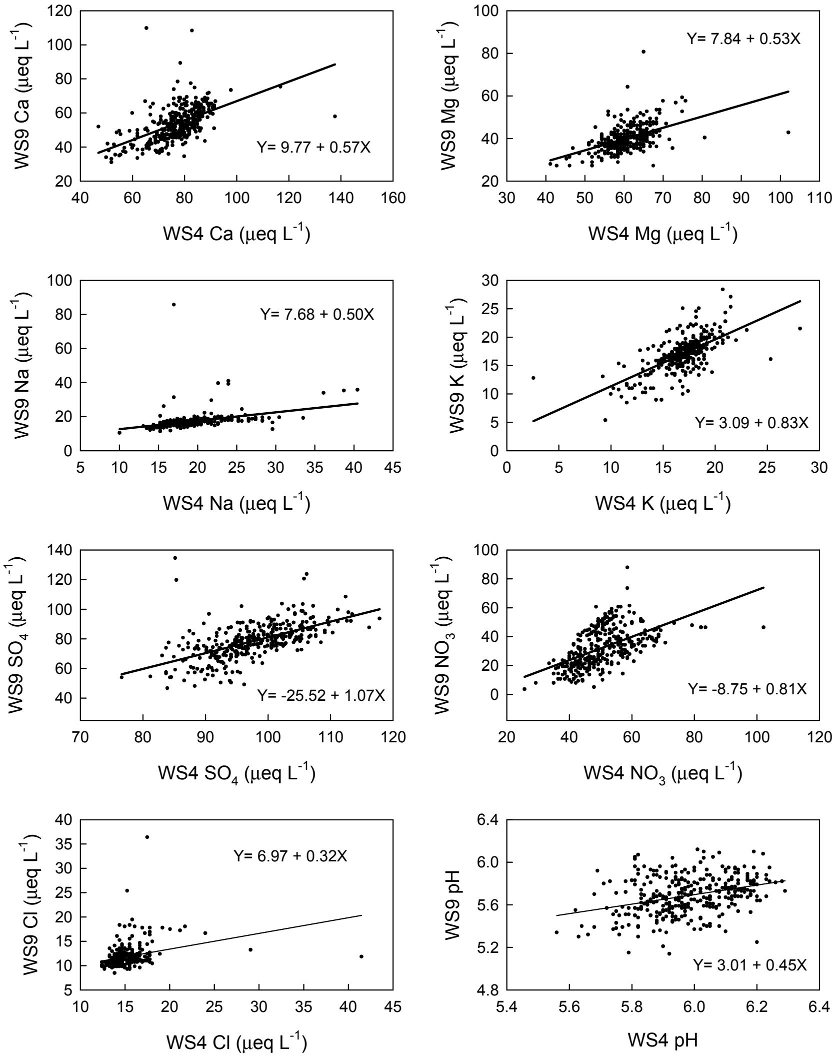

Figure 4-23. Stoichiometric relationships between WS9 and WS4 for baseflow.

Calcium and Mg concentrations in WS9 baseflow increased significantly through 1991 and then decreased through 2002 (Fig. 4-24, Table 4-6), indicating that the watershed sources affecting baseflow could provide additional buffering of some of the increased acid anions (Stage II) but those levels of available cations were small and short-lived. Calcium and Mg remained in a state of progressive depletion after 1991 (Stage III) even though the elevated additions of S and N were terminated in 1994. Baseflow concentrations of both ions were slightly less than the concentrations in soil water at the beginning of the study, but the overall changes in their concentrations were much more muted in stream water (Fig. 4-24) than in soil water (Fig. 4-12).

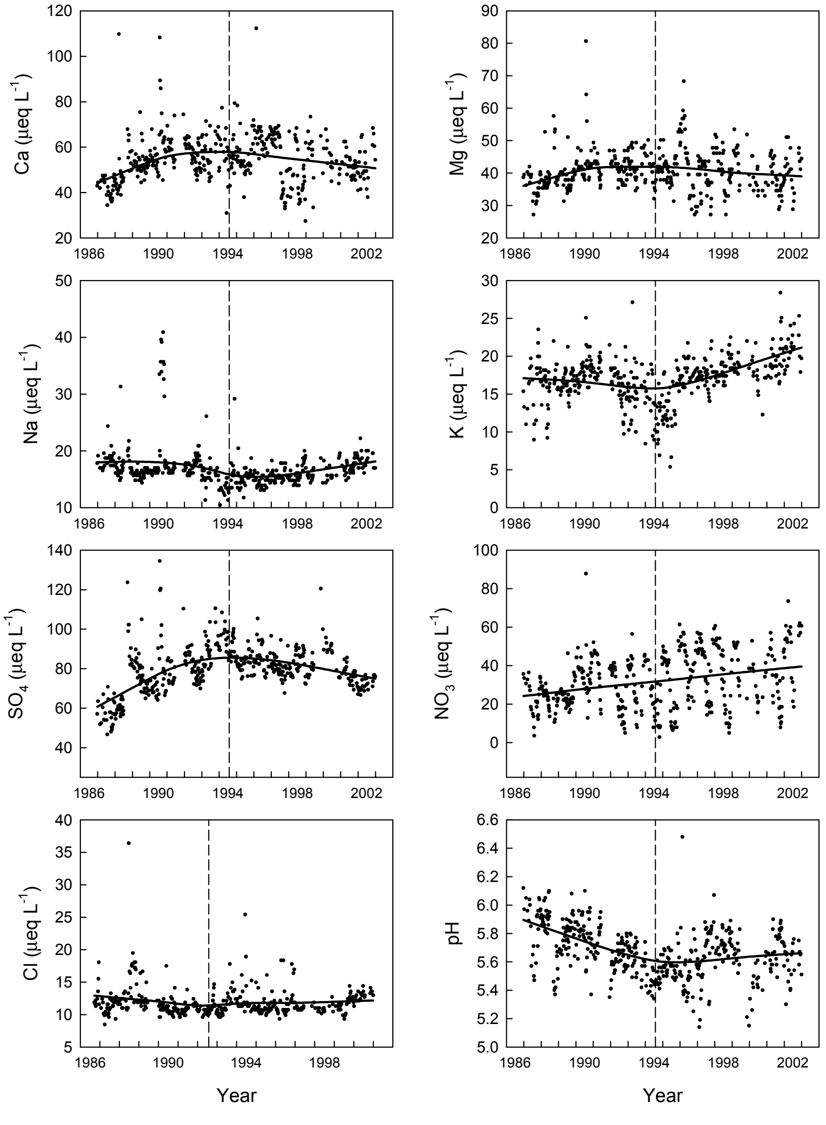

Figure 4-24. Chemical concentrations in baseflow for WS9 with trend lines overlaid. Vertical line marks end of treatment.

