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1988 Annual Report of the Integrated Forest Study

S. E. Lindberg
D. W. Johnson

Environmental Sciences Division
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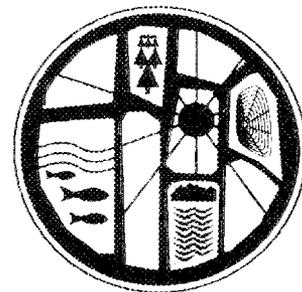
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1988 ANNUAL REPORT OF THE INTEGRATED FOREST STUDY

S. E. Lindberg and D. W. Johnson (Editors)

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Oak Ridge, Tennessee

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ABSTRACT

LINDBERG, S. E., and D. W. JOHNSON (Eds). 1989.
1988 Annual Report of the integrated forest study.
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Oak Ridge, Tennessee. 241 pp.

The summaries contained in this report describe the trends in atmospheric deposition, canopy interactions, soil solution fluxes, and ecosystem budgets for the major chemical species studied in the Integrated Forest Study (IFS). This document also includes summary reports of each supportive deposition and soils experimental task, and descriptions of specific field research performed at each site. This report is one of a series of reports on the IFS, including Site Descriptions, Measurement Protocols, and Project Summary.

Preliminary analysis of the deposition and nutrient cycling data indicates several interesting trends across sites. The deposition estimates confirm the expected increase in atmospheric deposition at high elevation sites compared to lower elevation forests. Input to the Smoky Mountains site in the Southeast exceeded that to all other sites for most chemical species. Cloudwater interception, enhanced dry deposition due to high wind speeds, and increased rainfall due to orographic effects all contribute to this trend. At the other sites dry deposition was important in the input of all ions, particularly at the dryer southeastern sites and most significantly for the base cations. Canopy interactions were minimal for deposited Na and S, but indicated significant canopy absorption of strong acidity and N, and foliar leaching of base cations at all forests.

The soil solution fluxes and ecosystem budget data illustrate the difficulties in predicting site nutrient status and the degree of sulfate and nitrate leaching. The magnitude of nitrate leaching from each forest is not readily predicted by any single parameter. Similarly, the sulfur input/output budgets do not fit with any expected soil series effects on sulfur retention. However, patterns of aluminum and base cation leaching do appear to match predictions from theoretical soil solution considerations. These observations indicate the need to quantify system fluxes for a variety of forests in different environments in order to understand the possible effects of deposition on nutrient cycling processes.

1. INTRODUCTION, PROJECT ORGANIZATION, AND STUDY SITES

The principal objective of the Integrated Forest Study on the Effects of Atmospheric Deposition is to determine the effects of atmospheric deposition of sulfur and nitrogen on forest nutrient cycling. The study integrates field measurements of atmospheric deposition and nutrient cycling in a variety of forest sites, and experimental research, including laboratory and field studies, to investigate selected atmospheric and soil processes in greater detail. The research is being conducted at forested sites in the northwestern, northeastern, and southeastern United States and in Canada and Norway (Fig. 1). These sites represent a range of conditions in climate, air quality, soils, and vegetation (Table 1), which will facilitate the testing of hypotheses regarding the effects of atmospheric sulfur and nitrogen deposition on forest nutrient cycles.

Responsibility for site operation throughout the IFS is in the hands of the principal investigators at each site. The separate experimental tasks underway at various sites are indicated in Figure 2. Coordination of synthesis activities for the IFS project is shared by several individuals with expertise in the areas of either atmospheric science or forest ecosystems. For the purpose of comparing data across a range of sites, these individuals have been designated as synthesis group leaders for the major chemical components being studied at each IFS research site: sulfur, nitrogen, acidity, and base cations. Data from the initial one to two years of field research was supplied to these individuals by the IFS site researchers for summary in this report.

The summaries reported here describe the trends in atmospheric deposition, canopy interactions, soil solution fluxes, and ecosystem budgets for the major chemical species studied. This document also includes summary reports of the various deposition and soils experimental tasks, and descriptions of specific field research performed at each site.

Preliminary analysis of the deposition and nutrient cycling data indicates several interesting trends across sites. The deposition estimates confirm the expected increase in atmospheric deposition at high elevation sites compared to lower elevation forests. However, the magnitude of this effect at the Smoky Mountains site in the Southeast was unexpected. Cloudwater interception, enhanced dry deposition due to high wind speeds, and increased rainfall due to orographic effects all contribute to this trend. At the other sites dry deposition was important in the input of all ions, particularly of the base cations and particularly at the dryer southeastern sites. Canopy interactions were minimal for deposited Na and S, but indicated significant canopy absorption of strong acidity and N, and foliar leaching of base cations at all forests.

The soil solution fluxes and ecosystem budget data illustrate the difficulties in predicting site nutrient status and the degree of sulfate and nitrate leaching. The magnitude of nitrate leaching from each forest is not readily predicted by any single parameter. Similarly, the sulfur input/output budgets do not fit with any expected soil series effects on sulfur retention. However, patterns of aluminum and base cation leaching do appear to match predictions from theoretical soil solution considerations. These observations indicate the need to quantify system fluxes for a variety of forests in different environments in order to understand the possible effects of deposition on nutrient cycling processes.

THE EPRI INTEGRATED FOREST STUDY

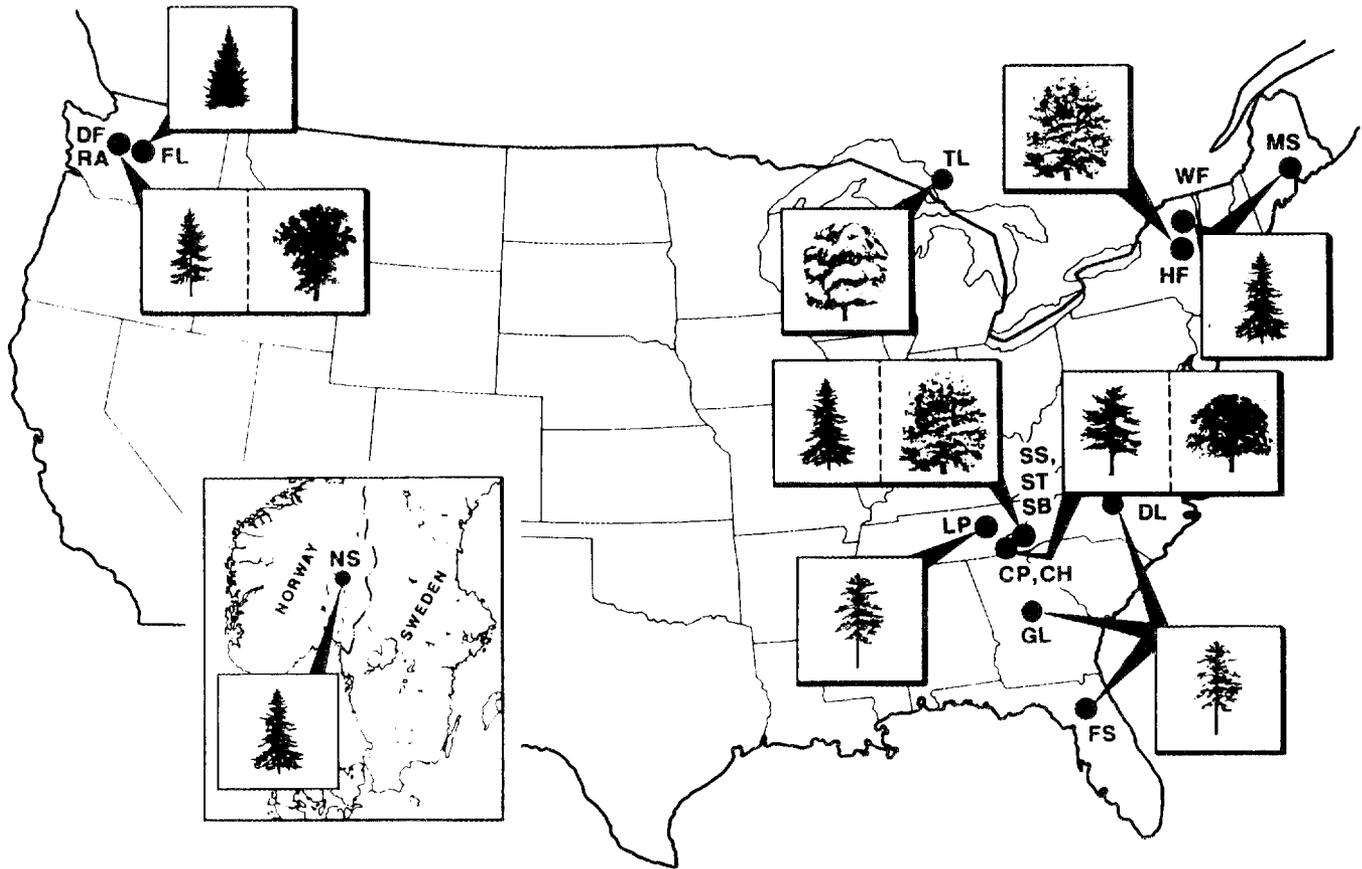


Fig. 1. Sites in the Integrated Forest Study

Table 1. Sites in the EPRI Integrated Forest Study (arranged from West to East, see Fig. 1 for site codes and locations).

INTENSIVE DEPOSITION MEASUREMENT SITES (see next section for equipment):

<u>SITE CODE</u>	<u>FOREST TYPE (~Elevation)</u>	<u>SITE LOCATION</u>	<u>PRINCIPAL INVESTIGATOR</u>
DF	Douglas Fir (220 m)	Thompson Forest, WA	D. Cole, H. Van Miegroet
RA	Red Alder (220 m)	Thompson Forest, WA	D. Cole, H. Van Miegroet
LP	Loblolly Pine (300 m)	Oak Ridge, TN	S. Lindberg, D. Johnson
ST	Red Spruce (1740 m)	Smoky Mountains, NC	S. Lindberg, D. Johnson
CP	White Pine (720-1100 m)	Coweeta Hyd. Lab., NC	W. Swank
GL	Loblolly Pine (175 m)	BF Grant Forest, GA	L. Ragsdale, J. Dowd
FS	Slash Pine (100 m)	Gainesville, FL	H. Gholz
DL	Loblolly Pine (215 m)	Duke Forest, NC	K. Knoerr, D. Binkley
TL	N. Hardwoods (350 m)	Turkey Lakes, Ontario	N. Foster
HF	N. Hardwoods (530 m)	Huntington Forest, NY	M. Mitchell
WF	Red Spruce, Balsam Fir (1000 m)	Whiteface Mt., NY	A. Friedland
MS	Red Spruce (60 m)	Howland, ME	I. Fernandez
NS	Norway Spruce (200 m)	Nordmoen, Norway	A. Stuanes

BULK DEPOSITION ONLY SITES:

FL	Fir, Hemlock (1100 m)	Findley Lake, WA	D. Cole
SS	Red Spruce (1800 m)	Smoky Mountains, NC	D. Johnson
SB	American Beech (1600 m)	Smoky Mountains, NC	D. Johnson
CH	S. Hardwoods (700-1000 m)	Coweeta Hyd. Lab., NC	W. Swank

EPRI RP - 2621 INTEGRATED FOREST STUDY ON EFFECTS OF ATMOSPHERIC DEPOSITION

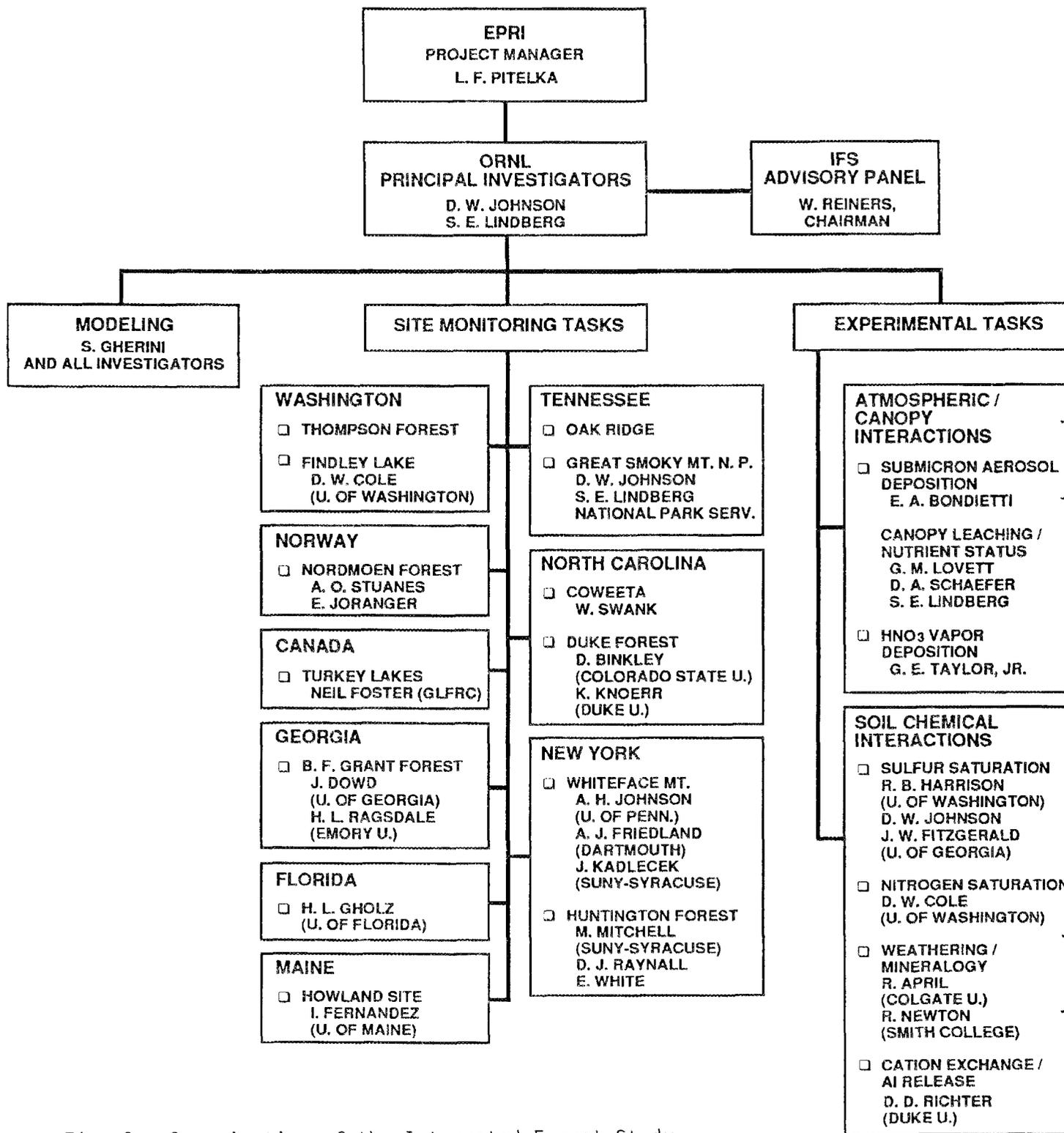


Fig. 2. Organization of the Integrated Forest Study

2. BRIEF SYNOPSIS OF MEASUREMENT AND COMPUTATION METHODS

2.1 Methods for Atmospheric Deposition Estimates to Forests in the Integrated Forest Study

Field Measurements

At the IFS forests designated as intensive deposition measurement sites, detailed data on atmospheric chemistry, wet deposition, and meteorology are collected continuously (meteorology) and on an event basis (atmospheric chemistry and wet deposition) throughout the year. Measurements of wet deposition of all major ions (including weak acidity, Al, total N and total P on smaller subsets of selected samples) are collected in nearby forest clearings (incident precipitation) and in replicate (N=2-20) below the canopy (throughfall and stemflow).

The air chemistry (major ions in aerosols and dry deposited coarse particles, SO₂, O₃, and HNO₃) and standard meteorological data are collected from towers which extend 5-10 meters above the surrounding canopy. All measurements are taken at or adjacent to the study plot used for collection of nutrient cycling data (Fig. 3). Samples are collected of both wet and dry events: wet deposition as wetfall/only using automatic collectors, air chemistry using filter pack and surrogate surface methods, and cloud water using passive string-type collectors. All of the methods described here and in the section on nutrient cycling, are described in detail in Lindberg et al (in press).

Deposition Calculations

Wet Deposition: The seasonal and annual input of ions in rain, throughfall, and stemflow are calculated from the product of precipitation-weighted mean ion concentrations in each solution times the appropriate hydrologic flux. Depending on site accessibility, from 40-100% (median 82%) of the wet deposition is sampled and analyzed. Hydrologic fluxes are based on continuous records of rain, throughfall, and stemflow (the latter two with extensive replicate-gage grids).

Dry Deposition of Vapors and Fine Aerosols: Dry deposition is calculated from the product of event mean air concentrations and appropriate deposition velocities (V_d). For vapors, V_d values are computed hourly using the inferential big-leaf model of Hicks et al (1987) based on site-specific hourly meteorological measurements and canopy structure/physiology data. For aerosols, V_d values are derived from site-specific canopy structure data using the submicron radionuclide tracer method of Bondietti et al (1984). Event dry deposition is computed from the product of the event mean concentrations and V_d values, and annual values from time-weighted means and measurements of total dry duration.

Dry Deposition of Coarse Particles: Dry deposition of coarse particles measured to inert surfaces must be scaled to the full forest canopy. This is done using scaling factors applicable to each forest. We have developed a linear regression model to separate ion fluxes in net throughfall into their component parts

of dry deposition washoff and foliar leaching based on event collections (Lovett and Lindberg, 1984). We have used this method to derive scaling factors for coarse particles based on the results of the regression model applied to Ca at each forest (Lindberg et al, 1988a). Calcium in throughfall is used because it is an excellent coarse particle tracer with no vapor phase component. These factors are determined as annual means from regressions on all sampled wet events over the year, and are multiplied by the mean measured fluxes of coarse particles to inert surfaces to estimate annual coarse particle dry deposition.

Cloud Water Interception: Cloud water deposition is calculated from the product of the weighted mean ion concentrations in cloud water (weighted by liquid water content) and the total annual hydrologic flux of cloud water. Hydrologic fluxes are determined by a number of independent methods, allowing an estimate of the range of cloud water fluxes. These include application of the model of Lovett (1984) to meteorological and canopy structure data for each site, direct measurements of cloudwater drip during selected events (extrapolated to a year based on estimates of cloud immersion time), and various methods involving hydrologic fluxes in throughfall (Lindberg et al, 1988b).

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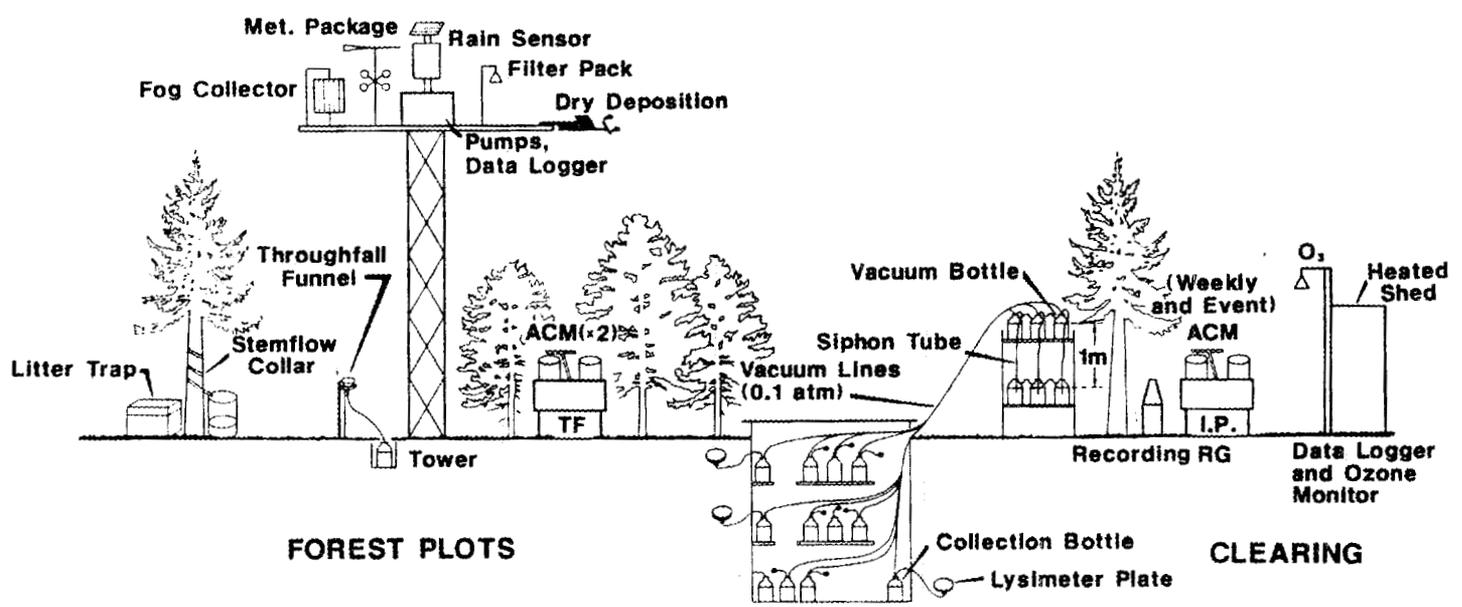


Fig. 3. Schematic of Sampling Plots in the Integrated Forest Study

2.2 Methods for Soils and Nutrient Cycling Measurements in the Integrated Forest Study

General

The basic unit of study is the plot, which ranges in area from approximately 0.05 to 0.10 ha, depending upon site conditions and protocols for previous plot-level studies that may have been conducted at the site. At each site, organic matter, N, P, S, K, Ca, and Mg contents of vegetation, forest floor, and soils and nutrient fluxes via litterfall, throughfall, and soil solution are estimated for a minimum of 3 years. The equipment layout typically used in a site is depicted in Figure 3.

Specific Methods

Vegetation Biomass and Nutrient Content

Aboveground vegetation biomass (foliage, branch, bole) is typically estimated from regression equations based upon diameter breast height (dbh, measured at 137 cm) or dbh and height. In some instances, foliage biomass is better estimated from litterfall, back calculating for weight loss from foliage during senescence. Root biomass is obtained if possible, in most instances by random coring. Vegetation is analyzed for nutrients by component and weighted average concentrations are multiplied by biomass to obtain nutrient content for each component.

Forest Floor and Soil Nutrient Content

Forest floor mass is determined by random destructive sampling within the plot. Soil mass and gravel contents are estimated from destructive measurements for bulk density (quantitative pit, core, or clod method, depending upon soil texture and structure) and coarse fragment (> 2mm sieving) content. Forest floor and the <2mm soil fraction are analyzed for total nutrient content, and Oa and soil samples are also analysed for extractable nutrients, extractable Al, and cation exchange capacity (by neutral NH_4Cl) as well. Forest floor and soil nutrient contents are estimated by multiplying concentrations by weights for each component. Nutrient content of the >2mm soil size fraction is not normally estimated.

Litterfall Flux

Litterfall is collected in screened traps of known area, separated into components (needles, leaves, wood, and reproductive parts) weighed, and analyzed for nutrient content.

Throughfall Flux

In addition to the wet-only event throughfall collections made as part of the atmospheric deposition studies, bulk throughfall is collected and analyzed at all sites.

Soil Solution Flux

Soil solutions are collected by means of tension lysimeters (set to 10-30 kPa tension, depending upon local soil conditions). Tension is supplied to lysimeters either by the hanging column method (Figure 1) or an electrical system with vacuum pump and vacuum control. Solutions are collected at monthly intervals or less and analyzed for major cations and anions, pH, conductivity, total N, and total P. Volumes are recorded at each collection, and volume-weighted means for each constituent are multiplied by independent estimates of soil water flux (obtained from nearby gauged streams, modeling, Cl⁻ balance, or subtraction of evapotranspiration estimates from total precipitation).

3. ANALYSIS OF UNCERTAINTIES IN THE IFS

The problem of assessing uncertainties in measured, calculated, and estimated quantities plagues all environmental research projects, and is often neglected. This is particularly true in nutrient cycling and deposition measurement projects which rely on numerous assumptions and applications of unique methods. The approach to evaluating uncertainties in the IFS involves both qualitative and quantitative analyses. We attempted to identify the most important sources of potential bias or error, and then to analyze the probable magnitude of these sources. Tables 2 and 3 illustrate the results of the qualitative analysis and provide a semi-quantitative ranking of these factors for both the Atmospheric Deposition and Soils/Nutrient Cycling tasks of the IFS. Since the time when these factors were identified, various IFS investigators have designed and performed special projects in an attempt to minimize potential problems, and to provide estimates of the most important sources of error.

An example of this analysis applied to the Smoky Mountain Spruce site (ST) is given in Table 4. Relative standard errors (RSE) were estimated from a combination of the measured standard errors in ion concentrations, analytical precision and accuracy, potential bias in certain physical measurements, and published sensitivity analyses of models used in the IFS. In addition, ranges of possible values based on "reasonable" physical bounds, where available, were used with these RSE values to derive overall estimates of uncertainty. Use of physical and other "bounds" often results in non-symmetrical ranges around the "best estimates" as illustrated in Fig. 4 for sulfur and nitrogen fluxes at the ST and LP IFS sites. We feel that this approach provides a reasonable idea of the level of uncertainty associated with IFS flux and pool size estimates.

Table 2.
UNCERTAINTIES IN IFS DEPOSITION ESTIMATES^a

Flux	Importance ^a	Uncertainty		Primary Source	Interaction ^b	Actions
		Level				
<u>Wet Deposition</u>						
Cloudwater	L-H	H		Immersion time, cloudwater amount, ion concentrations	**	More personal observations, intensive field experiments, collect more samples
Rain	H	L		Water flux in mountains		Replicate sites, snow boards
Throughfall	H	M		Spatial variability	*	Permanent replicates at some sites, intensives at others, permanent replicate TF gages
Stemflow	L-M	M		Spatial averaging		Increase replicates at some sites, eliminate SF at others
<u>Dry Deposition</u>						
SO ₂	L-H	M		Modeling surface resistance, wetness effects	*	Beyond scope of IFS, rely on NAPAP work, compare with micrometeorological data at some sites
HNO ₃	H	H		Atmosphere resistance	**	Gradient measurements at some sites, canopy balance to establish bounds, replicate filter packs, compare with real-time sensor, compare long- and short-term filter pack measurements
Fine Particles	L	H		Deposition velocity		Radionuclide measurements on several species
Coarse Particles	L-M	M		Scaling factors		Run throughfall model at all sites, improve model R ² with air chemistry measurements

^aL = low uncertainty (10-30%)

M = medium uncertainty (~50%)

H = high uncertainty (>100%)

L-H indicates a range in importance due to local characteristics and depends on the IFS site in question

^bInteraction represents a flux with both high importance and high uncertainty

** = serious problem

* = moderate problem

Table 3.
UNCERTAINTIES IN SOILS AND NUTRIENT CYCLING TASK

<u>Problem</u>	<u>Importance</u>	<u>Uncertainty Level</u>	<u>Source of Uncertainty</u>
Soil weathering	H	H	Measurement
Water flux estimation	H	L-M	Measurement
Plant uptake, retranslocation	M	L-M	Measurement
Disturbance due to lysimeter installation	L-H*	L-M	Length of time for measurement
Belowground biological processes (N transformations, root turnover)	M-H	H	Lack of data
Soil content estimates, i.e., bulk density and % gravel	M-H	L-H*	Lack of data
Deposition estimates	M-H	L-H	Measurement
Sorting year-to-year variation from long-term trends	L-H	L-H	Duration of sampling
Biomass estimates	M	M	Regression equations
Macropore and unsaturated flow	L-H	H	Measurement
Denitrification	L-H*	H	Measurement
Inter-laboratory analytical bias; sample aging effects	L-M	L	Lab accuracy, sampling interval

*Varies considerably from site to site.

Table 4. Uncertainty Analysis for Annual Deposition of SO₂ at Smoky Mountain IFS Site (ST)

	SAMPLING EFFICIENCY IN TIME	RSE* OF CONCENTRATIONS	SPATIAL VARIABILITY	WATER AMOUNT	DRY DEPOSITION VELOCITIES	RESULTANT OVERALL UNCERTAINTIES
RAIN	94%	12%	Unknown, but rain is measured at site	30% LOW?	-	20%
CLOUD	10-20%(EVTS)	16%	SEE DRY	27-52 cm (TF-PPT, Na BAL)	-	80%
DRY- SO ₂	26%	24%	?(NTF RANGE = +- 7%)	-	30%	10%
DRY- SO ₂ fine	26%	14%	?(NTF RANGE = +- 7%)	-	100%	80%
DRY- SO ₂ Coarse	26%	30%	?(NTF RANGE = +- 7%)	-	35% RSE of (S.F.)	60%
TOTAL DRY	-	-	-	-	-	60%
TOTAL DEPOSITION	-	-	-	-	-	50%
TF	94%	11%	SUM 4% LOW EVENTS=5-30% DIFFERENT	4.8% LOW	-	20%
SF	94%	10%	FLUX INSIG., EVEN AT +- 3X	-	-	80%
TF+SF	-	-	-	-	-	30%
NET CANOPY EFFECT (NCE = TF + SF - TOTAL DEPOSITION)	-	-	-	-	-	200%

*RSE = relative standard error of the mean (SE/mean).

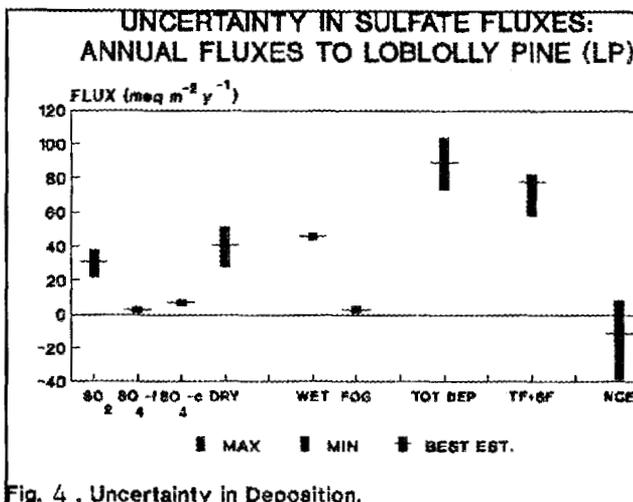
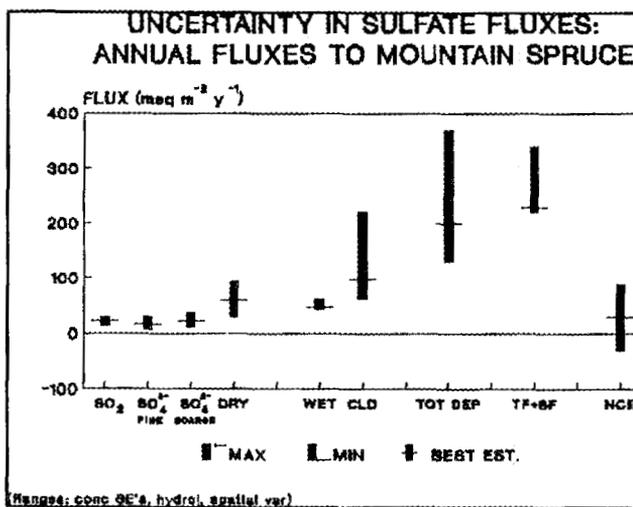
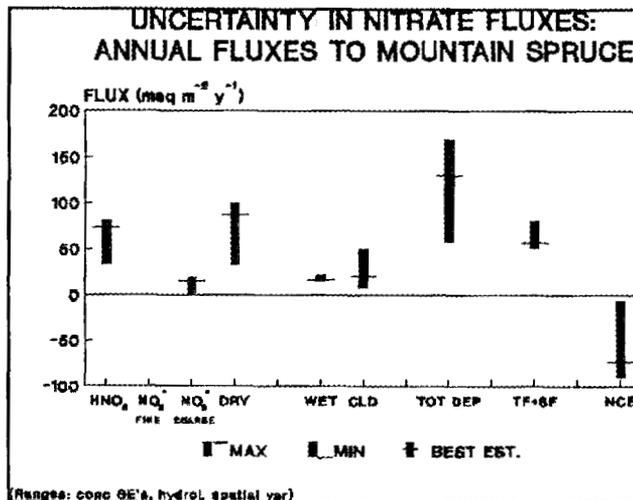


Fig. 4 . Uncertainty in Deposition.

Fig. 4. Results of uncertainty analysis for sulfate and nitrate deposition and throughfall stemflow (TF+SF) fluxes at IFS sites in the Smoky Mountains (site ST, upper 2 graphs) and Oak Ridge (site LP, lower graph).

SECTION 4. DEPOSITION AND NUTRIENT CYCLING SYNTHESIS SUMMARIES

4.1. SULFUR

4.1.1. ATMOSPHERIC DEPOSITION AND CANOPY INTERACTIONS OF SULFUR TO FORESTS IN THE INTEGRATED FOREST STUDY

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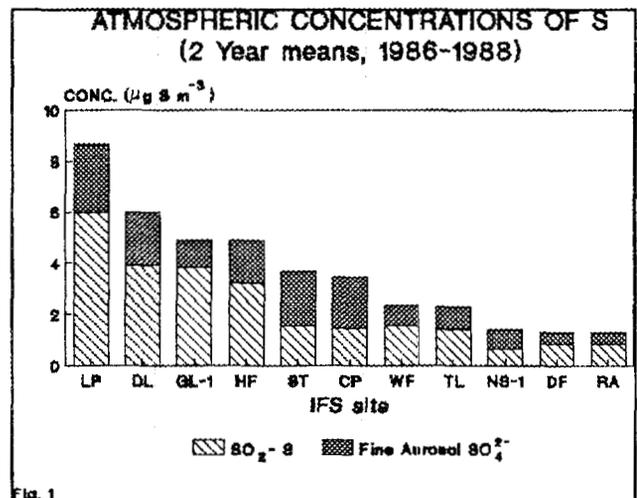
INTRODUCTION AND APPROACH

Atmospheric concentrations and fluxes of the major forms of airborne sulfur have been determined above and below the forest canopies at eleven of the IFS Intensive Deposition Measurement Sites for periods of 1-2 years: Washington red alder (RA) and Douglas fir (DF), Oak Ridge loblolly pine (LP), Smoky Mt. red spruce (ST), Coweeta white pine (CP), Duke loblolly pine (DL), Whiteface Mt. spruce/fir (WF), Huntington Forest mixed hardwood (HF) (all 2-y data sets), and Turkey Lakes mixed hardwood (TL), Nordmoen Norway spruce (NS), and Georgia loblolly pine (GL) (1-y data sets). The sampling years began between 4/86 and 11/86; hence somewhat different periods were summarized for each site. Data were also made available from the Turkey Lakes Watershed in Ontario for 1984 for comparison. Limited data were also available from the Maine spruce (MS) and Florida slash pine (FS) sites but were not included in this summary due to delayed startup (the first year of sampling will be completed during the summer of 1989).

At each site standard IFS deposition sampling protocols were followed for precipitation, throughfall, atmospheric aerosols and vapors, deposited coarse particles, cloud and fog water, and meteorological parameters (Lindberg et al, in press). Common protocols were also followed for computation of deposition fluxes as described earlier in this report (see Section 2). The site operators collected from 41 to 100% of the total rainfall (as wet-only events; mean 75%) and sampled from 8 to 100% of the dry periods (mean 50%). Results of studies of the spatial variability of fluxes within the forest plots for several of the IFS sites are described in the site reports in Section 6 of this report.

ATMOSPHERIC CONCENTRATIONS

Total airborne sulfur at the sites ranged from 1.3 to 8.6 $\mu\text{g S m}^{-3}$ and was dominated by SO_2 at most sites (Fig. 1). At the



more remote sites, SO_2 and particle SO_4^{2-} were comparable. The highest levels occurred in the Southeast, the lowest in the Northwest and in Norway. These trends were not reflected in the rain concentration data for SO_4^{2-} , with the highest concentrations ($\sim 50\text{-}60 \mu\text{eq/l}$, volume-weighted means) at the Norway and low elevation Northeastern and Southeastern sites, and the lowest concentrations ($\sim 20\text{-}25 \mu\text{eq/l}$) at the CP and RA/DF sites.

ATMOSPHERIC DEPOSITION

The estimates of total atmospheric deposition by wet, dry, and cloudwater processes to the forest canopy at each site are illustrated in Figure 2. The sites are ranked in order of total deposition. Total SO_4^{2-} fluxes ranged nearly over an order of magnitude from ~ 300 to $\sim 2000 \text{ eq ha}^{-1} \text{ y}^{-1}$ (dry deposited SO_2 is assumed to be converted to SO_4^{2-} within the ecosystem for these calculations). The highest flux occurred at the ST mountain site, with fluxes generally decreasing from the Southeast to the Northeast to the Northwest. The flux at the WF mountain site is comparable to the highest flux measured at a low elevation site (DL), and that at the Norway site is in the range of fluxes at low elevation Northeastern sites.

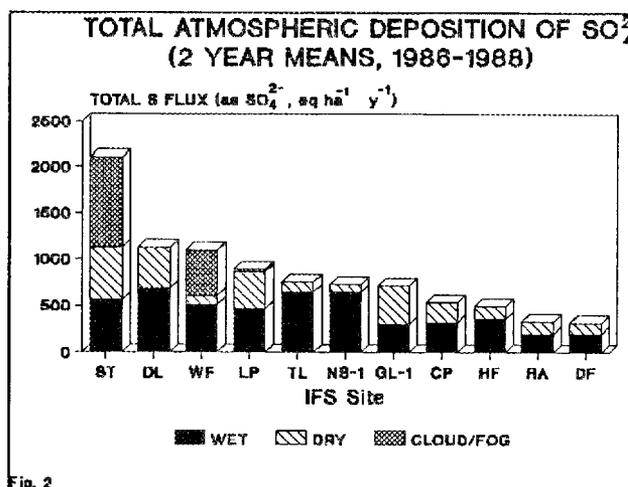


Fig. 2

Approximately 50% of the SO_4^{2-} flux at the ST and WF sites was due to cloudwater interception (we estimated an annual hydrologic flux of 37 cm cloudwater at ST and 13 cm at WF in addition to the 194 and 114 cm of precipitation, respectively). Inputs by dry deposition and precipitation were nearly equal at the ST site, while dry deposition was only 20% of wet at WF due to generally lower air concentrations and canopy surface area. Dry deposition was most important at the dryer low elevation Southeastern sites ($\sim 40\text{-}60\%$ of total), while wet deposition dominated at all other low elevation sites ($60\text{-}90\%$ of total), indicating that dry/wet input ratios are site specific, but may be regionally representative. Dry deposition at all North American sites was dominated by SO_2 ($\sim 50\text{-}90\%$ of total dry). At the Norway site, with the lowest SO_2 concentrations (which peaked during the dormant season), dry deposition was controlled by aerosols.

The results for the ST and WF sites support the idea that mountain forests are exposed to higher atmospheric loading because of climatologic factors and site characteristics (orographic effects, high winds, cloud immersion, and the gap nature of the high surface area spruce/fir canopy), despite their location distant from major emission sources. Although we expected this trend, the magnitude of the enhancement at the ST mountain site was a surprise (four

times higher S flux than at the nearby CP site, and two times higher than at the WF mountain site). These trends in S inputs are reflected by the deposition estimates for N, H⁺, and base cations, as well as the soil fluxes of S and N (summarized in the following reports), indicating that this enhancement is not specific to S alone.

All of these estimates are subject to considerable uncertainty. This is particularly true at the high elevation sites because of the presence of cloudwater which is difficult to quantify. The magnitude of the uncertainty in S deposition was determined for the ST site based on combined errors due to analytical, sampling, and hydrologic factors, and spatial variability (see Section 3). Using these data and applying physical bounds on fluxes wherever possible (eg. hydrologic fluxes based on independent measurements, see Section 6.1), it is possible to bound the best estimate of the S flux: minimum = 1500, best = 2100, maximum = 3800 eq ha⁻¹ y⁻¹). Despite this relatively large range, it is probable that the S flux to this site exceeds that measured at any other site.

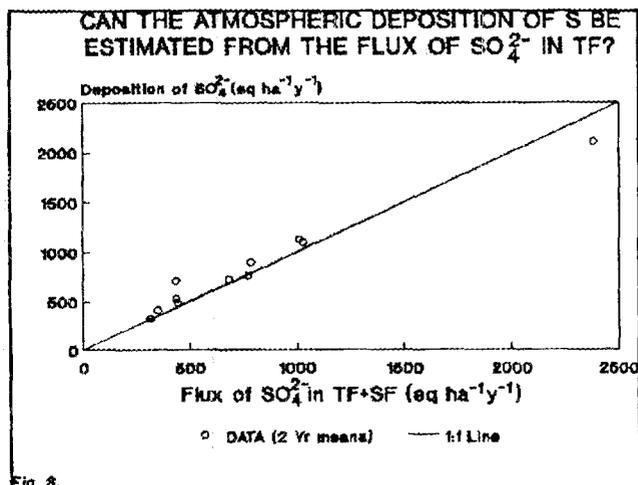
THROUGHFALL FLUXES

The fluxes of SO₄²⁻ below these canopies in throughfall plus stemflow (TF+SF) strongly reflect the trends in deposition described above. For example, the flux of sulfate in TF+SF at the ST site exceeds the next highest flux (WF) by a factor of 2.3, and exceeds that at the geographically nearest site (CP) by more than a factor of 6.

At any individual site, the fluxes in deposition and TF+SF are remarkably similar. Figure 3 illustrates the relationship between the estimated total annual wet plus dry deposition of SO₄²⁻ to the forest canopy and the measured flux in TF+SF at each site. At five of the IFS sites the fluxes are essentially the same above and below the canopy, and at the remaining sites the differences are generally within the range of uncertainty in the deposition estimates. The variance in the flux of S in TF+SF accounts for 97% of the variance in estimated total S deposition. This strongly suggests that measurements of TF+SF fluxes can provide a much simplified method for estimating the seasonal and annual S loading to forests and forested watersheds, as suggested by recent S isotope studies (Garten et al, 1987; Garten, in press).

CANOPY INTERACTIONS

Comparison of total deposition of SO₄²⁻ to the canopies with the fluxes of SO₄²⁻ below these canopies in TF+SF provides an indication of the interactions and fate of atmospheric S. These data indicate



that, relative to total S fluxes, canopy interactions (uptake and leaching) appear to be small. The two sites which represent the extremes in behavior of S in the canopy are ST and GL in Figure 3. The distance of each point from the 1:1 line indicates the magnitude of the canopy interaction for S which is given by the difference between the atmospheric flux and the flux in

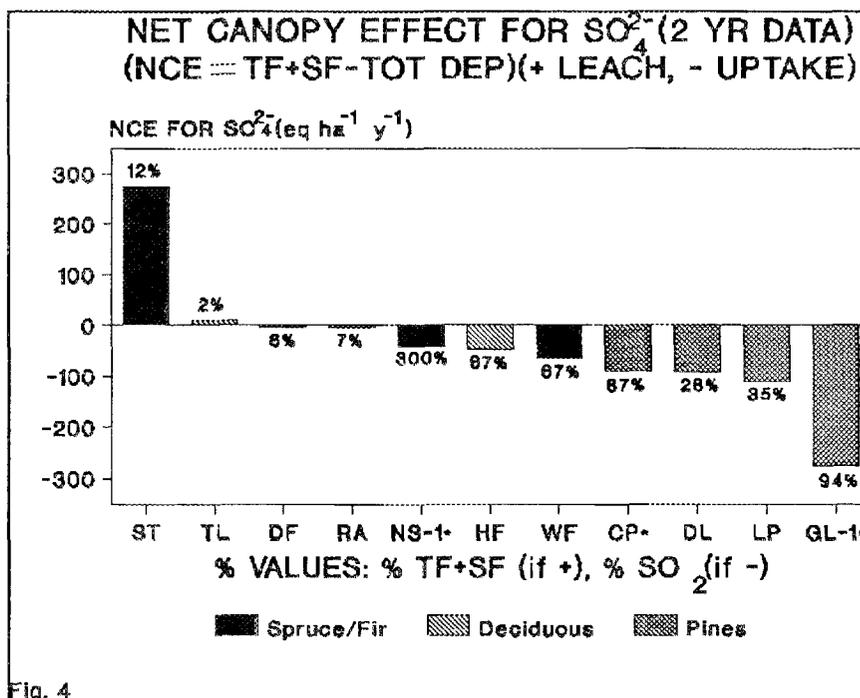


Fig. 4

TF+SF (termed the net canopy exchange, NCE = TF+SF-total deposition). The net canopy exchange at each site is summarized in Figure 4, which also shows the values as a % of TF+SF (for leaching) and as a % of dry deposited SO_2 (for uptake). At nearly all of the IFS sites deposition exceeds the flux below the canopy, yielding negative NCE values. The flux below the canopy exceeds that into the canopy only at ST and TL. However, given the uncertainty of these fluxes, NCE's of absolute magnitude $<70 \text{ eq ha}^{-1}$ are probably not significantly different from zero, and suggest an approximate balance of S in the canopies at the TL, DF, RA, NS, HF, and WF sites.

NCE values greater than zero indicate a source of S in the canopy (foliar leaching). NCE values less than zero indicate that the canopy is a sink for deposited S, most likely dry deposited SO_2 which is the only form known to readily enter the stomatal cavity. Such behavior is obviously specific to each tree species, but the IFS data suggest some generalities which are potentially useful for modeling. The most significant "sink" canopies are all southern pine sites (CP, DL, LP, GL), and the only "source" canopy is high elevation spruce. In between, more or less in balance, are a mixture of spruce, fir, and deciduous systems.

Given the relatively small contribution of foliar leaching of SO_4^{2-} to TF+SF measured with S isotopes for three pine and deciduous species near the LP site (~3% on the average; Lindberg and Garten, 1988), one might expect the general behavior of S in forest canopies in industrialized areas to lie somewhere between a balance and moderate uptake, depending on local SO_2 dry deposition. Leaching would be significant relative to TF+SF only when dry deposition is minimal. If this is an accurate generalization, the

relatively large foliar leaching at the ST site may simply reflect our inability to accurately quantify the fluxes to this mountain site. This could result from an underestimate of the total S deposition to this forest, or an overestimate of the flux in TF+SF (less likely, as discussed in Section 6.1).

Assuming that a small amount of foliar leaching does occur in most trees (Lindberg and Garten, 1988), our data suggest that uptake of dry deposited SO_2 in many forests is sufficiently large relative to foliar leaching to result in a negative canopy balance for SO_4^{2-} . Thus leaching becomes unimportant at sites with high S loading where deposition wash-off dominates the below canopy flux. When this is the case, leaching cannot be detected in the canopy balance due to uptake of SO_2 .

Expressing the uptake values relative to the flux of dry deposited SO_2 indicates that over an annual cycle, from ~30 to >90% of the dry deposited SO_2 remains fixed in the canopy (Fig. 4). Very high values for % uptake of SO_2 (NS, CP, GL) may indicate overestimates of S dry deposition, or underestimates of S fluxes in TF+SF. This is clearly reflected in the NCE for NS which far exceeds the very small dry deposition of SO_2 , and may also be suggested by the values for CP and GL which are nearly equal to dry deposition of SO_2 . There are reasons to suspect both the deposition and TF+SF estimates at these three sites.¹ The remaining NCE values (DL, LP, RA, DF, HF, WF) suggest that forest canopies release ~30-70% of dry deposited SO_2 into TF+SF.

SUMMARY

Atmospheric deposition of sulfur is highest at the mountain sites and Southeastern sites, and lowest in the Northwest. Cloudwater contributes significantly to input at the mountain sites, dry deposition is comparable to wet at the dryer Southeastern sites, and wet deposition dominates input at the northern sites. At all these forests, it appears that deposited S behaves more or less conservatively in the canopy, with uptake balanced to some extent by foliar leaching. With the exception of only the GL site,

¹[The dry deposition model used in the IFS is known to overestimate SO_2 input to forests during periods of soil moisture stress (Matt et al, 1987) which we expect occurred at GL and CP during this sampling period. At the NS site, the spruce canopy is covered with snow for much of the dormant season when SO_2 concentrations peak, creating a condition which is not directly addressed by the deposition velocity model (Hicks et al, 1987). Underestimates of TF+SF are also suspected at these three sites. At GL and CP less than 60% of total TF+SF was sampled as wet-only events, yielding fluxes which were smaller than fluxes derived from bulk TF+SF which was sampled continuously. Since TF fluxes were computed from weighted means using the same TF hydrologic fluxes for both event and bulk TF, this suggests that the smaller event population was not representative. At other sites, SO_4^{2-} fluxes in continuous bulk and wet-only event TF were comparable (as reported elsewhere, Richter and Lindberg, 1988). A TF sampling problem also affects the NS site where wintertime TF event samples as snow are difficult to obtain and interpret.]

estimated fluxes in total deposition are within 15% of the measured fluxes in TF+SF, indicating that useful estimates of total atmospheric deposition of S can be derived from TF networks. This is particularly important for forests in complex terrain where many micrometeorological methods are not readily applicable, and in watersheds where scaling up from single point measurements of atmospheric concentrations and modeled fluxes is difficult.

ACKNOWLEDGEMENTS AND REFERENCES

These data could not have been summarized without the help of the investigators at each IFS site. In particular the considerable efforts of the field researchers who collect these data are appreciated: D. Silsbee, J. Owens, D. Schaefer, G. Wolfe, J. Panec, L. Reynolds, J. Shepard, P. Conklin, D. Todd, E. Miller, P. Homann, R. Gonea, and R. Briggs.

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4.1.2 INTEGRATED FOREST STUDY

SULFUR DISTRIBUTION AND CYCLING IN FOREST ECOSYSTEMS

April 1989

Summarized by:
M.J. Mitchell
SUNY-CESF
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The quantification of sulfur budgets of forested ecosystems is an important component of the IFS project since sulfur inputs are major contributors to mineral acidity and the flux of sulfate through the soil affects the dynamics of other elements, such as base cations which are important for forest nutrition (Johnson et al., 1982; Nilsson and Grennfelt, 1988). A diagram of a generalized sulfur budget for a forest ecosystem is given in Figure 1. Major inputs are through dry and wet deposition. Major sulfur pools include the vegetation as well as inorganic and organic sulfur fractions in the soil. Fluxes include sulfate uptake by vegetation, litter and root input of sulfur to the forest floor and soil, microbial immobilization-mineralization, abiotic sulfate adsorption-desorption, and sulfate leaching (David et al., 1987).

The flux of sulfate through the strata of the forest ecosystem (total deposition, throughfall plus stemflow, forest floor leaching, and lower B horizon leaching) for IFS sites is given in Figure 2. The sites are ranked with respect to sulfur loading. For those sites in which atmospheric inputs have not been detailed, correlative information such as proximity to sites with known deposition and/or similarity of bulk throughfall sulfur fluxes was used for establishing the ranking. Among the sites, there is an order of magnitude difference of input from 2100 to 300 eq/ha/y. The high input sites are red spruce stands (ST, SS) in the high elevations of the Smokey Mountains with the lowest input sites being found in the Cascade Mountains of Washington which have low background levels of atmospheric sulfur. There is a general correspondence with the input of sulfur to the sites and the fluxes of sulfate through the canopy as throughfall and stemflow. Among the various sites, however, there are some notable increases and decreases in the flux of sulfate through the forest floor and mineral soils. The factors affecting these latter fluxes will be discussed below.

Accumulation of sulfur in the vegetation, forest floor and mineral soil could alter the flux of sulfate through the forest ecosystem. The information presently available on the sulfur content of IFS sites is shown in Figure 3. As has been established for other forest ecosystems, the mineral soil serves as the major sulfur pool (Johnson, 1984). The precise estimates of the sulfur content of forest soils is complicated by spatial heterogeneity and the presence of coarse fragments. However,

among IFS sites the sulfur content of the soil does not show marked variation with the exception of high levels of sulfur in the Duke Loblolly Pine Site (DL) and the B.F. Grant Forest Site (GL). The former site may have been fertilized with super-phosphate when the site was in agricultural use (D. Binkley, personal communication) and this may have contributed to its elevated sulfur levels.

An assessment of the relationship of sulfur inputs to the requirement (bole and branch increment plus current foliage production) of the forest vegetation is shown in Figure 4. In general the atmospheric inputs of sulfur are substantially greater than the requirement of the vegetation for sulfur. In those cases where it is less [Red Alder (RA) and Cowetta Pine (CP)] the additional sulfur would be met by internal cycling such as by litter inputs followed by mineralization.

It has often been hypothesized that sulfate adsorption is in steady state for soils with low sulfate adsorption capacity and sulfate outputs should equal inputs for these ecosystems (Rochelle et al., 1987). This hypothesis was tested by comparing sulfur inputs to outputs and in some cases sulfate is showing conservative behavior (Figure 5). The amount of sulfate retention (total deposition - leaching from B horizon) is also given (Figure 6). Sites with lowest sulfur inputs [red alder (RA), Douglas fir (DF), Howland Maine (HM)] tend to exhibit net retention of this element and this may be due to nutritional demands. However, other forest systems with higher sulfate inputs also have net retention which may be due sulfate adsorption and/or microbial immobilization [Cowetta Pine (CP), B.F. Grant (GL)]. The importance of sulfate adsorption (Johnson et al., 1980) and biological immobilization (Swank et al., 1984) as mechanisms of sulfur retention in forest soils has been previously established. A number of sites, especially those with high levels of input, appear to be exhibiting net losses of sulfur. These net losses could be due to underestimates of sulfur inputs, overestimates of sulfate losses, sulfate desorption, and/or net sulfur mineralization. For some regions sulfate inputs may be declining from earlier maxima (Fay et al., 1986) and hence maximal solution concentrations would also be decreasing. A decline in sulfate concentration in the soil would result in release of adsorbed sulfate (Figure 7) if desorption is a reversible reaction (Barrow and Shaw, 1977).

Experimental tasks have ascertained sulfate adsorption-desorption and the potential for organic sulfur immobilization-mineralization among sites. For example, data from Rob Harrison and Dale Johnson (Figure 8) have shown that sites with low sulfate retention generally have a higher capacity for sulfate adsorption. However, this retention is not related to inorganic iron and aluminum fractions which should affect adsorption

capacities (Fuller et al., 1985). John Fitzgerald has also shown that among the sites there is a high capacity for organic sulfur immobilization especially in the forest floor but there is no discernable pattern in these potentials with respect to sulfur loadings in these sites (Figure 9).

There is a notable relationship between nitrate and sulfate concentrations in solutions passing through the B horizon with those sites with highest nitrate concentrations having the lowest concentrations of sulfate (Figure 10). It has been shown that sulfate adsorption is enhanced with a depression of pH and nitrification which generates acidity may lead to increased sulfate adsorption (Nodvin et al., 1986; Mitchell et al., 1989). These results suggest that pH dependent sulfate adsorption may be affecting sulfate adsorption and hence sulfate flux from some sites.

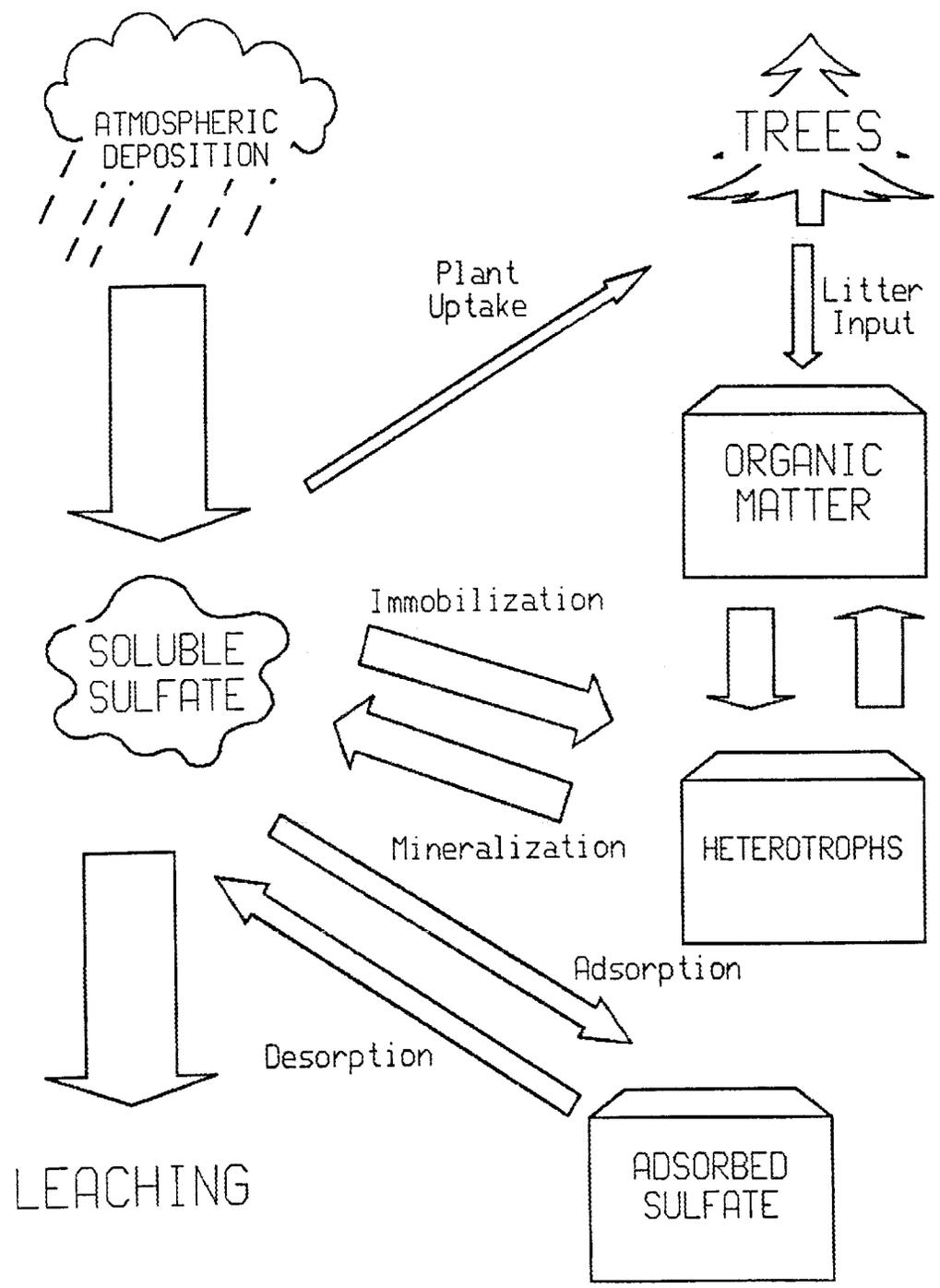
These findings demonstrate the need for independent estimates of inputs and outputs for sulfur budgets of forested ecosystems such as those being carried out in the IFS project. The assumption that dry deposition can be calculated by the difference between sulfate leaching and wet deposition would be incorrect for a wide range of forested ecosystems. The determination of whether sulfur is being retained or lost in forested ecosystems has important implications not only for estimating nutrient status of these sites, but also for predicting how changing atmospheric inputs of sulfur will affect surface water chemistry (Hornberger et al., 1986; Mitchell and Fuller, 1988). These results also show that the flux of sulfate through these forest ecosystems is tightly linked with the transformations and fluxes of other elements such as nitrogen.

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Figure 1



FOREST
SULFUR
CYCLE

Figure 2.

Sulfate Flux Through Ecosystem Strata

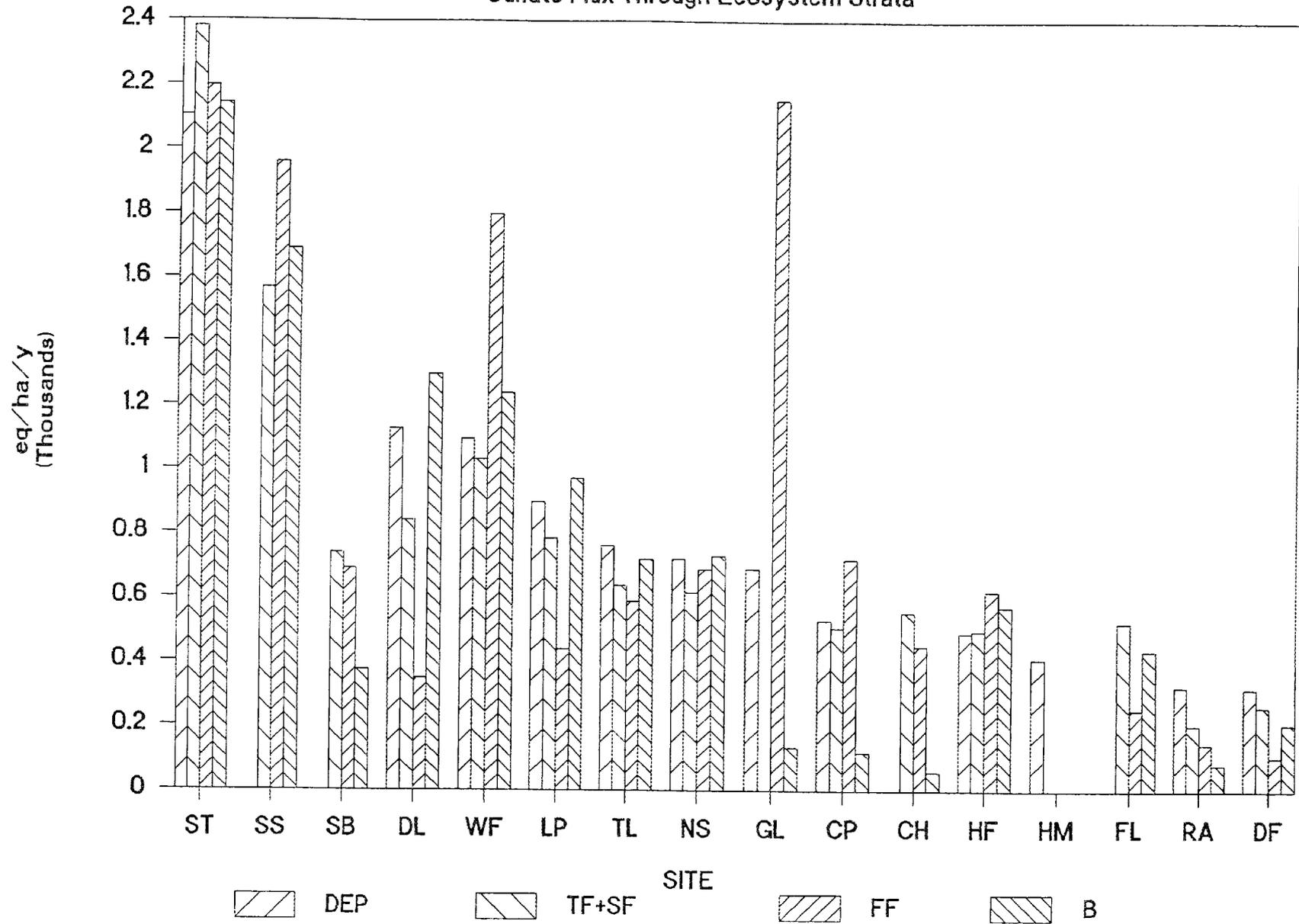


Figure 3.
S content of IFS Sites.

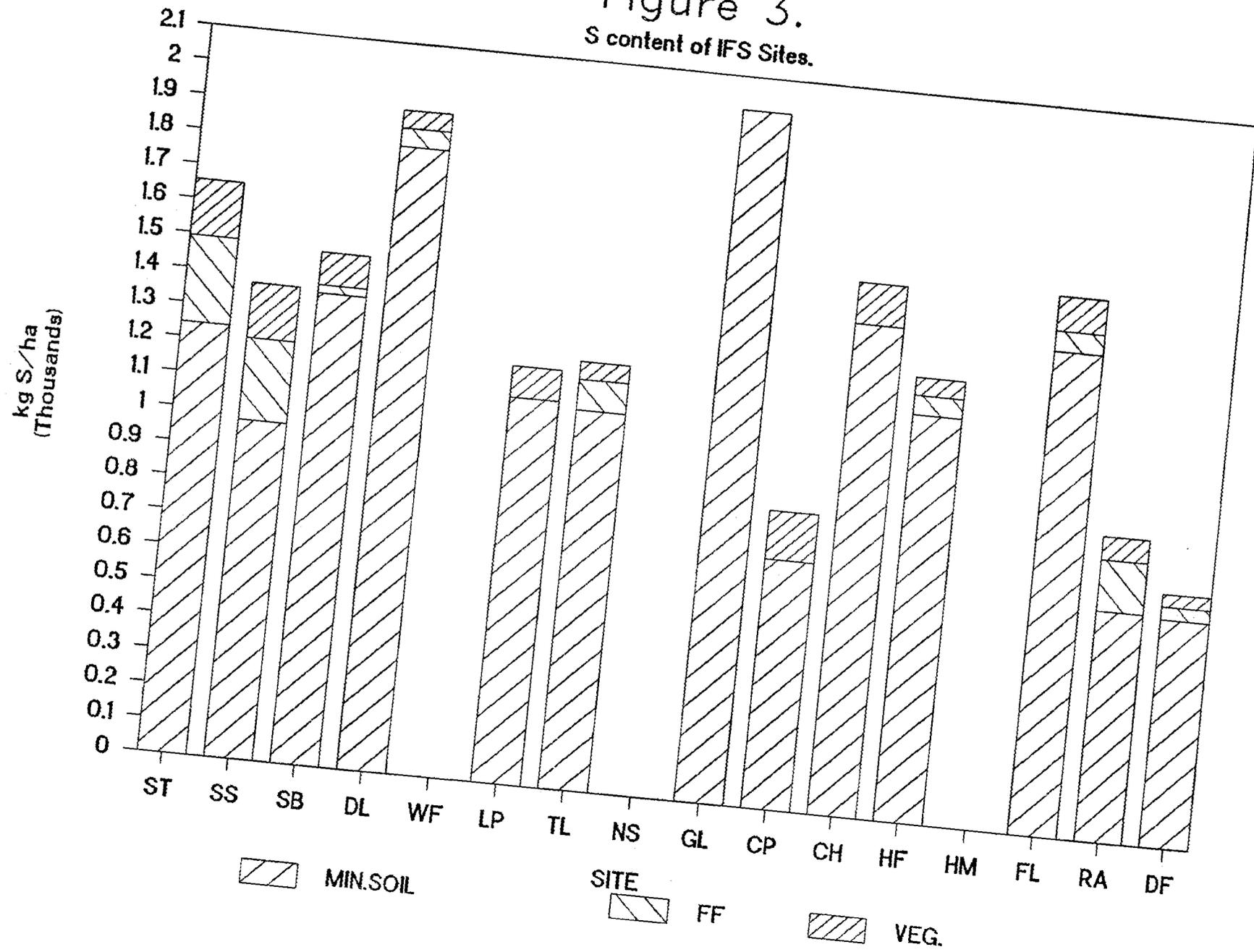


Figure 4.

