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SOIL LEACHATE RESPONSES DURING 10 YEARS OF INDUCED WHOLE-WATERSHED ACIDIFICATION

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Abstract. Soil solution was collected from zero-tension lysimeters for 10 yr on two small central Appalachian watersheds in West Virginia, U.S.A. Ammonium sulfate fertilizer was applied to one catchment 3 times per year during each year. The other watershed was used as a reference to account for ambient baseline conditions. Ca and Mg concentrations collected below the A- and B-horizons of the treated watershed increased and then decreased over time as a result of the treatment. By contrast, Ca and Mg concentrations in the C-horizon continued to increase throughout the study period. The depletion in Ca and Mg that occurred in the upper levels apparently occurred due to charge pairing and leaching of those base cations with NO₃ and SO₄. The progressively greater amounts of Ca and Mg carried through the soil with these acid anions provided their continued increasing concentrations in the C-horizon. NO₃ concentrations increased progressively with depth due to both the assimilation of NO₃ by vegetation and microorganisms in the upper soil layers and leaching of NO₃ into deeper soils by mesopore flow. NO₃ became a more important ion over time with respect to pairing and leaching with base cations because its concentrations continued to increase in all soil layers, whereas SO₄ became retained in all soil layers after several years of treatment, presumably induced by adsorption from increasing SO₄ concentrations.

Keywords: atmospheric deposition, charge pairing, leaching, lysimeters, soil solution chemistry

1. Introduction

Accelerated acidification of forested watersheds due to atmospheric deposition in northeastern U.S.A. has been discussed in terms of presenting real or potential problems for several decades. Effects to aquatic ecosystems, such as fish kills, fish migration to refugia during acidic episodes (Wigington, 1999), reductions in fish diversity (Carline *et al.*, 1999), and macroinvertebrate drift and shifts in species composition (Kimmel, 1999), have been documented. Acidification effects to soils and soil water also have been documented (DeWalle *et al.*, 1988, Drohan and Sharpe, 1997), though connecting those changes to vegetative stresses or species diversity changes in northeastern United States often has been difficult and sometimes more speculative (Hendershot and Belanger, 1999; Hendershot and Jones, 1989) than in Europe (e.g., Thimonier *et al.*, 1992, Fangmeier *et al.*, 1994).



Acidification by atmospheric deposition generally is caused by elevated inputs of sulfate (SO_4) and nitrate (NO_3) to a watershed. Because recent legislation has required and resulted in reductions of SO_4 emissions (Nat. Sci. Tech. Council Comm. Environ. Nat. Resour., 1998), most recent acidification research has focused on the role of NO_3 . However, because the effects of SO_4 are cumulative over time, SO_4 emissions are not required or expected to go to zero, organically-bound S is only slowly released from soils, and specifically-bound SO_4 is at best only partially reversible (Alewell and Matzner 1993), sulfate's role in acidification remains important and should not be ignored.

Acidification is signaled by decreases in pH and acid neutralizing capacity (ANC) (Hyer *et al.*, 1995) and accompanied by increases in sulfate and nitrate in soils and soil solution. Depending upon the degree of acidification already present, base cation and/or aluminum (Al) concentrations also increase (DeWalle and Swislock, 1994; Wigington *et al.*, 1996) to charge pair with the portion of these acid anions not retained in the watershed via assimilation, mineral precipitation, or adsorption (Rustad *et al.*, 1996).

In this study we examined the effects of 10 yr of induced acidification on soil leachate in a headwater catchment in the mid-Appalachians. Temporal trends in concentration responses are examined for major ions in soil water samples collected from the A-, B-, and C-horizons.

2. Methods

2.1. STUDY SITES

Two small adjacent watersheds, WS3 and WS4, on the Fernow Experimental Forest (FEF) in north central West Virginia, U.S.A. ($39^\circ 3' 15''$ N, $79^\circ 41' 15''$ W) were used in this study (Figure 1). The FEF is located in the unglaciated portion of the Allegheny Plateau region of the Appalachian Mountains, near the town of Parsons in Tucker County. WS4 was used as the reference watershed against which the responses of WS3, which was treated repeatedly to induce acidification, were compared.

WS3 and WS4 are very similar physically (Table I) and hydrologically (DeWalle *et al.*, 1997). Both watersheds have moderate to steep sideslopes with soil depth to bedrock typically 1 m or less. The dominant soil across both catchments is Calvin channery silt loam (loamy-skeletal, mixed mesic typic Dystrochep) with acidic sandstone and shale bedrock of the Hampshire formation (Losche and Beverage, 1967). Chemical characteristics of A- and B-horizon soil samples collected from WS3 and WS4 in 1988 during pretreatment are shown in Table II; few significant chemical differences existed. Precipitation averages 143 cm per year, with fairly even distribution throughout the year. The streams draining WS3 and WS4 are second-order channels. In the lower portion of the watersheds, surface flows are

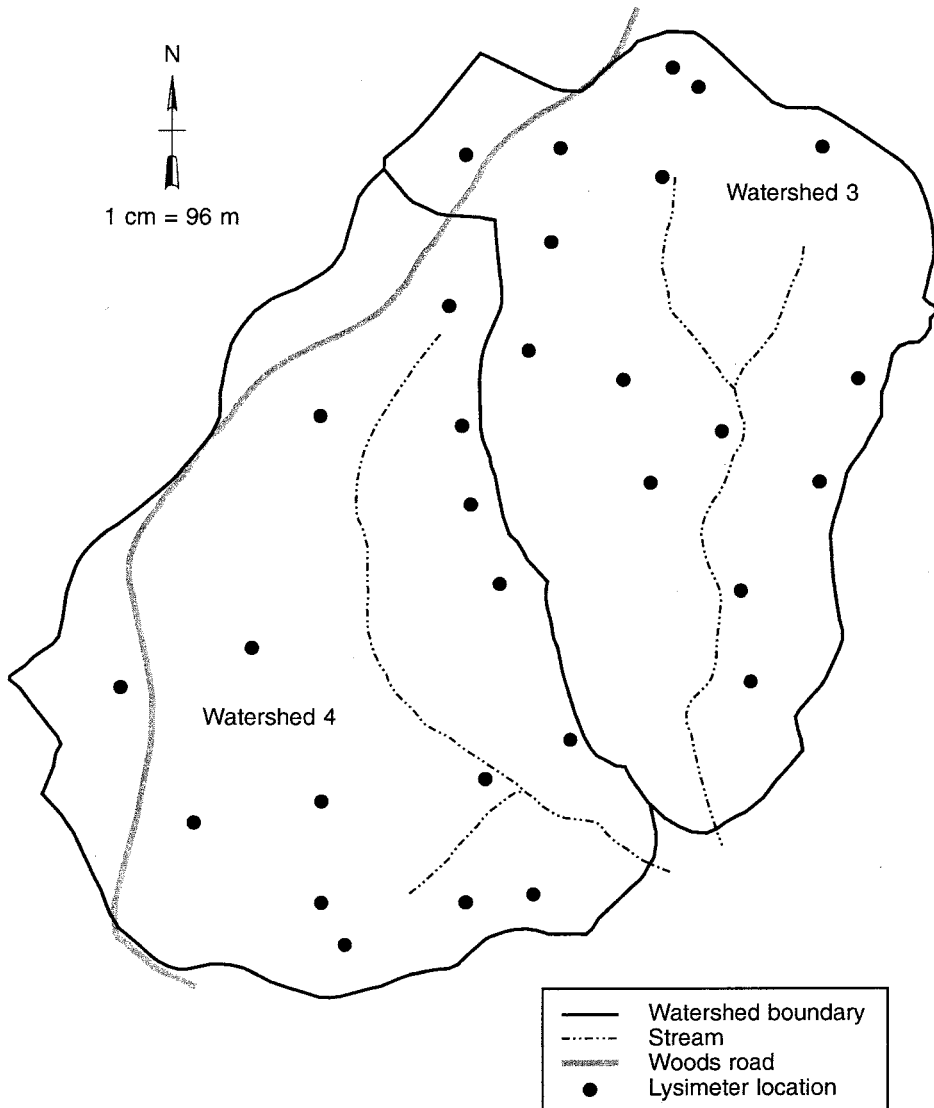


Figure 1. Locations of lysimeters on WS3 and WS4.