Table 4-6. Mann-Kendall and Sen slope results for baseflow from WS9.

Analyte	Period	Mann-Kendall probability	Sen slope
Ca	1986-1991	0.000	4.89
	1992-2002	0.000	-0.60
Mg	1986-1991	0.000	1.76
	1992-2002	0.007	-0.27
Na	1986-2002	0.001	-0.06
	1986-1995	0.000	-0.28
	1996-2002	0.000	0.50
K	1986-9/1994	0.003	-0.26
	10/1994-2002	0.000	0.76
SO_4	1986-9/1993	0.000	4.18
	10/1993-2002	0.000	-1.79
NO_3	1986-2002	0.000	1.09
Cl	1986-2002	0.731	0.00
pH	1986-2002	0.000	-0.02
	1986-11/1994	0.000	-0.05
	12/1994-2002	0.005	0.01
ANC	1986-2002	0.000	-1.36
	1986-7/1994	0.000	-2.51
	8/1994-2002	0.384	0.30

Potassium concentrations decreased until 1994 (Fig. 4-24, Table 4-6), as they did for WS4 baseflow (Fig. 4-17), suggesting that K concentrations in baseflow were depleting (Stage III) even before the study began. The termination of the N and S additions to the watershed appear to have resulted in an increase in K concentrations; however, this pattern does not follow the expected recovery phase of the base cation depletion model.

The SO_4 concentrations in baseflow throughout the study and the magnitude of change in SO_4 concentrations (Fig. 4-24) were much less than those in soil water (Fig. 4-12). Sulfate concentrations increased significantly through 1994 and decreased thereafter (Fig. 4-24, Table 4-6). The decreases in SO_4 following the termination of treatment show that SO_4 adsorption was at least partially reversible (Reuss and Johnson 1986). Nitrate concentrations in WS9 baseflow continued to increase in stream water even after the termination of fertilization in 1994. This was the only instance for treated watersheds in which NO_3 retention was not evident. The continued release of NO_3 even after N inputs were reduced to much lower ambient levels shows that streamflow from some watersheds may exhibit continued acidification symptoms long after reductions in NO_3 emissions or deposition reductions.

The pattern of baseflow pH responses from WS9 (Fig. 4-24) was very similar to that for WS3 (Fig. 4-19), though the starting pH of the trend line was slightly less on WS9 (about pH 5.9) and the ending pH of the trend line was slightly greater (about pH 5.6). However, the spread of the actual pH values was nearly the same by the end of the period of record; a major difference was that the very low pH values (~5.2) were present on WS9 throughout a much larger period of the study and not just primarily at the end. Those pH values still remain above those at which high levels of Al become solubilized. There was a slight but significant increase in pH on WS9 after the fertilization ceased (Table 4-6), so that increases in Al in any form are not expected in the future, at least in the short term.

The ANC of WS9 baseflow decreased significantly over time (Table 4-6); however, the data fall into two distinct groups – those during treatment (before 1994) and those after treatment (1994-2002) (Fig. 4-25). Prior to 1994, most of the data were between 0 and 45 μeq L^{-1}. Afterwards, about half of the data were positive and half were negative, between 30 and -40 μeq L^{-1} but the ANC did not significantly change during that time (Table 4-6), so it did not recover once the N and S applications stopped. The ANC values in WS9 baseflow did not become as negative as those on WS3, because the treatment was terminated after only 8 years on WS9, and the ANC values for WS9 baseflow also did not transition to negative values as quickly as they did on WS3 (3.5 years of treatment for WS3 vs. 6 years for WS9). Baseflow on WS9 was moving toward becoming chronically acidic, but the termination of treatment allowed the regular though not consistent occurrence of positive ANC values; thus, baseflow in WS9 remains episodically acidic.

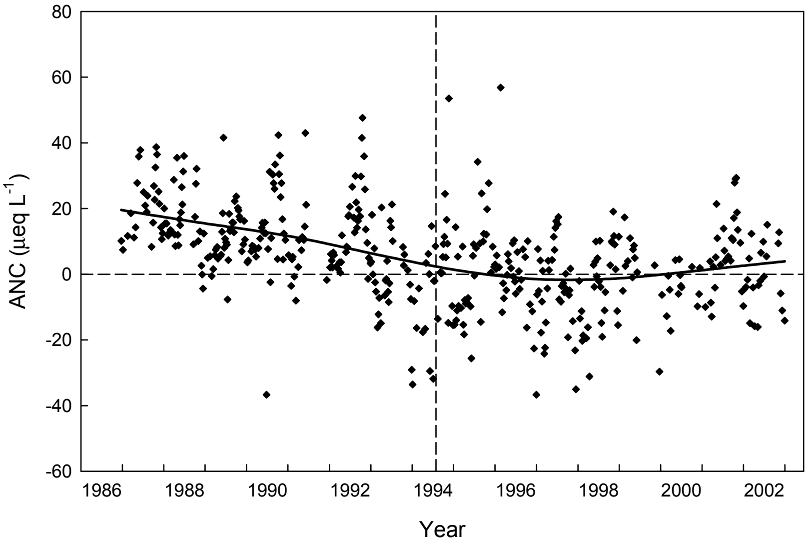

Figure 4-25. ANC concentrations of baseflow from WS9. Dashed vertical line marks end of treatment.

