

## Long-Term Ionic Increases from a Central Appalachian Forested Watershed

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### ABSTRACT

The electrical conductivity of stream water draining from an unmanaged and undisturbed control watershed has been increasing rather steadily, about  $0.03 \text{ mS m}^{-1} \text{ yr}^{-1}$ , since 1971. During this period,  $\text{NO}_3^-$  and  $\text{Ca}^{2+}$  concentrations increased and were shown to mathematically account for the ionic contribution to conductivity; therefore, they are believed to be primarily responsible for the increase. However, the percentage of conductivity explained by the two ions was different over time. The percentage of conductivity attributable to  $\text{NO}_3^-$  increased in a pattern very similar to concentration. In contrast, the percentage of conductivity attributable to  $\text{Ca}^{2+}$  decreased slightly over time. The  $\text{Ca}^{2+}$  is believed to be pairing with the  $\text{NO}_3^-$  as the  $\text{NO}_3^-$  ions leach through the soil. While nitrification in mature stands can be strongly inhibited, limited nitrification, especially in forest gaps, and high anthropogenic inputs of  $\text{NO}_3^-$  probably were primary sources of the leached  $\text{NO}_3^-$ . Preferential adsorption of  $\text{SO}_4^{2-}$ , rather than  $\text{NO}_3^-$ , on soil colloids is given as an explanation for the lack of retention of  $\text{NO}_3^-$  in the soil system and subsequent leaching to the stream.

SINCE THE INITIATION of experimentation on the Fernow Experimental Forest, Watershed 4 has been maintained as a control for use in paired watershed studies. As such, it has not been treated or managed. However, the mean annual electrical conductivity of the stream water from this catchment has increased rather steadily since 1971 (Helvey et al., 1982), indicating that the export of dissolved solids is increasing (Kunkle and Wilson, 1984).

This article attempts to identify the ionic constituents that were responsible for causing the long-term conductivity increase, quantify the percentages of conductivity composed of these ions, examine changes in these percentages over time, and discuss possible mechanisms that might control these ionic responses on this watershed.

### MATERIALS AND METHODS

#### Site History and Description

Watershed 4 is a 38.9-ha catchment, located about 4.8 km south of Parsons, WV ( $39^\circ 3'00''\text{N}$ ,  $79^\circ 41'00''\text{W}$ ). Between 1905 and 1910, the watershed was heavily cut, but not clear-cut. In general, the entire area that became the Fernow Experimental Forest was not cut as heavily as many of the surrounding areas in the central Appalachians. Most American beech (*Fagus grandifolia* Ehrh.), birch (*Betula* spp.), and maple (*Acer* spp.) trees were not cut if they were defective, relatively inaccessible, or under 250 mm dbh. On Watershed 4, the principal species left uncut was sugar maple (*A. saccharum* Marsh.). By 1948, when the Fernow was activated

as an experimental area, significant stands of old-growth timber existed throughout the Forest (Trimble, 1977). Today, the residual trees on Watershed 4 are estimated to be approximately 200 yr old; however, their rings cannot be counted to define their ages precisely because the boles are hollow.

After the cutting in the early 1900s, harvesting was permitted only one other time on Watershed 4. Most of the dead merchantable American chestnut [*Castanea dentata* (Marsh.) Borkh.] was cut during the 1940s after the chestnut blight (*Endothia parasitica*) had killed the majority of these trees. The volume of timber removed during that cutting is not known. Since that time, no other cutting or timber management techniques have been employed on Watershed 4.

Today, the catchment supports a stand composed of mixed hardwoods, principally northern red oak (*Quercus rubra* L.), American beech, red maple (*A. rubrum* L.), sugar maple, sweet birch (*B. lenta* L.), and black cherry (*Prunus serotina* Ehrh.). Currently, about 1206 trees  $\text{ha}^{-1}$  (all trees  $>25 \text{ mm dbh}$ ) with a basal area of  $38 \text{ m}^2 \text{ ha}^{-1}$  are growing on the watershed.