largely absent from August or September through mid-November in years of average precipitation and distribution. Baseflows are derived from water percolating vertically through the soil profile until it reaches bedrock and then draining laterally to the stream channel (DeWalle *et al.*, 1997). The rapidity with which precipitation reaches streams suggests that stormflow originates from shallow lateral subsurface flow (Edwards *et al.*, in press). Despite their similarities, WS3 and WS4 have

TABLE I
Characteristics of WS3 and WS4

Characteristic	WS3	WS4
Watershed area (ha)	34.3	38.9
Minimum elevation (m)	735	750
Maximum elevation (m)	860	870
Annual precipitation (mm)	1476	1457
Dominant overstory vegetation	<i>Prunus serotina</i> <i>Acer rubrum</i> <i>Betula lenta</i>	<i>Quercus rubra</i> <i>Fagus grandifolia</i> <i>Acer rubrum</i>
Overstory age (yr)	28	90
Average watershed slope (%)	20	25
Aspect	S	S-SE

different land use histories and, consequently, now support substantially different vegetation of different age classes (Table I).

WS4 was cut heavily about 1910. Unharvested trees at that time were primarily sugar maple (*Acer saccharum* Marsh.), American beech (*Fagus grandifolia* Ehrh.), and black birch (*Betula lenta* L.), along with some small trees of other species. Today, the surviving residuals are approximately 200 yr old (Edwards and Helvey, 1991). In the 1940's, some dead American chestnut (*Castanea dentata* (Marsh.) Borkh.) was salvage logged, but most if not all of this salvaged volume is believed to have been located along the watershed's upper boundary. Since that time, disturbance to WS4 has been minimal.

WS3 also was cut heavily about 1910, but was reharvested between July 1969 and May 1970. During the latter harvest, the entire watershed was clearcut to 2.54 cm dbh except for a 3-ha buffer strip surrounding the stream. In November 1972, the buffer was clearcut and all treetops and debris in the channel and within 2.4 m from the channel on both sides of the stream were removed manually. Equipment was prohibited in the buffer strip for any of the streamside harvesting or channel clearing (Kochenderfer and Edwards, 1991). The entire watershed has regenerated to native vegetation (Table I). Current overstory regeneration became established from both seeds and sprouts.

While the two watersheds support stands of vastly different ages, which affects nutrient cycling and soil solution chemistry, we believe that WS4 is a reasonable reference against which to compare the response of WS3. First, pretreatment soil chemistry of the two watersheds for the analytes available show few significant differences (Table II). Second, total monthly flow and volume-weighted monthly mean concentrations of stream chemistry on WS3 prior to treatment were strongly correlated to those of WS4 (Table III). While the concentrations of the two water-

TABLE II

Pretreatment (1988) soil chemistry means and standard deviations (in parentheses) for WS3 and WS4; horizon designations followed by an *a* indicate significant differences between watersheds at 0.05 level. Statistical differences were determined by either t-test or Mann-Whitney rank sum test, depending upon whether data were normally or non-normally distributed

Analyte	Horizon	WS3	WS4
pH	A ^a	4.48	3.95
	B	4.51	4.55
Exchangeable Ca (cmol kg ⁻¹)	A	4.79 (8.72)	0.49 (0.22)
	B	0.07 (0.08)	0.09 (0.05)
Exchangeable Mg (cmol kg ⁻¹)	A	0.59 (0.88)	0.23 (0.10)
	B ^a	0.02 (0.02)	0.07 (0.04)
Exchangeable Na (cmol kg ⁻¹)	A	0.07 (0.09)	0.08 (0.11)
	B	0.02 (0.03)	0.02 (0.01)
Exchangeable K (cmol kg ⁻¹)	A	0.34 (0.19)	0.20 (0.06)
	B	0.08 (0.06)	0.09 (0.01)
Exchangeable Al (cmol kg ⁻¹)	A ^a	1.39 (1.81)	8.70 (3.79)
	B	1.48 (2.28)	–
Cation Exchange Capacity (cmol kg ⁻¹)	A	11.77 (7.86)	9.35 (3.41)
	B	6.20 (1.47)	5.99 (1.54)
Total C (%)	A	9.1 (5.4)	11.2 (5.3)
	B	1.9 (2.3)	4.6 (2.7)

TABLE III

Regression relationships between WS3 (y) and WS4 (x) total monthly flows (cm) and volume-weighted monthly mean concentrations ($\mu\text{eq L}^{-1}$) from 1970–1988. Cl data were not available for this period

Parameter	Regression Equation	R ²
Flow	$y = 0.475 + 0.99x$	0.96
Ca	$y = 3.26 + 0.75x$	0.83
Mg	$y = 2.77 + 0.82x$	0.87
K	$y = -0.325 + 1.2x$	0.87
Na	$y = 1.63 + 0.88x$	0.78
NO ₃	$y = 6.55 + 0.66x$	0.66
SO ₄	$y = 2.78 + 0.73x$	0.78

sheds were not identical for each sampling period (i.e., slopes $\neq 1$), the R^2 values indicate fairly strong, consistent relationships between the two watersheds prior to treatment. And third, patterns of WS3 soil solution responses over time prior to and after accounting for background changes using WS4 concentrations (Figures 2 and 3, respectively; see Methods) are very similar to one another, suggesting that the reference watershed primarily influenced the y-axis values (or intercept) in Figure 3 rather than the shape or slope of the trend. Nitrate is the analyte that provides the weakest justification for using WS4 as a reference for WS3 because pretreatment soils data were not analyzed for N fractions or total N and the regression equation relating WS3 and WS4 stream water chemistry (Table III) had the lowest degree of correlation. However, the availability of 10 yr of soil solution data tempers those weaknesses for NO_3 as well as other analytes, by providing a moderately long picture of WS3 responses to the acidification that suggests the changes observed were due to treatment, rather than an aberration due to a very limited period of observation. Thus, while the two watersheds clearly did not have identical nutrient cycling processes, we believe they were sufficiently similar and consistent to one another that WS4 could be employed as a reasonable reference against which the treatment behavior of WS3 could be assessed.

2.2. WATERSHED INSTRUMENTATION, TREATMENT, AND SAMPLE COLLECTION

Zero-tension pan lysimeters were installed in 15 soil pits throughout both WS3 and WS4 (Figure 1). These pits represented the range of soils, landforms, and elevational ranges at both catchments. The pits were excavated to bedrock with a small bulldozer. Plastic pans (54 cm long \times 37 cm wide \times 3 cm deep) were installed into the uphill side of the pit as zero-tension pan lysimeters (DeWalle *et al.*, 1988). Lysimeters were installed at the base of the A- and B-horizons and, when possible, the C-horizon. The average depth of these horizons below the soil surface was 13, 79, and 119 cm, respectively. Gravity-drained soil leachate was captured in 4 L high-density polyethylene bottles connected to the lysimeters by Tygon tubing. The bottles were placed below ground in buckets which caught overflow during extremely wet periods, and were covered to eliminate precipitation contamination and shield the samples from direct sunlight and solar heating. Sample and overflow volumes were recorded to the nearest 1 ml; however, overflow was excluded from the samples due to the potential for contamination.