4.2 Concentrations at Peakflow

Episodic changes occurred on all the watersheds, including the reference WS4. The difference in concentrations between baseflow and storm peakflow concentrations for any of the analytes typically was <2 mg L^{-1}, even for the largest storms, and was often <1 mg L^{-1}. As acidification progressed, the magnitude of differences between baseflow and peakflow concentrations did not increase or decrease meaningfully, even if the data were adjusted to account for differences in flows. Instead, there was a wide variation in the differences between peakflow concentrations and baseflow concentrations within and across years.

Because storm sampling took place only from 1987 through 1997, with no sampling in 1996 and only one storm sampled in 1997, and there were many fewer observations per year than for baseflow or soil water samples, less information can be derived from the samples collected near peakflow. Furthermore, for all watersheds, including reference WS4, there was substantial variation in concentrations even over a short number of years; thus, while the trend lines suggest generally expected and explainable behavior, the variation in the data makes some of the trends less convincing than they are for soil water and baseflow.

4.2.1 WS4 Responses

Figure 4-26 shows the patterns of the concentrations of the various analytes over time from reference WS4. From these graphs, the trend lines and the data suggest that all the base cations in peakflow on WS4 went through an initial period of mobilization (in response to increasing NO_3 concentrations) followed by progressive depletion, but not all of the base cation increases or decreases were highly significant (Table 4-7). Whether SO_4 experienced true declines in concentrations after 1994 is questionable because of the limited amount of data, but the data certainly suggest that NO_3 concentrations at peakflow declined significantly beginning about 1991 (Fig. 4-26, Table 4-7). The reason for the decline in NO_3 concentrations is unknown, but the increases at peakflow in 1990 and 1991 (Fig. 4-26) also correspond to high NO_3 concentrations in baseflow (Fig. 4-17), so the same factor probably affected both flow regimes.

4.2.2 WS3 Responses

Watershed acidification appears to have induced cation mobilization (Stage II) for all four base cations through about 1992 or 1993 (Fig. 4-27). The increases in concentrations were statistically significant for all base cations (Table 4-8). Only a few samples were available after the downturns

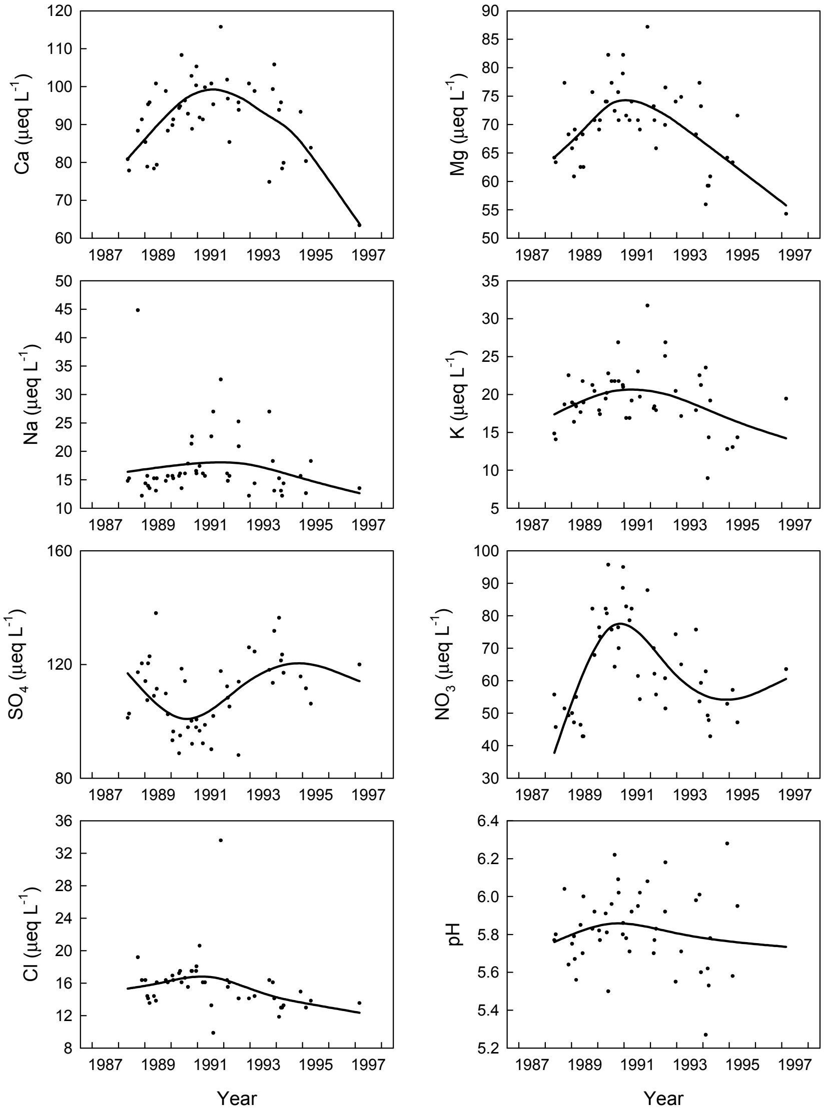

Figure 4-26. Chemical concentrations in peakflow from WS4 with trend lines overlaid.

began, so it is difficult to conclude with certainty that depletion (Stage III) of base cations was initiated, but the downturns for Mg and Na were significant. By contrast, the case for Ca and K depletion is particularly difficult to make since the downturns of those data were not significant (Table 4-8).

Table 4-7. Mann-Kendall and Sen slope results for peakflow from WS4.

