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A Comparative Evaluation of the Effects of Acid Precipitation, Natural Acid Production, and Harvesting on Cation Removal from Forests

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Environmental Sciences Division
Publication No. 2508

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ENVIRONMENTAL SCIENCES DIVISION

A COMPARATIVE EVALUATION OF THE EFFECTS OF ACID PRECIPITATION,
NATURAL ACID PRODUCTION, AND HARVESTING ON
CATION REMOVAL FROM FORESTS

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DISCLAIMER

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ABSTRACT

JOHNSON, D. W., J. M. KELLY, W. T. SWANK, D. W. COLE,
J. W. HORNBECK, R. S. PIERCE, and D. VAN LEAR. 1985.
A comparative evaluation of the effects of acid
precipitation, natural acid production, and harvesting
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National Laboratory, Oak Ridge, Tennessee. 114 pp.

A comparison was made of the effects of acid deposition, natural leaching, and harvesting on base cation export from coniferous forests in Maine, coniferous and deciduous forests in Tennessee, a coniferous forest in South Carolina, a deciduous forest in North Carolina, and coniferous and deciduous forests in Washington. Sulfate dominated leaching in the Tennessee sites, whereas HCO_3^- dominated leaching in the Maine, North Carolina, South Carolina, and Washington sites (the latter because of very high HCO_3^- and NO_3^- leaching rates). Nitrate leaching was negligible in all but a red alder site in Washington where nitrogen fixation resulted in net NO_3^- leaching. Total base cation export by leaching exceeded $\text{Ca}^{2+} + \text{Mg}^{2+} + \text{K}^+$ export that results from whole-tree harvesting in most sites. (The export of Na^+ via harvesting was assumed to be negligible compared with that of Ca^{2+} , Mg^{2+} , and K^+ .) However, leaching, even as augmented by acid deposition, does not appear to pose an imminent threat to soil base cation supplies on sites for which soil data are available. This is basically because soil base cation reserves are very large relative to leaching rates. Some sites showed a net Ca^{2+} or K^+ accumulation from atmospheric deposition until they were subjected to whole-tree harvesting. Thus, leaching need not cause a net export of all nutrient cations, even if total base cation export is accelerated by acid deposition.

I. INTRODUCTION

Early evaluations of the nutritional effects of intensive harvesting considered atmospheric inputs solely from the perspective of possible nutrient amendments (e.g., Boyle et al. 1973; Weetman and Webber et al. 1972). Conversely, early acid deposition research considered only the potential effects on cation nutrient loss (e.g., Engstrom et al. 1971). In reality, atmospheric deposition can have beneficial, adverse, or no effects on forest nutrient status. Which effects occur depends on site nutrient status, silvicultural practices, and amount of atmospheric input of nutrients and acids (reviewed by Johnson et al. 1982b).

Since harvesting and atmospheric deposition occur together, it is essential to consider their combined effects on forest nutrient status. This is particularly important because harvesting intensity is increasing, in terms of both shorter rotations and greater biomass utilization [e.g., whole-tree harvesting (WTH)]; concurrently, atmospheric pollutant inputs have increased also.

The overall goal of this project was to evaluate the combined effects of acid deposition, natural leaching processes, and intensive harvesting on cation removal from forests. Specific objectives included the following:

1. To determine the significance of anthropogenic inputs of acidity, natural internal production of acidity, and whole-tree harvesting to nutrient losses from forest soils;

2. To evaluate present and potential future adequacy of soil nutrients to sustain forest productivity, based on measurements of present nutrient pools in forests, nutrient status of soils, nutrient losses by acid deposition, natural internal processes, and tree harvesting; and
3. To evaluate ways of classifying soil sensitivity to acid deposition by examining soil systems at approximately 10 widely spaced sites in both the eastern and western United States.

II. TECHNICAL APPROACH

This project was added to an ongoing project funded by the Department of Energy (DOE) (West and Mann 1984) on the effects of conventional harvesting vs WTH and an ongoing Electric Power Research Institute (EPRI) study on the effects of acid rain on forest nutrient status. Both projects are coordinated at Oak Ridge National Laboratory (ORNL). The institutions and sites involved in these studies are listed in Table 1.

Lysimeters were in place and routine collections were being made on control, conventionally harvested, and whole-tree harvested sites as part of the DOE-funded project. This project required additional analyses on routinely collected samples and, in most cases, the installation of precipitation and throughfall collectors (open-bucket type). Under the EPRI-funded program, estimates of the effects of acid rain vs natural processes on cation leaching rates were being made at five sites. At three sites, the Environmental Protection Agency (EPA)

Table 1. Sites and forest types included in the study

Research group (Task leader)	Site location	Forest type
<u>Sites currently in DOE Whole-Tree Harvesting Program</u>		
Oak Ridge National Laboratory (D. W. Johnson)	Oak Ridge National Environmental Research Park (NERP), Tennessee	Mixed upland hardwoods loblolly pine (newly established)
Southeastern Forest Experiment station (W. T. Swank)	Coweeta Hydrologic Laboratory, North Carolina	Mixed deciduous
Northeastern Forest Experiment Station (R. S. Pierce/ J. M. Hornbeck)	Chesuncook Lake, Maine	Spruce-fir
Clemson University (D. Van Lear)	Clemson, South Carolina	Loblolly pine
University of Washington (D. W. Cole)	Charles Pack Forest, Washington	Douglas-fir, red alder
<u>Sites currently in the EPRI Acid Rain Research Program</u>		
Oak Ridge National Laboratory (D. W. Johnson)	Walker Branch Watershed, Tennessee	Chestnut oak, yellow-poplar
Tenn. Valley Auth. (J. M. Kelly)	Camp Branch Watershed, Tennessee	Mixed deciduous

project required construction of a full nutrient budget, including total nutrient distribution in biomass, litter, and soil.

The techniques for assessing acid rain and natural leaching processes paralleled those used in the EPRI study. Specifically, analysis of pH, SO_4^{2-} , and HCO_3^- in inputs and soil solution allowed a comparison of atmospheric H^+ inputs with internal H^+ generation from carbonic acid in the soil (i.e., $\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3 \rightarrow \text{H}^+ + \text{HCO}_3^-$).

Methods of assessing harvesting effects in the EPRI sites parallel those used in the DOE study (except that no actual harvesting has taken place). Namely, tree biomass was estimated using regression equations and soils, litter, and vegetation were analyzed for major nutrients. Knowledge of the distribution of nutrients in foliage, branch, bole, litter, and soils allows the effects of bole-only harvesting vs WTH to be calculated (assuming complete removal of the product).

Results from each site were reported in a standard format annually to ORNL. This report represents the first major synthesizing of these data at ORNL; an abbreviated version of the report which was submitted for the NAPAP meeting held in Asheville, N.C., November 13-15, 1984. Reports from individual sites are provided in Appendix B.

III. RESULTS AND DISCUSSION

Table 2 shows the three stages of the method used to evaluate the effects of acid deposition and harvesting on base cation export. These results allow some insight into (1) the potential long-term effects of

Table 2. Synthesis of results at ORNL

Three Stages of Evaluation of the Effects of Acid Deposition,
Harvesting, and Natural Leaching on Base Cation Export from Forests

- Stage I. Potential base cation removal due to acid deposition vs whole-tree harvesting (assumes 100% efficiency of H^+ exchange for cations)
- A. Measure inputs of H^+ , SO_4^{2-} , NO_3^- , Ca^{2+} , K^+ , Mg^{2+}
 - B. Estimate export of $\Sigma Ca^{2+} + K^+ + Mg^{2+}$ in biomass harvest
 - C. Compare H^+ inputs (A) to $\Sigma Ca + K + Mg$ output (B) in $Eq \cdot ha^{-1} \cdot yr^{-1}$ for a given rotation length
- Stage II. Actual base cation removal due to acid deposition, internal leaching processes, and whole-tree harvesting (requires measurement of leaching fluxes)
- A. Compare leaching rates of $\Sigma Ca^{2+} + K^+ + Mg^{2+}$ with leaching rates of SO_4^{2-} , NO_3^- , and HCO_3^- in $Eq \cdot ha^{-1} \cdot yr^{-1}$
 - B. Determine amount of cation leaching due to HCO_3^- , NO_3^- and SO_4^{2-} from (A)
 - C. Compare results of (B) to Σ cation removal in harvest
- Stage III. Integration: Relative effects of acid deposition, internal leaching processes, and harvesting on Ca^{2+} , K^+ , and Mg^{2+} removal from forests
- A. Estimate proportions of Ca^{2+} , K^+ , and Mg^{2+} leaching (individually) accounted for by HCO_3^- , NO_3^- and SO_4^{2-} in $Eq \cdot ha^{-1} \cdot yr^{-1}$ (individually)
 - B. Compare results of (A) to estimates of Ca, K, and Mg removal in harvesting in $Eq \cdot ha^{-1} \cdot yr^{-1}$
-

acid deposition and harvesting on soil cation nutrient status and
 (2) the validity of existing soil sensitivity classification schemes.

Stage I. Potential Base Cation Removal Due to Acid
 Deposition vs Whole-tree Harvesting

This simplest stage of analysis lends itself well to regional extrapolation, since regional patterns of deposition are being measured and basic forest biomass and nutrient content data are available for many forest types (see Marion 1979; Cole and Rapp 1981). (Recent advances in remote sensing will no doubt enhance the latter, also.) Thus, the potential base cation export due to acid deposition could be compared with estimated base cation removal by harvesting on a fairly large scale, if it is assumed that (1) accurate measurements of H^+ deposition are obtained and (2) all incoming H^+ causes equivalent exports of base cations. Both assumptions are questionable, as will be shown later, and natural leaching processes are ignored. However, the relative ease of obtaining data is a factor in regional assessments; thus, the utility of this crude approach is evaluated here, using the data sets on hand.

Table 3 gives bulk deposition of H^+ , SO_4^{2-} , and NO_3^- and the sum of $Ca^{2+} + Mg^{2+} + K^+$ (ΣBC) removed by WTH (annualized, or total removal divided by rotation age) at all sites. In assessing the effects of harvesting on base cation export, we consider only removals of Ca^{2+} , Mg^{2+} , and K^+ but not Na^+ . Sodium is not an essential nutrient, and its concentration in the tissues of temperate forest trees is normally very low relative to concentrations of the major base cation nutrients. That Na^+ can be ignored in assessments of base

Table 3. Bulk deposition and throughfall fluxes of H^+ , SO_4^{2-} and NO_3^- and annualized export of $Ca^{2+} + Mg^{2+} + K^+$ (ΣBC) in various forest site ($keq \cdot ha^{-1} \cdot yr^{-1}$)

Site	Vegetation	Potential ΣBC removal by atmospheric deposition			Σ cation removal by WTH ^a
		H^+	SO_4^{2-}	NO_3^-	
					<u>Removal in biomass</u>
Chesuncook, Maine	Spruce-fir	0.59	0.39	0.19	0.49
Clemson, S.C.	Loblolly pine	0.54	0.77	0.06	0.28
Oak Ridge, Tenn.	Loblolly pine	0.70	0.82	0.09	0.40
Pack Forest, Wash.	Douglas-fir	0.10	0.48	0.10	0.66
Coweeta, N.C.	Mixed deciduous	0.44	0.74	0.28	0.40
Oak Ridge, Tenn.	Mixed deciduous	0.60	0.80	0.16	1.22
Walker Branch, Tenn.	Mixed deciduous	0.70	0.88	0.14	1.63
Walker Branch, Tenn.	Mixed chestnut oak	0.70	0.88	0.14	1.43
Camp Branch, Tenn.	Mixed deciduous	0.17	1.25	0.31	0.40
Pack Forest, Wash.	Red alder	0.10	0.48	0.10	0.66
		<u>Throughfall</u>			
Chesuncook, Maine	Spruce-fir	0.32	0.53	0.08	
Clemson, S.C.	Loblolly pine	0.58	1.15	0.10	
Oak Ridge, Tenn.	Loblolly pine	0.51	1.29	0.26	
Pack Forest, Wash.	Douglas-fir	0.13	0.41	0.005	
Coweeta, N.C.	Mixed deciduous	0.12	1.92	0.13	
Oak Ridge, Tenn.	Mixed deciduous	0.32	1.14	0.03	
Walker Branch, Tenn.	Mixed chestnut oak	0.30	1.25	0.20	
Walker Branch, Tenn.	Mixed yellow-poplar	0.22	1.38	0.19	
Camp Branch, Tenn.	Mixed deciduous	0.06	1.21	0.29	
Pack Forest, Wash.	Red alder	0.11	0.43	0.005	

^aWTH = whole-tree harvesting.

cation removal via harvesting has been confirmed by foliage, wood, and root tissue analyses at ORNL. Sodium analyses on plant tissues remain to be done for the other sites.

It can be seen that, while variability among sites is great, H^+ deposition and ΣBC removal by WTH are generally of the same order of magnitude (i.e., one does not make the other trivial by comparison, therefore both must generally be considered in assessing base cation removal and soil acidification).

The absolute amount of H^+ input in bulk deposition does not correspond particularly well to a site's proximity to pollutant sources or to the amount of SO_4^{2-} deposition. The rates of H^+ deposition decrease from, Oak Ridge/Walker Branch, Tenn., > Chesuncook, Maine, > Clemson, S.C., > Coweeta, N.C., > Camp Branch, Tenn., > Pack Forest, Wash. The problems with measuring H^+ input from bulk deposition are well known, however, so it is useful to compare inputs of mineral acid anions in both bulk deposition and throughfall, as indices of the level of total deposition. In bulk deposition input of SO_4^{2-} , Camp Branch > Walker Branch/Oak Ridge \approx Coweeta \approx Clemson > Pack Forest > Chesuncook. The rather low SO_4^{2-} input at Chesuncook, Maine is surprising in view of the moderately high H^+ input at that site; apparently, much of the incoming H^+ is balanced by NO_3^- in this case.

Throughfall SO_4^{2-} can give a rough index of wet + dry S input in polluted regions, since several analyses of sulfur cycling show that foliar SO_4^{2-} leaching can seldom exceed 0.1 to $0.2 \text{ keq}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$ (Shriner and Henderson 1978; Meiwes and Khanna 1981; Stednick 1982; Johnson et al. 1982a; Johnson 1984; David et al. 1984). Using this as a rough guideline, it becomes apparent that in terms of total S deposition,

Coweeta > Oak Ridge/Walker Branch > Camp Branch > Clemson, S.C.
 > Chesuncook, Maine > Pack Forest, Wash. The Camp Branch and Pack Forest sites show no net foliar leaching of SO_4^{2-} [(throughfall SO_4^{2-}) - (precipitation SO_4^{2-})], possibly reflecting a generally lower level of dry sulfur deposition nutrition than at the other sites. Some foliar SO_4^{2-} uptake may be expected in N-rich sites, such as the N-fixing red alder site, however.

For NO_3^- deposition, the sites followed the order Camp Branch, Tenn., > Coweeta, N.C., > Chesuncook, Maine, > Oak Ridge/Walker Branch, Tenn., \approx Pack Forest, Wash. > Clemson, S.C. The Chesuncook, Pack Forest, Coweeta, and Oak Ridge mixed-oak sites show a net uptake of NO_3^- in the canopy, whereas the other sites show no change (Camp Branch site) or a net loss from the canopy (Oak Ridge, loblolly both Walker Branch sites and Clemson). The latter apparent net loss at the Oak Ridge loblolly and Walker Branch sites is thought to be due to HNO_3 vapor deposition to the forest canopy, probably followed by leaching from the canopy, in addition to an unknown amount of foliar NO_3^- uptake (Lindberg 1982). (Research on HNO_3 vapor deposition has not been done at other sites.)