The soils of this watershed are dominated by Calvin channery silt loam (loamy-skeletal, mixed, mesic Typic Dystrichrepts) derived from acidic sandstones and shales of the Hampshire formation (Losche and Beverage, 1967). Soils are acidic with pH values of the A, B, and C horizons averaging 4.3, 4.6, and 4.7 (Tomkowski, 1983). Depth to bedrock is approximately 1.5 m across most of the watershed.

Average annual precipitation is about 150 cm, with a fairly even distribution throughout the year. On average, daily streamflow from this watershed is  $1.83 \text{ m}^3 \text{ s}^{-1} \text{ km}^{-2}$ . Because of the transpirational demand during the growing season, the majority of stream discharge occurs between November and April.

#### Sample Collection and Analyses

Stream water was grab sampled at approximately weekly intervals, except for November 1984 through August 1987 during which time samples were taken biweekly. Samples were taken just upstream from the mouth of the watershed, using the same location each week to avoid differences in stream chemistry which might be caused by geological variations in the streambed or groundwater upwelling.

The grab samples were analyzed chemically at the USDA Forest Service's Timber and Watershed Laboratory in Parsons. Concentrations of Ca, Mg, Na, and K were determined by atomic absorption spectrophotometry. Alkalinity determinations were made using a double-endpoint titration, to pH 4.5 and 4.2 (APHA, 1985). Anion concentrations were determined by the Hach method (Hach Chemical Co., 1977) before 1981, and by ion chromatography since 1981 ( $\text{Cl}^-$  was not determined before 1981). Comparisons between the two anion analytical techniques indicated no significant differences between the methods. Data determined since 1971 are presented in the subsequent discussions, except alkalinity measurements that were determined since 1976 and  $\text{Cl}^-$  measurements that were determined since 1981.

Samples were not filtered prior to analysis, except for the anion concentrations determined by ion chromatography. They were filtered with a  $0.2\text{-}\mu\text{m}$  syringe filters at the time of sample injection into the instrument. Preservatives or acids also were not added to the samples prior to analyses; however, all samples were maintained at  $4^\circ \text{C}$  between analyses.

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### Data Analysis

Laboratory analyses provided concentration data that were examined graphically and with regression analysis to identify the ions primarily responsible for the conductivity increase.

Equivalent conductivity values were used to quantify the percentage contributions to conductivity by each of the major dissolved ions. Equivalent conductivity values were calculated by converting the mean annual concentrations to milliequivalents per cubic meter and then multiplying the results by the corresponding equivalent conductivities at infinite dilution (Weast, 1987). These results were divided by 10 to obtain units applicable to the conductivity units expressed in this article (i.e.,  $\text{mS m}^{-1}$ ). The percentage of conductivity attributable to each of the major chemical constituents was calculated by dividing each equivalent conductivity by the sum of the equivalent conductivities for the corresponding year.

### RESULTS

The mean annual pH of stream water for Watershed 4 has remained relatively constant at about pH 6.0 and has been discussed in other papers (Helvey et al., 1982; Helvey and Edwards, 1987); therefore, it will not be discussed further here. Subsequent discussions will focus on the major cations and anions in the stream water of this watershed.

Though certain ionic concentrations fluctuate slightly with flow during storm and snowmelt events in this catchment, streamflow volumes at the times samples were taken were related only very weakly to stream chemistry concentrations for all ions. Consequently, in the analyses presented, no flow factor or flow weighting procedures were applied to the concentration data.

Figure 1 shows the average annual electrical conductivity increase experienced from 1971 to 1987. A linear regression through these data indicates that conductivity increased an average of  $0.03 \text{ mS m}^{-1} \text{ yr}^{-1}$  during the 17-yr period. To determine the chemical components responsible for the increase, the concentrations of the major dissolved ions were examined over time (Table 1).

Only  $\text{Ca}^{2+}$  and  $\text{NO}_3^-$  concentrations showed what can be considered actual long-term increases. The other constituents either changed randomly over time, or

Table 1. Average annual concentrations of stream water draining from Watershed 4, from 1971 to 1987.