Analyte	Period	Mann-Kendall probability	Sen slope
Ca	1988-7/1991	0.002	5.86
	8/1991-6/1997	0.010	-5.59
Mg	1988-1990	0.000	5.49
	1991-1997	0.025	-2.46
Na	1988-7/1992	0.001	0.87
	8/1992-1997	0.274	-1.45
K	1988-3/1991	0.077	1.43
	4/1991-1997	0.045	-1.66
SO_4	1988-8/1990	0.327	-5.62
	9/1990-1997	0.001	5.76
NO_3	1988-11/1990	0.011	13.79
	12/1990-1997	0.000	-7.11
Cl	1988-11/1990	0.053	0.66
	12/1990-1997	0.002	-0.81
pH	1988-7/1991	0.506	0.04
	8/1991-1997	0.051	-0.06
ANC	1988-1997	0.505	-0.64
	1988-7/1991	0.038	2.92
	8/1991-1997	0.010	-11.56

While the SO_4 trend line for peakflow samples follows the general patterns that were seen for soil water on WS3 (i.e., increasing concentrations followed by retention), neither the increases nor decreases in concentrations were significant (Table 4-8). This lack of significance makes it impossible to show that the acidification treatment increased the mobilization of SO_4. This apparent lack of response is surprising given that SO_4 was applied in higher concentrations than N and the source of stormflow from WS3 is believed to be transported quickly through upper soil layers. The statistically unconvincing response of SO_4 in peakflow to treatment indicates that the source areas that ultimately contribute stormflow also behave different biogeochemically than the upland areas.

Nitrate and Cl responses provide strong evidence that they were affected by the ammonium sulfate additions (Fig. 4-27). Both increased significantly (Table 4-8) and did not have later downturns, though NO_3 did level off as it did in soil water. The maximum increases in Cl were only about 10-15 µeq L^{-1}, compared to ~100 µeq L^{-1} for the NO_3 trend line and as much as twice that for the actual concentrations.

The pH (Fig. 4-27) and ANC values (Fig. 4-28) for WS3 convincingly indicate increased acidification of peakflow: both declined significantly (Table 4-8). The pH dropped by about 0.5 units based on the trend line and ANC moved from almost all positive or ~0 µeq L^{-1} concentrations to all negative values with most in the -40 to -80 µeq L^{-1} range. Thus, like baseflow, chemistry at peakflow on WS3 has shifted from being episodically acidic to chronically acidic.

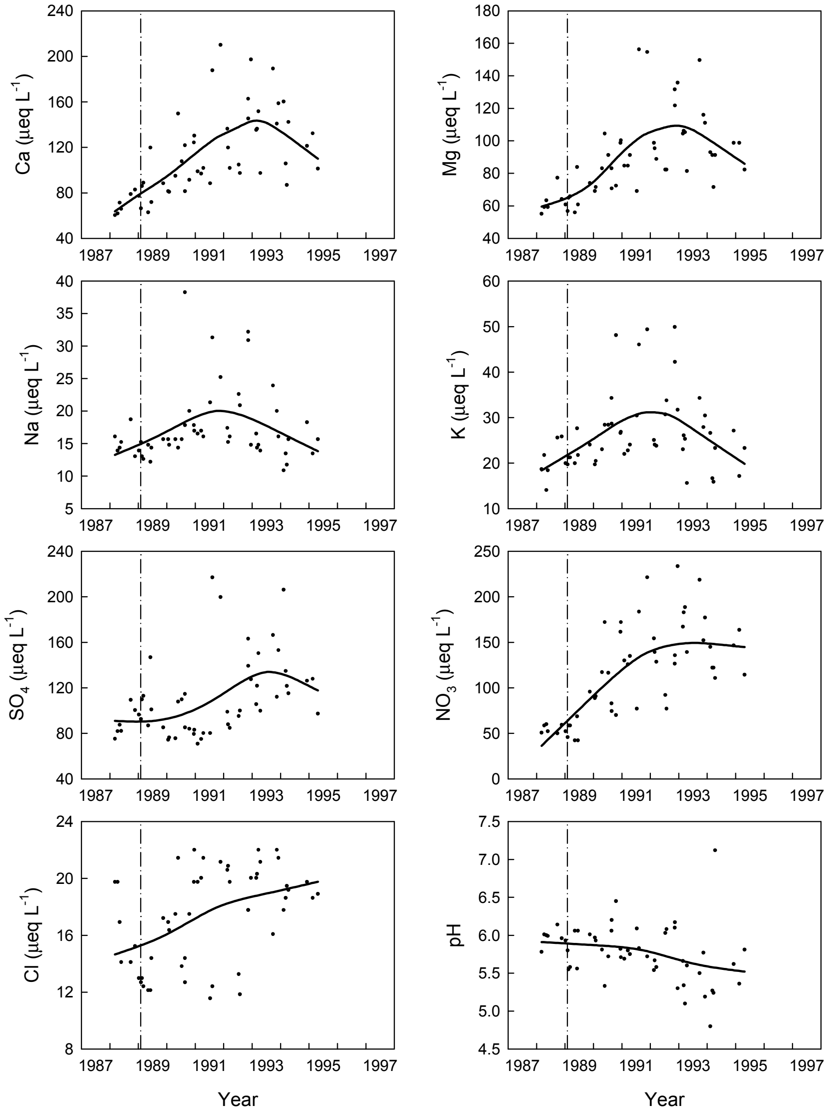

Figure 4-27. Chemical concentrations at peakflow from WS3 with trend lines overlaid. Dashed vertical line marks beginning of treatment.

4.2.3 WS9 Responses

While the trend lines for Ca and Mg concentrations in peakflow on WS9 suggest that base cation mobilization occurred through the beginning of 1991 and was followed by progressive depletion thereafter (Fig. 4-29), the Mann-Kendall tests do not show significant concentration increases or decreases for either period (Table 4-9). Thus, the results infer that the source areas that contribute stormflow on WS9 were depleted of excess Ca and Mg prior to the initiation of acidification treatments, and weathering rates were controlling Ca and Mg concentrations during storm events (Stage IV).

Table 4-8. Mann-Kendall and Sen slope results for peakflow from WS3.