The ΣBC removal by WTH appears to be generally greater in deciduous species than in coniferous ones (although there are uncertainties in defining rotation age in mixed deciduous stands). This is most likely due to the greater concentrations of cations in hardwood species, especially oaks and hickories (Marion 1979; Johnson et al. 1982c). Since acid deposition potentially has the same effect in both coniferous and deciduous forests, it would seem that the

combined effects of acid deposition and WTH would be more pronounced in deciduous forests (primarily due to greater Σ BC export by WTH). As is shown in Appendix A of the Oak Ridge site report and later in the main body of this report, however, a more detailed analysis of the ecosystem shows this to be an oversimplification.

Stage II. Actual Base Cation Removal Due to Acid Deposition,
Internal Leaching Processes, and Whole-Tree Harvesting

This second stage of analysis required measurements of leaching, which quite considerably limits its regional-scale use. However, it adds two critical components to the overall assessment: estimates of natural leaching rates (by internal production of carbonic, organic, or nitric acid) and estimates of the mobility of the atmospherically deposited SO_4^{2-} and NO_3^- anions in the ecosystem. It is well known that immobilization of SO_4^{2-} or NO_3^- can preclude the leaching of base cations by atmospherically deposited H_2SO_4 or HNO_3 (Johnson and Cole 1977, 1980; Lee and Weber 1982; Singh et al. 1980; Richter et al. 1983; Johnson et al. 1983).

For this analysis, we used the leaching fluxes in the control sites as estimates of base cation fluxes over a rotation. Some sites show increased (Chesuncook, Maine) and some sites show decreased (Red Alder - Pack Forest, Wash.) rates of leaching following harvesting (primarily associated with NO_3^- ; see Appendix B). We assume such changes to be temporary, however, if the site is allowed to revegetate. Thus, the control site fluxes are taken to be the best (though probably slightly low) estimates of leaching rates for the full rotation.

An overall view of the results of this analysis is given in Fig. 1. The left-hand bar indicates Σ BC input and the right-hand bar indicates Σ BC output in each case, with output being divided into leaching balanced by SO_4^{2-} , leaching balanced by HCO_3^- , leaching balanced by NO_3^- total leaching, and added effects of WTH. Sulfate dominates Σ BC leaching at the Oak Ridge, Walker Branch, and Camp Branch sites whereas HCO_3^- dominates leaching at all other sites. Nitrate is a major anion at the Pack Forest red alder site, no doubt because of excessive N fixation and nitrification, as was noted by Van Miegroet and Cole (1984) for another red alder site. Reasons for the abnormally high HCO_3^- leaching rates at the Pack Forest sites are as yet unknown but are being investigated at this time.

The predominance of SO_4^{2-} in leachates from the Oak Ridge Walker Branch and Camp Branch sites suggests that leaching rates in these eastern sites have been accelerated considerably, assuming preindustrial SO_4^{2-} leaching was low. Preindustrial SO_4^{2-} leaching is and will remain unknown, however, thus, the assumption that it was low cannot be tested. Nevertheless, it is safe to assume that increased atmospheric H_2SO_4 deposition will lead to increased base cation leaching rates if (1) HCO_3^- and organic anion leaching decrease (Krug and Frink 1983) and (2) SO_4^{2-} is mobile. As to the former, it is likely that anions will shift some as concentrations of H^+ (as well as all other cations) increase, but only in extremely acidic soils will H^+ (and therefore HCO_3^-) respond significantly to increases in ionic strength produced by increased SO_4^{2-} concentrations. In any event,

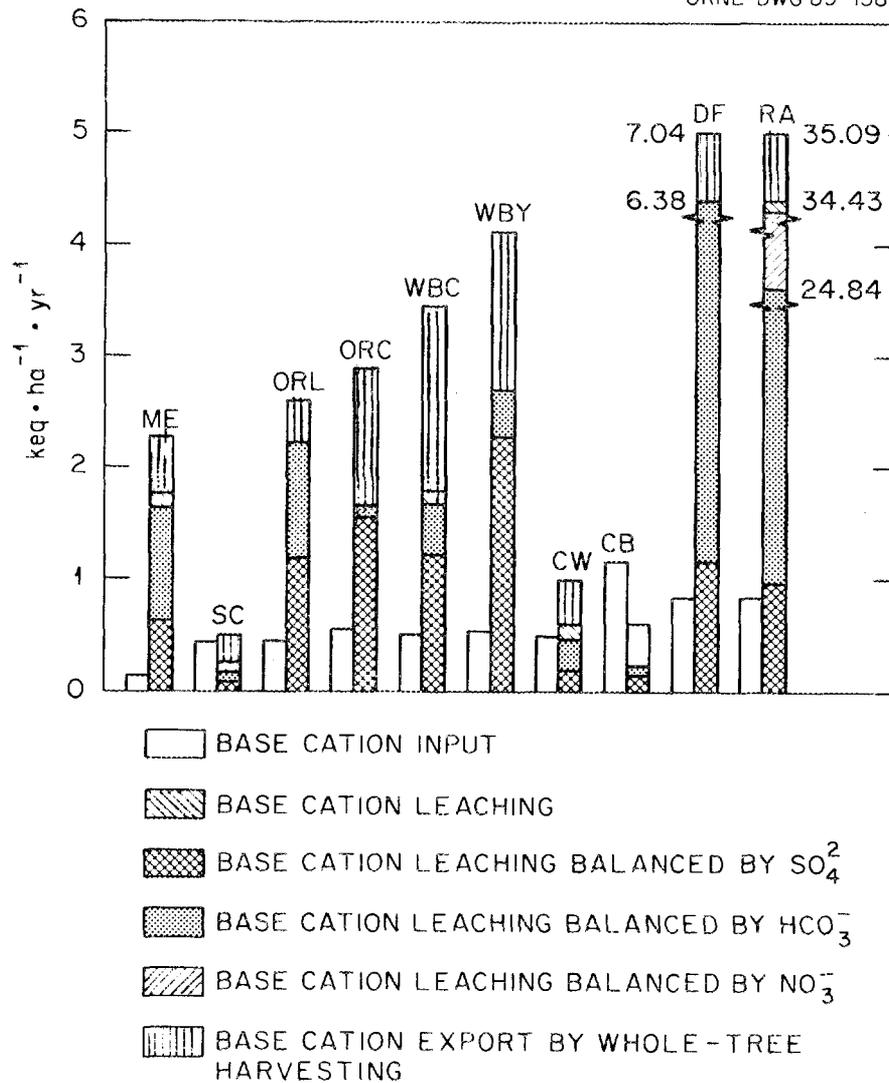


Fig. 1. Inputs of Σ Base cations (Σ BC) by bulk precipitation, leaching of Σ Base cations, SO_4^{2-} , HCO_3^- , and NO_3^- , and removal of Σ Base cations by whole-tree harvesting (WTH). Right-hand bars indicate additive effects of Σ Base cation leaching by SO_4^{2-} , HCO_3^- , NO_3^- , and other anions plus Σ Base cation removal by WTH. ME = Chesuncook, Maine; SC = Clemson, S.C., ORL = Loblolly pine, Oak Ridge, Tenn., ORC = Chestnut oak, Oak Ridge, Tenn., WBC = Chestnut oak, Walker Branch Watershed, Tenn., WBY = Yellow-poplar, Walker Branch Watershed, Tenn., CW = Coweeta, N.C., CB = Camp Branch, Tenn., DF = Douglas-fir, Pack Forest, Wash., RA = Red alder, Pack Forest, Wash.

it can be said that the increases in SO_4^{2-} concentrations in soil solution are very unlikely to be exactly matched by decreases in HCO_3^- and organic anion concentration, thus, overall leaching rates will increase in response to H_2SO_4 inputs. To the extent that a pH-induced anion shift has occurred, we have underestimated natural leaching rates and overestimated the degree to which acid deposition has accelerated these natural leaching rates. For the sites studied here, it is unlikely that a significant anion shift has occurred, and most H_2SO_4 input has caused base cation rather than H^+ and Al^{3+} concentrations to increase. This assumption is testable in field and laboratory manipulative studies and is worthy of further study.

It appears that SO_4^{2-} is immobilized in the Clemson, Coweeta, and Camp Branch sites (input > output); thus, the potential for SO_4^{2-} -mediated leaching has yet to be realized (Table 4). Since estimates of soil water flux have a major effect on estimates of SO_4^{2-} and other ionic fluxes, errors in soil water flux can significantly affect all budgets. Some sites used water flux estimates based upon models (Pack Forest, Clemson, Oak Ridge), and others used estimates based upon ancillary watershed-level studies (Chesuncook, Walker Branch, Coweeta, Camp Branch; see Appendix A). Some investigators reported stream water export (Chesuncook, Camp Branch) and Clemson reported surface runoff. Streamflow and runoff data show net SO_4^{2-} retention at Clemson, Camp Branch, Coweeta, and Walker Branch but no SO_4^{2-} retention at Chesuncook, Maine (Table 4).

Table 4. Weighted average annual SO_4^{2-} concentrations ($\text{meq} \cdot \text{L}^{-1}$) and SO_4^{2-} fluxes ($\text{keq} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$) in solutions from various forest ecosystems

Site	Vegetation	Bulk precipitation		Throughfall		Soil solution		Stream	
		Conc.	Flux	Conc.	Flux	Conc.	Flux	conc.	Flux
Chesuncook, Maine	Spruce-fir	0.038	0.39	0.073	0.53	0.171	0.61	0.137	0.47
Clemson, S.C.	Loblolly pine	0.057	0.77	0.098	0.83	0.020	0.05	0.100	0.21
Oak Ridge, Tenn.	Loblolly pine	0.061	0.82	0.112	1.29	0.259	1.21	— ^a	—
Pack Forest, Wash.	Douglas-fir	0.043	0.48	0.075	0.41	0.141	1.15	—	—
Coweeta, N.C.	Mixed deciduous	0.038	0.74	0.192	1.92	0.019	0.20	—	—
Oak Ridge, Tenn.	Mixed deciduous	0.060	0.80	0.092	1.14	0.248	1.54	—	—
Walker Branch, Tenn.	Mixed chestnut oak	0.069	0.88	0.114	1.25	0.166	0.94	—	0.56
Walker Branch, Tenn.	Mixed yellow-poplar	0.069	0.88	0.119	1.38	0.379	2.16	—	0.56
Camp Branch, Tenn.	Mixed deciduous	0.108	1.25	0.118	1.21	0.134	0.15	0.084	0.64
Pack Forest, Wash.	Red alder	0.043	0.48	0.057	0.43	0.119	1.15	—	—

^aThe dash indicates no data.

A further check on site SO_4^{2-} retention was made by comparing SO_4^{2-} concentrations in precipitation with concentrations in soil solution. If soil solution SO_4^{2-} concentration is less than or equal to that in precipitation or throughfall, the site will show a net accumulation of SO_4^{2-} (because soil water flux must be less than precipitation or throughfall flux). By this measure, it is clear that Clemson, Coweeta, and Camp Branch are accumulating SO_4^{2-} , just as the ecosystem budgets indicate (Table 4).

It is somewhat surprising that none of the Oak Ridge or Walker Branch sites showed net SO_4^{2-} accumulation, in view of previous research on both plot and watershed levels (Shriner and Henderson 1978; Johnson et al. 1982a). [The yellow-poplar stand on Walker Branch is known not to accumulate SO_4^{2-} , because of its low soil SO_4^{2-} adsorption capacity (Richter et al. 1983)]. Recent comparisons suggest that although the Fullerton soils (which occupy all but the Walker Branch - yellow-poplar site) contain adsorbed sulfate and the Walker Branch Watershed as a whole retains SO_4^{2-} (Shriner and Henderson 1978; Johnson and Henderson 1979), these soils are less able to adsorb additional SO_4^{2-} than many other southeastern soils [e.g., Porters and Saluda series at Coweeta; Johnson and Todd (1983)].

It should also be noted that some of the Oak Ridge and Walker Branch sites may actually be adsorbing SO_4^{2-} , since bulk deposition underestimates S deposition (Lindberg 1982). Similarly, unmeasured inputs may account for part or all of the apparent net SO_4^{2-} export from the Chesuncook, Maine, site and the Pack Forest sites. However, the very large net SO_4^{2-} exports from the latter suggest an internal source, perhaps an S-bearing mineral.

The lag times involved for the SO_4^{2-} -accumulating sites to reach steady state are unknown but could be addressed through soil SO_4^{2-} adsorption studies and modeling. Johnson and Todd (1983) tested several of these soils for SO_4^{2-} content and adsorption properties (Chesuncook, Coweeta, Camp Branch, Walker Branch) and overall patterns generally matching SO_4^{2-} budgets but did not measure SO_4^{2-} adsorption isotherms for these soils. Such isotherms would be necessary to model breakthrough times (i.e., time needed to reach steady state). This is a matter worthy of future research.

The Pack Forest sites are unique in their extremely high internal production of HCO_3^- (Fig. 1)). The red alder site shows a large internal production of NO_3^- as well, similar to that documented by Van Miegroet and Cole (1984) for the Thompson site. (All other sites in this study accumulate NO_3^- .) Even in the red alder site at Pack Forest, however, internal HCO_3^- production clearly dominates. For this reason, and not because of particularly low rate of SO_4^{2-} leaching, SO_4^{2-} plays a relatively minor role in base cation leaching at these Washington sites.

All sites except Clemson and Camp Branch show net exports of ΣBC by leaching alone (Fig. 1). The Clemson and Camp Branch sites show a net gain due to low soil leaching rates. Camp Branch also shows very high ΣBC inputs. With the exceptions of the Clemson and Camp Branch sites, total ΣBC leaching exceeds ΣBC removal by WTH. Sulfate-mediated leaching alone exceeds ΣBC removal by WTH in the Maine, Oak Ridge loblolly pine, and Walker Branch yellow-poplar sites (Fig. 1). With the combined effects of leaching and WTH, all sites except Camp Branch show a net ΣBC loss.

Data for soil exchangeable cations and total base cations (in this case, $\text{Ca}^{2+} + \text{Mg}^{2+} + \text{K}^+$ only) were available for some sites, allowing comparisons of ΣBC loss rates with soil pool sizes. For the sites for which we have data, annual ΣBC losses by leaching equal only 0.3% (Coweeta) to 2.0% (Oak Ridge, Walker Branch) of the exchangeable cation capital and 0.003 to 0.1% of the total soil cation capital (Camp Branch and Clemson show a net gain.) (See Table 5). With WTH, annual ΣBC losses equal from 0.06% (Clemson) to 7.0% (Oak Ridge, mixed deciduous) of the exchangeable cation capital and 0.01 to 0.2% of the total soil cation capital. None of these rates of loss appears to threaten soil-exchangeable (or total) ΣBC supplies, even with WTH, in view of the probability of replenishment of exchangeable cations by weathering and deep rooting. Unfortunately, soil ΣBC capital values are unavailable for Pack Forest, thus hindering comparisons, with the very high ΣBC leaching rates there.