S Requirement vs. Inputs for IFS Sites

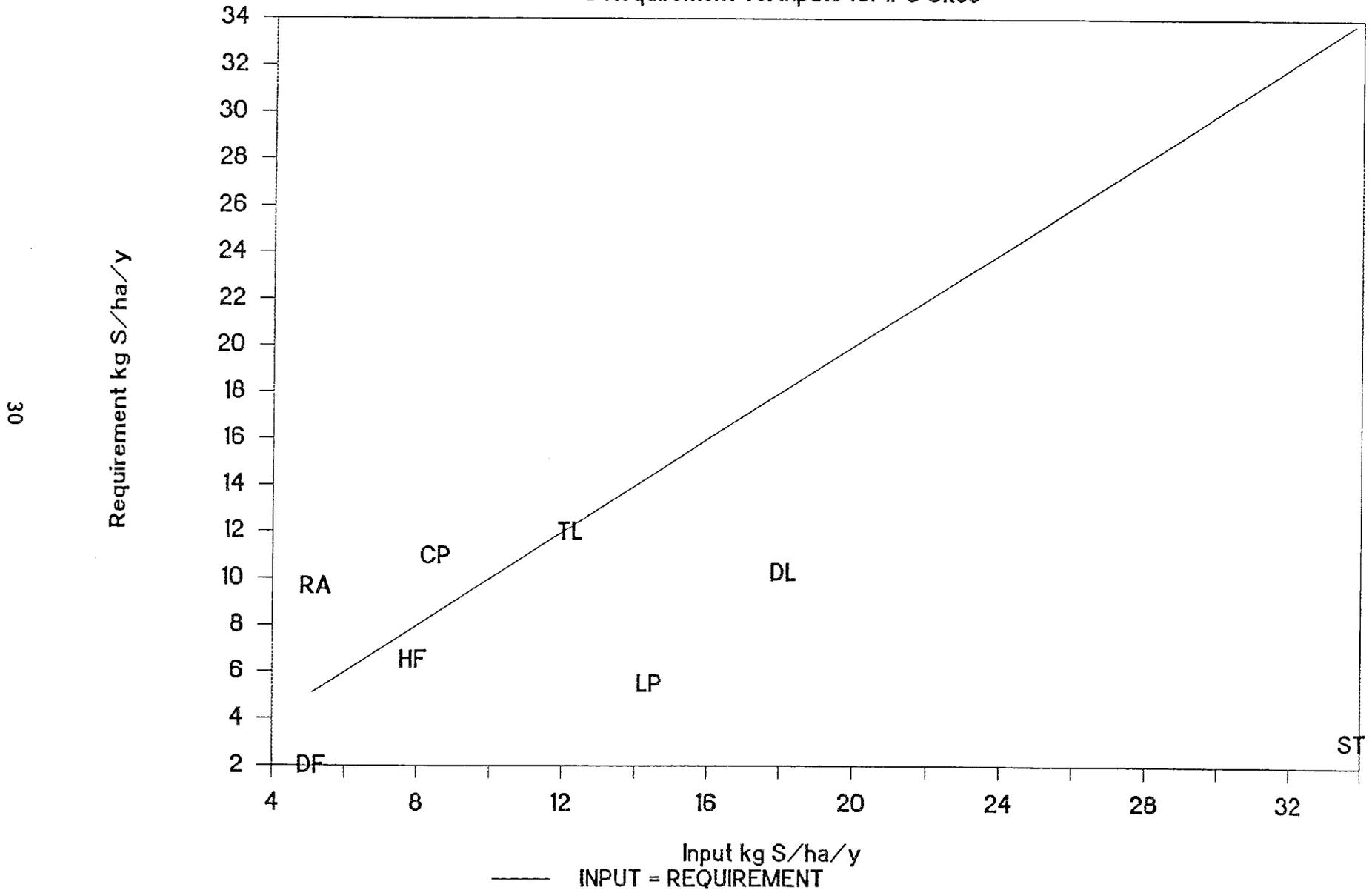


Figure 5.
S Output vs. S Input

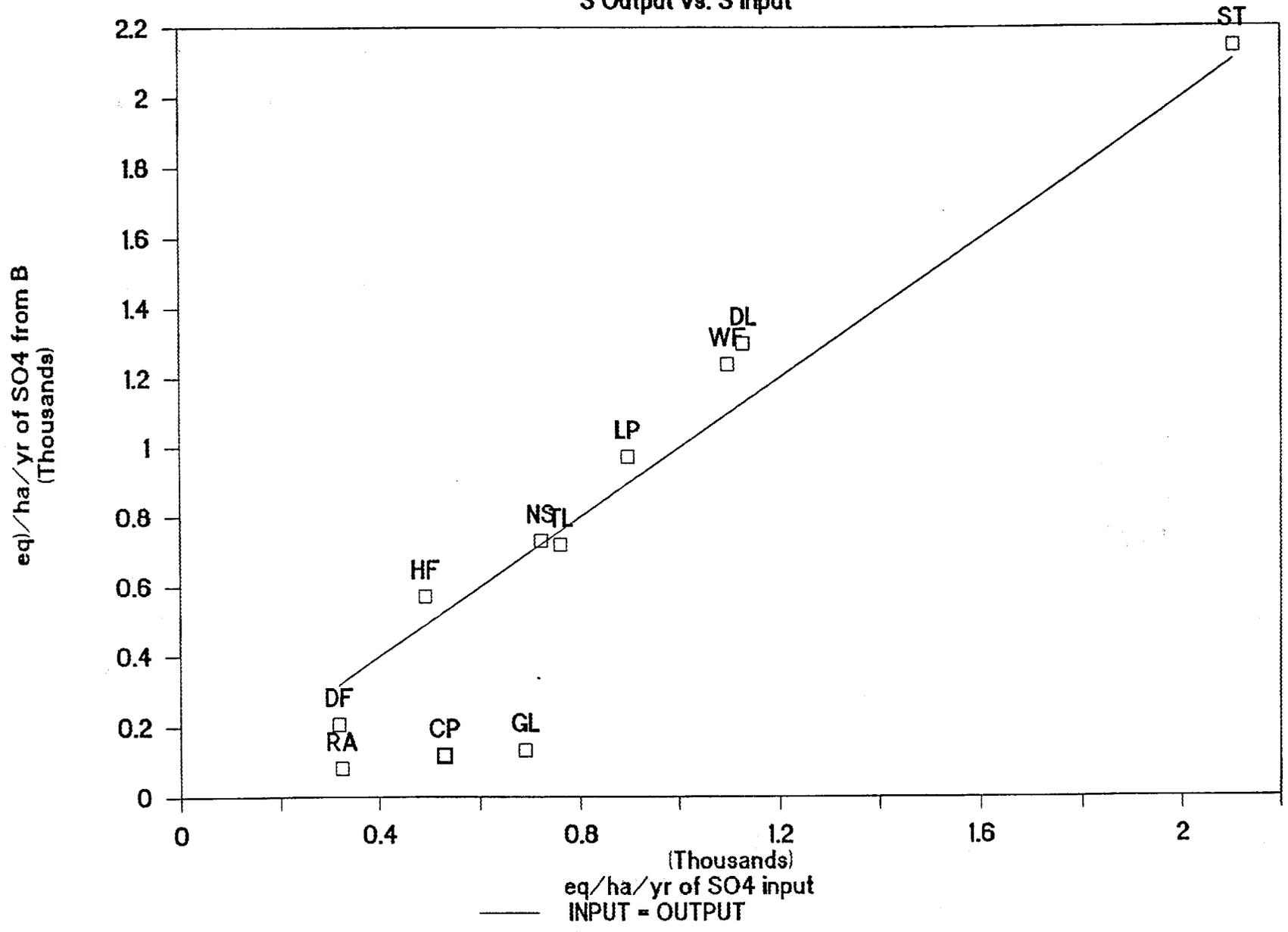


Figure 6.

Net Retention of Sulfate

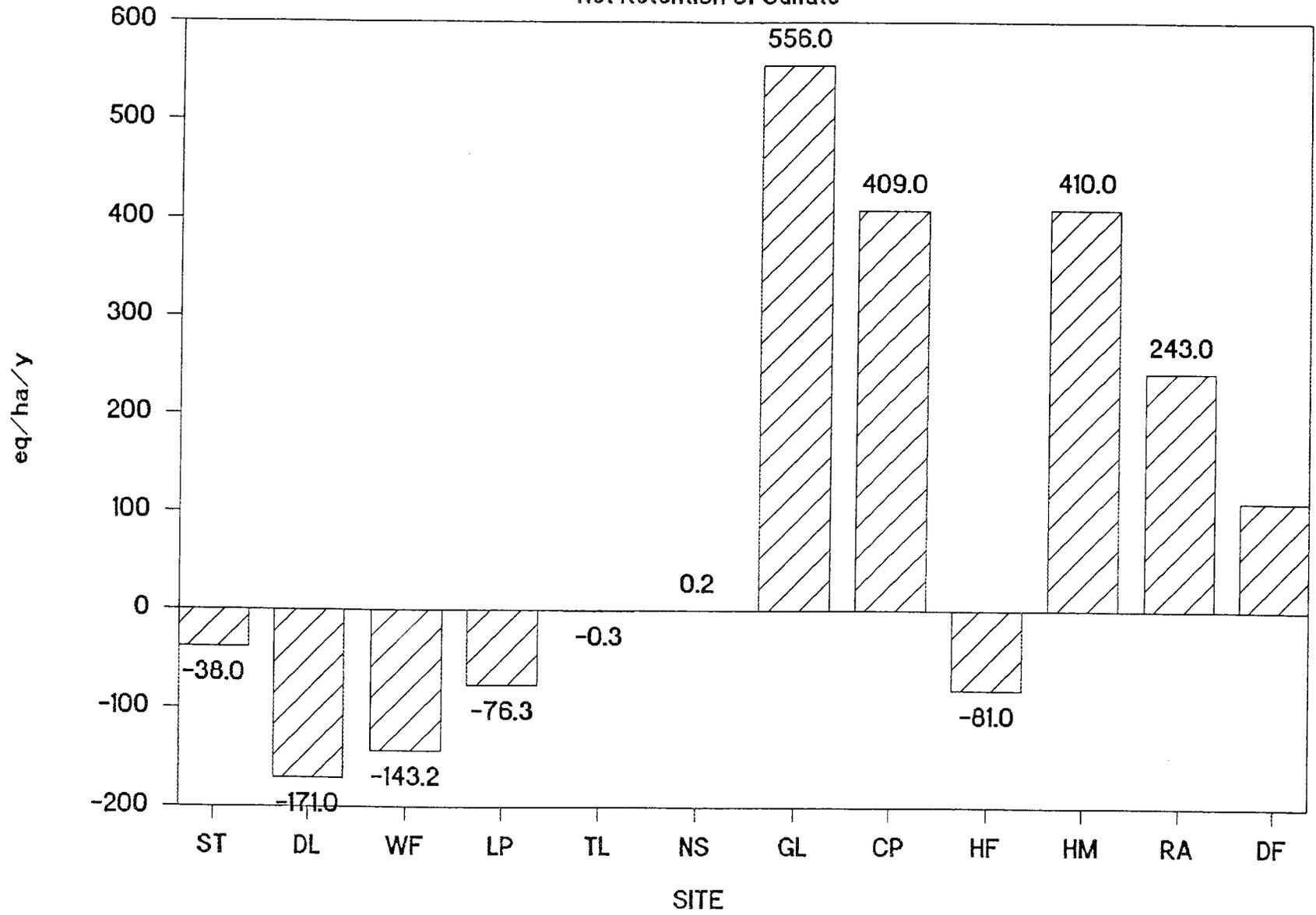


Figure 7.
Isotherm of sulfate adsorption.

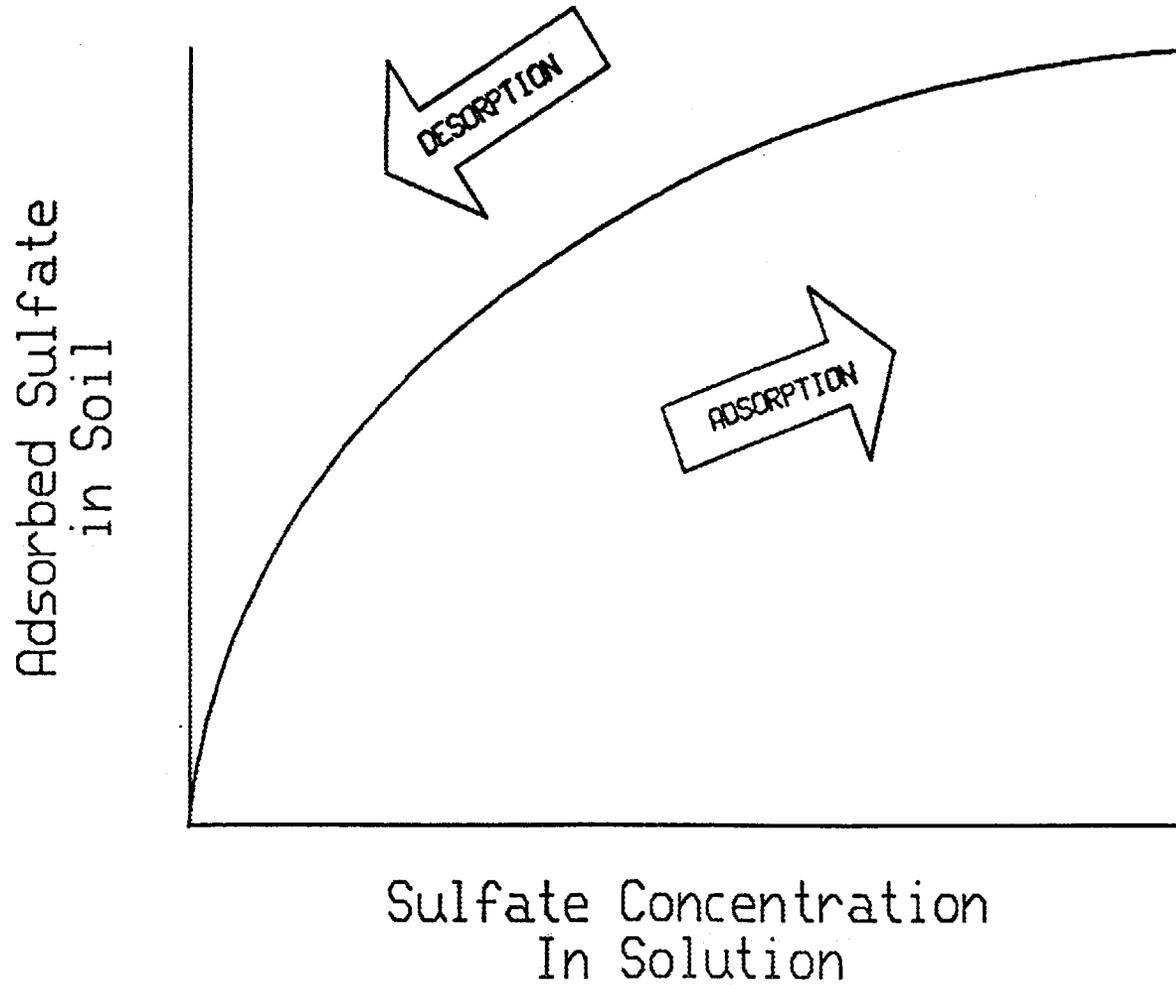


Figure 8.

Sulfate Adsorption vs. Conc. Below B

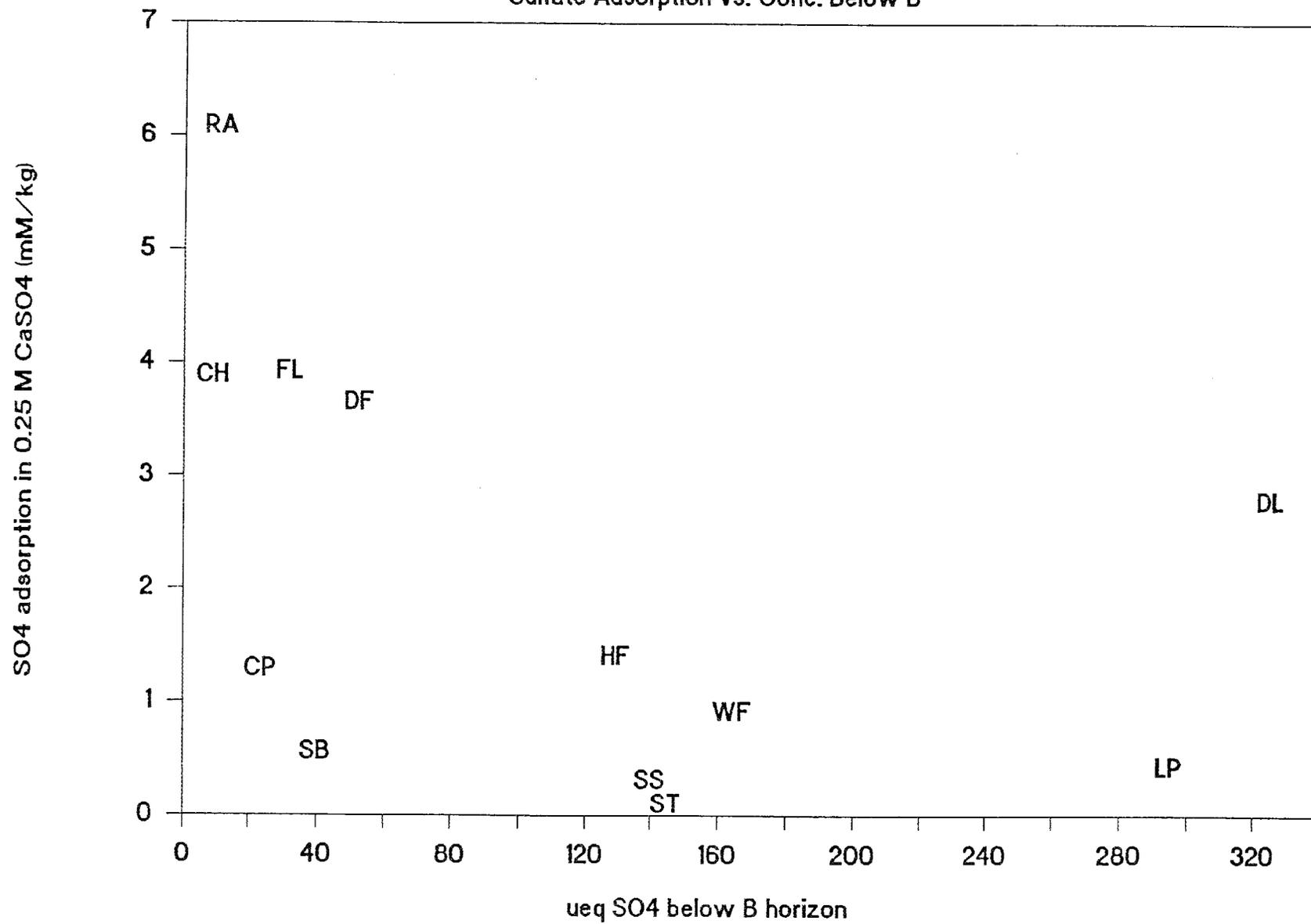


Figure 9
Organic S Formation Potential

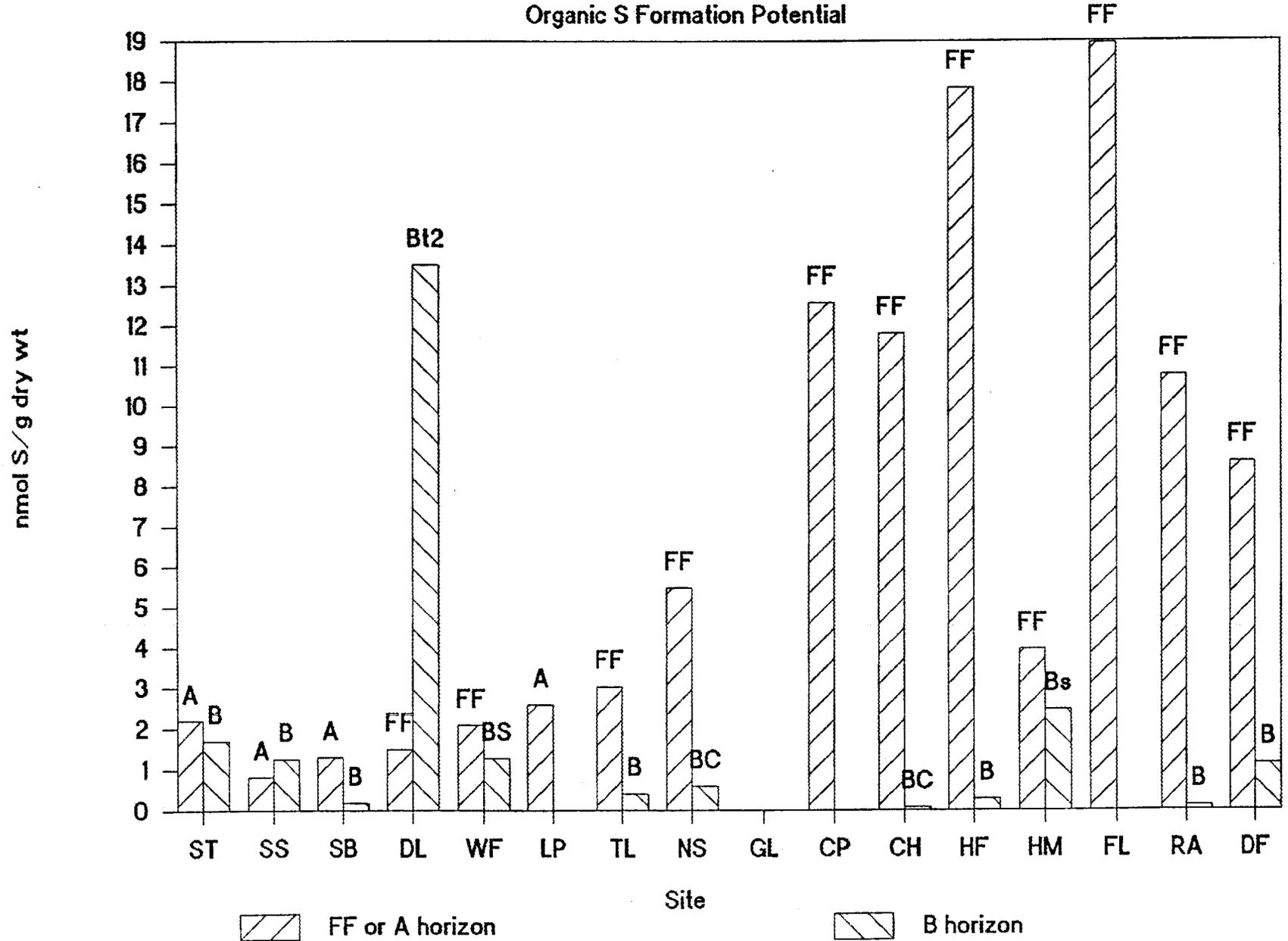
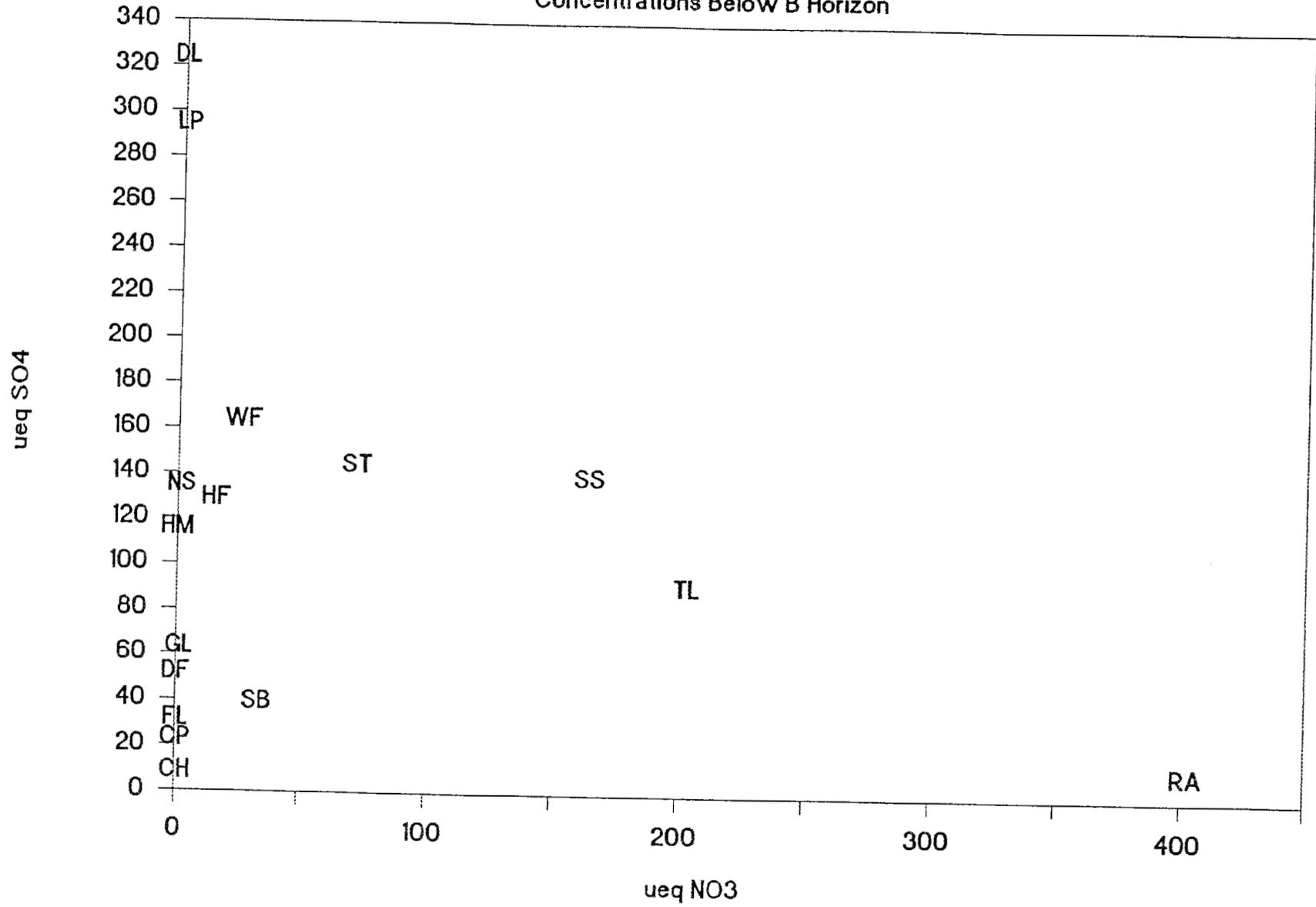


Figure 10.

Concentrations Below B Horizon



4.2 NITROGEN

4.2.1 Atmospheric Deposition and Canopy Exchange of Nitrogen at the IFS Sites 1989 Summary

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This report summarizes the atmospheric deposition of nitrogen species to the IFS intensive deposition sites, and includes the behavior of nitrogen in the canopy as determined by comparing deposition with stemflow and throughfall. The data presented here were collected and analyzed by the principal investigators and site researchers at the various IFS sites. This summary is merely a compilation of their considerable efforts.

The data used here are, for the most part, two-year averages beginning in 1986 and ending in 1988. The exceptions are the Norway Spruce (NS) and B.F. Grant (GL) sites, which have only one year's data (1987-88) available at this time. The precipitation and throughfall fluxes reported here represent wet-only deposition, except for organic N, which in several sites was only measured in bulk deposition. Dry deposition fluxes were estimated using air concentration data, a deposition model, and direct collection of coarse particles, using methods described in the IFS protocols.

We measured atmospheric concentrations of fine-particle NO_3^- and NH_4^+ , plus HNO_3 vapor at these sites. Because of possible artifacts in the simple filter pack we used, HNO_3 vapor may be overestimated and particulate NO_3^- underestimated in these data. Nonetheless, the comparison in Figure 1 shows that atmospheric N is dominated by particulate NH_4^+ , which exists as small aerosols, probably associated with SO_4^{2-} . The concentrations of N ranged from 0.55 to 2.27 $\mu\text{g N/m}^3$ at these sites.

However, Figure 2 shows that the dry deposition of N is dominated by HNO_3 vapor for most of the sites. This occurs because the deposition velocities calculated for HNO_3 vapor are quite high, ranging from 1.1 to 7 cm/s across the sites, while the deposition velocities for fine particles are less than one-tenth as high. Total dry deposition of N is highest at the ST site, where relatively high concentrations, combined with high wind speeds and a high leaf area index, enhance the dry deposition process. While we did not measure NO_2 deposition to these canopies, Hanson et al. (Task A4 report, this volume) estimated this input based on chamber studies and ambient concentration data. Their analysis indicates that NO_2 contributes from 6 (WF site) to 60 (DL site) moles of N/ha/yr to these sites. At the

western sites (DF and RA), coarse-particle nitrate dominates the dry deposition of N.

Figure 3 compares the total deposition of inorganic nitrogen at the sites, including wet, dry, and cloud water deposition. The highest deposition occurs at the two high-elevation sites (ST and WF) because of the cloud water input and the enhanced wet and dry deposition. The N deposition of 1814 moles N/ha/yr at the ST site corresponds to over 25 kg N/ha/yr, a very high deposition rate, especially in view of the fact that the annual N requirement of this forest is only 32 kg N/ha/yr. The lowest deposition values are at the western sites (DF and RA), although it should be noted that biological N fixation at the RA site is a massive N input not accounted for in this graph. Figure 3 illustrates several general trends in N deposition:

1. For low elevation sites in the eastern U.S., total N deposition is about 500-1000 moles N/ha/yr (7-14 kg N/ha/yr).
2. The principal factors causing variation around this general amount are elevation and proximity to NO_x sources (primarily cities).
3. For the eastern low-elevation sites, wet and dry deposition each contribute approximately 50% of the total.

We do not know the reasons for the apparently low wet deposition of N at the GL site or the high wet deposition of N at the NS site. As both of these sites are currently reporting only one year's results, we consider these data tentative until a longer sampling record has been obtained.

Our collections of stemflow and throughfall (TF + SF) permit us to evaluate the behavior of N in the canopies of these forests. We calculate the net canopy exchange (NCE) as $\text{TF} + \text{SF} - \text{total deposition}$. For all of these forests, NCE is negative for both NO_3^- and NH_4^+ , indicating canopy uptake of both ions. Organic N can be a significant fraction of throughfall N, however, so for a total N balance in the canopy we add the organic N component of both wet deposition and TF + SF (we have assumed that dry and cloud water deposition of organic N are negligible). The N balance for the canopies is shown in Figure 4 as a scatter plot of TF + SF nitrogen vs. total N deposition. The GL and DL sites (circled) have no organic N data available; if it were available, the points would move up on the graph. The 1:1 line represents the situation $\text{NCE} = 0$. All points except CP lie below this line, indicating canopy uptake of total N, even with organic N included. The maximum N uptake values are 418 and 357 moles N/ha/yr (5.9 and 5.0 kg N/ha/yr) at the WF and ST sites, respectively. These two high-elevation sites also have the highest canopy biomass of epiphytic lichens, which are known

to take up inorganic N. The nitrogen uptake may indicate that the total N pool in canopy epiphytes is increasing in these canopies, or that the absorbed N becomes particulate litterfall, which is not included in the balance shown in Figure 4. Alternatively, the N may be taken up by the foliage of the trees themselves, and thus contribute to the N nutrition of the forest. The data in Figure 4 do not show any strong relationship between foliar uptake (distance of a point below the 1:1 line) and N deposition.

Figure Captions

Figure 1. Atmospheric concentrations of N species at the IFS sites. FP = fine particle.

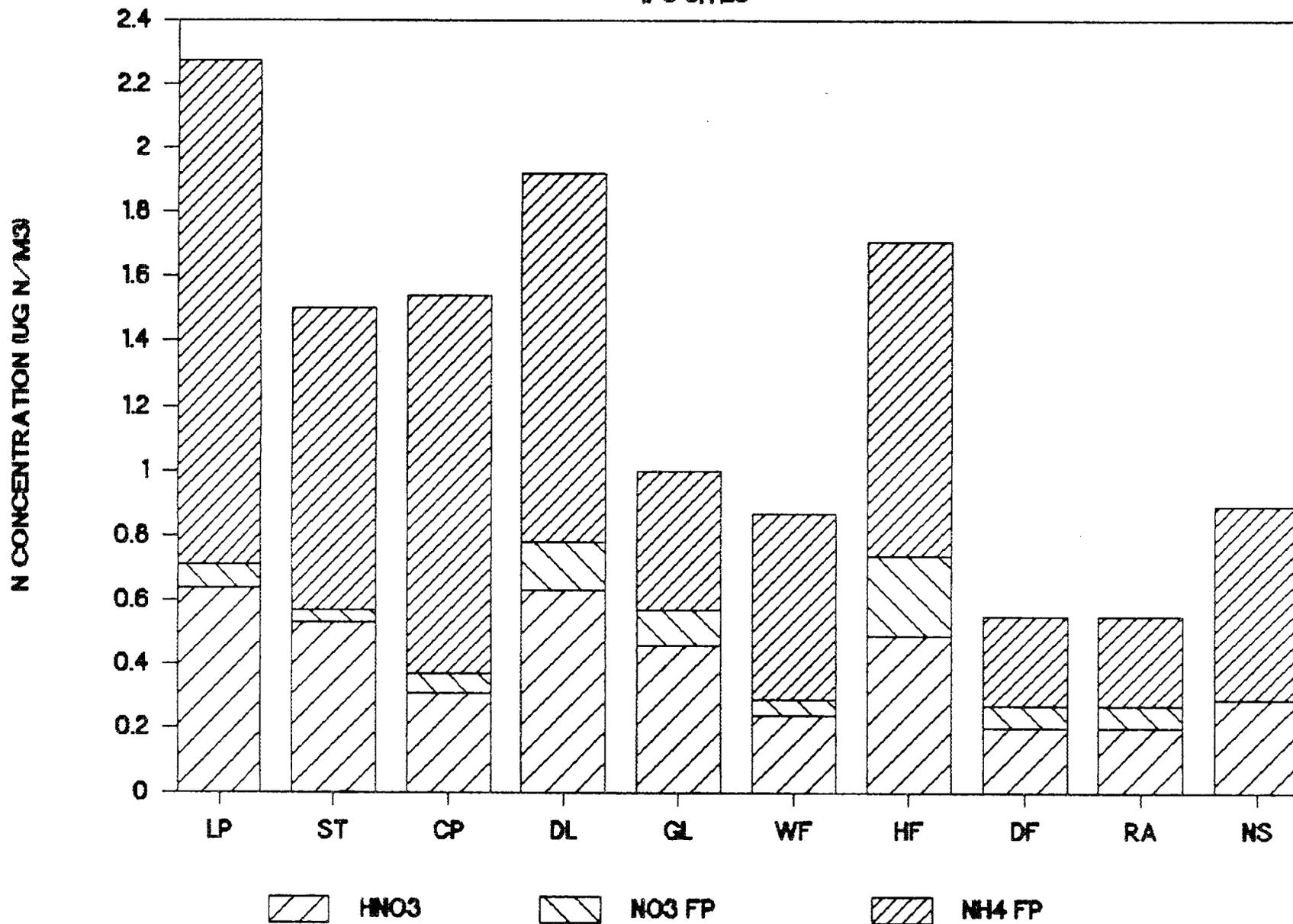
Figure 2. Dry deposition of N species at the IFS sites. FP = fine particle, CP = coarse particle.

Figure 3. Total deposition of inorganic N at the IFS sites by wet, dry, and cloud water deposition processes.

Figure 4. Canopy inputs (total deposition) vs. outputs (TF + SF) of total N (organic + inorganic) at the IFS sites. Line indicates equal inputs and outputs. Circled points had no organic N data available.

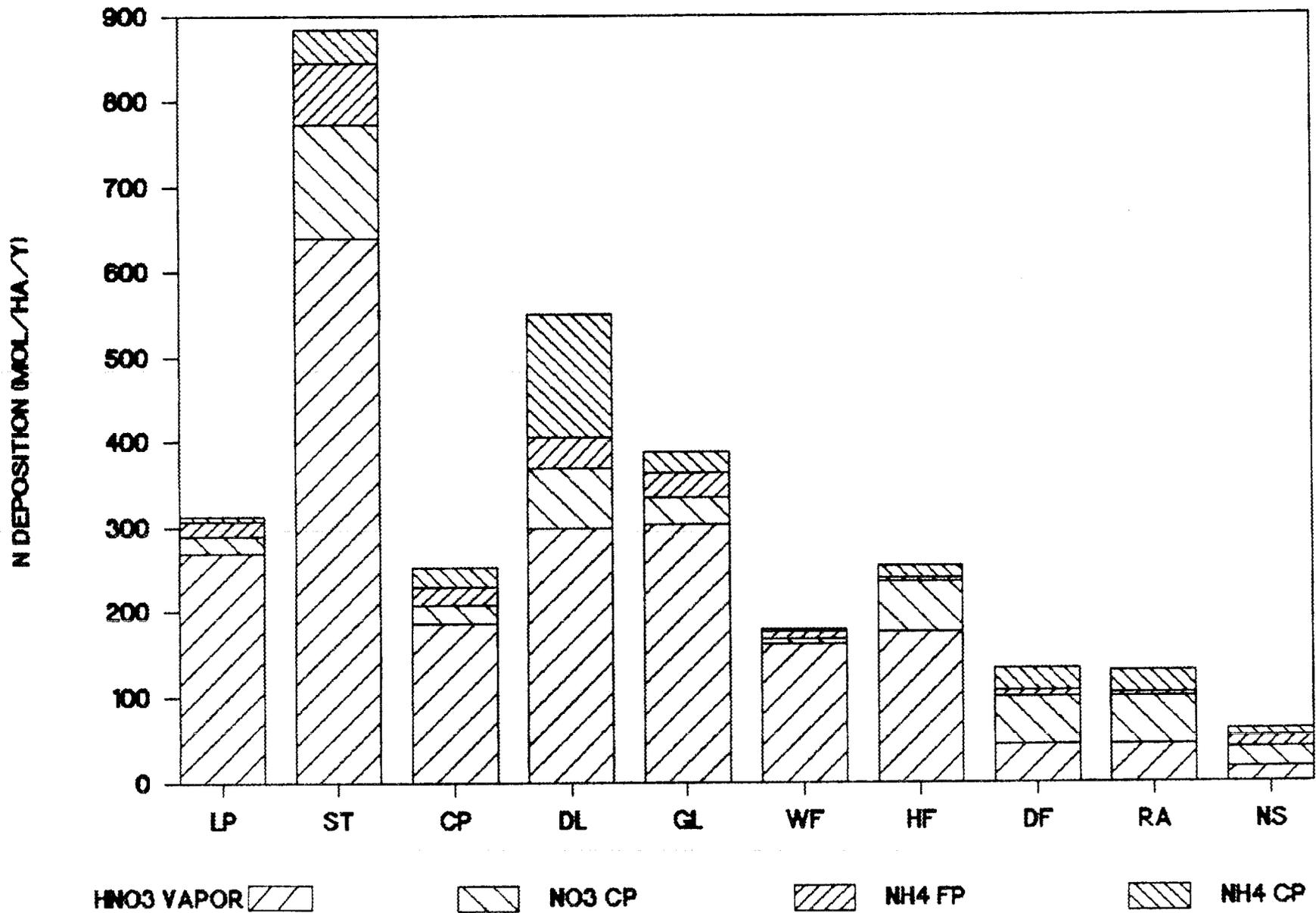
NITROGEN IN ATMOSPHERE

IFS SITES



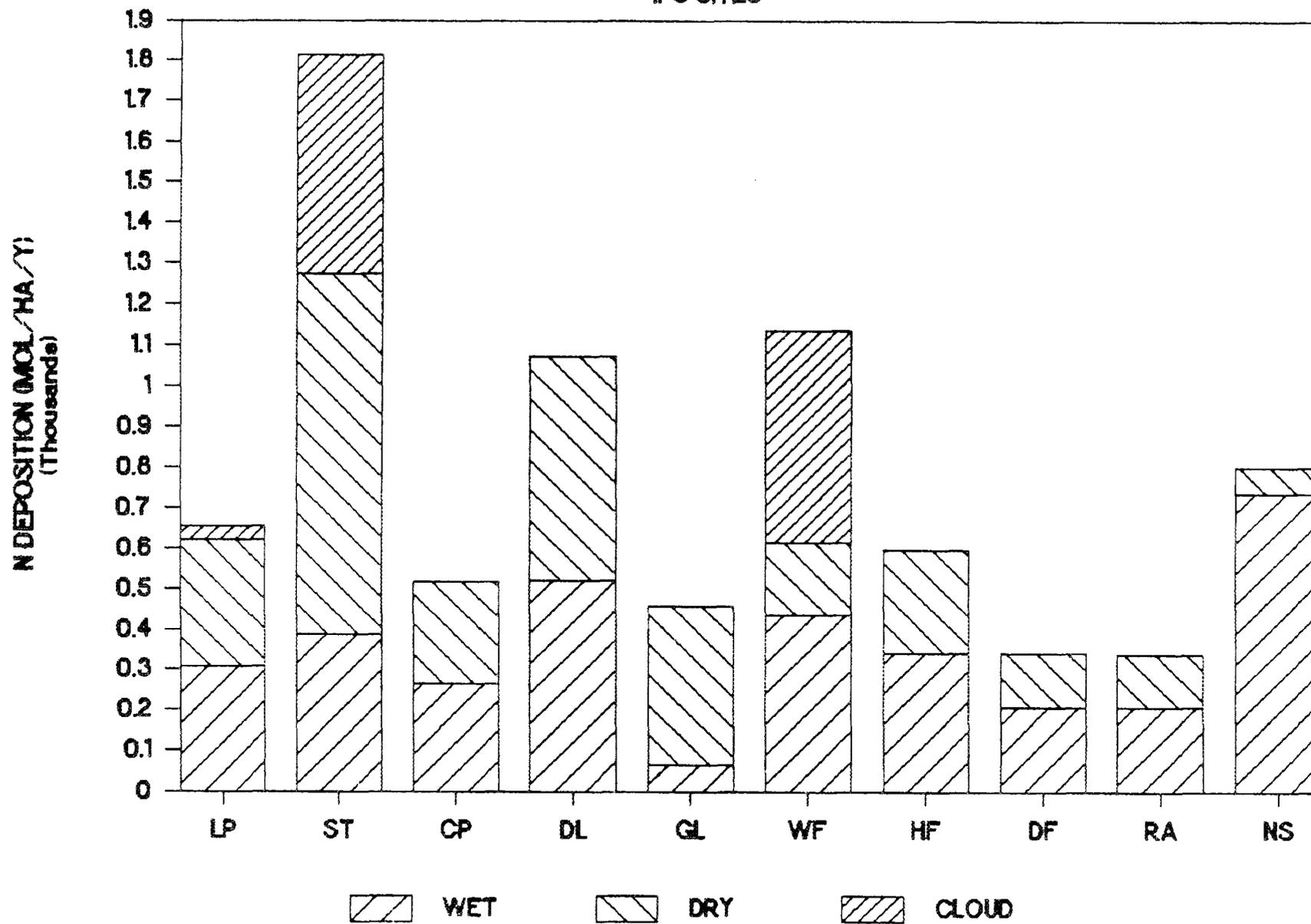
NITROGEN DRY DEPOSITION

IFS SITES



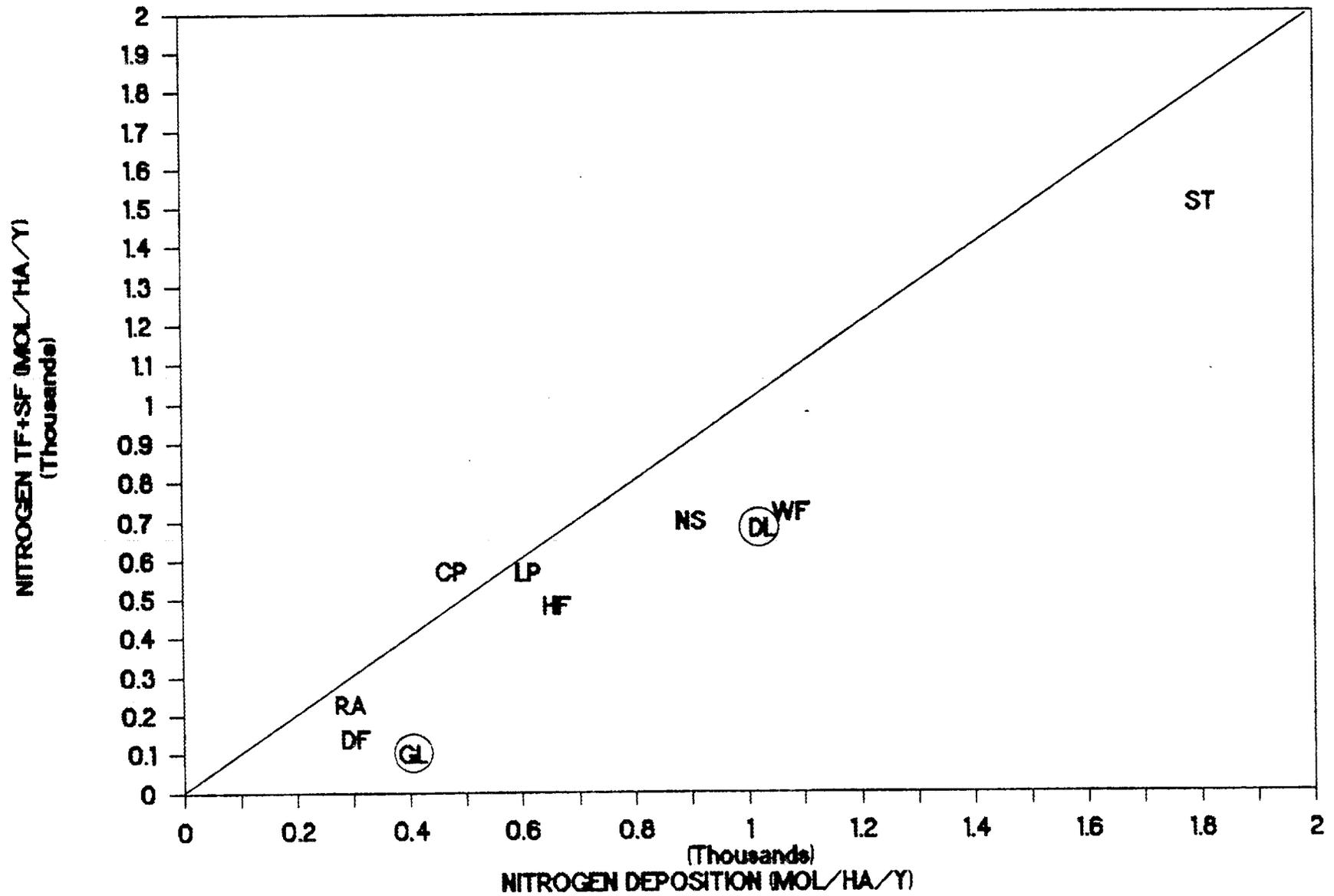
NITROGEN DEPOSITION

IFS SITES



CANOPY NITROGEN INPUTS VS. OUTPUTS

IFS SITES



4.2.2
1989 Summary Report
Nitrogen Synthesis Task

Dale W. Cole, University of Washington
Helga Van Miegroet, Oak Ridge National Laboratory

The primary goal of the N task has been to investigate the role of atmospheric N inputs in causing N saturation and excess NO₃ leaching from forest ecosystems. With two-years worth of dry and wet N input and soil solution data now available, and nutrient pools and fluxes better defined for most of the IFS sites, we are now in a position to better evaluate patterns which emerge from this integrated study. The following set of study questions were used in the analysis and refer to the source or origin of N saturation:

- (1) Are there IFS sites where active NO₃ leaching is currently taking place?
- (2) Do these N-saturated sites follow a consistent pattern?
- (3) Does atmospheric N deposition add to this NO₃ leaching?

As to the first question, a simple ranking of the IFS sites by NO₃ leaching output (Fig. 1) demonstrates that some IFS sites are clearly leaching large amounts of NO₃-N, whereas there are others that show little or no N leaching loss. Although the Smokies sites (SS, ST and SB) rank among the highest both in terms of atmospheric N deposition and NO₃ leaching rates, and low NO₃ leaching are generally observed in sites at the lower end of the N input scale (e.g., DF, CP, CH), two-year averages for total input and output fluxes reaffirm the earlier suggestion that no strong direct correlation between total N input and N leaching output exists (Fig. 1 and 2). Indeed, at some of the the Smoky Mountains sites (SS) and the Turkey Lakes site in Ontario (TL), leaching losses far exceed annual atmospheric N input rates, while at Whiteface (WF) N leaching is substantially lower than in the Smokies sites despite similar high N inputs. Net N retention is also observed for most of the other IFS sites, except for the red alder (RA) site in Washington (Fig. 1).

This suggests that although the N input regime may contribute to N saturation and NO₃ leaching, additional sources and sinks within the ecosystems must certainly be considered. There are several features that characterize the sites that rank high on the NO₃ leaching scale: First of all, they all have larger amounts of N accumulated in the forest floor and mineral soil in contrast to the sites at the lower end of the N output scale (Fig. 3). In the case of alder (RA), this N accumulation has occurred over a fairly short time period and is the result of large N inputs from the atmosphere via N-fixation (in the order of 50-100 kg/ha). For the other "N-saturated" sites, the N accumulation likely took place more slowly, and over a longer geological time period.

Associated with the higher total N contents are higher N mineralization and nitrification rates. For most of the sites, data from the field incubation experiments are now available for at least one full year, either from quarterly or monthly measurements. Although the buried bag technique has its limitations in terms of providing a real measure of

mineralization rates occurring in the field, and spatial variability was often very high, the numbers obtained were nevertheless useful for comparison between sites. The IFS sites represent a wide array of soil mineralization and nitrification rates, but once again sites with the highest NO_3 leaching rates generally rank the highest in terms of calculated annual nitrification rates in the upper soil and forest floor (Fig 4). At Whiteface (WF) only forest floor mineralization and nitrification rates from nearby sites were available from an earlier observation period. They indicated low nitrification potential in the forest floor, despite elevated forest floor N levels and mineralization rates in the order of those calculated for the spruce sites in the Smokies (SS and ST). Even though no N transformation processes were directly measured in the soil, low nitrification rates are also expected in the mineral soil.

In spite of the many similarities between the spruce forests at Whiteface (WF) and in the Smoky Mountains (ST and SS), especially in terms of N input regime and total N contents (Fig. 1 and 3), tree N uptake rates are significantly higher at Whiteface (Fig. 5). These higher N demands by the vegetation at the latter site could help to explain lower nitrification potential and NO_3 leaching rates, compared to the Smokies sites where the lowest N uptake among the IFS sites are observed (Fig. 5). Nitrogen uptake rates greater than or equal to annual mineralization estimates at, for example, the North Carolina sites (CP, CH, DL) coupled with relatively low total soil N contents are indicative of systems still at the stage of active N accumulation and illustrate the potential role of N uptake in curtailing NO_3 leaching. Conversely, the Turkey Lakes results illustrate that those same N uptake rates may be insufficient to effectively limit NO_3 leaching from systems which have large amounts of N already accumulated in the soil, and now release part of these large pools through mineralization. At this point, it is not entirely clear why the Huntington forest site (HF), which bears many similarities with the Turkey Lakes site (e.g., N input, total N content, high N mineralization and nitrification rates in excess of tree N uptake) is not showing larger NO_3 leaching losses, especially in view of the lower N uptake rates.

Integrating the above information on N dynamics, the IFS sites can basically be divided into three categories according to total (past) N accumulation and the potential for N inputs to cause N saturation and accelerated NO_3 leaching (Fig. 6). The first category consists of forest systems at the lower end of total ecosystem N content (either because soils are still relatively young, or because organic C and N pools have been reduced through prior disturbances) and which are still actively immobilizing N in the soil, forest floor and biomass. Nitrification is generally limited in such systems mainly due to N substrate limitation. Such systems can be called relatively stable, in that no or little NO_3 leaching takes place and N inputs are unlikely to cause accelerated NO_3 leaching losses. A whole array of IFS sites belong to this category as indicated in figure 6. At the other end of the spectrum are those ecosystems characterized by large past accumulation of organic matter and N, either over a long period without significant reduction of the organic C and N pool through disturbances, or relatively rapidly through the presence of N-fixers. Such systems are N saturated in function of their current C content, and N immobilization in organic matter has reached its upper

limit. Consequently, competition for N among the organisms is low, mineralization and nitrification rates are high, and NO_3 leaches out of the system. Nitrogen inputs are no longer completely retained, and atmospheric N deposition may add significantly to N saturation and NO_3 leaching. Stand age and vigor also play a critical role in the regulation of NO_3 leaching: In young stands N uptake for biomass increment will be able to curtail NO_3 leaching losses somewhat, but in stands at the end of their natural life cycle N uptake is generally insignificant, and stand disturbance with tree mortality may actually further accelerate N release via mineralization. The site in the Smoky Mountains and at Turkey Lakes, and the red alder forest in Washington belong to this category.

Finally, there are those sites which occupy an intermediate position from the standpoint of N capital, N input rates and forest growth. Ecosystems are at a transition with respect to N saturation when N accumulation is approaching its upper limit but NO_3 leaching rates are still significantly lower than annual N input rates. In such systems, a change in N retention via tree uptake (e.g., through aging of the stand) and/or a change in the atmospheric N deposition regime can be critical in that it may cause the system to become N saturated and leach excess $\text{NO}_3\text{-N}$. Both the Huntington Forest and the spruce forest on Whiteface Mountain can be considered in this category.

In the next analysis step we can then look at the effect of N saturation as expressed by the following questions:

- (4) To what extent does NO_3 leaching change soil and solution properties?
- (5) Will these changes affect ecosystem productivity?
- (6) Are these changes reversible, will the system recover, and if so, over what time period?

The potential effects of nitrification and NO_3 leaching on soil and solution properties that need to be considered are:

- A decrease in soil solution pH caused by the proton release during nitrification
- An increase in the ionic strength of the soil solution during periods of peak nitrification and NO_3 leaching
- An increase in solution Al activity associated with the increase in ionic strength and displacement reactions from the cation exchange complex of acid forest soils
- An increase in exchange acidity and a decrease in soil base saturation due to cation displacement by H^+ produced during nitrification followed by cation leaching through the soil profile in association with mobile NO_3 .
- A decrease in soil pH due to the changes in the exchange complex listed above
- Change in nutrient availability (e.g., P) due to changes in soil and solution pH listed above

Some of these projected changes were indeed observed in the alder (RA) site in Washington which has been receiving large amounts of atmospheric N over a 50-year-period via N-fixation and where the highest nitrification and NO_3 leaching rates among the IFS sites have been measured. As to possible recovery from N saturation and nitric acid input, results from the

alder forest conversion experiments in Washington have shown that a reduction in N input (in this case through the removal of the symbiotic N-fixers) has caused a significant decrease in NO_3 solution concentration at all collection levels, and a concomittent decline in base cation leaching which has persisted for at least four years. However, no significant changes in solution pH or Al concentrations have been observed sofar and soil properties have not yet been remeasured. Such results indicate that recovery is indeed possible, but that the recovery of some properties clearly takes longer than others. On the other hand, the repercussions of nitrification and NO_3 leaching on nutrient availability and eventually on site productivity are not entirely clear yet and are currently still under investigation.

TOTAL N INPUT AND OUTPUT FLUXES

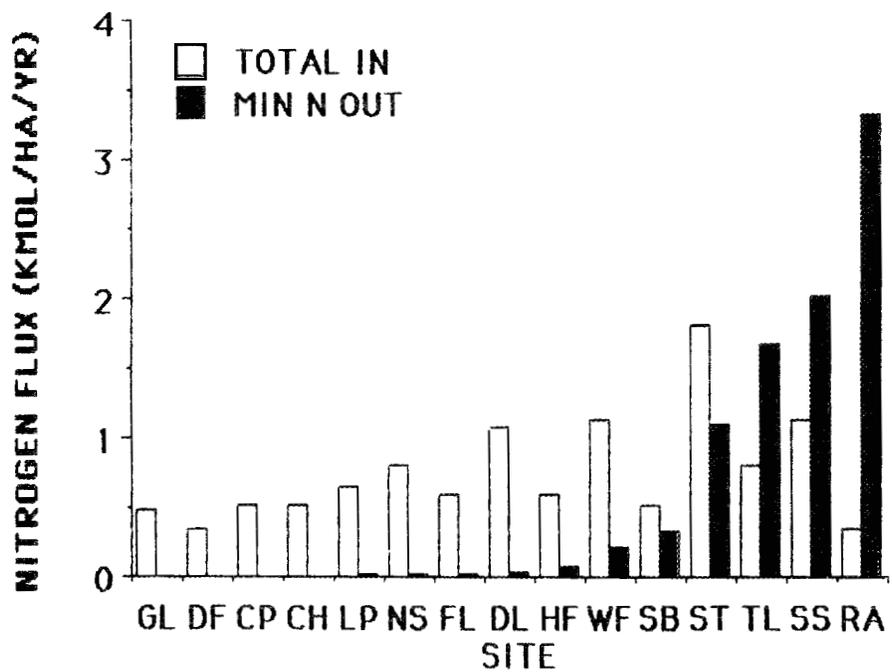


Figure 1. Two-year average total N input (wet + dry deposition) and N output via leaching of $\text{NH}_4 + \text{NO}_3$ at the EPRI-IFS sites ($\text{kmol ha}^{-1} \text{yr}^{-1}$).

NITROGEN OUTPUT VS TOTAL INPUT

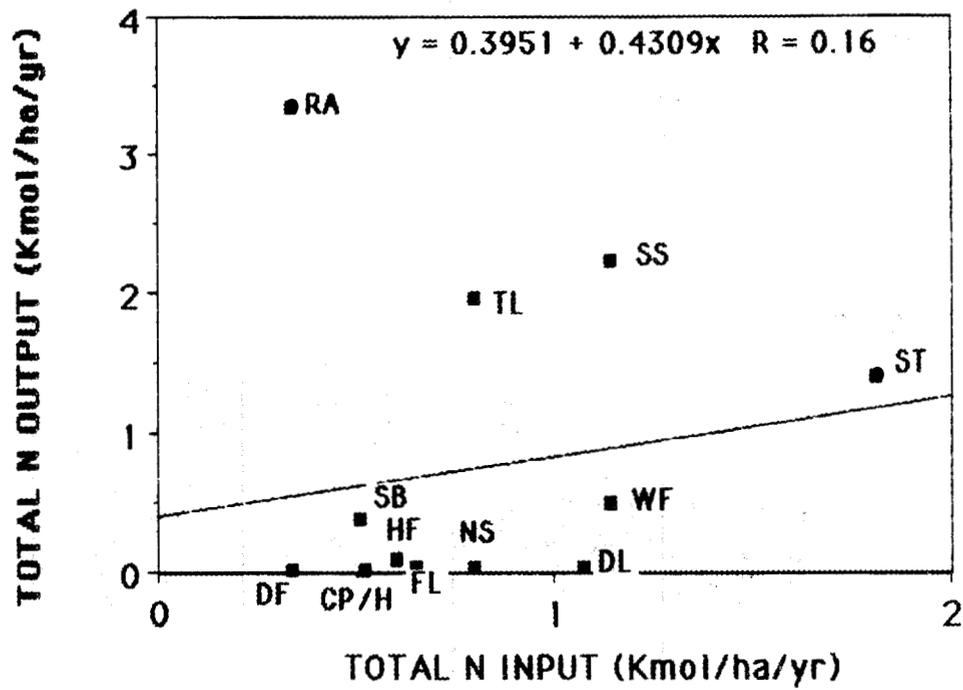


Figure 2. Total N output vs. total N input with correlation coefficient at the EPRI-IFS sites.

SOIL AND FOREST FLOOR N CONTENT

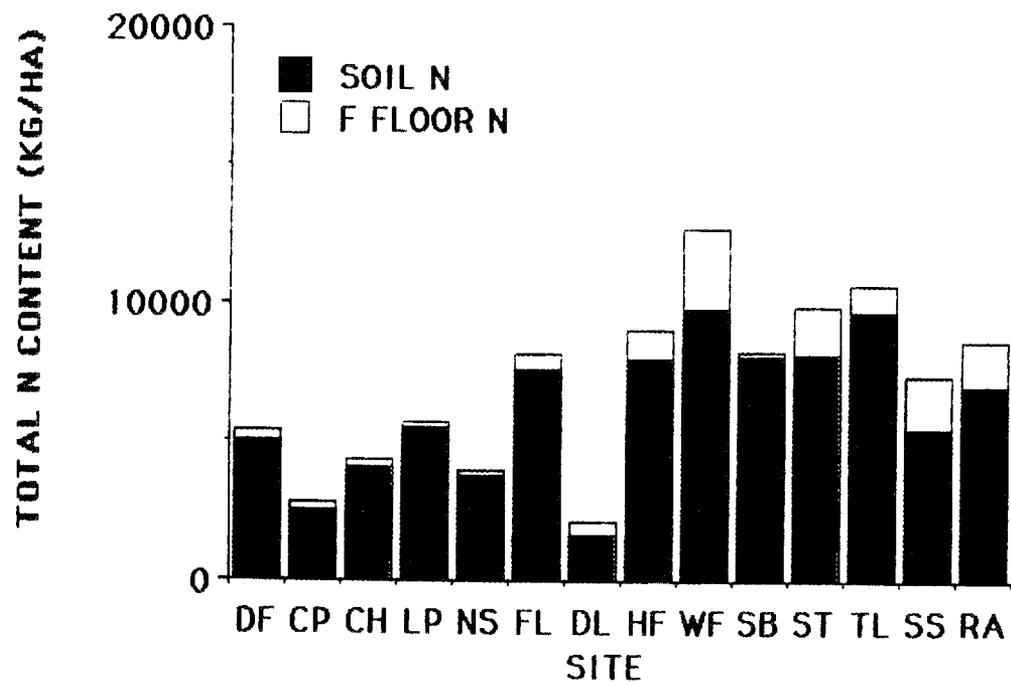


Figure 3. Total soil and forest floor nitrogen content (kg ha^{-1}) for the EPRI-IFS sites ranked by annual N leaching output.

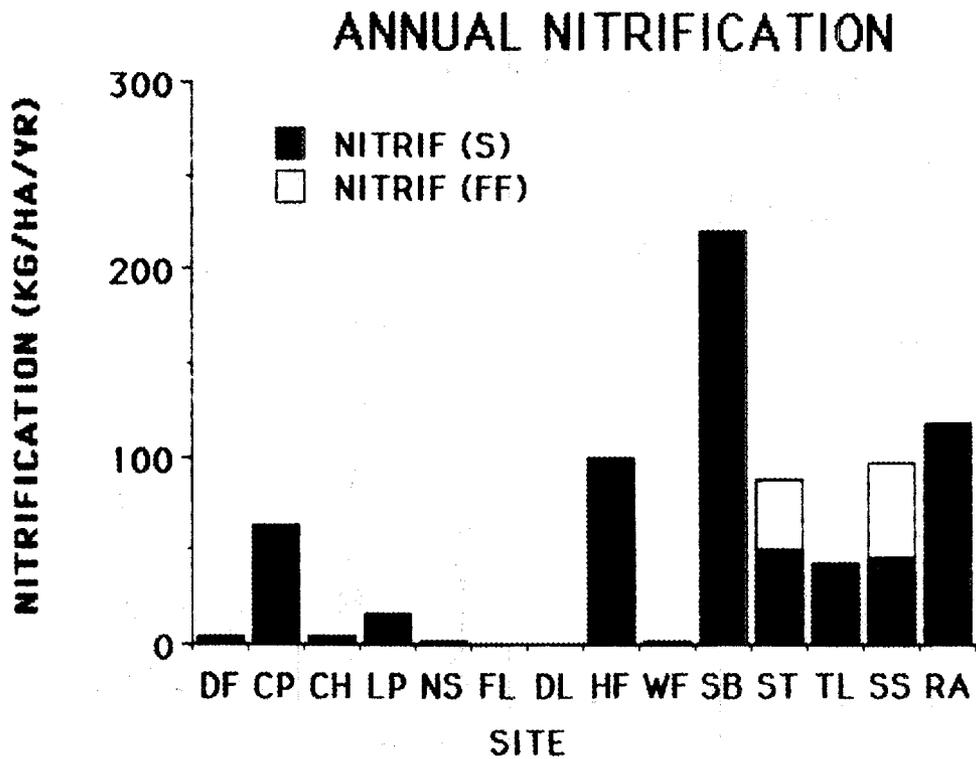


Figure 4. Calculated annual nitrification rates ($\text{kg ha}^{-1} \text{ yr}^{-1}$) in the upper 10 cm of the mineral soil and the forest floor of the EPRI-IFS sites ranked by annual N leaching output.

N RELEASE AND RETENTION FLUXES

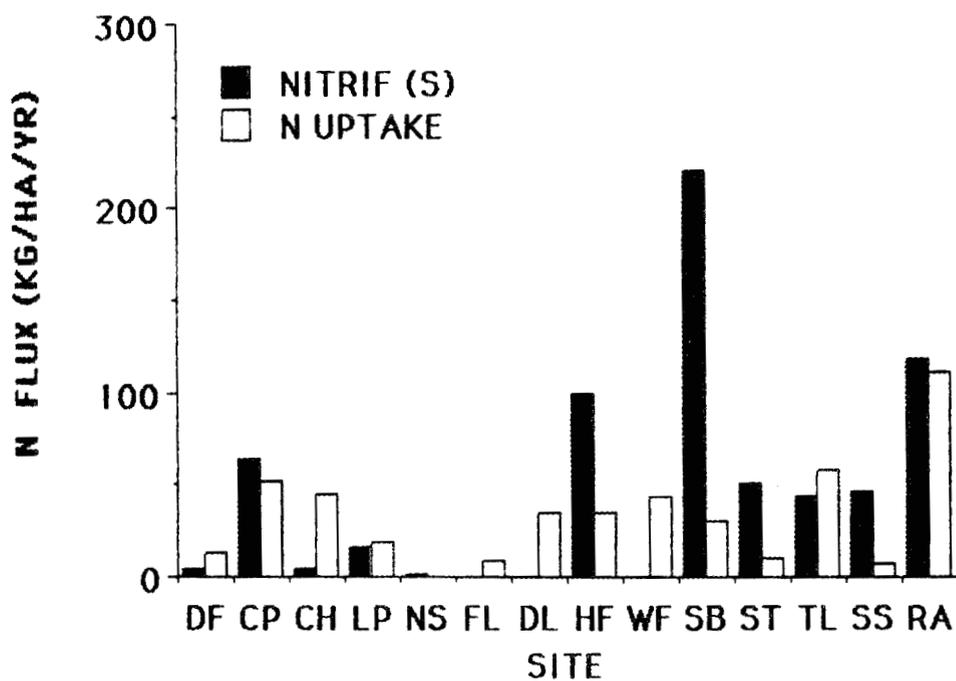


Figure 5. Calculated annual nitrification in the upper 10 cm of the mineral soil compared to N uptake by the overstory vegetation in the EPRI-IFS sites ranked by annual N leaching output.