Lysimeters were allowed to equilibrate in the soil for approximately 5 months before the first samples were collected to minimize the influences of any contamination or altered mineralization rates with lysimeter installation and soil exposure to the air. Beginning in January 1989, soil lysimeter samples were collected approximately monthly except in extremely wet periods, during which they were collected more frequently and during some extended periods in some summers

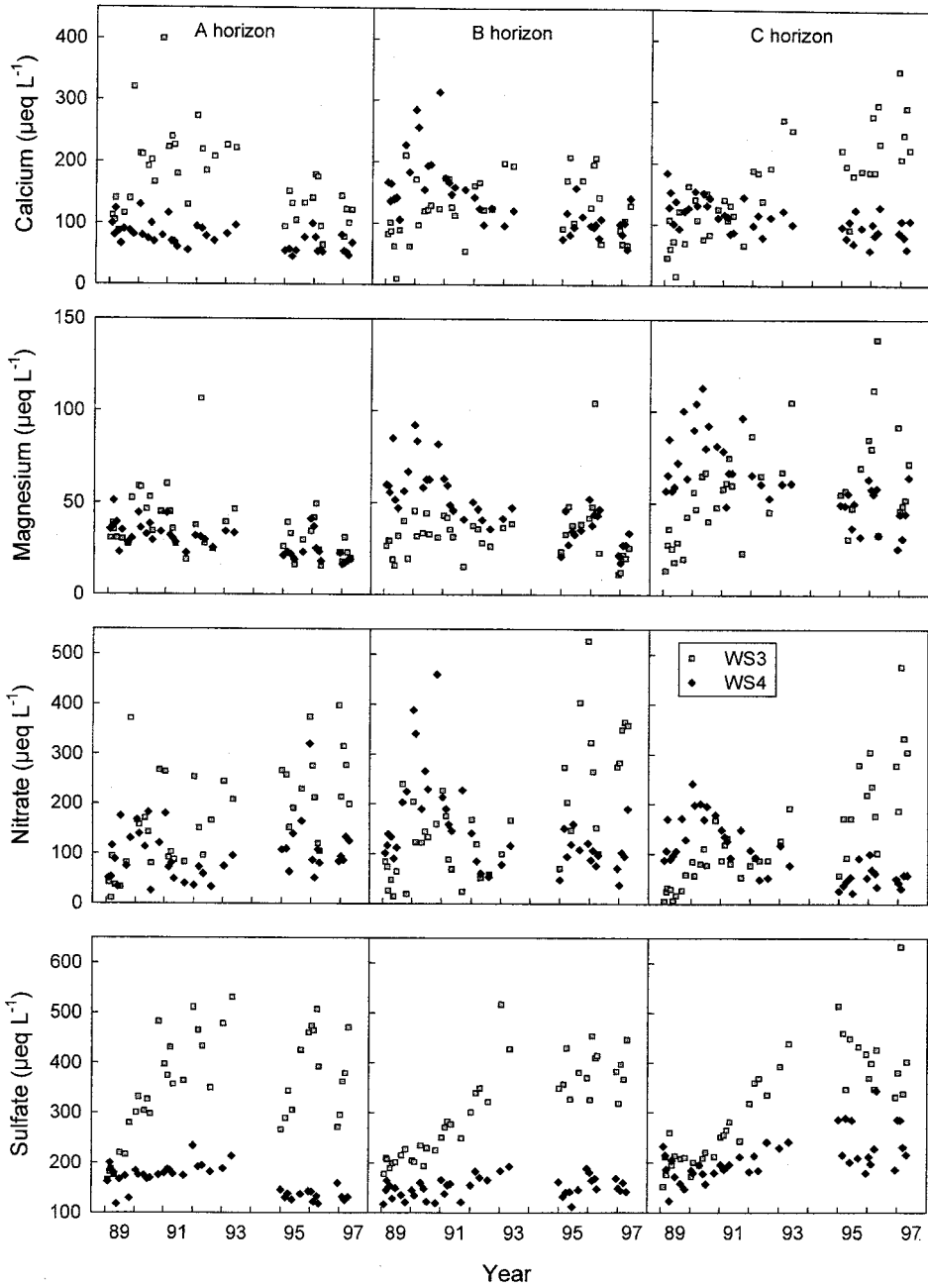


Figure 2. Volume-weighted mean concentrations for A-, B-, and C-horizon lysimeters in WS3 and WS4.

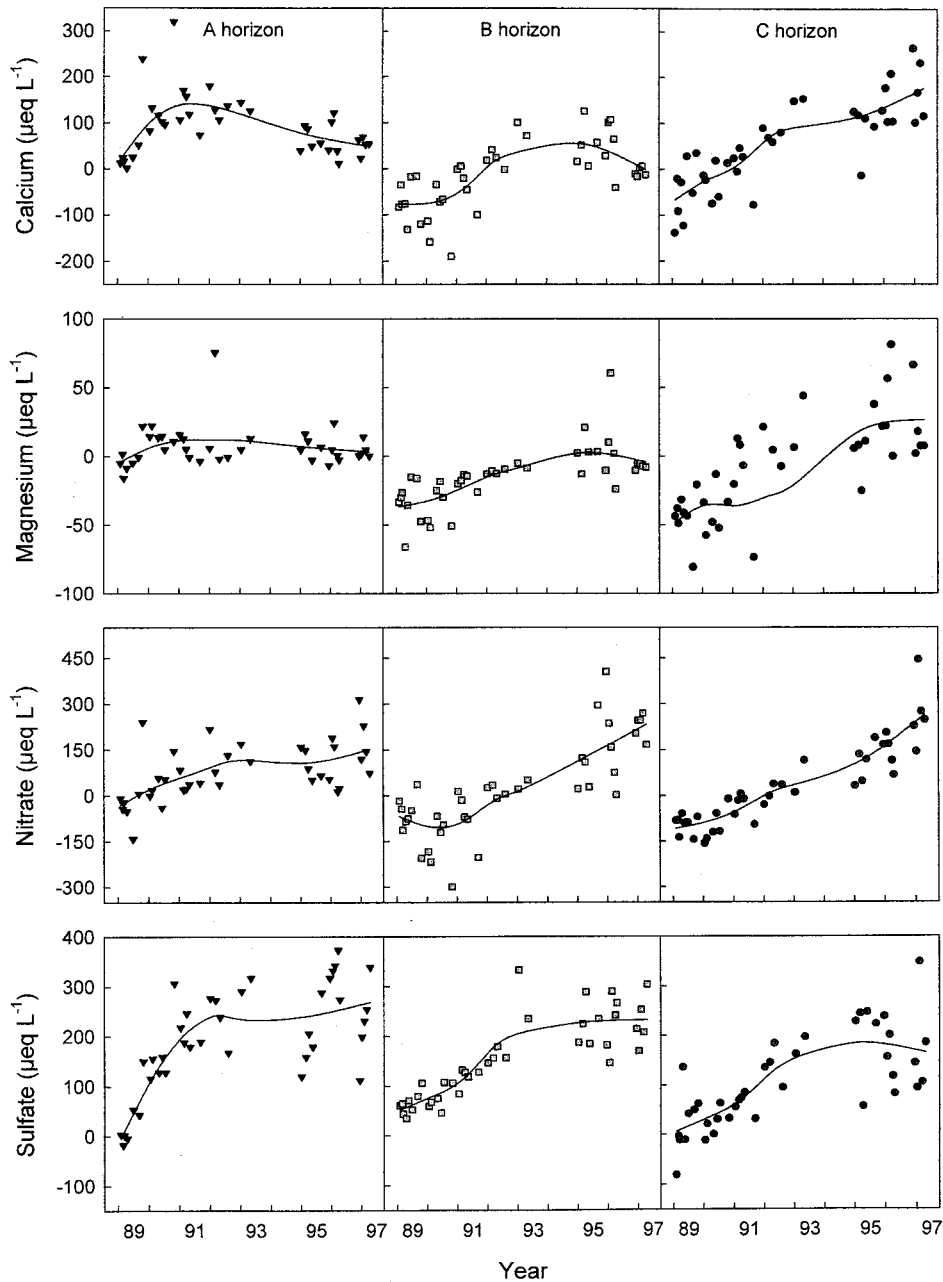


Figure 3. Volume-weighted mean differences (WS3-WS4) for A-, B-, and C-horizon lysimeters.

when sample collections were less frequent due to the lack of gravity draining soil water. Lysimeter samples were not collected in 1994 due to budget constraints.