Stage III. Integration: Relative Effects of Acid Deposition,
Internal Leaching Processes, and Harvesting on
 Ca^{2+} , K^+ , and Mg^{2+} Removal from Forests

Both biomass removal and leaching can cause the net export of base cations from the ecosystem. However, there are fundamental differences in the basic processes involved (i.e., plant uptake vs cation exchange) that lead to very different effects of harvesting vs those of leaching (whether due to acid deposition or natural, internal processes) on the export of individual cations.

Since each cation nutrient has a unique set of functions in plants, (i.e., Ca^{2+} in cell wall formation, Mg^{2+} in chlorophyll, K^+ in regulating stomatal opening) plants require each of these

Table 5. Net exports of Σ base cations, Ca^{2+} , K^+ , and Mg^{2+} ($\text{keq ha}^{-1} \text{ yr}^{-1}$) compared with soil-exchangeable and total contents (keq ha^{-1}).

Site vegetation	Chesuncook, Maine Spruce-fir	Clemson, S.C. Loblolly pine	Oak Ridge, Tenn. Loblolly pine	Oak Ridge, Tenn. Chestnut oak	Walker Branch, Tenn.		Coweeta, N.C. Mixed deciduous	Camp Branch, Tenn. Mixed deciduous
					Chestnut oak	Yellow-poplar		
Σ Base Cations								
<u>Soil capital</u>								
Total	3800	--	1370	1450	3000	1700	5540	--
Exchangeable	85	71	83	35	84	113	68	95
<u>Net export with:</u>								
Leaching ^a	-1.61	+0.23	-1.21	-1.11	-1.25	-2.22	-0.18	+0.99
WTH ^b	-2.10	-0.04	-1.61	-2.33	-2.88	-3.65	-0.58	-0.59
Ca^{2+}								
<u>Soil capital</u>								
Total	540	756	255	245	200	200	125	--
Exchangeable	67	46	64	18	50	80	47	40
<u>Net export with:</u>								
Leaching ^a	-0.94	+0.07	-0.76	-0.33	+0.07	-1.14	+0.13	+0.46
WTH ^b	-1.29	-0.14	-0.92	-1.42	-1.33	-2.28	-0.17	+0.13
K^+								
<u>Soil capital</u>								
Total	260	392	596	593	500	500	3170	--
Exchangeable	2.9	4.1	5.7	5.4	10	9	13.1	15
<u>Net export with:</u>								
Leaching ^a	-0.04	+0.04	-0.10	-0.12	-0.01	-0.05	0	+0.07
WTH ^b	-0.12	-0.08	-0.19	-0.18	-0.12	-0.17	-0.06	+0.03
Mg^{2+}								
<u>Soil capital</u>								
Total	3000	--	520	610	1040	560	2240	--
Exchangeable	15	21	13	12	27	17	8	40
<u>Net export with:</u>								
Leaching ^a	-0.52	+0.01	-0.26	-0.54	-0.20	-0.39	-0.16	+0.05
WTH ^b	-0.58	-0.13	-0.37	-0.61	-0.31	-0.56	-0.19	+0.01

^a(Bulk precipitation) - (soil leaching).

^b(Bulk precipitation) - (soil leaching) - (removal by WTH).

nutrients and substitutions cannot be made. On the other hand, H^+ can exchange for any cation sufficiently abundant on exchange sites to allow cation exchange to occur.

The inability of plants to substitute among cations, the diminished leaching of cations with diminishing exchangeable supplies, and the biological conservation of limiting nutrients make it apparent that harvesting will have a greater impact on the export of growth-limiting cations than will leaching, either by acid deposition or natural processes.

Considering each of the three major nutrient cations individually, some interesting patterns emerge that differ substantially from those in ΣBC export. Without harvesting, the Clemson, Coweeta, and Camp Branch sites show a net Ca^{2+} gain from atmospheric deposition and the Walker Branch Chestnut oak site is approximately in balance (Fig. 2). As was stated earlier, the Coweeta and Walker Branch sites showed a net ΣBC export by leaching, whereas Clemson and Camp Branch showed a net ΣBC gain (Fig. 1). Only the latter two sites show net gains of Mg^{2+} and K^+ , and Coweeta is in balance for K^+ (Fig. 2). Calcium removal by WTH varies considerably, being highest in the eastern deciduous forests and lowest in the loblolly pine forests (Fig. 2). At the Oak Ridge site, there are interesting contrasts in Ca^{2+} , K^+ , and Mg^{2+} removals by leaching and WTH; these are described in detail in Appendix B. Briefly, it appears that the much greater Ca^{2+} accumulation by deciduous trees than by loblolly pine has caused differences in soil-exchangeable Ca^{2+} , which in turn affect Ca^{2+} leaching rates, both of which are lower in the deciduous

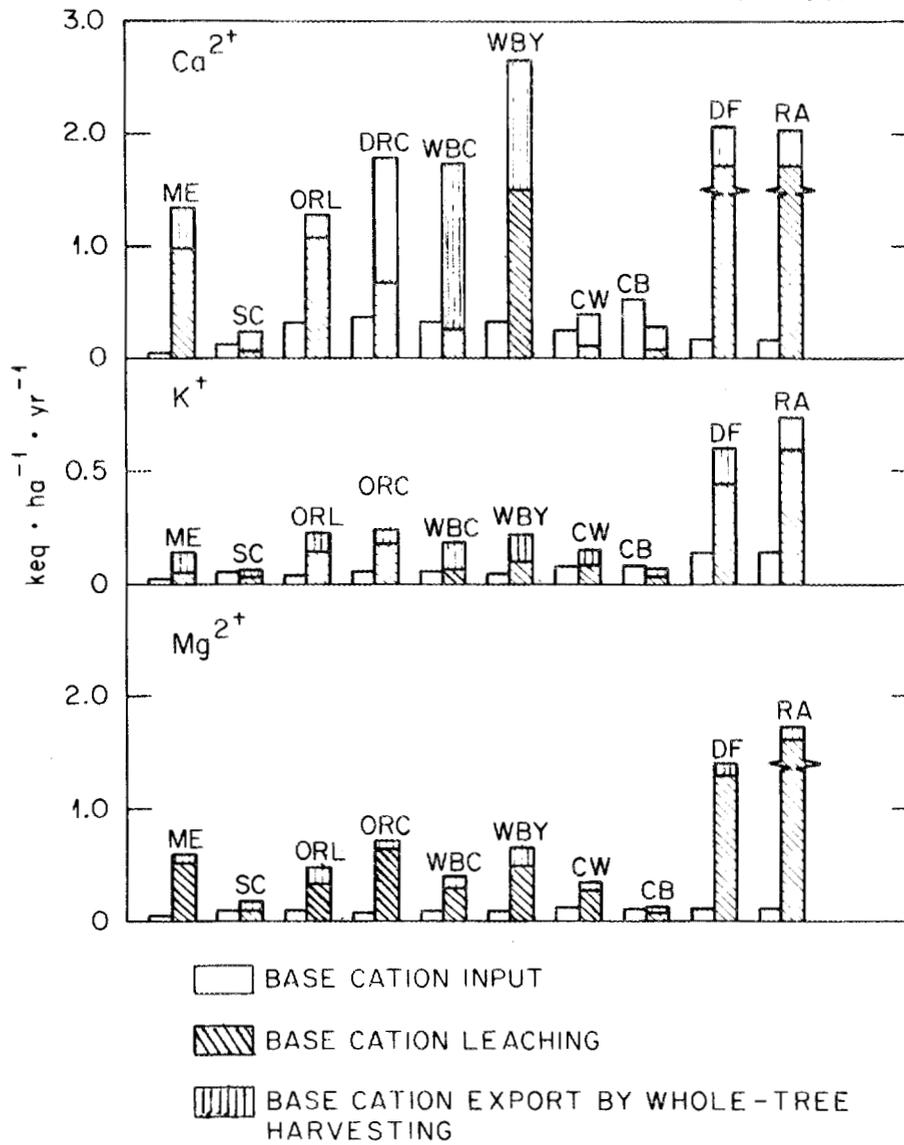


Fig. 2. Inputs of Ca^{2+} , K^+ , and Mg^{2+} by bulk precipitation and exports by leaching and whole-tree harvesting (additive). See Fig. 1 for legend.

site (Fig. 2). Since both sites are subject to basically the same leaching pressure from SO_4^{2-} , ΣBC leaching rates are similar (Fig. 1); and thus the rates of Mg^{2+} , K^+ , and Na^+ leaching in the deciduous site are greater than in the loblolly pine site (Fig. 2, Appendix B).

This contrast in leaching rates of individual base cations seems to be a direct consequence of differences in soil-exchangeable Ca^{2+} produced by differences in vegetation Ca^{2+} accumulation (and thus removal of Ca^{2+} by WTH). WTH may pose a problem for Ca^{2+} removal in the deciduous site (Johnson et al. 1982c) but not in the loblolly pine site. This interesting contrast supports the hypothesis that WTH will more strongly affect the budget of potentially limiting cations than will leaching.

Calcium leaching does not appear to pose a threat to soil Ca^{2+} supplies in those sites for which the latter data are available; net annual losses (for those sites experiencing a net loss) equal only 0.02 to 2.0% of exchangeable Ca^{2+} and >0.01 to 0.2% of total soil Ca^{2+} (Table 5). Leaching that occurs in conjunction with harvesting accounts for 0.4 to 8.4% of soil-exchangeable Ca^{2+} (the higher amount occurring in the Oak Ridge deciduous forest) and 0.1 to 0.6% of total soil Ca^{2+} (Table 5).

Net K^+ leaching constitutes a fairly small (0.8 to 1.3%) proportion of soil exchangeable K^+ in all sites showing a net K^+ leaching loss, with the exception of the Oak Ridge deciduous forest, where net K^+ leaching equals 5.4% of the soil-exchangeable K^+ (Table 5). However, soil total K^+ is large at this site and even

modest rates of weathering could offset net K^+ leaching losses (Table 5). The relative importance of WTH to K^+ budgets varies considerably among sites. All sites except Camp Branch show a net K^+ loss with WTH, and this loss equals 0.5 to 6.5% of exchangeable K^+ (the highest occurring in the Oak Ridge deciduous forest) and only 0.002 to 0.06% of total soil K^+ (Table 5).

With the exception of the Clemson and Camp Branch sites (which show net gains of Mg^{2+}), all sites show a greater Mg^{2+} loss from leaching than from WTH [sometimes by a considerable amount (e.g., Pack Forest, Oak Ridge)] (Fig. 2; Table 5). This reflects lower tree Mg^{2+} demand relative to Ca^{2+} . Net Mg^{2+} leaching losses (where they occur) generally equal greater proportions of soil-exchangeable Mg^{2+} (0.9 to 3.5%) than was the case for Ca^{2+} or K^+ . (K^+ leaching in the Oak Ridge site being an exception) (Table 5). Total soil Mg^{2+} pools are large, however; thus, no immediate problems in Mg^{2+} supplies are foreseen. WTH adds little to Mg^{2+} loss by leaching and generally poses little threat to soil Mg^{2+} supplies.

It is not possible at this time to assess the degree to which leaching rates of Ca^{2+} , Mg^{2+} , and K^+ are affected individually by acid deposition. It can be stated from theoretical selectivity relationships, however, that Ca^{2+} and Mg^{2+} (M^{2+}) leaching have been affected more than K^+ . The change in M^{2+} activity is proportional to the square of the change in K^+ activity (Reuss 1983). Thus, for a doubling of the M^{2+} leaching rate, the K^+ leaching rate would increase by a factor of 1.41 ($\sqrt{2}$). A modeling

approach (e.g., Reuss 1983) to the issue of increases in individual cation leaching rates would be both useful and interesting but is at present beyond the scope of this project.

IV. IMPLICATIONS FOR SOIL SENSITIVITY CLASSIFICATION SCHEMES

Soil sensitivity criteria have employed basically three major criteria for terrestrial effects: cation exchange capacity (CEC), base saturation (%BS), and sulfate adsorption capacity, the last relying on the use of soil Fe + Al oxide and organic matter content as surrogates (Wiklander 1974; McFee 1980; Klopatek et al. 1980; Johnson 1980, 1981). Wiklander (1974) argued that soils with low CEC and moderate %BS are most sensitive to change; this concept would be valid for our budgeting approach for Σ BC. That is, soils low in CEC will generally have low Σ BC content and thus small reserves relative to a given rate of Σ BC loss. Wiklander (1974) correctly argued that soils with very low %BS will conserve base cations and thus will not change as rapidly as soils with moderate %BS. Wiklander (1974) did not account for Al^{3+} mobilization in soils with very low %BS (e.g., Ulrich 1980; Seip 1980) in his assessment of soil sensitivity to acidification, however. Clearly, it is important to specify the type of sensitivity (i.e., to %BS change, Al^{3+} mobilization, etc.) before proposing criteria for classifying sensitivity.

None of the sites investigated in this study showed either significant Al^{3+} concentrations in solution or the potential for significant changes in soil base cation content due to leaching. Unfortunately, complete soils data are not available for all sites and

methods were not comparable (e.g., NH_4Cl vs NH_4OAc extractions for CEC), so that a complete analysis of appropriate sensitivity criteria is not possible with the data at hand. Analyses of CEC and %BS on all soils could be done at one laboratory, using standard methods, if further information on sensitivity criteria are desired. However, it is important to recall that no site was considered to be in serious danger of experiencing soil changes due to leaching (i.e., all sites are relatively "insensitive"), especially when the potential (but unknown) replenishment by weathering is considered.

Johnson (1980) proposed adding soil sulfate adsorption to soil sensitivity criteria and Johnson and Todd (1983) suggested that this could be related to soil Fe + Al oxide and organic matter content, which in turn may broadly relate to soil order or suborder. Specifically, it is suggested that Ultisols will generally retain more SO_4^{2-} than Spodosols (Johnson and Todd 1983). While it is clear that SO_4^{2-} immobilization greatly inhibited leaching in the Ultisols at Coweeta, Clemson, and Camp Branch, little or no apparent SO_4^{2-} immobilization occurs in the Ultisols at the Oak Ridge sites. More research is needed (once again, standard extractions and tests in one lab) to sort out the reasons for differences in SO_4^{2-} retention among these Ultisols.

Finally, these studies show the need to assess soil sensitivity on the basis of individual cations. These results show that a site losing ΣBC at a high rate may not necessarily be losing each cation, and furthermore that potentially limiting cations will be conserved. The same cation exchange principles that dictate ΣBC conservation and

Al^{3+} leaching in very acid (low %BS) soils dictate that a given cation in very short supply will be conserved and less scarce cations will be lost. There are, of course, complexities within the above generalization in terms of susceptibility of monovalent vs divalent cations to leaching and the effects of changes in the percentage of Ca^{2+} , K^+ , or Mg^{2+} saturation on exchange sites (the latter caused by uptake and leaching). From a nutritional standpoint (i.e., from the standpoint of Ca^{2+} , K^+ , and Mg^{2+} losses), it is clear that sites low in a particular cation are least susceptible to leaching losses of that cation (although one could argue that the site is "sensitive" to these losses since the soil reserves are low). It is also clear that Ca^{2+} removal by WTH is a greater threat to low soil supplies than leaching is in the stands studied here. Eastern deciduous stands seem particularly susceptible to large Ca^{2+} loss by WTH.