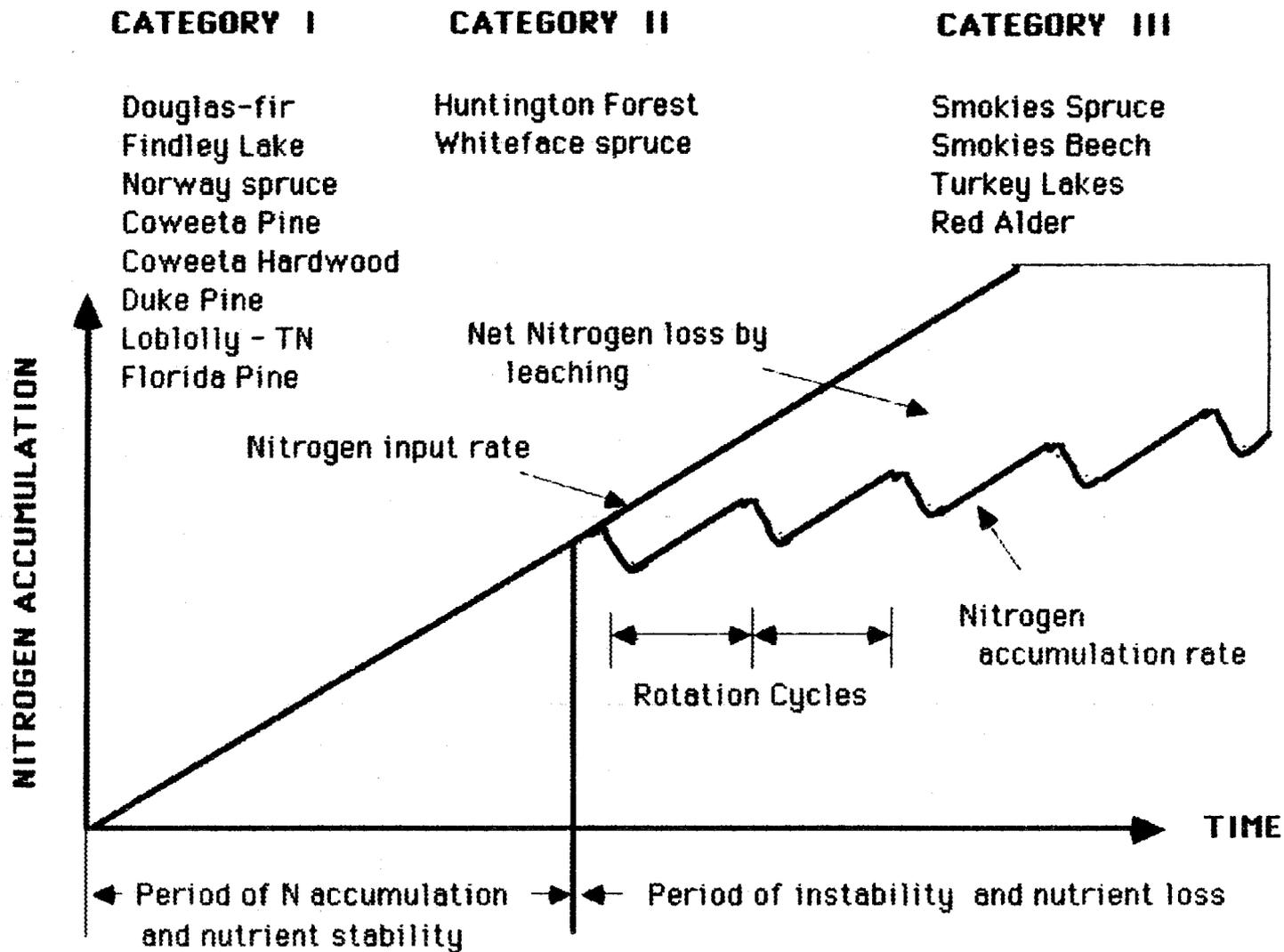


Figure 6. Schematic representation of the EPRI-IFS sites with respect to N accumulation, N saturation, and the potential impact of atmospheric N input on NO_3 leaching.

4.3 HYDROGEN ION

4.3.1

ANNUAL H⁺ ION DEPOSITION AND CANOPY EXCHANGE - IFS SITES 1987/88

by

Kenneth R. Knoerr and Paul S. Conklin

Duke University

Annual H⁺ ion precipitation wet deposition ranged from a low value of about 250 eq/ha/yr at the pacific northwest DF/RA sites to nearly 740 eq/ha/yr at the DL and NS sites (Fig. 1). While there was a wide variation in this deposition, there was only a small variation in the amount of precipitation in which it was received. Thus, there was a poor correlation between H⁺ wet deposition and the amount of precipitation (Fig. 2), while there was a good correlation between H⁺ wet deposition and the H⁺ ion concentration of the precipitation.

For some of the sites the precipitation ratio of H⁺/(SO₄²⁻ + NO₃⁻) was close to 1, indicating a near balance between the acidity and the sulfate and nitrate ions (Fig. 3). However, for other sites, this ratio was considerably less than 1. In these cases the precipitation acidity was partially neutralized by base aerosols or some of the sulfate and nitrate ions were from non-acidic sources. For most of the sites the sulfate source was about one and one-half to three times the nitrate source of H⁺ ions (Fig. 3).

H⁺ dry deposition was dominated by the two gaseous components, SO₂ and HNO₃ (Fig. 4). Fine particles generally contributed an insignificant amount of acidic deposition. The largest amount of dry deposition occurred at the southeastern sites which have frequent air mass source trajectories from the Ohio Valley (Fig. 4).

For many of the sites total H^+ deposition was about equally divided between wet deposition and dry deposition (Fig. 5). Exceptions were the DF/RA, NS and WF sites where dry deposition was somewhat less than wet deposition. At the two high elevation WF and ST sites, H^+ cloud water deposition accounted for about half of the total H^+ wet deposition (Fig. 5).

Canopy exchange generally depleted H^+ ions. Thus, the precipitation reaching the forest floor as throughfall and stemflow had less H^+ ions than the total deposition (Fig. 6). The exceptions were the DF and ST sites where there was almost no net canopy exchange. The canopy exchange (depletion) of H^+ ions was not related to either total wet H^+ deposition (Fig. 7) or the H^+ ion concentration of precipitation (Fig. 8).

H+ Precipitation Deposition

ppt deposition vs ppt depth

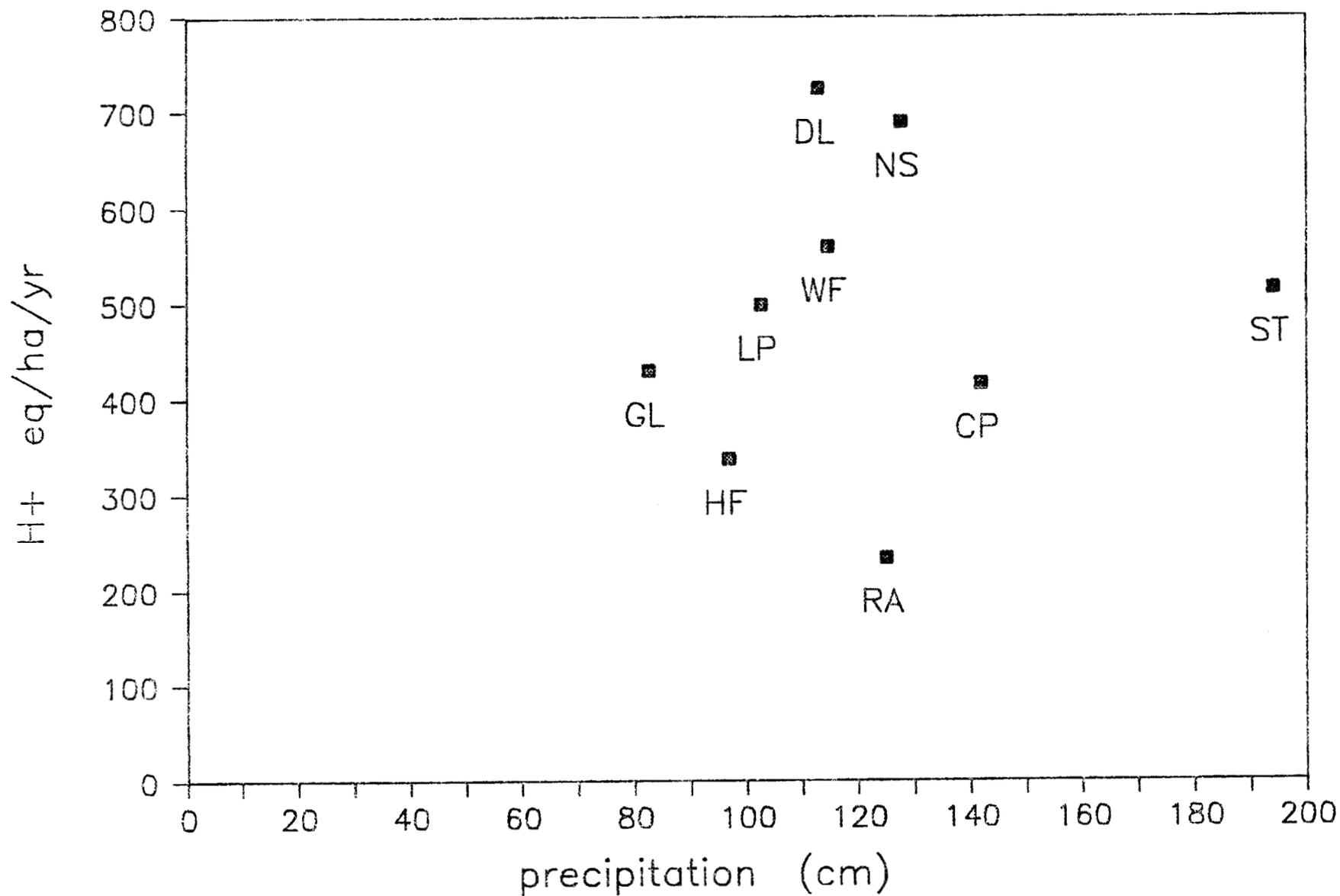


Figure 1

H⁺ Precipitation Deposition deposition vs. concentration

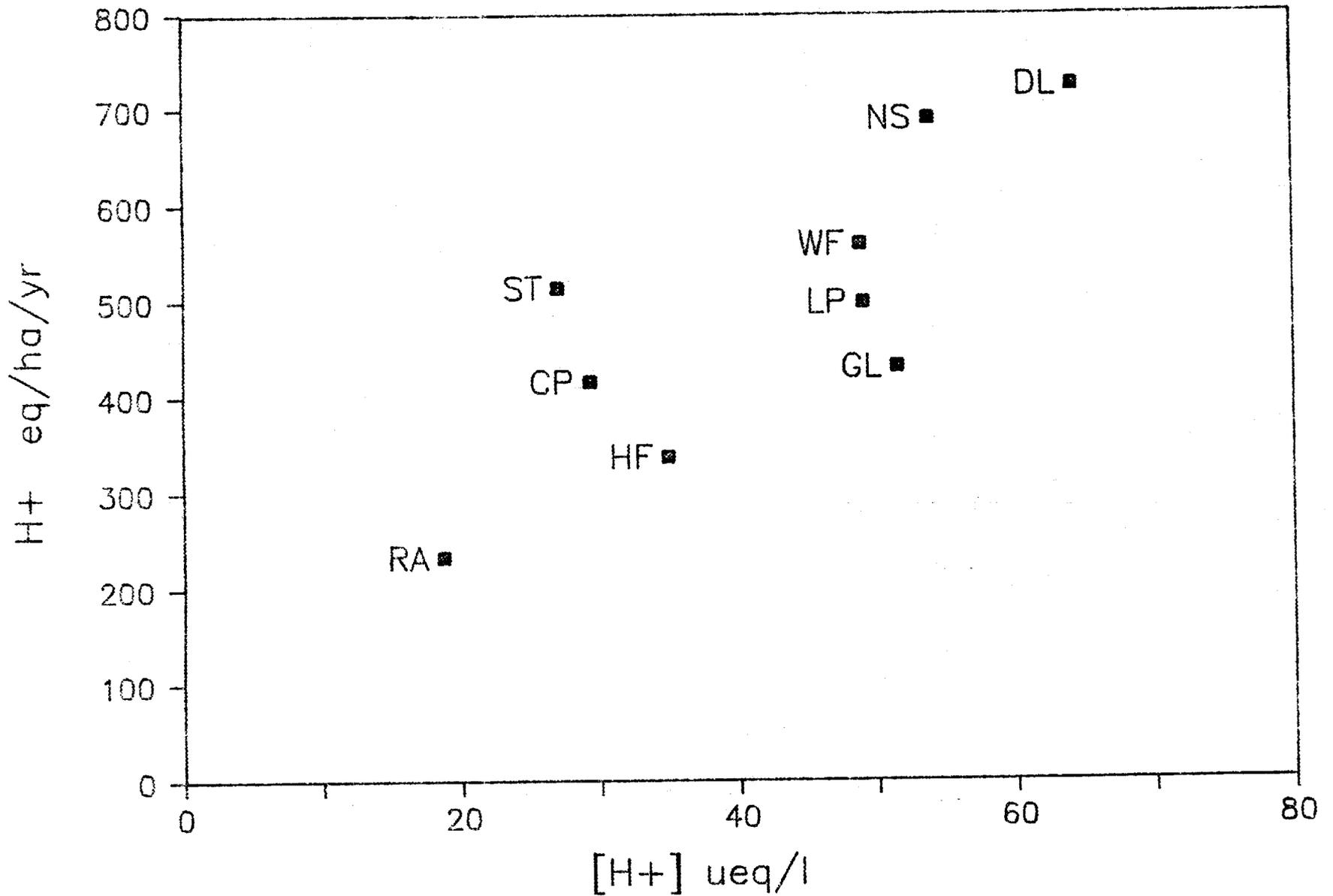
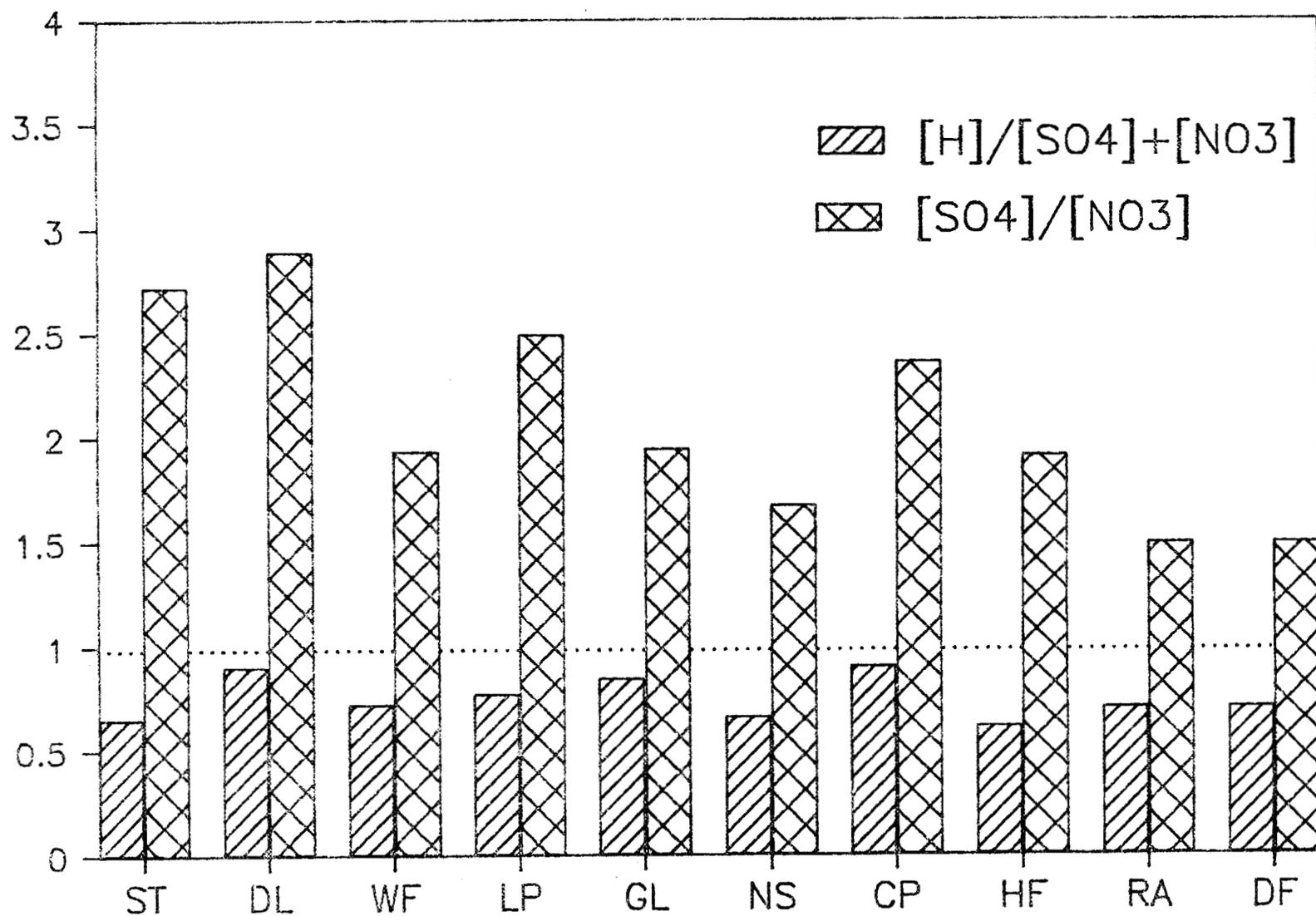


Figure 2

Precipitation Ion Ratios

deposition components



H+ Dry Deposition Sources

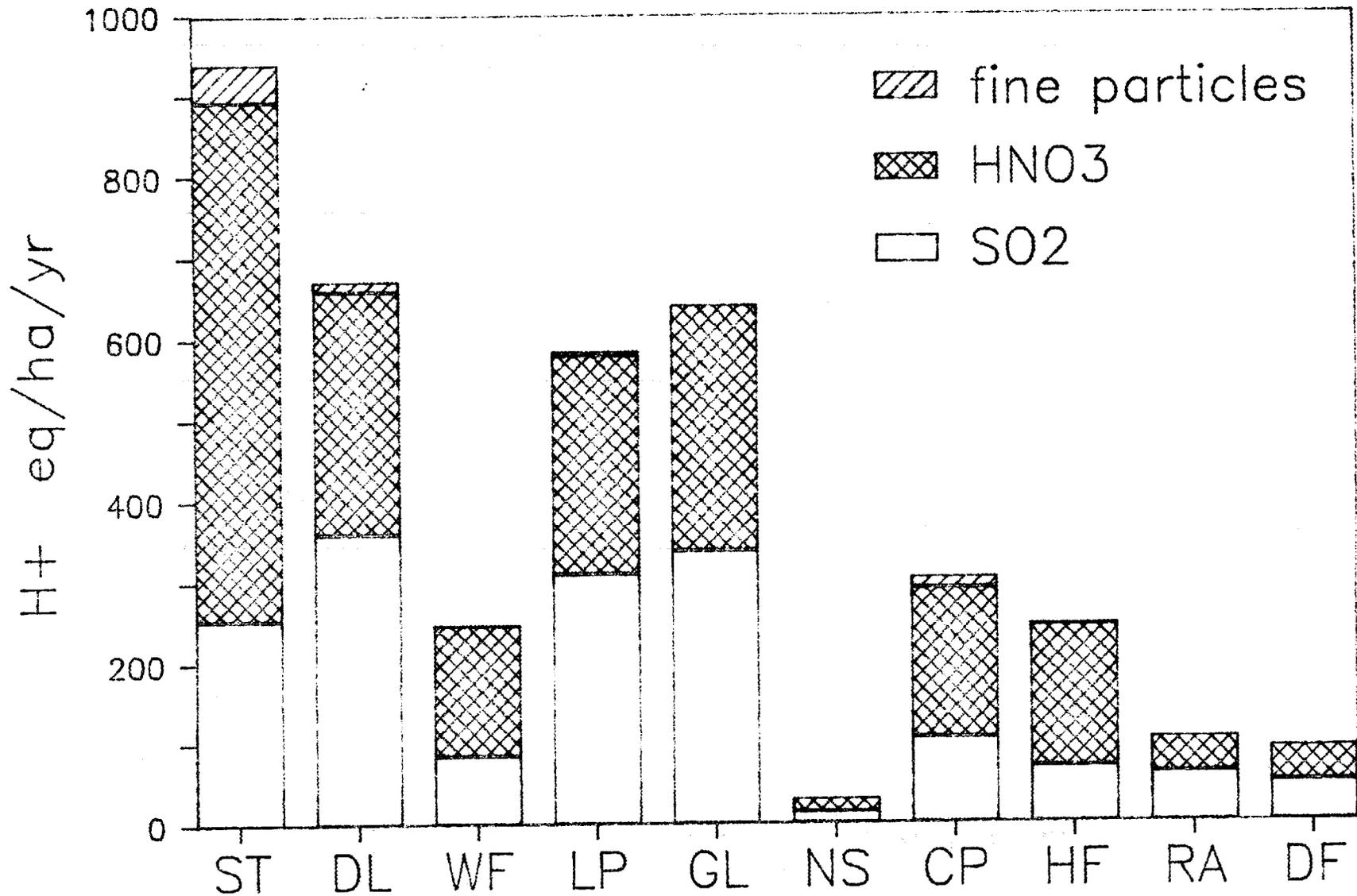


Figure 4
59

Hydrogen Ion Deposition

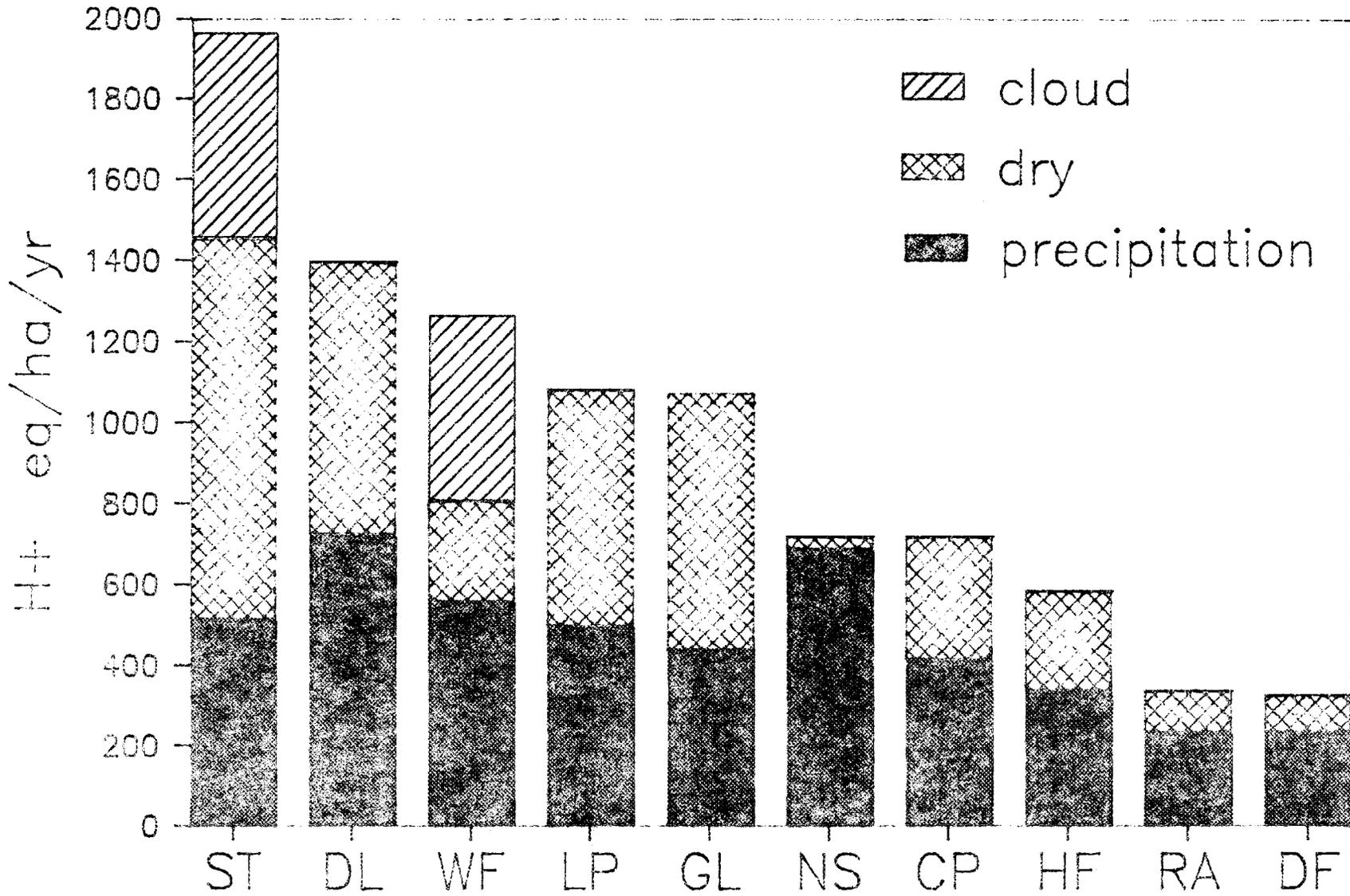


Figure 5
60

Hydrogen Ion -- Net Canopy Effect

TF + SF vs. Total Deposition

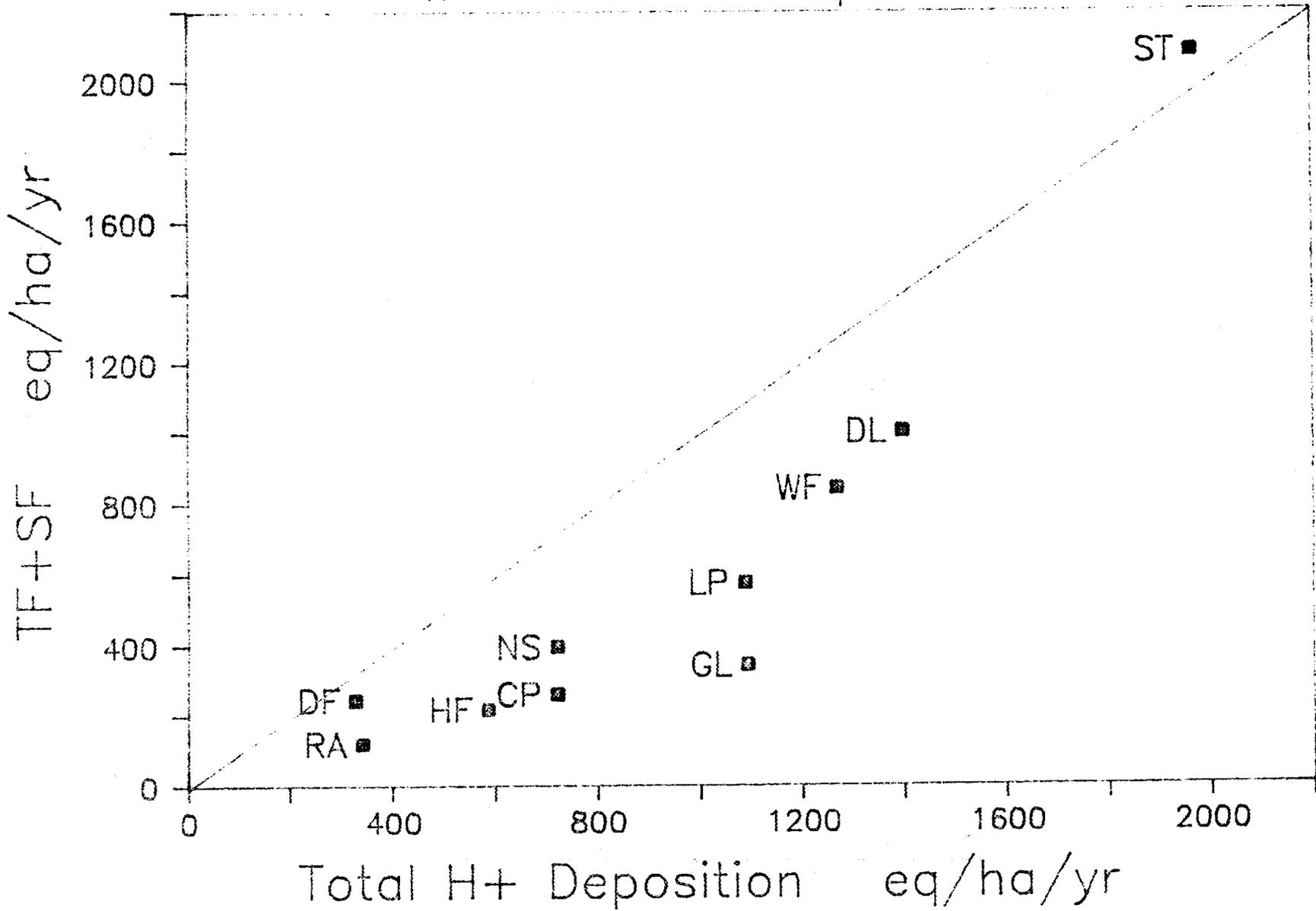


Figure 6

H⁺ Canopy Exchange

exchange vs. total wet deposition

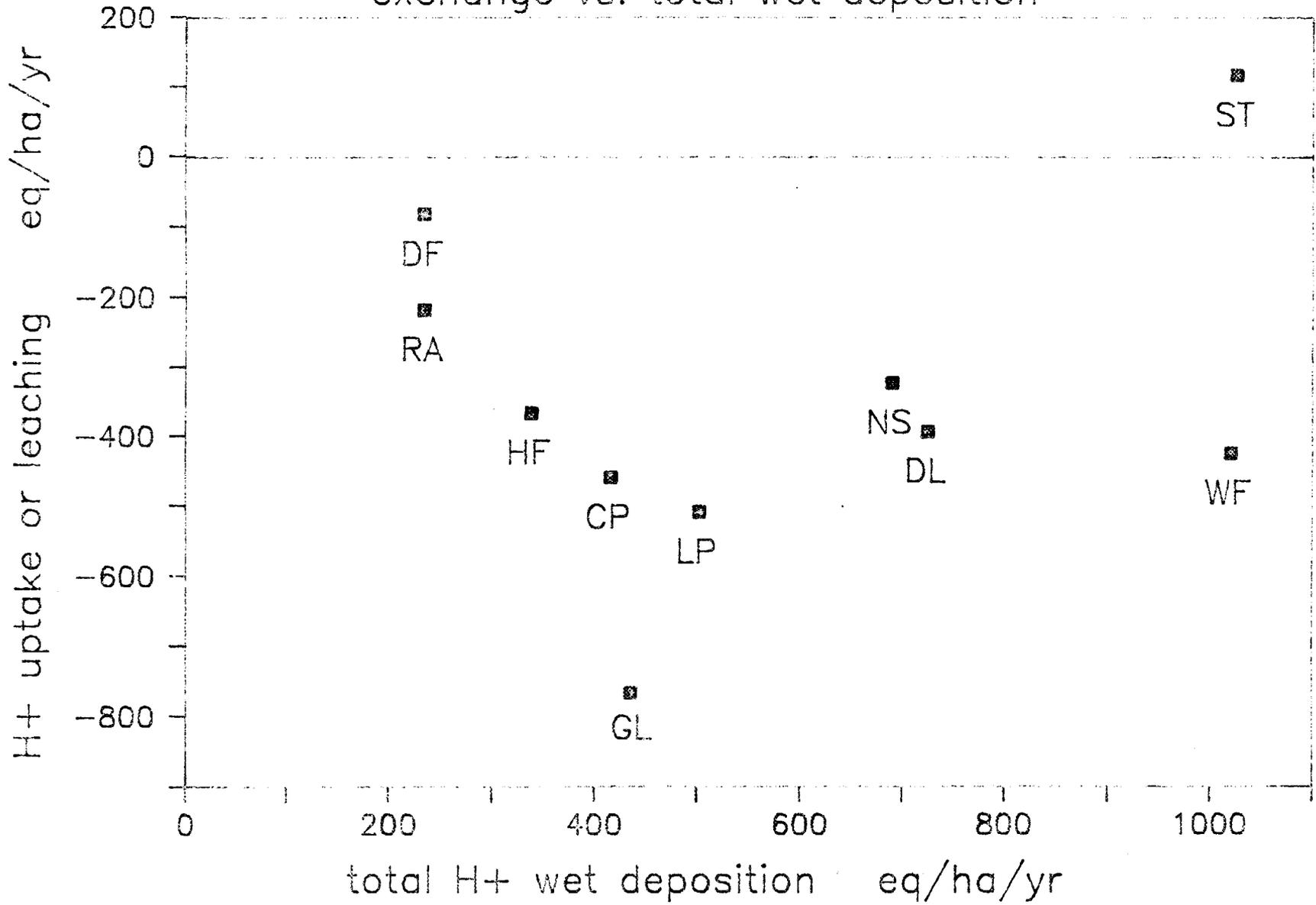


Figure 7

H⁺ Canopy Exchange

exchange vs. ppt. concentration

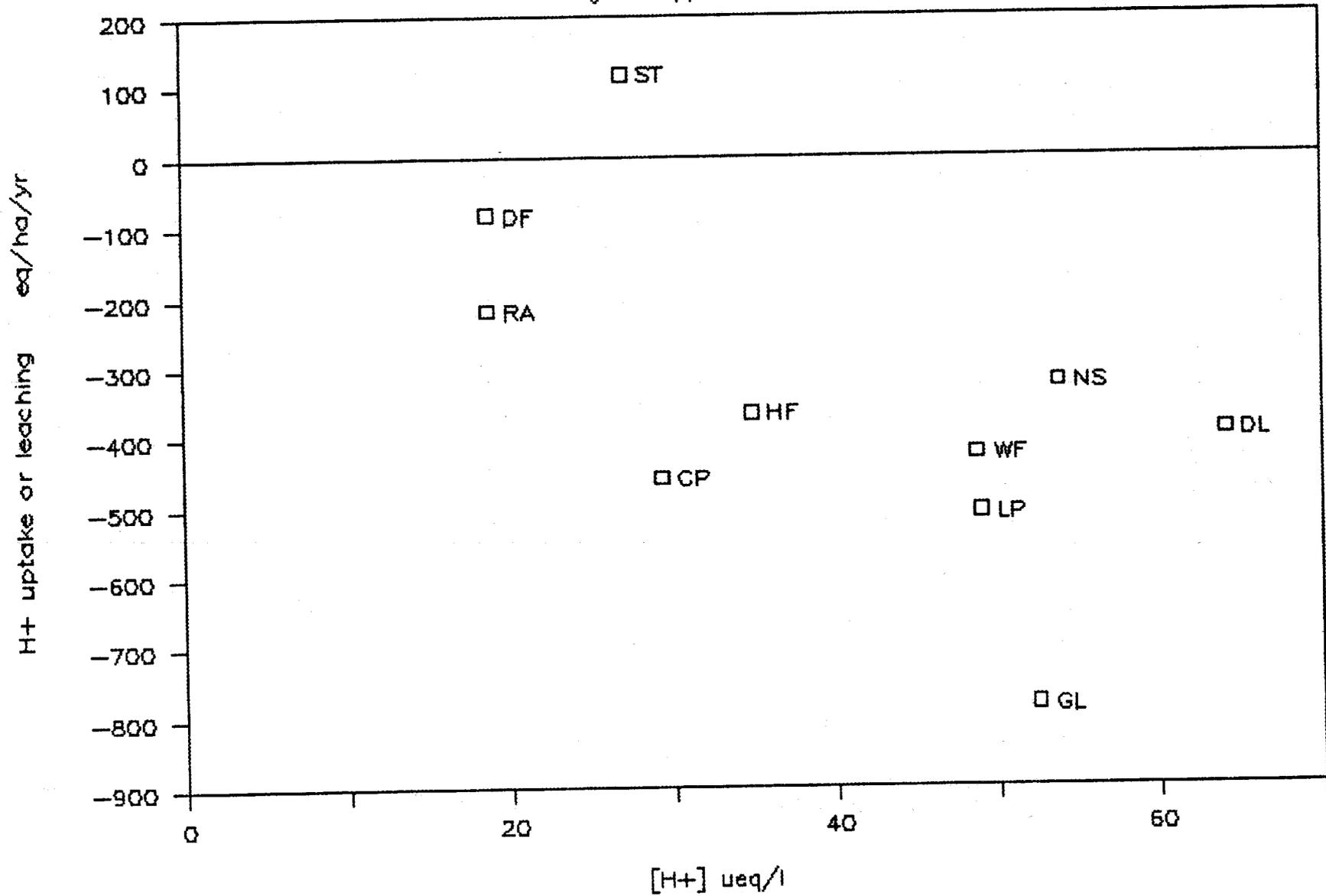


Figure 8
63

IFS H⁺ Budgets

Summary for April, 1989

Dan Binkley

The pH and ion concentrations in soil solutions are determined by the equilibrium between the readily exchangeable pools of ions in the soil and the soil solution. Changes in the soil solution are driven either by changes in the ionic strength of the solution (due to atmospheric deposition, soil respiration, nitrification, or other processes) or to changes in the exchange complex. Two general changes may occur in the chemistry of the exchange complex: quantitative replacement of one ion (such as Ca²⁺) by another (such as Al³⁺), and qualitative changes in the affinity of the exchange sites for different ions. Such qualitative changes result from either changes in soil pH (which protonates or deprotonates exchange sites) or the quality of organic exchange sites. In both cases, the selectivity of the residual exchange complex would appear to shift by the protonation or change in selectivity of the sites.

As with any accounting framework, the line items in a H⁺ budget vary with the perspective of the accountant and the objective of the exercise. In this summary, the focus of the H⁺ budgets is on the exchange complex. The net H⁺ value calculated for each site represents the charge of "basic" cations that must be either weathered (since this is currently unknown for the sites) or stripped from the exchange complex. A net H⁺ value of 1 kmol_c/ha annually would mean that maintenance of overall electroneutrality in the ecosystem would require that 1 kmol_c/ha of "basic" cations be weathered or stripped from the exchange complex. Furthermore, if the net H⁺ budget value were 1.0 kmol_c/ha, but only 0.5 kmol_c/ha of "basic" cations were observed to leach, then an overall mass and charge balance error of 0.5 kmol_c/ha would be indicated.

The net accounting system used for these H⁺ budgets is:

H⁺ input - H⁺ output
 Ammonium input - ammonium output
 Aluminum input - aluminum output
 Cation increment in biomass
 Nitrate output - nitrate input
 Sulfate output - sulfate input
 Bicarbonate output

If H⁺ input exceeds output, there would be a net increase in the load of H⁺ in the ecosystem from this portion of the H⁺ budget. Similarly, if inputs of ammonium exceeded outputs, the storage of ammonium would involve a loading of H⁺. Aluminum input is essentially 0 for all sites; Al³⁺ leaving the ecosystem represents the removal of H⁺. The increment of

cations in biomass results in an efflux of H^+ into the soil. If the nutrient cation had come from decomposing organic matter, this H^+ efflux would merely neutralize the H^+ consumed in decomposition. If the nutrient cation came from the exchange complex, the efflux of H^+ would acidify the exchange complex (unless neutralized by some other component of the H^+ budget).

If the output of nitrate exceeded the input, the net production of nitrate within the ecosystem would be accompanied by net production of H^+ ; if the ecosystem received more nitrate than was leached from the soil, a net consumption of H^+ occurred. The same pattern holds for sulfate and bicarbonate (bicarbonate inputs are negligible in all sites).

The input and output of "basic" cations is not included, as their charge effects are already accounted for by the differences between the anion budgets and the acid cation budgets (including them would represent double counting).

Figure 1 shows that only the Smokey spruce sites leached substantial quantities of H^+ ; for most of the others, the deposition of H^+ was not substantially balanced by H^+ output in soil leachate. Ammonium was also strongly retained in all sites (Figure 2). The increment of cations in biomass (from the current woody increment values in Spreadsheet #7 from each site) graphed in Figure 3 assumes all cations were removed from the exchange complex, with no recycling from the decomposition of soil organic matter (see discussion later). The value for Turkey Lake looks like an overestimate; the woody increment rate of over 10,000 kg/ha annually may have been too high? This anomaly carries through the H^+ budget for Turkey Lake. The output of aluminum was substantial at the spruce sites in the Smokies and on Whiteface (Figure 4), representing a removal (or consumption) of up to 0.8 keq/ha from the Smokies sites. While this represents a reduction in the net H^+ load of these ecosystems, it also represents a substantial H^+ load into downstream ecosystems.

The net retention of deposited nitrate varied greatly among sites (Figure 5). The Smokies Tower site lost about the same quantity of nitrate in soil leachate as it received in deposition, and therefore made little contribution to the net loading of H^+ on the ecosystem. The loss of nitrate from the red alder site greatly exceeded inputs from the atmosphere, resulting in a net H^+ load on the forest of over 3 keq/ha annually. Net sulfate retention also varied greatly across sites (Figure 6); most sites experienced a marginal net consumption of H^+ associated with a net retention of sulfate. The most acidic sites had no net production of H^+ from carbonic acid (Figure 7), as their solutions were too acidic to promote dissociation into H^+ and HCO_3^- . Less acidic sites experienced about 0.1 to 0.2 keq/ha annual loading of H^+ due to dissociation of carbonic acid.

With the exception of the red alder (high nitrification) site, H^+ deposition represented roughly half of the total H^+ load experienced by each ecosystem (Figure 8). The processing of the nitrate and sulfate anions in acid deposition consumed part of the deposited H^+ in all ecosystems except the high-elevation sites and the red alder site (Figure 9). The net

retention of sulfate and nitrate essentially neutralized all the H^+ deposited at the Norway spruce, Douglas-fir, and Coweeta sites. Note that the net retention of these ions may be reversible in the future, re-releasing the H^+ currently being consumed.

After accounting for all the net production and consumption of H^+ , the net H^+ load ranged from about 0.3 keq/ha annually in the Douglas-fir site (Figure 10) to over 5 keq/ha for the red alder site. This net H^+ load must be balanced by the leaching of "basic" cations, which would be derived from either stripping of the exchange complex or mineral weathering. The base cation output bars in Figure 10 show close agreement with the net H^+ load in some sites, but not in others. Figure 11 graphs the difference between these two as the "residual" or error associated with the ecosystem budgets. Sites such as the Huntington Forest appear to have perfectly balanced budgets of ions in the ecosystem; other sites (such as Findley Lake and Red Alder) are substantially unbalanced. Where the residuals are positive, an excess production of H^+ is indicated. Possible causes of the excess H^+ include:

1. Assuming all cation increment in biomass came from the exchange complex rather than from recycled soil organic matter. The 7 sites with the greatest H^+ production due to cation increment in biomass are also the 7 with the largest positive residuals. This could account for about 0.5 to 0.8 keq/ha annually for these 7 sites.
2. An overestimation of the output of nitrate, sulfate and bicarbonate.
3. An underestimate of the leaching loss rates of "basic" cations.

Note that an overestimate of the rate of deposition of nitric acid or sulfuric acid (and allied chemicals) could not account for the excess H^+ residual; if the rate of H^+ input from nitric acid were reduced, the input of nitrate would be reduced, cancelling the effect of lowered H^+ input.

Only the Findley Lake site showed a substantial deficit in H^+ . Most of the H^+ budget components for Findley Lake were small relative to the other sites; the only explanation I could find is the charge imbalance in the B horizon (40 cm depth) leachate. The leaching rate of cations was 0.6 kmol_c/ha greater than anions; the H^+ budget deficit indicates that sufficient H^+ were not generated in the other budget components to account for this excess leaching of cations. If the charge balance of the soil leachate were adjusted to electroneutrality, the H^+ deficit would drop down to only 0.2 to 0.3 kmol_c/ha annually.

H⁺ input/output budget

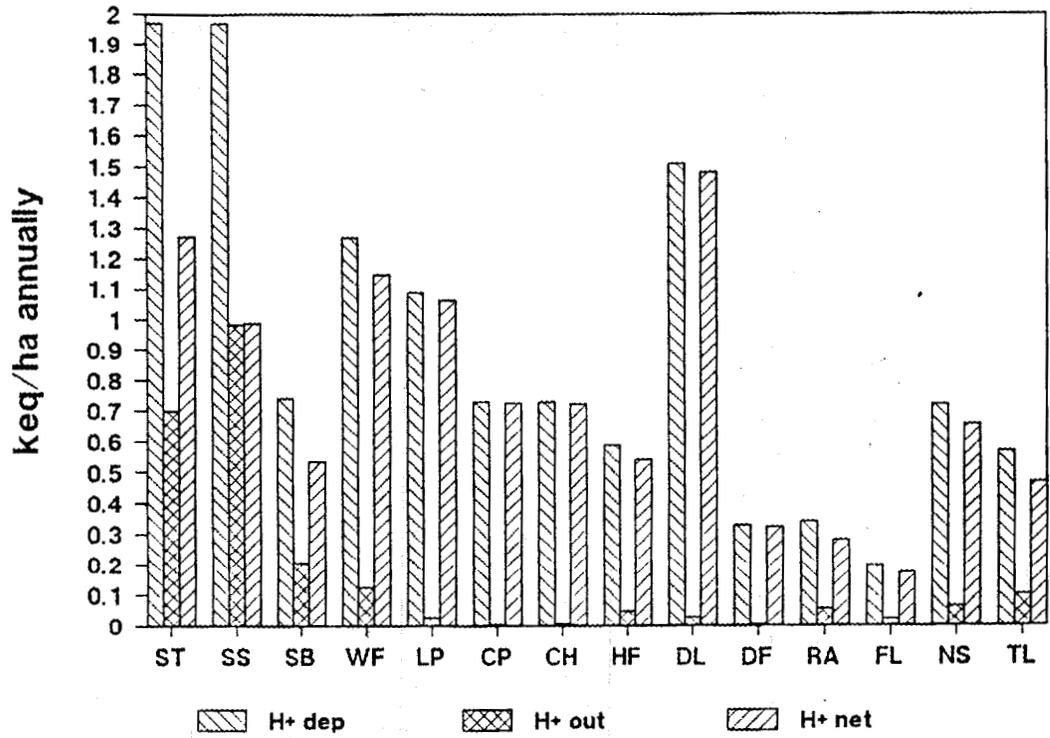


Figure 1. Atmospheric deposition of H⁺; leaching loss of H⁺; and net H⁺ input remaining from atmospheric deposition. A positive value for the net budget indicates H⁺ loaded into the ecosystem.

NH₄⁺ input/output budget

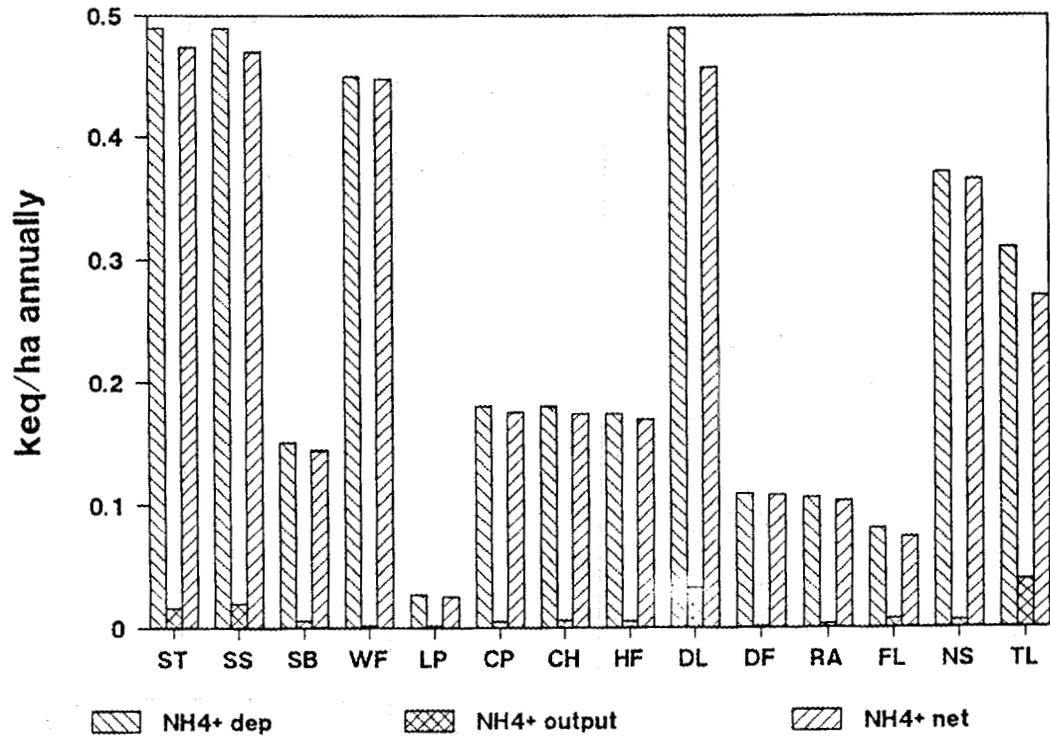


Figure 2. Ammonium deposition; ammonium output; and the net ammonium retained from atmospheric deposition. A positive value for the net budget indicates H⁺ loaded into the ecosystem.

Woody biomass cation increment

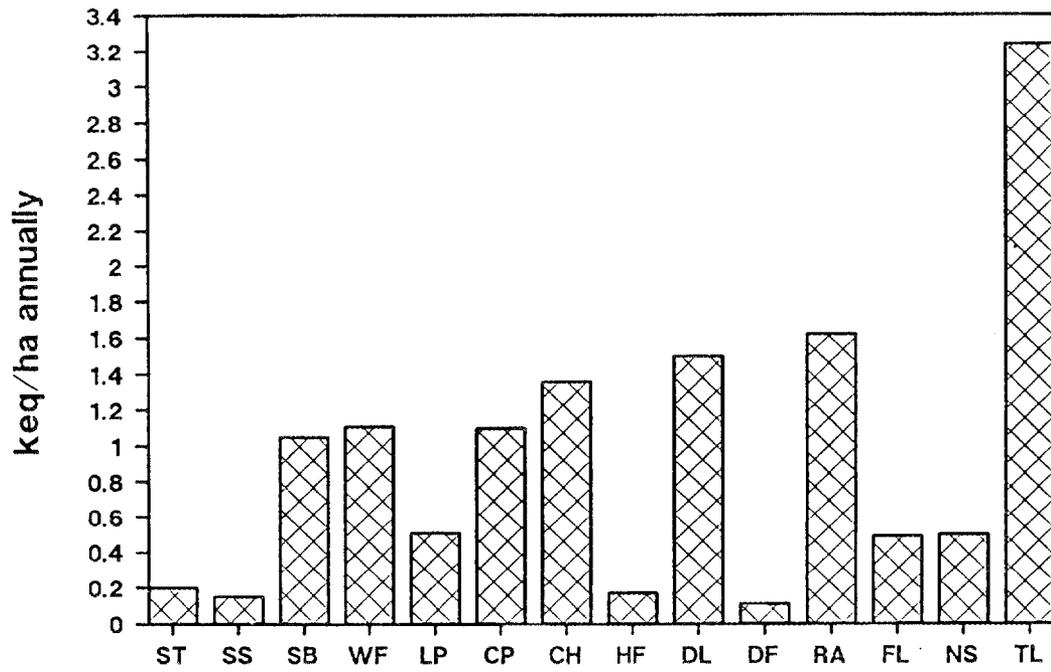


Figure 3. Content of "basic" cations in woody increment. A positive value indicates H⁺ loaded into the ecosystem.

Aluminum output (-)

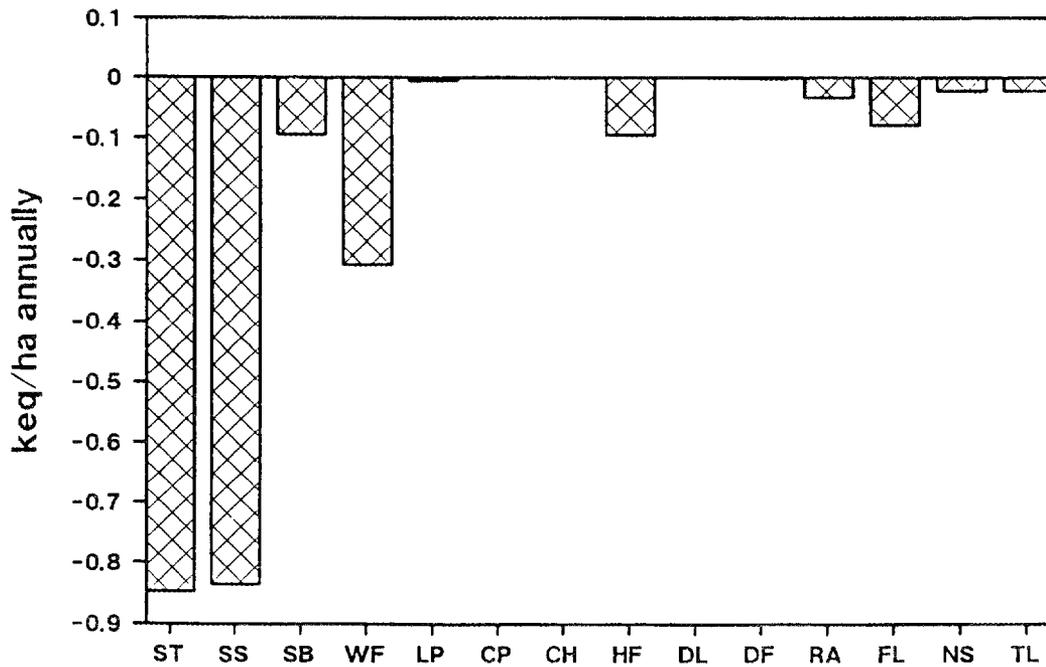


Figure 4. The negative of aluminum output, plotted to represent the net removal of H⁺ from the ecosystem.

Nitrate input/output budget

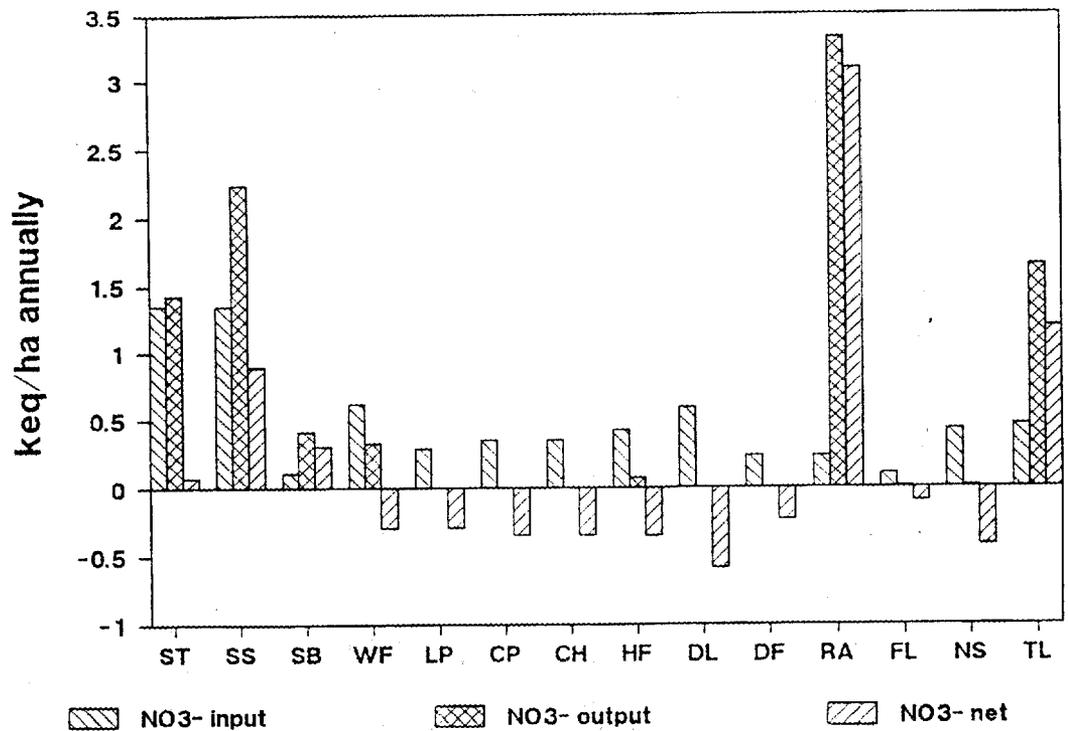


Figure 5. Nitrate deposition; nitrate output; and the net nitrate retained. Net retention involves consumption of H^+ (negative net values), and net loss involves H^+ production (positive net values).

Sulfate input/output budget

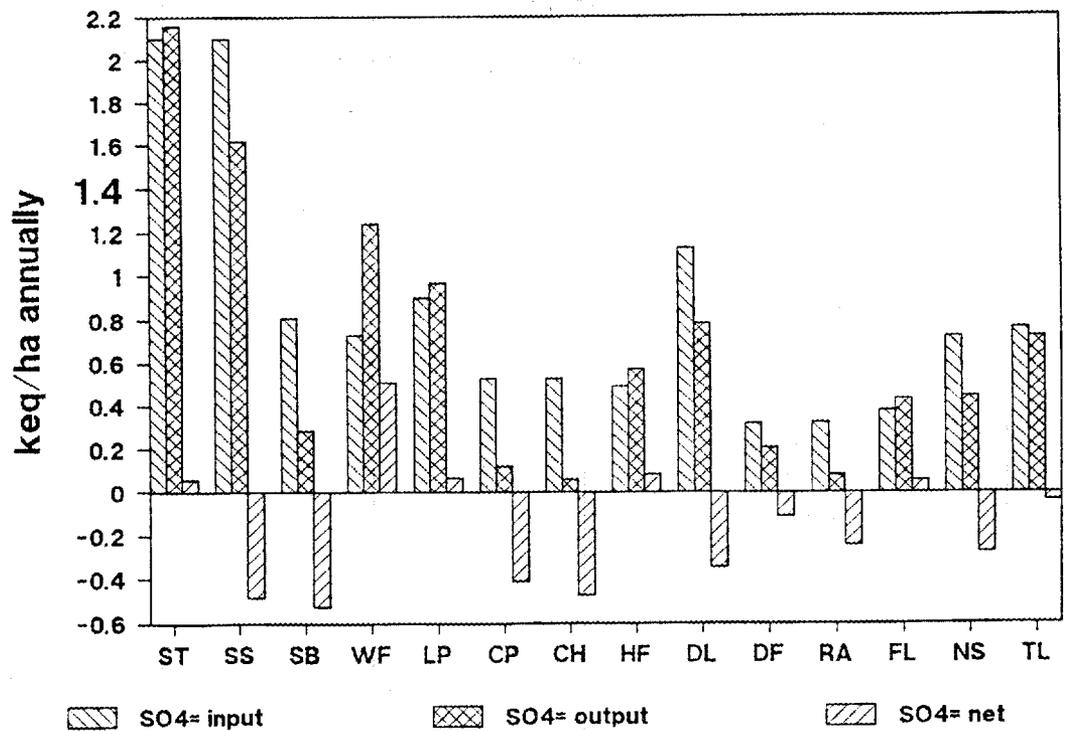


Figure 6. Sulfate deposition; sulfate output; and the net sulfate retained. Net retention involves consumption of H^+ (negative net values), and net loss involves H^+ production (positive net values).

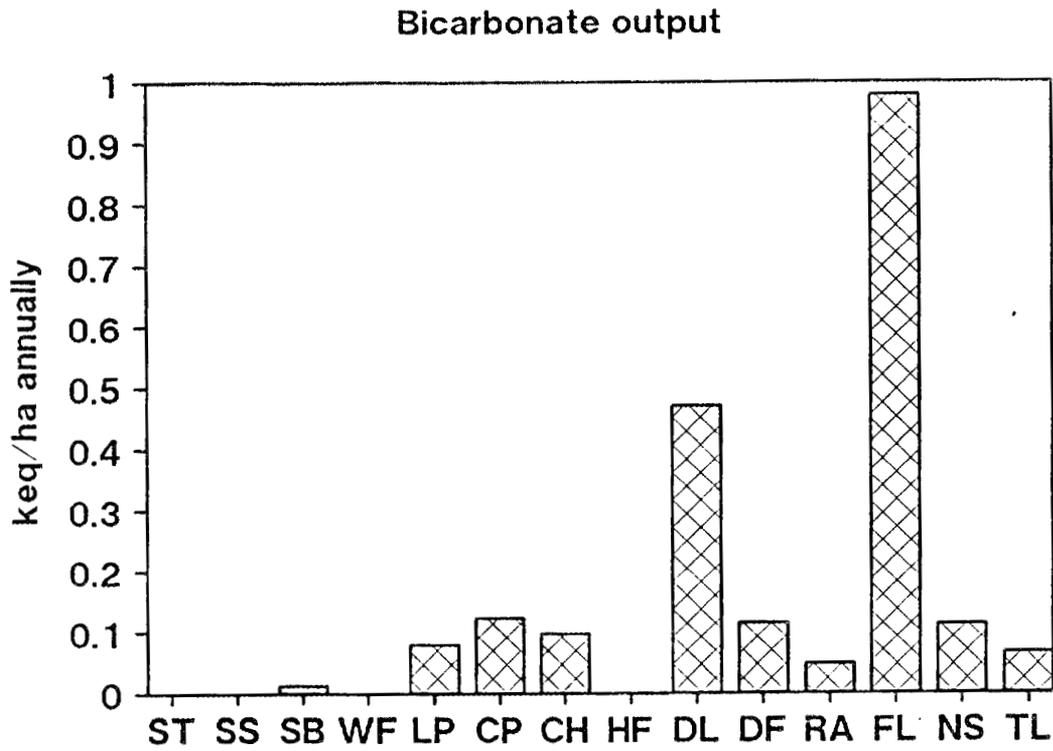


Figure 7. Bicarbonate input was negligible, so the net output of bicarbonate represents the net addition of H^+ to the ecosystem.

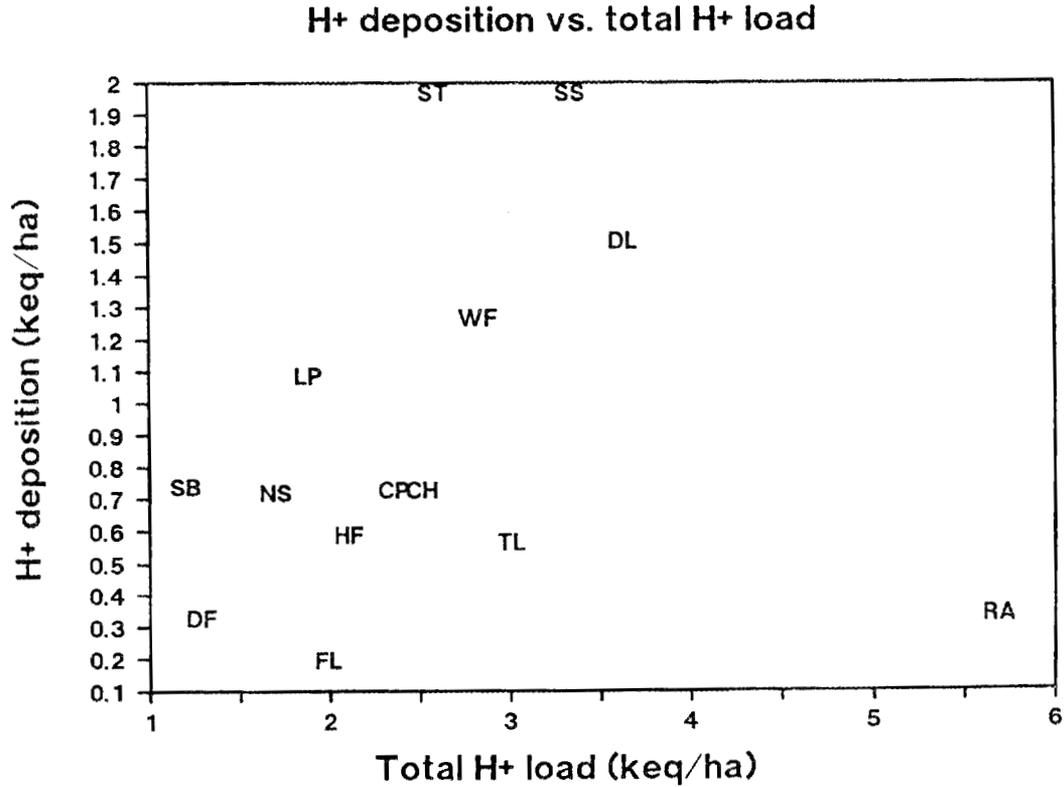


Figure 8. Excluding the high-nitrate-leaching red alder site, the total load of H^+ in the ecosystem (deposition + internal generation) was roughly double the rate of deposition across the sites.

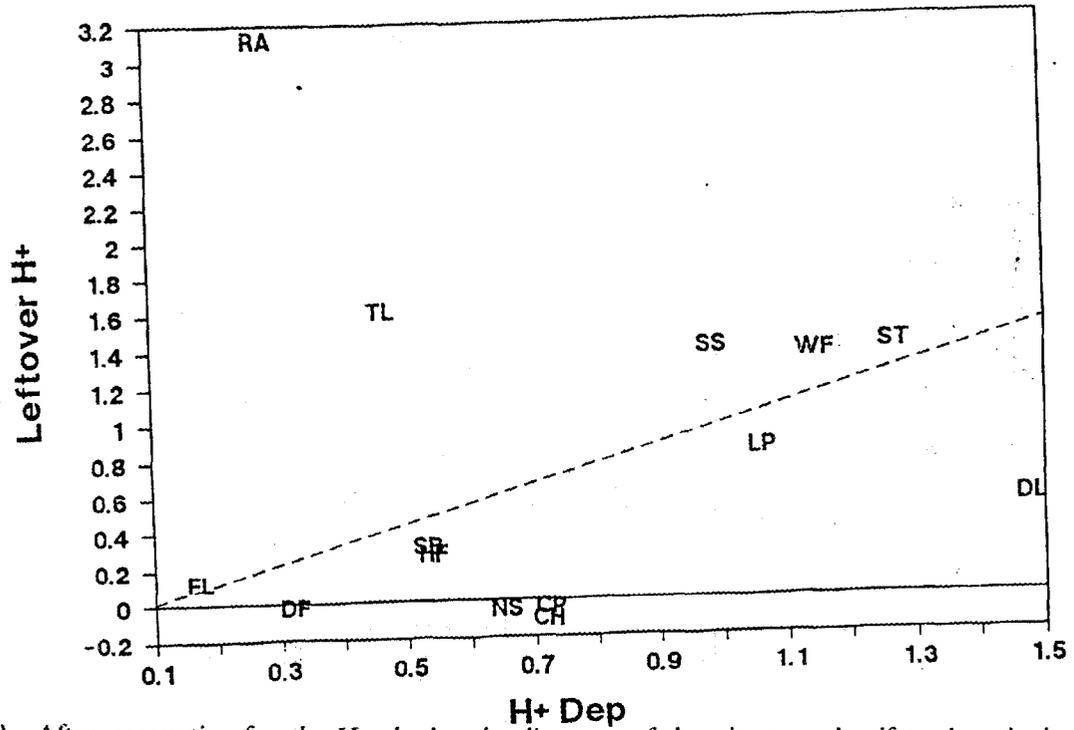


Figure 9. After accounting for the H⁺ budget implications of the nitrate and sulfate deposited as acidic deposition, 4 sites showed no net H⁺ loading from the atmosphere (0 "leftover H⁺"); 4 sites showed slightly lowered net H⁺ loading; and 5 showed a net loss of nitrate and sulfate indicating no potential for H⁺ neutralization through retention of these anions.

Net H⁺ load and base cation output

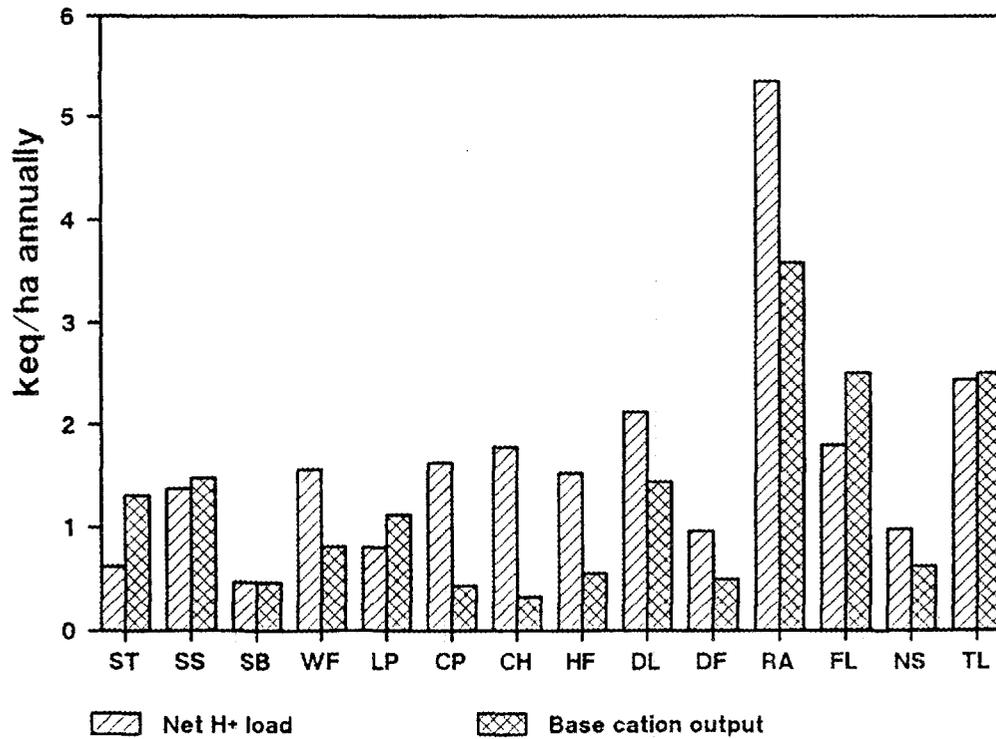


Figure 10. The overall net H⁺ budget should match the leaching losses of "basic" cations, as all other components of the ecosystem fluxes were accounted for. If the overall net H⁺ budget exceeds the leaching loss of "basic" cations, inaccuracies in the nutrient budgets indicate overestimates of the rates of H⁺ generation (see text).