Year	Analyte							
	$\text{HCO}_3^-$	$\text{Mg}^{2+}$	$\text{K}^+$	$\text{Na}^+$	$\text{Ca}^{2+}$	$\text{SO}_4^{2-}$	$\text{Cl}^-$	$\text{NO}_3^-$
	$\text{g m}^{-3}$							
1971	—	0.43	0.59	0.46	1.11	3.30	—	0.66
1972	—	0.44	0.65	0.51	1.10	3.13	—	0.69
1973	—	0.44	0.67	0.52	1.17	3.32	—	0.96
1974	—	0.46	0.62	0.53	1.19	3.36	—	1.74
1975	—	0.41	0.63	0.55	1.13	3.29	—	2.77
1976	1.12	0.45	0.60	0.52	1.26	3.19	—	1.91
1977	0.88	0.51	—	0.44	1.11	4.23	—	2.02
1978	1.00	0.52	—	0.46	1.24	6.63	—	2.50
1979	1.20	0.49	0.72	0.43	1.27	5.40	—	1.83
1980	1.26	0.51	0.65	0.30	1.40	5.76	—	3.64
1981	0.88	0.75	—	—	—	3.61	0.08	4.73
1982	0.88	0.77	0.45	0.42	1.50	3.32	0.06	4.49
1983	0.95	0.73	0.47	0.41	1.46	3.67	0.06	3.82
1984	0.95	0.77	0.70	0.46	1.47	4.32	0.07	3.52
1985	0.93	0.77	0.73	0.46	1.48	4.43	0.12	3.38
1986	0.90	0.76	0.70	0.49	1.40	4.43	0.07	3.23
1987	1.04	0.73	0.64	0.49	1.44	4.39	0.07	3.06

the changes found are considered the result of instrument changes. The latter situation is the case for Mg. The significant and sustained increase in Mg concentrations beginning in 1981 corresponds to an instrument upgrade for cation analyses. Later analyses showed that the Mg concentrations determined prior to 1981 were significantly lower than the true values. Consequently, the actual early concentrations probably were similar to the post-1981 values. These same tests showed that  $\text{Ca}^{2+}$ ,  $\text{K}^+$ , and  $\text{Na}^+$  were not affected by the instrument change.

The increases in average annual  $\text{Ca}^{2+}$  and  $\text{NO}_3^-$  concentrations are shown in Fig. 2 and 3, respectively. Linear regressions through these data show an average annual increase (determined from the regression slopes) of  $0.03$  and  $0.19 \text{ g m}^{-3}$ , respectively, for the two ions.

Their contributions to conductivity were examined to determine if they could be shown to account for the average  $0.03 \text{ mS m}^{-1} \text{ yr}^{-1}$  conductivity increase. To accomplish this, the slope values for the  $\text{Ca}^{2+}$  and  $\text{NO}_3^-$  equations were converted to equivalent conductivities as explained previously, and the two results were summed. If the two ions could account for the

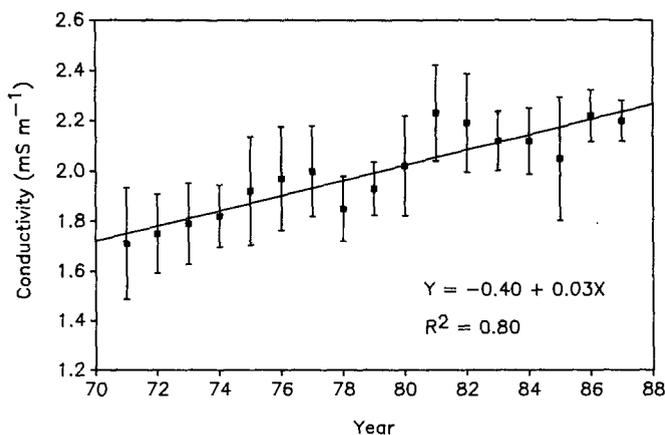


Fig. 1. Mean annual electrical conductivity of Watershed 4 stream water, from 1971 to 1987. Error bars indicate  $\pm 1$  SD.