V. SUMMARY AND CONCLUSIONS

The effects of acid deposition, harvesting, and natural leaching on base cation export was investigated in forest sites at Chesuncook, Maine (spruce-fir), Clemson, S.C. (loblolly pine), Oak Ridge and Walker Branch Watershed, Tenn. (mixed deciduous, loblolly pine), Camp Branch, Tenn. (mixed deciduous), Coweeta, N.C. (mixed deciduous) and Pack Forest, Wash. (red alder and Douglas-fir). Sulfate was the major anion in soil solutions from the Tennessee sites, suggesting that leaching rates had been significantly accelerated by acid deposition. Bicarbonate dominated leaching in the Maine, North Carolina, South Carolina, and Washington sites. In the Washington sites, SO_4^{2-} was

of minor importance (although comparable in magnitude to that in the eastern sites) compared to the extremely high internal generation of HCO_3^- . In addition, NO_3^- was of major importance in the red alder site. At three of the southeastern sites (Clemson, S.C., Coweeta, N.C., and Camp Branch, Tenn.), most incoming SO_4^{2-} was immobilized in the soil (presumably by adsorption and incorporation into organic soil sulfur), considerably reducing the potential for accelerated leaching by H_2SO_4 deposition. For this reason, regional assessments of acid deposition vs WTH effects on base cation (ΣBC) removal based upon atmospheric deposition and stand inventory data only (Stage I of analysis), may seriously overestimate acid deposition effects in southeastern forests. The Oak Ridge and Walker Branch sites showed little or no SO_4^{2-} retention, and reasons for differences in SO_4^{2-} mobility among these sites (especially among the southeastern sites, which shared Ultisols) merits further study in laboratory soil column experiments.

Leaching, even from soils accelerated by acid deposition, does not appear to pose a threat to soil ΣBC supplies in sites for which soil data are available. (This is basically because soil pools are large relative to leaching rates). Indeed, some sites (e.g., Clemson and Camp Branch) appear to accumulate ΣBC from atmospheric deposition, in part because of a high degree of SO_4^{2-} immobilization.

WTH causes the net ΣBC budgets of all but the Camp Branch site to become negative (the latter being subject to unusually high atmospheric ΣBC inputs). WTH has the greatest effect on ΣBC export in eastern deciduous sites.

The effects of leaching and harvesting on Ca^{2+} , Mg^{2+} , and K^+ individually are quite different from those on ΣBC . Calcium removal by WTH is very high in some eastern deciduous forests, which accumulate Ca in biomass. Studies at Oak Ridge in loblolly pine and deciduous forests show less Ca leaching but more Ca export in biomass in the deciduous forest. This suggests that Ca accumulation in biomass may reduce soil Ca^{2+} , and thus Ca^{2+} leaching rates, while increasing Ca^{2+} removal by WTH. Potassium and Mg^{2+} , which are accumulated to a much lesser extent by these deciduous forest trees, show a higher leaching rate in the deciduous site than in the loblolly pine site. Overall, these results support the hypothesis that scarce or potentially limiting cations are less susceptible to export by leaching than by WTH, whereas the reverse is true for more abundant, nonlimiting cations.

The results of this study show that current soil sensitivity criteria for soil acidification -- CEC, %BS, SO_4^{2-} adsorption -- can be used to assess ΣBC export to a limited extent (with the realization that soil weathering is an important but unaccounted for factor). However, sensitivity schemes to determine nutritional effects must be oriented toward individual cations (Ca^{2+} , K^+ , and Mg^{2+} separately) and must consider both biological and chemical mechanisms which act to conserve those cations when in short supply.

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APPENDIX A
Publications

APPENDIX A
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- Federer, C. A. and J. W. Hornbeck. The buffer capacity of soils in New England. *Water, Air, and Soil Pollut.*, vol. 25.
- Hornbeck, J. W., and C. A. Federer. Acid rain and the buffer capacity of forest soils. IN Quebec Conf. on Acid Rain and Forest Resources. Environment Canada, Ottawa.
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- Reuss, J. O. and D. W. Johnson. 1985. Effects of soil processes on the acidification of water by acid deposition. *J. Environ. Qual.* 14:26-31.

Submitted:

- Hornbeck, J. W. and C. A. Federer. A method for indicating susceptibility of forest soils to acid precipitation. *J. of Forestry* (submitted).

In Preparation:

Hornbeck, J. W., C. T. Smith, C. W. Martin, C. A. Federer,

R. S. Pierce. Combined effects of whole-tree harvesting and acid deposition in a spruce-fir forest. Proposed outlet is J. of Environmental Quality.

Johnson, D. W., D. W. Cole, J. W. Hornbeck, J. M. Kelly, W. T. Swank, and D. Van Lear. Combined effects of acid deposition, natural acid production, and whole-free harvesting on base cation budgets in a variety of forest ecosystems. Forest Ecol. Manage. (in prep.).

Abstracts:

Smith, C. T. and J. W. Hornbeck. 1983. Changes in soil solution chemistry after forest harvest depend on soil drainage class. Bull. Ecol. Soc. Amer. 64:(2):65.

Hornbeck, J. W. and C. A. Federer. 1984. Acid rain and the buffer capacity of forest soils in New England. Bull. Ecol. Soc. Amer. 65:(2):271-72.

Hornbeck, J. W., and R. S. Pierce. 1985. Comparative impacts of forest harvest and acid precipitation. Bull. Ecol. Soc. Amer. (in press).

Dissertation:

Smith, Charles Tattersall. 1984. Nutrient removals and soil leaching from a whole-tree harvest of red spruce-balsam fir stand in central Maine. Univ. of Maine at Orono. PhD thesis. 214 p.

APPENDIX B
Individual Site Reports

A COMPARATIVE EVALUATION OF THE EFFECTS OF ACID PRECIPITATION,
NATURAL ACID PRODUCTION, AND HARVESTING ON
CATION REMOVAL FROM FORESTS

CAMP BRANCH SITE

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INTRODUCTION

Data on precipitation, throughfall, soil solution, and stream water chemistry from the Camp Branch study site are presented in this report. Data reported span the period from May 1983 through April of 1984 and thus represent the most recent 12 months of observation. The main focus of this report will be a summarization of these most recent data.

STUDY SITE

The Camp Branch Experimental Watershed is located on the Cumberland Plateau within the boundaries of Fall Creek Falls State Park in Bledsoe County, Tennessee (35°38' N; 85°18' W). The watershed covers an area of 94 ha and ranges in elevation from 598 m at its highest point to 518 m at the weir. The climate of the Cumberland Plateau is temperate and continental. The winters are moderate, with short cold periods, and the summers are mild to hot. Precipitation is well distributed over the year with an average annual input of 144 cm. The soils on the study site are derived primarily from weathered sandstone and siltstone and represent two orders, Ultisols and Inceptisols. Average depth for most profiles is less than 120 cm. The dominant soils are typically well drained, highly leached, acidic (pH 4.6-4.8), and relatively infertile (CEC 6.8-10.7). The study site is vegetated with a second growth forest in which various species of oak combine to provide approximately 70 percent of the basal area. Quercus coccinea, Q. stellata, Q. alba, and Q. velutina are the dominants. Additional information on stand characteristics and soils can be found in Remseur and Kelly (1981), Kelly (1979), and Kelly (1984).

METHODS

Bulk precipitation samples for chemical analysis were collected in a cleared area in the forest. Two replicate samples were collected on a weekly basis and composited for the month for chemical analysis. Rainfall amount is determined at three locations in the watershed and averaged to provide an estimate of total input for the watershed. Total monthly estimates of rainfall amount are then combined with monthly concentration values to obtain precipitation flux estimates. Throughfall samples were collected on a weekly basis from ten locations in the study area and bulked for the month for chemical analysis as was precipitation. A typical-funnel bottle arrangement was used (Kelly 1979) with the amount of throughfall being based on actual volume measurements and appropriate conversions to an area basis. Throughfall volumes and monthly analytical values were used to calculate flux estimates. Soil solution chemistry was sampled using porous plate lysimeters located at three depths within the soil profile. Three plates were located at each of three levels, bottom of the A horizon, mid B, and near the bottom of the profile. A constant tension was applied to the plates through the use of an automated vacuum system. Soil solution samples were collected on a weekly basis, moisture conditions permitting, and also composited for analytical purposes on a monthly basis. Estimates of water flux to each depth were derived using regression techniques and throughfall input. Actual measured volumes from the plates at the bottom of the profile consistently exceeded precipitation input, indicating significant lateral movement of water to the plate through this horizon. Water flux estimates were

again combined with monthly analytical values to calculate elemental flux. Streamflow volume was calculated from continuous measurements of stage height. Stream water was sampled in proportion to flow with samples being collected and analyzed chemically on a weekly basis. Weekly flow and concentration values were combined to produce monthly estimates of flux from the study site. All precipitation, throughfall, soil solution, and stream water concentrations reported in Table 1 are volume weighed.

RESULTS

The amount of precipitation occurring during the study period if projected to an annual basis is 28 cm or 19 percent below the long term annual mean. This fact could have a significant impact on both concentration and flux estimates presented in Tables 1 and 2. Precipitation volume was reduced by 12 percent in the conversion to throughfall while soil solution volume at the bottom of the soil profile represented approximately 11 percent of the incoming throughfall volume. This value is thought to be a reasonable estimate based on the dryer than normal conditions observed during the study period. Stream water output represents 64 percent of precipitation input. The flashy nature of the stream should be borne in mind, along with the observation that a significant amount of the water loss from this system occurs as a consequence of lateral flow in the upper soil horizons, which is consistent with the relatively low level of soil water flux below the B2t horizon.

Table 1. Volume weighted mean concentrations of selected constituents in precipitation, throughfall, soil, and stream water at the Camp Branch study site based on the period May 1983 through April 1984

COMPONENT	Total Volume (cm)	meq • L ⁻¹														Conduc- tivity
		H	Ca	Mg	K	Na	NH ₄	Al	Σ cations	HCO ₃	SO ₄	NO ₃	Cl	PO ₄	Σ Anions	
Precipitation	116	0.015	0.042	0.009	0.006	0.044	0.036	0.011	0.164	0.018	0.108	0.027	0.018	0.006	0.176	19.2
Throughfall	102	0.006	0.078	0.022	0.056	0.056	0.013	0.012	0.242	0.050	0.118	0.028	0.020	0.007	0.223	28.1
SOIL SOLUTION																
A	70	0.007	0.055	0.039	0.026	0.010	0.002	0.027	0.165	0.030	0.128	0.001	0.019	0.003	0.181	21.3
A/B	50	0.007	0.061	0.046	0.009	0.014	0.001	0.013	0.150	0.022	0.146	0.001	0.020	0.003	0.189	22.3
B	11	0.002	0.028	0.058	0.003	0.076	0.001	0.011	0.180	0.074	0.134	0.001	0.020	0.003	0.229	22.2
Stream Water	75	0.006	0.007	0.020	0.010	0.016	0.005	0.011	0.075	0.021	0.084	0.003	0.017	0.005	0.130	12.9

Table 2. Annual flux of selected constituents in precipitation, throughfall, soil solution, and stream water at the Camp Branch study site based on the period May 1983 through April 1984

COMPONENT	eq • ha ⁻¹											
	H	Ca	Mg	K	Na	NH ₄	Al	HCO ₃	SO ₄	NO ₃	Cl	PO ₄
Precipitation	168	489	107	68	511	419	128	207	1250	306	206	64
Throughfall	60	796	224	567	575	128	121	508	1205	285	206	74
SOIL SOLUTION												
A	49	387	273	180	68	17	187	209	893	10	133	20
A/B	37	305	233	43	72	4	63	110	732	5	102	15
B	2	32	66	4	87	1	13	85	152	1	22	3
Stream Water	48	51	154	74	117	36	82	162	637	23	130	34

There continues to be a definite bias in the cation/anion balance for streamwater toward a predominance of anions, while no strong bias is evident in the precipitation or throughfall samples. Soil solution, especially in the B-horizon samples, exhibits a bias in charge balance similar to that observed for streamwater. Although various possible explanations for this difference have been explored no reason can be offered at this time. Hydrogen ion input by precipitation and throughfall appears to be effectively reduced by the soil with 29 percent of precipitation hydrogen ion input leaving the system in stream water (Table 2). It is also interesting to note that while there is a substantial retention of calcium input (89%), there is a net loss of magnesium by a factor of 1.4. Comparing throughfall NH_4 values with precipitation values suggests direct foliar absorption of approximately 70 percent of NH_4 precipitation input. An additional 21 percent is absorbed by the soil resulting in NH_4 losses equivalent to 9 percent of input (Table 2). Nitrate appears to be even more tightly conserved with only 8 percent of precipitation input leaving the system via streamflow. There does not appear to be a significant canopy-precipitation interaction with respect to absorption of NO_3 . From these data it would not appear that significant amounts of excess nitrogen occur in this system. In fact only in the case of Mg and K do exports in streamflow exceed precipitation inputs.

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A COMPARATIVE EVALUATION OF THE EFFECTS OF ACID PRECIPITATION,
NATURAL ACID PRODUCTION, AND HARVESTING ON
CATION REMOVAL FROM FORESTS

COWEETA SITE

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INTRODUCTION

This report summarizes the results of a study to evaluate the impacts of acid precipitation on forest soils. The experimental site is a 0.7 ha catchment at Coweeta Hydrologic Laboratory and the study is part of a broader effort to assess the effects of whole-tree harvesting on soil nutrients. Study objectives, experimental sites, sampling methods, and data analysis have previously been given in detail in previous documents.

METHODS AND RESULTS

Bulk precipitation samples are collected weekly at Rain Gage 5; chemical analyses are performed on each sample and average annual values are calculated by weighting concentrations by volumes of precipitation. Throughfall quantities and chemistry were taken from previous studies at Coweeta and presented in the first annual progress report. For purposes of this project, these data remain unchanged and are not repeated here. Soil solution samples are collected weekly at a 100-cm depth with 10 porous cup lysimeters located over the experimental area. Mean chemistry values are based on all samples collected during the June 1983-May 1984 period. The water flux at 100 cm was derived from long-term hydrologic records at Coweeta and from experimental measures of streamflow responses to treatment.

Annual water fluxes and concentrations and fluxes of cations-anions are summarized in Table 1 and a comparison of values for 3- and 4-year-old hardwood coppice regrowth are given in Table 2. In both years, substantial depletions of both total cations and total

Table 1. Annual (June 1983–May 1984) water and ion data for Coweeta Watershed 4B for a 4-year-old hardwood coppice stand

Sampling location	H ₂ O (cm)	H	Ca	Mg	K	Na	NH ₄	E+	HCO ₃	SO ₄	NO ₃	Cl	PO ₄	Σ-
Concentrations in $\mu\text{eq l}^{-1}$ and annual fluxes ($\text{eq ha}^{-1} \text{ year}^{-1}$)														
Precipitation	221.0	25.77	10.28	4.36	3.45	4.31	8.21	56.38	0.93	38.29	14.28	6.32	0.88	60.70
		(570)	(227)	(96)	(76)	(95)	(181)	(1245)	(20)	(846)	(316)	(140)	(20)	(1342)
Soil solution at 100 cm	100.7	1.09	10.13	26.07	7.67	13.48	0.21	58.65	19.18	19.36	0.93	9.53	0.08	49.08
		(11)	(102)	(263)	(77)	(136)	(2)	(591)	(193)	(195)	(9)	(96)	(8)	(494)

Table 2. Comparison of annual water and total ion fluxes for a coppice stand at ages 3 and 4 years

Parameter	Stand age		Annual change Percent
	3 years	4 years	
Precipitation (cm)	220.7	221.0	<1
Estimated drainage at 100 cm (cm)	106.4	100.7	-5
Precipitation cations	1080	1245	+15
Precipitation anions	1254	1342	+7
Soil solution cations	714	591	-17
Soil solution anions	661	494	-25

anions occur in the soil profile. Annual precipitation for the 2 years was nearly identical, drainage was about 5 percent greater in the second year, fluxes of precipitation cations and anions were 7 to 15 percent less in the second year. These trends in nutrient losses are primarily due to high rates of net primary production in incorporation of nutrients in woody biomass.