Acidification was induced on WS3 by applying granular ammonium sulfate fertilizer to the entire watershed area by a helicopter. A granular form assured that the fertilizer would fall to the forest floor and not remain in the canopy to chemically burn the foliage. Treatment on WS3 began on January 31, 1989, and continues; data reported in this paper are inclusive through 1997. Three applications per year were approximately double ambient bulk N and S deposition inputs, as estimated from throughfall concentrations (Helvey and Kunkle, 1986). Except for occasional deviations generally related to helicopter availability or weather, WS3 was treated in the spring, summer, and autumn (usually March, July, and November) of each year. The spring and fall applications of 34 kg fertilizer per ha (7.1 kg N ha^{-1} and 8.1 kg S ha^{-1}) were approximately double the deposition rates for January to April and September to December, respectively. The summer applications of 101 kg fertilizer per ha ($21.3 \text{ kg N ha}^{-1}$ and $24.4 \text{ kg S ha}^{-1}$) were approximately double the deposition rates between May and August. Fertilizer application rates varied by season because ambient N and S inputs vary seasonally. Multiple applications per year in combination with this low rate of fertilizer application avoids inducing toxicity and minimizes altering partitioning of N and other nutrients (Schleppi *et al.*, 1999).

2.3. SAMPLE ANALYSES AND STATISTICS

Soil water samples were analyzed by horizon for calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), nitrate (NO_3), sulfate (SO_4), and chloride (Cl) using EPA-approved protocols at the Northeastern Research Station's Timber and Watershed Laboratory at Parsons. Sample handling, processing, and analytical techniques are detailed in Edwards and Wood (1993). Concentrations of all analytes except pH were expressed as $\mu\text{eq L}^{-1}$.

Only the major ions Ca, Mg, SO_4 , and NO_3 are detailed in this paper; however, Na, K, and Cl concentrations were used in the calculation of ANC as the difference in concentrations ($\mu\text{eq L}^{-1}$) between the sum of mineral bases (Ca, Mg, Na, and K) and the sum of mineral acids (SO_4 , NO_3 , and Cl). ANC provides an approach to examining soil solution chemistry as a whole (Rustad *et al.*, 1993); if ANC is negative, the solution has a strong acid acidity (Reuss and Johnson, 1986) or alternatively stated, mineral acids are supporting or counterbalancing hydrogen ions (or Al species) (Baker *et al.*, 1990). If ANC is positive, the solution has net mineral base or alkalinity, or all or some of the hydrogen ions are being countered by other anions, such as organic anions (Rustad *et al.*, 1993).

Volume-weighted mean concentrations by horizon and date were used in analyses. Sample volume included the volume in the lysimeter bottle plus overflow, when overflow existed. When the amount of soil water movement was so substan-

TABLE IV

Sen slopes and Mann-Kendall probability levels of soil leachate differences (WS3-WS4) for years indicated. Statistical significance is probability ≤ 0.05

Parameter	Dates	A-horizon		B-horizon		C-horizon	
		Sen Slope	Probability	Sen Slope	Probability	Sen Slope	Probability
Ca	1989-93	28.76	0.003				
	1994-97	-9.48	0.621				
	1989-97			15.36	0.000	28.50	0.000
Mg	1989-97	0.003	1.000	4.36	0.000	9.25	0.000
NO ₃	1989-97	18.22	0.000	39.58	0.000	40.86	0.000
SO ₄	1989-97	29.66	0.000	26.10	0.000	25.95	0.000
ANC	1989-97	-52.73	0.000	-42.31	0.000	-26.08	0.000

tial that the bucket also overflowed, overflow was recorded as 16,148 ml, which was the maximum volume the bucket could hold with bottle displacement.

To isolate only treatment effects, WS4 volume-weighted mean concentrations were subtracted from WS3. Statistical analyses are done on these difference values. Trend lines determined by locally-weighted regression are overlain on the mean differences to better visually illustrate trends.

Mann-Kendall tests (Mann, 1945) were used to test whether the mean differences in concentrations (i.e., not the trend line) between WS3 and WS4 increased or decreased significantly over time. Because Mann-Kendall tests can detect only monotonic trends, the local regression trend lines were used to identify substantial changes in the direction of data trends. Where directional changes occurred, separate Mann-Kendall test statistics were calculated for data on both sides of that change, as recommended by Hipel and McLeod (1994).

3. Results

Mean Ca concentration responses in the A- and B-horizons were similar (Figures 2 and 3). Both showed initial increases followed by decreases, though the A-horizon concentrations began decreasing about the start of 1991 and the B-horizon concentrations started declining in early 1995 (Figure 3; the exact timing of the decrease may be slightly earlier but cannot be determined without any 1994 data). While the increases attributable to treatment were significant, the decreases were not (Table IV). Ca concentrations (Figure 2) started and ended at approximately the same concentrations in the A-horizon and B-horizon, even though they experienced increases of $\geq 100 \mu\text{eq L}^{-1}$ prior to the end of the study period (Figure 3). By contrast Ca concentrations for WS3 in the C-horizon increased throughout

the study (Figure 2). An increase of approximately $225 \mu\text{eq L}^{-1}$ was experienced, with ending volume-weighted concentrations between $200\text{--}300 \mu\text{eq L}^{-1}$ (Figure 2). Based on the beginning and ending position of the trend lines (Figure 3), the treatment induced an increase of approximately $125 \mu\text{eq Ca L}^{-1}$ in the C-horizon (Figure 3), which was similar to the maximum changes observed in the A- and B-horizons.

Overall, Mg concentrations were lower than Ca concentrations in all lysimeter depths (Figure 2). Treatment resulted in little change in Mg concentrations in soil solution in the A-horizon (Table IV, Figure 3), but significant increases occurred in the B- and especially the C-horizons (Table IV, Figure 3). The rate of Mg increases in the C-horizon was about double that of the B-horizon (Table IV).

The fertilizer induced significant increases in NO_3 concentrations in all horizons (Table IV, Figure 3). The trend line for the B-horizon data shows an initial small decline in concentrations for 1–1.5 yr, but a steep increase thereafter (Figure 3). Rates of NO_3 increases were approximately $40 \mu\text{eq L}^{-1} \text{yr}^{-1}$ in the B- and C-horizons, but only about half that in the A-horizon (Table IV).

SO_4 responses to acidification treatments were similar across horizons (Figure 3). After an initial period of increase, concentrations began to level off, though the variation in the data during the latter period was greater than during the initial increasing period. Leveling off began slightly earlier in the A- and B-horizons ($\sim 1992\text{--}93$) compared to about ~ 1994 for the C-horizons. The dominant high concentration occurring across the 3 horizons was approximately $500 \mu\text{eq L}^{-1}$ (Figure 2), but the change in the C-horizon SO_4 concentrations attributable to treatment was somewhat tempered by an increase in background SO_4 concentrations in WS4 (Figure 2).