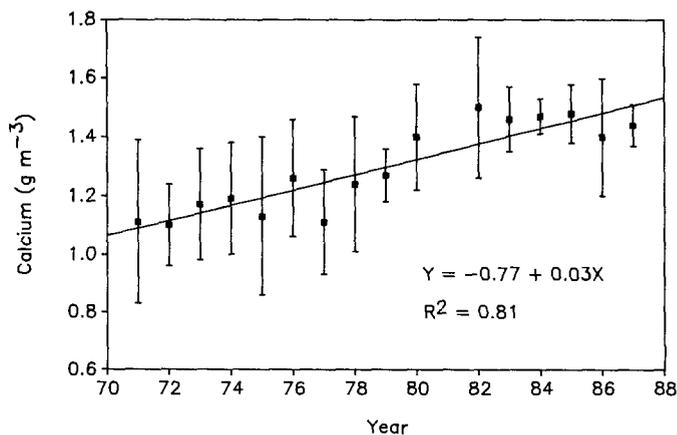


Fig. 2. Mean annual  $\text{Ca}^{2+}$  concentrations of Watershed 4 stream water, from 1971 to 1987. Error bars indicate  $\pm 1$  SD.

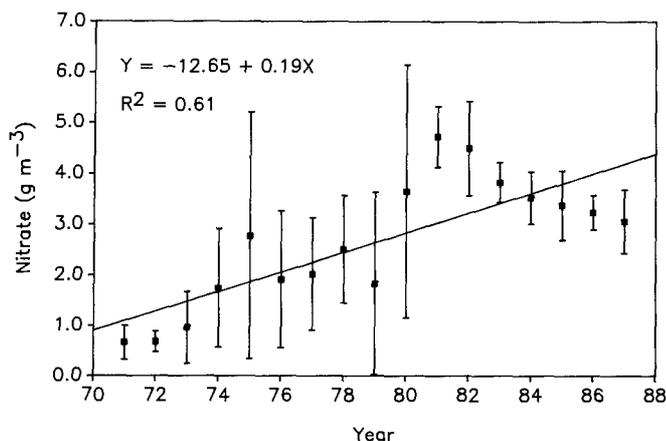


Fig. 3. Mean annual  $\text{NO}_3$  concentrations of Watershed 4 stream water, from 1971 to 1987. Error bars indicate  $\pm 1$  SD.

increase, the sum should approximate the slope of the conductivity increase, 0.03. In fact, the sum is equal to 0.03, thus supporting the hypothesis that  $\text{Ca}^{2+}$  and  $\text{NO}_3$  concentration increases were principally responsible for the conductivity increase.

The next step in analysis was to determine if the percentage contributions to conductivity changed over time. The percentage contributions to conductivity by each of the major dissolved ions will not necessarily follow the same patterns as concentration over time. Some ionic contributions may become increasingly important, whereas the importance of others may remain relatively constant or even decrease.

Before examining the actual percentages, the calculated equivalent conductivities were compared to the laboratory-measured conductivities to assure that the values compared sufficiently to perform the percentage calculations. No equivalent conductivities were calculated for 1981 because  $\text{Ca}^{2+}$ ,  $\text{K}^+$ , and  $\text{Na}^+$  were not determined that year. Equivalent conductivities prior to 1976 and 1981 were calculated without the bicarbonate contribution and  $\text{Cl}^-$  contribution, respectively. Potassium was not included in equivalent conductivity calculations in 1977 or 1978. Even with

Table 2. Comparisons between calculated annual equivalent conductivities and mean annual laboratory-measured conductivities.

Year	Equivalent conductivity	Measured conductivity	Difference [(Eq. - Meas.)	Difference
				[(Eq. - Meas.)/Meas.]
				mS $\text{m}^{-1}$
				%
1971	1.36	1.71	-0.35	-20.5
1972	1.35	1.75	-0.40	-22.9
1973	1.44	1.79	-0.35	-19.6
1974	1.54	1.82	-0.28	-15.4
1975	1.62	1.92	-0.30	-15.6
1976	1.63	1.97	-0.34	-17.3
1977	1.65	2.00	-0.35	-17.5
1978	2.16	1.85	0.31	16.8
1979	2.02	1.93	0.09	4.7
1980	2.29	2.02	0.27	13.4
1981	-	-	-	-
1982	2.10	2.19	-0.09	-4.1
1983	2.06	2.12	-0.06	-2.8
1984	2.21	2.12	0.09	4.2
1985	2.23	2.05	0.18	8.8
1986	2.17	2.22	-0.05	-2.3
1987	2.15	2.20	-0.05	-2.3

these omissions, the equivalent conductivity values compared well with the measured values (Table 2), and the percent differences are all within acceptable quality assurance limits for conductivities between 0.5 and 3.0  $\text{mS m}^{-1}$  (Peden, 1981). In fact, had the missing concentrations been available for inclusion in the calculations, the percent differences would have been closer to zero for 1971-1977, and larger only for 1978-1980.