A COMPARATIVE EVALUATION OF THE EFFECTS OF ACID PRECIPITATION,
NATURAL ACID PRODUCTION, AND HARVESTING ON
CATION REMOVAL FROM FORESTS

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In the course of this project we were able to complete chemical analysis of soil solution samples collected from November 1982 to November 1983 in the Douglas-fir [Pseudotsuga menziesii] (Mirb.) Franco] and Red Alder (Alnus rubra Bong.) ecosystems at Pack Forest, Washington. A summary of the weighted average ion concentration and pH values for these solutions and the annual nutrient flux through both soils can be found in Tables 3 and 4. Tables 1 and 2 provide comparable information on precipitation and throughfall solutions collected over the same period of time. The weighted average concentrations of most anions and cations in the incoming rainwater solution (Table 1) are similar to those reported earlier: only alkalinity and NH_4^+ measurements are higher, the latter causing an increase in the estimate annual atmospheric $\text{NH}_4\text{-N}$ deposition to $7.7 \text{ kg N}^- \text{ ha}^{-1} \text{ yr}^{-1}$, which represents up to 85% of total N input ($9 \text{ kg ha}^{-1} \text{ yr}^{-1}$) respectively, which closely approximates the estimates given in previous reports. The same is true for the total annual influx of the other anions and cations investigated.

Interaction between the incoming rainwater and the forest canopy causes changes in solution chemistry (Table 1) which can be summarized as follows:

- (1) an enrichment in exchangeable bases -- primarily K^+ and to a lesser extent Mg^{2+} and Ca^{2+} -- most pronounced in alder throughfall
- (2) an increase in SO_4^{2-} concentration which is greatest in the coniferous forest
- (3) a noticeable drop in solution pH which amounts to nearly 0.5 of a pH unit in the Douglas-fir ecosystem

84-206--1

Table 1. Average pH, conductivity and ion concentration of the precipitation and throughfall solution samples collected from Douglas-fir and red alder ecosystems from November 1982 through October 1983

	pH	H ⁺	NH ₄ ⁺	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Total Posit.	Alka	NO ₃ ⁻	PO ₄ ⁻	SO ₄ ²⁻	Cl ⁻	Total Anion	Conductivity
								meq/l							mmhos cm ⁻¹
Precipitation	5.05	0.009	0.049	0.037	0.011	0.016	0.009	0.132	0.062	0.009	0.003	0.043	0.052	0.168	0.031
Alder Throughfall	4.85	0.014	0.001	0.034	0.072	0.022	0.047	0.190	0.026	0.001	0.005	0.057	0.071	0.159	0.032
Douglas-fir Throughfall	4.62	0.024	0.003	0.039	0.051	0.043	0.024	0.185	0.012	0.001	0.005	0.075	0.071	0.164	0.072

84-206--2

Table 2. Annual water flux area a 12-month period November 1982 through October 1983 and annual ion flux in the precipitation and throughfall solution for Douglas-fir and red alder ecosystems

	H ₂ O	H ⁺	NH ₄ ⁺	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Total Posit.	Alka	NO ₃ ⁻	PO ₄ ⁻	SO ₄ ²⁻	Cl ⁻	Total Anion
	cm							eq ha ⁻¹ yr ⁻¹						
Precipitation	111	99	550	418	127	177	103	1475	687	95	31	479	585	1878
Alder Throughfall	75	107	8	256	543	167	351	1431	199	5	38	427	532	1201
Douglas-Fir Throughfall	54	131	18	212	277	231	131	999	62	5	28	407	385	886

- (4) an almost total disappearance of inorganic N (NH_4^+ and NO_3^-) from the percolating solution
- (5) a decline in alkalinity which is most pronounced in the throughfall samples collected underneath the Douglas-fir canopy
- (6) an increase in Cl^- concentration.

Two mechanisms are thought to be involved, especially in view of the fact that the type of vegetative cover (i.e., deciduous vs coniferous) seems to influence the nature and the extent of chemical changes observed.

- (1) The oxidation and dissolution of dry S deposition and subsequent dissociation of the H_2SO_4 formed into H^+ and SO_4^{2-} ions. This filtering action of S particles by forest canopies has been shown to be more efficient in conifer canopies compared to deciduous forests (Mayer and Ulrich 1980). Such difference in filtering efficiency thus explains the greater SO_4^{2-} enrichment and stronger acidification observed in the throughfall solution collected under Douglas-fir (Table 1) in comparison to the one under Red Alder. The actual (observed) rise in H^+ concentration, however, is less than what could be expected from the increase in SO_4^{2-} concentration, indicating that part of the H^+ load released during dissociation of H_2SO_4 is subsequently neutralized. A further analysis of the alkalinity data (Table 1), notably the decline in HCO_3^- in throughfall vs precipitation solution suggested that the $\text{HCO}_3^- - \text{H}_2\text{CO}_3$ equilibrium may be the buffer mechanism involved. The remainder of the decrease in alkalinity measurements can then largely be explained as a simple pH effect (Stumm and Morgan 1982).

(2) Leaf surface exchange reactions leading to the displacement of cations (especially K^+) from the exchange sites in the foliar free space by incoming displacing agents such as H^+ and NH_4^+). This process seems to be most pronounced in deciduous vegetation types and was shown to exhibit seasonal fluctuations, which the strongest K^+ release during the period of leaf senescence (Cronan and Reiners 1983). Our data set is for the most part consistent with the findings from the above-mentioned study (difference deciduous vs conifers, seasonality, washout of Cl^-) with the exception of NO_3^- by both canopy types, the cause of which is not immediately clear.

The chemical composition of the soil solution samples obtained from 10 and 50 cm in both forest types (Table 3) is also quite comparable to the observations from the previous collection year (see first annual report).

In both soil types a significant rise in solution pH can be observed between 10 and 50 cm soil depth, accompanied by a 5- to an almost 100-fold increase in alkalinity measurements (Table 3) and an acceleration of mainly Ca^{2+} and Mg^{2+} leaching (Table 3 and 4). This accelerated nutrient flux is once again more pronounced in the N-saturated (Red Alder) site (Table 4) which is further characterized by the intensive production and leaching of NO_3^- (Table 3), raising NO_3^- (Table 3), raising NO_3^- levels far above EPA standards for drinking water and transporting nearly 150 kg of N to the groundwater in one year. A major difference from previous collection year is that intensive nitrification is not limited to the zone between 0 and 10 cm

soil depth, but is also occurring deeper into the profile. As a result of the nitrification process, a total amount of $10 \text{ keq H}^+ \text{ ha}^{-1}$ is released annually into solution exceeding atmospheric H^+ inputs by a factor of 100. Expressed alternatively: this natural process has the same acidifying potential as 120 cm of annual rainfall with an average pH of 3.1! In spite of the magnitude of this natural H^+ generation process under Red Alder, no protons are observed leaching below 50 cm soil depth. It is still believed that weathering of Ca^{2+} and/or Mg^{2+} carbonates is the main H^+ consuming mechanism involved.

Our soil leachate studies further show that both soils are saturated with respect to S, as SO_4^{2-} S leaching outputs significantly exceed annual inputs to the site from the atmosphere, even if actual deposition rates are doubled to account for dry deposition. It would further appear from the leachate data that some SO_4^{2-} retention is taking place between 10 and 50 cm in the N-rich soil, whereas a net release of SO_4^{2-} seems to be occurring in the Douglas-fir soil. A more detailed study of the S transformation processes, the S cycle and its linkages to the N cycle will be necessary to further elucidate the mechanism(s) responsible for observed changes in solution chemistry.

A COMPARATIVE EVALUATION OF THE EFFECTS OF ACID PRECIPITATION,
NATURAL ACID PRODUCTION, AND HARVESTING ON
CATION REMOVAL FROM FORESTS

CHESUNCOOK, MAINE, SITE

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INTRODUCTION

The paired control and treatment watersheds being used in this study are located on the east side of Chesuncook Lake, about 72 km west of Millinocket, Maine. The area is forested predominantly by even-aged, spruce-fir stands that developed after the massive spruce budworm epidemic of 1919-20.

Data collection on the 72-ha control watershed and 47-ha treatment watershed began in summer, 1979. Right-of-way clearing for the main haul road on the treatment watershed was completed in July 1980, and a gravel roadbed was laid in February 1981. The whole-tree harvest began June 8, 1981. The mechanical portion of the harvest was completed July 13, at which time hand crews were brought in to harvest saw timber and fell unmerchantable timber. All harvesting was completed by August 12, 1981.

Data collected to date are summarized in Tables 1 through 4. Tables 1 and 2 present concentration data for the control and harvested watersheds, respectively, and Tables 3 and 4 present data on nutrient flux. The data for the control watershed are averages for 4 water years (a June 1-May 31 water year is used), while data for the treatment watershed are averages for the three harvest (1981-82 through 1983-84).

Table 1. Average annual concentrations of solutions from control watershed at Chesuncook Maine for water years 1980-81 through 1983-84.

Sampling Location	H ₂ O	H ⁺	Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺	NH ₄ ⁺		HCO ₃ ⁻	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	PO ₄ ³⁻	{cations + anions}	DOC	Measured Conductance
	cm	Average Annual Concentrations, meq l ⁻¹											mg/l	μ S		
Precipitation	105.2	.0560	.0041	.0014	.0008	.0024	.0074	.0720	.0075	.0380	.0177	.0071	a .0703	1.02	5.3	33
Throughfall	73.6	.0426	.0431	.1050	.0600	.0108	.0049	.2264	.0276	.0730	.0103	.0710	a .1819	1.26	62.9	50
Soil Solution:																
15 cm ^{b/}	—	.0135	.1239	.0786	.0216	.0390	.0021	.2787	.0244	.1903	.0006	.0409	a .2562	1.09	10.7	46
30 cm ^{b/}	—	.0038	.1296	.0827	.0109	.0436	.0006	.2712	.0350	.1732	.0013	.0286	a .2381	1.14	4.3	38
60 cm ^{b/}	—	.0021	.2740	.1481	.0154	.0596	.0006	.4998	.2950	.1716	.0004	.0292	a .4962	1.01	7.7	62
Streamflow	35.6	.0074	.1037	.0660	.0119	.0378	.0025	.2294	.0293	.1368	.0032	.0326	a .2019	1.14	16.7	34

a. PO₄³⁻ was always below detection levels (.003 mg/l).

b. All soil solution values are for frost-free months only (May-October).

Table 2. Average annual concentrations of solutions from harvested watershed at Chesuncook, Maine for water years 1981-82 through 1983-84

Sampling Location	H ₂ O	H ⁺	Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺	NH ₄ ⁺	(Cations)				CO ₃ ⁻	BO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	PO ₄ ³⁻	{Anions	(Cations + Anions)	DOC	Measured Conductance
	cm	Average Annual Concentrations, mg l ⁻¹																	mg/l	μ S
Precipitation	111.5	.0531	.0040	.0011	.0009	.0018	.0068	.0675	.0075	.0345	.0166	.0078	b	.0662	1.02	5.3	33			
Throughfall	a	a	a	a	a	a	a	a	a	a	a	a	a	a	a	a	a	a	a	a
Soil Solution:																				
15 cm ²	--	.0337	.1199	.0639	.0401	.0406	.0090	.3072	.0083	.1371	.1733	.0319	b	.3506	0.88	11.2	51			
30 cm ²	--	.0901	.1083	.0864	.0281	.0461	.0028	.3618	.0289	.1111	.1623	.0265	b	.3290	1.10	4.3	47			
60 cm ²	--	.0096	.4551	.2230	.0206	.0835	.0006	.7924	.4652	.1585	.0744	.0295	b	.7276	1.09	7.7	84			
Streamflow	68.7	.0005	.2173	.1012	.0413	.0461	.0084	.4147	.2313	.0863	.0148	.0435	b	.3759	1.10	15.1	52			

a. Throughfall has not been sampled in the first two years of stand regeneration.

b. PO₄³⁻ was always below detection levels (.003 mg/l).

c. All soil solution values are for frost-free months only (May-October).

Table 3. Average annual flux of nutrient ions for control watershed at Chesuncook, Maine for water years 1980-81 through 1983-84

Sampling Location	H ₂ O	H ⁺	Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺	NH ₄ ⁺						PO ₄ ³⁻	(Cations + {Anions	
								{Cations							{Anions
cm		Average Annual Flux, eq·ha ⁻¹ ·yr ⁻¹													
Precipitation	105.3	592.7	43.4	14.5	8.7	23.5	71.8	754.6	61	393.0	185.1	93.4	a	661	1.07
Throughfall	73.9	317.0	319.0	345.1	459.4	74.0	33.1	1621.5	275.0	528.2	75.2	653.8	a	1532.2	1.06
Streamflow	35.6	25.8	356.8	228.5	42.5	130.8	8.5	792.9	98	469.7	10.7	111	a	684	1.14

a. PO₄³⁻ was always below detection levels (.003 mg/l).

Table 4. Average annual flux of nutrient ions for harvested watershed at Chesuncook, Maine for water years 1981-82 through 1983-84.

Sampling Location	H ₂ O	H ⁺	Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺	NH ₄ ⁺	{Cations				{Anions		{Cations + Anions}	
	cm	Average Annual Flux, eq·ha ⁻¹ ·yr ⁻¹													
Precipitation	111.5	602.2	44.6	13.0	10.1	20.0	70.3	760.1	66	386.3	184.4	88.6	b	612	1.13
Throughfall	a	a	a	a	a	a	a	a	a	a	a	a	a	a	a
Streamflow	68.7	3.9	1524.5	707.5	293.0	320.4	53.1	2902.3	1756	595.4	98.6	315.0	b	2879	1.15
Cation Removal in Harvest (eq·ha ⁻¹ ·yr ⁻¹) : (Removal in Biomass, eq·ha ⁻¹) ÷ (Rotation Age = 60 yrs)															
Whole-Tree			352	61	82										
Conventional			179	23	40										

a. Throughfall has not been sampled in the first three years of stand regeneration.

b. PO₄³⁻ was always below detection levels (.004 mg/l).

PRECIPITATION

Volume of precipitation is sampled at a site 15 km east of the study watersheds using a standard rain gage read at daily intervals. Samples for chemical content are obtained with a bulk, polyethylene collector located in an opening on the treatment watershed. Samples are collected and the sampler changed at about 2-week intervals.

We compared precipitation chemistry from our study sites with four surrounding Maine NADP sites located at Greenville, Bridgeton, Caribous, and Acadia. While there is considerable scatter among all stations, our study site seems representative of the chemical content of precipitation in Maine. The comparative data are available on request.