H⁺ Residual

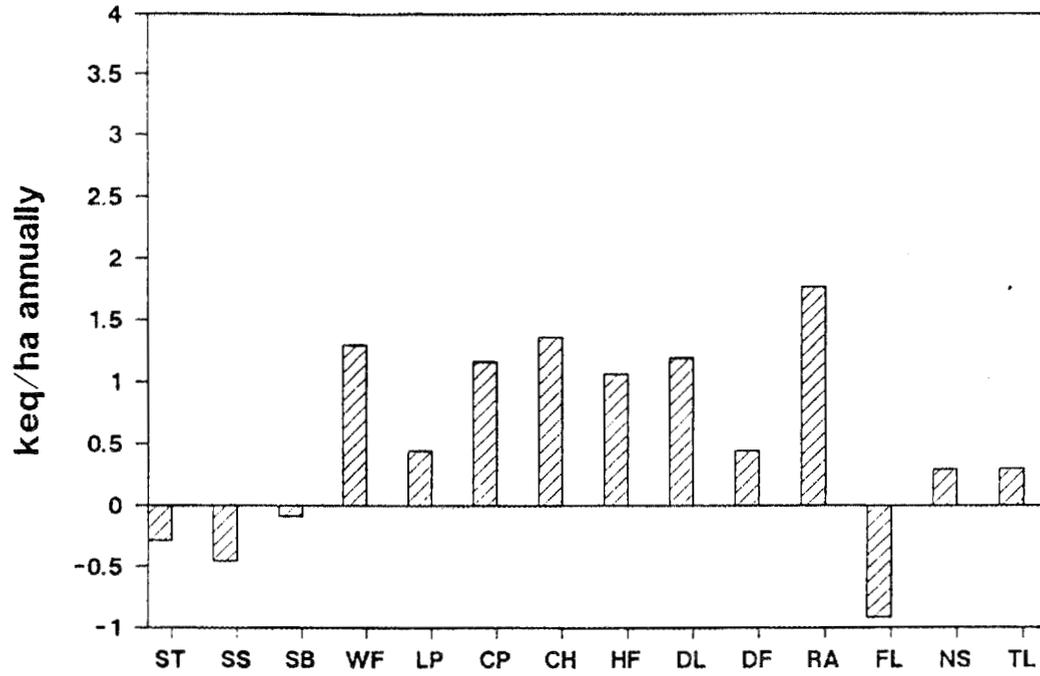


Figure 11. Subtracting the leaching losses of "basic" cations from the overall net H⁺ budget provides an estimate of the overall residual (or error) in the biogeochemical fluxes tabulated for each site (see text).

4.4 BASE CATIONS

4.4.1 Deposition and Throughfall Fluxes of Base Cations

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Emory University

Dry deposition of the "base" cations; K, Na, Ca, and Mg; consists of coarse and fine particle fractions. The base cation positive charge input of dry particles to the IFS forest sites ranged from about 70 to greater than 510 eq/ha/yr (Fig. 1). The lowest values, 74 and 82 eq/ha/yr were reported for the White Face (WF) and Georgia Loblolly (GL) sites. The highest dry deposition, 510 eq/ha/yr, was recorded for the eastern Smokies Tower (ST) site. Dry deposition of base cation charge for the eastern sites (excluding (ST); Oak Ridge (LP), Georgia Loblolly (GL), Coweeta (CP), Huntington Forest (HF), and Duke (DL); ranged from about 100 to 300 eq/ha/yr. Dry charge deposition at the western Douglas Fir (DF) and Red Alder (RA) sites was about 180 eq/ha/yr, quite similar to dry deposition at the eastern IFS sites. The Norway Spruce (NS) site had dry deposition of 126 eq/ha/yr, a value comparable to the eastern GL, CP, and HF sites.

Coarse particle deposition is the dominant form of cation deposition for the forested IFS sites (Fig. 1). Among most sites, coarse particle deposition represented about 95% or more of the base cation charge deposition with a narrow range of 1 - 17% of the total dry deposition attributed to fine particle deposition. Whiteface (WF) was the exceptional site with coarse and fine particle deposition each contributing 50% to the total dry deposition.

Total wet deposition (precipitation and cloud) of base cation charge was generally greater in magnitude than total dry deposition (Figs. 1 and 2). Total wet deposition was 60 to 75% of total atmospheric deposition for 7 sites (DL, GL, DF, NS, RA, WF and ST). Total wet deposition was 42 to 46% at LP, CP, and HF. The high elevation Smokies Tower (ST) site had a base cation wet deposition of 860 eq/ha/yr, about 6.5 times greater than occurred in the other eastern sites. The remaining eastern sites; LP, GL, CP, and HF; clustered around a value of 130 eq/ha/yr except for the DL site which had 445 eq/ha/yr total wet deposition. The remaining sites generally had higher wet deposition than the eastern sites with 540 eq/ha/yr for the western sites, DL and RA, and 248 eq/ha/yr for the Norway Spruce site.

Most of the wet deposition came in the form of precipitation. Cloud deposition occurred at the Oak Ridge (LP) site but it was not recorded for any other low elevation site in the eastern or western U.S. (Fig. 2). Wet deposition from clouds accounted for 12% of the total wet deposition at the LP site. Cloud deposition occurred at both high elevation sites. Cloud deposition was the dominant wet deposition process for the high elevation Smokies Tower (ST) site where over three-quarters of the total wet deposition occurred as cloud deposition. About one-fourth of the total wet deposition at WF was deposited by cloud.

The IFS sites were quite similar in the ratio of base cation charge deposition for wet and dry deposition, with about 60% of the total coming as wet deposition. Coarse particle deposition accounted for most (about 95%) of the dry deposition of base cation charge. Precipitation was the dominant wet deposition process for most IFS sites except at the high elevation Smokies Tower site where cloud deposition was the dominant wet deposition process.

Deposition of base cations to the forest floor occurs as the precipitation moves over the leaf surfaces and the bark of tree stems. Previously deposited dry deposition, scavenged from leaf and bark surfaces, and additional cations directly from the vegetation and bark are added to the incident precipitation. The sum of throughfall and stemflow fluxes is the total base cation flux to the organic layer of the forest floor. The total TF+SF fluxes ranged from about 600 to 1000 eq/ha/yr for most sites (Fig. 3). The total throughfall for the high elevation Smokies Tower site, 1750 eq/ha/yr, was about twice that at the other IFS sites.

The stemflow component of total throughfall was small to non-existent for most sites (Figure 3). At three sites (GL, CP and HF), however, the stemflow was a significant fraction, 12 - 29%, of the total throughfall. The significance of the stemflow component depends on the number of stems per unit area. The trees at the Georgia site (GL) are planted on 6 by 8 foot spacings and stemflow is 12% of the total throughfall. The loblolly pines at the Duke site have twice the spacing of the GL site and stemflow is only 2 % of the total throughfall. At Oak Ridge, the loblolly pines are widely spaced and stemflow is essentially unmeasurable.

The Net Canopy Effect (Fig. 4) is the difference between total atmospheric deposition and total throughfall (Wet + Dry - (TF +SF)). Approximately one-half of the total throughfall (stemflow + throughfall, Fig 3.) base cation charge is contributed by the trees (Figure 4). Among IFS sites the Net Canopy Effect was similar, varying between 230 and 480 eq/ha/yr. The low site at 151 eq/ha/yr was DF while CP had the highest Net Canopy Effect, 650 eq/ha/yr. There was relatively little difference, about a factor of 2, among the IFS sites for base cation charge contributed to total throughfall by the forest vegetation.

Ion Composition of Base Cation Fluxes

Ion specific analysis of the "base" cation charge flux shows the importance of Ca, Na, Mg and K for each of the base cation charge fluxes (Figures 5,6,7 and 8). Either Ca or Na dominate the coarse particle dry flux at the IFS sites (Figure 5). Sodium is the dominant base cation in coarse particle flux at the DF, RA, DL and NS sites, each of which has a strong coastal influence. Calcium is the dominant cation, 50% + of the total base cation charge flux, at the ST, LP, and CP sites. The high calcium contribution at ST, LP and CP is explained by the high soil calcium concentrations characteristic of this limestone region. While the Coweeta site (CP) is not on a limestone derived soil, significant dry calcium could be carried to Coweeta through the westerly winds blowing across Tennessee to Coweeta.

The contribution of Ca, Na, Mg, and K to the precipitation charge flux differs somewhat from that for the coarse particle dry flux (Fig. 6). Sodium is the dominant cation in precipitation at the DF, RA, NS and GL sites. This is due to the proximity of these sites to their respective coast lines. Calcium is the dominant cation in the precipitation flux at the ST, LP and CP sites. This is similar to the results for the coarse particle deposition at these sites (above).

The dominant cations in total throughfall (TF+SF) charge flux are Ca and K which together account for 50% or more of the total throughfall charge flux for all sites (Fig. 7). At the DF and RA sites, Na and Ca dominate the total throughfall charge flux. This results from the fact that dry flux is relatively insignificant at the DF and RA sites while Na is the dominant cation in precipitation charge flux at these two sites (Figures 5,6, and 7).

Unlike the DF and RA sites, Na accounts for very little of the total throughfall charge flux at the remaining IFS sites (Figure 7). The contribution of Mg to the charge flux is similar to that for Na, although the charge contributed by Mg is usually greater than for Na.

The considerable contribution of K to total throughfall charge flux (Figure 7) at the IFS sites is almost wholly due to K flux from the forest vegetation (Figure 8). The relative balance of K and Ca in dominating the total throughfall flux of the IFS sites is, as well, a result of Ca contributions from the forest canopy. Potassium charge dominates the net canopy flux of most IFS sites (Figure 8). Either Ca or Mg is second to K in accounting for the total cation charge flux and in most cases there is little difference in the charge contributed by either Ca or Mg. Sodium contributed very little charge to net canopy charge flux. Sodium is not a required element for forest trees and the balance of Na deposition and loss through the forest canopy is expected to be near zero.

FIGURE 1

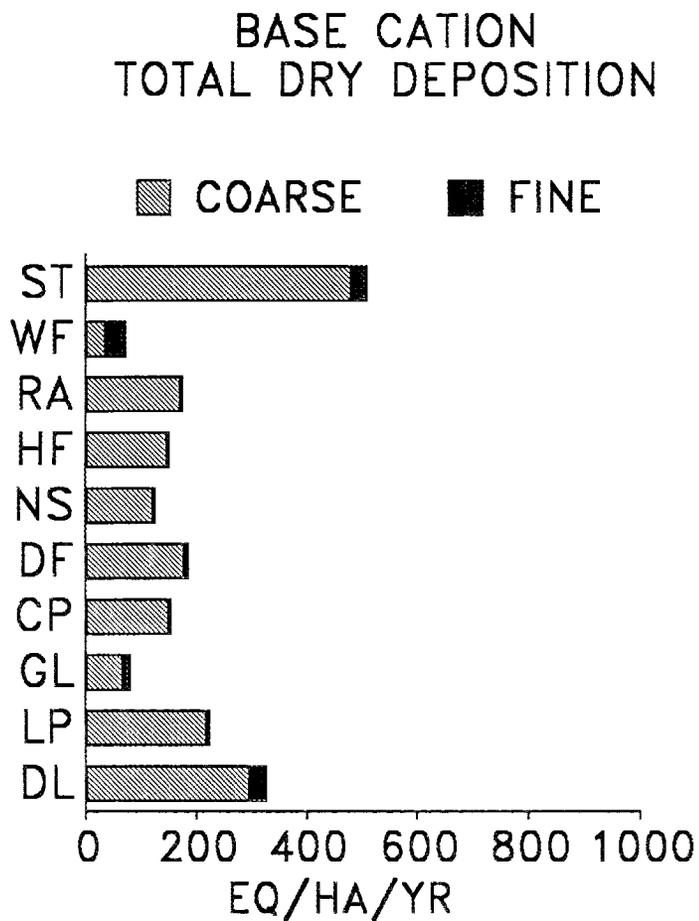


FIGURE 2

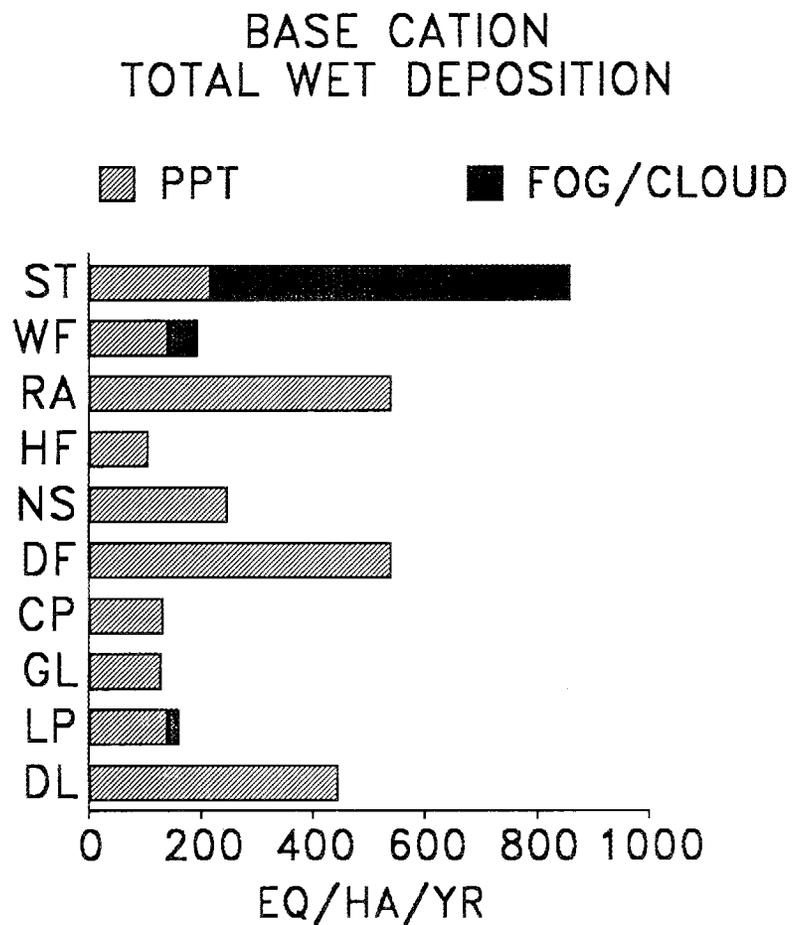


FIGURE 3. BASE CATION
THRUFALL+STEMFLOW
DEPOSITION TO FOREST FLOOR

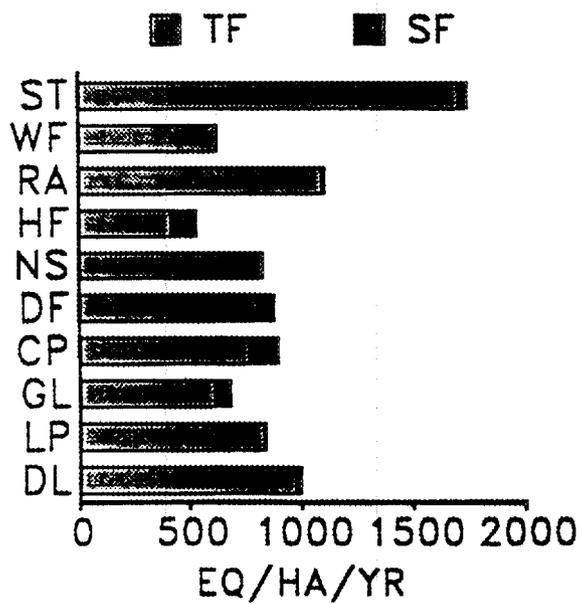


FIGURE 4. BASE CATION
NET CANOPY EFFECT

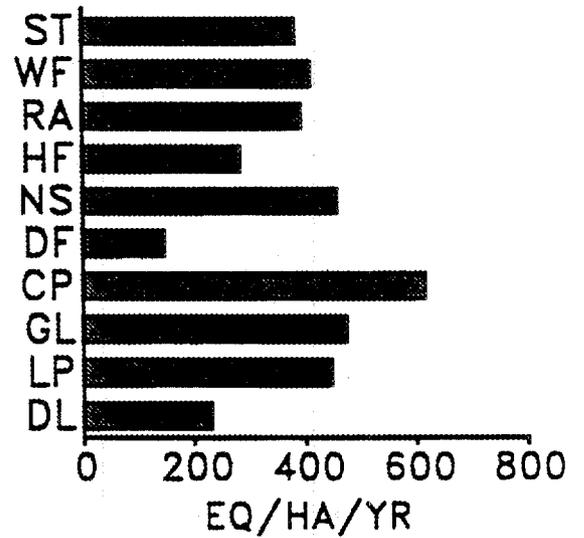


FIGURE 5. COARSE DRY FLUX

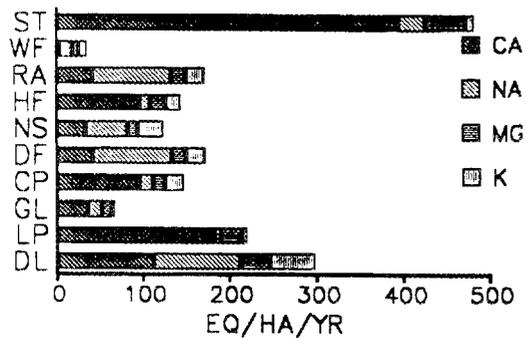


FIGURE 6. PPT FLUX

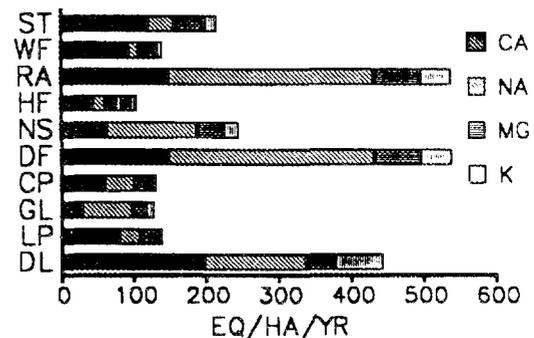


FIGURE 7. TF+SF DEPOSITION

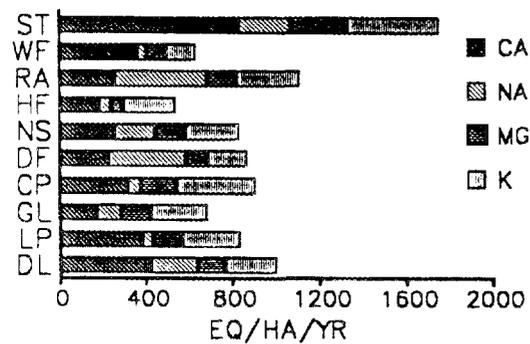
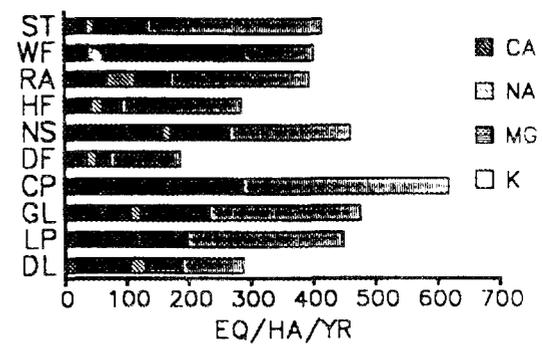


FIGURE 8. NET CANOPY EFFECT



4.4.2. Cation Cycling Synthesis

The Integrated Forest Study Cation Cycling Synthesis

Dale W. Johnson
March 1989

Introduction

One of the major driving forces (if not the major driving force) behind the Integrated Forest Study (IFS) is to determine the extent to which acid deposition is causing cation losses and soil acidification in the sites under study. With the aid of the IFS Nutrient Cycling Model (NUCM), it is our intention to extrapolate the data collected from these sites in time and space to gain a more general understanding of how forest ecosystems respond to acid inputs, both anthropogenic and natural. As we near final stage of IFS, some patterns in cation distribution and flux are beginning to emerge that can be further explored through an analysis of the cation cycles, the H⁺ budget analysis by Dan Binkley, and the NUCM model.

Ecosystem Cation Distribution

As a general rule, soils from the low-elevation and southern sites within the project are richer in exchangeable base cations and are less acid than soils from the high-elevation and southern sites. Figures 1 and 2 illustrate this with base saturation data from the B horizons and ecosystem Ca distribution data for most of the IFS sites. Soils from glaciated sites (whether high-elevation/northern or low-elevation) tend to have higher total cation contents, reflecting greater reserves of weatherable minerals (see report by Bob Newton). It is noteworthy that none of the sites has a substantial proportion of Ca in biomass, as has been noted in some eastern deciduous forests (Cole and Rapp, 1981; Johnson et al 1988).

Cation Fluxes

There is no particular pattern of base cation loss that relates to site location (Figure 3). Three sites (both beech sites in the Smokies, SB1 and SB2) and the Douglas-fir site in Washington (DF) show a net base cation gain from atmospheric deposition, the Smokies red spruce sites (SS1, SS2, ST1, ST2) are approximately in balance, and the others show a net loss. It is interesting to note that the greatest net losses occur in the relatively less polluted red alder (RA) and Turkey Lakes (TL) sites. In these sites, nitrate production within the soil plays a major role in soil leaching (See the Nitrogen Synthesis report by Cole and Van Miegroet). A somewhat different pattern emerges when looking at ecosystem balances for individual cations. About an equal number of sites show a net gain of Ca as show a net loss of Ca from atmospheric deposition (Figure 4), whereas all sites show a net loss of Mg (Figure 5).

There is a clear pattern of Al leaching in relation to base saturation and, therefore, site location. The more acid high-elevation/northern sites release a greater amount of Al when subjected to inputs of mineral acid anions (Figure 8). This is to be expected and is consistent with soil chemical equilibria (Reuss and Johnson, 1986). It should be recognized that extremely acid soils (such as those that occur in high-elevation and northern sites) will not in themselves necessarily cause high soil solution Al concentrations; a combination of extremely acid soils and mineral acid anion inputs are necessary. Thus, extremely acid soils, which can be produced naturally such as at the Findley Lake site, are a necessary but not sufficient condition for the mobilization of Al. The mobilization of Al in the Smokies red spruce sites may be of special significance in that soil solution Al levels are approaching levels found to be toxic to red spruce seedlings in solution culture studies (see the ORNL site report).

Cation Fluxes and Soil Reserves

In order to evaluate the degree to which these cation budgets might affect soil reserves, the fraction of soil exchangeable and total cations lost via leaching are shown in Figures 6 and 7. It is clear that Mg is the cation whose soil reserves are most likely to be affected by leaching in most cases; the export of Mg equals 5-10% of exchangeable Mg reserves in the Turkey Lakes (TL), Smokies Becking and Tower (SS AND ST), Whiteface (WF), Norway (NS), and red alder (RA) sites (Figure 6). The exports of Ca and K equal less than 5% of exchangeable reserves in all cases except Ca in the Turkey Lakes site. In contrast, net export as a fraction of soil total cation reserves is greatest in the case of Ca at the Duke (DL) and Oak Ridge Loblolly (LP1 and 2) sites. Even in these cases, however, depletion of soil total reserves is not likely to occur in the near future; net Ca export equals only 0.1-0.2% of total soil reserves, and the effects of deep rooting and recycling by vegetation is not accounted for.

Cation Cycles

Cation cycles for some of the IFS sites have now been constructed from the data tables as a prelude to modeling activities. Figure 8 illustrates the Ca cycles for the Duke Loblolly and Douglas-fir sites to provide a comparison of Ca cycles in ecosystems under differing pollutant loads (the Duke site being more polluted). The Duke site has greater soil solution Ca concentrations and greater Ca leaching rates than the Douglas-fir site, a direct result of greater inputs and leaching of sulfate in the Duke site. Both Ca uptake and accumulation of Ca in woody tissues are also greater at the Duke site, which is a young, vigorously growing stand. The net result is that the total export of Ca from the soil (Leaching + Wood Increment - Deposition) at the Duke site (31 kg/ha/yr) is over three times greater than that from the Douglas-fir soil (9 kg/ha/yr). It is noteworthy that wood increment is a substantial fraction of this total export in both sites. The potential for change in the Duke soil, while rather small in itself, is greater than in the Douglas-fir soil for two reasons. First, the net export from the soil is a greater fraction of exchangeable Ca at the Duke site (1.5%) than at the Douglas-fir site (0.8%), and secondly, weathering studies by Bob Newton

and Rich April indicate that there is a very low supply of weatherable minerals in the Duke soil whereas the supply of weatherable minerals in the Douglas-fir soil is relatively large. This is reflected by the differences in soil total Ca content in Figure 8. The cycles of Mg and K for these two sites (not shown) show essential similar patterns, except that wood increment is less significant relative to leaching in the case of Mg.

Conclusions

1. Soils from high-elevation/northern sites are generally more acid and have lower exchangeable base cation reserves than soils from low-elevation/southern sites.
2. Glaciated soils generally have the greatest soil total cation reserves
3. Soil solution Al concentrations may be approaching toxicity levels in the Smokies red spruce sites.
4. Extremely acid soils are a necessary but not sufficient condition for Al mobilization into soil solution. (Mineral acid anions must also be present.)
5. Many sites (especially high-elevation/northern) accumulate one or more base cations from atmospheric deposition.
6. The greatest potential for soil change is in the case of Mg (highest net export/exchangeable ratio).
7. Analysis of selected cation cycles indicates that uptake usually exceeds leaching, and wood increment can equal or exceed leaching.

References

- Cole, D. W., and M. Rapp. 1981. Elemental cycling in forest ecosystems. Pages 341-409 in D. E. Reichle (ed.), *Dynamic Properties of Forest Ecosystems* Cambridge University Press, London
- Johnson, D.W., G.S. Henderson, and D.E. Todd. 1988. Changes in nutrient distribution in forests and soils of Walker Branch Watershed over an eleven-year period. *Biogeochemistry* 5:275-293.
- Reuss, J.O., and D.W. Johnson. 1986. *Acid deposition and the acidification of soil and water*. Springer-Verlag, New York.

- Figure 1. Base saturation (NH_4Cl extraction) in B horizon soils from the IFS sites. HF=Huntington Forest, NY; TL=Turkey Lakes, Ontario; ST=Smokies Tower, NC; MS=Howland site, ME; SS=Smokies Becking, NC; SB=Smokies Beech, NC; FL=Findley Lake, WA; WF=Whiteface Mt. NY; DF=Douglas-fir, Thompson site, WA; NS=Aamli site, Norway; GA=B.F. Grant Site, GA; CP=White pine site, Coweeta, NC; CH=hardwood site at Coweeta, NC; CB=Camp Branch site, TN; FS=slash pine site, FL; FT=Fullerton site, Walker Branch, TN; DL=Duke loblolly site, NC; TK=Tarklin site, Walker Branch, TN; RA=red alder site, Thompson site, WA; LP=Loblolly pine site, Oak Ridge, TN. Duplicate abbreviations indicate separate or duplicate plots.
- Figure 2. Calcium distributions from the IFS sites. See Figure 1 legend for code.
- Figure 3. Base cation budgets for the IFS sites. See Figure 1 legend for code.
- Figure 4. Calcium budgets for the IFS sites. See Figure 1 legend for code.
- Figure 5. Magnesium budgets for the IFS sites. See Figure 1 legend for code.
- Figure 6. Fraction of soil exchangeable Ca, Mg, and K lost annually by leaching ($[\text{Leaching-Deposition}]/\text{Exchangeable}]$) in the IFS sites. See Figure 1 legend for code.
- Figure 7. Fraction of soil total Ca, Mg, and K lost annually by leaching ($[\text{Leaching-Deposition}]/\text{Exchangeable}]$) in the IFS sites. See Figure 1 legend for code.
- Figure 8. Calcium cycles for the Duke Loblolly and Douglas-fir sites.

B2 Horizons

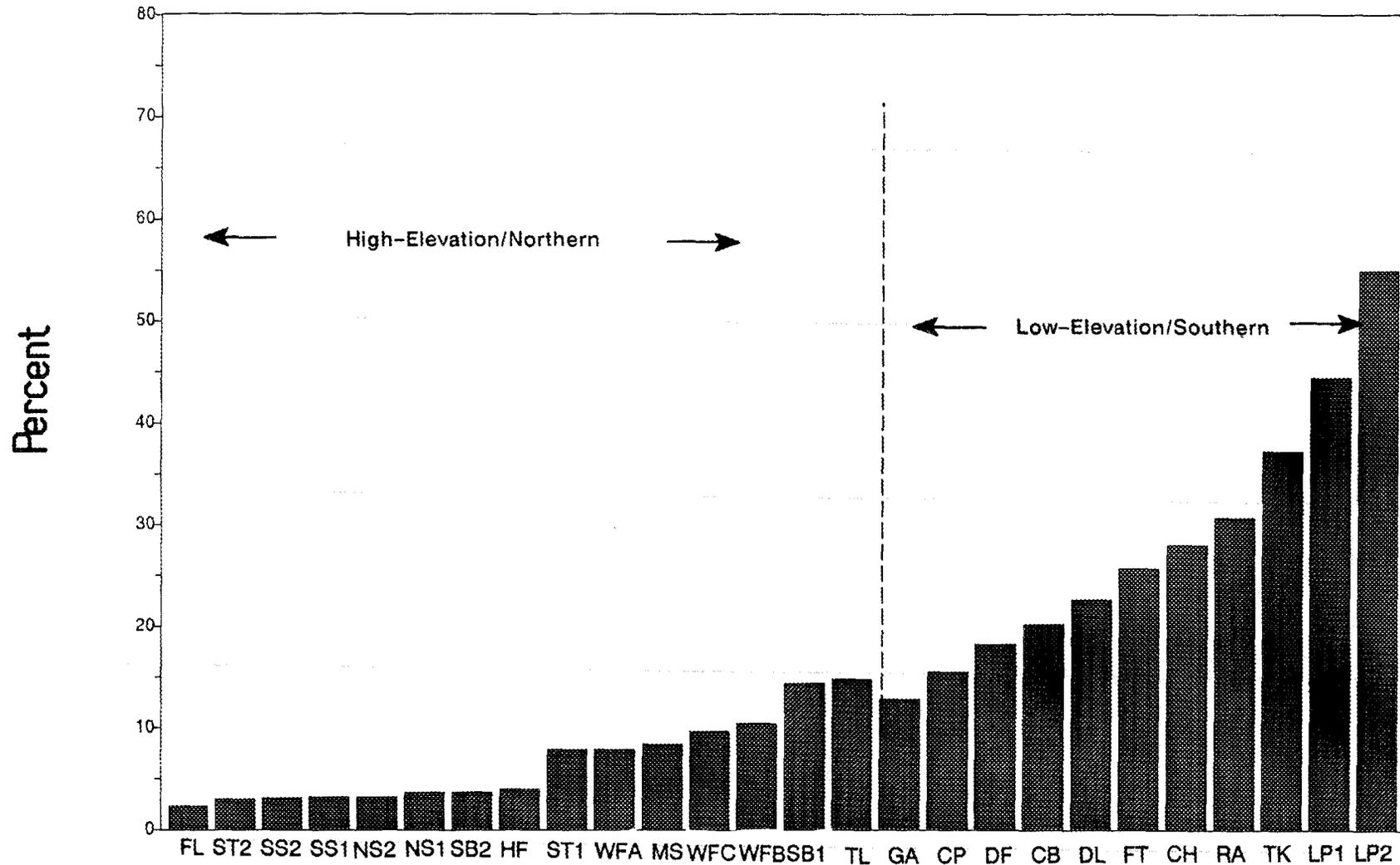


Figure 1. Base saturation (NH₄Cl extraction) in B horizon soils from the IFS sites. HF=Huntington Forest, NY; TL=Turkey Lakes, Ontario; ST=Smokies Tower, NC; MS=Howland site, ME; SS=Smokies Becking, NC; SB=Smokies Beech, NC; FL=Findley Lake, WA; WF=Whiteface Mt., NY; CH=hardwood site at Coweeta, NC; CB=Camp Branch site, TN; FS=slash pine site, FI; FT=Fullerton site, Walker Branch, TN; DL=Duke Loblolly site, NC; TK=Tarkin site, Walker Branch, TN; RA=red alder site, Thompson site, WA; LP=loblolly pine site, Oak Ridge, TN. Duplicate abbreviations indicate separate or duplicate plots.

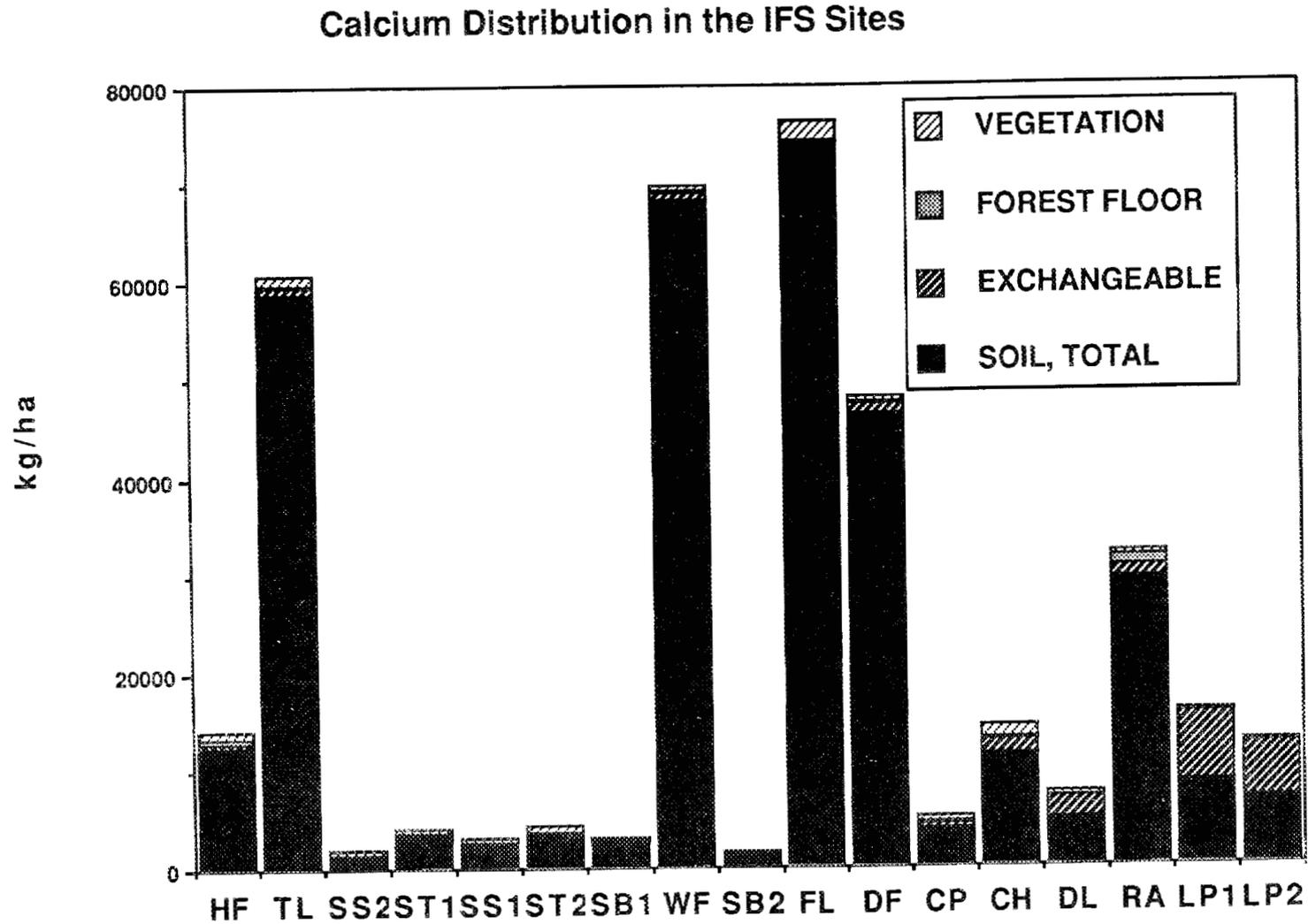


Figure 2. Calcium distributions from the IFS sites. See Figure 1 legend for code.

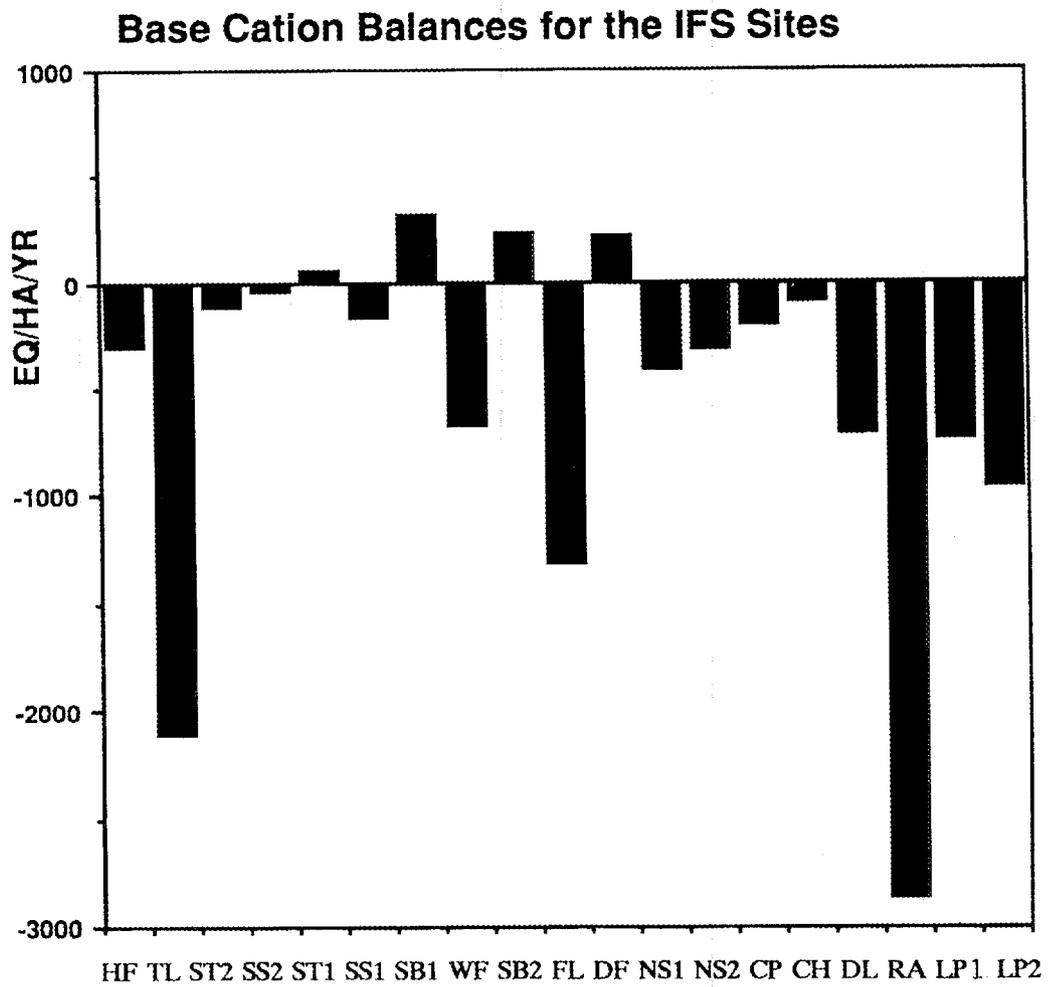


Figure 3. Base cation budgets for the IFS sites. See Figure 1 legend for code.

Calcium Budgets for the IFS Sites

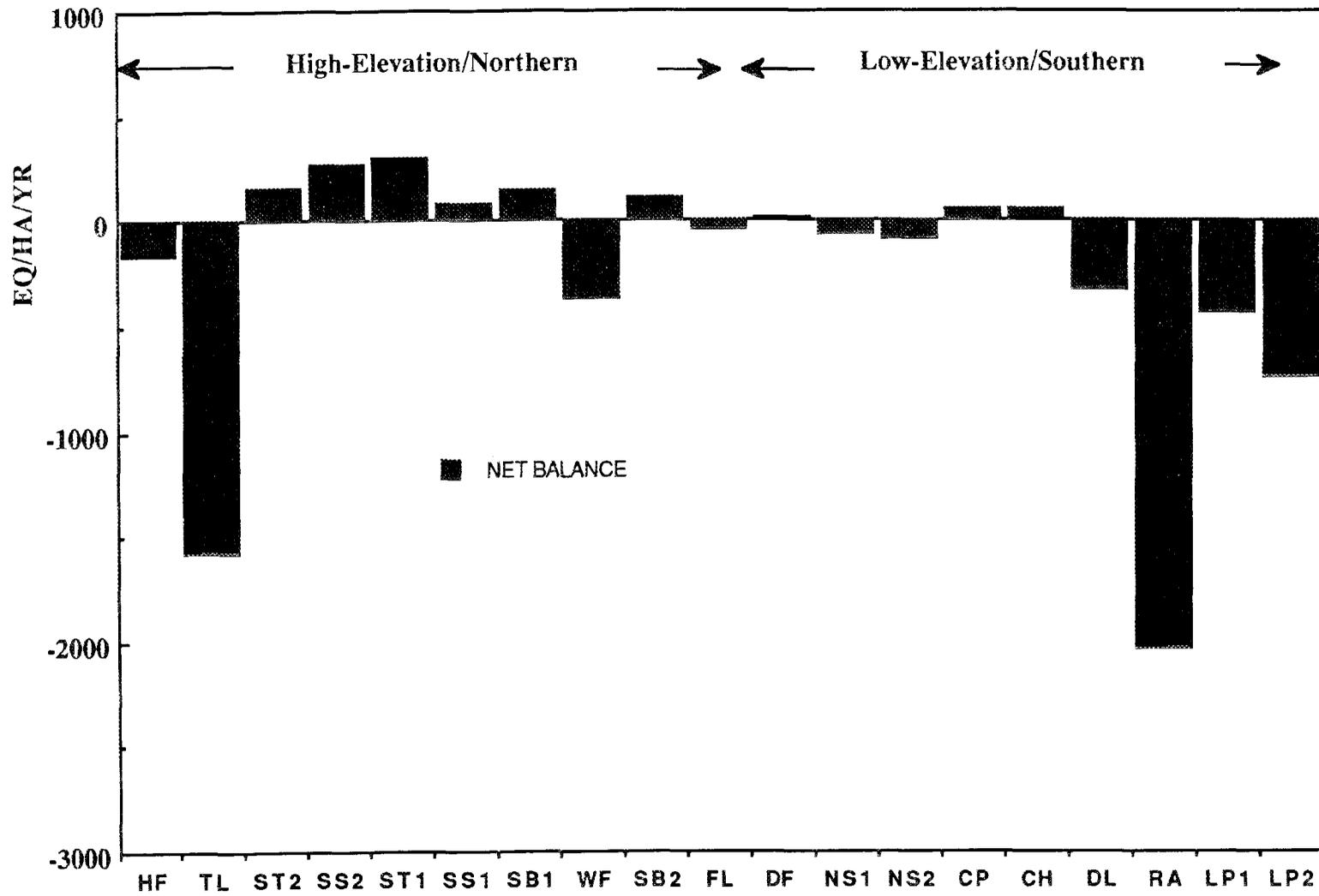


Figure 4. Calcium budgets for the IFS sites. See Figure 1 legend for code.

Magnesium Budgets for the IFS Sites

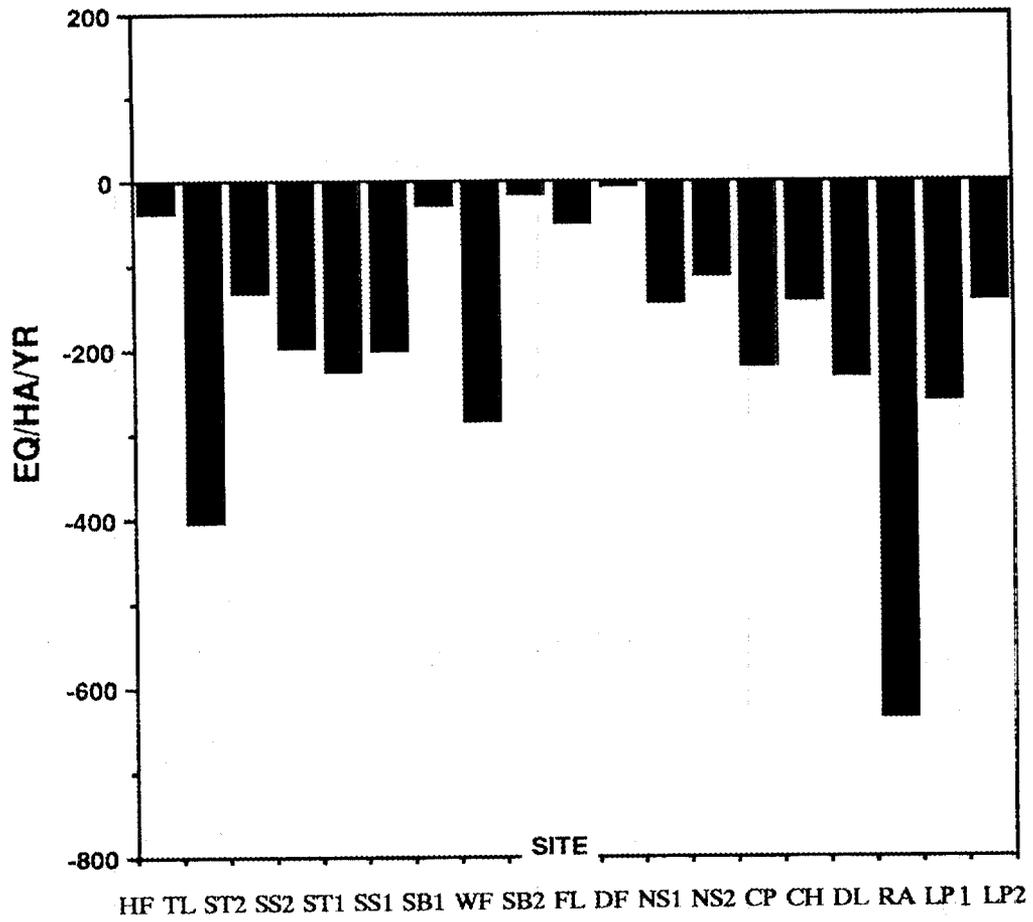


Figure 5. Magnesium budgets for the IFS sites. See Figure 1 legend for code.

Fraction of Soil Exchangeable Cations Exported
or Imported Annually

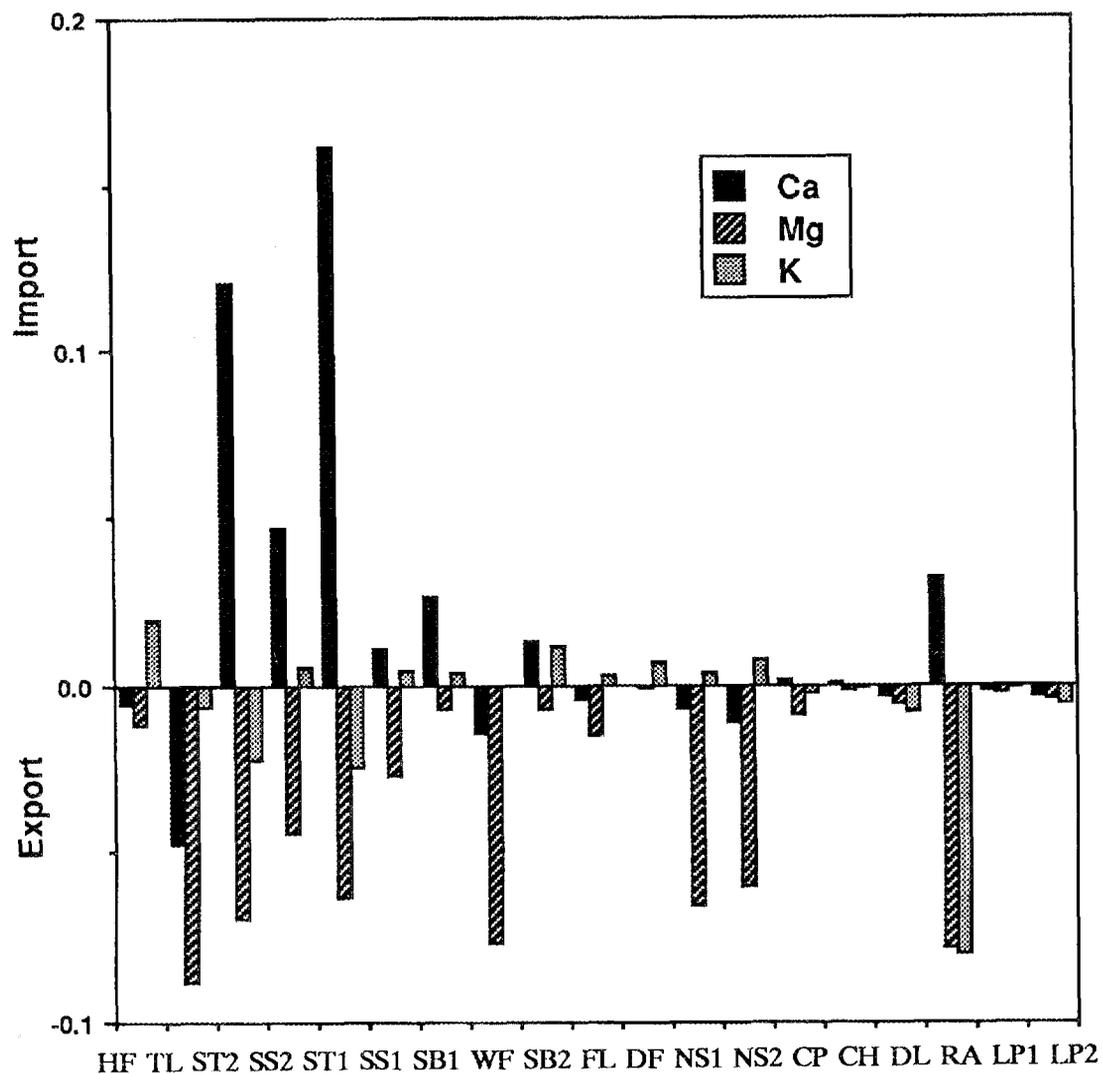


Figure 6. Fraction of soil exchangeable Ca, Mg, and K lost annually by leaching ((Leaching-Deposition)/Exchangeable) in the IFS sites. See Figure 1 legend for code.

Fraction of Soil Total Cations Exported or Imported Annually

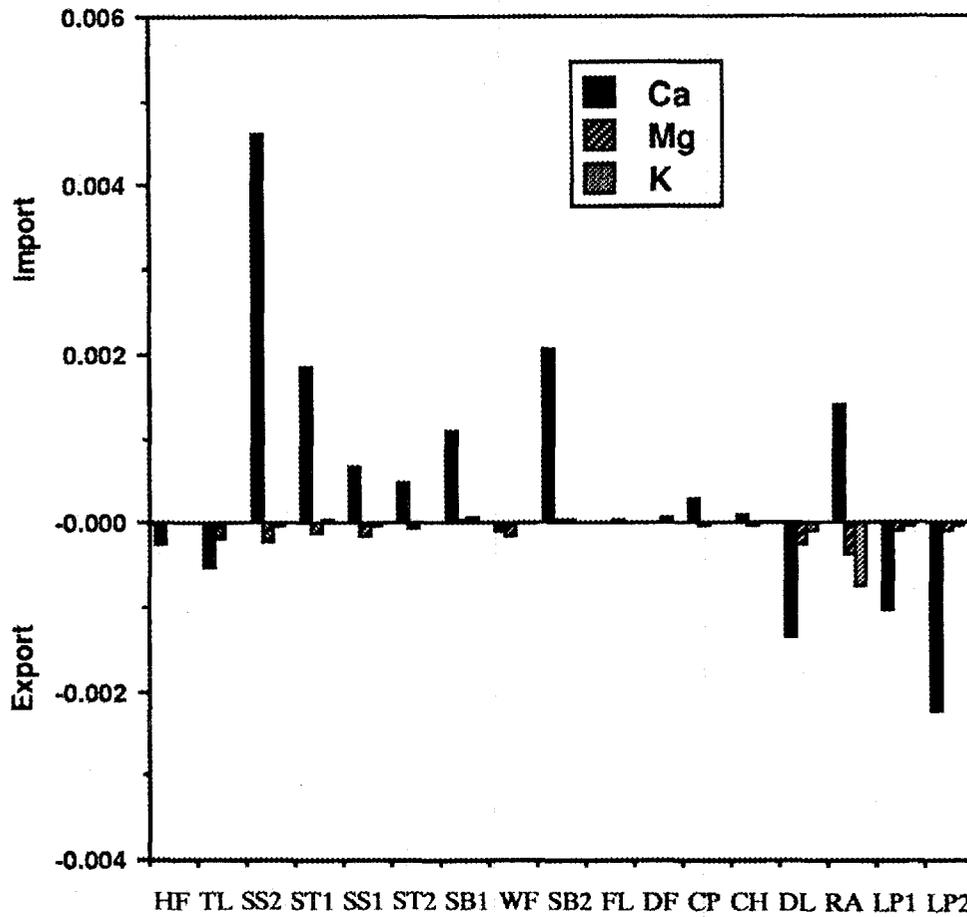


Figure 7. Fraction of soil total Ca, Mg, and K lost annually by leaching ($[(\text{Leaching}-\text{Deposition})/\text{Exchangeable}]$) in the IFS sites. See Figure 1 legend for code.

Calcium

(KG/HA/YR)

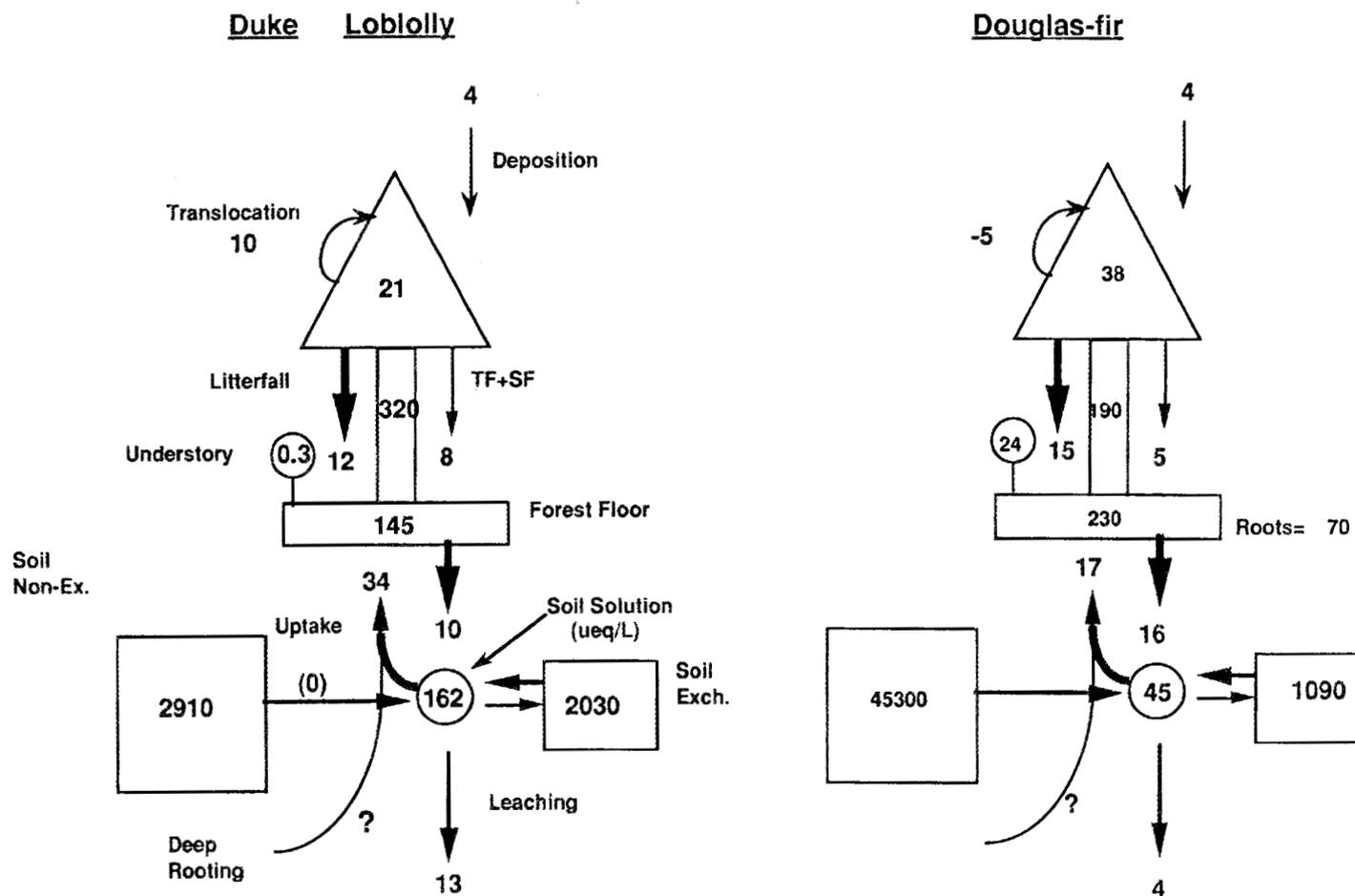


Figure 8. Calcium cycles for the Duke Loblolly and Douglas-fir sites.

SECTION 5. EXPERIMENTAL TASK SUMMARY REPORTS

5.1 ATMOSPHERIC DEPOSITION TASKS

5.1.1

Integrated Forest Study
1989 Annual Report

Task A2 Submicron Aerosol Deposition

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March 1989

Directly measuring the flux of submicron aerosol sulfate to forest canopies is impossible because aerodynamic factors (foliage surfaces, micrometeorology, etc.) dominate the uncertainty in deposition. Ambient sulfate aerosols are "tagged" with natural radioactivity, ^{212}Pb and ^7Be . These tracers allow empirical measurements of submicron aerosol deposition to be made to complex surfaces like vegetation. In humid climates ^7Be cannot be used as a particle tracer since rainfall is the dominant deposition mechanism. Measurements in dry summer climates have been made to evaluate submicron aerosol deposition, however. Lead-212 is very useful in humid climates but suffers from being associated with aerosols that are a factor of 3 to 6 smaller in median diameter than sulfate. However by doing intercomparison studies with the isotopes it is possible to derive an air-to-vegetation transfer rate (AVTR) which is useful in deriving sulfate flux estimates.

1. For average daily wind speeds of 1 to 2 m s^{-1} empirical AVTRs for conifers are between 1 to 2 $\times 10^{-3} \text{ m}^3 \text{ kg}^{-1} \text{ s}^{-1}$. For deciduous species the estimate is 2 to 4 $\times 10^{-3} \text{ m}^3 \text{ kg}^{-1} \text{ s}^{-1}$. The range represents judgment based on various measurements. If the air concentration of sulfate (mg m^{-3}) is multiplied by the foliage biomass density (kg m^{-2}) and AVTR, the product is the deposition flux of sulfate ($\text{mg m}^{-2} \text{ s}^{-1}$).

2. For canopies with windspeeds less than 1 m s^{-1} (average) the AVTR is lower. Two studies, one with field-grown white pine and ^{212}Pb and one with Loblolly pine saplings and ^7Be in the greenhouse indicate that at windspeeds below 0.5 m s^{-1} the empirical deposition velocity of both isotopes is about 50% of the values referenced above, or 0.5 to 1 $\times 10^{-3} \text{ m}^3 \text{ kg}^{-1} \text{ s}^{-1}$.

3. Windspeeds higher than several m s^{-1} pose problems because the best empirical tracer in humid climates, ^{212}Pb , is on the small side of the aerosol size spectrum. This means that AVTRs derived using ^{212}Pb are biased towards diffusion-driven depositional processes, whereas impaction will dominate aerosol deposition at wind speeds such as are found on mountains. Thus an AVTR for spruce is impractical.

5.1.2

DRY DEPOSITION VELOCITIES AND SURFACE-TO-CANOPY SCALING FACTORS FOR AEROSOL CALCIUM FROM FOREST CANOPY THROUGHFALL*

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Oak Ridge, TN 37831-6038

Introduction Important problems in quantifying dry deposition to plant canopies include spatial and temporal representativeness of modeled fluxes and scaling from point measurements to the landscape. Micrometeorological approaches are limited to simple terrain and short intervals and are not applicable to coarse particles. Quantifying dry deposition of aerosols in the coarse mode, such as Ca and Mg in soil dust, is necessary to predict the effects of acidic deposition on lake acidification and forest nutrition. Although inert or surrogate surfaces can be used to measure particle fluxes, they do not reproduce foliage.

Analysis of throughfall (TF) beneath forests addresses these problems. TF is the water which drips from plant canopies following interception of rain and includes ions in the incoming rain, those leached from plant tissue, and those washed from plant surfaces as accumulated dry deposition. Net TF, defined as the flux in TF flux minus the flux in rain, consists of foliar leaching and dry deposition washoff. We previously developed a model to separate net TF into its component parts using rain event samples from a limited data set at a single forest (Lovett and Lindberg, 1984). The model has now been applied at several forests at different sites and elevations. The model was applied to examine spatial variability in dry deposition fluxes of aerosol Ca^{2+} within and between forest stands and to develop factors to scale up to tree canopies the fluxes of coarse aerosols measured to inert surfaces.

Methodology The model is based on an understanding of the general behavior of ions in plant canopies during rain events (Lovett and Lindberg, 1984). The approach involves a linear regression of measured net TF fluxes of an ion on these variables: antecedent period (ANT = duration of dry period prior to each rain event) and rain duration (DUR = duration of the rain event) (Eqn. 1). The coefficient of the parameter ANT (A) represents the mean dry deposition rate and that of the parameter DUR (B) represents the mean leaching rate from the canopy for a given ion. Term C

$$\text{Net TF flux} = \text{TF flux} - \text{rain flux} = A \cdot (\text{ANT}) + B \cdot (\text{DUR}) + C \quad (1)$$

is the intercept (not generally significant and not reported here). The model requires that samples be collected on an event basis so that ANT and DUR can be quantified. Data from at least 15 events are necessary to produce significant regression coefficients. TF measurements include only that material which is washed from the canopy by rainfall. Dry deposition that is irreversibly sorbed by the canopy or deposited to areas of the canopy not reached by rain is not measured. Hence, the model results are most reliable for water-soluble components of aerosols. The assumptions of the model are discussed in detail in Lovett and Lindberg (1984).

We report here model results from the following sites: an oak forest (Quercus prinus) in Tennessee sampled from 1981-1983, a low-elevation (300-m) loblolly pine (Pinus taeda) stand and a high-elevation (1730-m) red spruce (Picea rubens) stand in Tennessee, and a low-elevation (430-m) Norway spruce (Picea abies) stand in West Germany (all sampled during 1986-1988). Automatic collectors were used to collect precipitation in forest clearings and TF beneath the canopies as wetfall-only (Lovett and Lindberg, 1984). Replicate TF collectors were used in each forest (N = 6 for pine, N = 2 for oak and red spruce, and N = 9 for Norway spruce). Grids of 10-20 collectors were used for selected events to establish the representativeness of the

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permanent sampling points and were used continuously for measurements of hydrologic fluxes. Aerosols and dry-deposited coarse particles were collected from towers above the canopies (30-45 m above the ground) using Teflon filters and polycarbonate deposition plates (Lindberg and Lovett, 1985).

Results and Discussion The results of the TF regression model are summarized in Table 1. This simple model accounted for 54 to 87% of the variance in the mean net TF fluxes of Ca^{2+} at these sites and resulted in significant dry deposition coefficients for each forest ($P < 0.05$), suggesting that the model originally developed for the oak stand may be more generally applicable.

Table 1. Dry deposition rates of aerosol Ca^{2+} determined from a regression model applied to rain and throughfall event data from four forests, and a summary of the regression statistics for each site. The upper portion of the table includes results based on mean throughfall fluxes calculated from all replicate samplers used at each site. The lower portion describes results for each replicate collector in the pine forest for year 1. All of the regressions and resulting coefficients are significant at $P < 0.05$.

Site	N*	Model r^2	Mean dry deposition rate ($\mu\text{g m}^{-2} \text{h}^{-1}$)	SE†
All forests				
Pine (year 1)	38	0.72	46	6
Pine (year 2)	35	0.83	44	4
Red spruce	20	0.54	110	30
Oak	21	0.87	86	12
Norway spruce	15	0.78	68	10
Pine forest (year 1)				
Pine replicate 1	38	0.68	28	4
Pine replicate 2	38	0.38	54	16
Pine replicate 3	38	0.66	24	4
Pine replicate 4	37	0.56	88	20
Pine replicate 5	38	0.82	36	4
Pine replicate 6	38	0.85	58	6
Mean and SE for 6 pine replicates:			48	8

*N = number of rain events used in regression model.

†SE represents the standard error of the mean dry deposition rate determined from the regression model.

The mean dry deposition rates of Ca^{2+} were highest at the high-elevation spruce stand, reflecting elevational effects on deposition despite generally lower concentrations of airborne Ca^{2+} (Table 2). The spruce site differs from the nearby pine site in significant ways. The mean wind speed exceeds that at the pine site by a factor of 2.5, and the leaf area index (LAI) exceeds that at the pine site by a factor of 2-3. The fact that the spruce stand is located on a steep, exposed slope in the mountains creates an edge effect further enhancing dry deposition rates (Lindberg *et al.*, 1988). It is likely that net throughfall Ca^{2+} is also enhanced at the mountain site by cloud water interception, which would lead to overestimates of dry deposition rates by the TF model. The data from 2 consecutive years at the pine site suggest comparable dry deposition of Ca^{2+} during each year, providing confidence in the reproducibility of the approach.

Table 2. Summary of mean values for airborne concentrations, dry deposition rates measured to inert surfaces and resulting dry deposition velocities. The standard errors are indicated in parentheses.

Site	N	Airborne Ca ²⁺ (μg/m ³)	Ca ²⁺ dry deposition rate (μg m ⁻² h ⁻¹)	V _d for inert surface (cm/s)
Pine (year 1)	37	0.50 (0.05)	34 (2)	1.8 (0.1)
Pine (year 2)	38	0.55 (0.06)	35 (5)	1.8 (0.2)
Red spruce	22	0.26 (0.04)	22 (3)	3.2 (0.6)
Oak	26	0.92 (0.13)	31 (4)	1.1 (0.1)
Norway spruce	10	1.40 (0.22)	---	---

The model yields two measures of uncertainty when it is applied to sites with replicate collectors. The first is the standard error (SE) of the regression coefficient for dry deposition. This value indicates uncertainty in the mean dry deposition rate due to the temporal variability of the events used in the model. The second is the SE of the mean dry deposition rate for a site, determined by averaging the results from each replicate sampler. This value indicates uncertainty due to the spatial variability. These results are shown for the pine data in the lower portion of Table 1 (Pine #1, etc.). The SE's of the regression coefficients (right-hand column) range from 11 to 30% of the means, and the SE of the overall site mean (bottom line) is 17% of the mean. Together, these values indicate uncertainties of -40-60% (± 2 SE's) in seasonal or annual mean dry deposition rates of Ca²⁺ due to actual variability in canopy cover and meteorologic conditions within a forest stand.