Percentage contributions were calculated for each year except 1981, since such a large portion of the conductivity generally was composed of the three missing ions, especially  $\text{Ca}^{2+}$ . Contributions for the remaining years were calculated with the data available; missing constituents (i.e.,  $\text{HCO}_3^-$  prior to 1976,  $\text{Cl}^-$  prior to 1981, and  $\text{K}^+$  in 1977-1978) were not included in calculations for those respective years.

Most of the ions did not show large change in percentage contributions over time, so they are not discussed in detail. However, the most frequently occurring trend, when one was present, was that of decreasing contributions by most ions to conductivity. Sodium,  $\text{K}^+$ , and  $\text{HCO}_3^-$  contributions all showed such a trend (Table 3). For  $\text{Na}^+$  and  $\text{K}^+$ , part of this trend can be accounted for by the fact that the pre-1976 percentages were calculated without  $\text{HCO}_3^-$  concentrations included in the calculations. The inclusion of  $\text{HCO}_3^-$  in the calculations, had the data been available, would have reduced the other pre-1976 ionic contributions by a factor of probably less than 1 to 2%, thereby dampening the decreasing trend. Chloride also was not included in the pre-1981 percentage calculations, but its contribution is so minor that it probably made little difference in the calculations.

Calcium and  $\text{NO}_3$  percentage contributions did provide some interesting results, particularly when compared to the concentration results. The  $\text{Ca}^{2+}$  percentage contribution decreased about 0.28% annually (Fig. 4). However, the exclusion of  $\text{HCO}_3^-$  from calculations for the pre-1976 years slightly inflated the  $\text{Ca}^{2+}$  contributions during those years. Thus, the true downward trend is probably a bit less pronounced than that shown in Fig. 4.

The  $\text{NO}_3$  percentage contribution results (Fig. 5) followed a pattern similar to the concentration results.

Table 3. Annual percentage contributions of major dissolved ions in stream water to conductivity.

Year	Percent of conductivity attributable to—							
	$\text{HCO}_3^-$	$\text{Mg}^{2+}$	$\text{K}^+$	$\text{Na}^+$	$\text{Ca}^{2+}$	$\text{SO}_4^{2-}$	$\text{Cl}^-$	$\text{NO}_3^-$
1971	-	13.92	8.23	7.34	24.32	40.59	-	5.64
1972	-	14.21	9.04	8.17	24.22	38.57	-	5.87
1973	-	13.31	8.72	7.90	24.03	38.38	-	7.68
1974	-	12.87	7.59	7.47	22.91	36.17	-	12.98
1975	-	11.08	7.35	7.36	20.64	33.84	-	19.73
1976	5.05	11.97	6.89	6.92	23.01	32.65	-	13.52
1977	3.88	13.38	-	5.77	20.06	42.81	-	14.12
1978	3.36	10.42	-	4.67	17.08	51.12	-	13.33
1979	4.32	10.67	6.73	4.68	18.68	44.52	-	10.43
1980	4.00	9.74	5.33	2.80	18.06	41.79	-	18.27
1981	-	-	-	-	-	-	-	-
1982	3.01	15.89	4.00	4.31	21.22	26.34	0.59	24.64
1983	3.34	15.47	4.27	4.35	21.04	29.58	0.61	21.33
1984	3.12	15.13	5.98	4.52	19.70	32.53	0.69	18.32
1985	3.02	14.99	6.16	4.44	19.62	33.16	1.16	17.45
1986	3.01	15.22	6.05	4.86	19.07	33.91	0.73	17.13
1987	3.51	14.75	5.57	5.00	19.96	34.07	0.72	16.42