For the 4 full years of study, precipitation has averaged 105 cm. The precipitation is acidic, having an average H^+ of .0560 meq/l. The dominant anion is SO_4^{2-} averaging .0380 meq/l, and the dominant cation next to H^+ is Ca averaging .0041 meq/l (Table 1).

THROUGHFALL

A throughfall study was conducted in the growing season, 1983. Eight trough collectors (240 cm l. x 10 cm w. x 8 cm d.) were located under the canopy on the control watershed and 3 collectors were placed in an opening on the treatment watershed. The locations of the collectors under the canopy were changed after each storm.

The summer of 1983 had below-average precipitation, but samples were obtained from 14 storms. The data indicate that about 30% of the precipitation is lost to interception, and that H^+ concentration in precipitation is reduced by about 24% during passage through the

canopy. Calcium, Mg^{2+} , K^+ , Na^+ , HCO_3^- , SO_4^{2-} , and Cl were concentrated as precipitation passed through the canopy, while NH_4^+ and NO_3^- were diluted.

An attempt was made to pick logical uncorrelated variables for multiple regression equations of throughfall concentrations (Table 5). Independent variables included respective nutrient concentrations in the open, days since last rain, and rain amount in mm. In the case of SO_4 , H concentration in the open was included as an independent variable. The mean of the three open samples comprised the nutrient concentration in the open for regression purposes. The low R^2 values (Table 5) are discouraging and indicate that models for estimating throughfall will not be easily obtained.

We have not obtained throughfall data on the harvested watershed. Regeneration is now between 1 to 2 m in height and throughfall measurements are being contemplated for 1985.

SOIL SOLUTION

Ceramic cup tension lysimeters are used to sample soil solution at monthly intervals. Lysimeters are located at 15, 22.5, 30, 45, and 60 cm depths at two locations on both the control and treatment watersheds. The data for 15, 30, and 60 cm are summarized in Tables 1 and 2 and Figures 1 and 2.

Compared to precipitation, soil solution is less acidic with H^+ for the control watershed ranging from .0135 meq/l at 15-cm depth to 0.0021 meq/l at 60-cm depth. Ca^{2+} , Mg^{2+} , NO_3^- , and SO_4^{2-} are the

Table 5. Multiple regressions and R² values for throughfall prediction

$$\text{CA} = 1.6487 * \text{EXP}(-.82426 + .03530 * \text{LASTRAIN} + 1.88829 * \text{CA OPEN}) \text{R}^2 = .13$$

$$\text{NH}_4 = 1.3293 * \text{EXP}(-.59416 * \text{LN}(\text{RAMOUNT}) + .58946 * \text{LN}(\text{NH}_4 \text{ OPEN}) \text{R}^2 = .38$$

$$\text{NO}_3 = 1.2870 * \text{EXP}(.97471 - .80102 * \text{LN}(\text{RAMOUNT}) + .20944 * \text{LN}(\text{NO}_3 \text{ OPEN}) \text{R}^2 = .31$$

$$\text{NA} = 1.4714 * \text{EXP}(-3.75253 + .02197 * \text{LASTRAIN} + 28.81844 * \text{NA OPEN}) \text{R}^2 = .35$$

$$\text{SO}_4 = 1.0553 * \text{EXP}(.18977 * \text{LN}(\text{RAMOUNT}) + .82497 * \text{LN}(\text{SO}_4 \text{ OPEN}) + .14078 * \text{LN}(\text{LASTRAIN}) \text{R}^2 = .64$$

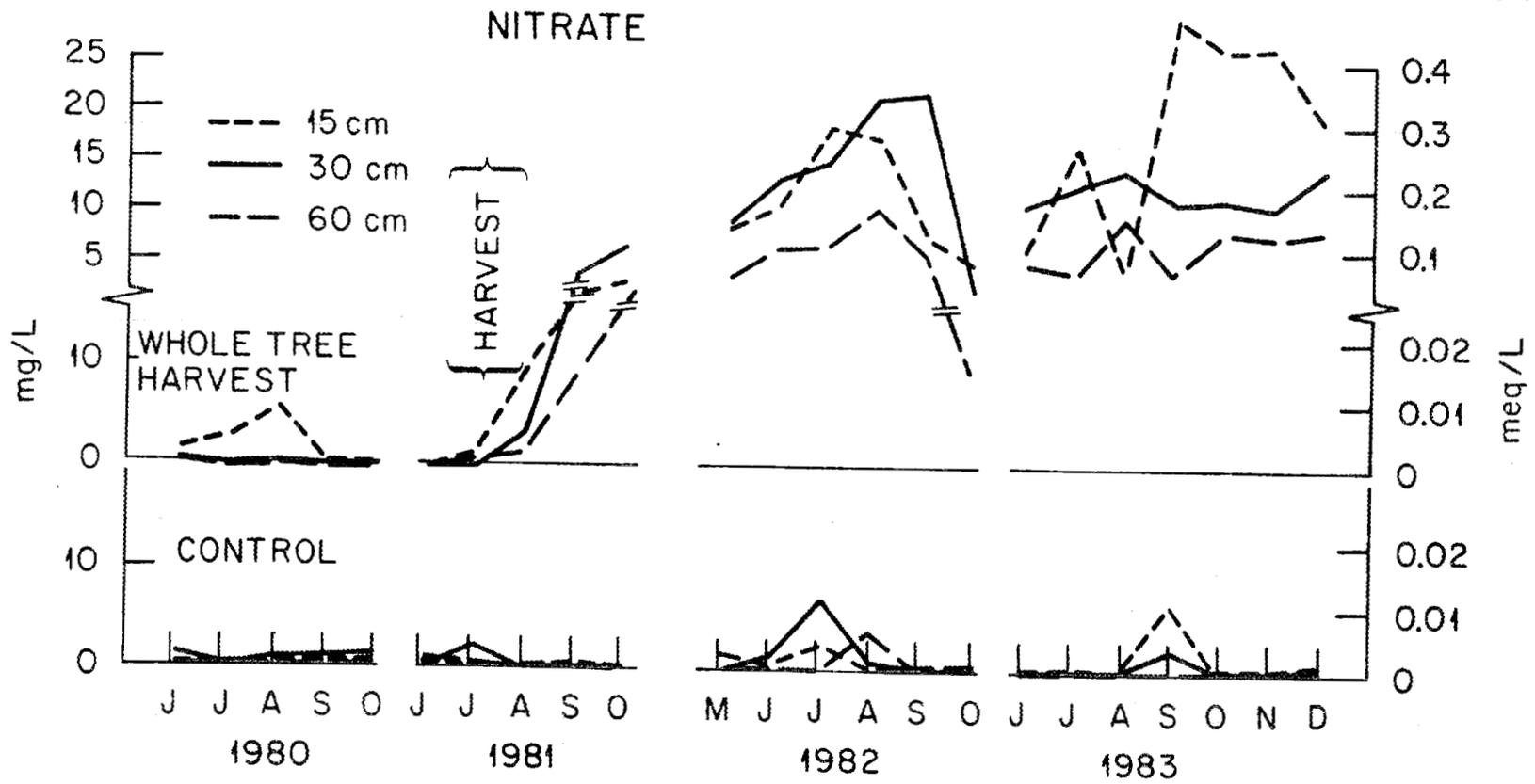


Fig. 1. NO_3^- concentrations in soil solution

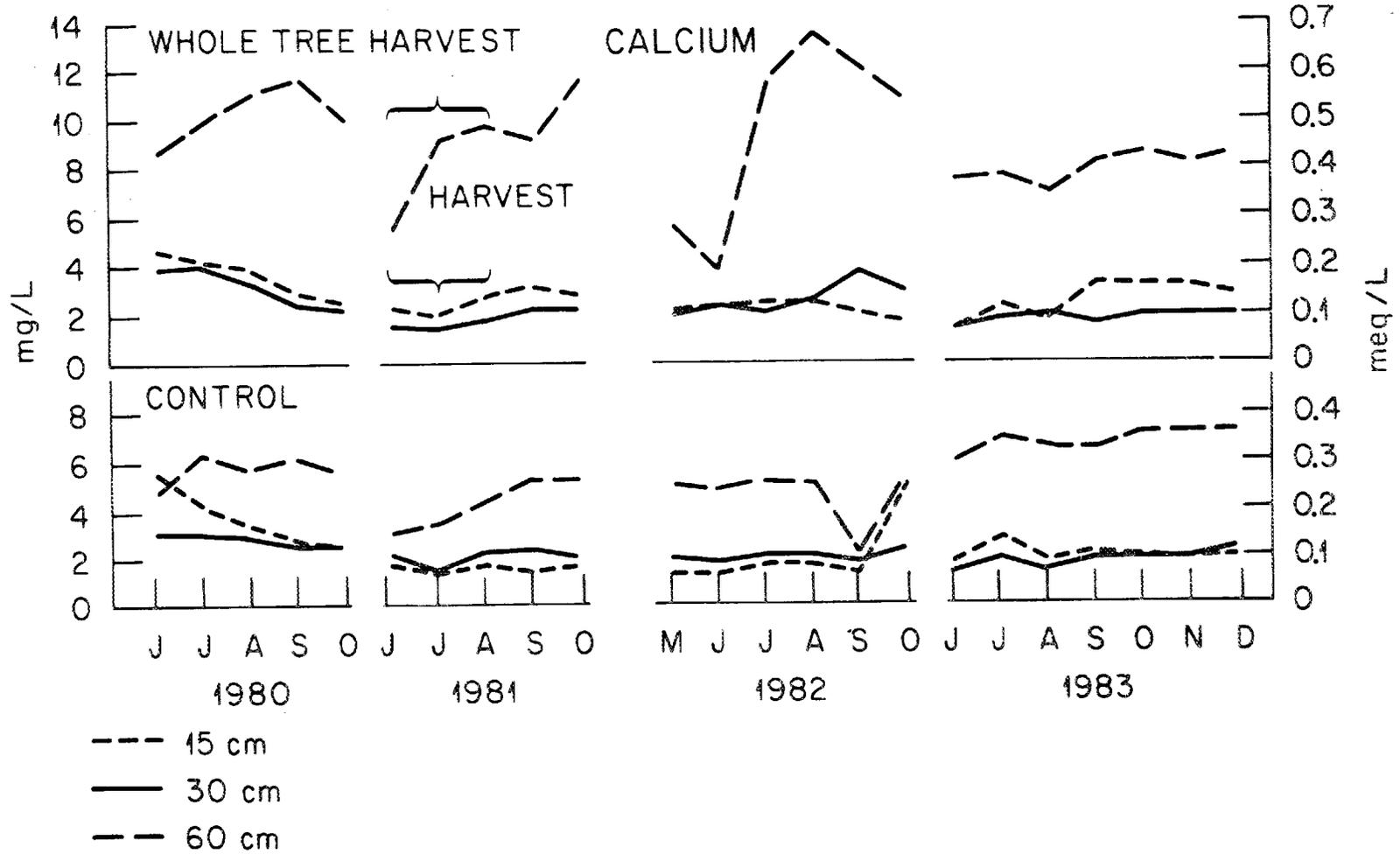


Fig. 2. Ca²⁺ concentrations in soil solution

dominant ions at the 15 and 30 cm depth with HCO_3^- playing an important role at 60 cm depth.

In response to the whole-tree harvest, NO_3^- and Ca^{2+} increased (Figs. 1 and 2) and SO_4^{2-} decreased. The changes in NO_3^- and SO_4^{2-} are greatest at the shallow soil depths while the change in Ca^{2+} was primarily at the deepest depth.

We are presently working on a hydrologic model that will allow simulation of fluxes of water and ions in soil solution.

STREAMFLOW

Amount of streamflow was estimated on a daily basis using the BROOK hydrologic model. To insure that BROOK was applicable, and to test input parameters, we obtained 5 years of data from a gaged watershed in the Province of New Brunswick. The test watershed has topography and forest cover similar to our study watersheds in Maine. With adjustment of input parameters we were able to obtain good agreement between simulated and measured flow for the New Brunswick watershed. This gave us confidence that the BROOK model is satisfactory for simulating streamflow for our watersheds at Chesuncook.

For the control watershed, estimated annual streamflow averaged 35.6 cm, or 34% of precipitation. Ion concentrations of streams are generally similar to those found in soil solution at the 15- and 30-cm depths (Table 1). Exceptions are NH_4^+ and D.O.C., which are always greater in streamflow than in soil solution. Ca^{2+} , Mg^{2+} , and SO_4^{2-} are the dominant ions, both in terms of concentrations

(Table 1) and flux (Table 3). To date the most obvious changes in streamwater concentrations due to harvest has been periodic increases in NO_3^- (Fig. 3). Ca^{2+} and HCO_3^- increased slightly and H^+ and SO_4 decreased.

The simulated streamflow data showed that streamflow increased by an average of about 60% over the 3 years since harvest. This means that even if stream concentrations remained unchanged, ion flux in streamflow would be increased by 1.6 x after harvest. The actual magnitude of the changes in output fluxes cannot be obtained by comparing values in Tables 1 through 4 since Tables 1 and 3 (control watersheds) are for 4 water years and Tables 2 and 4 (harvested watersheds) are for 3 years. We have worked out a procedure for determining nutrient increases based on a short calibration period when both watersheds were uncut (1979-1980 and 1980-1981). Increases in streamflow and ions showing major changes are summarized by year in Table 6.

CATION REMOVAL IN HARVEST

A rotation of 60 years was used to calculate the cation removal in harvest as $\text{eq}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$ (Table 4). Silviculturalists suggest that the rotation age for spruce-fir is highly variable and could be anywhere between 40 and 100 years. In any case, the order of cation removal is: $\text{Ca}^{2+} > \text{K}^+ > \text{Mg}^{2+}$.