Expressing the mean dry deposition rates in Table 1 relative to the mean aerosol concentrations (Table 2) yields average dry deposition velocities (V_d) for aerosol Ca²⁺ for each canopy. These values are 1.4 cm/s for the Norway spruce, 2.4 cm/s for the pine, and 2.6 cm/s for the oak stand, and exceed the deposition velocities of Ca²⁺ measured to inert surfaces above each canopy (Table 2). An accurate value for the red spruce stand cannot be determined until the influence of cloud water on TF fluxes has been quantified. The V_d's for the canopies are high relative to theoretical results, but are consistent with other field observations for both Ca²⁺ and coarse aerosols in general (Davidson and Wu, in press).

The results of the TF model applied to the Ca²⁺ data from these forests provide information on the dry deposition of coarse particles in general. Aerosol Ca²⁺ is a useful tracer of coarse particle behavior in atmosphere/canopy interactions. Impactor samples collected over 2 years near the oak and pine sites indicate that aerosol Ca²⁺ exhibits a mass median diameter generally >2 μm (mean = 2.7, SE = 0.9, N = 7; Lindberg et al., 1986). The importance of coarse particle dry deposition has been established, even for ions such as SO₄²⁻ that are typically associated with submicron aerosols (Davidson et al., 1985). Although the TF model can be used directly for SO₄²⁻, uncertainty in the behavior of dry-deposited SO₂ suggests that an unambiguous coarse particle tracer may be more useful.

Inert surfaces have been widely used to measure the dry deposition of various ions in different environments (Davidson and Wu, in press); however, the need to scale these measurements to the plant canopy is a major research need. The scaling factors needed to address this problem can be derived by comparing the Ca²⁺ dry deposition estimates from the TF model with those from inert surface measurements. The ratio of the mean dry deposition rate of Ca²⁺ to the forest canopy determined from the TF regression model (Table 1) divided by the measured deposition of Ca²⁺ to polycarbonate surfaces (Table 2) yields a useful scaling factor for coarse particles. The scaling factors (canopy/plate) for these forests range from 1.3 to 2.8 to 5.0 at the pine, oak, and red spruce stands, respectively. The similarity in the factors for the

pine stand for years 1 and 2 (1.3 and 1.4) is encouraging, as one would expect such scaling factors to be relatively constant over time in mature forests.

It is also expected that such scaling factors would be influenced by the surface area of the associated canopy and would be smaller than the canopy LAI. LAI which expresses canopy surface area on a ground-area basis, has often been considered an estimate for scaling from individual surfaces to full canopies, assuming all surfaces behave similarly. However, overlapping and shading of some surfaces, reduced turbulence in the subcanopy layers, and differences between leaf and flat plate capture characteristics suggest that these scaling factors should be lower than the full LAI of the canopy.

The LAI of these stands increase in the same order as the scaling factors, from 3.6 to 5.1 to 9 for pine, oak, and spruce, respectively. These three scaling factors and those determined for four other forests in the Integrated Forest Study are strongly related to canopy LAI ($r^2 = 0.90$), as illustrated in Fig. 1. These relationships establish confidence in the model and its assumptions, because the scaling factors should be physically bounded between 1 and the canopy LAI and should generally increase with canopy area. Such factors improve models for scaling point measurements of aerosol dry deposition to forest canopies.

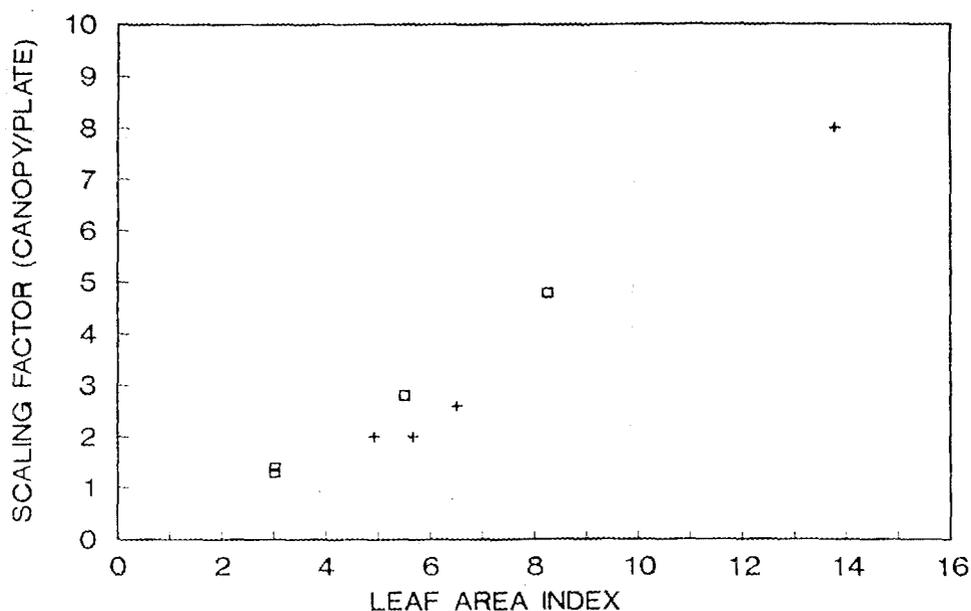


Fig. 1. Relationship between canopy leaf area index (LAI) and scaling factor for coarse aerosol dry deposition. Squares represent data from this paper; pluses represent data from other low-elevation forests in the Integrated Forest Study (Lindberg et al., 1988).

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5.1.3

Deposition of Reactive Nitrogen Gases to Landscape Surfaces (Experimental Task A4)

P. J. Hanson, G. E. Taylor Jr., S. E. Lindberg, Oak Ridge National Laboratory; and G. M. Lovett, Institute for Ecosystem Studies.

The objective of this experimental task was to characterize the role of environmental and physiological factors governing the deposition of nitric acid vapor (HNO_3) and nitrogen dioxide (NO_2) to vegetative surfaces in terrestrial landscapes. Nitrogen dioxide is the dominant form of atmospheric oxides of nitrogen (NO_x), whereas HNO_3 is the principal chemical sink for removal of NO_x . The deposition data are needed in the IFS to estimate the atmospheric inputs of gaseous nitrogen to each of the forest sites.

Measurements of HNO_3 and NO_2 deposition were conducted in an open gas exchange system operating at the whole-plant level. The system simultaneously monitored CO_2 , H_2O , and pollutant gas exchange under controlled conditions of temperature, light, vapor pressure, and soil water availability. Deposition rates ($\text{nmol m}^{-2} \text{s}^{-1}$) were calculated as the product of flow rate and the inlet/outlet concentration differential normalized for surface area and corrected for losses to chamber walls. Shoot conductance to a reactive nitrogen gas, a leaf level measurement analogous to the "deposition velocity" presented in cm s^{-1} , was determined by dividing the rate of deposition by the ambient concentration of the gas being measured. Measurements of HNO_3 and NO_2 deposition to foliage shoots were conducted under light and dark conditions to establish patterns of diurnal variability, and rates of NO_2 deposition were explored relative to shoot conductance to water vapor ($\text{mol m}^{-2} \text{s}^{-1}$; the reciprocal of diffusive conductance).

NO_2 deposition

Under daylight conditions and a mean concentration of 33 nl l^{-1} ($63 \mu\text{g m}^{-3}$), NO_2 deposition to foliage of forest tree species varied by more than an order of magnitude, ranging from 0.35 (loblolly pine) to $5.75 \text{ nmol m}^{-2} \text{s}^{-1}$ (sycamore), and the flux to most broadleaf species was greater than deposition to conifers. The broadleaf species exhibiting the highest rates of NO_2 deposition had greater shoot conductance to water vapor (Fig. 1) suggesting that interspecific variation in shoot conductance to NO_2 reflects variation in stomatal frequencies and stomatal apertures. The contrasting light-dark measurements of NO_2 deposition indicated that the principal foliar site of NO_2 deposition was the leaf interior, comprising typically greater than 90 % of total deposition to individual leaves.

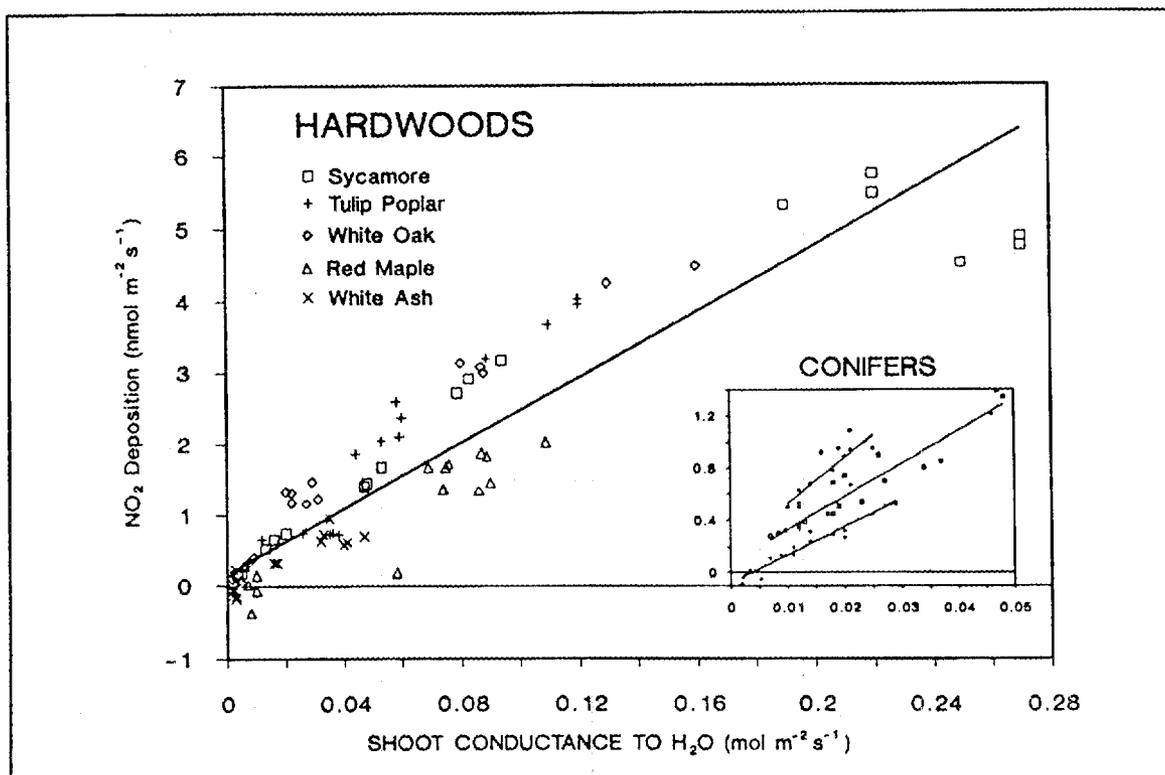


Fig. 1. Linear relationship between NO_2 deposition and shoot conductance to water vapor. The symbols represent individual measurements for 5 broadleaf (main graph) and 3 conifer species (inset). The data for broadleaf species is expressed on a projected leaf area basis, and that for conifers on a total area basis. Mean NO_2 concentration was 33 nl l^{-1} ($63 \mu\text{g m}^{-3}$).

Deposition of NO_2 varied among forest elements measured. Foliar, bark and forest floor surfaces showed greater conductance to NO_2 than distilled water alone, and forest floor surfaces showed a disproportionately high conductance when compared to bark or foliage (Fig. 2). The average conductance to NO_2 of the materials measured ranged from -0.0045 to 0.48 cm s^{-1} . As expected, conductance to NO_2 of Teflon was virtually zero. Conductance to NO_2 of dry bark was similar to that of conifer shoots (0.047 and 0.049 cm s^{-1} , respectively), and conductance to NO_2 of wet bark was similar to values for broadleaf shoots (0.093 and 0.093 cm s^{-1} , respectively). Conductance to NO_2 was not influenced by species of bark.

HNO_3 deposition

Comparisons of HNO_3 and NO_2 deposition showed little deposition of either gas to Teflon surfaces and much greater deposition of HNO_3 versus NO_2 to hardwood shoots, conifer shoots, and tree bark (Fig. 3). This dissimilarity between the two trace gases is consistent with field observations which employ micrometeorological techniques.

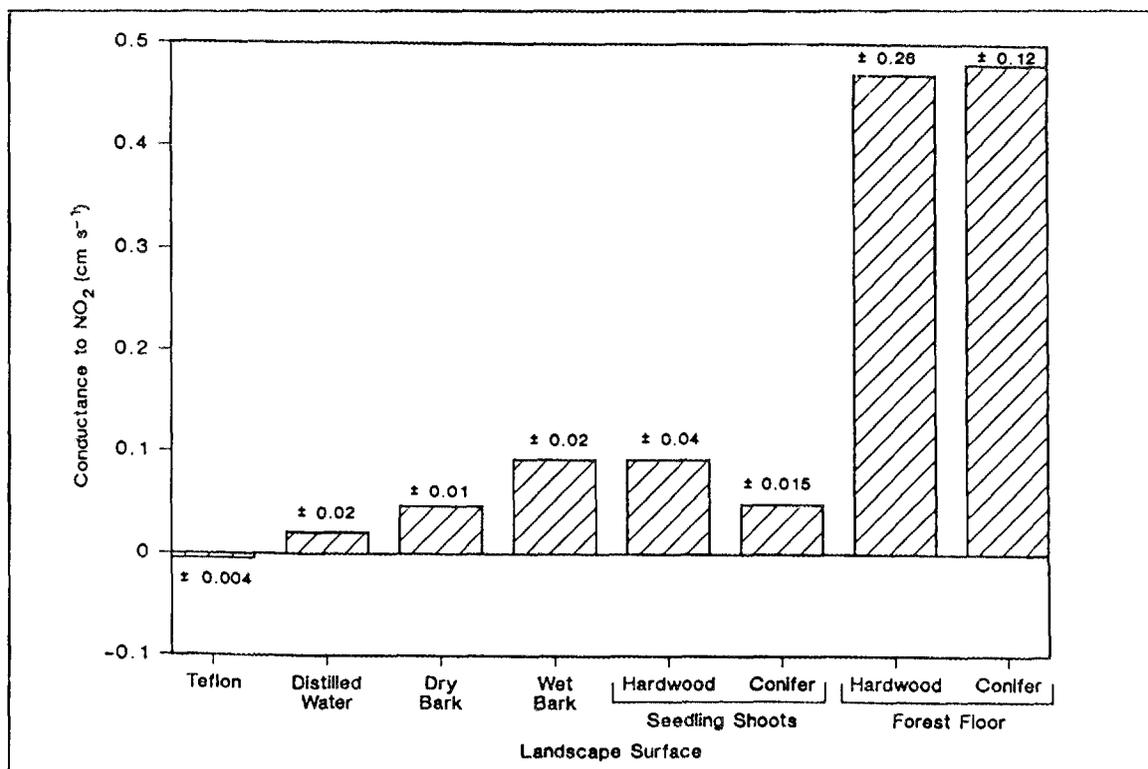


Fig. 2. Conductance of various terrestrial surfaces to NO₂ deposition. Each bar is topped by a number corresponding to the 95 percent confidence interval around the data. All data are expressed on a total area basis (planar for the intact forest floor cores).

Because the HNO₃ deposition measurements were necessarily limited to conditions of low humidity and therefore low shoot conductance to water vapor, comparisons of deposition between HNO₃ and NO₂ were restricted to those NO₂ measurements with correspondingly low water vapor conductances. Although variability was great, precluding rigorous quantification, our data indicated a small component of HNO₃ deposition to the leaf interior coincident with a large component of surface deposition. This observation is not consistent with the assumption of zero internal deposition used by current "stand-level" deposition models. However, modeling errors caused by this assumption should be small (i.e., <10%).

Modeling Deposition to Leaves

To support our experimental observations concerning the location and extent of deposition of HNO₃ to leaves, we developed a model based on pollutant gas diffusivities in air and their Henry's Law coefficients that addresses gas-surface interactions at the "leaf" scale of resolution. For a 3 nl l⁻¹ (5.7 μg m⁻³) concentration gradient, the model predicts initial pollutant fluxes to leaf interiors to be similar for

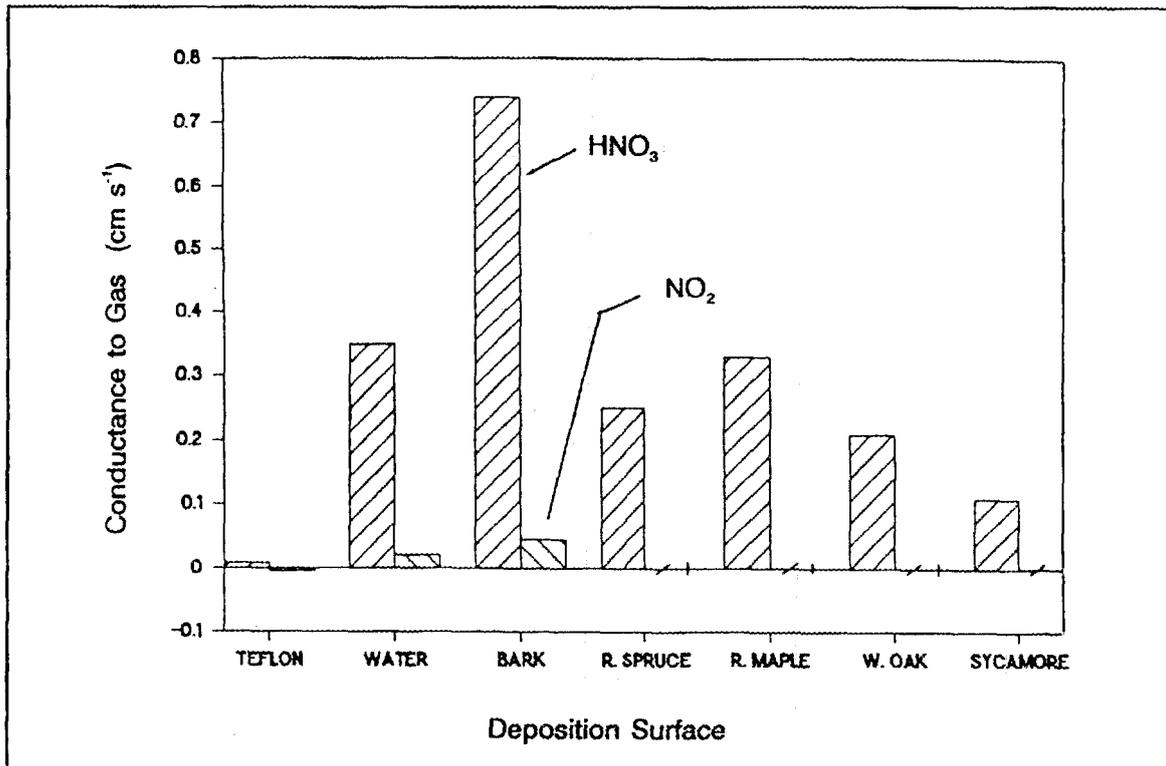


Fig. 3. Deposition of HNO₃ and NO₂ to tree bark and seedling shoots.

HNO₃, NO, O₃, and SO₂. However, diffusion flux is predicted to decline rapidly over time for NO and O₃, at a slower rate for SO₂, and very little for HNO₃. The rate of change in flux corresponds to the gas' water solubility; gases of low solubility saturate the leaf interior faster. Flux of HNO₃ vapor to the leaf was predicted to be 4 to 7 orders of magnitude higher than for the less soluble gases (a prediction that agrees with the observed data; Fig. 3). Although this model focuses on deposition at the "leaf" level of resolution, its principles can be used to generate reasonable estimates of variables for use in whole-plant or stand level models of pollutant deposition (e.g. big-leaf or stratified layer stand models).

Estimates of NO₂ Deposition to Forest Canopies

Laboratory data for several forest species were extrapolated to stand-level rates of NO₂ deposition using leaf area index as a scaling factor. Based on appropriate NO₂ concentrations, NO₂ deposition was calculated to provide annual nitrogen inputs between 0.08 and 1.9 kg ha⁻¹ y⁻¹ of NO₂-derived nitrogen (NO₂-N) for natural forests (Table 1). These rates of N deposition are similar to inputs expected from nonsymbiotic nitrogen fixing bacteria (0-3 kg NO₂-N ha⁻¹ y⁻¹) in temperate forest

ecosystems. In or near urban environments where NO_2 concentrations can easily exceed $30\text{-}50 \text{ nL L}^{-1}$ ($57\text{-}95 \mu\text{g m}^{-3}$) deposition of $\text{NO}_2\text{-N}$ could easily reach $12 \text{ kg NO}_2\text{-N ha}^{-1} \text{ y}^{-1}$.

Table 1. Estimates of $\text{NO}_2\text{-N}$ deposition to IFS forests

Stand	NO_2 conc.	$\text{NO}_2\text{-N}$ deposition	Total dry N deposition
	nl l^{-1}	$\text{kg ha}^{-1} \text{ y}^{-1}$	$\text{kg ha}^{-1} \text{ y}^{-1}$
WF	2	0.08	6.5 (1)
ST	2	0.2	13.8 (1)
NS	1	0.09	3.2 (3)
LP	8	0.6	4.3 (13)
DL	5	0.8	9.1 (9)
CP	2	0.7	4.4 (16)
DF	1	0.4	0.8 (49)
HF	2	0.4	4.4 (8)
WB	8	1.9	4.8 (39)

Numbers in parentheses are $\text{NO}_2\text{-N}$ deposition expressed as a percent of total dry N deposition. Multiply nL L^{-1} by 1.91 to get $\mu\text{g m}^{-3}$.

Conclusions

- * Deposition occurs along pathways leading to foliage, bark, and forest floor surfaces.
- * NO_2 deposition to broadleaf species exceeds that to conifers.
- * Deposition of $\text{HNO}_3 > \text{NO}_2$.
- * NO_2 deposition occurs mainly to leaf interior spaces and is controlled by stomatal aperture.
- * HNO_3 vapor exhibits significant deposition to leaf cuticular surfaces, but a finite amount of internal deposition probably occurs.
- * Nitrogen dioxide's contribution to total dry N deposition may be more important than previously recognized, especially in or near urban or polluted areas.

Ozone Patterns in Forested Landscapes: Spatial and Temporal Characteristics

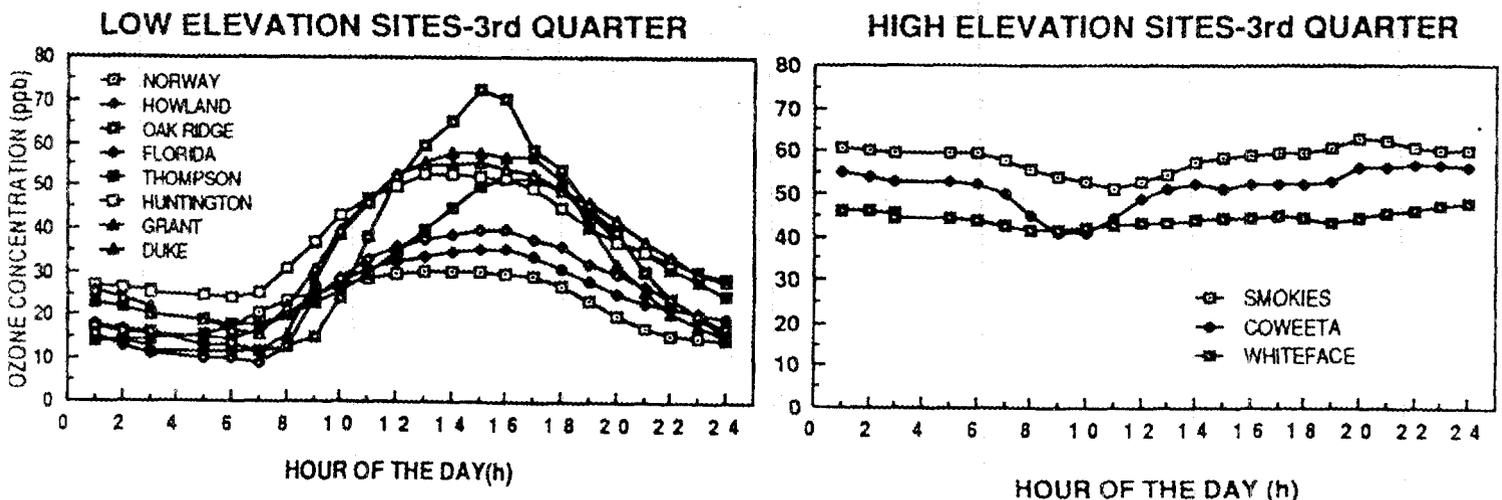
G. E. Taylor, Jr., B. M. Ross-Todd, and IFS Site Representatives

Ozone (O₃) measurements are being made at all of the IFS sites in conjunction with the atmospheric deposition and mineral cycling research. The intent is to provide a record of O₃ concentrations at all sites and to compare patterns of O₃ across sites. This highlight presents a preliminary summary of the O₃ data for 1988, focusing specifically on the second (April, May, and June) and third (July, August, and September) quarters using 1-h means as the base statistics from which to aggregate over time. The objective is to characterize the variability among and within sites as a function of (1) time (e.g., diurnal, seasonal, annual) and (2) space (e.g., elevation, latitude). Figure 1 summarizes O₃ concentrations as a function of time of day in both the low and high elevation IFS sites for solely the third quarter of 1988.

In the lower elevation IFS sites, O₃ concentrations exhibited the characteristic pattern of a photochemically-driven pollutant (i.e., predawn minimum and middle to late afternoon maximum). Independent of the site, the predawn value approached 20 ppb (± 10 ppb), whereas the late afternoon maxima were more variable (30 to 70 ppb) and the max:min ratio ranged from 2 (Norway) to 7 (Oak Ridge). Unlike urban landscapes, the daytime maxima showed a broad shoulder, lasting from 1 to 5 hours and oftentimes extending into the evening hours (1800-2200 h). On the average, the O₃ concentrations in the low elevation IFS sites were 10-20% higher in 1988 than in 1987 and were greater in the second rather than the third quarter.

A contrasting O₃ pattern was recorded in the three higher elevation sites (Smokies, Coweeta, Whiteface). In particular, the diurnal variability was substantially muted, with each 1-h mean being ± 5 ppb of the 24-h mean. There was no evidence of a mid-afternoon to evening peak in O₃ concentration. One unique feature of the high elevation sites, particularly those in the more southern latitudes, was the pronounced early morning (0600 to 1100 h) drop in O₃ concentration, attributed to the thermal upwelling of O₃ depleted air from lower elevations. In comparison to the lower elevation sites, the 24-h means were generally 20-40% higher.

The salient feature of these patterns in O₃ concentrations is the necessity of data summaries that do not mask the rather pronounced temporal and spatial variability among forested sites. Because of this variability, the final summary of the O₃ concentrations across sites will focus on methodologies that attempt to describe patterns that are physiologically and ecologically important.



5.1.5

Effects of Ozone Exposure, Acid Deposition, and Nutrient Supply on Foliar Leaching

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Acid Deposition, Ozone Exposure, and Foliar Leaching

The purpose of this project was to examine whether foliar leaching of ions is affected by acidic deposition or ozone exposure. Both of these pollutants have been suggested by others to increase foliar leaching of base cations (K, Ca, and Mg in particular) from trees, but the proposed mechanisms are different. For acid deposition, the mechanism is identified as cation exchange between deposited H^+ and foliar base cations on exchange sites on or in the leaf (Tukey 1980). However, experimental studies have not shown statistically significant effects of acidity on foliar leaching until acidity was raised to pH 3.3 or below (Wood and Bormann 1975, Scherbatskoy and Klein 1983, Schier 1987). For ozone, the proposed mechanism is damage to leaf cellular membranes, causing leakage of cell contents which are then leached by subsequent rainfall (Krause et al. 1982). Krause et al. reported this effect on Norway spruce (*Picea abies*) seedlings, but without statistical analysis of the data. Skeffington and Roberts (1985) could not demonstrate this effect on Scots pine (*Pinus sylvestris*).

We used a branch chamber apparatus, described in previous reports and by Hubbell and Lovett (1988), to expose canopy branches of mature trees of white pine (*Pinus strobus*) and sugar maple (*Acer saccharum*) to ozone and acid mist and determine the leaching response. Treatments included a 5h ozone exposure at 25, 70, or 140 ppb, followed by a 1h leaching with mist acidified to pH 5.0 or 3.8. Thus the treatment sequence mimicked a typical summer day, with elevated ozone concentrations in the afternoon followed by a brief rainshower.

The results of the experiments were very similar for both white pine and sugar maple. In both cases, the 5h ozone exposures had no effect on leaching of any ions. Increasing mist acidity from pH 5.0 to 3.8 more than doubled the leaching of Ca and Mg from both species (a highly statistically significant effect), but had no effect on leaching of K. For both species, H^+ was released in the pH 5.0 treatment and absorbed in the pH 3.8 treatment, indicating a buffering of the incident precipitation acidity by the foliage. Figure 1 shows the treatment means for sugar maple for Ca, Mg, K and H^+ .

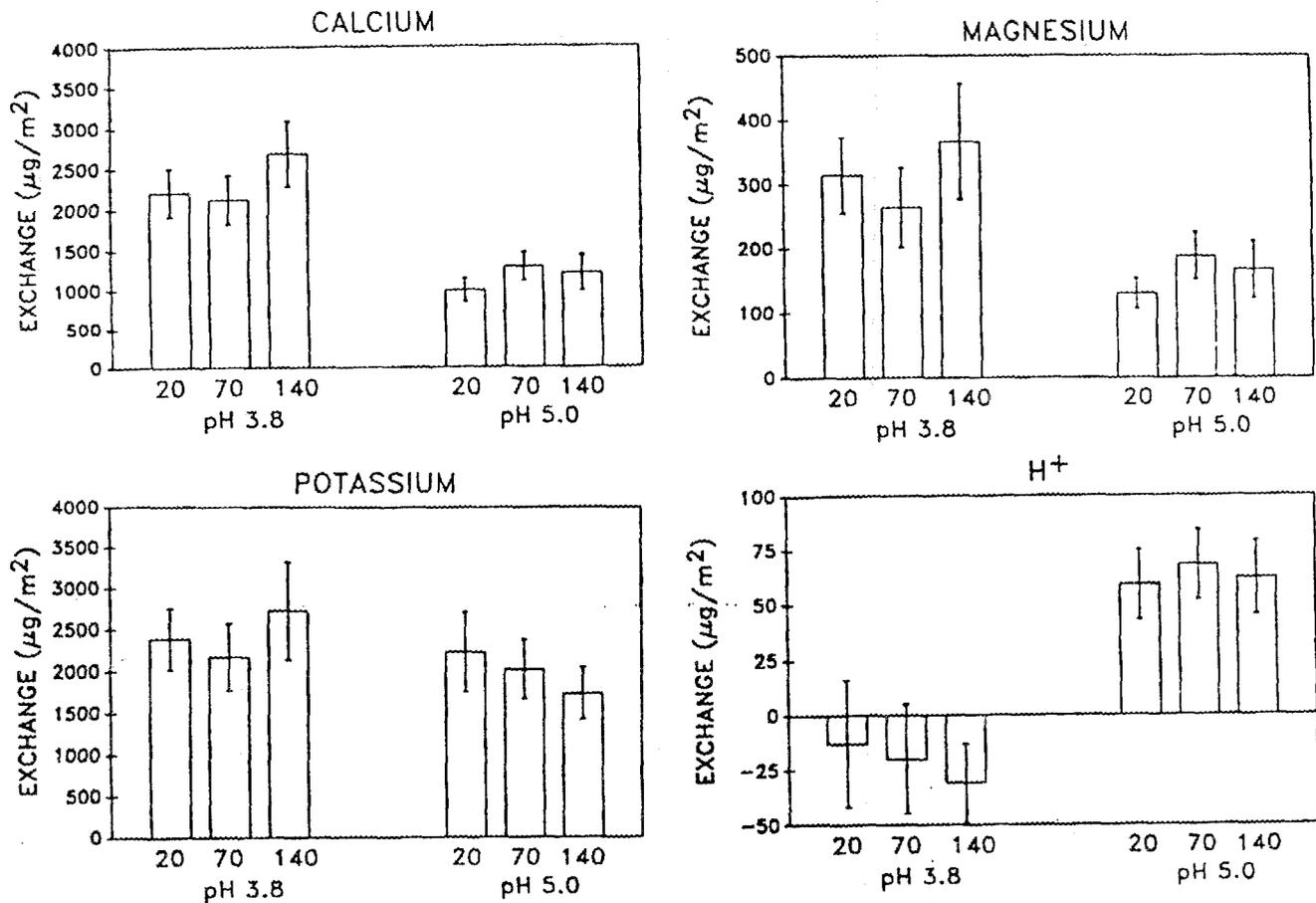


Figure 1. Treatment mean (\pm standard error) values for sugar maple canopy exchange, in $\mu\text{g}/\text{m}^2$ of foliage surface. Individual bars represent ozone treatments (20, 70, or 140 ppb) grouped by acid mist treatment (pH 3.8 or 5.0).

Table 1 compares the sugar maple and white pine results for all ions in the two pH treatments. The loss of both cations and anions was higher from sugar maple than from white pine. The anion deficit in Table 1 indicates that in some cases, unmeasured anions were released into the leachate solution. These are most probably organic acid anions, which represent part of the pH-buffering capacity of these canopies. In all cases except the white pine pH 3.8 treatment, these organic anions provide a major portion of the leached negative charge.

We conclude from these experiments that short-term ozone exposure, in the absence of visible leaf damage, does not affect

Table 1. Mean amounts of canopy release (positive numbers) or uptake (negative numbers) from white pine and sugar maple branches at two different pH levels. Data expressed as micro-equivalents per square meter of foliar surface area (one-sided) for 1h misting treatments.

	White Pine		Sugar Maple		
	pH	<u>3.8</u>	<u>5.0</u>	<u>3.8</u>	<u>5.0</u>
Ca		19	8	117	60
Mg		8	3	26	13
K		14	11	62	51
Na		8	5	6	7
NH ₄ ⁺		8	3	-3	-8
H ⁺		-17	41	-21	63
Cation Sum		40	71	187	186
SO ₄ ²⁻		21	21	57	75
NO ₃ ⁻		15	11	52	53
Cl ⁻		7	4	1	3
Anion Sum		43	36	110	131
Anion Deficit		-3	35	77	55

foliar leaching. However, acid wet deposition, at acidity levels commonly experienced in the eastern U.S. and Europe, can have a strong effect on canopy exchange of Ca, Mg, and H⁺.

Foliar Leaching and Compensatory Root Uptake

The strong effects of acid mist on foliar leaching of Ca and Mg prompted us to ask whether increased root uptake can compensate for losses of nutrients from the foliage. The question is relevant from two points of view. From the perspective of the plant, lack of compensatory uptake could result in a decline in the foliar nutrient pool and thus affect the nutrition of the leaf cells. From the ecosystem perspective, lack of compensatory uptake would indicate an acidification of the foliage, and subsequently the litterfall, in effect creating a delay in the deposition of the acidity to the soil. At the same time, Ca and Mg return would be increased in throughfall solution and decreased in litterfall. If compensatory uptake did occur, increased hydrogen ion expulsion from the roots would balance the increased cation uptake, in effect resulting in a shunting of the acid deposition from the canopy to the rooting zone, and

decreasing the potential for neutralization of the acidity in the litter layer of the forest floor.

Testing for a decrease in foliar nutrients after exposure to acid deposition would probably not answer this question, because the total foliar pool of cations is large relative to the exchangeable pool, which is located in the foliar apoplasm and provides the nutrients for cell growth. We know of no way to measure this apoplastic pool, so our approach was to examine the relative magnitude of nutrient inputs (uptake) and outputs (foliar leaching) in whole plants under different foliar leaching and cation availability treatments.

In a greenhouse, we grew white pine seedlings in sand culture, and calculated their nutrient uptake from measurements of inputs and outputs (in drainage water) from the sand-filled pots. Twenty-four plants were divided into four treatment groups, which received either high or low cation concentrations in nutrient solution (Table 2) and either 3 h/wk of foliar

Table 2. Concentrations (mg/L) of N, K, Ca, and Mg in the two nutrient solutions supplied to white pine seedlings. Nitrogen was supplied 60% as NH_4^+ and 40% as NO_3^- .

	<u>High Cations</u>	<u>Low Cations</u>
N	150	150
K	72	12
Ca	8.0	1.2
Mg	8.2	1.3

leaching or no leaching at all. Six sand-filled pots without plants were used as controls. The nitrogen content of the nutrient solution was high and identical for both nutrient solutions. The nitrogen:cation ratios in the high-cation treatment were optimal for pines (Ingestad 1979), whereas in the low-cation treatment, the ratios were approximately 1/6 the optimal ratio (Table 2). The results were analyzed statistically using an analysis of variance procedure.

Our results included the following:

1. Plants in the high-nutrient treatment took up more Ca, Mg, and K than those in the low-nutrient treatment, and the cation uptake was linearly proportional to N uptake, indicating incorporation of the cations into tissue.

2. Cation leaching was small relative to cation uptake (e.g., Figure 2). Uptake/leaching rates were generally 10 or greater.
3. The leached plants did not take up significantly more cations than the unleached plants, probably because the leaching rates were small compared to the uptake rates.

Our overall impression from these results is that nutrient availability controlled the uptake, and that there was no tight linkage between leaching and uptake. We plan to further investigate this linkage under the conditions of low nutrient availability and high foliar leaching "intensity" characteristic of high-elevation forests.

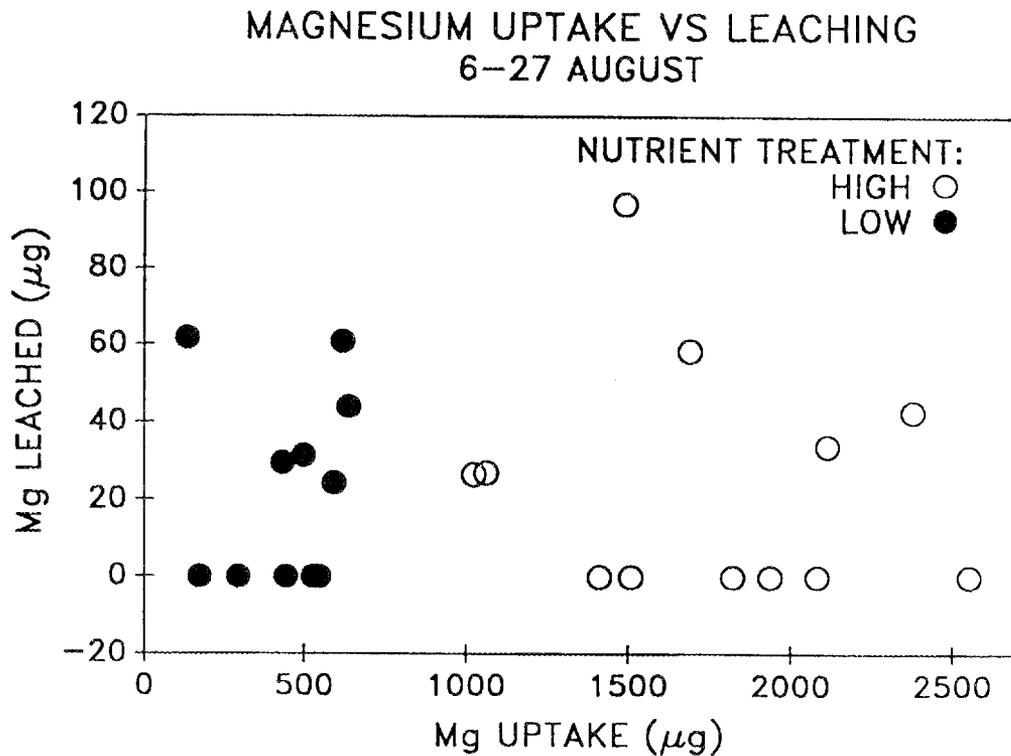


Figure 2. Amounts of Mg leached from foliage and taken up by roots of white pine seedling during the period 6-27 August. Points showing zero leaching represent the unleached plants. Qualitatively similar results were obtained for K and Ca.

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5.1.6

Integrated Forest Study Experimental Task Report:

Canopy Acid Balance and Foliar Cation Exchange

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One experimental task of the Integrated Forest Study (IFS) is to explore the extent to which atmospheric deposition of acidity can increase cation losses from foliage. In this study, we compared net canopy cation exchange with fluxes of free and undissociated acidity in net TF to interpret the mechanism of acidity consumption across several IFS canopies.

The presumptive mechanism of cation exchange for protons involves fixed exchange sites at or near foliar surfaces (Mecklenburg et al. 1966). However, this cation exchange *per se* is not the the only mechanism which could lead to to the coupled appearance of cations, and the disappearance of free acidity from throughfall (TF), as indicated in Figure 1. Panel A shows the cation exchange mechanism, with free acidity consumed as cations are released. Panel B illustrates inorganic cation release coupled with organic acid anions (which become protonated in TF). Both processes release cations from foliage and decrease the free acidity of water descending the canopy as TF (Cronan and Reiners 1983), but only in the former will the increased deposition of acidity necessarily increase cation release from foliage (Lovett et al. 1985).

Because both of these processes increase inorganic cation concentrations in TF and raise the pH of TF, they are difficult to distinguish. Net canopy

cation exchange in TF (based on the canopy charge balance described below) can be used to estimate of cation exchange at fixed sites (Lovett et al. 1985). This estimate is conservative because it assumes that all organic acid anions lost from foliage are accompanied by cations other than H⁺, so those cations in net TF do not arise from fixed cation exchange sites in the canopy.

Net TF fluxes of undissociated acidity were determined from Gran's plot titrations (undissociated acidity equals Gran's total acidity minus free acidity from pH; Lindberg et al. 1984) of TF and rain, multiplied by the hydrologic fluxes of TF and rain (Schaefer et al. 1989). Net TF fluxes of all major inorganic anions and cations were determined from TF minus rain and estimated dry deposition fluxes (IFS Technical Highlight #12). Net TF cation exchange was determined as net canopy cation retention minus anion retention (Lovett et al. 1985). Samples titrated from the Smoky Mtns. red spruce (ST), the Oak Ridge loblolly pine (LP), the Washington Douglas fir (DF), red alder (RA) and the Norway spruce (NS) sites represented essentially complete annual fluxes. Samples representing less than 50% of the annual fluxes were titrated from the other sites. Lovett et al. (1985) performed this analysis for three deciduous forests in Tennessee and found that all three exhibited net canopy cation exchange.

This analysis showed that all sites exhibited net canopy cation losses, but not all cation exchange per se (Figure 2). At the ST, LP, DF and RA sites, net canopy anion retention (primarily from dry-deposited nitrate) exceeded cation retention (primarily the protonation of weak organic acid anions). Therefore fixed foliar cation exchange sites need not be invoked

there, and increased acidic deposition would not necessarily increase canopy cation losses from the ST, LP, DF and RA forests.

However, at the Coweeta white pine (CP), the Whiteface Mtn. red spruce/balsam fir (WF), the Huntington Forest beech/maple (HF) sites and NS, canopy cation retention exceeded anion retention. At those four sites, we concluded that cation exchange in the canopy did occur, and that increased acidic deposition would increase cation losses from those forests.

The ST and DF sites were at opposite extremes of acidic inputs among IFS sites, and neither showed canopy cation exchange. This argued against an acidic deposition effect across sites, but experimental evidence from other IFS studies (Schaefer and Lovett, in prep.) has clearly shown the effect of acidity on cation exchange for several tree species. The presence of cation exchange in both NS and CP showed that coniferous as well as deciduous canopies could exhibit cation exchange.

The preceding analysis was based on the conservative assumption that all organic acid anions lost from foliage were accompanied by cations other than H⁺. With the more liberal assumption that some organic acids were protonated when released from foliage, calculated canopy proton retention increased and canopy cation exchange was observed at all sites except ST and DF (Figure 3). The absence of cation exchange at ST and the lack of a consistent pattern across the other sites (shown in Figure 3 along a gradient of decreasing acidic deposition) again failed to support an acidic deposition effect on cation exchange.

The IFS sites measure total acid inputs and outputs. Free and undissociated acid fluxes in canopy inputs (assuming that dry deposition fluxes of undissociated acidity are negligible; Schaefer et al. 1989) and outputs can be used to construct a total canopy acid balance (Figure 4). In such an acid balance, organic acids in TF water that released cations and became protonated would be detected by titration, and canopy outputs of acidity would equal the inputs. However, cation exchange at fixed sites in the canopy would result in proton retention in the canopy, and canopy acid inputs would exceed the outputs. By this method, the WF, NS, CP, HF and RA sites showed reduced total acidity in canopy outputs compared to the inputs. This shows that cation exchange took place in those canopies to at least a limited extent.

Both charge balance estimates indicated that cation exchange was less than the net canopy release of cations, regardless of whether the organic acids were presumed to be released with protons or with other cations. Nitrate retention in the canopy was a major term in the charge balance, suggesting the possibility that the acidity delivered to the canopy as HNO_3 could also be retained. To explore this possibility, we compared total acid inputs to the sums of total acid outputs plus nitrate retention and both low and high estimates of cation exchange (Figure 5). Linear regressions (excluding ST) based on the low and high estimates of cation exchange are both significant, and neither slope differs significantly from unity. Thus both cation exchange and HNO_3 uptake appear to interact in the canopy total acid balance. The total acidity increase of ST was unusual among IFS sites, and may have resulted from organic acids released from decomposition or

from living canopy tissue. If these acids exhibited pK_a lower than the pH of TF, their dissociation would lower the pH of TF.

In summary, a subset of both the deciduous and coniferous canopies in the IFS have been shown to release cations to TF in exchange for free acidity. We anticipate that at these sites, increased acidic deposition would lead to additional canopy cation losses. This process may occur in the other canopies as well, but when assessed by charge balance, can be masked by the presence of undissociated acidity in TF. Both deciduous and coniferous canopies showed release of undissociated acids and (at least) the potential for cation exchange in the canopy. This suggests that the widely-reported differences in "pH neutralization" between deciduous and coniferous canopies may result from dry-deposited acidity or the pK_a of the undissociated acids released, not solely from the presence or absence of cation exchange in the canopy.

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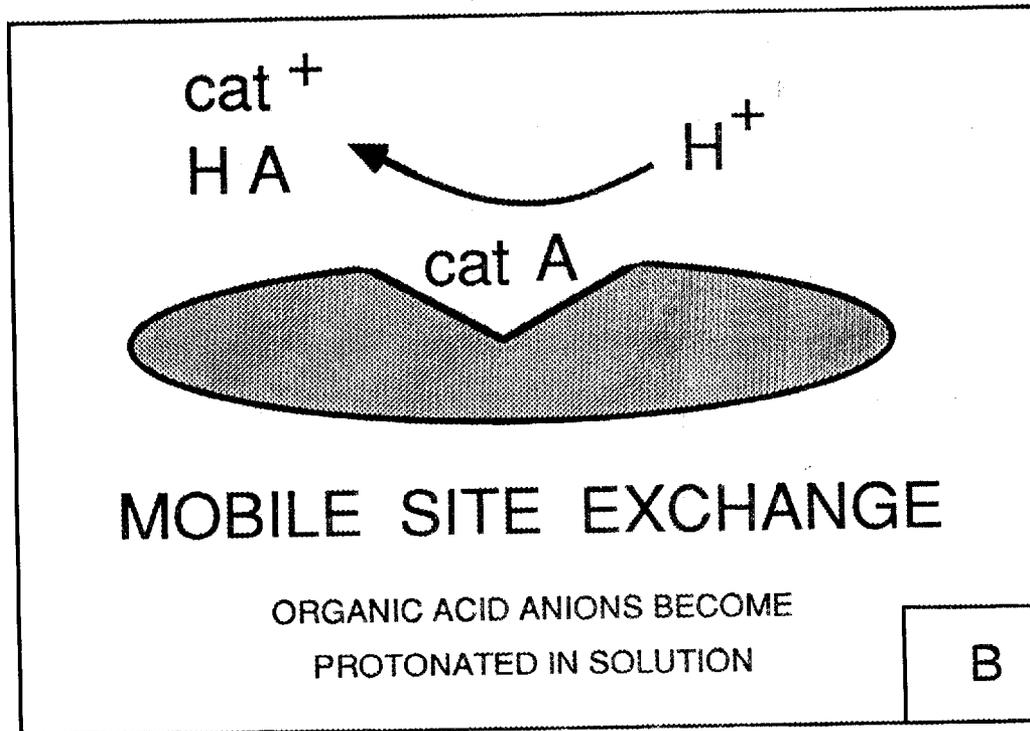
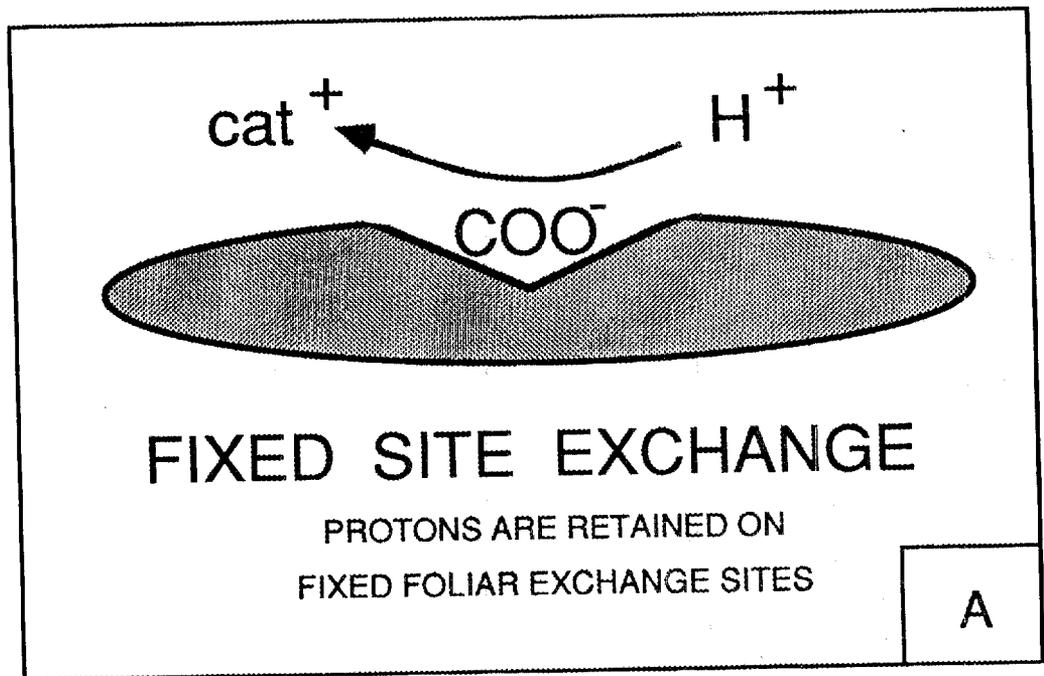


Figure 1. A) A schematic representation of H^+ ions in solution displacing basic cations from fixed foliar exchange sites, and B) Of mobile organic acid anions associated with basic cations diffusing out of foliage. In throughfall water, the cations dissociate and H^+ ions protonate the acid anions.

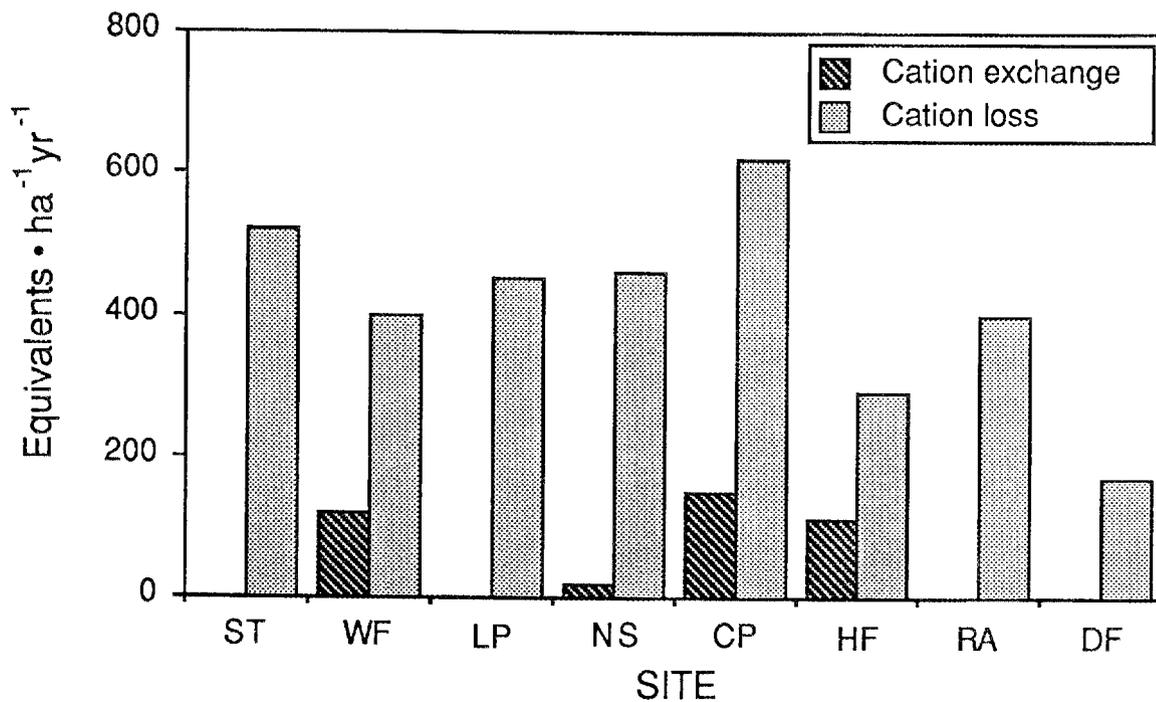


Figure 2. A comparison of net throughfall fluxes of cations and a conservative estimate of net canopy cation exchange, based on the assumption that the organic acidity released from the canopy consumes protons. Units are equivalents ha⁻¹ y⁻¹. IFS sites are defined in the text.

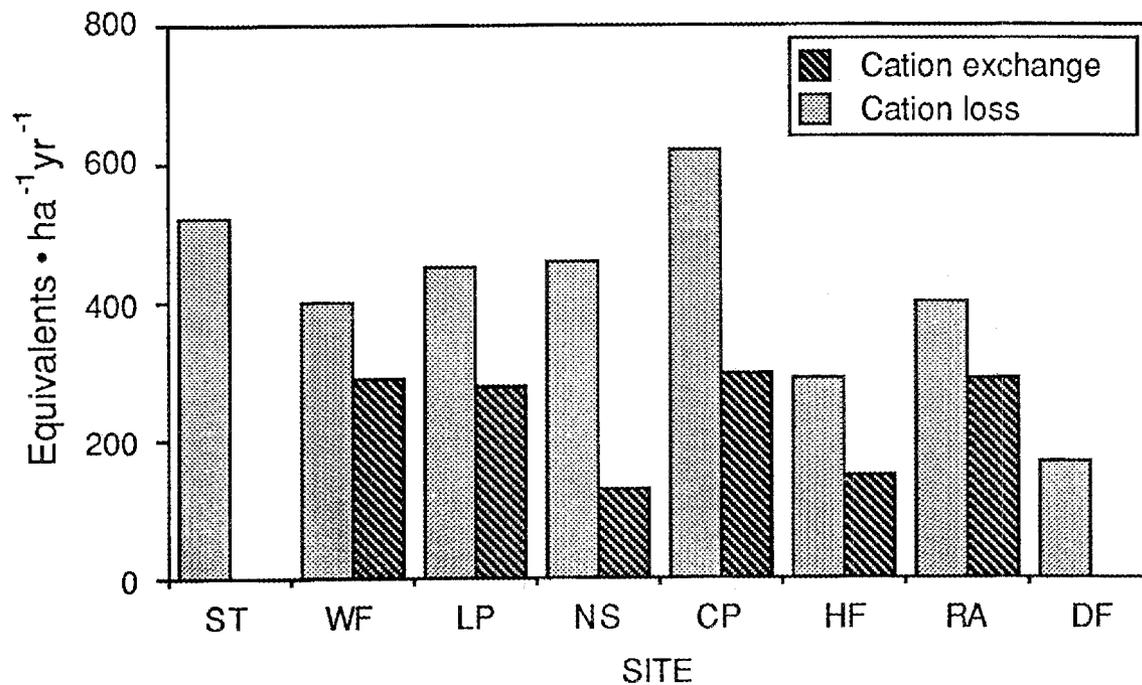


Figure 3. A comparison of net throughfall fluxes of cations and a liberal estimate of net canopy cation exchange, based on the assumption that organic acidity released from the canopy does not consume protons. Units are equivalents ha⁻¹ y⁻¹. IFS sites are defined in the text.

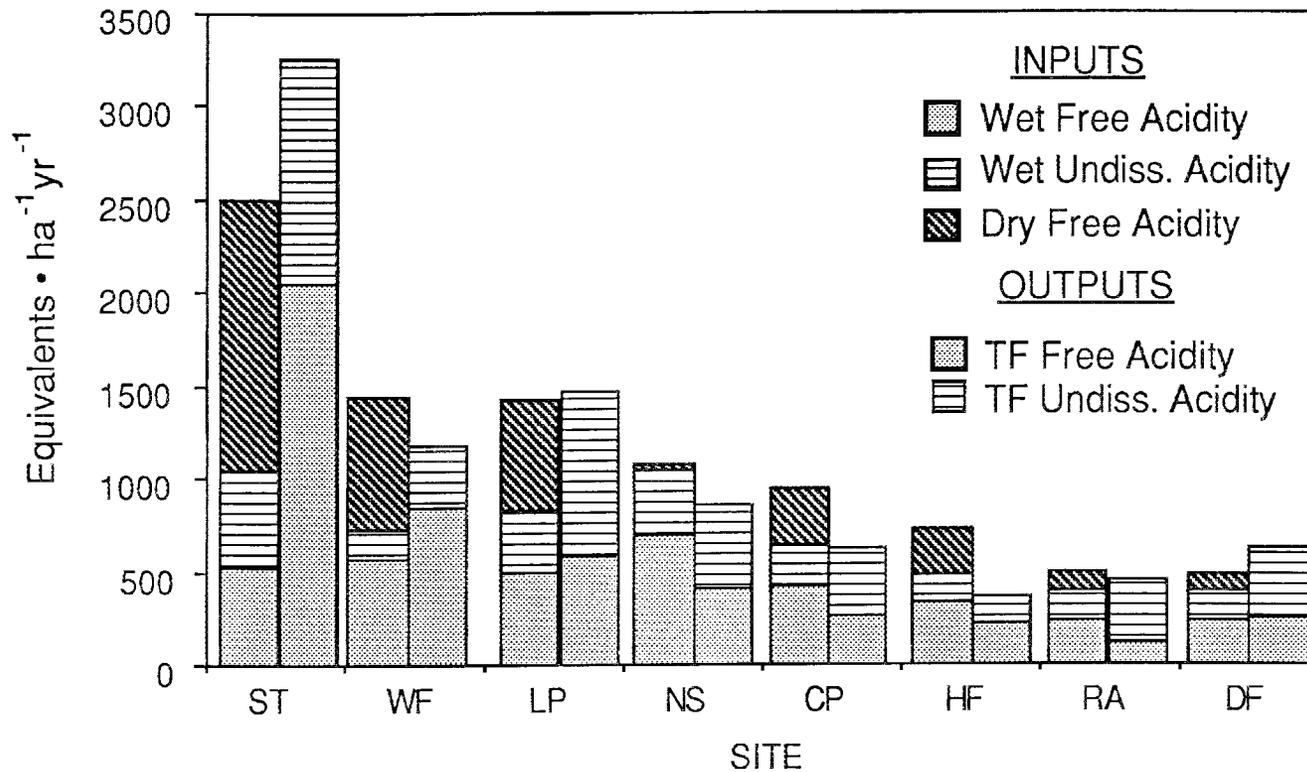


Figure 4. Total acid inputs and outputs (in equivalents ha⁻¹ y⁻¹) for 8 IFS sites (defined in the text). Dry free acidity is H⁺ from aerosols and vapors, and cloud deposition at ST and WF. Rain and snow provide both free and undissociated wet acidity. Throughfall (TF) is the output flux of free and undissociated acidity. Where total inputs exceed outputs, H⁺ was retained in the canopy, presumably at fixed cation exchange sites.

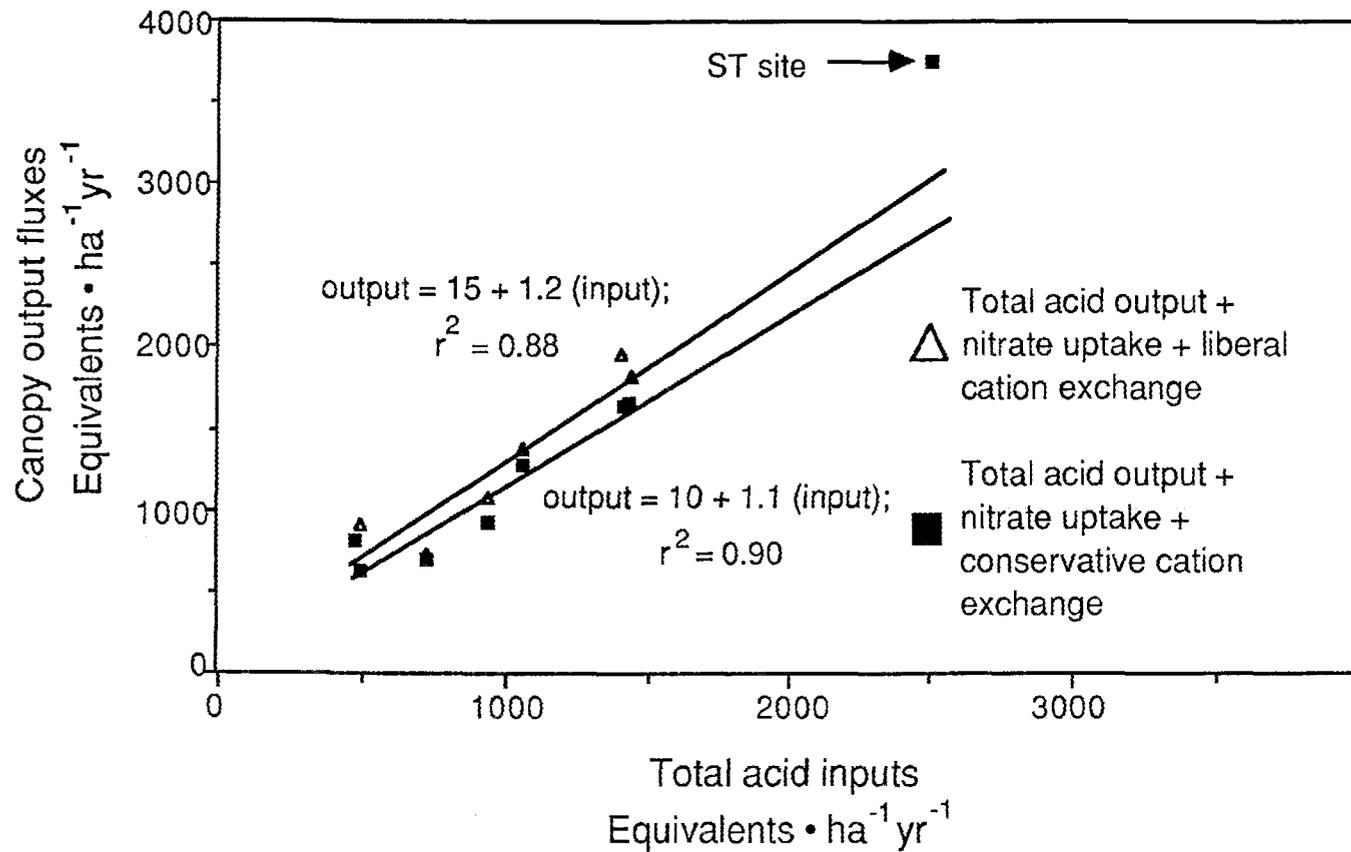


Figure 5. Canopy acid inputs and outputs at 7 IFS sites show a 1:1 correspondence when outputs include the H⁺ associated with nitrate deposition, and either estimate of canopy cation exchange. The ST site is not included in the regression (see text). Units are equivalents ha⁻¹ y⁻¹.

5.2 SOILS AND CYCLING TASKS

5.2.1

EFFECTS OF ATMOSPHERIC DEPOSITION ON CATION EXCHANGE REACTIONS IN ACID FOREST SOILS

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Over time, the most insidious problem resulting from acid deposition is likely to be the "erosion" of soil cations caused by the displacement of exchangeable cations into solution and accelerated leaching of cations from soil solutions into drainage waters. Despite its biological significance, cation exchange is not well documented in acid forested soils with solutions of low ionic strength. Cation exchange reactions are significant to soil ecosystems because cation exchange not only retains cations within the soil profile, but these reactions help control the plant-availability of nutrients and the chemistry of drainage waters.

In addition to the atmosphere, natural processes such as the mineralization of organic matter, chemical weathering, rainfall, evapotranspiration, and leaching control ionic concentrations of the soil solution and affect cation exchange. Increasing concentrations of ions in solution (i.e., ionic strength) can increase exchange of polyvalent cations into soil solutions, and consequently there is considerable concern that atmospheric deposition elevates aluminum, calcium, and magnesium in soil solution and increases their export to drainage waters.

A major objective of this research is to evaluate the susceptibility of various soils to release exchangeable polyvalent cations into soil solutions. Three questions are central to understanding how soils respond to atmospheric additions of electrolytes: (1) Are soil cation exchange reactions affected by relatively small changes in ionic strength of the soil solution? (2) Do soils have a critical Al saturation of cation exchange capacity (CEC) above which exchangeable Al is readily released into soil solution? (3) Can such changes in cations in soil solution be predicted, based on cation exchange reactions? Much progress has been made in addressing these questions about cation exchange reactions that occur in dilute soil solutions.

Experiments with the Becking and Fullerton soils (from the Smoky Mountains and the Ridge and Valley, respectively) illustrate how increasing concentration of ions in solution affects the species of cations that exchange from soil exchange sites (Fig. 1B and 1C, respectively). The Becking soil is far more acidic than the Fullerton soil: 95% vs 79% Al saturated, respectively. In both soils, however, small increases in ionic concentration in solution greatly favors the exchange of polyvalent cations, Mg and Al over that of monovalent cations, K and Na. In general, divalent Mg is readily exchanged by relatively small increases in ionic strength in nearly all soils of the IFS study. In contrast, trivalent Al tends to be retained by soil exchangers more strongly than Mg. In extremely acid soils such as the Becking, Al is released readily by small increases in ionic strength of soil solution (Fig. 1B). In moderately acid soils such as the Fullerton B horizon, exchangeable Al is strongly adsorbed to exchange sites even when the ionic

strength of solution is relatively high (Fig. 1C).