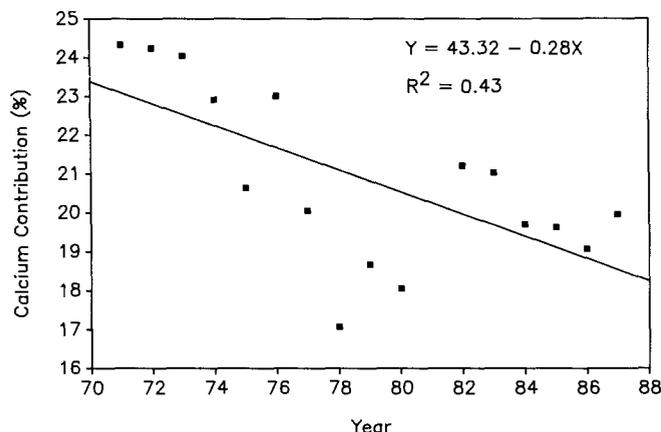


Fig. 4. Percentage contributions to electrical conductivity by  $\text{Ca}^{2+}$  in Watershed 4 stream water.

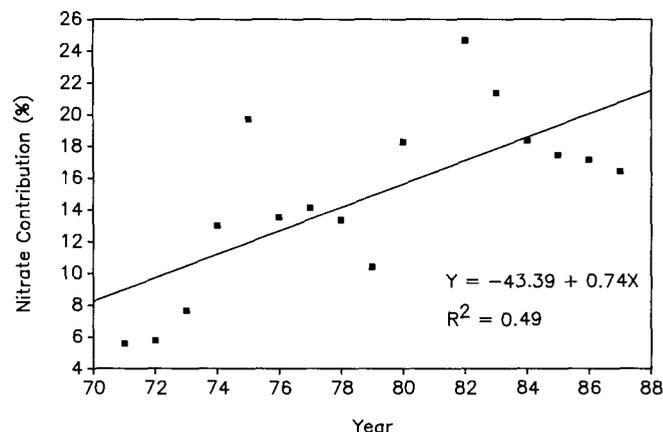


Fig. 5. Percentage contribution to electrical conductivity by  $\text{NO}_3^-$  in Watershed 4 stream water.

This ion was the only one for which a percentage increase was found, though some variation occurred throughout the period of record. During the 1970s, the  $\text{NO}_3^-$  contribution to stream water conductivity was approximately 11.5%. This percentage nearly doubled to approximately 21% during the 1980s. Had pre-1976  $\text{HCO}_3^-$  data been included in the calculations, the early  $\text{NO}_3^-$  percentages would have been somewhat lower than those reported, resulting in a slightly greater slope. The average annual  $\text{NO}_3^-$  contribution actually exceeded the  $\text{Ca}^{2+}$  contribution during this latter period.

Only sulfate's percentage contributions to stream conductivity surpassed that of  $\text{NO}_3^-$  during the 1980s. Sulfate and  $\text{NO}_3^-$  tend to complement one another; when  $\text{SO}_4^{2-}$  contributions increase,  $\text{NO}_3^-$  contributions decrease, and vice versa. As expected from an electrical equivalent basis, since  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  are the primary anions in the stream water, their sum of contributions composes approximately 50% of the electrical conductivity during almost all years (Table 3).

### DISCUSSION

A long-term record of precipitation chemistry is not available for this site, so the attribution of increasing exports of  $\text{NO}_3^-$  and/or  $\text{Ca}^{2+}$  to atmospheric inputs cannot be supported or disproved. However, the available wet precipitation data determined weekly from an automatic wet/dry collector (Table 4) do not show consistent changes over time. Neither simple concentrations nor precipitation-weighted concentrations of  $\text{NO}_3^-$  or  $\text{Ca}^{2+}$  have consistently increased (or decreased) since 1983. In addition, while atmospheric inputs may

have some control over exports, the system is not driven by wet precipitation inputs. That is, the exports of  $\text{NO}_3^-$  and  $\text{Ca}^{2+}$  do not respond directly or proportionally to precipitation inputs. For example, from 1983–1987  $\text{NO}_3^-$  discharge actually decreased, while the unweighted and precipitation-weighted concentration inputs increased slightly through 1985 and 1986. Therefore, one or more other controlling factors is inferred.