ANC concentrations decreased due to treatment at approximately the same rates in all lysimeter depths (Table IV, Figure 4). By contrast, WS4 ANC concentrations were quite stable over time and were approximately equal to WS3 ANC concentrations at the beginning of the study (Figure 4). Decreases in WS3 ANC values occurred first in the A-horizon, by about 1990, and are most evident in the steeper initial slope of the trend line in the A-horizon compared to the B- and C-horizons (Figure 4). Approximately 2 additional years were needed for ANC to decline as much in the lower 2 horizons and for the trend lines to steepen (Figure 4).

4. Discussion

The decreases in Ca concentrations attributable to treatment (Figure 3) in the A- and B-horizons suggest that the onset of Ca depletion was induced first in the organic and upper mineral soil layers as a result of repeated additions of NO_3 and SO_4 . White *et al.* (1999) concluded that initial cation pool mobilization and depletion would begin in upper soil layers and then continue downward through the soil. Initial decreases in available Ca were expressed as early as the start of

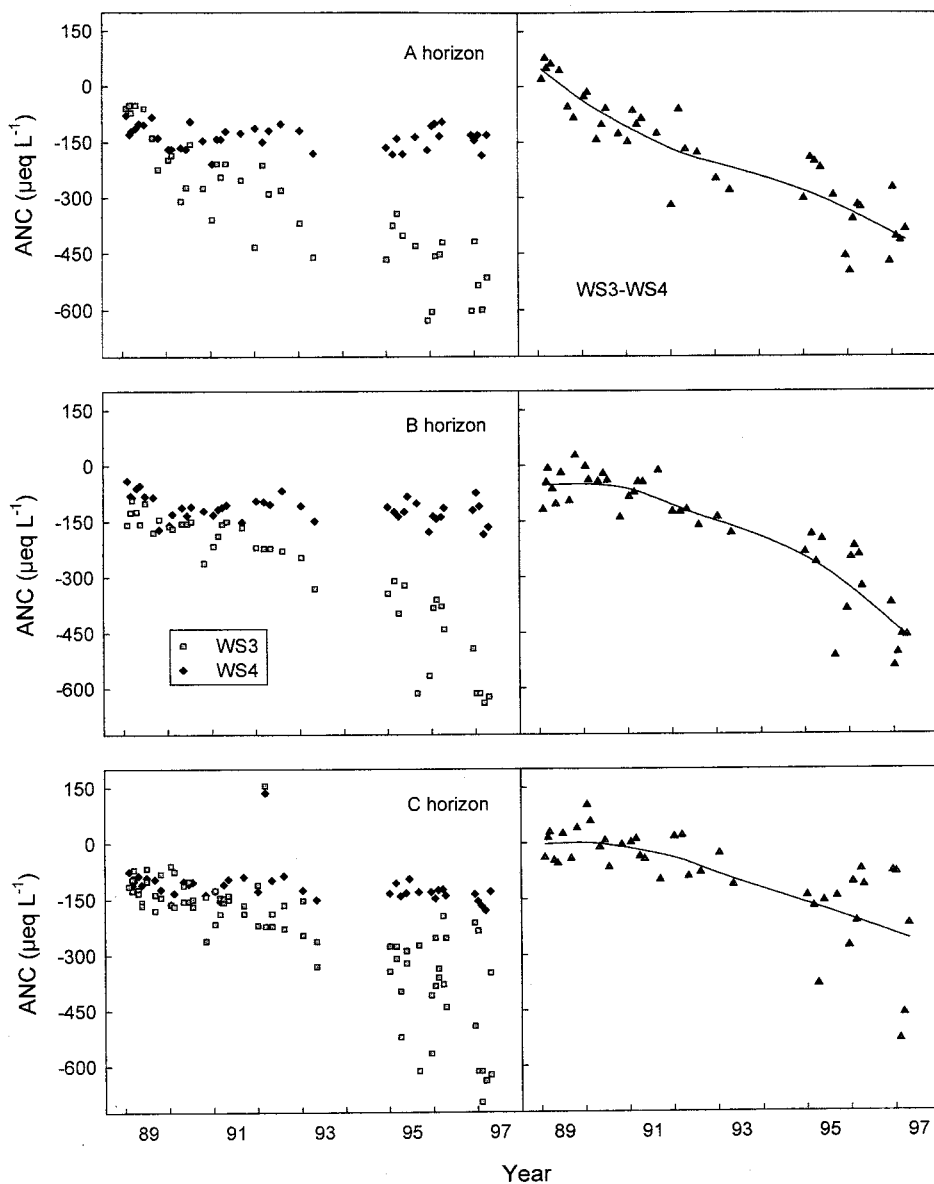


Figure 4. Volume-weighted ANC concentrations for WS3 and WS4 A-, B-, and C-horizon lysimeters, and corresponding volume-weighted mean differences (WS3-WS4).

1991 in the A-horizon, but did not begin to occur until about 1995 in the B-horizon (Figure 3). While changes in Mg concentrations were not as great as for Ca, the pattern and timing of the Mg response in the B-horizon were very similar to B-horizon Ca, suggesting the same processes controlled Mg and Ca availability and leaching. The virtual lack of Mg response in the A-horizon to repeated fertilization suggests that available Mg was largely depleted from the organic and A-horizons before the study began. The pattern of Ca concentrations were similar to Ca and Mg concentrations from zero-tension lysimeters in a nearby clearcut watershed that had ammonium sulfate fertilizer applications of the same frequency and loads as WS3 (Edwards *et al.*, 1999b). They too reported the decreases to be due to depletion as the result of charge paring and leaching with NO_3 , but primarily SO_4 . There, the initial nutrient status of the watershed was so poor from past land use, that most of the N additions were assimilated by plants and microorganisms rather than being leached.

The continued increases of both base cations in C-horizon leachate throughout the study indicate that Ca and Mg remained available for neutralization of acidic compounds near the bottom of the soil profile. The source of these cations may be from labile Ca and Mg leached from above and/or greater Ca and Mg reserves in deeper soils and parent material. These are acidic to very strongly acidic residual soils, and Ca and Mg are in limited supply in the acidic parent material and bedrock. Therefore, the increasing availability of deep Ca and Mg over time likely was due more to their displacement by protons and subsequent leaching from the forest floor and upper soil layers than from primary mineral weathering deep in the soil.

David *et al.* (1990) observed similar leaching of base cations from the forest floor and accumulation in lower soils at Bear Brook watershed with increasing additions of acids. This base cation mobilization in the upper layers initially resulted in increased base cation concentrations in soil leachate in these same layers (Rustadt *et al.*, 1993, 1996), such as were observed in the A- and B-horizons on WS3 during the first few treatment years. At Bear Brook, after 4 yr of fertilizing plots with several permutations of S and N, soil leachate in the upper B-horizon consistently maintained higher Ca and Mg concentrations than in the lower B-horizon (Rustad *et al.*, 1996), suggesting that the degree of Ca and Mg depletion in the upper horizons was not as advanced as in WS3 after 10 yr of fertilizer treatments. The most obvious signs of Ca depletion on WS3 in the A-horizon did not occur until about the fourth year after treatment started (Figures 2 and 3).

The NO_3 effect from the fertilizer on soil leachate chemistry was much greater in B- and C-horizons than in the A-horizon. Because the soil leachate in the zero-tension lysimeters is captured primarily by gravity drainage, the lower NO_3 concentrations near the soil surface suggest that: 1) NO_3 was assimilated substantially by microbes and vegetation, and/or 2) it was transported downward in the soil primarily by capillary forces and not by gravity potential during storms. It seems likely that both processes are occurring.