Analyte	Period	Mann-Kendall probability	Sen slope
Ca	1988-3/1993	0.000	15.18
	4/1993-1995	0.244	-20.18
Mg	1988-10/1992	0.000	9.23
	11/1992-1995	0.009	-15.09
Na	1988-11/1991	0.001	1.40
	12/1991-1995	0.020	-2.07
K	1988-2/1992	0.000	3.44
	3/1992-1995	0.108	-3.19
SO_4	1988-3/1993	0.059	4.70
	4/1993-1995	0.534	-17.25
NO_3	1988-6/1992	0.000	27.32
	7/1992-1995	0.861	-3.25
Cl	1988-1995	0.003	0.75
pH	1988-1995	0.003	-0.08
ANC	1988-1995	0.004	-4.08
	1988-7/1991	0.797	-0.55
	8/1991-1995	0.021	-18.02

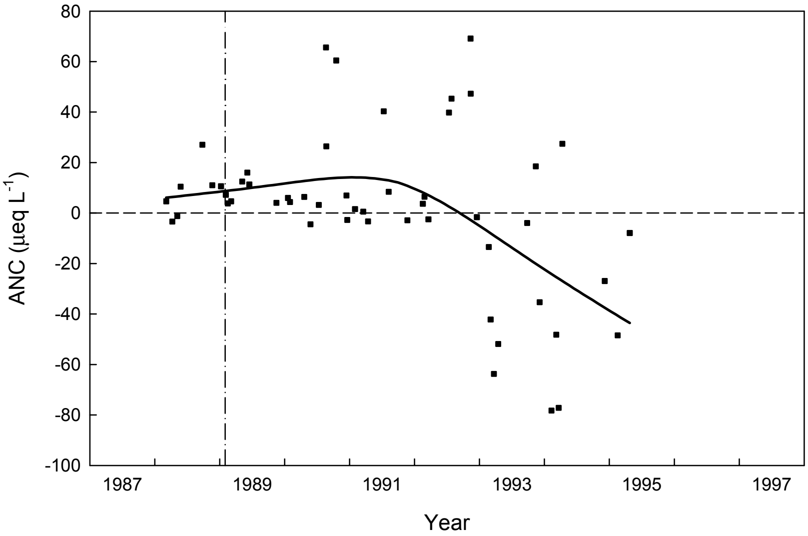

Figure 4-28. ANC concentrations of peakflow from WS3. Dashed vertical line marks beginning of treatment.

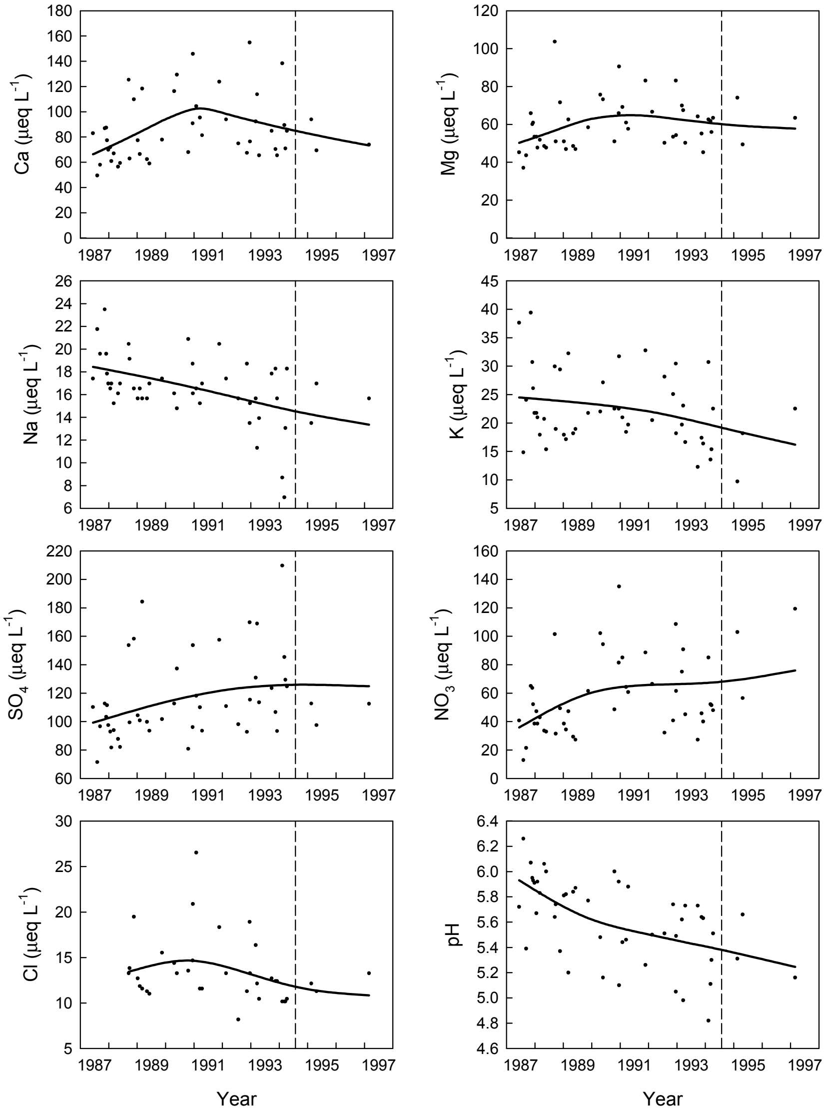

Figure 4-29. Chemical concentrations at peakflow from WS9 with trend lines overlaid. Dashed vertical line marks end of treatment.

By contrast, Na and K concentrations decreased significantly throughout the entire period that fertilizer was applied to WS9 (Fig. 4-29, Table 4-9). Consequently, exchangeable levels of Na and K were available at the

Table 4-9. Mann-Kendall and Sen slope results for peakflow from WS9.

Analyte	Period	Mann-Kendall probability	Sen slope
Ca	1987-1990	0.082	7.56
	1991-1997	0.135	-3.96
Mg	1987-10/1990	0.214	3.83
	11/1990-1997	0.350	-1.54
Na	1987-1997	0.001	-0.49
K	1987-1997	0.042	-0.80
SO_4	1987-1997	0.014	3.03
NO_3	1987-1997	0.017	3.59
Cl	1987-1997	0.031	-0.35
pH	1987-1997	0.000	-0.07
ANC	1987-1997	0.000	-5.81

beginning of the study, but they were already in a depleted state (Stage III) presumably due to long-term ambient inputs of acidic deposition.