For this watershed, the high inputs of  $\text{SO}_4^{2-}$  may be indirectly causing increased  $\text{NO}_3^-$  leaching from the soil. This catchment receives an annual average bulk  $\text{SO}_4^{2-}$  input of  $39.9 \text{ kg ha}^{-1}$  (Helvey and Kunkle, 1986), placing it within the region of greatest  $\text{SO}_4^{2-}$  deposition in the USA (NADP/NTN, 1987). In addition, net  $\text{SO}_4^{2-}$  accumulation has been reported for this catchment (Helvey and Kunkle, 1986). Because soil has a limited capacity to adsorb anions, and  $\text{SO}_4^{2-}$  is more preferentially adsorbed due to its 2- charge and specific adsorption (Bohn et al., 1985),  $\text{NO}_3^-$  consequently is adsorbed to a lesser degree. The result of the lower preference for  $\text{NO}_3^-$  retention allows it to be leached more easily from the soil.

Nitrification and the occurrence of  $\text{NO}_3^-$  in forest soils typically decreases with stand age (Bormann and Likens, 1979). In climax stands, a strong inhibition of nitrification has been reported (Rice and Pancholy, 1972), and  $\text{NH}_4^+$  replaces  $\text{NO}_3^-$  as the N compound used by plants. But nitrification probably is not entirely inhibited in any aerobic soil, even in climax stands (Mladenoff, 1987). Therefore,  $\text{NO}_3^-$  from nitrification would still be present in the soil. Anthropogenic inputs also provide a very significant input of  $\text{NO}_3^-$  to forest soils in this region (NADP/NTN, 1987).

Table 4. Average annual wet precipitation concentrations, precipitation-weighted concentrations, and total yearly precipitation for Watershed 4 from 1983 to 1987.

Year	pH	Cond. $\text{mS m}^{-1}$	$\text{Cl}^-$	$\text{NO}_3^-$	$\text{SO}_4^{2-}$	$\text{Ca}^{2+}$	$\text{Mg}^{2+}$	$\text{K}^+$	$\text{Na}^+$	Precip. cm	Precip. weighted	Precip. weighted
											$\text{Ca}^{2+}$	$\text{NO}_3^-$
						$\text{g m}^{-3}$			$\text{g m}^{-3}$			
1983	4.17	3.21	0.01	1.83	2.98	0.23	0.02	0.05	0.04	140	0.21	1.94
1984	4.14	3.32	0.02	1.94	3.31	0.22	0.03	0.08	0.06	160	0.24	2.22
1985	4.14	3.49	0.02	2.11	3.20	0.19	0.02	0.05	0.06	169	0.25	2.34
1986	4.12	3.65	0.03	2.19	3.45	0.23	0.03	0.12	0.07	147	0.22	2.04
1987	4.20	3.42	0.03	1.98	3.10	0.22	0.01	0.05	0.16	109	0.16	1.55

In a mature stand, such as that on Watershed 4, the  $\text{NO}_3^-$  present from nitrification and atmospheric inputs may be less important to vegetation than in younger stands because of the switch to  $\text{NH}_4^+$  utilization. This situation, coupled with the lower potential for  $\text{NO}_3^-$  adsorption in soils receiving heavy  $\text{SO}_4^{2-}$  loads, may explain the increasing  $\text{NO}_3^-$  export from Watershed 4.

However, in addition to these factors, physical changes in older stands also may heighten the potential for excess  $\text{NO}_3^-$  formation. The creation of gaps in the forest stand on Watershed 4 may augment nitrification, creating more  $\text{NO}_3^-$  available for leaching. Gap formation is a natural process in all forest stands. Although openings are produced throughout a stand's life, older stands have higher occurrences of gap formation, and the gaps caused by noncatastrophic factors tend to be larger and longer-lived than in young stands (Romme and Martin, 1982; Runkle, 1982; Barden, 1989). Gap formation could have accelerated mineralization as soil temperature and moisture increased when canopy openings were created. In turn, the C/N ratio may have been reduced as  $\text{CO}_2$  was liberated during microbial respiration, allowing for elevated nitrification (Carlyle, 1986).