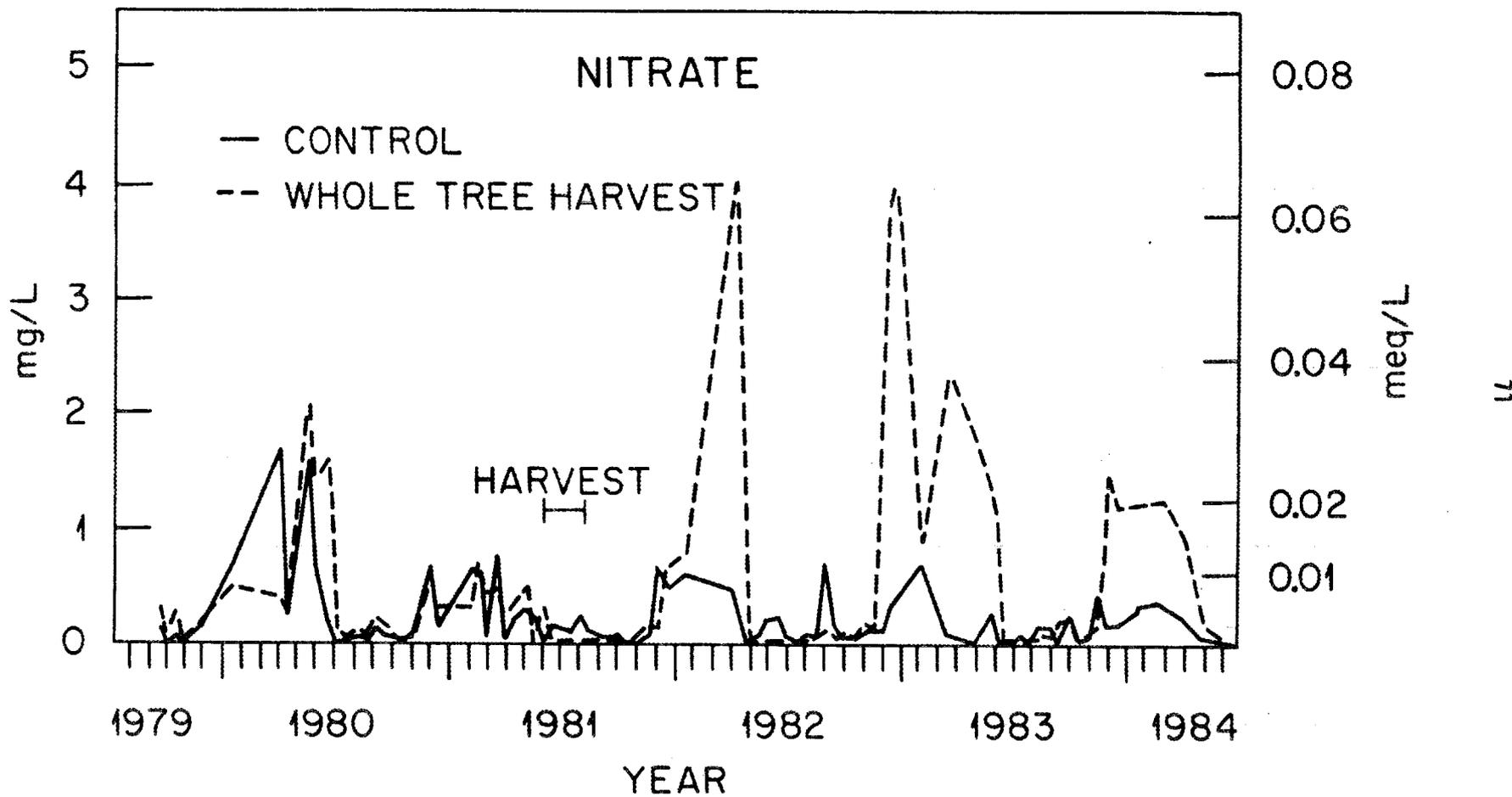


Fig. 3. NO_3^- concentrations in streamflow

Table 6. Increases in water yield and ion flux
due to whole-tree harvest

Year after harvest	H ₂ O	Ca ²⁺	Mg ²⁺	K ⁺	NH ₄ ⁺	NO ₃ ⁻
	cm	----- flux, eq.ha-1.yr-1 -----				
1	31	1148	494	435	50	66
2	30	648	329	205	99	133
3	23	329	214	115	11	66

Table 7. Total exchangeable cations and percent of total contributed by each cation. Values are means of 2 samples from uncut forest.

Horizon	H ⁺	Al ⁺³	NH ₄ ⁺	Ca ⁺²	Mg ⁺²	K ⁺	Na ⁺	base saturation	total exchange	o.m.
	----- Percent -----							meq kg _s ⁻¹	kg _o kg _s ⁻¹	
Oe	10	3	2	70	9	6	0	87	217.2	.947
Oa	28	4	1	49	12	5	1	68	192.1	.902
E	51	41	0	4	2	1	0	8	51.7	.030
Bsh	12	79	0	5	2	2	0	9	77.0	.162
Bs	0	84	1	7	3	4	2	16	23.3	.103

SOILS

Soils at the study site belong to the Chesuncook catena and are Typic Fragiorthods. For later use in interpreting the data collected on the study watersheds, we have determined a number of soil chemical characteristics. These data are summarized in Table 7 and show that the base cations dominate in the organic horizon while H^+ and Al^{3+} dominate in the upper mineral horizons.

DISSEMINATION OF RESULTS

The following publications, abstracts, and dissertation have resulted wholly or in part from funding provided for this study:

IN PRESS

Hornbeck, J. W., and C. A. Federer. 1984. Acid rain and the buffer capacity of forest soils. IN Quebec Conference on acid rain and forest resources. Environment Canada, Ottawa.

SUBMITTED

Federer, C. A., and J. W. Hornbeck. The buffer capacity of soils in New England. Submitted 5/84 to WATER, AIR, and SOIL POLLUTION.

ABSTRACTS

Smith, C. T., and J. W. Hornbeck. 1983. Changes in soil solution chemistry after forest harvest depend on soil drainage class. Bull. Ecol. Soc. Amer. 64(2):65.

Hornbeck, J. W., and C. A. Federer. 1984. Acid rain and the buffer capacity of forest soils in New England. Bull. Ecol. Soc. Amer. 65(2):271-72.

DISSERTATION

Smith, Charles Tattersall. 1984. Nutrient removals and soil leaching from a whole-tree harvest of a red spruce-balsam fir stand in central Maine. University of Maine at Orono. PhD thesis. 214 pp.

A COMPARATIVE EVALUATION OF THE EFFECTS OF ACID PRECIPITATION,
NATURAL ACID PRODUCTION, AND HARVESTING ON
CATION REMOVAL FROM FORESTS

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INTRODUCTION

This report outlines the accomplishments for the Clemson University portion of the Oak Ridge National Laboratory-funded study comparing effects of natural and anthropogenic factors on cation removal from forests. Acidification from atmospheric deposition and internally generated acids may accelerate leaching of calcium, magnesium, potassium, and sodium, thereby reducing soil fertility. This study was initiated in June 1982 with the objective of quantifying losses of cations from a loblolly pine forest ecosystem due to leaching by acid rain, natural leaching by organic acids, and removal by harvesting. The study focuses on a near-maturity loblolly pine plantation and two recently clearcut loblolly pine watersheds in the Piedmont of South Carolina.

RESULTS

The impact of harvesting methods (conventional or whole-tree) is shown in table 1. Magnesium drain in harvest is included in this report.

Tables 2-7 show concentrations and fluxes of nutrients in precipitation, throughfall, soil solution, and stormflow.

Table 1. Cation removal in conventional and whole-tree harvest. Cation removal in harvest ($\text{eq ha}^{-1}\text{yr}^{-1}$):
(Removal in biomass, eq ha^{-1})
÷ (Rotation age, yrs).

	<u>Nutrient concentrations</u>		
	<u>Ca</u>	<u>Mg</u>	<u>K</u>
Conventional	85	54	22
Whole-tree	163	72	42

Table 2. Average nutrient concentrations in hydrologic components on the control watershed (#63)

Watershed 63 (control)	Nutrient concentrations										
	H	Ca	Mg	K	Na meq/l	NH ₄	HCO ₃	SO ₄	NO ₃	Cl	PO ₄
Precipitation*	.038	.010	.006	.005	.013	.018	.014	.057	.004	.014	.003
Throughfall**	.049	.028	.016	.034	.018	.033	.023	.098	.008	—	.006
Soil Solution***	.003	.031	.035	.010	.030	.0003	.021	.020	.0001	—	.0003
Stormflow****	.010	.064	.054	.036	.031	.007	.017	.100	.003	—	.0003

* Based on 6 years data

** Based on 2 years data

*** Based on 3 years data

**** Based on 6 years data

Table 3. Average nutrient concentrations in hydrologic components on the whole-tree harvested watershed (#64)

Watershed 64 (whole-tree harvest)	Nutrient concentrations										
	H	Ca	Mg	K	Na	NH ₄	HCO ₃	SO ₄	NO ₃	Cl	PO ₄
	meq/l										
Precipitation*	.038	.010	.006	.005	.013	.018	.014	.057	.004	.014	.003
Throughfall**	.034	.015	.009	.016	.010	.017	.003	.067	.005	—	.002
Soil Solution***	.036	.089	.063	.011	.031	.0002	.050	.071	.0004	—	.002
Stormflow****	.073	.052	.040	.048	.020	.004	.021	.090	.001	—	.0004

* Based on 6 years data

** Based on 2 years data

*** Based on 3 years data (1980-1983)

**** Based on 3 years data

Table 4. Average nutrient concentrations in hydrologic components on the conventionally harvested watershed (#66)

Watershed 66 (Conventional Harvest)	Nutrient concentrations										
	H	Ca	Mg	K	Na	NH ₄	HCO ₃	SO ₄	NO ₃	Cl	PO ₄
	meq/l										
Precipitation*	.038	.010	.006	.005	.013	.018	.014	.057	.004	.014	.003
Throughfall**	.045	.013	.007	.011	.012	.013	.013	.063	.005	—	.002
Soil Solution***	.004	.055	.042	.009	.021	.0004	.014	.053	.003	—	.0007
Stormflow****	.073	.052	.040	.048	.020	.004	.002	.105	.001	—	.004

* Based on 6 years data

** Based on 2 years data

*** Based on 3 years data (1980-83)

**** Based on 3 years data

Table 5. Annual fluxes of nutrients in hydrologic components on Watershed 63

Watershed 63	Annual fluxes											
	H ₂ O cm	H	Ca	Mg	K eq ha ⁻¹ yr ⁻¹	Na	NH ₄	HCO ₃	SO ₄	NO ₃	Cl	PO ₄
Precipitation	132	538	135	85	63	178	222	188	768	61	190	28
Throughfall	117	576	332	190	394	212	386	271	1148	97	—	66
Soil Solution	40	6	68	77	22	66	1	45	45	1	—	1
Stormflow	5	94	47	70	75	48	2	10	205	1	—	1

Table 6. Annual fluxes of nutrients in hydrologic components on Watershed 64

Watershed 64	Annual fluxes											
	H ₂ O cm	H	Ca	Mg	K Na eq ha ⁻¹ yr ⁻¹		NH ₄	HCO ₃	SO ₄	NO ₃	Cl	PO ₄
Precipitation	132	538	135	85	63	178	222	188	768	61	190	28
Throughfall	117	454	198	116	214	136	226	36	879	64	—	31
Soil Solution	42	8	207	147	26	72	1	116	165	1	—	4
Stormflow	4	12	30	27	13	19	1	12	57	1	—	0

Table 7. Annual fluxes of nutrients in hydrologic components on Watershed 66

Watershed 66 (Conventional Harvest)	Annual fluxes											
	H ₂ O cm	H	Ca	Mg	K eq ha ⁻¹ yr ⁻¹	Na	NH ₄	HCO ₃	SO ₄	NO ₃	Cl	PO ₄
Precipitation*	132	538	135	85	63	178	222	188	768	61	190	28
Throughfall	117	590	177	91	151	159	173	174	833	70	—	21
Soil Solution**	27	3	48	36	8	18	1	12	46	3	—	1
Stormflow***	18	94	47	70	75	48	2	4	205	1	—	1

A COMPARATIVE EVALUATION OF THE EFFECTS OF ACID PRECIPITATION,
NATURAL ACID PRODUCTION, AND HARVESTING ON
CATION REMOVAL FROM FORESTS

OAK RIDGE AND WALKER BRANCH SITES

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INTRODUCTION

The overall goal of this project is to evaluate the combined effects of acid deposition, natural leaching processes, and intensive harvesting on cation removal from forests. This project was initiated in FY 1982 when EPA provided support for the determination of atmospheric inputs and analysis of certain elements (e.g., SO_4^{2-} , Cl^- , etc.) which facilitate the construction of budgets to estimate the relationship of acid deposition-caused nutrient losses to losses by whole-tree harvesting and natural leaching processes. These budgets are used to estimate the extent to which acid deposition is depleting soil nutrients at selected sites and the potential significance of this depletion based on nutrient uptake by vegetation and nutrient pools in soils. This report describes second-year results from four sites at Oak Ridge, Tennessee: chestnut oak and yellow-poplar sites on Walker Branch Watershed not actually harvested but subject to intensive studies of soil leaching and chestnut oak and loblolly pine sites near Walker Branch that were actually harvested but subject to less intense leaching process-level studies.

METHODS

Methods were outlined previously and thus are only briefly reviewed here. At the Walker Branch sites, EPRI funding called for bulk precipitation, and throughfall collections with plastic funnels fitted to bottles and soil solutions are collected at 4 depths (O2, A1, A2, and B2 horizons) by means of tension lysimeters at a chestnut oak (Fullerton) and yellow poplar (Tarklin) site. To estimate cation

export in harvesting, EPA funding contributed time for synthesis of data on Ca, Mg, and K content of vegetation from biomass of nearby permanent inventory plots and nutrient concentrations of biomass components from Johnson et al. (1982) and Henderson (unpubl. data). It was assumed that 40% of bole biomass would be removed in bole-only harvest, and 95% of aboveground biomass would be removed in whole-tree harvesting, as was the case in the nearby harvested site (Johnson et al. 1982). Rotation age was assumed to be 50 years.

At the chestnut oak harvest site, Mg^{2+} , Cl^{-} , and Na^{+} analyses were added to water collections under the existing DOE project beginning in April 1982 to complete cation-anion balance and vegetation samples were analyzed for Mg^{2+} to add to existing Ca^{2+} and K^{+} data. Bulk precipitation and throughfall were collected at Walker Branch, but soil solution was collected by tube lysimeters placed to 50-cm depths at various points in the watershed.

At the loblolly site, procedures were the same as for the chestnut oak harvest site except that duplicate plots in each of 3 treatment areas were set up with triplicate throughfall and tube lysimeter collectors per plot. Biomass estimated by the Clemson regressions, which were checked out by destructively sampling 5 trees in June 1983, and analysis of tree tissues by the Analytical Chemistry Division at ORNL provided nutrient content.

In May of 1983, the whole-tree harvest site was logged for merchantable timber (to a 7.6-cm diameter top). Prior to this, sampling equipment was removed to avoid being damaged. In September, the site was KG-bladed, raked, and disked. Slash was piled and burned.

The site was replanted in March 1984 after which lysimeters were re-installed in previous locations.

RESULTS AND DISCUSSION

Despite the inputs of acid rain and interval generation of carbonic acid (Richter et al. 1983), the chestnut oak intensive study site on Walker Branch had virtually no net export (i.e., output minus input) of Ca^{2+} , or K^+ via leaching (Johnson and Richter, in press; Table 1). Of the cations considered here, only Mg^{2+} and Na^+ show substantial net exports. In contrast to the chestnut oak site, the yellow-poplar intensive study site had a substantial net export of all four major cations via leaching (Table 2). The differences in total cation leaching rates between these two sites are due to differences in sulfate adsorption properties [caused by differences in amorphous Fe- and Al-oxide content (Richter et al. 1983, Johnson et al. 1981) and differences in percent base saturation (Fullerton B horizon had a 10% BS whereas Tarklin B horizon had 43% BS)]. As reported previously, reasons for the large Na^+ flux are not clear. Sulfate concentrations have been steadily increasing in the Walker Branch chestnut oak site (Fig. 1), and SO_4^{2-} now accounts for 85% of total anions at this site. Sulfate accounts for 76% of total anions at the yellow-poplar site, the remainder being attributable to HCO_3^- and Cl^- , respectively. Thus, it appears that leaching at both sites is dominated by atmospheric H_2SO_4 input and that SO_4^{2-} breakthrough may have occurred in the chestnut oak site.