Peakflow concentrations of SO_4 and NO_3 increased during the period of treatment (Fig. 4-29). Their concentrations were distributed widely but the increases were enough to result in significant upward trends (Table 4-9). By contrast, Cl decreased (Table 4-9) and the magnitude of the change was much smaller than for SO_4 or NO_3 (Fig. 4-29).

ANC and pH responses indicate that peakflow became increasingly acidic over time. As on WS3, ANC on WS9 decreased significantly over time (Table 4-9) and ANC values transitioned from primarily positive values between 0 and 40 μeq L^{-1} in 1989 and 1990 to almost consistently negative concentrations after 1992 with values between 0 and -60 μeq L^{-1} (Fig. 4-30). The pH values at peakflow on the trend line dropped almost 0.75 units from nearly pH 6 in 1987 to about pH 5.25 in 1997 (Fig. 4-29). As a result of treatment, acidification of peakflow became chronic.

5. DISCUSSION

5.1 Application of Base Cation Results

For solution samples collected from WS3 and WS9, it is clear that different interpretations of cation availability or depletion states can result, depending upon whether soil water or stream water responses are evaluated. Even evaluations based upon chemistry from different streamflow regimes can be different. On both WS3 and WS9, soil water and peakflow results reflected processes of cation mobilization (Stage II) followed by progressive depletion (Stage III). In some cases base cation losses were great enough to move the soils to equilibrium with weathering inputs (Stage IV). By

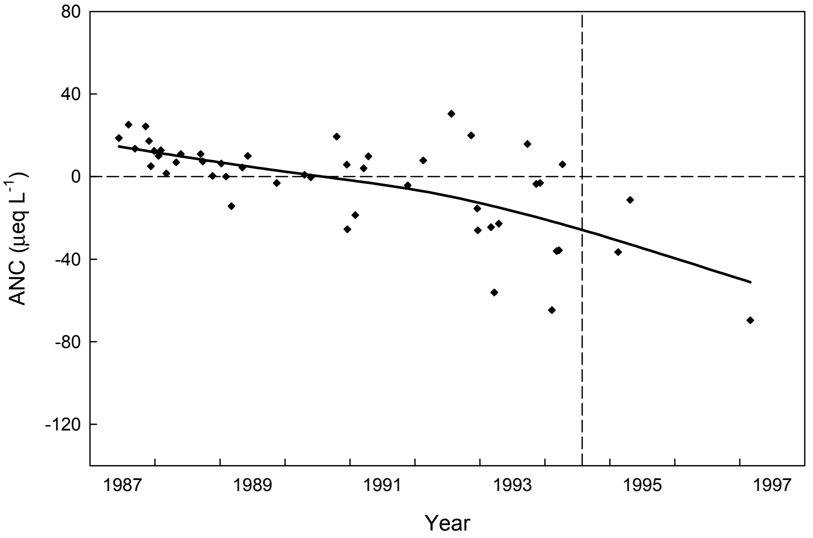

Figure 4-30. ANC concentrations of peakflow from WS9. Dashed vertical line marks end of treatment.

contrast, baseflow results generally indicated that the watersheds still had at least small reserves of exchangeable base cations (Stage II).

The dissimilarity in soil nutrients and/or biogeochemical processing of nutrients must be considered and understood to realistically evaluate the base cation and buffering status of the component of the watershed of interest. Sufficiently long time series data are more commonly available from stream water than from soil water, and stream water chemistry often is considered an integrator of all the processes within a watershed. Thus, there may be a tendency to apply those stream water data to the entire watershed. Since baseflow predominates the duration of annual flows, and groundwater can make up as much as 75-85 percent of stormflow (Hewlett and Nutter 1969, Swistock et al. 1989) in forested headwater streams, the bias of long-term stream water data sets will be toward baseflow conditions which, at least for WS3 and WS9, were much more different from soil water than concentrations at peakflow.

If the application of stream water results is to determine the acid/base status of the aquatic environment, it is reasonable to use interpretations from stream water. However, if the application is to obtain information about the soils or potential effects on vegetation or soil fauna across the greater watershed area, stream water interpretations may not be applicable if stream water is dominated by deep groundwater sources. In order to make interpretations about upland soil conditions from stream water, one should first ensure that stream water and soil water originate from the same sources or assess that they are in similar states of cation availability or depletion. If they are not, soil water should be substituted for stream water in the assessment.

We cannot speculate whether interpretations about soil base saturation levels collected from the uplands over time would have resulted in findings similar to soil water because soil samples were not collected frequently enough (Chapter 3) to examine trends closely, and the number of soil samples collected may have been too small to make a meaningful interpretation given the spatial variability of soil chemistry. However, the conceptualized base cation depletion model presented by Fernandez et al. (2003) also included conceptualized trends in base saturation.

5.2 Application of Nitrate Responses

Stoddard (1994) described N saturation in a series of stages based on seasonal stream NO_3 concentrations. In Stage 0, stream NO_3-N concentrations are near zero year round. In Stage 1, NO_3-N becomes elevated (0.5 to 0.8 mg NO_3-N L^{-1}) in the dormant season due to a lack of microbial and vegetative uptake. Stage 2 is characterized by elevated stream NO_3-N concentrations year round. WS4 has been cited as the best example of a Stage 2 N saturated watershed in the northeastern United States, exhibiting elevated year-round NO_3 concentrations (Stoddard 1994, Peterjohn et al. 1996, Fenn et al. 1998, Williard et al. 2003). At the beginning of the study, WS3 stream water (i.e., weekly grab samples and baseflow) had approximately the same concentrations of NO_3 as WS4, but WS3 now is at about three times that level (Figs. 4-17 and 4-19), so it too clearly is in Stage 2 N saturation. WS9 stream water concentrations were lower at the beginning of treatment (Fig. 4-22) than on WS3 or WS4, but the most recent years of data show that NO_3 concentrations in stream water on WS9 are now approximately equal to that on WS4 and equal to that on WS3 in the mid 1980s. The degree of seasonality for WS9 NO_3 concentrations is somewhat greater than WS3 but similar to WS4. Thus, stream water concentrations on WS9 also indicate that it is now behaving in accordance with Stage 2 N saturation.