The difference among soils in Al exchangeability suggests that soils have a critical Al saturation above which exchangeable Al is readily displaced into the soil solution. Thirty-three IFS soils, that represented a range of exchange conditions, were tested to evaluate the relationship between Al saturation of CEC and the exchangeability of soil Al. Figure 2 demonstrates that exchangeable Al saturation is directly related to the Al that is released by addition of only 0.5 mMc/L (meq/L), a low concentration typical of soil solutions in field conditions. In very acid soils that have exchangeable Al saturations of >80% of CECE (effective CEC), increasing ionic strength of soil solution by only 0.5 mMc/L causes Al to become a major soluble cation. The extremely acid soils that release exchangeable Al to solution in the laboratory include those from the Becking, Tower, and Beech sites in the Smoky Mountains, and soils at Whiteface Mountain in New York and Findley Lake in Washington. Moreover, the soils that exchange Al in the laboratory tend to be the same soils that have relatively high soluble Al in soil solutions in the field. Provided solutions of these soils have elevated ionic strength due to atmospheric deposition or other causes, Al is released to solution. Extreme soil acidity is not a sufficient condition but is a necessary condition to releasing Al to soil solutions.

Exchange reactions among Al, Ca, Mg, K, and Na have been quantified and reactions are predictable in extremely acid soils with low ionic strength solutions. Even for soils with mixtures of cations and with different types of cation exchange charge, Schofield's activity ratios and the Gapon selection coefficients were remarkably independent of ionic strength (Fig. 3, 4A, 5A). Such activity ratios or selection coefficients ranged widely among IFS soils due to widely different populations of exchangeable cations. For individual soils, activity ratios and Gapon selection coefficients were markedly constant despite widely variable ionic strength.

Relatively constant activity ratios and Gapon coefficients suggest that they are suitable expressions for predicting exchange reactions in soil solutions in response to variable but low ionic strength of soil solutions. In contrast, Figure 4B and 5B illustrate that exchange of Al-Mg or Al-K could not be described by Gaines-Thomas formulations of the same solid-solution data as those in Figures 3, 4A, and 5A. We attribute these differences to different numerical formulations of the solid and solution data.

Recently we have documented markedly strong relationships between exchangeable Al saturation of CECE (i.e., the reciprocal of "base saturation" in traditional soil science terminology) and a soil's Gapon selection coefficients. In other words, we can make relatively good predictions of Gapon coefficients for Al-divalent cation exchange based solely on a soil's Al saturation of CECE for the wide range of soils within the IFS study. This relationship is being further tested with Spodosols from the Norwegian site which have been experimentally acidified in the field (in cooperation with Dr. A. Stuanes), and with Ultisols (that resemble soils of the Duke and the Georgia sites) that have been naturally acidified by a rapidly aggrading pine plantation. These soils will provide excellent tests for elaborating exchange relationships developed from the IFS soils.

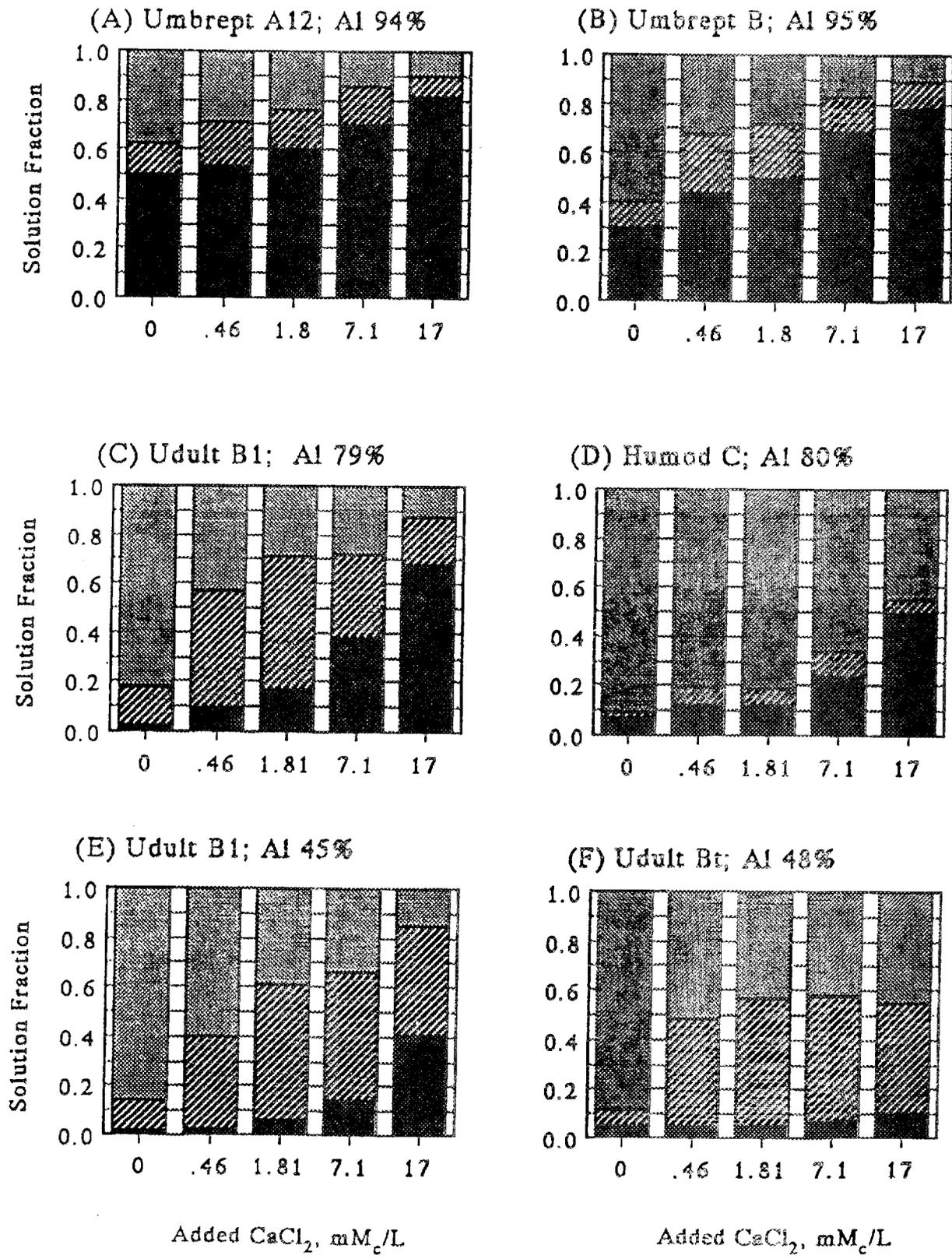


Figure 1. Effect of ionic strength on displacement of Al⁺³ (dark), Mg⁺² (striped), and K⁺ plus Na⁺ (light) in six soils. Figure 2A to 2F represented soils # 7, 11, 25, 20, 28, 33, respectively.

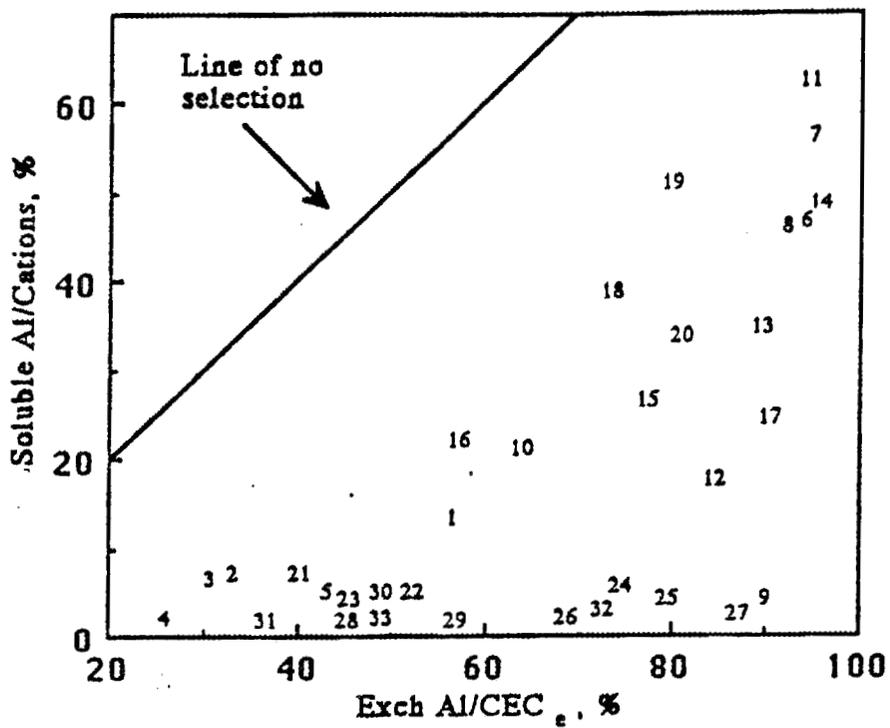


Figure 2. Effect of exchangeable Al saturation of soil CEC_e on Al displaced by 0.5 mM_e/L BaCl₂.

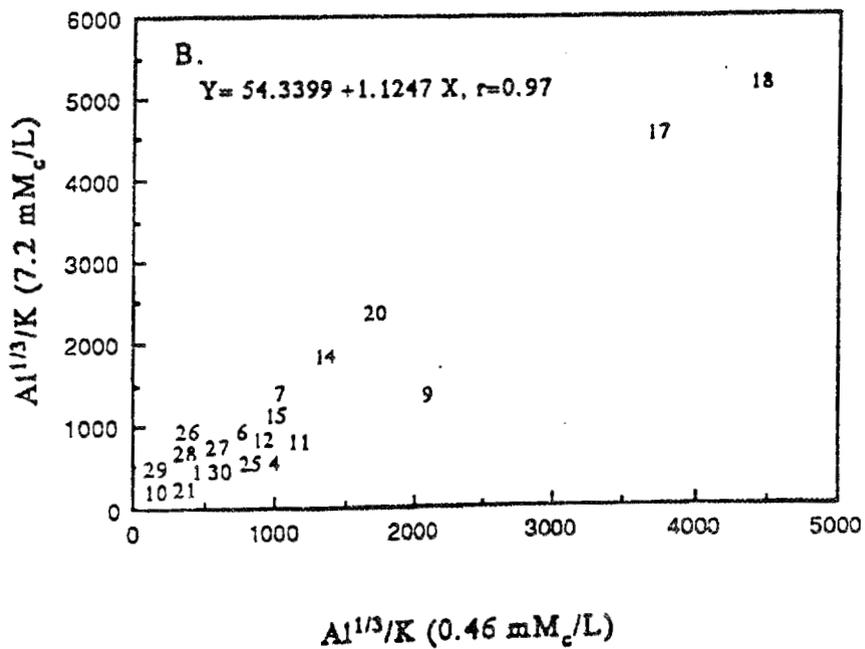
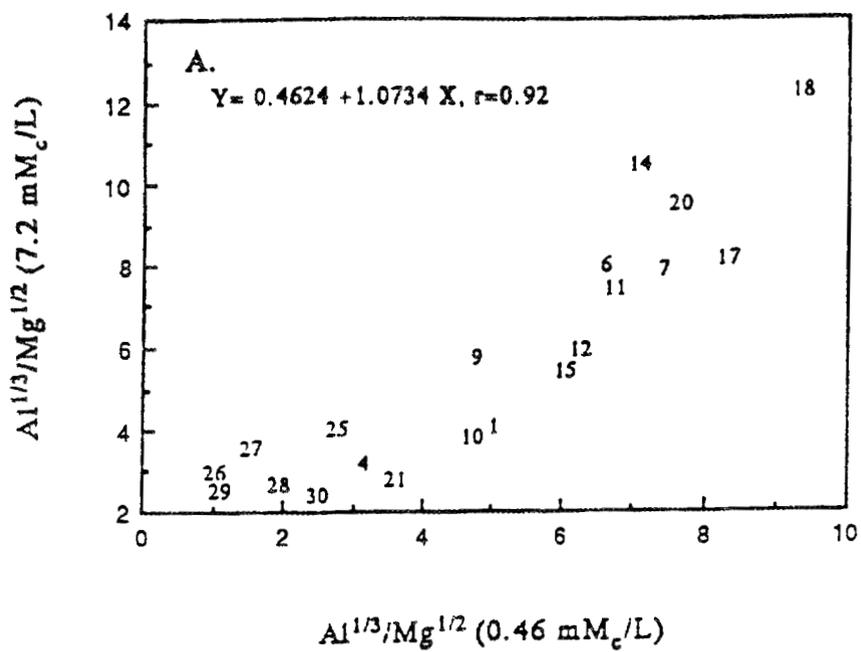


Figure 3. Schofield's activity ratios of Al-Mg (A) and Al-K (B) exchange at 0.46 and 7.2 mM_c/L CaCl₂.

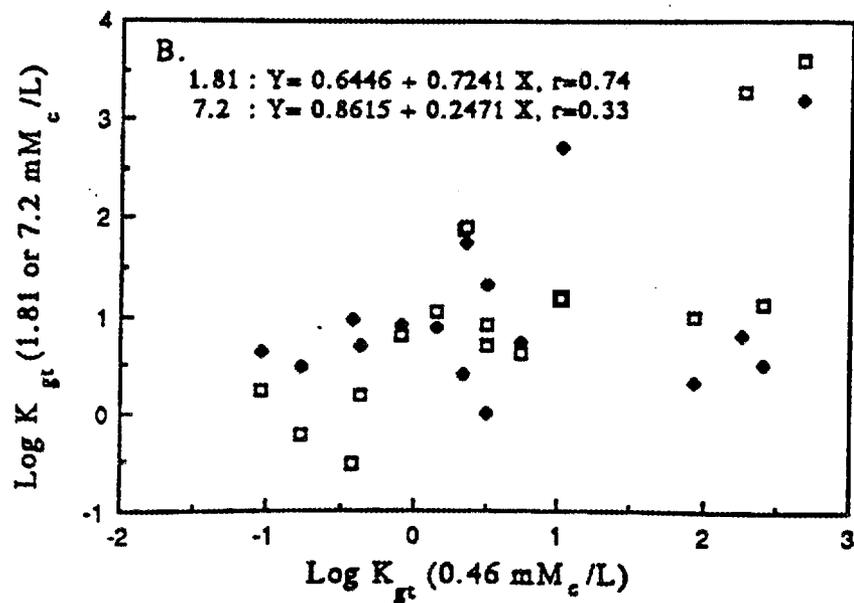
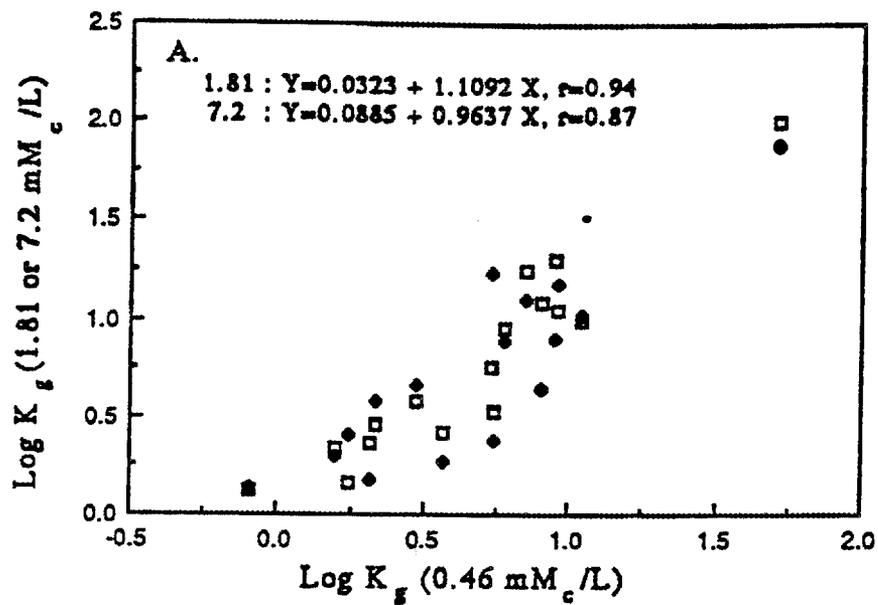


Figure 4. Gapon (A) and Gaines-Thomas (B) selection coefficients for Al-Mg exchange at 0.46 as compared to 1.81 or 7.2 mM_c /L CaCl₂ (□ or ●, respectively).

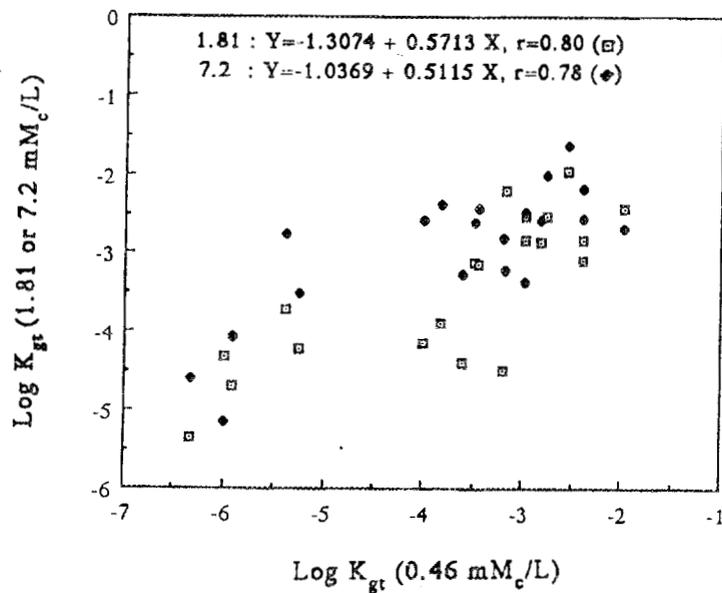
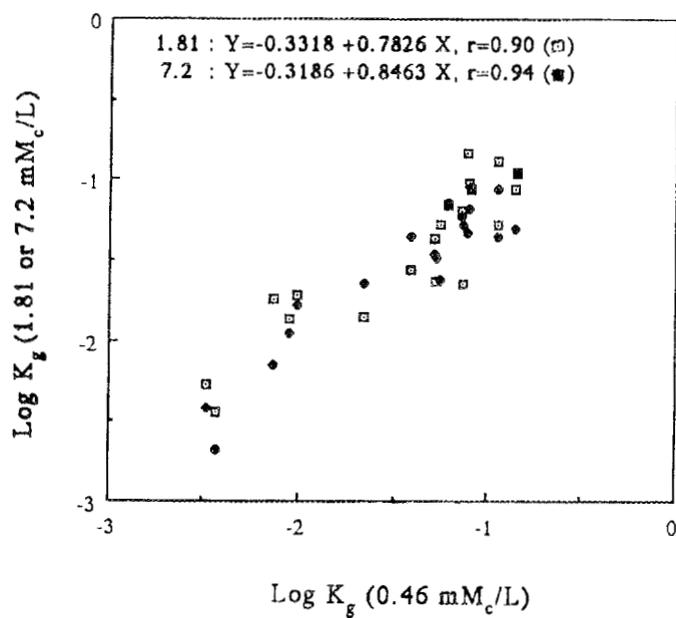


Figure 5. Gapon (A) and Gaines-Thomas (B) selection coefficients for Al-K exchange at 0.46 as compared to 1.81 or 7.2 mM_c/L CaCl₂ (□ or ●, respectively).

5.2.2
IFS Project
Annual Summary Report
Colgate University
March, 1989

MINERALOGY AND CHEMISTRY
OF SOILS AND RHIZOSPHERE

R. April

Introduction

This report contains a brief summary of the IFS research carried out at Colgate University, with emphasis on the results obtained in 1988. The two primary objectives of our work are: (1) to characterize the mineralogy and chemistry of the forest soils in each of the IFS sites, and (2) to characterize in detail the mineralogy and chemistry of the rhizosphere in selected IFS sites. Also, we are working closely with Bob Newton at Smith College to determine weathering rates in the soils by providing mineral chemistries for formulating stoichiometric equations of mineral weathering. Completion of these tasks is necessary in any attempt to understand and model processes related to cation release and uptake, mineral weathering and the importance of rhizosphere processes in forest soils.

Characterization of the Soils

To date, we have received and analyzed 103 soil samples from all 18 sites (and sub-sites) included within the IFS study. Because most of the data from these analyses were presented previously (in the 1987 annual report), we have included here only the summary tables of the clay mineralogy and bulk soil chemistry. Results of these analyses, together with the grain size and heavy mineral analyses (conducted at Smith College), will be presented at the Atlanta review meeting in April.

Semi-quantitative ranking of clay mineral species present in the less than 2 micron fraction
(error of + or - 20 percent)

Location	Site Code	Vermiculite*	Mica**	Kaolinite	Gibbsite	Chlorite	Smectite	Mixed-layer M/V
ThompsonDF	DF	70	5	10	0	15	tr	0
ThompsonRA	RA	65	5	20	0	5	5	0
FindleyLake	FL	65	0	15	0	10	10	0
Huntington	HF	90	0	10	0	0	0	0
Maine	MS	70	10	10	0	0	10	0
Norway	NS	35	20	20	0	10	0	15
Turkey Lakes	TL	60	5	20	0	15	0	0
Whiteface	WF	80	5	15	0	0	0	0
Camp Branch	CB	55	5	30	5	5	0	0
Coweet:WS2	CH	40	20	20	10	0	0	10
Coweet:WS1	CP	40	15	25	15	0	0	5
Duke	DL	30	0	65	5	0	0	0
Florida	FS	15	0	80	5	0	0	0
Georgia	GL	15	0	85	tr	0	0	0
Oak Ridge	LP	30	20	40	10	0	0	tr
SmokyMtn SB	SB	35	20	10	10	0	0	25
SmokyMtn SS	SS	25	10	20	20	0	tr	25
SmokyMtn ST	ST	30	15	20	15	0	0	20
Walker Branch FT	FT	65	0	25	5	0	5	0
Walker Branch TK	TK	70	0	25	5	0	tr	0

*hydroxy-interlayered vermiculite present in many samples

**includes both muscovite and biotite

— IFS Bulk Soil Chemistry / Wt % Oxides —

Site Code	Forest	Code #	Horizon	Fe2O3	MnO	TiO2	CaO	K2O	P2O5	SiO2	Al2O3	MgO	Na2O	Total	LOI
GL	B.F. Grant		A	2.97	0.14	0.91	0.17	1.66	0.06	85.34	8.75	0.01	0.28	100.29	7.35
GL	B.F. Grant		E	2.62	0.09	0.57	0.08	1.54	0.04	84.82	11.30	0.01	0.31	101.38	4.50
GL	B.F. Grant		BE	3.73	0.24	1.30	0.05	0.75	0.06	85.03	8.74	0.01	0.08	99.99	4.50
GL	B.F. Grant		Bt	8.55	0.09	1.22	0.04	0.69	0.05	70.48	17.92	0.17	0.22	99.43	7.09
GL	B.F. Grant		BC	9.94	0.04	0.98	0.01	0.71	0.06	62.80	25.07	0.22	0.16	99.99	8.77
GL	B.F. Grant		AVERAGE*	5.56	0.12	1.00	0.07	1.07	0.05	77.69	14.36	0.08	0.21	100.22	6.44
CB	Camp Branch	34550	0 - 15	2.02	0.03	1.16	0.10	0.72	0.03	90.47	5.52	0.01	0.06	100.00	5.13
CB	Camp Branch	34551	15 - 30	2.46	0.02	1.16	0.10	0.80	0.03	88.31	7.21	0.01	0.01	100.00	3.62
CB	Camp Branch	34552	30 - 60	3.13	0.02	1.18	0.10	0.72	0.04	86.83	7.91	0.01	0.01	99.84	3.36
CB	Camp Branch	34559	60 - 100	6.54	0.01	1.21	0.10	0.61	0.05	78.06	13.21	0.01	0.05	99.74	5.40
CB	Camp Branch		AVERAGE	3.54	0.02	1.18	0.10	0.71	0.04	85.92	8.46	0.01	0.03	99.90	4.38
CH	Coweeta	34522	A	11.45	0.10	1.99	0.10	1.97	0.05	63.85	18.95	1.40	0.24	100.00	9.42
CH	Coweeta	34523	BA	12.23	0.09	2.10	0.10	2.06	0.05	63.97	18.38	1.44	0.54	100.86	6.31
CH	Coweeta	34524	Bt	12.59	0.09	1.96	0.10	2.22	0.11	60.62	21.19	1.05	0.16	100.00	6.47
CH	Coweeta	34525	BC	12.99	0.09	2.00	0.10	2.59	0.05	60.50	21.62	1.84	0.24	101.91	5.97
CH	Coweeta		AVERAGE	12.32	0.09	2.01	0.10	2.21	0.07	62.24	20.04	1.43	0.30	100.69	7.04
CP	Coweeta	34526	A	11.75	0.08	1.68	0.10	3.68	0.10	57.51	23.19	2.01	0.01	100.00	6.66
CP	Coweeta	34527	BC	11.02	0.11	1.98	0.10	3.64	0.07	60.69	20.28	1.84	0.38	100.00	10.20
CP	Coweeta	34528	B4	10.96	0.06	1.82	0.10	3.75	0.09	60.61	20.83	1.34	0.54	100.00	6.38
CP	Coweeta	34540	Bt	11.57	0.07	1.67	0.10	3.76	0.10	58.06	23.67	1.46	0.04	100.40	8.17
CP	Coweeta		AVERAGE	11.33	0.08	1.79	0.10	3.71	0.09	59.22	21.99	1.66	0.24	100.10	7.85
DL	Duke	34544	0 - 20	0.48	0.03	0.48	0.10	0.16	0.10	95.93	2.76	0.01	0.01	99.96	1.54
DL	Duke	34545	20 - 35	3.25	0.02	0.79	0.10	0.37	0.02	86.24	9.32	0.01	0.01	100.00	3.67
DL	Duke	34546	35 - 60	10.29	0.02	1.10	0.10	0.68	0.02	64.13	23.77	0.01	0.01	100.00	8.86
DL	Duke	34547	60 - 80	10.82	0.02	1.01	0.10	0.75	0.02	60.52	27.28	0.04	0.01	100.46	9.67
DL	Duke		AVERAGE	6.21	0.02	0.85	0.10	0.49	0.04	76.71	15.78	0.02	0.01	100.11	5.94
FL	Findley	34509	A2	5.08	0.09	0.76	5.47	1.02	0.07	62.68	17.79	2.81	4.25	100.00	6.20
FL	Findley	34510	B2hr	5.55	0.06	1.15	3.23	0.98	0.11	67.45	16.80	1.77	2.90	100.00	12.12
FL	Findley	34511	B3	8.65	0.11	0.88	0.61	1.34	0.17	61.67	22.31	3.69	2.18	101.61	11.61
FL	Findley		AVERAGE	6.43	0.09	0.93	3.10	1.11	0.12	63.93	18.97	2.76	3.11	100.54	9.98
FS	Florida		A	0.10	0.01	0.33	0.02	0.01	0.02	99.91	0.66	0.01	0.01	101.08	2.14
FS	Florida		E	0.07	0.01	0.30	0.01	0.01	0.02	96.62	0.70	0.01	0.21	97.96	0.37
FS	Florida		E1	0.09	0.01	0.36	0.01	0.01	0.04	100.30	0.92	0.01	0.18	101.93	0.34
FS	Florida		Bh	0.13	0.01	0.34	0.01	0.01	0.02	99.95	1.22	0.01	0.10	101.80	1.99
FS	Florida		Bt	0.12	0.01	0.32	0.05	0.01	0.02	98.17	1.22	0.01	0.08	100.01	3.11
FS	Florida		C	0.36	0.01	0.70	0.05	0.01	0.05	92.45	6.20	0.01	0.20	100.04	2.17
FS	Florida		AVERAGE	0.15	0.01	0.39	0.03	0.01	0.03	97.90	1.82	0.01	0.13	100.47	1.69
HF	Huntington	34549	Bs1	7.80	0.09	1.53	3.21	4.11	0.15	64.52	15.14	1.56	1.90	100.00	7.87
HF	Huntington	34516	Bs2	7.12	0.08	1.44	3.19	3.88	0.20	64.46	15.41	1.75	2.47	100.00	5.70
HF	Huntington	34517	Bs3	7.11	0.08	1.40	3.68	4.03	0.19	64.90	14.76	1.65	2.20	100.00	3.45
HF	Huntington	34518	C	6.93	0.08	1.46	4.14	4.04	0.15	65.12	13.45	1.88	2.75	100.00	1.12
HF	Huntington		AVERAGE	7.05	0.08	1.43	3.67	3.98	0.18	64.83	14.54	1.76	2.47	100.00	3.42

— IFS Bulk Soil Chemistry / Wt. % Oxides —

Site Code	Forest	Code *	Horizon	Fa2O3	MnO	TiO2	CaO	K2O	P2O5	SiO2	Al2O3	MgO	Na2O	Total	LOI
MS	Maine		E	1.00	0.02	0.99	0.28	1.25	0.02	90.42	5.72	0.06	0.83	100.59	2.43
MS	Maine		B	5.64	0.03	0.78	0.84	2.06	0.06	75.02	12.97	0.70	1.90	100.00	10.40
MS	Maine		Bs (2 cm)	8.11	0.03	0.88	0.81	1.94	0.07	73.22	12.60	0.61	1.71	99.98	13.54
MS	Maine		Bs (5 cm)	6.96	0.03	0.78	0.89	1.98	0.11	71.40	13.58	0.73	1.54	98.00	12.34
MS	Maine		AVERAGE	6.90	0.03	0.81	0.85	1.99	0.08	73.21	13.05	0.68	1.72	99.33	12.09
NS	Norway	A2S3S11	Bs	3.94	0.08	0.58	1.23	1.81	0.29	79.13	9.83	0.87	1.43	99.19	4.07
NS	Norway	A2S3S11	BC	3.87	0.04	0.58	1.55	2.20	0.30	78.56	10.80	1.46	1.75	101.11	2.56
NS	Norway	A2S3S11	C	4.11	0.05	0.59	1.53	2.34	0.30	76.49	10.95	1.55	1.82	99.73	2.17
NS	Norway	A2S4S10	E	1.89	0.04	0.58	1.10	1.62	0.33	82.58	8.45	0.59	1.49	98.67	7.83
NS	Norway	A2S4S10	Bs	3.67	0.09	0.52	1.04	1.85	0.33	81.16	9.88	0.82	1.43	100.79	3.75
NS	Norway	A2S4S10	BC	3.58	0.03	0.49	1.24	2.13	0.29	79.24	10.39	1.23	1.88	100.50	2.29
NS	Norway	A2S4S10	C	3.43	0.03	0.45	1.08	2.26	0.29	78.77	10.04	1.33	1.42	99.10	2.02
NS	Norway	A4R1G1G2	E	2.40	0.03	0.59	1.22	1.73	0.39	82.53	8.80	0.84	1.48	100.01	9.87
NS	Norway	A4R1G1G2	Bs	3.64	0.12	0.56	1.24	1.87	0.38	79.74	10.02	1.13	1.32	100.02	4.39
NS	Norway	A4R1G1G2	BC	3.49	0.03	0.48	1.21	2.07	0.30	78.64	10.11	1.40	1.76	99.49	2.82
NS	Norway		AVERAGE	3.40	0.05	0.54	1.24	1.99	0.32	79.68	9.93	1.12	1.58	99.86	4.18
LP	Oak Ridge	3601	Ap	8.82	0.16	1.00	0.03	2.95	0.21	69.90	16.14	0.63	0.15	99.99	6.60
LP	Oak Ridge	3602	B1	9.49	0.07	1.08	0.06	3.57	0.18	65.27	19.37	0.88	0.21	100.18	6.08
LP	Oak Ridge	3603	B	9.92	0.02	1.14	0.09	4.04	0.16	61.27	22.40	0.88	0.10	100.02	6.76
LP	Oak Ridge	3604	Ap	3.87	0.24	0.99	0.14	1.13	0.15	83.93	6.93	0.15	0.19	97.72	4.05
LP	Oak Ridge	3605	A	4.03	0.22	0.98	0.10	1.12	0.17	88.79	7.26	0.04	0.24	102.85	3.36
LP	Oak Ridge	3606	B	3.17	0.11	1.09	0.11	1.14	0.09	84.14	8.16	0.18	0.09	98.28	3.32
LP	Oak Ridge		AVERAGE	6.55	0.14	1.05	0.09	2.33	0.16	75.55	13.38	0.46	0.16	99.84	5.03
SS	SM Becking	3609	A	6.67	0.06	1.32	0.10	2.40	0.29	74.32	16.33	0.36	1.19	102.94	28.68
SS	SM Becking	3610	B	6.71	0.06	1.20	0.10	2.55	0.17	73.00	14.89	0.49	0.94	100.01	10.86
SS	SM Becking	3611	C	5.95	0.12	1.01	0.10	3.02	0.13	72.66	15.97	1.02	1.23	101.11	4.83
SS	SM Becking	3615	A	5.17	0.04	1.31	0.10	2.55	0.21	76.46	13.89	0.27	1.38	101.28	16.09
SS	SM Becking	3616	B	4.17	0.04	0.97	0.10	2.22	0.12	78.77	10.58	0.22	1.68	98.77	5.03
SS	SM Becking	3617	C	5.44	0.08	1.08	0.10	2.65	0.12	74.62	13.86	0.69	1.45	99.99	5.12
SS	SM Becking	3618		8.48	0.11	1.22	0.10	5.14	0.15	62.47	20.21	1.56	0.46	99.80	5.64
SS	SM Becking		AVERAGE	6.08	0.07	1.16	0.10	2.93	0.17	73.19	15.10	0.66	1.19	100.56	10.89
SB	SM Beech	3619	A	9.09	0.48	1.15	0.10	3.40	0.44	67.04	17.51	0.52	0.69	99.96	16.98
SB	SM Beech	3620	B	9.02	0.40	1.16	0.10	3.22	0.31	67.31	17.44	0.53	0.62	100.01	9.10
SB	SM Beech	3621	BC	8.93	0.38	1.12	0.10	3.20	0.24	65.66	17.37	0.87	0.73	98.50	7.59
SB	SM Beech	3622	A	8.02	0.28	1.19	0.10	2.56	0.49	71.74	15.65	0.54	0.61	101.08	26.76
SB	SM Beech	3623	B1	7.93	0.27	1.16	0.10	2.60	0.29	69.57	15.13	0.48	0.65	98.09	11.03
SB	SM Beech	3624	B	8.23	0.23	1.15	0.10	2.63	0.25	68.50	16.37	0.82	0.62	98.80	8.45
SB	SM Beech		AVERAGE	8.54	0.34	1.16	0.10	2.94	0.34	68.30	16.58	0.63	0.65	99.41	13.32

— IFS Bulk Soil Chemistry / Wt. % Oxides —

Site Code	Forest	Code #	Horizon	Fe2O3	MnO	TiO2	CaO	K2O	P2O5	SiO2	Al2O3	MgO	Na2O	Total	LOI
ST	SM Tower	3627	A11	6.75	0.07	1.17	0.10	2.43	0.15	71.26	14.09	0.78	1.38	98.09	15.75
ST	SM Tower	3628	A12	7.27	0.07	1.15	0.10	2.96	0.18	72.31	16.04	0.73	1.32	102.02	14.92
ST	SM Tower	3629	B1	6.80	0.07	1.06	0.10	2.94	0.15	71.01	15.45	0.69	1.28	99.45	11.24
ST	SM Tower	3630	B2	6.52	0.10	1.04	0.10	3.00	0.12	72.83	16.24	1.17	1.22	102.25	6.53
ST	SM Tower	3634	A1	3.09	0.05	1.17	0.10	2.17	0.16	79.35	12.79	0.15	1.08	100.00	25.74
ST	SM Tower	3635	AB	3.73	0.05	1.17	0.10	2.19	0.07	78.46	12.03	0.07	0.90	98.67	8.33
ST	SM Tower	3636	A2	6.11	0.06	1.14	0.10	2.20	0.11	73.77	12.81	0.22	1.33	97.75	10.29
ST	SM Tower	3637	B1	6.21	0.06	1.07	0.10	2.23	0.10	74.51	14.01	0.68	1.13	100.00	8.97
ST	SM Tower	3638	B2	6.24	0.10	1.06	0.10	2.41	0.08	72.28	15.16	1.01	1.14	99.48	6.82
ST	SM Tower	3639	B	3.90	0.08	0.96	0.10	1.74	0.11	81.51	12.51	0.43	0.53	101.77	4.27
ST	SM Tower		AVERAGE	5.66	0.07	1.10	0.10	2.43	0.12	74.73	14.11	0.59	1.13	99.95	11.29
DF	Thompson DF	34501	A1	5.64	0.24	0.97	3.23	1.12	0.32	69.50	14.35	1.89	2.74	100.00	18.63
DF	Thompson DF	34503	B21	6.46	0.15	0.92	3.00	1.14	0.23	67.98	17.53	2.20	2.96	102.59	7.73
DF	Thompson DF	34504	B22	6.14	0.10	0.89	2.69	1.11	0.14	66.55	17.44	2.39	2.55	100.00	6.14
DF	Thompson DF		AVERAGE	6.08	0.16	0.93	2.97	1.12	0.23	68.01	16.44	2.16	2.75	100.86	10.83
RA	Thompson RA	34505	A1	6.78	0.25	0.99	2.97	1.16	0.28	66.05	18.03	2.28	2.62	101.41	27.96
RA	Thompson RA	34506	A2	6.10	0.23	0.96	3.13	1.02	0.32	67.82	15.84	2.26	2.32	100.00	12.27
RA	Thompson RA	34507	B21	6.80	0.19	0.97	2.88	1.14	0.20	65.01	18.47	2.60	2.56	100.82	14.80
RA	Thompson RA	34508	B22	6.46	0.14	0.94	3.02	1.15	0.16	68.02	17.35	2.54	2.53	102.31	10.53
RA	Thompson RA		AVERAGE	6.54	0.20	0.97	3.00	1.12	0.24	66.73	17.42	2.42	2.51	101.14	16.39
TL	Turkey Lake	34519	Bf1	7.66	0.07	0.81	3.11	1.91	0.13	67.49	13.94	1.75	3.13	100.00	11.80
TL	Turkey Lake	34520	Bf2	5.38	0.07	0.63	3.20	1.76	0.07	69.66	15.46	1.99	3.61	101.83	9.30
TL	Turkey Lake	34521	Bf	5.26	0.07	0.65	3.39	1.83	0.08	70.15	15.19	2.33	3.95	102.90	6.73
TL	Turkey Lake	34548	Bf	4.34	0.07	0.55	3.45	1.83	0.08	70.81	14.41	1.99	3.54	101.06	3.02
TL	Turkey Lake		AVERAGE	5.66	0.07	0.66	3.29	1.83	0.09	69.53	14.75	2.02	3.56	101.45	7.71
FT	Walker Branch	34553	A2	1.67	0.04	0.89	0.01	0.25	0.31	92.57	3.87	0.01	0.42	100.02	2.48
FT	Walker Branch	34554	B1	2.67	0.03	0.92	0.10	0.38	0.02	90.97	5.02	0.01	0.01	100.00	2.41
FT	Walker Branch	34555	B22t	3.51	0.03	0.90	0.10	0.44	0.04	87.73	7.34	0.01	0.01	100.00	3.12
TK	Walker Branch	34556	Ap	1.54	0.10	1.08	0.10	0.47	0.09	91.71	4.52	0.01	0.01	99.51	3.93
TK	Walker Branch	34557	B1	1.68	0.06	1.07	0.10	0.48	0.01	91.88	4.69	0.01	0.12	100.00	3.09
TK	Walker Branch	34558	B2	2.81	0.04	1.09	0.10	0.52	0.02	89.54	5.96	0.01	0.01	100.00	2.92
TK	Walker Branch		AVERAGE	2.31	0.05	0.99	0.09	0.42	0.08	90.73	5.23	0.01	0.10	99.92	2.99
WF	Whiteface	34529	FF	4.65	0.15	1.05	5.25	2.55	1.18	69.89	12.15	1.74	1.39	100.00	84.59
WF	Whiteface	34530	Bup	5.94	0.05	1.19	4.10	2.23	0.13	69.29	13.52	1.90	1.65	100.00	14.81
WF	Whiteface	34531	Blo	5.56	0.06	1.02	4.69	2.13	0.14	67.37	14.83	2.20	2.03	100.00	10.15
WF	Whiteface	34532	Bup	5.27	0.06	1.20	3.78	2.45	0.19	72.53	13.35	1.52	1.91	102.26	17.36
WF	Whiteface	34534	Blo	5.68	0.08	1.20	4.97	2.24	0.14	67.69	13.84	2.38	1.77	100.00	8.27
WF	Whiteface	34535	C	4.66	0.06	0.95	5.70	2.32	0.10	67.76	14.46	2.71	2.24	100.95	3.52
WF	Whiteface	34537	Bup	4.27	0.05	1.10	5.11	2.14	0.48	63.36	19.19	1.74	2.54	99.98	24.34
WF	Whiteface	34538	Blo	5.48	0.08	1.06	5.53	2.12	0.21	64.57	17.57	2.49	2.38	101.50	13.31
WF	Whiteface	34539	C	5.94	0.07	1.24	5.80	2.14	0.12	65.82	14.13	3.00	2.01	100.27	4.93
WF	Whiteface		AVERAGE	5.27	0.07	1.11	4.99	2.26	0.30	67.59	14.78	2.19	1.99	100.55	20.14

*averages are unweighted for soil horizon thicknesses

Summary of Rhizosphere Studies

The mineralogy and chemistry of forest soils from six IFS sites in the northeastern and southeastern United States were determined using X-ray diffraction, X-ray fluorescence, and scanning electron microscopy with energy dispersive spectrometric capabilities. Special attention in this study was given to the nature of rhizosphere soils whose proximity to root surfaces exposes them to unique biotic influences.

Results of the chemical and mineralogical analyses showed that southern soils are more extensively weathered than northern soils and contain greater amounts of clay material and significantly greater quantities of advanced weathering products such as gibbsite and kaolinite. Additionally, total base cation concentrations in southern soils are approximately half those recorded for northern soils. These regional differences in soil characteristics that exist between northern and southern sites are primarily determined by differences in climate, parent material, and glacial history.

Examination of the rhizosphere soils revealed that mineral grains within this area of soil are affected mechanically, chemically and mineralogically by the invading root bodies. In SEM/EDS analyses, phyllosilicate grains contiguous to roots commonly align with their long axis tangential to the root surface. Numerous mineral grains were also observed for which the edge abutting a root surface is significantly more fractured than the rest of the grain. Both the alignment and fracturing of mineral grains by growing roots influence pedogenic processes within the rhizosphere by exposing greater quantities of mineral surface area to weathering processes operating in the root-zone microenvironment. Chemical interactions between roots and rhizosphere minerals include possible preferential dissolution of mineral grains adjacent to root bodies, and biomineralization of amorphous aluminum oxide /hydroxides, opaline and amorphous silica, and calcium oxalate within the cells of mature roots. Mineralogical analyses using X-ray diffraction techniques, indicate that kaolinite in the rhizosphere has a higher thermal stability and is better crystallized than kaolinite in the bulk forest soil. In addition, XRD analyses of clay minerals from one of the southern sites showed a sharp 10Å peak for

STATUS OF THE RHIZOSPHERE STUDIES

<u>SITE</u>	<u>DATE SAMPLED</u>	<u>ANALYSES IN PROGRESS OR COMPLETED</u>
Coweeta CP	Summer 1987	yes
Coweeta CH	Summer 1987	yes
Duke LP	Summer 1987	yes
Oak Ridge	Summer 1987	yes
Smoky Mtns. SB	Summer 1987	yes
Smoky Mtns. ST	Summer 1987	yes
Huntington HF	Fall 1987	yes
Whiteface WF	Fall 1987	yes
Findley Lake FL	Summer 1988	<div style="display: flex; align-items: center; justify-content: center;"> <div style="border-left: 1px solid black; border-right: 1px solid black; border-bottom: 1px solid black; width: 40px; height: 40px; margin-right: 5px;"></div> <div style="text-align: center;">1989</div> </div>
Thompson DF	Summer 1988	
Thompson RA	Summer 1988	
Turkey Lakes TL	Summer 1988	
Norway NS	Fall 1988	

micas adhering to root surfaces indicating that these micas are well crystallized and, therefore, contain sufficient structural potassium. By contrast, diffuse 10Å mica peaks, characteristic of weathered, potassium-poor illites, were noted for rhizosphere and bulk forest soil clays from the same site.

Phyllosilicate weathering studies focused on biotite because of its abundance in these soils and its propensity toward chemical alteration. SEM/EDS analyses using quantitative analysis programs showed biotites in all sites to weather along grain boundaries and cleavage surfaces by potassium loss and increases in (octahedrally-coordinated) aluminum, structural water and hydroxyl ions. In addition, altered biotites in southern soils are depleted in magnesium. Biotite weathering schemes in northern soils proceeded through mixed-layer biotite/vermiculite to vermiculite and ultimately to smectite in some upper soil horizons. By contrast, biotite alteration in southern soils progressed through vermiculite to kaolinite and finally, to a gibbsite precipitate. Biotite was also observed to change directly to kaolinite in some southern soil samples.

Rhizosphere Studies - Conclusions to Date

To date, studies of the mineralogy and chemistry of bulk forest soils and rhizosphere soils from six of the IFS watersheds in the eastern United States have led to the following conclusions:

- 1) Significant differences exist between northern and southern soil mineralogy and chemistry which primarily reflect differences in parent material, climate, and glacial history.
 - a) Bulk mineralogy principally reflects the composition of parent materials, both bedrock and glacial detritus.
 - b) Clay mineralogy is largely indicative of the extent of weathering that has occurred. Clay analyses from this study reveal that southern soils are distinctly more weathered than northern soils.
 - c) Bulk soil chemistry reflects both the parent material content and the extent of soil weathering, and complements the mineralogical findings.

2) Root-soil interactions change the character of the mineralogy (especially clay mineralogy) in the rhizosphere, suggesting that pedogenic processes differ in the root zone from those operating in the bulk forest soil.

a) Mechanical effects of the root on adjacent mineral grains are thought to expose greater amounts of fresh, mineral material to the weathering regime of the rhizosphere.

1) Fracturing of mineral grains was commonly observed in areas of the grain that abutted root bodies.

2) Tangential alignment and bending of phyllosilicate minerals was noted frequently.

b) Chemical effects

1) Dissolution of a few mineral grains was suggested by replication of the shape of the root surface by an adjacent grain edge that faced it.

2) Biomineralization of amorphous aluminum oxides/hydroxides, opaline and amorphous silica, and calcium oxalate was common in the cells of mature root bodies.

3) No chemical gradients with respect to proximity to root surfaces were observed by the analytical methods employed in this study.

c) Effects on rhizosphere mineralogy

1) Greater thermal stability of rhizosphere kaolinite compared to bulk soil kaolinites indicates that the former was better crystallized. Mechanisms suggested for this enhanced crystallinity include:

1) recrystallization due to a more intensive weathering environment within the rhizosphere, and

2) interference by organic ligands causing more aluminum to remain in a form that is available for kaolinite formation.

- 2) Weathered micas (i.e., illites) within the rhizoplane were potassium-saturated in contrast to those within rhizosphere and bulk forest soils. Interference by polyvalent cations, especially aluminum, is favored as the causal mechanism because aluminum compounds are found precipitated within the peridermal cells of these roots and because transpiration rates, in this region, are not expected to be greater than potassium uptake rates throughout the majority of the year.
- 3) Biotites weather more rapidly than muscovites in these soils and are, therefore, a more important source of potassium for plant nutrition.

- 4) Biotites weather by the following reactions:

Northern Soils

biotite → (mixed-layer biotite/vermiculite) → vermiculite

Southern Soils

biotite → mixed-layer biotite /vermiculite →
 → vermiculite → kaolinite → gibbsite

or

biotite → kaolinite → gibbsite

Mineral Weathering at the IFS Sites

A Progress Report

February, 1989

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INTRODUCTION

Mineral weathering is being evaluated at the IFS sites using two different approaches. The first involves the physical characterization of the soils. In this part of the study important variables such as grain-size distribution, the abundance and composition of the heavy mineral, light mineral, and clay mineral fractions are being determined. These variables are a measure of the overall weathering potential of the soil. In addition, the chemistry of the weatherable minerals together with the chemistry and mineralogy of the secondary weathering products (clay minerals) provides the stoichiometry of the weathering reactions.

An experimental approach is being used to estimate the actual weathering rates at each of the IFS sites. Soil samples are being leached with a series of acidic solutions to determine the relative release rates of base cations and silica. The results of these experiments will be used together with the stoichiometry of the weathering reactions determined in the characterization work to calculate the weathering rates of the various minerals in the soil. The hydrogen ion dependency of these reactions will also be determined. It is planned that the results of these experiments will be integrated with D. Richters work in order to determine the relative importance of weathering and cation exchange in neutralizing acidic inputs.

PHYSICAL CHARACTERIZATION

Grain-size distributions have been determined for samples from all the IFS sites. The sites fall within two basic categories; the glaciated soils, which are generally rich in sand and poor in clay, and the non-glaciated soils, which generally have higher concentrations of clay-sized material (Figure 1). In contrast, the percentage of heavy minerals in glaciated soils is generally much higher than those in non-glaciated soils (Figure 1). Sites located on steep slopes are exceptions to this rule. In

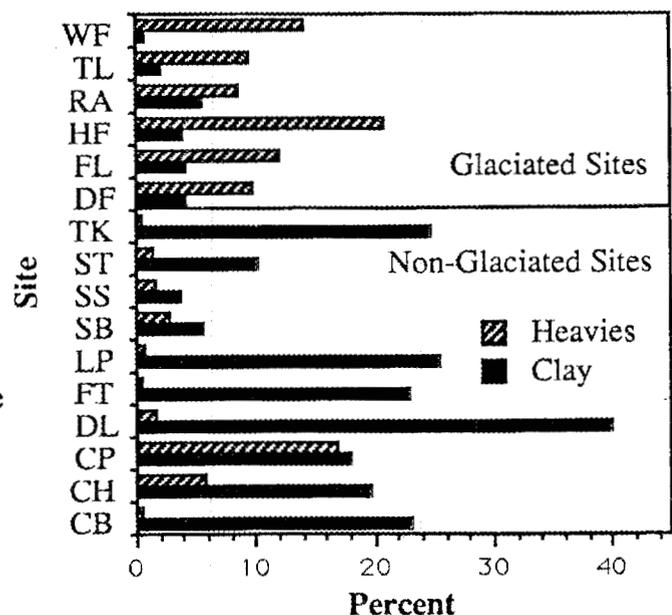


Figure 1. The glaciated sites tend to have more heavy minerals and less clay than the non-glaciated sites. This reflects the immaturity of the glaciated soils.

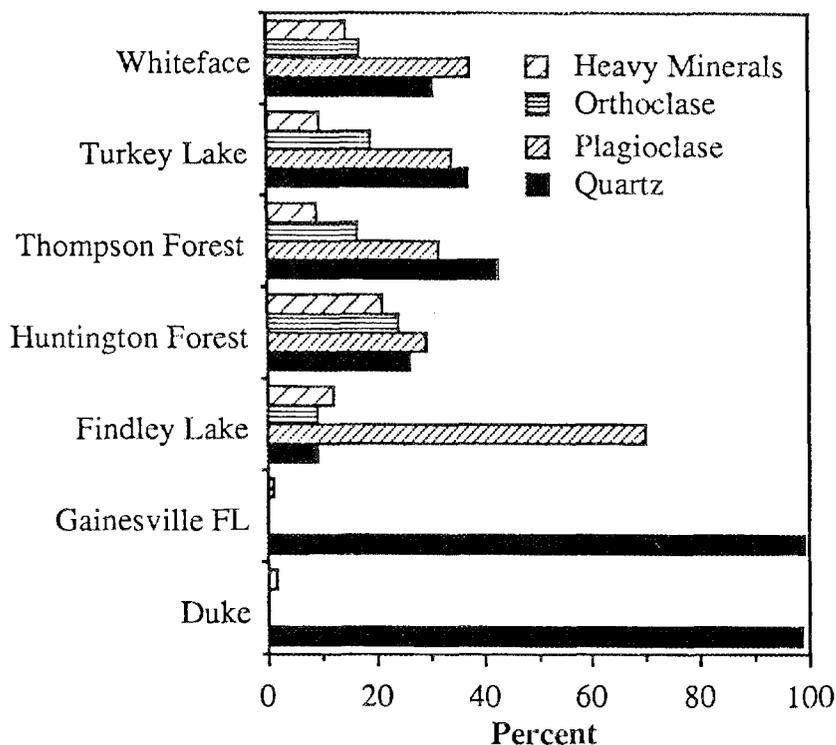


Figure 2. The relative concentration of heavy minerals, orthoclase feldspar, plagioclase feldspar and quartz at some of the IFS sites. Note the difference between glaciated and nonglaciated sites.

Coweeta, for example, one of the sites has an average of more than 16 percent heavy minerals.

The low concentration of clay-sized material at the glaciated sites reflects the immaturity of these soils. The recent retreat of Pleistocene glaciers approximately 15,000 years ago means that there has not been sufficient time for mineral weathering reactions to have produced a lot of secondary clay minerals. The relatively high concentrations of heavy minerals in these soils also reflects their immaturity. Although not all heavy minerals are weatherable, the vast majority weather more rapidly than the more abundant light minerals. In contrast, the unglaciated southern soils have developed over a much longer period of time, thus, the weatherable heavy minerals have been removed leaving behind abundant secondary clay mineral weathering.

The light mineral fraction of many of the IFS sites has been examined by scanning

electron microscopy (SEM) coupled with an energy dispersive x-ray spectrometer (EDS). The relative abundance of quartz, plagioclase feldspar, and potassium feldspar has been determined (Figure 2). In addition the average chemical composition of the plagioclase feldspar has been measured. The chemical composition of the abundant heavy minerals is currently being measured using these techniques. Many times it is possible to see evidence of weathering of different minerals by observing their surface morphology under the SEM.

This data can be combined with the mineralogy and chemistry of the clay mineral fraction collected by R. April to produce a series of stoichiometrically correct mineral weathering reactions for the important minerals at each of the IFS sites. The relative importance of mineral weathering in producing base cations can then be determined for each site.

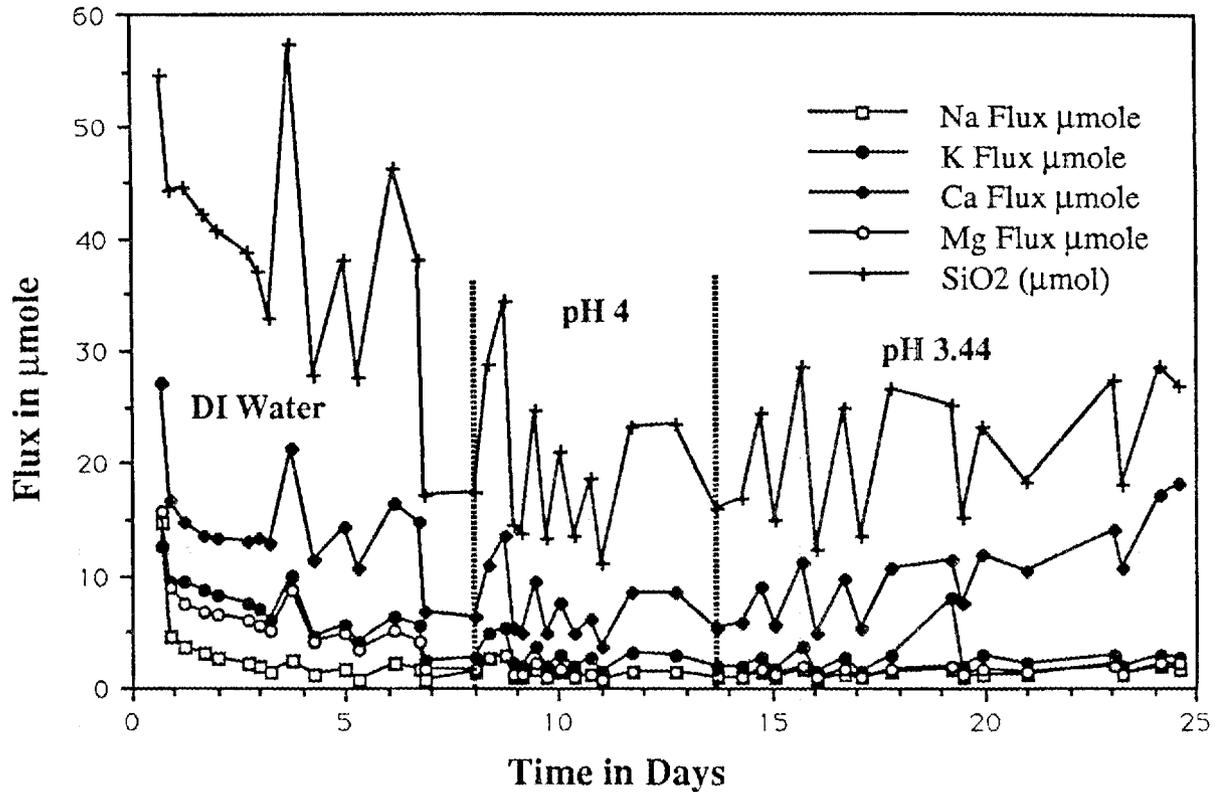


Figure 3. Column leachate chemistry from the Douglas Fir site at Thompson Forest as a function of time. Note the very high flux rates at the beginning of the experiment.

Experimental Studies

A series of column experiments are being run in order to quantify the release rate of base cations due to primary and secondary mineral weathering. The columns are 3.5 cm in diameter, approximately 25 cm long, and are filled with B horizon soil. Each column goes through a sequential leaching with deionized water, pH 4 and pH 3.44 sulfuric acid solutions. Approximately 5 liters of each solution is passed through the columns over a period of 25 days. The leachate is analyzed for; pH, Ca, Mg, Na, K, SiO₂, SO₄, and NO₃.

Figure 3 shows the characteristic trends of base cation and silica flux as a function of time for the Thompson Forest column. Initially the columns leach very high amounts of base cations and silica, presumably produced by weathering which occurred within the soil since the last flushing event. The flux contin-

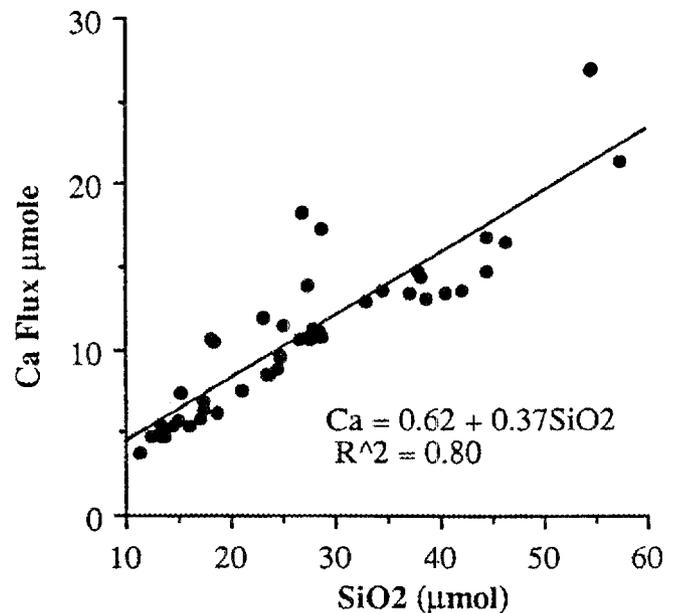
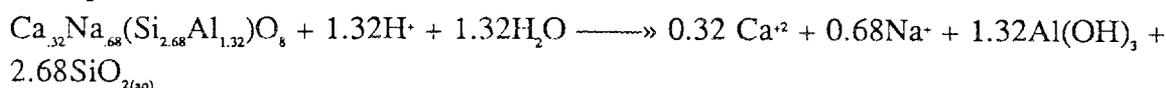


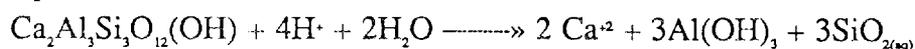
Figure 4. The close correlation between silica and calcium in the Thompson Forest column indicates that most of the calcium comes from weathering.

Important Weathering Reactions at Thompson Forest

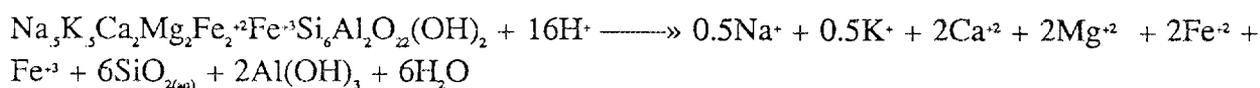
Feldspar



Epidote



Hornblende



ues to decrease into the pH 4 treatment. The pH 4 treatment did not appear to stimulate much additional weathering, perhaps because there was very little change in soil water pH. With the application of the pH 3.44 solution there was some increase in the Ca and SiO₂ flux, but the other base cations remained unchanged.

Preliminary interpretation of these results suggests a relatively high weathering rate in the glaciated soils. This is particularly true for the Douglas Fir site at Thompson Forest, Washington. Considerable amounts of base cations were released from this soil. Based on the remarkably good correlation between base cations and silica (Table 1), it appears that virtually all these base cations came from mineral weathering (Figure 4). The mineral characterization work reveals three potential source minerals for the bulk of the base cations at this site. These minerals are; plagioclase feldspar, epidote, and hornblende. The stoichiometry of these three weathering reactions can be used to predict the ratio of base cations to silica released by weathering and these values can be compared with the observed values. A series of simultaneous equations can be written relating the release of base cations to the weathering of each mineral. The

Table 1
Relationships Between Base Cations and Silica

Thompson Forest (DF)

Mg = -2.86 + 0.22SiO ₂	r ² = 0.78
Ca = 0.616 + 0.38SiO ₂	r ² = 0.80
K = -1.64 + 0.22SiO ₂	r ² = 0.84
Na = 0.114 + 0.058SiO ₂	r ² = 0.62

Whiteface Mountain

Mg = 0.115 + 0.038SiO ₂	r ² = 0.087
Ca = 1.03 + 0.53SiO ₂	r ² = 0.65
K = 0.371 + 0.035SiO ₂	r ² = 0.48
Na = 0.810 + 0.064SiO ₂	r ² = 0.49

Smoky Mountains

Mg = 1.92 + 0.11SiO ₂	r ² = 0.28
Ca = 2.41 + 0.38SiO ₂	r ² = 0.94*
K = 3.55 + 0.26SiO ₂	r ² = 0.45
Na = -0.41 + 0.20SiO ₂	r ² = 0.92*

* These samples were leveraged by a single data point

solution of these equations gives the amount each mineral contributes base cations from weathering. For Thompson Forest, epidote weathering is most important with hornblende and plagioclase feldspar secondary in importance.

Summary

The mineral characterization work shows that the glaciated sites are distinctly different from the nonglaciated sites both in their grain-size distribution and in their mineral composition. In general, soils in the glaciated sites are

sandy and contain abundant weatherable minerals, while the non-glaciated sites are clay-rich and in many cases lack any significant amounts of weatherable minerals. On this basis alone it can be concluded that for at least some of these sites (the Florida site for example) there are no base cations contributed by mineral weathering from the B horizons. In contrast, some of the glaciated sites appear to have very high mineral weathering rates.

Task B2: Sulfate Adsorption and Desorption Reversibility Studies.

ABSTRACT Subsurface soil samples were collected from 20 forest sites of differing soil and cover type, atmospheric deposition history and physiographic location. Samples were analyzed for S pools, sulfate adsorption capacity, desorption reversibility and associated soil properties in order to compare the relative S chemistry and sulfate retention capacities of the sites. Sulfate adsorption capacity was determined by sequential equilibration of air-dried soil samples with a percolating solution of 0.25 mM CaSO_4 , and desorption reversibility by leaching both sulfate saturated and untreated soil samples with deionized water. Phosphate extractable sulfate was measured at the end of each series of equilibrations as a means of estimating irreversibly adsorbed sulfate.

INTRODUCTION The input of certain anions (notably sulfate and nitrate) and associated acidity from the atmosphere has been hypothesized to increase cation leaching from soils to ground and surface waters in some forest ecosystems. Many factors may influence ecosystem response to acid inputs, including vegetation and soil factors, topographic factors, and natural and man-caused factors such as land use and fire. The mobility of sulfate has received considerable attention because net sulfate retention by soils can result in reductions in cation leaching. Where an equivalent displacement of OH^- or other anion does not occur during the sulfate retention process, cations are coadsorbed with sulfate. The generic term "sulfate adsorption" has been given to the variety of inorganic processes whereby sulfate is retained by soil from a solution, whether this retention results in a stoichiometric displacement of another anion or not.

Soils that exhibit a substantial amount of sulfate adsorption are considered to be resistant to accelerated cation leaching, whereas soils that do not adsorb sulfate are more susceptible. Sulfate adsorption is concentration dependent; that is, when the ambient concentration of sulfate in water equilibrating with soil is increased, the amount of sulfate a given soil will adsorb also increases. Many forest ecosystems, particularly in the Northeastern U.S. and some parts of Canada, are presently subjected to much higher sulfate loading compared to pre-industrial levels, and considerable effort has been made to evaluate the potential sulfate adsorption properties of these soils. Results have shown that many forest ecosystems retain additional sulfate with elevated sulfate input levels and ambient solution concentrations, though the variety of methodology utilized has made comparisons between studies difficult.

The net effects of increased sulfate inputs on soil solution chemistry for sulfate adsorbing and nonadsorbing soils is shown in Fig. 1. In sulfate adsorbing soils the increase of soil solution sulfate (and associated cations) is reduced over time until the soil becomes saturated; whereas in the nonadsorbing soil the sulfate concentration increases immediately.

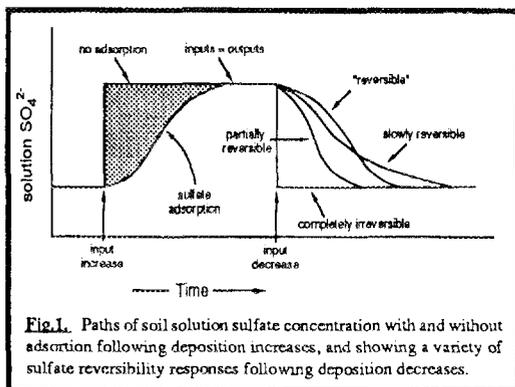


Fig. 1. Paths of soil solution sulfate concentration with and without adsorption following deposition increases, and showing a variety of sulfate reversibility responses following deposition decreases.

Air pollution reductions in many regions have resulted in a decrease in sulfate inputs, and the effect of decreasing sulfate deposition levels on soil solution chemistry is largely unknown. The degree to which sulfate adsorption is reversible is an important consideration in projecting recovery of acidified surface waters and acidified soils to pre-acidified levels following decreases in atmospheric deposition. Reductions in ambient sulfate concentrations of solutions in forest ecosystems would be prolonged considerably if sulfate (along with an equivalent quantity of acidic and basic cations) desorbs from acidified soils once atmospheric inputs decrease, whereas large decreases in sulfate concentrations could be virtually instantaneous if sulfate does not desorb, or desorbs very slowly. The net effects of varying degrees of reversibility of sulfate adsorption following a reduction in inputs is shown in Fig. 1.

PROCEDURES Sulfate adsorption, desorption and desorption reversibility was measured by use of a constant-rate vacuum extractor. Two leaching sequences were followed with an influent rate of 1.4 cm hr^{-1} (25 g soil loosely packed in a cylinder 2.5 cm in diameter). Each sequence was followed in order: the sulfate from a soil sample (with 3 replications) was desorbed with deionized water (procedure "1a") and then extracted with phosphate solution ("1b").

A separate soil sample (with 3 replications) was treated first with 0.25 mM CaSO_4 (procedure "2a") until saturated, then sulfate was desorbed with deionized water ("2b"), and finally extracted with phosphate solution ("2c"). A measure of the reversibility of sulfate adsorption is calculated by making two comparisons: 1) by the difference in phosphate extractable fractions, and 2) by comparing the desorption of sulfate following the adsorption treatment with sulfate desorption from the untreated soil. Comparisons are as follows:

$$\text{Irreversibly adsorbed sulfate} = "2c" - "1b" \quad [1]$$

$$= "2a" - ("2b" - "1a") \quad [2]$$

Thus, an overall evaluation of the conservation of sulfate during the sequences of these equilibrations can be made by comparing irreversibly adsorbed sulfate calculated by the use of Eq. [1] with that calculated by Eq. [2].