Though no measurements have been taken to quantify the extent or changes of gap formation over time, mortality measurements have been taken on the watershed using 25 0.08-ha plots distributed throughout the catchment. The results of these measurements are given in Table 5. Eighty-one percent of the dead trees were in the 127 to 279 mm dbh classes, which were intermediate and codominant trees. The gaps formed by the intermediate trees probably were not large; however, the gaps formed by the codominant and few dominant trees were probably larger and clearly more important in influencing nitrification. There was a ten-

dency for dead trees to occur in clusters. Many plots had only a few or no dead trees, while dead stems comprised up to 10% of the trees on several plots. Such clustering, even with only intermediate trees, would have introduced a greater potential for formation of gaps of sizes that would have been substantial enough to alter the biological and biochemical activity of the soil system in those finite areas.

Apparently,  $\text{Ca}^{2+}$  leached from the watershed as a consequence of the  $\text{NO}_3^-$  movement. To maintain electroneutrality,  $\text{Ca}^{2+}$  paired with  $\text{NO}_3^-$  during transport through the soil. Foster et al. (1989) found  $\text{Ca}^{2+}$  was highly correlated with  $\text{NO}_3^-$  in soil leachate studies, suggesting that they pair quite readily as  $\text{NO}_3^-$  leaches through the soil. The relatively high natural abundance of  $\text{Ca}^{2+}$  combined with its 2+ valence and ionic radius probably account for its preferential pairing with  $\text{NO}_3^-$ .

## CONCLUSION

Increases in electrical conductivity of stream water recorded over the past 17 yr from a control watershed have been attributed to accelerating exports of  $\text{Ca}^{2+}$  and  $\text{NO}_3^-$ . While an increasing loss of  $\text{NO}_3^-$  is not typically expected from a catchment supporting mature hardwood stands, the loss may be linked to the regional input of high  $\text{SO}_4^{2-}$  loads. The incoming  $\text{SO}_4^{2-}$  may effectively occupy the majority of the anion adsorption sites, so that  $\text{NO}_3^-$  in the soil, from whatever source, is maintained in solution, available for leaching. The formation of forest gaps may augment the amount of  $\text{NO}_3^-$  leached by elevating nitrification rates within the gaps. If this situation indeed occurs, special timber management practices may have to be considered in mature and overmature stands growing in areas with high  $\text{SO}_4^{2-}$  deposition so that  $\text{NO}_3^-$  losses do not become excessive and negatively affect soil nutrient status or stream productivity. The  $\text{Ca}^{2+}$  losses are believed to be a result of ion pairing to retain electroneutrality rather than a loss caused by some independent factor.

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Table 5. Tree mortality summary from 25 0.08-ha plots on Watershed 4, measured in 1990.

Plot	No. of dead trees	Mean dbh	Dead basal area	Percent dead trees	Percent dead basal area
		mm	m <sup>2</sup>	%	
1	2	178	0.06	2.0	1.5
2	10	213	0.38	9.9	11.9
3	1	178	0.03	1.3	0.9
4	7	175	0.18	5.1	6.2
5	7	168	0.17	5.6	5.2
6	0	0	0.00	0.0	0.0
7	11	183	0.31	8.5	11.1
8	5	198	0.17	7.2	5.6
9	5	269	0.35	6.8	13.7
10	3	462	0.76	2.7	23.5
11	4	193	0.13	2.8	3.3
12	4	224	0.17	3.5	5.0
13	4	282	0.31	4.0	9.3
14	0	0	0.00	0.0	0.0
15	1	528	0.22	1.7	7.3
16	4	348	0.41	9.1	15.2
17	2	462	0.33	2.5	10.2
18	2	162	0.04	2.4	1.2
19	2	183	0.06	2.0	1.8
20	6	312	0.56	5.2	14.8
21	2	287	0.16	2.2	9.0
22	3	323	0.26	4.5	8.0
23	3	162	0.07	2.5	2.0
24	2	190	0.06	2.1	2.3
25	2	226	0.08	1.7	3.6
Total	92		5.27	3.8	6.9
Per ha	46		2.64		

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