The soil water NO_3 concentrations from WS3 and WS9 show that some type of retention of NO_3 had occurred in the watershed soils even during prolonged elevated levels of N inputs. This behavior was demonstrated to a lesser extent in WS3 baseflow. That NO_3 retention can be induced after periods of elevated losses simply by continuing to add N to the system at elevated rates is intriguing because it provides a substantially different perspective on how long-term elevated atmospheric deposition may affect forest ecosystems in the long term. Other researchers have found some unexpected long-term NO_3 results in stream water (Goodale et al. 2003) and in studies with manipulated increases of N inputs (Fernandez, unpublished results). It is clear that our current understanding of N cycling in forests is incomplete. Some of the newer ideas about N retention processes are based on kinetic principles or are hypotheses (e.g., Davidson et al. 2003, Dail et al. 2001, Hansen et al. 2001) while others have been documented in soils in the field or laboratory (Fitzhugh et al. 2003), but there is still much to be learned about factors that control the processes and how important those processes are across an entire watershed (Fitzhugh et al. 2003).

5.3 Regional Susceptibility to Acidification

The geology and overlying soils on the study watersheds are considered to be only moderately sensitive to acidification (pers. comm. Stephanie Connolly, Monongahela National Forest Soil Scientist). Consequently, watersheds underlain by more acidic geologies in the area, such as Pottsville and Allegheny formations, have received the majority of attention in terms of defining critical loads, adjusting vegetation management strategies, and development of possible mitigation strategies (e.g., see the Monongahela National Forest Plan Revision). Indeed, at the start of this study, many people believed that there would be little or no measurable changes to solution chemistry because the amount of N and S added annually represented only a small proportion of the total pools within WS3 and WS9 and a moderate amount of buffering capacity existed. Consequently, the onset of acidification as evidenced by base cation depletion, decreasing pH and ANC, and perhaps most dramatically, the transition from episodic to chronic acidification in baseflow over such a short period of time was somewhat surprising.

These soils have been subjected to decades of S and N inputs that greatly exceed the cumulative loads added during treatment. That acidification effects were documented at these relatively modest input levels suggests that a large land base in this region may be more sensitive to acidification than previously believed. For example, watersheds that are classified as moderately sensitive to acidification occupy approximately 32 percent of the land base within the proclamation boundary of the Monongahela National Forest. In a synoptic survey of 27 watersheds located in close proximity to and on similar geology as the Fernow Experimental Forest, Williard et al. (2003) found that NO_3 concentrations in baseflow for many streams (Fig. 4-31) were greater than the highest NO_3 concentrations observed on WS9, and several streams had concentrations that were approximately equal to those found after 3-5 years of treatment on WS3. The latter concentrations also correspond to NO_3 concentrations that were present at the time the ANC of WS3 baseflow was transitioning from positive to negative values. The NO_3

concentrations at the beginning of the study for WS3 and WS4 were similar, and more than 10 of the streams surveyed by Williard and his colleagues had NO_3 concentrations in baseflow that were greater than WS4.

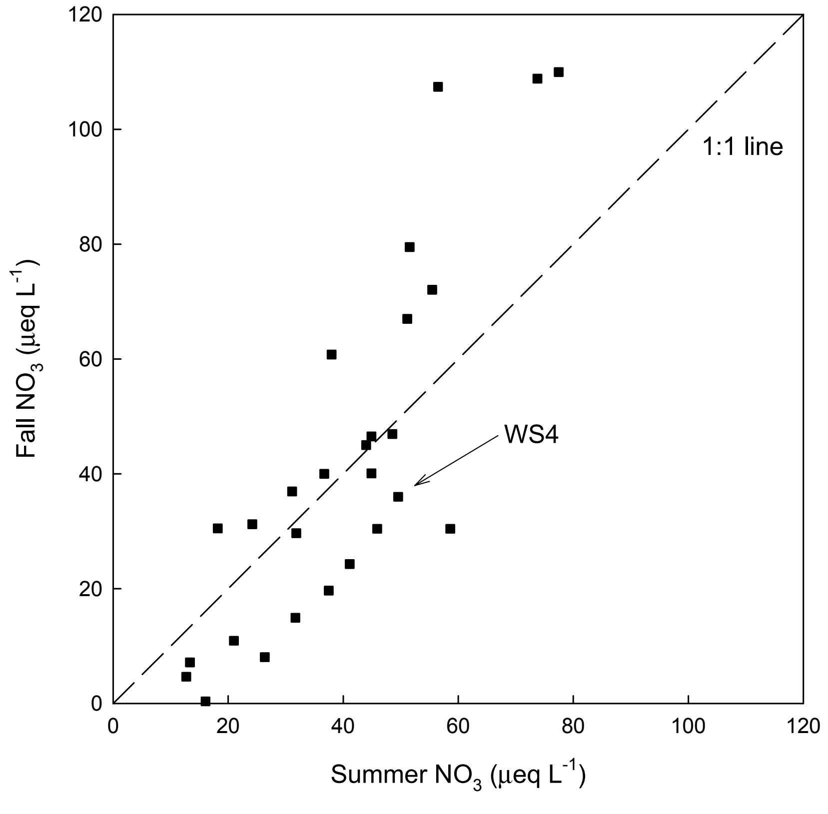

Figure 4-31. Summer and fall stream NO_3 concentrations for 27 watersheds located near WS4.