Kochenderfer (unpublished data) found evidence of NO₃ uptake by WS3 over-story vegetation. On WS3 Gilliam *et al.* (1996) found elevated nitrification and NO₃ uptake by *Viola rotundifolia*, *Liriodendron tulipifera* L., *Prunus serotina* Ehrh., *Betula lenta* L., and *Acer rubrum* L. compared to 2 untreated adjacent watersheds. These species are common on WS3; together the latter 4 species comprise approximately 53% of the total number of trees on the watershed (unpublished data). Their combined uptake would have reduced the NO₃ concentrations available for leaching into A-horizon lysimeters. Unfortunately, no data concerning changes in microbial populations resulting from the fertilizer applications were collected during this study, so the extent that microbes affected N leaching and retention is not known. But since much of the fertilizer was applied to WS3 in the spring and fall outside of the growing season, soil microorganisms would have been at a distinct advantage over vegetation with regard to competing for N inputs (Schleppi *et al.*, 1999). The July applications were during the growing season, but they were not optimal relative to the nutrient uptake. May and June are the months of greatest growth and nutrient demand by vegetation. Therefore, the timing of fertilizer applications also contributed to nitrate's opportunity to move downward into the B- and C-horizons.

Support for capillary transport of NO₃ comes from the timing of NO₃ leaching. In these streams, NO₃ typically reaches its peak concentrations in streamflow hours and sometimes days after peak stormflow (Edwards *et al.*, 2001), meaning that NO₃ transport is greatest after the periods of maximum gravity potential transport of water and other ions. From stormflow and associated chemistry data, Edwards *et al.* (in press) hypothesized that much of the soil water movement in WS3 is attributable to mesopore flow, which involves a pressure range of -0.3 to -30 kPa. In the noncapillary range of -0.3 to -3 kPa (Nelson and Baver 1940), mesopore flow includes movement that allows some gravity transport of soil water into the soil lysimeters, but the vast majority of the pressure range (-3 to -30 kPa) of mesopores involves capillary movement of moisture and associated ions. This larger proportion of capillary pores, depending upon pore size distribution with depth, could move substantial amounts of NO₃ deeper into the soil profile between storms. Once in deeper soils, when gravity moisture is present NO₃ would be transported into the zero-tension lysimeters and yield higher concentrations because biological controls (and delays in transport) are much less important than near the surface.

The behavior of NO₃ in this study was markedly different than that of the NITREX experiments in Switzerland, though hydrologic control of NO₃ also was important. Whereas we observed progressively larger increases in NO₃ with depth, in the NITREX experiments N additions resulted in increases in NO₃ only in the topsoil and in runoff because of preferential flow to the stream through shallow macropores (Tietema *et al.*, 1995); no increases in NO₃ were observed in lower soil layers. Little contact existed between the soil matrix and soil solution (Hagedorn *et al.*, 1997) so that assimilation of the added N by plants was minimal (Tietema *et al.*, 1995). This is in contrast to the relatively low rates of NO₃ increases in the

A- and B-horizons compared to the C-horizon observed for WS3 (Figure 3, Table IV), where N uptake occurred and the influence of macropores apparently was less. However, we observed no lag between the start of treatment and the time at which increases in the C-horizon occurred. Thus, while the hydrologic mechanisms controlling movement may have been largely different, both macropores in the NITREX and mesopores in this study efficiently conveyed NO_3 .

While evidence for transport of NO_3 exists, the reduction in NO_3 concentrations attributable to treatment during the first 1–2 yr of treatment in the B-horizon (Figure 3) illustrates that retention of NO_3 occurred initially. Since SO_4 did not simultaneously show signs of retention (i.e., no downturns in concentration responses, Figure 3), adsorption of NO_3 was not the retention mechanism. Instead, retention was by either uptake, assimilation, or incorporation into organic matter. Schleppei *et al.* (1999) reported incorporation into organic matter and adsorption of N as NH_4 onto clay minerals as principle mechanisms of retention in Gleysols in a spruce forest in Switzerland. However, organic matter levels in WS3 were substantially lower in the B-horizon than the A-horizon or forest floor before treatment (Table II) and throughout the study (Adams and Kochenderfer, 1999), so greater incorporation into organic matter in the B-horizon than in the A-horizon is questionable. Instead, vegetative uptake and microbial assimilation seem most likely, particularly since much of the rooting depth occurs in the B-horizon because the A-horizon is quite thin (~ 13 cm). While NH_4 levels in soil were not measured, NH_4 adsorption onto clay minerals is not believed to have been very important in WS3; NH_4 concentrations in soil leachate were low (unpublished data) due to the rapid nitrification rates (Gilliam *et al.*, 1996). Comparison of NO_3 and SO_4 responses shows that NO_3 played a large role in base cation leaching, especially in the mid and late 1990s. NO_3 concentrations increased and remained available as a mobile anion to charge pair with and leach base cations while SO_4 concentrations leveled off. This influence of NO_3 on base cation leaching might be more common under situations of increasing N availability than previously believed, since many types of coniferous forest soils have been found to have high nitrification rates (Stark and Hart 1997) and Fernandez *et al.* (2000) found that hardwood forests throughout Maine had much higher potential nitrification rates than softwood forests.

The leveling off or decreasing concentrations of SO_4 in all horizons by the middle of the decade suggests that SO_4 adsorption was occurring, which effectively acts to buffer acid loads (Ulrich 1994). SO_4 adsorption occurred first in the A-horizon and then in progressively lower horizons, most likely because some time was required for SO_4 to move deeper into the soil. The smaller slope values (Table IV) progressing from the A- to C-horizons illustrate the lag in time required for SO_4 to move deeper in the soil. A similar delay in SO_4 availability with depth was observed seasonally by Edwards *et al.* (1999a) in an unfertilized forested watershed.

SO_4 adsorption in WS3 may have been induced by a number of mechanisms, with the most important probably due to increasing SO_4 concentrations from fer-

tilization. SO_4 adsorption sites are created under conditions of increasing SO_4 concentrations, as SO_4 displaces OH^- ions located on neutral soil exchange sites (Chao *et al.*, 1962a, 1962b). Additional SO_4 adsorption also could have resulted from decreases of soil pH. As soil pH decreases, OH^- groups on soil exchange sites are neutralized by H^+ (Mattson, 1931; Chang and Thomas, 1963). The resulting H_2O molecule is replaced by SO_4 (Schofield and Samson, 1954). In the A-horizon, soil pH declined from 4.48 prior to treatment to 4.20 in 1997, though soil pH changes were not evident below the A-horizon (Edwards *et al.*, in press). The pH of the soil solution decreased significantly (unpublished data) over time in the A- and B-horizons, so there was a significant increase in available H^+ ions for OH^- neutralization. The limited change in soil pH (Adams and Kochenderfer, 1997) or soil leachate pH (unpublished data) through the soil profile suggests that heightened SO_4 adsorption probably was due more to SO_4 concentration increases than pH dependent processes. Precipitation of aluminum hydroxy sulfates, such as basaluminite, may have provided additional SO_4 immobilization under these conditions (Neary *et al.*, 1987; Nordstorm, 1982; Courchesne and Hendershot, 1990).

SO_4 concentrations also could have been tempered by increased S assimilation by vegetation and microbes. As N uptake increases, S uptake also must increase for protein synthesis (Turner *et al.*, 1977, Mitchell *et al.*, 1992). However, because the SO_4 concentration responses attributable to treatment tended to level off rather than simply slowing their rate of increase (Figure 3), adsorption as the primary retention mechanism seems more likely than substantial increases in S uptake.

Loss of mineral bases and negative ANC values were not unexpected, particularly in the A- and B-horizons where Ca and Mg concentrations leveled off or declined. However, even at the onset of the study ANC concentrations in all soil horizons were less than 0 (Figure 4), indicating the presence of mineral acidity at all depths in the soil without any acidification treatments. ANC concentrations declined even more over time due to the additional S and N contributions from the fertilizer, meaning the concentrations of mineral acidity relative to mineral bases increased further, though the effect was less in deeper soils.