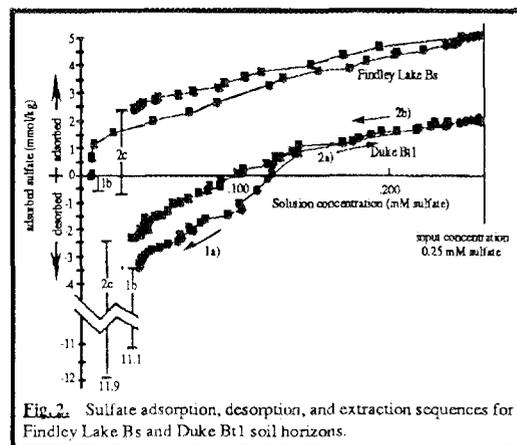


Fig. 2. Sulfate adsorption, desorption, and extraction sequences for Findley Lake B3 and Duke Bt1 soil horizons.

RESULTS A total of 31 out of 36 soil horizons studied adsorbed some sulfate. The Findley Lake Bs soil, for instance, adsorbed 5.0 mmol/kg (Fig. 2; Tab. 1). Levels of soluble sulfate in the Findley soil were very low; it did not support a solution concentration above 0.025 mM. Native insoluble sulfate was also relatively low (0.7 mmol/kg). The Duke Bt1 soil horizon had much higher levels of native soluble sulfate (3.58 mmol/kg), and native insoluble adsorbed sulfate (7.6 mmol/kg), but still adsorbed 1.8 mmol/kg from solution.

Tab. 1—Selected soil properties and sulfate adsorption data for the sites.

Site	Vegetation	soil horizon	soil pH	total C	oxalate Al	adsorption studies				
						2a	2b	2c	1a	1b
Oak Ridge	Loblolly pine	B1	5.2	182	67	.42	2.46	.35	.96	.07
Oak Ridge	Chestnut Oak	B1	4.7	13	36	.37	1.45	1.09	1.18	.95
Oak Ridge	Chestnut Oak	B2	4.8	13	37	.75	1.26	1.82	.90	1.94
Oak Ridge	Yellow Poplar	B1	5	23	41	-.15	.40	.08	.49	.11
Oak Ridge	Yellow Poplar	B2	5	23	41	.03	.62	.92	.92	.42
Camp Branch	White Oak	B	4.7	-	59	.50	1.16	.54	.79	.30
Camp Branch	White Oak	C1	4.9	-	48	1.38	1.34	1.82	.67	1.14
Camp Branch	White Oak	C2	5	-	67	7.22	5.08	5.10	.10	3.02
Smoky Mts.	Red Spruce 1	B	4.1	3017	170	.31	.88	.32	1.08	.20
Smoky Mts.	Red Spruce 1	C	4.7	407	145	.47	.97	.71	.49	.15
Smoky Mts.	Red Spruce 2	B1	4.3	2853	182	.03	2.24	.98	2.60	.89
Smoky Mts.	American Beech	A	4	5290	133	-.76	.86	.37	1.62	.27
Smoky Mts.	American Beech	B	4.6	2190	170	.28	1.21	.54	1.20	.44
Smoky Mts.	American Beech	BC	4.8	1404	245	.84	3.30	5.95	2.26	5.90
Cowoceta	Oak-hickory	Bt	5.3	-	37	1.34	1.90	1.92	1.35	1.07
Cowoceta	White Pine	Bt	5.6	375	59	2.67	2.56	2.70	.56	1.91
Cowoceta	White Pine	BC	5.8	167	41	3.89	2.33	3.00	.10	1.46
Duke Forest	Loblolly pine	Bt1	4.8	214	63	1.75	3.79	9.29	3.58	7.62
Duke Forest	Loblolly pine	C	4.8	114	67	2.78	5.31	11.90	3.62	10.30
B.F. Grant	Loblolly pine	Bt	5.2	263	47	3.09	2.22	3.98	.00	3.00
B.F. Grant	Loblolly pine	BC	5.2	75	51	6.39	4.65	5.59	.00	3.69
Florida	Slash pine	Bt	4.6	180	51	1.00	.80	.77	.37	.58
Florida	Slash pine	C	4.7	102	32	.93	.70	.57	.00	.34
Maine	Red spruce	Bs	4.2	-	803	1.05	.77	2.22	.00	2.15
Cedar River	Red Alder	B21	5.1	6524	778	2.31	2.19	.56	.29	.14
Cedar River	Red Alder	B22	5.2	4033	826	1.93	1.65	.67	.44	.39
Cedar River	Douglas-fir	B21	5.6	2199	730	3.18	2.40	3.31	.87	1.47
Cedar River	Douglas-fir	B22	5.5	1191	693	2.42	3.53	2.68	.79	1.79
Findley Lake	P. Silver fir	Bs	4.6	5402	1012	4.97	3.17	2.68	.00	.64
Whiteface Mt.	Red Spruce	Bap	4.8	5436	663	.64	1.16	.49	.62	.43
Horsington For.	Sugar maple	Ba1	4.9	2787	693	1.54	1.89	1.23	.63	.70
Turkey Lakes	Sugar maple	BfL1	4.6	4291	296	1.24	1.58	.62	.63	.29
Turkey Lakes	Sugar maple	BfH2	4.9	3281	493	.82	1.34	.41	.49	.33
Turkey Lakes	Sugar maple	Bf	4.9	2345	400	.75	.93	.39	.23	.37
Norway	Norway Spruce	Bs	4.8	795	128	-.41	1.31	.86	1.93	.83
Norway	Norway Spruce	BC	5	78	123	-.28	.94	1.78	1.32	1.66

Several soil properties appeared to be correlated with observed sulfate adsorption. The concentration of oxalate extractable Al was most closely correlated with sulfate adsorption for Spodosols and Inceptisols. This observation has been seen in several previous studies. For instance, Fig. 3 shows the relationship between sulfate adsorption and oxalate extractable Al. Very noticeable in this figure is the lack of high levels of oxalate Al in the weathered Ultisols despite a wide range of sulfate adsorption. The observed sulfate adsorption vs Al relationship for Inceptisols and Spodosols are plotted together in the figure ($r^2 = 0.68$).

No clear relationship between sulfate adsorbed and total C was seen in this study. As in the comparison of sulfate adsorbed vs Al above, there was a sharp distinction between Ultisols and the other soils analyzed in the study. A highly variable positive relationship between sulfate adsorption and pH was seen, which is in contrast to what has been seen in several other studies.

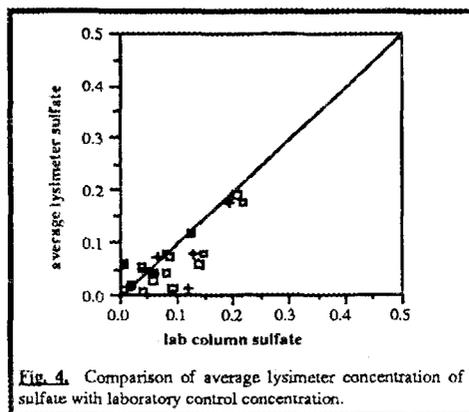


Fig. 4. Comparison of average lysimeter concentration of sulfate with laboratory control concentration.

Subsoil horizons showed sulfate adsorption ranging from -0.4 to 7.2 mmol/kg (Tab.1). There were no consistent patterns in observed sulfate adsorption between soil horizons within the same site. In general, native sulfate levels (soluble and insoluble) increased with soil depth. There were large differences in observed sulfate adsorption and native sulfate levels in similar soil horizons between sites in the same area, though not as great as the differences between soil horizons.

In the present study there are two measures of sulfate adsorption reversibility. One is the increase in phosphate-extractable sulfate (Eq. [1]) brought about by sulfate adsorption from solution during equilibration "2a". The second measure of irreversibly adsorbed sulfate is the difference between native water soluble sulfate, sulfate adsorbed from procedure "2a", and sulfate desorbed after procedure "2a" (Eq. [2]).

A total of 29 out of 36 subsoils showed irreversible adsorption based on increases in phosphate-extractable sulfate (Eq. [1]) while 28 of 36 subsoils showed irreversible adsorption based on the adsorption/desorption criteria of Eq. [2]. Thus, most soil samples showed relative conservation of added sulfate. In other words, sulfate adsorbed from solution was recovered quantitatively by water or phosphate extraction, or:

$${}^{2}c - {}^{1}b \approx {}^{2}a - ({}^{2}b - {}^{1}b) \quad [3]$$

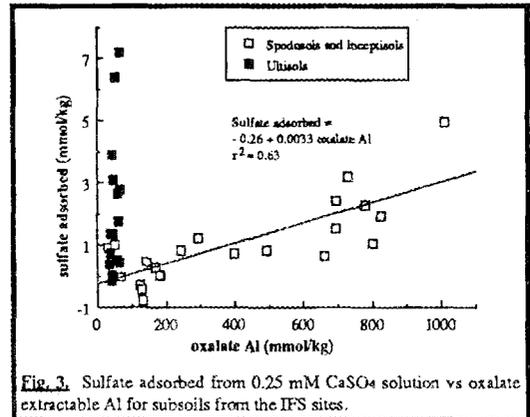


Fig. 3. Sulfate adsorbed from 0.25 mM CaSO₄ solution vs oxalate extractable Al for subsoils from the IFS sites.

Sulfate desorbable after saturation was directly related to pH, indicating the soils at low pH have more native soluble sulfate, possibly as a result of greater historical deposition, but also have a greater tenacity to retain any additional sulfate.

Laboratory studies indicated that soil chemistry has a strong control on the sulfate concentration of percolating water, and due to the fact that field studies of the IFS include monitoring soil solution chemical composition, a comparison between field and laboratory controls on sulfate concentration was possible. Fig. 4, for instance, includes a direct comparison of sulfate concentrations for solutions collected by lysimeter and initial percolates for equivalent soil horizons from several IFS sites. The imposed line is a 1:1 relationship; soils that fall on the line have equivalent sulfate concentrations in solution for field and laboratory studies. The relationship is direct, but extremely variable, indicating that the soil is important in controlling solution sulfate concentrations, but that our ability to estimate field results by laboratory studies is limited.

5.2.5

Integrated Forest Study Annual Report for 1988

Task B2: Inorganic and Organic Sulfur Retention Processes

John W. Fitzgerald, Department of Microbiology,
University of Georgia

Work in years prior to 1988 has concentrated on field incubations to determine to what extent laboratory determined potentials for organic sulfur formation reflect naturally occurring rates. Very good agreement was obtained at least for the Coweeta watersheds and a full length manuscript dealing with this was published in Soil Science Soc. of America, Journal. Other work has concerned an evaluation of surface samples from most IFS sites for various forms of organic S. Sites have been ranked in terms of existing levels of each form.

As first reported in an IFS technical highlight, we are now evaluating the relative importance of inorganic and organic sulfur accumulation by assaying soil samples taken by horizon for sulfate adsorption and organic S formation potentials. This work is aimed at evaluating a major hypothesis of the overall IFS project namely "all ecosystems are unsaturated with respect to higher rates of sulfur deposition". Briefly, assays for adsorption and organic S formation are made on the same samples at progressively increasing amounts of added sulfate. We have completed work on samples collected from all sites except Turkey Lakes, Huntington, and Maine. Work at these sites will be completed by September 1989.

Although it may be premature at this stage to draw conclusions, some general trends appear to be emerging as follows:

- 1) Irrespective of site, amounts of added sulfate required for saturation with respect to adsorption or organic S formation increased with sample depth.
- 2) At saturating amounts of sulfate and irrespective of site, sulfur retained by adsorption and by organic S formation generally increased with sample depth.

Although these results are not surprising for the adsorption process in view of increasing Fe and Al oxides with depth, these results were unexpected for organic S formation implying that microbial activity is far greater in the deeper soil horizons than previously anticipated. This realization means that sulfur retention by conversion to organic forms of S cannot be totally evaluated unless all major soil horizons are assayed.

- 3) Except for A horizon samples from a few sites, sulfur retention by adsorption was at least 4-fold greater than retention by organic S formation at saturating amounts of added sulfate.

- 4) Much higher amounts of sulfate were required to saturate samples collected from sites receiving lower amounts of S deposition (eg. Washington State sites) as opposed to those receiving high amounts of deposition (eg. Oak Ridge sites). Generally, this observation held true irrespective of process assayed for or soil horizon assayed.
- 5) Although some exceptions exist, samples from the less saturated sites (with respect to either process) tended to exhibit much higher potentials for organic S formation than those evident for the most saturated sites. Thus for example, the mean formation potential (all horizons considered) for the Douglas Fir site (Washington) was about 10-fold greater than that for the Loblolly Pine site (Oak Ridge). Although sulfate adsorption potentials followed this relationship in some cases, a trend between degree of saturation and activity for this process was less evident.

Anticipated Publications:

- 1) Watwood, M. E. and Fitzgerald, J. W. 1988. Sulfur transformations in forest litter and soil: Results of laboratory and field incubations. *Soil Sci. Soc. Am. J.* 52:1478-1483.
- 2) Autry, A. R., Fitzgerald, J. W. and Caldwell, P. R. 1989. Sulfur retention mechanisms in forest soils. *Can. J. For. Res.* (Submitted).
- 3) Autry, A. R. and Fitzgerald, J. W. 1989. Sulfonate-S: A major linkage group of forest soil organic sulfur. *Can. J. For. Res.* (Submitted).
- 4) Autry, A. R. and Fitzgerald, J. W. 1989. Sulfur saturation potentials for forest soils. *Soil Biol. Biochem.* (In preparation).

5.2.6

Interim Report: Trees as Recorders of Changing Soil Solution Chemistry

Ernest A. Bondiotti
Environmental Sciences Division
Oak Ridge National Laboratory

March 1989

Purpose: The purpose of this study funded largely by the Electric Power Research Institute is to examine cation trends in annual rings of trees and evaluate their use in reconstructing past changes in soil solution chemistry, especially as related to perturbations in base cation nutrition (Bondiotti et al. 1989a). Stated differently, "If we had monitored the soil solution over the past 50+ years, would the direction of the chemical changes observed in wood be consistent with those we would expect given the particular perturbation and our understanding of how that perturbation affects plant uptake".

Objectives: The principal objectives are to develop a better understanding of the factors influencing cation storage in wood, to develop empirical data on wood responses to known chemical perturbations, and to expand the diversity of existing data sets, especially by sampling the same species in different environments. With respect to acidic deposition the objective is to determine when acidic inputs into the forest floor began to alter cation availabilities.

Mechanistic rationale: The physiological rationale behind the approach is simple: plant cell walls are ion exchangers and the composition of cations bound in cell wall structures reflects the activities of ions in the aqueous phase, either at the time of wall formation or subsequently as wall constituents equilibrate with the bathing solution. In wood this is the relationship between the cell wall of the tracheid or vessel and the sap. Only native soil cations whose flux into the plant is largely or entirely influenced by apoplastic processes are examined.

Tasks underway in the current Electric Power Research Institute work:

1. Empirical measurements to document responses to known perturbations
2. Understanding cation binding in wood.
3. Increasing the data base on red spruce and other species which may be good "recorders" of changing soil solution chemistry.
4. Evaluating the significance of the data from Task 3 in terms of natural and anthropogenic acidification pressures.
5. Automating measurements on increment cores (not discussed here).

Results (referencing the task numbers above):

1a. Empirical Tests: Four situations regarding soil perturbations have been examined:

- A. A 1971 calcium nitrate disposal experiment at a mixed oak-pine forest at Oak Ridge.
- B. A 1971 liming-fertilization trial on red spruce in Maine.
- C. A 1971 liming-fertilization trial on jack pine in Ontario.
- D. Two decade-long (1960s) fertility trials in pecan orchards in Georgia

We have also received cores from Sweden from three liming trials on Norway spruce. We also hope to obtain stem sections or data from German liming experiments where radial increment responses have been documented. We want to

determine if the calcium levels in wood increased as well.

The results of the calcium nitrate disposal study were inconclusive; white oak showed no response in wood to calcium applications. Shortleaf pine showed (possibly) progressively increased calcium levels in the two highest applications but the differences were not statistically significant, largely because only one pine remained at the high treatment plots.

The red spruce liming trial results were also inconclusive. No differences between cation trends in three trees each from limed and unlimed plots were found that would reflect the liming response expected (increased calcium, decreased manganese, decreased or constant magnesium, barium, etc.).

The pecan results were more than satisfactory. In the 1960s two orchards were involved in a decade-long fertility trial. The Waycross, Georgia orchard was limed with various materials; we chose the calcium carbonate treatment based on the published foliar data collected during the experiment. The other study, in Tifton, Georgia, involved variable fertilization rates; we chose the highest rate, again based on foliar response data obtained at the time. In the Waycross study the results of the tree core analyses reflected the foliar data of two decades ago: higher calcium, and lower magnesium, manganese, and aluminum when compared to the controls. In the Tifton cores, the results also reflected the original foliar data. The high fertilization rates in the poorly-buffered coastal plain soil depressed soil pH, increasing aluminum and manganese in foliage (and in wood). The use of lime to counteract the acidification also increased foliar calcium slightly by the end of the trial; this was also detected in the wood.

The Jack pine results were also positive. Foliar measurements published in 1988 by Neil Foster showed that after seventeen years calcium levels had increased significantly in the highest lime application rate plots vs the control plots, and that the base saturation and pH of the humus horizons had been positively affected. Measurements on increment cores supplied by Neil Foster confirmed this response, as calcium concentrations were significantly higher, and magnesium and manganese concentrations significantly lower, than in the controls. Aluminum concentrations were not different. Unpublished foliar manganese data supplied by Neil Foster showed lower manganese after liming.

1b. Fallout Sr-90

Fallout ^{90}Sr distributions in seven species have been measured, including three red spruce. Longleaf pine and probably shortleaf pine will be examined in the next six months. The results of this work show that hickory and red spruce are "good" species but that diffuse porous species like yellow-poplar may not be useful. "Good" refers to the ^{90}Sr concentration profile in wood formed prior to the fallout period; the narrower it is the better. Sapwood functioning at the time of a perturbation will control the distribution of most cations. Detecting changes in cation uptake at a time scale of 5- to 10-years appears reasonable, although the amount of functioning sapwood will dominate the uncertainty in the temporal resolution of any record of a perturbation in divalent cation availability. Literature papers purporting to detect changes in cations at yearly time scales are suspect. The conclusion (below) that base cation mobilization occurred in the red spruce ecosystem in the 1940s and 1950s is based on calibrating for the sapwood effect using ^{90}Sr .

2. Cation binding in wood.

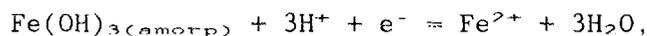
A major effort has been underway to understand divalent cation binding in red spruce and other species. We now understand why divalent cation concentrations often decrease at breast height in conifers with increasing age. This results from the fact that the concentration of pectic acid binding sites decreases with increasing radius. If divalent cations increase in wood at some date (as we have found in red spruce) it must be because either salt storage increases (oxalates, etc.) or because base saturation of the wood increases.

We have found that about 60% of the exchange sites in red spruce were saturated with divalent cations before about 1940 (or thereabouts) but in the 1940s-1970s this increased to about 80%. When aluminum, and especially iron, began increasing in the 1960s (and later), the base saturation of wood decreased, reflecting acidification of the transpiration stream. The timing of the change differs by geographic location for reasons that are not entirely clear.

3a. General nature of cation trends in red spruce and other species growing in low base-saturated environments.

Measurements of red spruce, eastern hemlock, Fraser fir, and yellow birch indicate that in general divalent cations were more available in the 1940s and 1950s than before or since that time. The existing data set is summarized in Table 1. Age seems to have little relationship to the measured trends. Decreasing divalent cation uptake, which begins to occur from the 1960s on, usually coincides with increasing aluminum and especially iron in wood. Increasing aluminum concentrations are presumably due to aluminum mobilization (Bondietti et al. 1989b) and acidification, or more specifically a decline in the Ca:Al ratio in the Donnan free space of the root.

Increasing iron availability in virgin stands of spruce at first seemed improbable and a physiological artifact was suspected. But based on all of the available data (over 100 trees of various species, of various ages, and with various site disturbance histories) the conclusion has been reached that acidification of the root zone of conifers growing on low base-saturated sites due to acidic deposition can account for the observed trends. Although the trends in young stands could be due to growth acidification, this natural mechanism cannot explain why the same trends occur in very old stands/trees. The proposed mechanism is straightforward and is based on the following model:



Amorphous ferric oxides in the root zone of acid, organic rich soils supply iron to solution in the divalent form. Small decreases in pH in the root zone, either episodically or permanently, will increase ferrous ion concentrations and thus plant uptake. A similar problem with iron toxicity was recognized 70 years ago when acid muck soils were first developed for agriculture. Experiments with humus from Vermont and Maine spodosols, in which redox potentials and Fe^{2+} concentrations have been measured, have confirmed that poorly crystalline ferric hydroxide controls ferric (and indirectly ferrous) iron concentrations. More importantly, soluble Fe^{2+} concentrations comparable to typical Ca^{2+} concentrations become increasingly probable when pHs drop several tenths of a unit below 4.0 even under oxygen-saturated conditions (pe+pH=13 in the laboratory). Organic complexes of Fe(II) were not found to be important in the laboratory studies.

This condition, like Al^{3+} , works to exclude other divalent cations from the root apoplast. The problem is compounded because the selectivity of spruce roots for Fe^{2+} over Ca^{2+} increases with decreasing pH below 4.0. Iron is much more toxic than Al^{3+} when present at similar activities in solution. Iron toxicity is a very rare condition in agricultural soils but probably not in a spruce-fir ecosystem being exposed to pH 3+ cloudwater for several decades.

This model and the evidence of increased iron uptake by trees is a possible explanation for why spruce with the highest wood iron come from sites with the highest mortalities. More importantly, it increases the importance of the finding that low elevation sites in Maine are just now showing the wood chemistry and radial increment declines that occurred at higher elevations several decades ago.

3b. Other trees

The other large tree data set now in hand involves shortleaf pine. Most of the

data was collected previously by Baes and McLaughlin and was supplemented by sampling at the calcium nitrate disposal site. What is striking about this data set, which is now about 60 trees, is the remarkable inverse correlation between iron and radial increment, much like the red spruce data set. Unlike the red spruce data set, however, we do not see the elevated divalent cations in the 1950s, except possibly in very calcium-poor sites. Evidence of a reduction in calcium uptake since the 1970s in Oak Ridge shortleaf pine appears to exist but a definitive conclusion awaits additional measurements. We are in the process of obtaining increment cores from shortleaf pine in Missouri to look at trees in a low deposition environment. So far we have only a few trees which are not showing a radial increment decline since the early 1970s; none show elevated iron or aluminum. Unlike the red spruce data set, however, the majority of these trees are less than 50 years of age and so greater caution must be exerted in assigning non-stand level causes to changing wood chemistry.

4. Relationships to acidic deposition

From the existing wood measurements, from similar measurements published in the literature, and from related research on how acidic deposition affects the humus horizons of forests, the available data indicate that the spruce-fir ecosystem underwent significant changes in cation cycling starting in the 1940s. Initially the response was positive as bases were transferred at an accelerated rate from the upper organic layers into the root zone and thus into bole and foliage. However this effectively sped up the divalent cation cycle beyond the capacity of the system to maintain a proper cation balance in the root zone. By the 1960s, solution Al:Ca and Fe:Ca ratios appear to have become detrimental to growth. Certainly calcium availability has declined since about the 1960s in both New England and the Smokies, and aluminum and iron availability is at a 250-y high.

References

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BONDIETTI, E. A., BAES, C. F. III and McLAUGHLIN, S. B. (1989b). Radial trends in cation ratios in tree rings as indicators of the impact of atmospheric deposition on forests. Canadian J. For. Res. (in press)

Table 1. Summary of Spruce-fir Ecosystem Tree Increment Chemical Data Set

<u>Location</u>	<u>Trees*</u>	Sample type	Date	Remarks

Maine				
	Penobscot N.F.	6 RS		stem 1988
	Beddington	2 RS		stem 1985
	Kossuth	2 RS		stem 1985
	Saddleback Mt.	4 RS		4-mm 1984 2 cores; 2 elevations
Vermont				
	Camels Hump	15 RS		4-mm 1983 3 elevations
		1 RS		5-mm 1982 Matusiewicz and Barnes (literature)
	Mt. Abraham	2 RS		stem 1985
New Hampshire				
	Crawford Notch	2 RS		stem 1985
Virginia				
	Whitetop Mt.			In progress
	Mt. Rogers			In progress
Tennessee/N. Carolina				
	GSMNP-1	23 RS		12-mm 1983 Baes and McLaughlin
		17 EH		12-mm 1983 Baes and McLaughlin
		12 FF		12-mm 1983 Baes and McLaughlin
	GSMNP-2	5 RS		stem 1988 fallen trees: 1985-1987
		1 YB		stem 1988 fallen tree: 1986
		2 EH		stem 1988 fallen trees: 1985-1987
		2 RS		5-mm 1988 1 core/tree
		2 YB		5-mm 1988 1 core/tree
New Brunswick				
		RS		1986 Arp et al. (literature)

* RS=red spruce; EH= eastern hemlock; YB= yellow birch; FF= fraser fir

**Integrated Forest Study Task Report
March 1989**

5.2.7

Task B3: Altering Natural Acid Inputs

Investigators: D.W. Cole, H. Van Miegroet, P.S. Homann, J.E. Compton, S. Brozek

The acidity generated through nitrification under N-fixing red alder is equivalent to 150 cm of rainfall per year at pH 3.5 over the lifetime of a stand. This acidity and subsequent cation leaching and decreased base saturation may affect the future growth of vegetation on a site. By removing the red alder from a site, and therefore removing the source of acid additions, soil recovery and future vegetation growth may be evaluated.

To determine the effects of acid generation on soils previously occupied by red alder, overstories were removed from 1-ha areas of adjacent 55-year-old red alder and Douglas-fir stands in September 1984 at the Thompson Research Center. Each 1-ha area was divided into two sections, one of which was replanted with red alder and the other with Douglas-fir.

Soil solutions are collected monthly from each plot and analyzed for chemical constituents. Seedling heights are measured each year. In the fall of 1988, through destructive sampling, regressions were derived for calculating seedling biomass from seedling height (Douglas-fir) and seedling height and diameter (red alder). In the summer of 1988, the understory species composition and biomass and forest floor biomass were measured.

By three years after harvesting the red alder, soil solution nitrate concentrations decreased to <1% of what they were the first year after conversion (Figure 1).

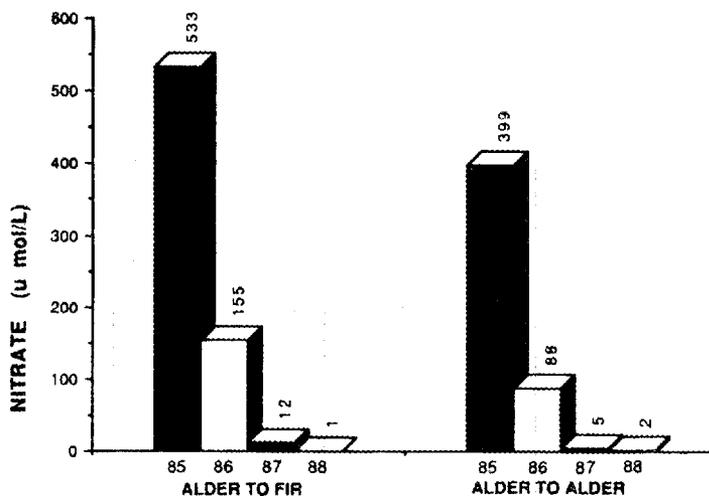


Figure 1. Nitrate concentration in soil solutions from A horizons in alder to fir and alder to alder conversion plots for four years following conversion.

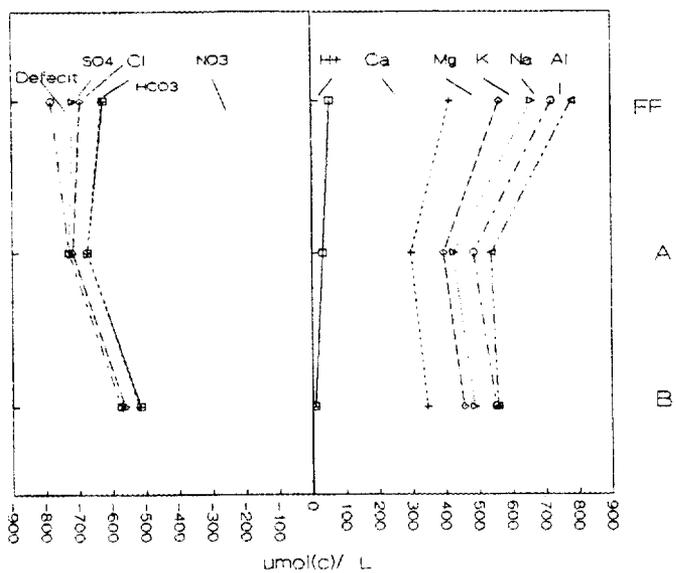
This indicates that nitrate leaching is mediated by removal of the source of nitrogen. The leaching may also be further reduced over time due to increased uptake by vegetation on the plots. Cation concentrations have also continued to decrease since overstory removal (Figure 2), suggesting that the leaching was nitrate-driven, and once the source of the acid was removed, cation depletion was ameliorated.



Figure 2. Cation concentrations in soil solutions from A horizons in alder to fir and alder to alder conversion plots for four years following conversion.

Soil profile cation/anion balances for the red alder control (nonharvested) plot and conversion plots previously containing alder are presented in Figure 3. The nitrate represents the largest anion charge in the control plot, whereas the nitrate concentrations in the conversion plots are a small part of the total anion concentration. The large anion deficits in the conversion plots suggest the presence of organic acids.

red alder control plot



alder to fir

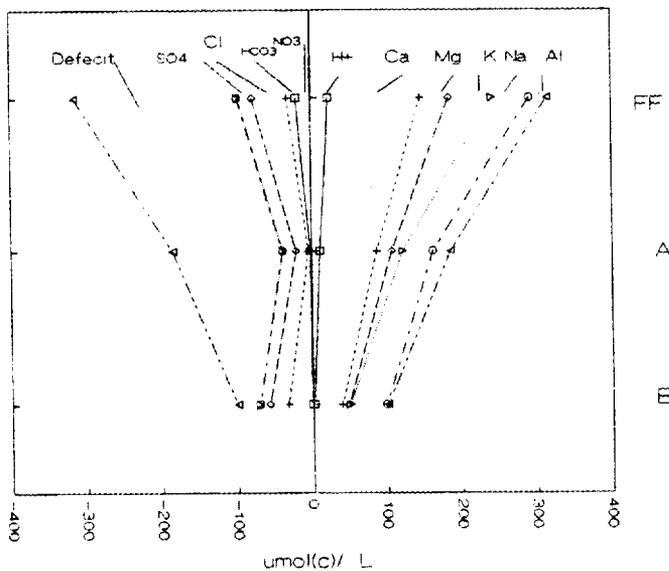


Figure 3. Cation/anion balance in soil solutions from red alder control plot, alder to alder conversion plot, and alder to fir conversion plot (1988 data).

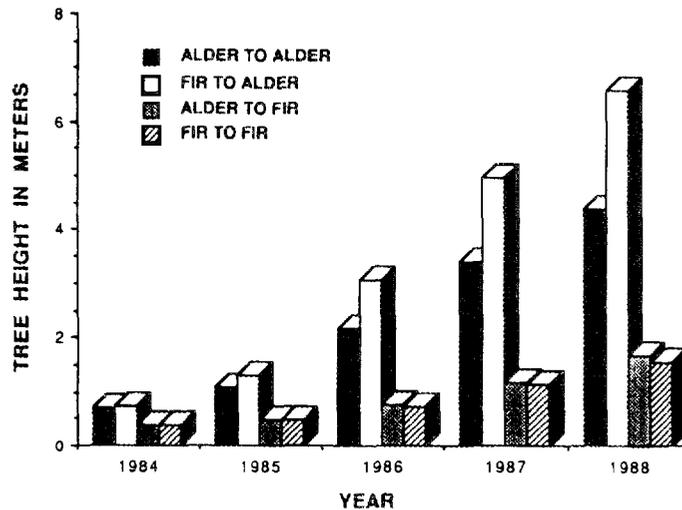


Figure 4. Red alder and Douglas-fir seedling heights for four years following stand conversion

Seedling heights each year after conversion are presented in Figure 4. The alder seedlings growing on the site previously occupied by alder have produced much less height growth and biomass accumulation than alder seedlings growing on soil previously occupied by Douglas-fir. This growth difference is most likely due to some residual effect associated with the acid generation under the red alder.

The Douglas-fir seedlings growing on soils previously occupied by red alder have produced slightly more height growth than those on soil previously occupied by Douglas-fir. Although this difference is less striking than that observed in the red alder seedling growth, it is expected to increase with time, due to the potential higher availability of nitrogen in the red alder soil.

Even as nitric acid-driven cation leaching has decreased over time after the removal of the source of acidity, subsequent vegetation growth has been dramatically affected by the previous 50 years of high nitrification rates. The decreased growth of alder on acidified soils may result from nutrient cation depletion, decreased viability of the N-fixing endophyte, and/or lowered phosphate or sulfate availability to the seedlings. There are also striking differences in understory composition between the two red alder seedling plots, and this may have resulted in differences in competition for nutrients and/or light.

5.2.8
WATER BUDGET ANALYSES

James M. Vose and Wayne T. Swank

Objective and Methods

The hydrologic subproject was not an original, planned task of the IFS project. It was not until the Annual Meeting in Pinehurst, NC, in February 1988, that a decision was made to conduct hydrologic modeling across IFS sites. Subsequently, EPRI provided supplemental funding to Coweeta scientists for water budget analyses and the cooperative agreement was amended in July 1988. Letters requesting the nature and format of input data needed for water budget simulations were transmitted to site investigators in August and September 1988. Therefore, this progress report covers only about 6 months of research effort.

The purpose of water budget analyses at IFS sites is to provide estimates of soil water fluxes commensurate with seasonal and annual assessments of ion concentrations in soil water collections and thereby provide a basis for estimating the hydrologic component of nutrient losses. We approached this need by selecting PROSPER, a phenomenological model of atmosphere-soil-plant water flow, to estimate water budgets for 12 forest stands at 9 IFS sites. This model was selected because (1) it has previously been evaluated against experimental watershed results for both conifers and hardwoods (Swift et al., 1975), for long-term hydrologic response (Huff and Swank, 1985), and for regional hydrologic studies (Troendle, 1979), and (2) input data required to run the model are generally available at IFS sites.

The model

A detailed description of PROSPER is given in Goldstein et al. (1974). Briefly, PROSPER links atmosphere, vegetation, and soils through the use of simultaneous equations that combine energy balance, mass transport, and soil moisture dynamics. The evapotranspiration (Et) surface combines canopy and litter, and Et is driven by an energy balance-aerodynamic equation. Network equations balance evaporative demands and liquid water flow through the soil and vegetation to the evaporating/transpiring surface. The soil is divided into several layers and rooting characteristics, soil porosity, unsaturated hydraulic conductivity, and saturated hydraulic conductivity, determine soil moisture and flow. PROSPER runs on a daily time step.

Current Status and Results

The status of PROSPER simulations for the IFS project is summarized in Table 1. Final results are available for the Coweeta mixed hardwood and white pine stands; initial simulations have been conducted for the Florida and Huntington sites; and at least some input data has been received for all sites except Turkey Lake, Duke, and the two Washington stands. To meet the objectives and timetable for nutrient flux analyses, hydrologic simulations for IFS sites will not be guaranteed if they have not provided all input data by March 31, 1989.

The hardwood and pine IFS study sites at Coweeta are located on watersheds where discharge has been measured with weirs for over 50 years. We evaluated model performance by comparing simulated annual outflow with measured annual discharge (Table 2). For the 1985 water year (May-April), simulated flow for mixed hardwoods was identical to measured flow while for white pine, simulated flow was 3 cm (6 percent) less than the measured value. Simulated annual evapotranspiration for hardwoods and pine was 59.6 cm and 89.7 cm, respectively; the 30 cm difference in Et obtained from the model compares

Table 1. Status of PROSPER simulations for IFS sites (February 1989)

IFS Site	Data Received		Simulation Status		
	Climate	Parameters	Data Input	Initial Runs	Final Results
COWEETA					
Pine	X	X	X	X	X
Hardwood	X	X	X	X	X
DUKE					
FLORIDA	X	X	X	X	
GEORGIA	X				
HUNTINGTON	X	X	X	X	
NORWAY	X	X			
OAK RIDGE					
GSMNP	X	partial			
Loblolly	X	partial	X		
TURKEY LAKE					
WASINGTON					
Douglas-fir					
Alder					

Table 2. Simulated annual water fluxes (cm) and measured flow for two Coweeta forest ecosystems.

Ecosystem	Simulated Flux			Measured Outflow
	Interception	Transpiration	Outflow	
Pine	44.4	45.3	53.7	57.1
Hardwoods	19.4	40.2	74.3	74.2

favorably with the 27 cm difference in water yield estimated by the paired watershed method of analysis for white pine on Watershed 1 (Swank, 1988). Comparisons of simulated and measured flows during subsequent years of the IFS study are not appropriate because of record drought conditions which began in 1986 and continues to the present time. PROSPER is an Et model and the

boundary of outflow is the bottom of the B soil horizon or 80 cm depth at Coweeta. In contrast, the regolith at Coweeta averages over 6 meters in depth and is the source for sustained stream discharge during extended precipitation deficits. Thus, during drought conditions some of the water flux from the B horizon replenishes storage deficits of deeper soil layers and does not appear as surface discharge.

Another level of model validation entails comparing ion fluxes based on lysimeter chemistry and water flux simulations with stream chemistry export. Assuming Cl^- is a conservative tracer, fluxes from the B horizon were calculated over a 19-month period, normalized to annual values, and compared to measured long-term export for both hardwood and pine-covered watersheds (Table 3). Calculated Cl^- fluxes ranged from 13 to 30 percent of measured exports. Stream export of base cations should be higher than calculated values, as illustrated by K^+ in Table 3, due to mineral weathering below the B horizon. Concentrations of NO_3^- are low in both soil solutions and streams of both ecosystems and fluxes are small.

Table 3. Comparison of calculated and measured export (kg/ha/yr) of select ions for two Coweeta forest ecosystems.

Ecosystem	Cl^-		NO_3^- -N		K^+	
	Calculated	Measured	Calculated	Measured	Calculated	Measured
Pine	5.1	4.5	0.02	0.20	2.0	3.4
Hardwood	4.3	6.2	.02	.02	1.6	4.7

These preliminary analyses indicate that reasonable estimates of both water and nutrient losses can be obtained using PROSPER and lysimeter data. Additional model evaluations will be possible for other IFS sites such as Florida, Huntington Forest, and Turkey Lake where independent hydrologic and/or nutrient flux estimates are available.

References

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INTEGRATED FOREST STUDY TECHNICAL HIGHLIGHT

JANUARY 1989

5.2.9

Task III: Development of Nutrient Cycling Model

S.A. Gherini, R.K. Munson, and S. Liu, Tetra Tech, Inc., Lafayette, CA 94549

To understand the cycling of nutrients in forested ecosystems, a mathematical model is being developed by Tetra Tech for the IFS project. The model will be used to simulate the response of forests to acid deposition and to various forest management practices. The acid-base status of the forest soils will be computed by the model to properly account for the interactions between soil pH and release of nutrients (base cations) from the various soil layers. The nutrient pools available in soil and vegetation components and the fluxes between them will be tracked (Figure 1). The model includes routing of water from the incident precipitation through the soil layers and includes evapotranspiration, deep seepage, and lateral flow out of the forest plot. The forested ecosystem is represented as a series of vegetation components (Figure 2) and soil layers. The major processes to be included are listed below:

Vegetation	Soil
Water Flux	Water Flux
Dry Deposition	Mineralization of Organic Matter
Foliar Leaching	Cation Exchange (Ca, Mg, K, Na, NH ₄ , H, Al)
Nutrient Uptake	Anion Adsorption (S, P, Organic anions)
Nutrient Translocation	Mineral Weathering
Litterfall	Aluminum Hydrolysis
Litter Decay	Solid-liquid-gas Phase Equilibrium
Tree Biomass Increment	Root Respiration

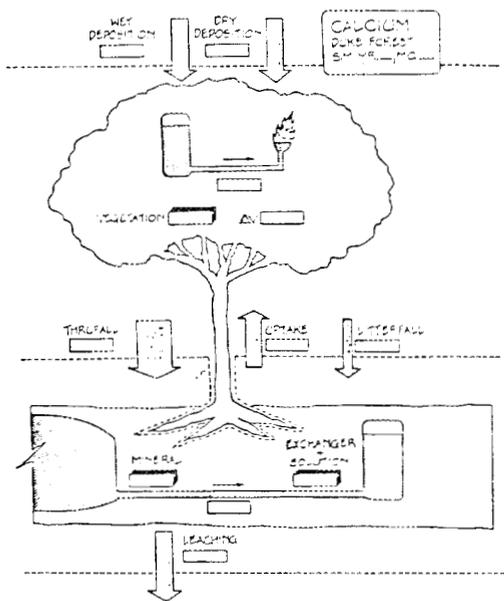


Figure 1. NUTRIENT CYCLING MODEL-POOL AND FLUX DIAGRAM
Nutrient Pools [solid rectangle] and Fluxes [dashed rectangle]

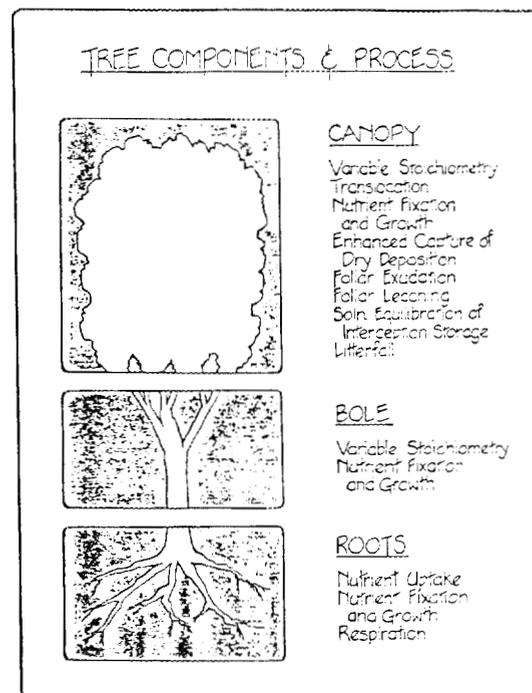


Figure 2. Tree components and processes simulated in NuCM.

Model output will also include total pool sizes, annual and monthly fluxes between components, and the relative contribution or loss by process (Figure 3). In addition, parameter versus time plots will be generated.

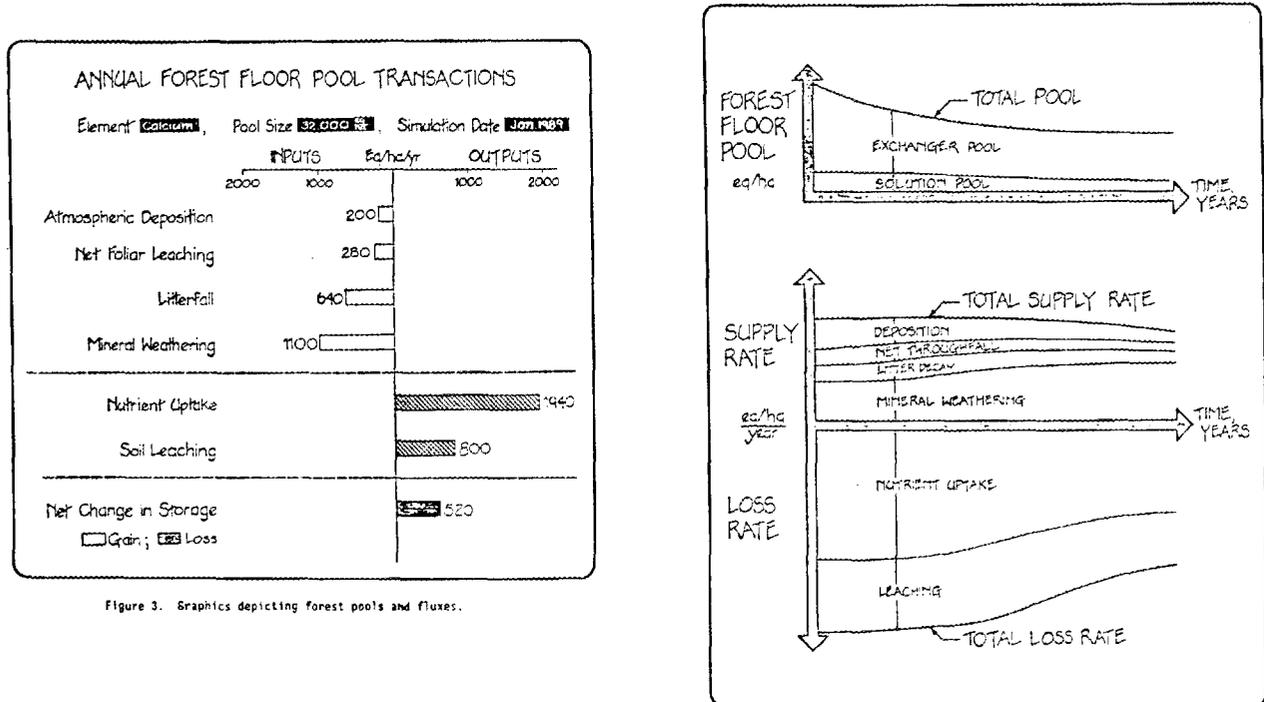


Figure 3. Graphics depicting forest pools and fluxes.

The model being developed has an interactive, menu-driven format for IBM-compatible microcomputers. Function keys are being programmed to enable the user to quickly move from one parameter or menu to another. Help menus to define the variables and to provide typical ranges of parameters are being included. The intent is to make the model easy to use with a variety of output options to investigate scientific hypotheses regarding specific soil and vegetation processes and to show the effects of deposition scenarios and forest management practices (e.g., clear cutting, full and understory burns, and use of fertilizers).

To assist in conceptualizing the model, two workshops were held with the group leaders from the IFS project. The Atmospheric Inputs Workshop, held at Oak Ridge, covered wet and dry deposition, and canopy processes. The Soils Workshop, held at Tetra Tech's Lafayette office, reviewed hydrologic processes as well as biogeochemical processes occurring in vegetation and soils. Of particular importance was the interaction of soil acid-base behavior and nutrient cycling. Additional information used to select processes to be included and modeling approaches has been obtained from literature and existing models (e.g., OR-NATURE, ILWAS, ENVSIM).

SECTION 6. SITE OPERATION AND SITE SPECIFIC RESEARCH REPORTS

Integrated Forest Study Site Report
March 1989

6.1

Sites: Douglas-fir (DF), Red Alder (RA), Findley Lake (FL)

Tasks: Atmospheric Deposition and Nutrient Cycling

Investigators: Dale W. Cole, Peter Homann, Gordon Wolfe, Jana Compton,
Helga Van Miegroet, Robert Edmonds, Bob Gonyea

November 1988 completed the field monitoring that will be included in the IFS Synthesis. This yields two years of atmospheric deposition data for the red alder and Douglas-fir stands, and more than two years of nutrient cycling data for all three stands, although only the two most recent years will be included in the Synthesis. Limited monitoring is being continued to better determine year to year variability.

Chemical deposition to the Douglas-fir stand is presented in Figure 1. Precipitation contributes greater than 70% of the estimated total deposition of calcium, magnesium, sodium, and chloride, and slightly less than this for the other species. Coarse particles are estimated to contribute nearly all the dry deposition of potassium, sodium, calcium, and magnesium, a majority of ammonium, and half of nitrate and sulfate, although there is much uncertainty associated with the absolute values.

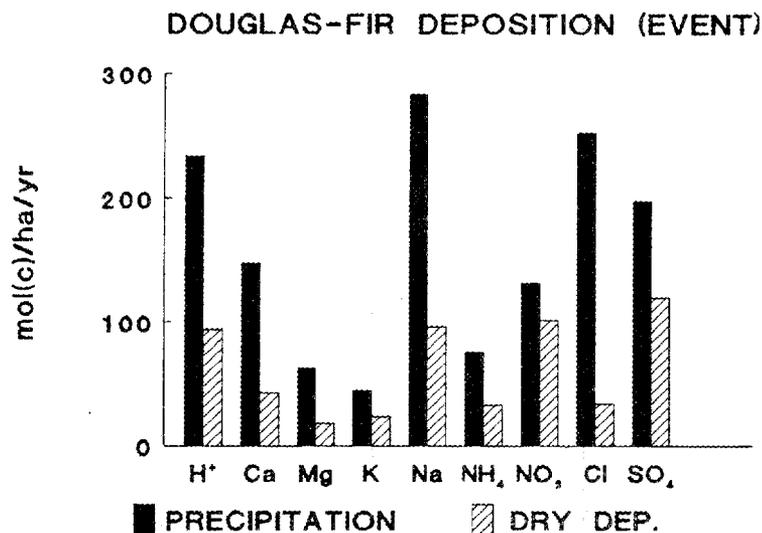


Figure 1. Precipitation and dry deposition in the Douglas-fir stand, Thompson Research Center, western Cascades, Washington.

The Douglas-fir canopy interacts considerably with the deposition and has a large effect on the element flux (Figure 2). The net canopy effect (throughfall + stemflow - total deposition) indicates a large uptake of hydrogen ion, ammonium, and nitrate by the canopy, a large release of potassium, and lesser interactions for the other elements. The red alder canopy shows a similar general pattern, although both the hydrogen ion uptake and the potassium release are greater than for the Douglas-fir canopy.

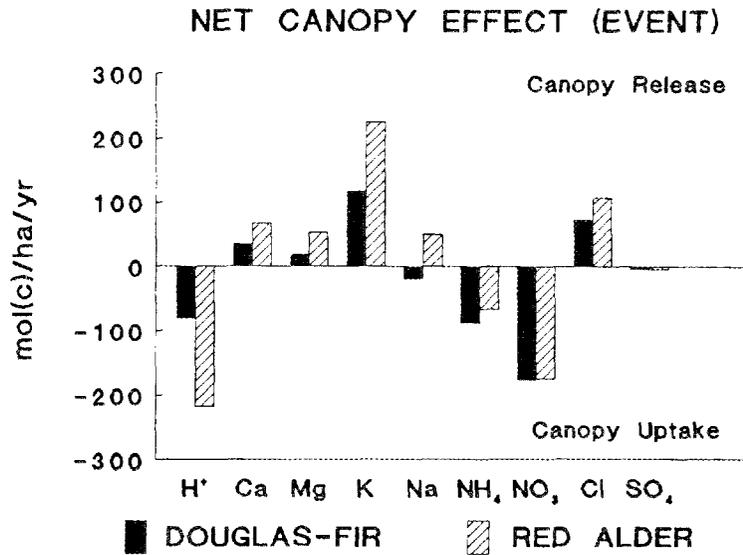


Figure 2. Net canopy effect in Douglas-fir and red alder stands.

The completion of soil sulfur analyses allowed a comparison between the different stands (Figure 3). Most of the soil sulfur is in the organic form. Of particular interest is comparison between the Douglas-fir and red alder stands which developed on same soil that presumably had the same properties 60 years ago. The effect of the nitrogen-fixing red alder has been a build-up of nitrogen in the soil. This produced a parallel build-up of organic sulfur (Figure 3), resulting in the maintenance of the nitrogen to organic sulfur ratio in the soil (Figure 4).

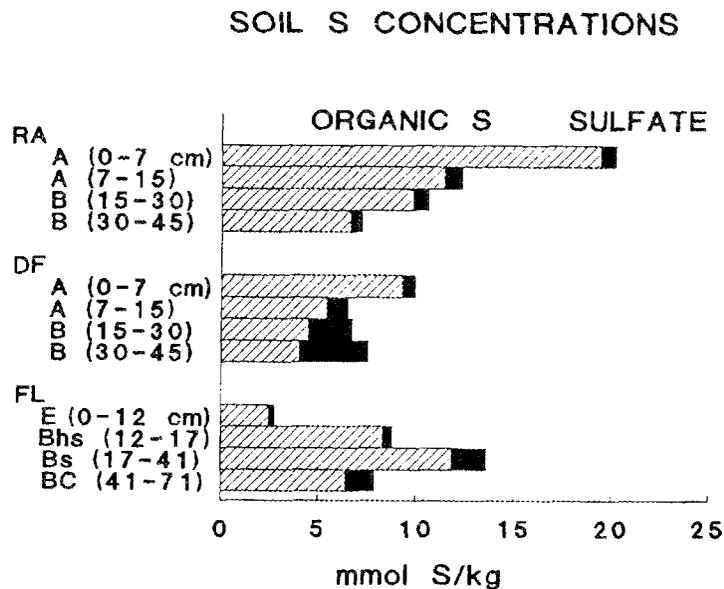


Figure 3. Soil sulfur concentrations in Douglas-fir, red alder, and Findley Lake stands.

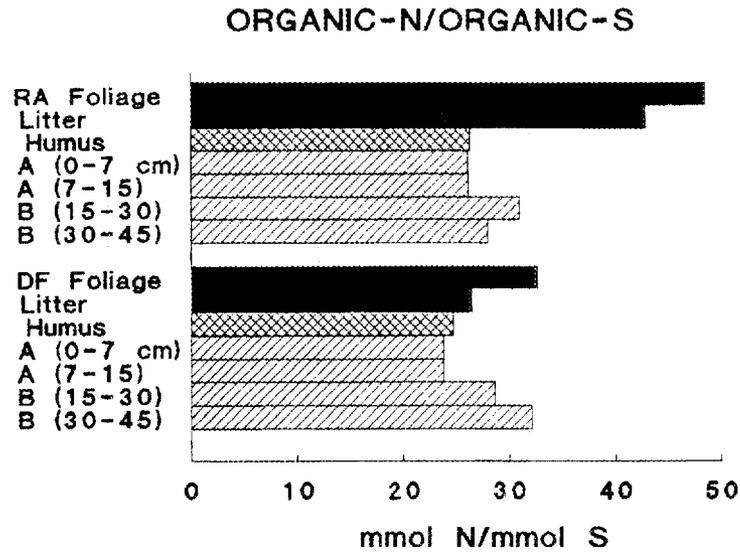


Figure 4. Organic-N/organic-S ratio (molar basis) throughout the Douglas-fir and red alder ecosystems.

The nitrogen to organic sulfur ratio in the forest floor is also similar in the two stands, inspite of the much higher ratio in the red alder litter that serves as a substrate for the forest floor. This suggests that microbial mineralization of the organic matter may control the relationship between organic sulfur and organic nitrogen in the forest floor and soil. However, organic sulfur and organic nitrogen in percolating soil solutions (Figure 5) suggest that leaching may also affect this relationship and the redistribution of organic sulfur and organic nitrogen within the soil.

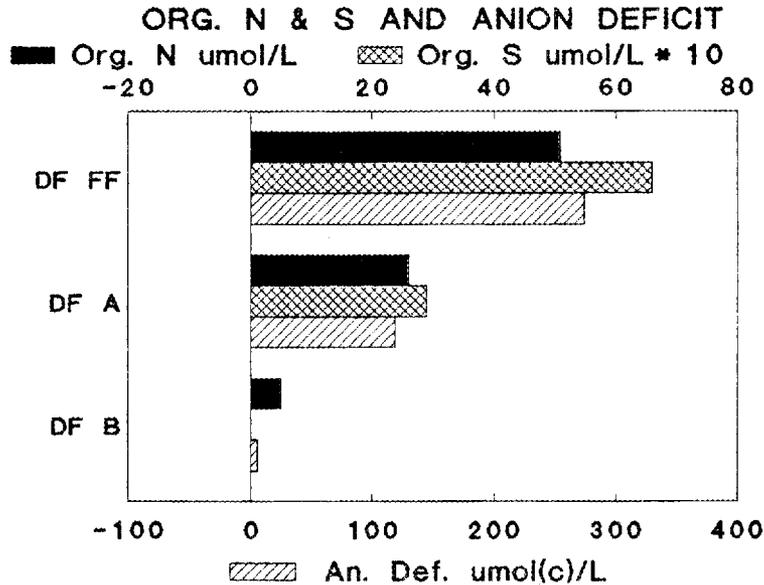


Figure 5. Organic-N, organic-S, and anion deficit of Douglas-fir soil solutions.

DEPOSITION RESEARCH AT THE SMOKIES TOWER SPRUCE (ST)
AND OAK RIDGE LOBLOLLY PINE (LP) IFS SITES

S. E. Lindberg, D. A. Schaefer, D. Silsbee,
J. G. Owens, and D. Nikoli

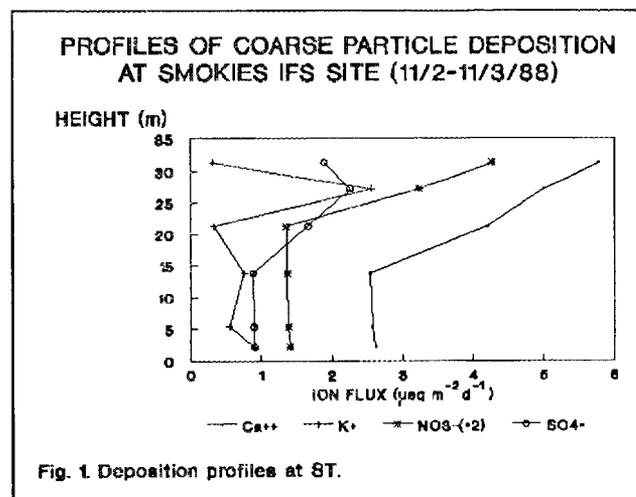
During 1988 several studies were performed at the ST and LP IFS sites to test assumptions or address questions regarding application of various methods within the IFS. These included 1) studies on the sources of ions in coarse particles dry deposited to inert surfaces, 2) development of plate-to-canopy scaling factors for coarse particles, 3) application of several methods for estimating cloudwater interception, and 4) evaluating spatial variability of ion fluxes in throughfall.

Sources of Dry Deposited Coarse Particles and Methods for Scaling to the Forest Canopy

Coarse particles in dry deposition are collected on inert deposition plates exposed on towers above the canopy at all IFS sites. There are two important questions regarding this method: how can fluxes measured to plates be extrapolated to the full canopy and what are the sources of coarse particles measured with this method? To address the first, we developed a scaling factor specific to each IFS forest canopy. The methods and results of this approach have now been published (Lindberg et al, 1989a) and are summarized below in the Experimental Task Reports.

Understanding the sources of dry deposited coarse particles involves two problems: the extent to which these particles are derived from locally derived resuspended dust (where local is defined as within the forest plot under study), and the specific sources which contribute to coarse particle dry deposition. Addressing the first question requires measurement of deposition or air concentration profiles in and above the forest canopy. Previous studies have shown that dry deposition to plates in open fields is dominated by local material (Davidson and Elias, 1982). This is indicated by deposition profiles which show an increasing deposition rate of ions as one moves closer to the ground-level source. The opposite pattern (deposition rates increasing with height above the ground) indicates that the primary source is the overlying air mass, and not soil dust immediately adjacent to the sampling site.

We have measured relatively high dry deposition rates of coarse particles at the ST site (Lindberg et al, 1988), although this site is distant from the extensive agricultural fields and gravel roads which act as sources of coarse aerosols at the valley IFS sites (LP, DL), suggesting local resuspension. The higher wind speeds at this mountain site can penetrate to the ground more effectively than at the valley site due to the patchiness of the canopy, particularly near the tower itself. We measured a deposition profile at this site for 48 hours to determine whether local soils were contributing this material (Fig. 1). The mean wind speed during these experiments was 6.2 m s^{-1} , and the wind direction was generally WSW (upslope).



The profile clearly shows that ground-level sources near the tower and in the forest plot do not contribute significantly to these fluxes during this experiment. The steep slope of the profiles for Ca^{2+} and NO_3^- indicate that these ions are efficiently scavenged by the upper canopy surfaces, more so than SO_4^{2-} . We have measured numerous similar profiles in forests such as LP in the Oak Ridge area (Lindberg and Lovett, 1985). In each case, the dry deposition rates of all major ions, except K^+ , consistently increase with increasing height above the forest floor, indicating insignificant local resuspension. This is not surprising given the rapid decay of the wind speed profile within these low-elevation forests, and the absence of bare soil on the forest floor, due to extensive litter cover.

The profiles for K^+ at both the ST and valley forests consistently exhibit a bulge within the canopy, decreasing with proximity to both the ground and the air, suggesting an in-canopy source, probably consisting of weathering products of needle cuticle and other biological material. However, because the flux of K^+ in these forests is dominated by foliar leaching in throughfall, this local source of coarse particles is not an important bias in our estimates of K^+ fluxes and behavior at these sites.

For the other base cations, the most logical sources of coarse particle dry deposition are resuspended soil and road dust (Gatz et al, 1985), originating outside of the forested areas. To estimate the relative importance of each source type at the LP site, we measured the major ion content of a limited number of samples of road and soil dust collected in the Oak Ridge area, and compared their composition as reflected in ion ratios with the average composition of suspended aerosols and particles collected in deposition plates over one year. The same extraction method was used for all sample types.

The best source indicator was the ratio of Ca/Mg which was very stable within any sample type, but differed by an order of magnitude between soil and road dust (Table 1). Because the two source types exhibit such different ion ratios, source apportionment methods can be used to estimate source contributions. Assuming that soil and road dust are the primary sources, and that they form an internally mixed aerosol, and that these samples are representative, it is apparent that soil dust dominates the composition of both

Table 1. Ratios of Ca/Mg in dry deposited particles, suspended aerosols, and two possible sources: soil and road dust.

Samples:	Mean ratio	Standard Error	Sources:	Mean ratio	Standard Error
<u>Coarse Particles</u>			<u>Road dust</u>		
LP-GS*	14	1	Sample 1	40	4
LP-DS	15	1	Sample 2	54	5
AVE	15		AVE	47	
ST-GS	16	2	<u>Soil dust</u>		
ST-DS	15	1	Sample 1	4.0	0.3
AVE	16		Sample 2	4.0	0.4
			AVE	4.0	
<u>Aerosols</u>					
LP-GS	9.1	0.9			
LP-DS	10	1			
AVE	10				
ST-GS	9.4	1.2			
ST-DS	9.9	1.4			
AVE	10				

*LP = Oak Ridge Loblolly Pine site, ST = Smoky Mountain Tower site

*GS = samples collected during the growing season, DS = dormant season

suspended aerosols and deposited particles, accounting for 72-88% of the material. The contribution of road dust ranges from ~10-15% in aerosols and ~25-30% in deposited particles. The higher contribution of road dust to dry deposited particles is a reflection of the generally larger particle size of material in road dust and deposited particles compared with that in suspended aerosols.

Estimates of Cloudwater Interception at ST Site

Quantifying deposition to mountain sites is more difficult than for low elevation sites for several reasons. One reason is the potential importance of cloudwater interception and the difficulty in accurately estimating its magnitude. With two years of record at the ST site, we can begin to apply several different methods for the estimate of annual cloudwater input. This approach yields a range of possible fluxes, based on different assumptions, and provides an indication of the level of uncertainty in annual ion fluxes by cloud interception. The methods include variations of four different approaches: modeling, direct measurements of canopy drip rates, throughfall hydrology, and ion balances (Lovett, 1988). The first two approaches require knowledge of annual in-cloud exposure duration. While this parameter is measured for events sampled at the ST site, the remoteness of the site makes any long-term estimates highly uncertain. Therefore, we have concentrated our efforts in development of hydrologic flux data.

We established a randomly-spaced grid of 1 automatic and 14 manual rain gages below the canopy at the ST site for continuous measurement of throughfall hydrologic fluxes on an event basis. The automatic sampler is a recording, weighing bucket rain gage allowing some analysis on a subevent basis. In combination with a similar gage in the open, this has been useful in distinguishing between cloud-drip-only and snow-melt events, and also serves as the backup gage during infrequent periods when the manual gages overflowed or became frozen. When the data from this network are expressed as net throughfall (NTF = throughfall-precipitation), these gages provide useful information on the spatial and temporal trends in cloud deposition.

Fig. 2 illustrates the variability in annual NTF within the ST forest plot. The annual hydrologic flux varied considerably from -30 to + 60 cm of water, with 5 sites showing a net water interception loss (NTF<0) and 10 sites a net gain due to cloud water deposition (NTF>0). Photographs of the canopy over each gage revealed that the sites with a net interception loss were generally characterized by either of the extremes of minimal canopy cover or very dense cover located near a tree trunk. The sites with net cloudwater input were located near the outer edges of individual tree crowns or near gaps in the canopy. A good example of this effect is illustrated in the gradient in NTF from gages T7 - T10. Gage 10 is located at the edge of a wintertime gap in the canopy created by deciduous overstory and gage 7 is several meters into the stand from the edge, with gages 8 and 9 between the two.

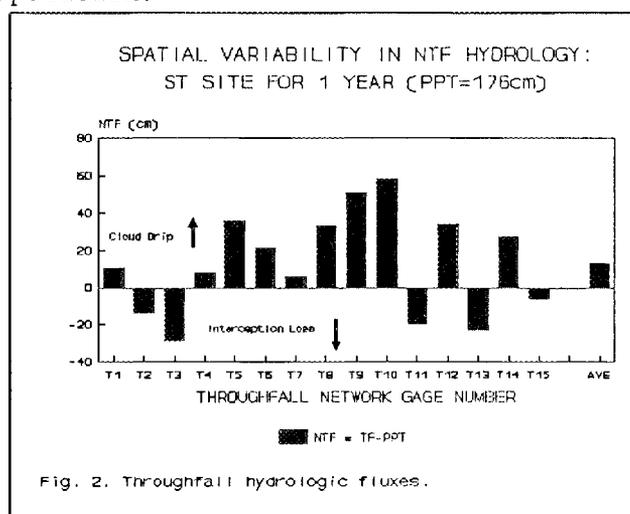


Fig. 2. Throughfall hydrologic fluxes.

Fig. 3 illustrates the temporal trend in the mean NTF from the complete grid of gages. These data suggest a consistent seasonal pattern in cloudwater interception at the ST site, with positive NTF values most common during the fall/winter periods of both years. Personal observations at the site confirm that cloud base moves down the mountain from the summit (2010 m) to the ST site (1740 m) during late summer/early fall, and that in-cloud exposure during the summer is minimal.

The straight mean NTF across this network ($\sim 14 \text{ cm y}^{-1}$, Fig. 2) provides a rough estimate of cloudwater input, but includes the negative effect of all of the interception losses during non-cloud periods. Summing only the events with $\text{NTF} > 0$ (Fig. 3) provides a better estimate of annual cloudwater deposition at this site ($\sim 24 \text{ cm}$), but does not account for interception losses due to evaporation from the canopy following cloud deposition. This effect can be estimated from the hydrologic behavior of the canopy during non-cloud periods (Fig. 3). When added to the 24 cm y^{-1} , this correction yields the best estimate of annual cloudwater input from the different hydrologic methods: $\sim 32 \text{ cm y}^{-1}$.

All of the estimates for annual cloudwater input to the ST site are summarized in Fig. 4. These estimates range nearly over a factor of 5, but the lowest value (straight NTF) is understood to be an underestimate, and is taken to represent the lowest cloudwater input rate that could occur. The model and drip rate estimates are consistently low, suggesting that our estimates of cloud immersion time ($\sim 800 \text{ h}$) are low, since each of these values is derived from either a modeled deposition or a measured drip rate, multiplied by an annual immersion time. The ion balance values are in relatively good agreement and are close to the "best" NTF value. These values are derived assuming no net foliar leaching of these ions, using cloudwater to balance the canopy input/output budgets for each ion. The overall mean of all estimates is $\sim 28 \text{ cm y}^{-1}$, but is an underestimate. We use as our best estimate the mean of the "loss-corrected" NTF and ion balance methods: $\sim 37 \text{ cm y}^{-1}$.