Harvesting would alter the cation budgets of these sites quite considerably. Both sawlog (SH) and whole-tree (WTH) harvesting would

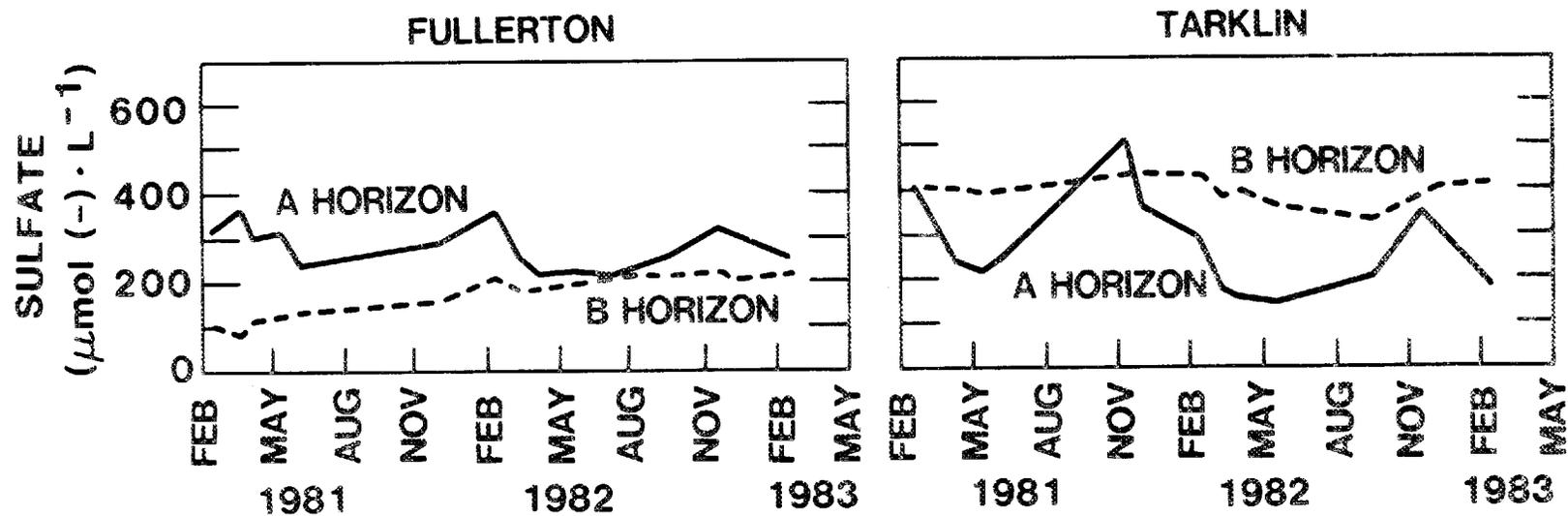


Fig. 1. Sulfate concentrations in soil solutions from Walker Branch Watershed (after Johnson et al., in press).

cause a considerable net export of Ca^{2+} from the chestnut oak site (Table 1). Both SH and WTH cause slightly less Ca^{2+} export from the yellow-poplar site (Table 2), and the increases in Ca^{2+} export by harvesting (relative to leaching) are much smaller than the chestnut oak site. The effect of harvesting on the net export of Mg^{2+} was much less than for Ca^{2+} (on both a total weight and equivalent basis, Tables 1 and 2). The effect of harvesting on net K^{+} export is pronounced at both sites (increases by 60–150% for SH and 340–600% for WTH, Table 5), but due to its high equivalent weight (39.1 for K^{+} vs 20 for Ca^{2+} and 12.2 for Mg^{2+}), total export of K^{+} is small on $\text{keq ha}^{-1} \text{ yr}^{-1}$ basis.

The chestnut oak and loblolly pine harvested sites, which are near one another on the same ridge, provide interesting contrasts to one another. Bulk precipitation inputs and SO_4^{2-} leaching rates at the two sites are roughly similar in magnitude (SO_4^{2-} accounts for 66% and 82% of total leaching at the loblolly pine and chestnut oak sites, respectively), but internal HCO_3^- production and Ca^{2+} leaching at the loblolly pine control plot was twice that at the chestnut oak control plot (Tables 3 and 4). This may be due to higher exchangeable Ca^{2+} in subsoils of the loblolly site (Table 9). However, variability in the chestnut oak site was great and further checking will be necessary to determine the significance of the differences in exchangeable Ca^{2+} . In any event, soil exchangeable Ca^{2+} differences are consistent with very different amounts of Ca in biomass (1200 kg ha^{-1} in chestnut oak vs 160 kg ha^{-1} in loblolly pine) as reflected by Ca removal via harvest (Tables 3 and 4). In short,

Table 1. Average annual fluxes in the Walker Branch chestnut oak site, May 1981-May 1984

Sampling location	H ₂ O (cm)	H ⁺	Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺	NH ₄ ⁺	Σ Cations	HCO ₃ ⁻	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	PO ₄ ³⁻	Σ Anions
A. Average annual fluxes (keq ha ⁻¹ yr ⁻¹) in solution														
Precipitation	131	.69	.35	.08	.05	.05	.09	1.31	0	.92	.14	.12	.004	1.18
Throughfall	112	.32	.73	.28	.36	.05	.19	1.93	.24	1.28	.20	.19	.014	1.92
Soil solution	61	.01	.27	.28	.06	1.16	.003	1.78	.58	1.22	.004	.29	.001	2.09
Stream (if applicable)														
B. Cation removal in harvest (keq ha ⁻¹ yr ⁻¹): Removal in biomass (keq ha ⁻¹) + (rotation age, yrs)														
Conventional			.45	.02	.03			.50						
Whole-tree			1.40	.11	.12			1.63						

Table 2. Average annual fluxes in the Walker Branch yellow-poplar site, May 1981-May 1984

Sampling location	H ₂ O (cm)	H ⁺	Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺	NH ₄ ⁺	Σ Cations	HCO ₃ ⁻	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	PO ₄ ³⁻	Σ Anions
A. Average annual fluxes (keq ha ⁻¹ yr ⁻¹) in solution														
Precipitation	131	.69	.35	.08	.05	.05	.09	1.31	0	.92	.14	.12	.004	1.18
Throughfall	120	.24	.99	.42	.58	.05	.16	2.44	.64	1.48	.21	.23	0.11	2.57
Soil solution	61	.01	1.49	.47	.10	.68	.002	2.75	.50	2.28	<.001	.23	.0003	3.01
Stream (if applicable)														
B. Cation removal in harvest (keq ha ⁻¹ yr ⁻¹): Removal in biomass (keq ha ⁻¹) + (rotation age, yrs)														
Conventional			.36	.04	.03			0.43						
Whole-tree			1.14	.17	.12			1.43						

Table 3. Average annual fluxes in the loblolly pine site, May 1981-May 1984

Sampling location	H ₂ O (cm)	H ⁺	Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺	NH ₄ ⁺	Σ Cations	HCO ₃ ⁻	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	PO ₄ ³⁻	Σ Anions
A. Average annual fluxes (keq ha ⁻¹ yr ⁻¹) in solution														
Precipitation	135	.70	.32	.06	0.03	.05	.05	1.21	0	.82	.09	.11	.003	1.02
Throughfall	116	.51	.88	.28	.43	.05	.13	2.28	.28	1.29	.26	.23	0.07	2.06
Soil solution	50	.02	1.09	.32	0.13	.12	.01	1.69	.47	1.30	.004	.20	.0005	1.98
Stream (if applicable)														
B. Cation removal in harvest (keq ha ⁻¹ yr ⁻¹): Removal in biomass (keq ha ⁻¹) + (rotation age, yrs)														
Conventional		.19	.09	.06				.34						
Whole-tree		.26	.11	.09				.46						

Table 4. Average annual fluxes in the chestnut oak harvested site, May 1981-May 1984

Sampling location	H ₂ O (cm)	H ⁺	Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺	NH ₄ ⁺	Σ Cations	HCO ₃ ⁻	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	PO ₄ ³⁻	Σ Anions
A. Average annual fluxes (keq ha ⁻¹ yr ⁻¹) in solution														
Precipitation	137	.60	.38	.07	0.5	.05	.13	1.28	0	.80	.16	.11	.004	1.07
Throughfall	123	.32	.84	.26	.47	.05	.08	2.02	0	1.14	.26	.20	.006	1.60
Soil solution	66	.07	.71	.61	.17	.09	.01	1.66	.26	1.64	.001	.18	.01	1.99
Stream (if applicable)														
B. Cation removal in harvest (keq ha ⁻¹ yr ⁻¹): Removal in biomass (keq ha ⁻¹) + (rotation age, yrs)														
Conventional			.41	.03	.02			.46						
Whole-tree			1.09	.07	.06			1.22						

vegetation uptake may have reduced base saturation in the chestnut oak site, thereby reducing soil solution pH and carbonic acid leaching. Thus, acid deposition has a greater effect than harvesting of Ca^{2+} export in the loblolly pine site (Table 3) whereas the reverse is true at the chestnut oak site (Table 4).

Magnesium, on the other hand, leaches at a greater rate from the chestnut site than the loblolly pine site (Tables 3 and 4). This may be in part due to higher subsoil exchangeable Mg^{2+} in the chestnut oak site (Table 9), but it may also be due to the lower leaching rate of Ca^{2+} at the chestnut oak site. That is, since both sites are basically under the same SO_4^{2-} leaching pressure (Tables 3 and 4) total cation leaching rates must be similar, and thus differences in Ca^{2+} leaching must be reflected in reverse patterns in the leaching of one or more of the other cations. There were slightly greater leaching rates of K^+ in the chestnut oak site, but this was due to differences in estimated water flux (Tables 3 and 4) since soil solution K^+ concentrations were virtually identical (Tables 7 and 8).

CONCLUSIONS

Sulfate was the major anion in soil solution in all cases, accounting for over 50% of total cations or anions in all cases (Tables 5-8). Nitrate was of minor importance in soil solution, even after harvesting in the chestnut oak site. Thus, the internal acidification processes in these sites are dominated by carbonic acid formation (as manifested by net HCO_3^- production) and tree uptake, the latter being in turn manifested by base cation removal in whole-tree harvesting). Harvesting has its greatest effect in the deciduous

Table 5. Weighted average annual concentrations at the Walker Branch chestnut oak site, May 1981-May 1984

Sampling location	H ⁺ (pH)	Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺	NH ₄ ⁺	Σ Cations	HCO ₃ ⁻	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	PO ₄ ³⁻	Σ Anions	Σ Cation ÷ SC/CC*	Σ Anions
A. Average annual fluxes (keq ha ⁻¹ yr ⁻¹) in solution															
Precipitation (4.3)	.053	.027	.006	.004	.004	.007	.101	0	0.70	0.11	.009	.0003	.090	1.12	22.8/26.9
Throughfall (4.6)	.028	.065	.025	.032	.004	.017	.171	.022	.115	.018	.017	.001	.173	0.99	28.1/31.6
Soil solution (5.7)	.002	.044	.046	.009	.189	.0005	.291	.094	.199	.0009	.048	.0001	.342	0.85	37.9/39.8

*Specific conductance/calculated conductance

Table 6. Weighted average annual concentrations at the Walker Branch yellow-poplar site, May 1981-May 1984

Sampling location	H ⁺ (pH)	Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺	NH ₄ ⁺	Σ Cations	HCO ₃ ⁻	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	PO ₄ ³⁻	Σ Anions	ΣCation ÷ ΣAnions	SC/CC*
A. Average annual fluxes (meq/l) in solution															
Precipitation	.053 (4.3)	.027	.006	.004	.004	.007	.101	0	.070	.011	.009	.0003	.090	1.12	22.8/26.9
Throughfall	.021 (4.7)	.082	.034	.048	.004	.014	.203	.053	.123	.017	.019	.001	.213	0.95	30.8/33.7
Soil solution	.0003 (6.5)	.245	.078	.016	.111	.0006	.451	.082	.374	.0002	.039	<.0001	.497	0.91	52.4/53.0

*Specific conductance/calculated conductance

Table 7. Weighted average annual concentrations at the loblolly pine site, May 1981-May 1984

Sampling location	H ⁺ (pH)	Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺	NH ₄ ⁺	Σ Cations	HCO ₃ ⁻	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	PO ₄ ³⁻	Σ Anions	Σ Cation ÷ Σ Anions	SC/CC*
A. Average annual fluxes (meq/l) in solution															
Precipitation (4.3)	0.053	.024	.004	.002	.003	0.004	.090	0	.061	.007	.008	.0002	.078	1.15	21.3/25.1
Throughfall (4.3)	.044	.076	.023	.038	.004	.012	.197	.024	.112	.023	.021	.0005	.185	0.94	33.9/38.8
Soil solution (6.4)	.004	.217	.063	.025	.023	.0024	.335	.094	.259	.0007	.040	.0001	.394	0.85	47.5/48.8

*Specific conductance/calculated conductance

Table 8. Weighted average annual concentrations in the chestnut oak, May 1981-May 1984

Sampling location	H+ (pH)	Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺	NH ₄ ⁺	Σ Cations	HCO ₃ ⁻	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	PO ₄ ³⁻	Σ Anions	ΣCation : SC/MC ΣAnions	
A. Average annual fluxes (meq/l)															
Precipitation	.044 (4.4)	.028	.005	.004	.004	.009	.094	0	.058	0.11	.008	.0003	.077	1.12	18.0/23.1
Throughfall	.026 (4.6)	.068	.021	.038	.004	.007	.164	0	.093	.021	.016	.0005	.131	1.25	24.9/28.0
Soil solution	.017 (4.8)	.108	.093	.025	.014	.0001	.251	.038	.249	.0003	.028	.0001	.315	.79	36.6/39.6

*Specific conductance/calculated conductance

Table 9. Exchangeable Ca^{2+} , K^{+} , and Mg^{2+} in soils from the chestnut oak and loblolly pine control plots (means \pm standard errors)

Depth	Chestnut oak	Loblolly pine
cm	(meq) (100 g) ⁻¹	
	Ca^{2+}	
0-15	1.29 \pm 1.98	0.91 \pm 0.17
15-30	0.49 \pm 0.62	0.53 \pm 0.11
30-45	0.54 \pm 0.82	1.06 \pm 0.14
	Mg^{2+}	
0-15	0.27 \pm 0.78	0.22 \pm 0.03
15-30	0.15 \pm 0.17	0.15 \pm 0.03
30-45	0.48 \pm 0.82	0.23 \pm 0.03
	K^{+}	
0-15	0.23 \pm 0.11	0.12 \pm 0.01
15-30	0.12 \pm 0.08	0.11 \pm 0.01
30-45	0.15 \pm 0.17	0.10 \pm 0.01

forests, where ΣBC (despite shorter rotations) which in turn may have led to greater internal HCO_3^- production (due to higher %BS, soil solution pH, and thus HCO_3^- concentrations). Even in this case, however, atmospheric H^+ and SO_4^{2-} inputs exceed net HCO_3^- production, as is the case in the deciduous forests.

Overall, it seems clear that atmospheric inputs dominate soil leaching at all four sites and that sulfate adsorption is no longer a significant mitigating influence upon this. Fullerton soils (which characterize all but the Walker Branch yellow-poplar site) are known to process sulfate adsorption properties, and thus further research on this is needed.

Harvesting effects equal or exceed leaching in all but the loblolly pine site where there is some evidence that lower tree Ca^{2+} and HCO_3^- leaching. Further aspects of this will be pursued in the final year of this project.

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