S and N additions to plots at Bear Brook also resulted in decreasing ANC, but in that case the net change was to drive the plots from having net available base to a net mineral acidity (Rustad *et al.*, 1993) and the change was greater in the shallower Bhs horizon than the Bs horizon (Rustad *et al.*, 1996). They attributed the lesser change in the Bs horizon to mineral weathering and consequent acid neutralization. Changes in ANC reductions in the A- and B-horizons of WS3 were greater than changes in the C-horizon due to the combination of both increased acid anions and base cation depletion processes in the former two horizons. Reductions to ANC concentrations in the C-horizon were tempered because Ca and Mg concentrations continued to increase throughout the measurement period in the C-horizon from base cation leaching from above. Thus, mineral acidity continued to increase in the C-horizon without simultaneous occurrence of Ca and Mg depletion. Based on

average slope values (Table IV), base cation increases in the C-horizon were able to support approximately 40–50% of the acid anion increase attributable to fertilization compared to the A- and B-horizons. As treatment continues and base cation availability from above disappears, C-horizon ANC will be decreased at least as much as ANC in the A- and B-horizons since the parent material is acidic and weathering will provide little opportunity for acid neutralization; acidic weathered products could even increase the acidity of the deeper soil material.

5. Conclusion

Soil solution from 10 yr of acidification treatments on a watershed supporting an approximately 30 yr old hardwood stand showed that elevated N and S inputs could result in changes to nutrient availability. SO_4 moved efficiently throughout the soil profile for several years until its elevated concentrations induced adsorption. Added NH_4 nitrified quickly to NO_3 and leached fairly rapidly, even though the forest stand was aggrading. Thus, the timing of N inputs as atmospheric deposition can play a large role in whether N is used significantly by biota or lost to leaching. Both acid anions carried available base cations with them during transport in the soil, which eventually resulted in a gradual depletion of base cations. The increasing SO_4 and NO_3 concentrations combined with decreasing Ca and Mg concentrations resulted in driving soil solution ANC values to much greater negative levels than where they began. The similarities and dissimilarities of this study to others where acidification or nutrient levels have been manipulated illustrate how site-specific biogeochemical and hydrologic conditions control nutrient cycling.

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References

- Adams, M. B. and Kochenderfer, J. N.: 1999, 'The Fernow Whole-watershed Acidification Study: Soil Chemistry', W. E. Sharpe and J. R. Drohan (eds), *The Effects of Acidic Deposition on*

- Pennsylvania's Forests*, Proceedings of the 1998 PA Acidic Deposition Conference, Vol. 1, Environmental Resources Research Institute, University Park, PA, pp. 119–127.
- Alewel, C. and Matzner, E.: 1993, 'Reversibility of soil solution acidity and of sulfate retention in acid forest soils', *Water, Air, Soil Pollut.* **712**, 155–165.
- Baker, J., Gherini, S. A., Christensen, S. W., Driscoll, C. T., Gallagher, J., Munson, R. K., Newton, R. M., Reckhow, K. H. and Schofield, C. T.: 1990, 'Adirondack Lakes Survey: An Interpretive Analysis of Fish Communities and Water Chemistry, 1984–1987', Adirondack Lakes Survey Corporation, Ray Brook, NY.
- Carline, R. F., McGarvey, D. J. and Peterman, D. A.: 1999, 'Effects of Acidic Episodes on Fish Populations and Diversity in Pennsylvania', in W. E. Sharpe, and J. R. Drohan (eds), *The Effects of Acidic Deposition on Pennsylvania's Forests, Proceedings of the 1998 PA Acidic Deposition Conference*, Vol. 1, Environmental Resources Research Institute, University Park, PA, pp. 11–16.
- Chao, T. T., Harvard, M. E. and Fang, S. C.: 1962a, 'Adsorption and desorption phenomena of sulfate ions in soils', *Soil Sci. Soc. Am. Proc.* **26**, 234–237.
- Chao, T. T., Harvard, M. E. and Fang, S. C.: 1962b, 'Soil constituents and properties in the adsorption of the sulfate ion', *Soil Sci.* **94**, 286–293.
- Chang, M. L. and Thomas, G. W.: 1963, 'A suggested mechanism for sulfate adsorption by soils', *Soil Sci. Soc. Am. Proc.* **27**, 281–283.
- Courchesne, F. and Hendershot, W. H.: 1990, 'The role of basic aluminum sulfate minerals in controlling sulfate retention in mineral horizons of two spodosols', *Soil Sci.* **150**, 571–578.
- David, M. B., Fuller, R. D., Fernandez, I. J., Mitchell, M. J., Rustad, L. E., Vance, G. F., Stam, A. C. and Nodvin, S. C.: 1990, 'Spodosol variability and assessment of response to acidic deposition', *Soil Sci. Soc. Am. J.* **54**, 541–548.
- DeWalle, D. R., Edwards, P. J., Swistock, B. R., Aravena, R. and Drimmie, R. J.: 1997, 'Seasonal isotope hydrology of three Appalachian forest catchments', *Hydrol. Process.* **11**, 1895–1906.
- DeWalle, D. R., Sharpe, W. E. and Edwards, P. J.: 1988, 'Biogeochemistry of two Appalachian deciduous forest sites in relation to episodic stream acidification', *Water, Air, Soil Pollut.* **40**, 143–156.
- DeWalle, D. R. and Swistock, B. R.: 1994, 'Causes of episodic acidification in five streams on the northern Appalachian plateau', *Water Resour. Res.* **30**, 1955–1963.
- Drohan, J. R. and Sharpe, W. E.: 1997, 'Long-term changes in forest soil acidity in Pennsylvania, U.S.A.', *Water, Air, Soil Pollut.* **95**, 299–311.
- Edwards, P. J., Gregory, J. D. and Allen, H. L.: 1999a, 'Seasonal sulfate deposition and export patterns for a small Appalachian watershed', *Water, Air, Soil Pollut.* **110**, 137–155.
- Edwards, P. J. and Helvey, J. D.: 1991, 'Long-term ionic increases from a central Appalachian forested watershed', *J. Environ. Qual.* **20**, 250–255.
- Edwards, P. J., Kochenderfer, J. N. and Helvey, J. D.: 1999b, 'Soil Water and Stream Water Acidification Caused by Nitrogen and Sulfur Amendments', in W. E. Sharpe and J. R. Drohan (eds), *The Effects of Acidic Deposition on Pennsylvania's Forests*, Proceedings of the 1998 PA Acidic Deposition Conference, Vol. 1, Environmental Resources Research Institute, University Park, PA, pp. 91–105.
- Edwards, P. J., Kochenderfer, J. N. and Wood, F.: 2001, 'Using Specific Conductance to Predict Stream Water Chemistry During Storms', in J. J. Warwick (ed.), *Proc. AWRA Spring Specialty Conference*, Water Quality Modeling, San Antonio, TX, April 30 May 2, 2001, pp. 225–230.
- Edwards, P. J. and Wood, F.: 1993, 'Fernow Experimental Forest Watershed Acidification Project: Field and Laboratory Quality Assurance/Quality Control Protocols', US Forest Service Gen. Tech. Rep. NE-177, 15 p.
- Edwards, P. J., Wood, F. and Kochenderfer, J. N.: (in press), 'Baseflow and peakflow chemical responses to induced watershed acidification', *Hydrol. Process.*
- Fangmeier, A., Hadwiger-Fangmeier, A., Van Der Eerden, L. and Jäger, H.-J.: 1994, 'Effects of atmospheric ammonia on vegetation – a review', *Environ. Pollut.* **86**, 43–82.