The relatively rapid progression toward acidification on these watersheds has potential implications in relation to future forest management decisions. The S and N loads added as fertilizer to the watersheds represent about 16-30 years of ambient deposition. During that treatment period, approximately 187 kg Ca ha^{-1} were exported from WS3 in stream water. This loss was, on average, 46 percent of the base cation loss and Ca was the cation that had the greatest effect on ANC. A major pool of Ca in WS3 is in the bolewood of trees. Calcium stored in the bolewood of WS3 is estimated to be approximately 155 kg ha^{-1} (see Chapter 7). Therefore, removal of all of the bolewood from WS3 by clearcutting would effectively remove about as much Ca as was exported by the elevated S and N inputs. As a result, intensive harvesting may affect the moderate to long-term susceptibility of soil to acidification even on sites classified as only moderately sensitive to acidification.

6. SUMMARY AND CONCLUSION

There was strong evidence of acidification of both soil water and stream water by the ammonium sulfate treatments on WS3 and WS9. With respect to soil water, WS3 and WS9 went through periods of increased base cation exchange and mobility due to increasing concentrations of SO_4 and NO_3, followed by periods of progressive base cation depletion in soil water. Some of the base cations in some soil horizons eventually became sufficiently depleted that they reached equilibrium levels, such that supplies of exchangeable base cations to soil solution were derived only from weathering, while others continued to be depleted through the end of data collection. Potassium concentrations increased on both watersheds due to inputs of the acid anions, but there was a lag in K increases in WS3. Exchange and mobilization of K occurred much later than for the other cations, which was surprising since it typically is exchanged more easily into soil solution than Ca and Mg. The reason for the delayed release of K is unknown.

Base cation recovery was observed in WS9 soil water following the termination of acidification treatments in 1994. Calcium and Mg concentrations in soil water declined below equilibrium concentrations as available base cations became associated with soil exchange sites. Eventually they transitioned even further through the recovery period and again moved toward equilibrium condition.

Nitrate and SO_4 leaching were obvious in soil water; the concentrations increased immediately and rapidly in response to the first fertilizer application and continued to increase for a number of years. However, as time progressed retention of both NO_3 and SO_4 were observed. The retention of SO_4 was believed to be at least partially due to the creation of anion adsorption sites by increasing SO_4 inputs and by pH-dependent charge development on clay particles that resulted in increased SO_4 adsorption as the pH decreased. The delayed retention of NO_3 was unexpected based on N-saturation theory. Nitrogen retention in forest soils occurs only if they are N deficient and should begin at the time that N inputs become elevated. The reasons for the much later retention are unknown, but are believed to be due largely to abiotic immobilization, which is a focus of contemporary N cycling research. Even after N inputs were terminated on WS9, NO_3

concentrations in soil water did not increase so, at least in the short term, N retention has not been reversible. The retention of these acid anions did not have a substantial effect on controlling base cation depletion; by the time anion retention occurred most of the base cations already had transitioned from the mobilization phase into the depletion phase.

Soil water acidity was substantially affected by the increased mobility of NO_3 and SO_4 and counterbalancing base cations. At the beginning of treatment, ANC levels on WS3 and WS9 were negative but always >-100 μeq L^{-1}. With progressive S and N additions, soil water ANC on WS9 dropped to as low as ~ -300 μeq L^{-1}, and on WS3 they fell to as low as -800 μeq L^{-1}. The smaller ANC drop on WS9 reflects the shorter period of treatment than on WS3 (8 yr vs. 15 yr). On WS9, the ANC concentrations in soil water returned toward pretreatment levels after fertilization was terminated in 1994. The increasing deficit in available counterbalancing charge by base cations relative to acid anions was believed to be fulfilled by Al^{3+}. Depending upon the horizon, approximately 60 to 80 percent of the negative charge in soil solution was counterbalanced by Al^{3+} in WS3, and in WS9 about 70 to 80 percent of the negative charge was counterbalanced by Al^{3+}.

While the patterns of base cation responses in baseflow and peakflow were not as marked as they were in soil water, acidification of both streamflow regimes was documented. On WS3, base cations were in sufficient supply in the soil source areas and bedrock that provide nutrients to baseflow so that only base cation mobilization was evidenced through the 15 years of treatment; the depletion phase was not entered for any of the four measured base cations. By contrast, on WS9, the supply of major base cations to buffer baseflow must have been substantially less because depletion of Ca and Mg began about 2-3 years into treatment. Sulfate retention, again presumably because of adsorption was observed for WS9 baseflow, but not for WS3 baseflow. Conversely, NO_3 retention was observed for WS3 baseflow but not for WS9. The pH of baseflow declined for both watersheds, but more on WS3 than WS9. On average, the drop was about 0.75 pH units on WS3 and about 0.3 pH units on WS9. The pH of baseflow on both watersheds remained above 5.0, so Al that came into solution to help fulfill cation charge deficits probably existed primarily as Al^{2+}. The changes to acidity on WS3, which was treated almost twice as long as WS9, were very significant and resulted in WS3 baseflow moving from being only episodically acidic to chronically acidic. WS9 was moving toward being chronically acidic but the termination of treatment allowed baseflow on WS9 to remain largely episodically acidic.

The base cations in peakflow on WS3 generally showed initial periods of mobilization followed by progressive depletion. On WS9, there were no significant changes to Ca or Mg, inferring these two ions largely were depleted from the source areas that contribute nutrients to streamflow during storm events, and weathering rates were controlling the amounts of Ca and Mg in peakflow. Potassium and Na concentrations showed these ions also were in limited supply before treatment began and were becoming progressively depleted over time. Increases to NO_3 were more marked and significant than for SO_4 in peakflow on WS3. The NO_3 data for peakflow also suggested retention was occurring for it, but the broad spread of the data make this a bit less certain than the NO_3 retention that was suggested especially for soil water. Sulfate and NO_3 increased throughout the entire period of record, though the data were spread rather widely. The pH of peakflow on both WS3 and WS9 fell through the period of record. The general decline on both watersheds was less than 0.5 pH units, though for individual storms the decline was as much as a full pH unit or more over the life of the study. For all but one or two storms on each watershed, the pH at peakflow remained above 5.0. The ANC of storm runoff for both watersheds moved from being only episodically acidic at the beginning of treatment to being chronically acidic by the time stormflow sampling was terminated.

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