- Fernandez, I. J., Simmons, J. A. and Briggs, R. D.: 2000, 'Indices of forest floor nitrogen status along a climate gradient in Maine, U.S.A.', *For. Ecol. Manag.* **134**, 177–187.
- Gilliam, F. S., Adams, M. B. and Yurish, B. M.: 1996, 'Ecosystem nutrient responses to chronic nitrogen inputs at Fernow Experimental Forest, West Virginia', *Can. J. For. Res.* **26**, 196–205.
- Hagedorn, F., Schleppei, P., Bucher, J. B. and Flühhler, H.: 1997, 'Nitrogen transformations in an alpine gleyic forest soil subjected to increased nitrogen deposition', *Annales Geophysicae* **15** (suppl.II): C287.
- Helvey, J. D. and Kunkle, S. H.: 1986, 'Input-output Budgets of Selected Nutrients on an Experimental Watershed near Parsons, West Virginia', US Forest Service Res. Pap. NE-584, 7 p.
- Hendershot, W. and Belanger, N.: 1999, 'The Role of Soil Acidification in Forest Decline', in W. E. Sharpe and J. R. Drohan (eds), *The Effects of Acidic Deposition on Pennsylvania's Forests*, Proceedings of the 1998 PA Acidic Deposition Conference, Vol. 1, Environmental Resources Research Institute, University Park, PA, pp. 21–27.
- Hendershot, W. H. and Jones, A. R. C.: 1989, 'The sugar maple decline in Quebec: a discussion of probable causes and the use of fertilizers to limit damage', *For. Chron.* **65**, 280–287.
- Hipel, K. W. and McLeod, A. I.: 1994, 'Time Series Modelling of Water Resources and Environmental Systems', Elsevier Science B.V., New York, 1013 p.
- Hyer, K. E., Webb, J. R. and Eshleman, K. N.: 1995, 'Episodic acidification of three streams in Shenandoah National Park, Virginia, U.S.A.', *Water, Air, Soil Pollut.* **85**, 523–528.
- Kimmel, W. G.: 1999, 'Macroinvertebrate Community Responses to Episodic Stream Acidification on the Laurel Hill in Southwestern Pennsylvania', in W. E. Sharpe and J. R. Drohan (eds), *The Effects of Acidic Deposition on Pennsylvania's Forests*, Proceedings of the 1998 PA Acidic Deposition Conference, Vol. 1, Environmental Resources Research Institute, University Park, PA, pp. 17–22.
- Kochenderfer, J. N. and Edwards, P. J.: 1991, 'Effectiveness of Three Streamside Management Practices in the Central Appalachians', in S. S. Coleman and D. G. Neary (eds), Proceedings 6th Biennial Southern Silvicultural Research Conference Vol. 2, Oct. 30–Nov. 1, 1990, Memphis, TN, US Forest Service Gen. Tech. Rep. SE-70, pp. 688–700.
- Losche, C. K. and Beverage, W. W.: 1967, 'Soil Survey of Tucker County and Part of Northern Randolph County, West Virginia', USDA Soil Cons. Serv., For. Serv. and West Virginia Agric. Exp. Stn., Washington, DC, 78 p.
- Mann, H. B.: 1945, 'Nonparametric tests against trend', *Econometrica* **13**, 245–259.
- Mattson, S.: 1931, 'The laws of soil colloidal behavior: VI. Amphoteric behavior', *Soil Sci.* **32**, 343–365.
- Mitchell, M. J., David, M. B. and Harrison, R. B.: 1992, 'Sulfur dynamics of forest ecosystems', *SCOPE* **48**, 215–254.
- National Science and Technology Council Committee on Environment and Natural Resources.: 1998, 'National Acid Precipitation Assessment Program Biennial Report to Congress: an Integrated Assessment', www.nnic.noaa.gov/CENR/NAPAP/NAPAP_96.htm.
- Neary, A. J., Mistry, E. and Vanderstar, L.: 1987, 'Sulphate relationships in some central Ontario forest soils', *Can. J. Soil Sci.* **67**, 341–352.
- Nelson, W. R. and Baver, L. D.: 1940, 'Movement of water through soils in relation to the nature of the pores', *Soil Sci. Am. Proc.* **5**, 69–76.
- Nordstrom, D. C.: 1982, 'The effect of sulfate on aluminum concentrations in natural waters: stability relations in the system Al₂O₃-SO₃-H₂O at 298 K', *Geochim Cosmochim Acta* **46**, 681–692.
- Reuss, J. O. and Johnson, D. W.: 1986, 'Acid Deposition and the Acidification of Soils and Waters', Springer-Verlag, New York, 119 pp.
- Rustad, L. E., Fernandez, I. J., David, M. B., Mitchell, M. J., Nadelhoffer, K. J. and Fuller, R. B.: 1996, 'Experimental soil acidification and recovery at the Bear Brook watershed in Maine', *Soil Sci. Soc. Am. J.* **60**, 1933–1943.

- Rustad, L. E., Fernandez, I. J., Fuller, R. D., David, M. B., Nodvin, S. C. and Halteman, W. A.: 1993, 'Soil solution response to acidic deposition in a northern hardwood forest', *Agric., Ecosys. and Environ.* **47**, 117–134.
- Schleppi, P., Muller, N., Edwards, P. J. and Bucher, J. B.: 1999, 'Three years of increased nitrogen deposition do not affect the vegetation of a montane forest ecosystem', *Phyton* **39**, 197–204.
- Schofield, R. K and Samson, H. R.: 1954, 'Flocculation of kaolinite due to the attraction of oppositely charged crystal faces', *Discuss. Faraday Soc.* **18**, 135–145.
- Stark, J. M. and Hart, S. C.: 1997, 'High rates of nitrification and nitrate turnover in undisturbed coniferous forests', *Nature* **385**, 61–64.
- Tietema, A., Wright, R. F., Blanck, K., Boxman, A. W., Bredemeier, M., Emmett, B. A., Gundersen, P., Hultberg, H., Kjonaas, O. J., Moldan, F., Roelofs, J. G. M., Schleppi, P., Stuanes, A. O. and VanBreeman, N.: 1995, 'NITREX: the timing of response of coniferous forest ecosystems to experimentally-changed nitrogen deposition', *Water, Air, Soil Pollut.* **85**, 1623–1628.
- Thimonier, A., Dupouey, J.-L. and Timbal, J.: 1992, 'Floristic changes in herb-layer vegetation of a deciduous forest in the Lorraine Plaine under the influence of atmospheric deposition', *For. Ecol. Manage.* **55**, 149–167.
- Turner, J., Lambert, M. J. and Gessel, S. P.: 1977, 'Use of foliage sulfate concentrations to predict response to urea application on Douglas Fir', *Can. J. For. Res.* **7**, 476–480.
- Ulrich, B.: 1994, 'Nutrient and Acid-base Budget of Central European Forest Ecosystems', in D. L. Godbold and A. Huttermann (eds), *Effects of Acid Rain on Forest Processes*, Wiley-Liss, New York, pp. 1–50.
- White, G., Fernandez, I. and Wiersma, G.: 1999, 'Impacts of ammonium sulfate treatment on the foliar chemistry of forest trees at the Bear Brook watershed in Maine', *Environ. Monitor. Assess.* **55**, 235–250.
- Wigington, P. J. Jr.: 1999, 'Episodic Acidification: Causes, Occurrence and Significance to Aquatic Resources', in W. E. Sharpe and J. R. Drohan (eds), *The Effects of Acidic Deposition on Pennsylvania's Forests*, Proceedings of the 1998 PA Acidic Deposition Conference, Vol. 1. Environmental Resources Research Institute, University Park, PA, pp. 1–5.
- Wigington, P. J., Jr., Baker, J. P., DeWalle, D. R., Kretser, W. A., Murdoch, P. S., Simonin, H. A., Van Sickle, J., McDowell, M. K., Peck, D. V. and Barchet, W. R.: 1996, 'Episodic acidification of small streams in the northeastern United States: episodic response project', *Ecol. Applic.* **6**, 374–388.