Variability in ion Fluxes in Throughfall

Throughfall fluxes are a critical component of the nutrient cycling measurements at IFS sites because the difference between deposition and throughfall is used to determine the fate of ions deposited to the canopy (Lindberg et al, 1988). However, their inherent variability puts throughfall fluxes among the most uncertain estimates made. Application of the dry deposition regression model to IFS data requires collection of throughfall as wetfall-only on an event basis, making large numbers of replicate collectors impractical. Numbers of replicate automatic collectors used at IFS sites

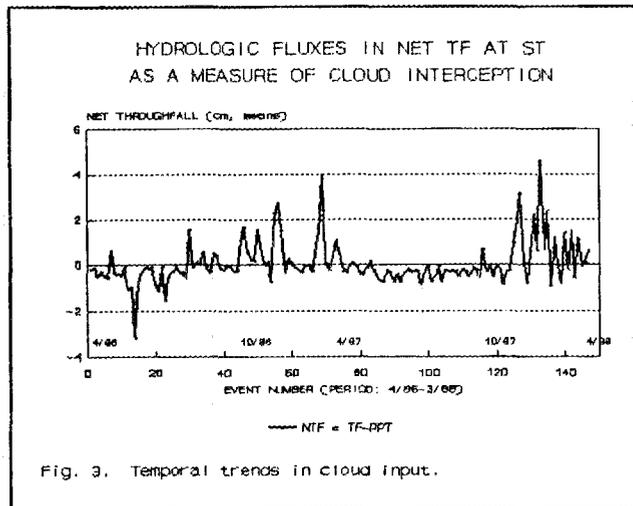


Fig. 3. Temporal trends in cloud input.

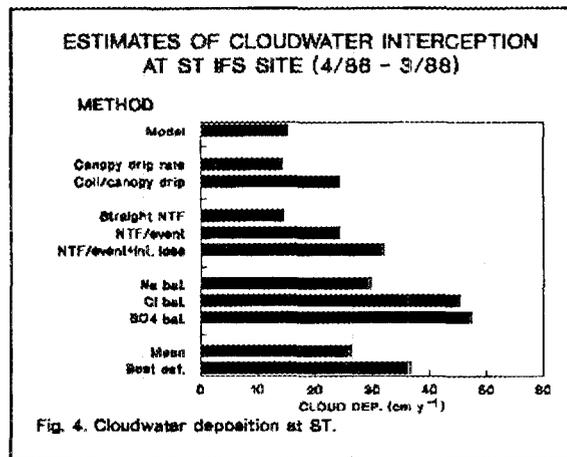


Fig. 4. Cloudwater deposition at ST.

generally range from 2-6 (the WF site employs 20 manual event throughfall collectors because of extreme canopy and terrain complexity). To quantify variability at these sites, special studies have been performed on selected events using replicate manual collectors in large networks.

At the ST (2 permanent collectors) and LP (6 permanent collectors) sites we established temporary grids of 12-18 samplers to collect throughfall for 4 (LP) to 7 (ST) events. Two of the ST events were mixed rain/cloudwater, the others rain only. Table 2 summarizes the results as relative standard errors (RSE) of the spatial mean ion fluxes for each event at the ST site, and includes

Table 2. Relative standard errors (RSE=SE/mean) of mean ion fluxes in throughfall for events sampled as wetfall-only at the Smokies Tower (ST) IFS site. The 1987 events were rain only, and were sampled with 17-18 replicate collectors. The 1988 events were mixed rain and cloudwater drip, and were sampled with 12 replicate collectors. Position of the 12 primary collectors remained fixed throughout the study, and were occasionally supplemented with 5-6 extra collectors

Event	TF-cm ^a	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	H ⁺	NH ₄ ⁺	K ⁺	Na ⁺	Ca ²⁺	Mg ²⁺
7/29/87	7.1%	5.5%	8.9%		8.5%		9.8%		9.3%	
8/14/87	14.0%	30.7%	39.3%		24.6%		33.7%		37.4%	
8/18/87	6.8%	9.6%	11.3%		12.3%		7.7%		10.4%	
9/11/87	7.6%	8.8%	10.8%		9.2%		12.4%		9.0%	
9/14/87	6.2%	13.0%	12.0%		12.3%		11.6%		14.9%	
11/7/88	8.2%	8.5%	10.4%	9.9%	9.1%	9.4%	9.4%	10.4%	8.6%	11.8%
11/17/88	8.3%	10.3%	12.1%	10.5%	8.8%	14.9%	10.9%	11.9%	10.1%	13.2%
Means	8.3%	12.4%	15.0%	10.2%	12.1%	12.1%	13.6%	11.1%	14.2%	12.5%
Mean LP*	2.3%	3.9%	5.0%	6.1%	7.8%	18.0%	10.3%	7.7%	10.6%	9.2%

^aTF-cm is the throughfall amount in cm.

*LP is the low elevation Loblolly Pine site at Oak Ridge where throughfall was sampled with 12 replicate collectors for 4 events.

the mean RSE for all events at the LP site for comparison. As expected from canopy and terrain heterogeneity, the mean RSE values for ST events generally exceeded those for events at the low elevation LP site. At the ST site the RSE values were surprisingly similar for all ions, suggesting that canopy characteristics influence the variability in throughfall fluxes of all ions similarly.

An important use of these data is in evaluation of the representativeness of the permanent sampler points at each site. Fig. 5 illustrates the spatial patterns in the total fluxes of SO₄²⁻ and NO₃⁻ in the 7 throughfall events sampled at the ST site, where collectors ACM1 and ACM2 represent the permanent sites. The spatial trends in total throughfall fluxes for both ions are similar, and are generally comparable with the patterns seen for each individual event (eg. site t4- located near the edge of a dense canopy- is consistently among the highest, and t6 the lowest).

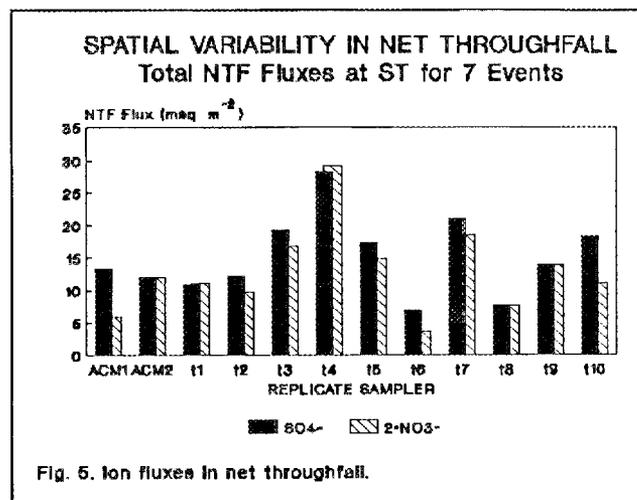


Fig. 5. Ion fluxes in net throughfall.

Summing the fluxes over all 7 events, the 2 permanent ACM samplers measured throughfall fluxes near the median value of the spatial replicates for SO_4^{2-} , but somewhat below the median for NO_3^- . The mean fluxes at the permanent sampling points are also less than the mean fluxes for the 12-site network for most of the individual events, as shown in Fig. 6 for SO_4^{2-} . For these 7 events, the permanent samplers underestimated the total throughfall ion fluxes averaged across the network by 10% for H^+ , 13% for SO_4^{2-} , 21% for K^+ , 22% for NO_3^- , and 25% for Ca^{2+} . Although the effect on annual throughfall fluxes cannot be quantified directly, these data (if representative) suggest that the permanent throughfall collectors may be an important source of bias for some ions at the ST site. The magnitude of this bias has been used to estimate the uncertainty in fluxes measured at the ST site, as discussed elsewhere in this report.

At the LP site (with its flat terrain, more uniform canopy, and 6 permanent samplers), the fluxes measured at the smaller permanent and larger temporary grids consistently agreed to within 10% (all but NH_4^+ and K^+ were within 4%).

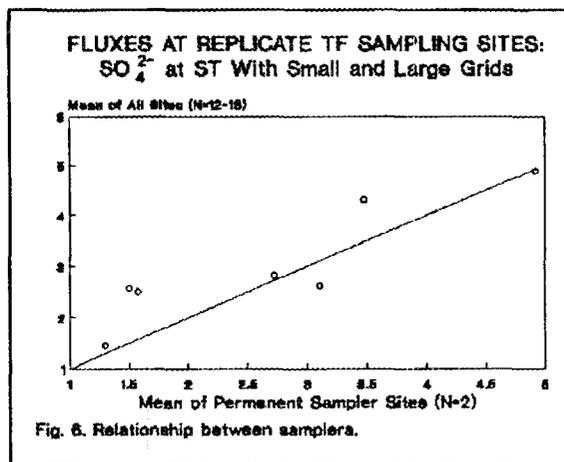


Fig. 6. Relationship between samplers.

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NUTRIENT CYCLING IN THE LOBLOLLY PINE AND SMOKIES SITES**D.W. Johnson, H. Van Miegroet, S.E. Lindberg, and D.E. Todd****March, 1989**Introduction

During 1988, we summarized two years of flux data (April 1986 - March 1988) and the stand biomass and nutrient contents. This data allows us to begin to construct nutrient cycles for the sites and assess the effects of acid deposition upon them. The latter is currently underway, with significant progress having been made in analyzing the nitrogen cycles and how our views of them must be modified when large amounts of foliar uptake occur.

It is not possible to summarize all the available nutrient cycling data for these four sites in this brief report. Instead, we will briefly review some of the highlights of our findings. Specifically, we review the contrasts in nitrogen, sulfur and calcium distributions and fluxes in these sites, and we will show recent temporal data on soil solution NO_3^- , SO_4^{2-} , and Al in the Tower red spruce site.

Distribution of Organic Matter, N, S, and Ca

The organic matter, N, S, and Ca distributions of the four sites vary considerably, as expected. The Smokies sites have greater vegetation nutrient contents than the Loblolly site; this is due to greater biomass in the Smokies sites and higher concentrations in the Beech site. The red spruce sites have considerably greater forest floor organic matter and nutrient contents than the Beech and Loblolly sites, whereas the Beech and Tower sites have greater soil organic matter and N contents than the Loblolly and Becking sites. Soil total S and Ca do not follow the same trends as organic matter and N, reflecting the greater importance of inorganic forms in the cases of S and Ca. Soil SO_4^{2-} was greatest in the Beech plot and least in the two spruce plots. Robb Harrison has noted previously the unusually high soil SO_4^{2-} in the Beech site; this may be related to the pyrite in the bedrock (Anakeesta formation) at this site.

The most striking difference among these sites is in exchangeable Ca^{2+} : levels in the Loblolly site are approximately two orders of magnitude greater than those in the Smokies sites. Values in the Becking site are particularly low. Yet soil total Ca contents vary by only a factor of 3, reflecting the much greater proportion of soil Ca on exchange sites in the Loblolly site (80%) than in the Smokies sites (0.4-4%).

Nitrogen, Sulfur, and Calcium Fluxes

Nitrogen, S, and Ca fluxes vary considerably among these sites as well (Table 1). As is typical of N-deficient forests, the Loblolly site accumulates over 90% of incoming N, whereas the Smokies sites show either no accumulation or a net loss. The major form of N in soil solutions in the Loblolly site is organic whereas the major form of N in soil solutions from the Smokies sites is NO_3^- . These differences in leaching cannot be attributed to total ecosystem N content, since the Becking site is relatively low in N yet it shows a large net annual N loss. It is also unclear as to how much of the NO_3^- leaching is directly attributable to current levels of atmospheric N deposition. The large forest floor and upper soil horizon N pools along with the lower C/N ratios in upper horizons in the Smokies sites (7-8 in the Smokies sites vs 12 in the Loblolly site) point strongly toward excessive net N mineralization (i.e., in excess of uptake) as the major cause of higher NO_3^- leaching rates. This is confirmed by the results from the field mineralization experiments which indeed indicate much higher mineralization and nitrification rates in the Smokies forest floor and mineral soil than in the Loblolly site. Atmospheric deposition certainly has contributed to the current high levels of NO_3^- leaching in the Smokies sites in that the atmosphere is the ultimate source of N for the ecosystem. The extent and duration which the currently high rates of NO_3^- leaching would be maintained under lower atmospheric N inputs is unclear, however; this is a scenario that we are interested in testing with the IFS nutrient cycling model.

Soil Solution Al in the Smokies Sites

Soil solution chemical equilibrium equations dictate that Al^{3+} concentrations will increase with the introduction of mineral acid anions to an acid soil (Reuss and Johnson, 1986). We have noted in earlier reports that soils from the red spruce (Becking and Tower) Smokies sites are extremely acid (base saturations of 3-8%, neutral salt CEC) and that concentrations of mineral acid anions (NO_3^- followed

closely by SO_4^{2-}) are relatively high. Thus, it is not surprising that the cationic component of soil solutions from these sites is dominated by H^+ and Al^{3+} (Johnson et al in press). Thornton et al (1987) find that red spruce roots begin to show morphological effects of Al^{3+} at concentrations of 200 $\mu\text{Mol/L}$ or more.

In the late winter/early spring of 1987-88, we noted soil solution total Al levels approaching 200 $\mu\text{Mol/L}$ associated with pulses of both NO_3^- and SO_4^{2-} in the A horizon of the Tower Site (Figure 1). We did not analyze for monomeric Al in these particular solutions, but analyses in other solutions have indicated that total Al was >80% monomeric in solutions from this horizon.

The concentrations of both NO_3^- and SO_4^{2-} vary with time, but the concentrations of NO_3^- vary to a greater extent, and NO_3^- was by far the predominant anion during the spring 1988 pulse (Figure 1). This NO_3^-/Al pulse may well have been associated with the drought of the previous summer, as has been shown for NO_3^- pulses at the Solling Site in Germany (Ulrich 1987). Monitoring of soil solutions from the Tower site (including more analyses for monomeric Al) will continue through 1989, thanks to funding from the Spruce-Fir Cooperative, and we will be watching carefully for further NO_3^-/Al pulses.

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Table 1. Organic Matter, Nitrogen, Sulfur, and Calcium Distributions and Fluxes in the Oak Ridge Loblolly pine, Smokies Beech, Becking Spruce, and Tower Spruce Sites

<u>Component</u>	<u>Site</u>			
	<u>Loblolly</u>	<u>Beech*</u>	<u>Becking</u>	<u>Tower</u>
	-----kg · ha ⁻¹ or kg · ha ⁻¹ · yr ⁻¹ -----			
<u>Organic Matter</u>				
<u>Vegetation</u>	118100	190800	263900	273300
<u>Forest Floor</u>	9600	27300	166100	151100
<u>Soil**</u>	116340	142500	86400	206100
<u>Nitrogen</u>				
<u>Distribution</u>				
<u>Vegetation</u>	190	560	390	520
<u>Forest Floor</u>	110	70	1920	2200
<u>Soil</u>	5260	9050	5360	9040
<u>Flux</u>				
<u>Deposition</u>	9	7	11	26
<u>Leaching</u>	0.5	7	35	24
<u>Sulfur</u>				
<u>Distribution</u>				
<u>Vegetation</u>	85	100	160	162
<u>Forest Floor</u>	250	N.D.	240	305
<u>Soil, Extr.</u>	250	560	100	200
<u>Soil, Total</u>	1160	1570	1270	1490
<u>Flux</u>				
<u>Deposition</u>	14	13	30	34
<u>Leaching</u>	15	5	26	35
<u>Calcium</u>				
<u>Distribution</u>				
<u>Vegetation</u>	160	400	510	470
<u>Forest Floor</u>	60	30	170	310
<u>Soil, Exch.</u>	6900	100	10	130
<u>Soil, Total</u>	8570	2560	2480	3240
<u>Flux</u>				
<u>Deposition</u>	6	8	12	16
<u>Leaching</u>	14	5	15	10

* The Beech site flux values are very tentative because of the predominance of a large nitrate pulse from the fall of 1985 to the spring of 1987.

** Assumes soil organic matter is 44% carbon

N.D.: Data not available as of this writing.

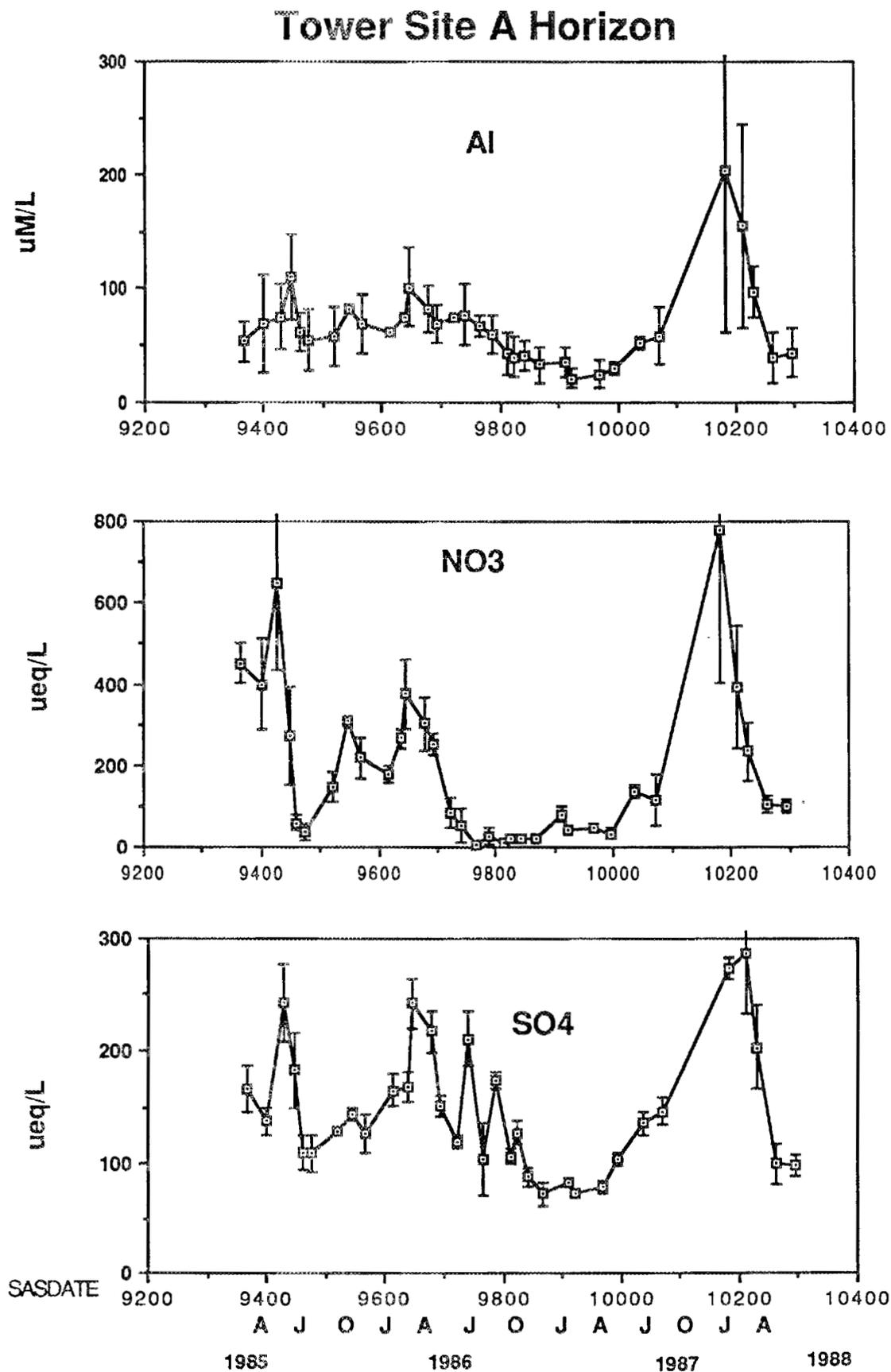


Figure 1. Soil solution Al (total), NO_3^- , and SO_4^{2-} in A horizon of the Smokies Tower site. (Standard Errors are shown.)

6.3

PROGRESS REPORT

COWEETA HYDROLOGIC LABORATORY

March 1989

Wayne T. Swank and Lee J. Reynolds

Overview

During the past year, routine sample collection was conducted following established protocols. Sampling for the nutrient cycling tasks was concluded in October 1988 and sampling for deposition tasks was terminated in March 1989. Monitoring of ambient O₃ has continued to present. A separate in situ study on HNO₃ uptake by white pine foliage was initiated (Vose et al., In Press), forest floor and soils were assayed for nitrogen transformation, and several small studies were conducted to assess uncertainty and variability for components of nutrient flux estimates. Results from most of our research are included in group leader and experimental task reports. Therefore, this site report will only include findings from the small separate studies.

Throughfall Variability

Event-only throughfall was routinely sampled during the 1988 growing season by three Aerochem Metrics (Model 301) automatic wet/dry collectors. Four storms during June and July 1988 were more intensively sampled to assess spatial variability in throughfall. The additional collectors were white plastic buckets mounted on stakes about 4 feet high--the same type of bucket and height as used in the Aerochem collectors. The buckets were opened

manually, 4 hours or less before the onset of rain. The stakes were never moved during the course of the study. Buckets were washed and soaked in distilled water between storms, or after being left open for several hours in anticipation of rain that did not materialize.

A comparison of throughfall and ion fluxes for each storm and for the total period are shown in Table 1. Differences in throughfall amounts between Aerochem and other throughfall collectors ranged from less than 1 percent to 12 percent for individual storms and averaged less than 1 percent for the total volume of the four storms sampled. These results are consistent with a similar study of throughfall variability conducted in 1987 in which 11 storms totaling 16 cm of precipitation showed an average difference in throughfall volumes of only 4 percent between Aerochem and other collectors. Thus, the number and location of Aerochem samplers appear to provide reliable, representative estimates of plot throughfall volume. Examination of ion flux data in Table 1 indicate the same level of confidence in estimates of SO_4 , Cl, Na, Ca, and Mg fluxes. Comparison of other ion fluxes shows that Aerochem values for NO_3 and H are 15 to 20 percent higher than the additional collectors while PO_4 , NH_4 , and K are lower. Thus, there appears to be no consistent bias across ions represented in the Aerochem flux estimates. The standard error of estimates for water and ion fluxes are 10 percent or less in most cases, even though means are based on only four storms (Table 2). The low variability and relatively high level of certainty obtained from the small sample sizes in this forest stand is probably due to the complete, uniform canopy of a single species.

Precipitation Variability

We have two independent sources with which to compare the EPRI results for temporal variability in event-only precipitation. (1) It is routinely monitored at Coweeta Watershed 6 (WS 6), a site about 650 meters distant from the pine and hardwood plots, and at a similar altitude. At the WS 6 site, event-only precipitation is collected with an Aerochem Metrics wet/dry sampler. Nearly all precipitation is analyzed for pH and major ions (but not for TKN or TP) on site at Coweeta. Samples are normally collected once each week, if there has been sufficient rainfall (approximately 2 mm). There were 85 such collections during the period of interest, 4/1/86 to 3/31/88. A few weeks were not sampled due to equipment failure. These samples include much precipitation that occurred in events of less than 0.35 cm, usually too small to sample by the EPRI protocols since there is insufficient throughfall under the white pine canopy for analysis. (2) There is also an NADP station located at Coweeta about 600 meters from the EPRI plots. Event-only precipitation is collected here and sent to the NADP laboratory for analysis. Bulk precipitation chemistry is also measured weekly at the NADP sampling site and is included for comparative purposes.

In the first year (4/86-3/87) of comparison, the WS 6 and NADP anion-cation balance shows good agreement but the EPRI analysis shows a 12 ueq/l anion deficit. Sulfate dominates the anion composition of Coweeta precipitation and H dominates the cations. EPRI values for SO_4 are 4 to 5 ueq/l lower than the other station values and H is 2 to 5 ueq/l higher. For the second year of comparison, WS 6 again shows good charge balance but the EPRI analysis gives a 12 ueq/l anion deficit. Values of H ions are within 3 ueq/l but EPRI SO_4 values are about 12 ueq/l lower than WS 6. Differences in solute concentrations between sites could be expected because the amount of precipitation sampled varied substantially between sites; however, this does

not explain a discrepancy in charge balance. Chemical analyses of paired samples across laboratories currently underway may provide insight into reasons for these differences. Otherwise, ion concentration data for precipitation events during the year for the EPRI study indicates that values are representative of the entire year.

TABLE 1. Comparison of throughfall water and ion fluxes measured in three Aerochem Metrics wet/dry collectors and in six manually operated event-only throughfall collectors ("VAR TF"). Differences expressed as a percentage of the flux measured in the VAR TF collectors.

			THROUGHFALL FLUX (ueq/m ²)									
Event#	Collector Type	Amount (cm)	SO4=	NO3-	Cl-	PO4---	H+	NH4+	K+	Na+	Ca++	Mg++
72	Aerochem:	1.01	1983	353	244	51	473	133	1953	100	1157	620
72	VAR TF:	.98	1945	316	268	152	392	284	2176	101	1057	628
	Percent Difference	3.1	1.9	11.7	-8.8	-66.3	20.7	-53.2	-10.2	-1.0	9.5	-1.3
73	Aerochem:	1.09	2294	711	229	96	1361	125	1313	77	1237	564
73	VAR TF:	1.06	2317	619	248	162	1121	160	1635	79	1180	586
	Percent Difference	2.5	-1.0	14.9	-7.7	-41.0	21.4	-22.0	-19.7	-1.9	4.8	-3.6
75	Aerochem:	.42	729	41	99	22	304	46	465	48	362	196
75	VAR TF:	.48	779	24	115	42	260	44	617	54	409	228
	Percent Difference	-12.0	-6.5	74.8	-14.2	-47.2	17.1	3.7	-24.6	-10.8	-11.5	-14.2
77	Aerochem:	1.12	857	169	134	39	532	52	691	66	529	245
77	VAR TF:	1.13	837	144	155	52	465	74	895	67	522	267
	Percent Difference	-.9	2.4	17.0	-13.1	-25.2	14.6	-29.6	-22.8	-2.2	1.4	-8.2
TOTAL	Aerochem:	3.64	5863	1275	706	208	2670	355	4423	291	3284	1625
TOTAL	VAR TF:	3.65	5878	1104	785	409	2237	562	5323	300	3168	1709
	Percent Difference	-.3	-.3	15.5	-10.1	-49.1	19.3	-36.7	-16.9	-3.3	3.7	-4.9

TABLE 2. Relative standard errors in throughfall water and ion fluxes at nine sites under the White Pine canopy, combining data from both Aerochem and manually operated collectors. [(Standard error/ mean) * 100]

PERCENT STANDARD ERROR IN THROUGHFALL FLUX											
EVENT #	Amount	SO4=	NO3-	Cl-	PO4---	H+	NH4+	K+	Na+	Ca++	Mg++
72	2.9	4.3	22.7	8.3	27.1	13.7	21.0	7.4	7.3	6.9	5.6
73	3.0	2.6	7.4	13.7	9.3	10.0	17.7	13.7	13.3	8.7	10.3
75	5.1	3.1	42.4	7.0	30.1	10.3	34.2	9.6	3.0	7.5	7.5
77	2.5	4.5	12.9	12.4	23.7	6.9	16.9	14.0	9.7	13.3	13.3
TOTAL (4 storms)	2.6	3.1	11.1	10.3	15.9	7.5	16.3	9.9	8.1	8.4	8.1

TABLE 3.

FIRST YEAR

EVENT-ONLY PRECIPITATION CONCENTRATIONS

PERIOD 4/1/86 to 3/31/87

TOTAL PRECIPITATION**..... 150.3 cm

SOURCE	Sampled		CONCENTRATION (ueq/liter)											
	Amt (cm)	pH	SO4=	NO3-	Cl-	PO4---	H+	NH4+	K+	Na+	Ca++	Mg++	Anions	Cations
EPRI	65.2	4.51	24.7	9.3	3.0	.34	31.0	10.6	.54	2.4	4.1	1.3	38	50
WS 6	141.0	4.54	29.2	12.7	3.3	.22	28.6	8.7	1.1	2.9	4.3	1.8	45	47
NADP	146.0	4.59	29.4	11.3	3.7	.22	25.4	6.7	.47	3.2	2.6	1.2	44	40
BULK PRECIP*	148.0	4.45	33.4	14.1	4.1	.42	35.3	9.62	1.9	3.76	6.3	1.9	52	59

SECOND YEAR

EVENT-ONLY PRECIPITATION CONCENTRATIONS

PERIOD 4/1/87 to 3/31/88

TOTAL PRECIPITATION**..... 133.5 cm

SOURCE	Sampled		CONCENTRATION (ueq/liter)											
	Amt (cm)	pH	SO4=	NO3-	Cl-	PO4---	H+	NH4+	K+	Na+	Ca++	Mg++	Anions	Cations
EPRI	50.2	4.47	25.6	11.6	5.0	.18	33.7	10.1	.60	3.7	4.1	2.0	42	54
WS 6	120.6	4.43	36.2	17.3	8.0	.20	36.7	9.9	1.7	7.3	4.0	2.2	64	62
BULK PRECIP*	131.4	4.40	42.5	17.4	9.4	.86	39.1	10.8	2.2	9.2	7.4	3.2	69	72

*Bulk precip measured at Coweeta climatic station #1, the same site as the NADP sampling.

**TOTAL PRECIP AMT. is the average of climatic station #1 and Raingage 20,

which is slightly closer to the EPRI plots. This amount was used to calculate fluxes.

Annual precipitation is typically slightly greater at raingage 20 than at Climatic Station # 1 or watershed 6.

6.4a
INTEGRATED FOREST STUDY REPORT
B. F. GRANT FOREST, GEORGIA
(GL SITE)

Harvey L. Ragsdale and John M. Croom
Emory University

The B. F. Grant loblolly pine site which has operated continuously from April, 1987 to the present, is an intensive measurement site in the IFS program. Field collection of "Event" and "Bulk" samples at the B. F. Grant site began approximately one year later than most other IFS Sites.

A major study on throughfall replicability is being conducted at the B. F. Grant pine forest. The first study consisted of a direct comparison of the similarity of precipitation collection results from seven, calibrated Aerochemetric collectors. The "Aerochems" were placed in an open grassy area for precipitation collection between October and December, 1986. Precipitation was collected for each rainfall event and analyzed for volume(mm), pH, and the concentration of K, Na, Ca, and Mg. Replicability of results was judged on the basis of the relative standard error, RSE, the ratio of standard error to mean.

Variability was minimal for precipitation volume and pH (Table 1), ranging from 0.1 to 0.7% for four events which represent the range of volumes collected over ten events. These results, including one event with a 4% RSE for volume, suggest that a single aerochem collector is adequate for measurements representing precipitation input to the IFS forest plots.

The variability for base cation concentrations among the replicate aerochem collectors was a factor of 10 or more greater than for pH and precipitation measurements (Table 1). Sodium, Mg, and Ca had RSE's of 1 to 5% with an occasional value up to 10% out of the full set of ten events. Potassium had RSE's of 4 to 14% with some values as high as 20%. The potassium concentrations were near detection limits which may explain the decreased precision for the K measurements.

The aerochemetric wet-dry fall collectors, if properly calibrated, will provide measurements of precipitation and pH with extremely low variability. Although precision for cation concentrations was significantly higher, the RSE's were low (5 to 10%) indicating good replicability among the aerochemetric collectors.

Variability of the annual throughfall flux of chemical elements was assessed by chemical and volumetric measurements of throughfall solutions taken from 6 aerochem collectors which were randomly located under a homogeneous loblolly pine canopy. Storms were collected as discrete events for one year from 4/1/87 to 5/1/88. The relative standard error is used as an index of precision since the standard error is routinely reported for the IFS event data.

The annual volume-weighted throughfall flux for an element is calculated by summing the total microequivalents over all storms, dividing this by the hydrological flux for the storms to determine the weighted average concentration, and finally multiplying the average concentration by the total throughfall for the annual period. The error term appropriate for this annual flux is obtained from the fluxes for each event. The standard error for the mean event fluxes is scaled to an annual flux.

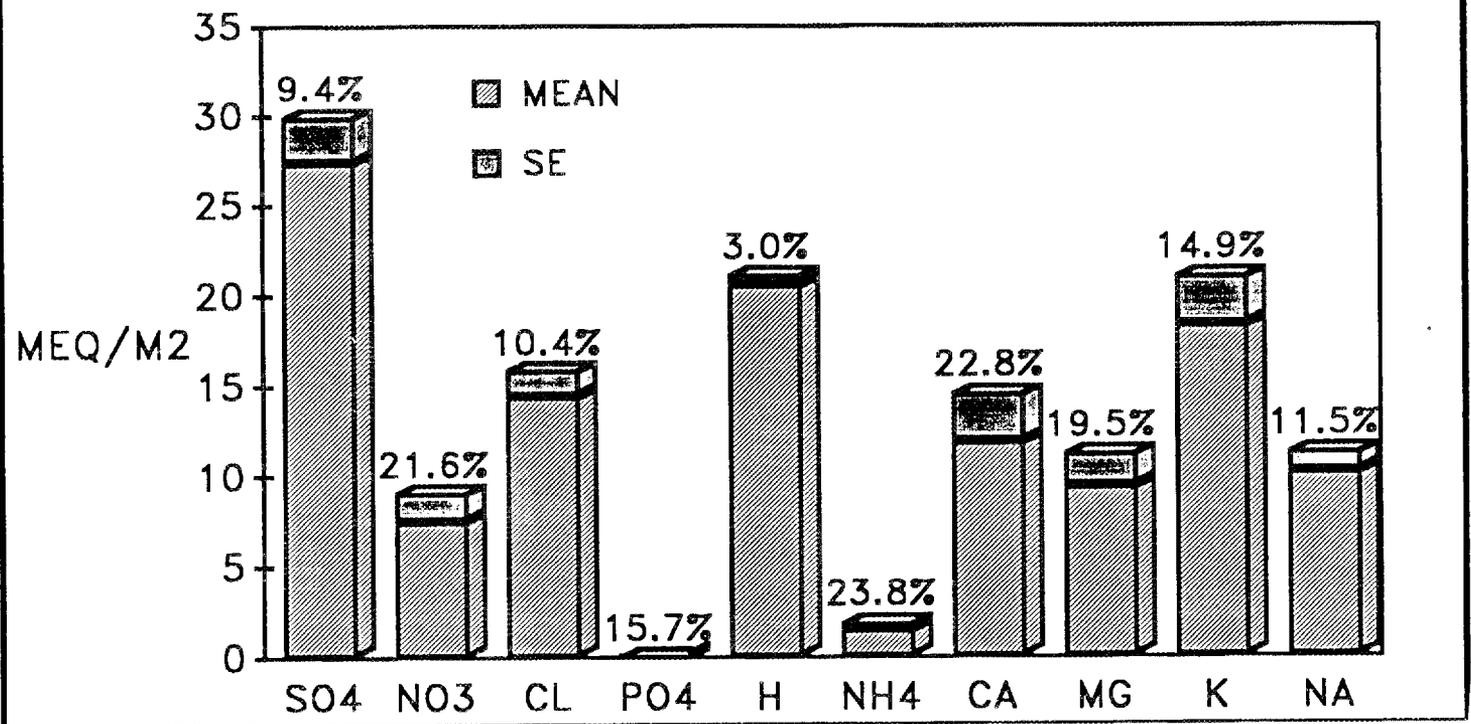
The throughfall results for the 1987-88 year suggest good to reasonable variability for the throughfall measurements (Figure 1) with 24% being the highest RSE calculated for the year. The RSE's for throughfall at this uniform loblolly pine canopy ranged from 3 to 24%. The lowest variability, 3 to 12%, was found for SO₄, Cl, H, and Na. Variability was higher, 15 to 24%, for NO₃, Ca, Mg, and K. The results for phosphate and ammonium are questionable due to a relatively small set of measurements.

These throughfall results represent a typical loblolly pine "monoculture" of the southern Piedmont. There is, however, a hardwood component associated with these pine forests. Deciduous plants may occur as occasional trees within the pine canopies, as understory plants reaching 20 to 30 foot heights and as climbing vines which can reach pine canopy height. Examination of the throughfall data for the individual Aerochems reveals one aerochem collector with fluxes that are consistently different from the others. The canopy of that collector has a greater deciduous canopy than the others. While the B. F. Grant site may be considered "homogeneous", the RSE for each element would be lower in the absence of the deciduous canopy effect.

Table 1. Variability among Aerochem wet-dry fall collectors for four precipitation events in 1986. RSE is the ratio of standard error to mean expressed as a percent value.

EVENTS		PPT (mm)	pH	NA (mg/L)	K (mg/L)	MG (mg/L)	CA (mg/L)
OCT. s1	MEAN	384	4.52	0.037	0.009	0.005	0.057
	SE	0.8	0.01	0.002	0.001	0.0003	0.002
	N = 7						
	RSE%	0.21%	0.20%	4.56%	5.95%	6.75%	3.32%
NOV. s2	MEAN	246	4.21	0.224	0.031	0.031	0.014
	SE	1.5	0.01	0.003	0.004	0.0007	0.001
	N = 6						
	RSE%	0.59%	0.15%	1.18%	14.16%	2.33%	7.24%
NOV. s4	MEAN	189	4.37	0.314	0.080	0.048	0.086
	SE	0.5	0.01	0.001	0.003	0.0003	0.001
	N = 6						
	RSE%	0.25%	0.16%	0.19%	3.56%	0.58%	1.37%
NOV. s3	MEAN	138	4.33	0.082	0.014	0.012	0.018
	SE	0.9	0.00	0.004	0.002	0.0006	0.001
	N = 6						
	RSE%	0.68%	0.09%	4.60%	14.97%	5.09%	6.96%

FIG. 1. Mean annual through-fall fluxes at the B. F. Grant Forest (GL-Georgia Loblolly Site), 1987-88. The relative standard error (SE/MEAN) is shown as a % value.



THE INFLUENCE OF WATER FLUX ON THE LEACHING OF IONS BF GRANT FOREST

J. Dowd and T.M. Keith

March 1989

The influence of water flux on the annual mass flux of ions is illustrated in this report. The water flux is calculated by 1) a model using a form of the Richard's Equation and 2) assuming uniform annual water movement below 20 cm. The latter method has been used by several IFS sites in their preliminary analyses.

WATER FLUX

The Richard's Equation calculation of water movement was performed using the one-dimensional model WATFLO, a component of LEACHM (Wagenet and Hutson, 1987). The model is a finite difference approximation of the equation:

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z} \left(K(\theta) \frac{\partial h}{\partial z} \right) - U(z,t)$$

where:

θ is the volumetric moisture content

h is the hydraulic head

$K(\theta)$ is the unsaturated hydraulic conductivity

z is the depth

$U(z,t)$ is a sink term representing transpiration

The domain of the model is from the top of the mineral soil to a depth of 120 cm. The annual transpiration distribution was based upon a Thornthwaite calculation, adjusted downward to agree with regional watershed estimates of actual evapotranspiration and to remove the canopy evaporation component. Canopy evaporation was estimated to be up to 2 mm per day. This value, selected as the best fit of observed versus modeled soil moisture and soil suction, is the curve labeled forest floor in Figure 1. Cumulative daily estimates of precipitation and model estimated water flux at 20, 80, and 120 cm are also plotted in Figure 1. These curves graphically illustrate that the water flux at 80 and 120 cm is approximately half the flux at 20 cm. This difference is due to transpiration.

The root distribution chosen for the simulation assumed that 55 percent of the roots were located between zero and 20 cm in the A and A/B horizons, and that 45 percent of the roots were located between 20 and 60 cm in the B_t horizon. Several other root distribution were simulated with no substantive differences in water flux.

The annual flux pools are very similar to the results obtained using the model PROSPER.

SELECTED ION FLUXES

Ion fluxes were calculated using the WATFLO water flux estimates of 42.7 cm at 20 cm depth, 22.1 cm at 80 cm depth, and 21.3 cm at 120 cm depth (labeled *model* in Figures 2 through 6). For comparison, ion flux estimates using a constant of 42.7 cm were calculated (labeled *constant*). In all cases, because of the higher water flux at depth with the constant flux assumption, the *constant* mass flux is greater than the *model* mass flux. For Calcium (Figure 2), the trends are similar, if less pronounced in the *constant* flux. Similarly with chloride (Figure 3), the reduction of mass flux in the B_t by *constant* is less pronounced than by *model*. Again, the trends are similar, with the *constant* method predicting a greater mass flux than the *model* method at depth.

Figure 4 illustrates the estimated sulfate flux. The trends are clearly similar, and the water prediction method has little affect on the results. Total nitrogen flux (Figure 5) and

nitrate flux (Figure 6) illustrate the problem that one can encounter using the *constant* water flux estimate. In both Figure 5 and Figure 6 the mass flux at the bottom of the B_t is greater than the input to the B_t by the *constant* method. In contrast, the *model* method yields a decrease in mass flux in both cases.

DISCUSSION

These results illustrate potential difficulties encountered in interpretation of the mass flux results. IFS sites that assume constant flux may show flux trends considerably different from those of the BF Grant Forest. If the chemical concentrations with depth are nearly uniform, the assumption of constant water flux with depth can reverse the depth trend, indicating a leaching of ions in the soil that may not be occurring. When the concentration with depth declines, the general depth trend based upon *constant* flux will agree with the more realistic *model* results, but will be less pronounced in the trend. This difference will be greatest where transpiration is high, such as in the southeastern US.

LITERATURE CITED

Wagenet, R.J. and J.L. Hutson. 1987. *LEACHM: leaching estimation and chemistry model. A process model of water and solute movement, transformation, plant uptake and chemical reactions in the unsaturated zone.* Water Resources Institute, Cornell University, Ithaca, NY 14853. 80pp.

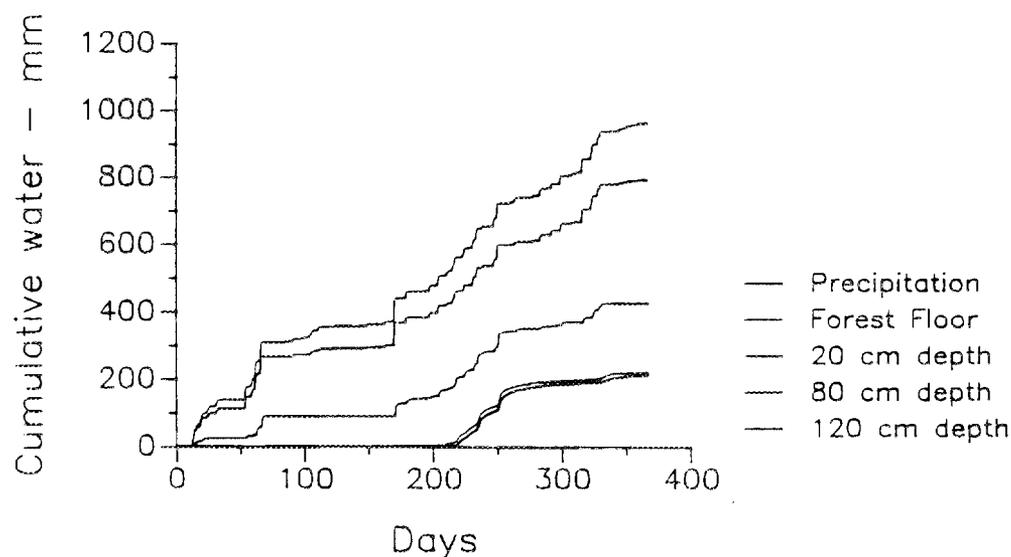


Figure 1. Selected cumulative water volumes.

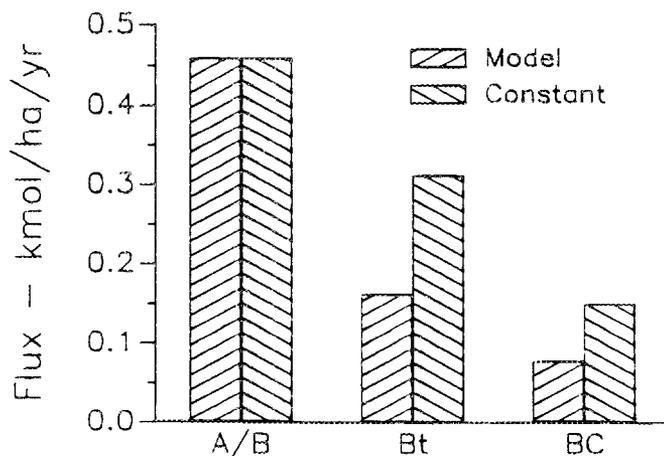


Figure 2. Calcium flux.

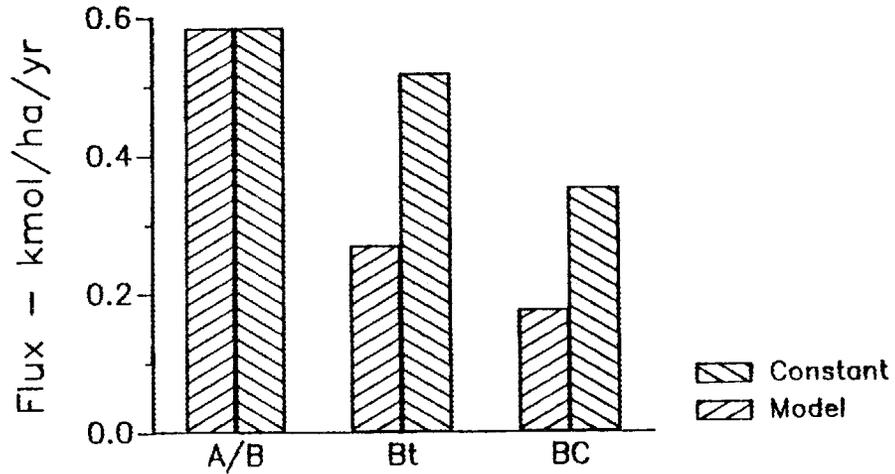


Figure 3. Chloride flux.

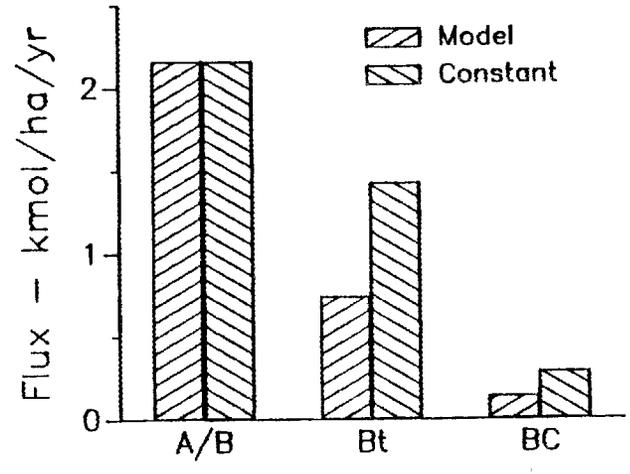


Figure 4. Sulfate flux.

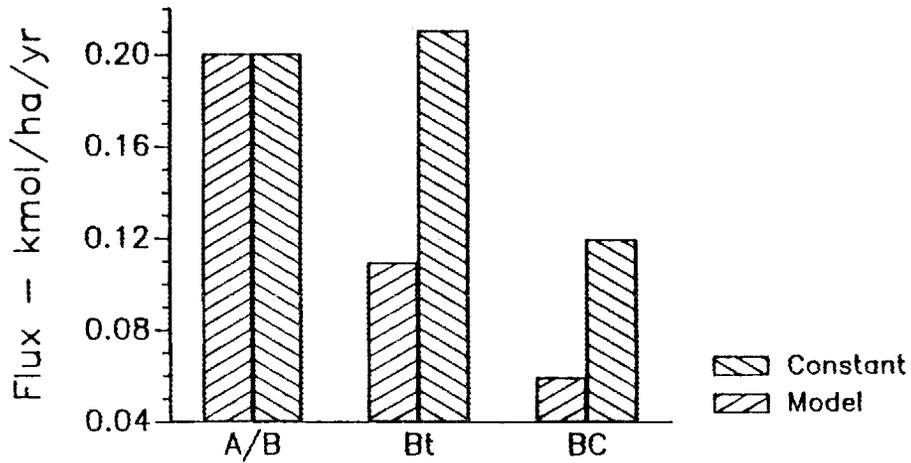


Figure 5. Total nitrogen flux.

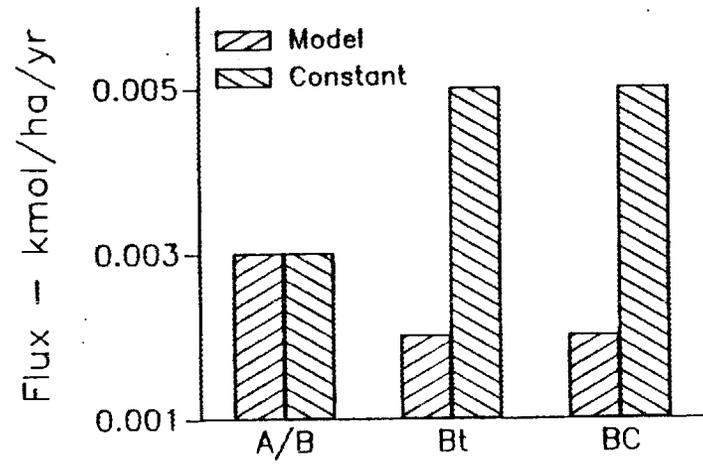


Figure 6. Nitrate flux.

Integrated Forest Study on Effects
of Atmospheric Deposition

1988 Annual Report

6.5

Duke Forest Loblolly Pine (DL) Site

Investigators:

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Assistants:

Paul Conklin, Terry Schneider, Ute Valentine, Dave Valentine

Summary

The Duke Forest Loblolly Pine (DL) Site has now been operating all of its field data collection tasks since September 1, 1986. Thus as of December 31, 1988 we had accumulated twenty-eight (28) months of data. In conjunction with investigators from the other sites we have initiated some preliminary cross-site comparison in both the atmospheric deposition and soil nutrient cycling areas. Ken Knoerr and Dan Binkley are serving as the H⁺ ion task coordinators. In addition to serving as initial steps in synthesis, these cross-site comparisons have helped us to evaluate the reasonableness and quality of our field data. As a result of this we have identified concentrations for several of the ions that appear too high for some of our field samples. Thus we have been re-evaluating this section of our data.

Because of our moderate climate we are able to maintain regular field data collection for both the atmospheric deposition and soil nutrient cycling tasks on a regular basis. For deposition event tasks we strive to set up for every wet and dry event. For the wet events, our success ratio has been quite high. Between 80 and 90 percent of these events have been collected. For the dry events, our success ratio has been lower. Between 40 and 50 percent of these events have been sampled. The greatest difficulty in the dry deposition event sampling is getting a good forecast of the end of the event (i.e. the start of precipitation) during the winter season. As currently designed, the protective covers for the coarse particle deposition plates do not respond rapidly enough to protect them from precipitation.

A brief summary of our measurements of ozone concentrations above and beneath the forest canopy and our evaluation of throughfall variability at this site follows.

Ozone Gradient Sampling at the Duke Forest Site

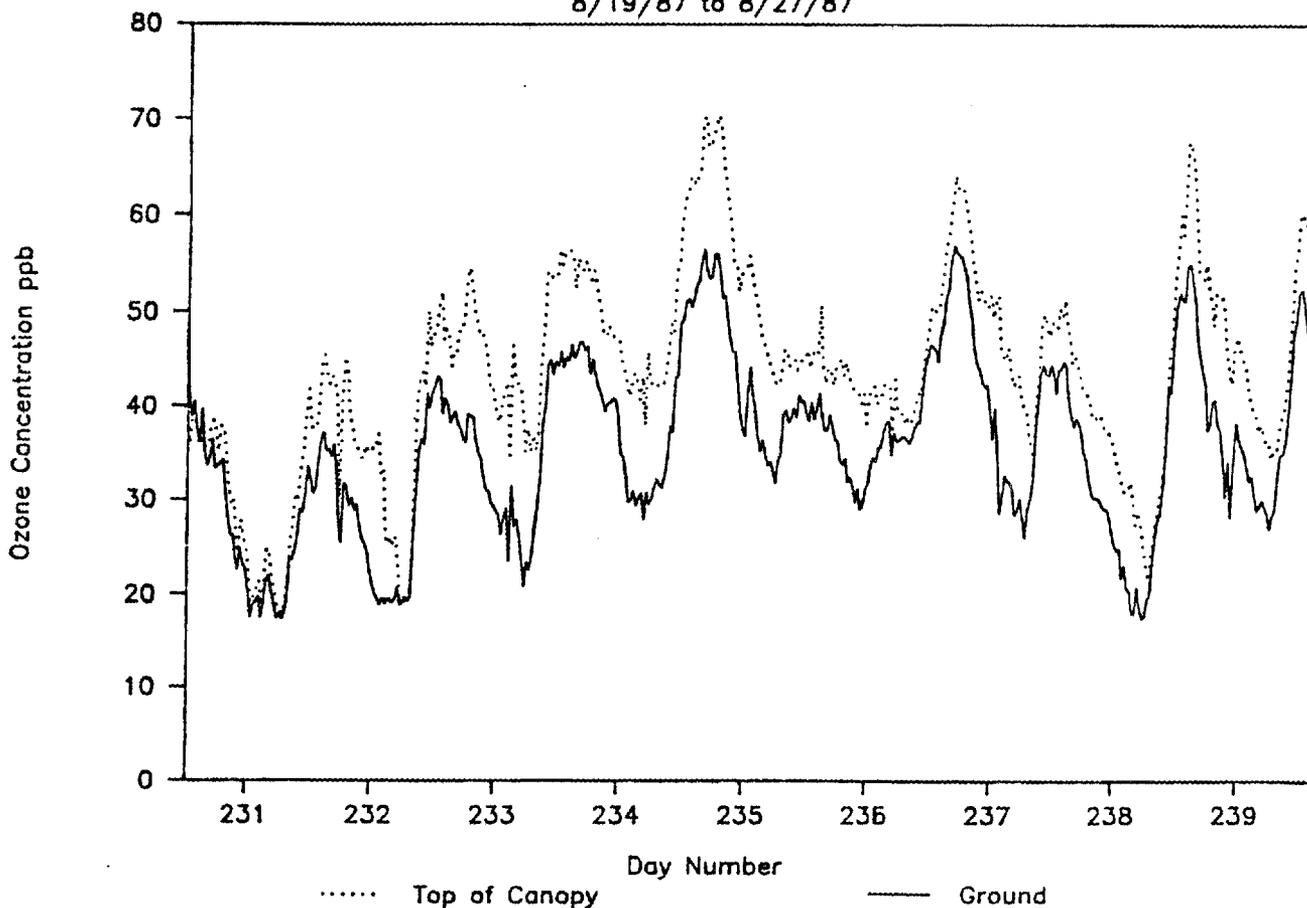
During the fall of 1987 we made two point measurements of the ozone gradient within the forest canopy at the Duke Site. We used two equal length sample lines and a high volume pump to draw samples from our instrument tower to the work shed. A pair of solenoid valves allowed alternating samples from the two lines to be fed into a single ozone monitor.

After sampling with the two lines side by side to ensure that line losses were similar, we measured two different two point gradients. First we sampled with one line two meters above the top of the canopy and the other 1.5 meters above the ground. Then we moved the ground line up to the bottom of the canopy, about 18 meters above the ground and 9 meters below the top line.

Our results show a small but measurable decrease in ozone through this loblolly canopy. The ozone concentration above the canopy averaged 38 ppb for the entire measurement period. The concentration decreased by 6% from the top of the canopy to the bottom of the canopy and by 15% from the top of the canopy to the ground.

Ozone Profile

8/19/87 to 8/27/87



Throughfall Variability

Throughfall measurements from five (5) replicate collectors have been made for over two (2) years (9/86 through 11/88) at this site. The following table summarizes the variations in the volume weighted mean concentrations for the various ions over this period. The relative standard error of these means ranges from 2 to 13 percent. Thus on the average we believe that the estimates of the throughfall fluxes at our site are within about 10 percent.

Throughfall Variability for Duke Loblolly Site
Shown by variation in the Volume weighted mean concentration
for 5 replicate collectors, for the period 9/86 through 11/88

Collector	Concentrations in ueq/l									
	SO4=	NO3-	Cl-	PO4≡	H+	NH4+	K+	Na+	Ca++	Mg++
1	94	58	67	0	123	26	34	26	49	16
2	71	38	46	0	92	23	25	25	45	12
3	62	29	62	0	95	24	18	20	35	9
4	89	47	63	0	100	23	27	24	47	17
5	72	32	40	0	74	23	17	18	33	8
Arithmetic Mean	78	41	56	0	97	24	24	23	42	12
Standard Error	5	5	5	0	7	0	3	1	3	2
Relative Standard Error	7%	12%	9%	0%	7%	2%	12%	6%	7%	13%

6.6

INTEGRATED FOREST STUDY SUMMARY

N. Foster
Canadian Forest Service
Turkey Lakes Watershed

Introduction

This report summarizes the results of IFS research carried out by Forestry Canada at the Great Lakes Forestry Centre during 1988. A summary of nutrient leaching at TLW is included.

Spreadsheets relating to the nutrient content of vegetation and soil at TLW and three years data on solution nutrient concentrations and fluxes have been prepared by Neil Foster, Ian Morrison and Paul Hazlett and distributed to study site and task leaders. Analyses relating to mineralization of nitrogen in soil were completed and the results are being summarized by Paul Hazlett.

In 1988 Diane Keller of Colgate U. visited TLW in August to collect additional samples for mineral weathering studies. TLW hydrologic data, including stream parameters are being summarized by John Nicolson for W. Swank for input into the PROSPER hydrologic model. Additional soil samples were supplied to J. Fitzgerald for sulphur experimental task studies.

A report entitled "Changes in cation leaching from a tolerant hardwood soil in response to acidic deposition and nitrogen mobilization in soil" was prepared and submitted to Water, Air, Soil Pollution.

Nutrient Leaching from Deciduous Vegetation and Podzolic Soils at TLW

Year-to-year changes in mean annual ion concentrations and ion fluxes in precipitation induced by contact with a maple-birch forest and soil were determined for 1981 to 1985 at the Turkey Lakes Watershed (Lat. 47°03'N, Long. 84°15'W).

Changes in Ion Concentrations within the Ecosystem

Solutions collected below the canopy and within the tree rooting zone were generally enriched in ions in relation to precipitation (Table 1). The exceptions were H^+ at all levels, NH_4^+ in throughfall, stemflow and mineral soil solution, and NO_3^- in stemflow. The increases in total concentration of anions and cations below canopy and a decrease in H^+ concentration were consistent with results from events (Cronan and Reiners 1983)¹ and 5- to 7-month examinations of tolerant hardwood forest in other areas (Eaton et al. 1973², Mollitor and Raynal 1982³).

¹Oecologia 59:216-223.

²J. Ecol. 61:495-508.

³Soil Sci. Soc. Am. J. 46:137-141.

The enrichment/depletion patterns at TLW were generally consistent from year to year, although the magnitude of the ratios varied. The highest cation ratios were K^+ in stemflow, forest floor percolate and throughfall, and Ca^{2+} and Mg^{2+} in mineral soil solution,. The anion with the highest ratio in throughfall and stemflow was HCO_3^- , and in forest floor and mineral soil solution it was NO_3^- .

Changes in Ion Fluxes within the Ecosystem

Acid deposition, by increasing the content of SO_4^{2-} and NO_3^- in soil solution, increased the potential for cation leaching from the soil of basin 31. This is particularly true for SO_4^{2-} , even though we have found indirect evidence suggesting that S transformations in soil are contributing SO_4^{2-} to mineral soil solution and water percolating from the mineral soil (Table 2). Nitrogen transformations in soil, on the other hand, added inorganic N, particularly NO_3^- , to soil solution. Even if all NH_4^+ -N in precipitation is assumed to nitrify, atmospheric inputs of inorganic N were equivalent to only 50% of the output of NO_3^- -N from the rooting zone (Table 2). The additional output must be derived from soil organic N resources in the forest floor and surface mineral horizons. Potential N mineralization in the upper soil profile of the TLW soil may approach $14 \text{ kmol ha}^{-1}\text{yr}^{-1}$, under soil moisture and temperature conditions that are optimum for microbial activity (Foster et al. 1986⁴). Only N that is in excess of the needs of the vegetation, along with any N produced during the dormant season, is likely to accumulate in soil, nitrify, and contribute to cation leaching. Atmospheric NO_3^- , therefore, largely augments that which is produced naturally in the TLW soil.

Acid deposition in the TLW watershed was partially neutralized by ion exchange in the deciduous forest canopy and mineral soil. We estimate that only 25% of the H^+ that enters basin 31 leaches through the vegetation and soil to ground and surface waters (Table 2). The actual passage of precipitation H^+ is probably even less because H^+ produced within the soil undoubtedly accounts for some of the H^+ leached. Water percolating through the forest floor gained H^+ (Table 2), possibly from organic acid production, nitrification or an excess uptake of cations by the vegetation. The dominant cation leached from the soil was Ca^{2+} , accounting for approximately half of the positive charge in the leaching solution. Sulfate was an important counter-ion for K^+ leached from the vegetation. Acid deposition had a minor impact on the quality of stemflow and forest floor percolate, which were enriched in K^+ and Ca^{2+} mobilized in association with organic anions. Calcium and Mg^{2+} were leached from the mineral soil in association with SO_4^{2-} and NO_3^- .

⁴Water, Air, Soil Pollut. 31:879-889.

Table 1. Solution flux (mm) and mean annual volume-weighted ion concentrations ($\mu\text{equiv L}^{-1}$) in solution (\pm standard deviation for spatial variation per collection and coefficient of variation in parentheses for year-to-year variability).

	H ⁺	Ca ²⁺	Cations	SO ₄ ²⁻	NO ₃ ⁻	Anions
Precipitation ^a	38±4 (7)	16±2 (27)	86.8 (9)	50±2 (11)	28±2 (18)	85.8 (14)
Throughfall ^a	19±4 (25)	32±6 (12)	129.7 (6)	70±8 (11)	33±7 (22)	130.2 (10)
Stemflow ^b	10±15 (61)	240±336 (9)	719.5 (26)	268±274 (4)	18±16 (61)	452.4 (10)
Forest floor ^a	28±11 (30)	156±52 (10)	313.1 (22)	78±22 (10)	79±47 (29)	156.1 (18)
Mineral soil ^c	20±8 (71)	176±36 (12)	288.7 (2)	106±14 (9)	142±39 (16)	270.0 (7)

^a1981-1985

^b1981-1983

^c1983-1985

Table 2. Mean annual fluxes of ions (kg ha^{-1}) in solution (with range)

	H ⁺	Ca ²⁺	NH ₄ ⁺ -N	SO ₄ ²⁻	NO ₃ ⁻ -N
Precipitation ^a	0.5 0.4-0.5	3.9 2.9-5.1	3.0 2.6-3.4	29.2 26.6-31.9	4.7 4.0-5.7
Throughfall	0.2 0.1-0.3	7.0 5.8-7.7	2.9 2.5-3.3	37.1 32.1-44.4	5.1 4.0-6.5
Stemflow ^b	0.1	0.2 0.2-0.2	0.1	1.0 0.7-1.5	0.1
Forest floor ^a	0.3 0.2-0.4	29.8 24.6-41.1	5.7 2.2-10.5	34.9 28.3-41.5	10.5 5.6-13.1
Mineral soil ^c	0.1 0.1-0.15	2.6 27.3-34.0	0.3 0.2-0.4	37.9 35.1-40.2	17.9 15.5-21.7

^a1981-1985

^b1981-1983

^c1983-1985 (calculated from water balance equation (Thorntwaite and Mather 1957))

6.7

HUNTINGTON FOREST SITE INTEGRATED FOREST STUDY

1989

Personnel:

Dr. Myron J. Mitchell, Dr. Dudley J. Raynal, Dr. Edwin H. White, Dr. James Shepard, Mr. Thomas Scott, Mr. Neal Buelow, Ms. Marianne Burke, Ms. Ann Moore, Mr. James Porter, and Mr. Yi-Min Zhang.

HIGHLIGHTS FOR YEAR:

A net loss (wet + dry deposition minus soil leaching) of Ca^{2+} and Mg^{2+} was observed at the Huntington Forest (3.3 and 0.5 $\text{kg ha}^{-1} \text{y}^{-1}$, respectively) but the amount was small compared with the amounts in the exchangeable pools (600 and 40 kg ha^{-1} , respectively). These small losses are likely to be smaller than the amount added to the site by mineral weathering. The relatively young soil has a greater fraction of heavy minerals than most other IFS sites and thus mineral weathering is potentially a very important source of base cations. Thus, although this site is subjected to acidic deposition, depletion of nutrient cations should not occur unless it is coupled with another source of removal such as that of whole-tree harvesting.

In other areas of the northeastern United States and Southeastern Canada, it has been hypothesized that sugar maple decline may be attributable to accelerated losses of nutrients including calcium and magnesium due to acidic deposition. At the Huntington Forest, sugar maple along with American beech are the dominant species and no indication of decline has been noted and this may be attributed to the adequate availability of these base cations at this site.

The wet input, dry input, and leaching loss of SO_4^{2-} were estimated at 5.7, 2.1, and 9.2 $\text{kg ha}^{-1} \text{y}^{-1}$ at the Huntington Forest, resulting in a net loss of 1.3 $\text{kg ha}^{-1} \text{y}^{-1}$. Some studies have circumvented the difficulty of measuring dry deposition by measuring wet inputs and soil losses in a watershed and calculating dry SO_4^{2-} input assuming that S is entirely conservative, with inputs equal to losses. Such an assumption at the Huntington Forest would result in a dry input of 3.4 $\text{kg ha}^{-1} \text{y}^{-1}$, 1.6 times the dry input we measured. The fluxes of anions

and cations at this site is driven primarily by the movement of SO_4^{2-} both in the canopy and the soil. The inputs of this ion are less than other sites closer to point sources of pollution and this results in less nutrient cation flux in the canopy (Figure 1) and the soil than those sites with higher sulfur loadings.

The study of root dynamics has been emphasized at the Huntington Forest since the below ground portion of northern hardwood ecosystems have been shown to be major loci of nutrient turnover. Fine root (<3 mm) production and turnover were quantified during the past two years. Periodicity of root growth was measured using root observation boxes (rhizotrons). Production and mortality were estimated using the sequential coring method. Decomposition was measured using buried litter bags. Fine root production began in mid-April, peaked in July and August and culminated in October; a total of 5 months of production. Fine root periodicity was governed by soil temperature. Soil moisture was not a factor in this forest which rarely experiences moisture deficits. Fine root production and mortality averaged $1.9 \text{ Mg ha}^{-1} \text{ y}^{-1}$, and thus the fine root pool is at a steady state. Decomposition averaged $1.1 \text{ Mg ha}^{-1} \text{ y}^{-1}$. Fine root mortality was about 40% of the total detrital pool. The contribution of fine roots is within the range found previously for other northern hardwood sites.

In the Huntington Forest site dominant trees are approximately 100 years old. The standing crop of biomass is likely at or near steady state and net primary production appears to be low. Presently we observe small amounts of net nitrate leaching from this ecosystem on an annual basis (Figure 2). However, we have evidence from long term studies of soil solution chemistry and nearby surface waters, that nitrate leaching may be increasing especially during the spring snow melt period. Other IFS sites with younger forests characterized by greater net primary production and thus greater nitrogen requirements have no nitrate leaching whereas older forests with low net production show net nitrate leaching. The Huntington Forest is apparently reaching the stage of nitrogen saturation due to its maturity and elevated levels of nitrogen inputs.

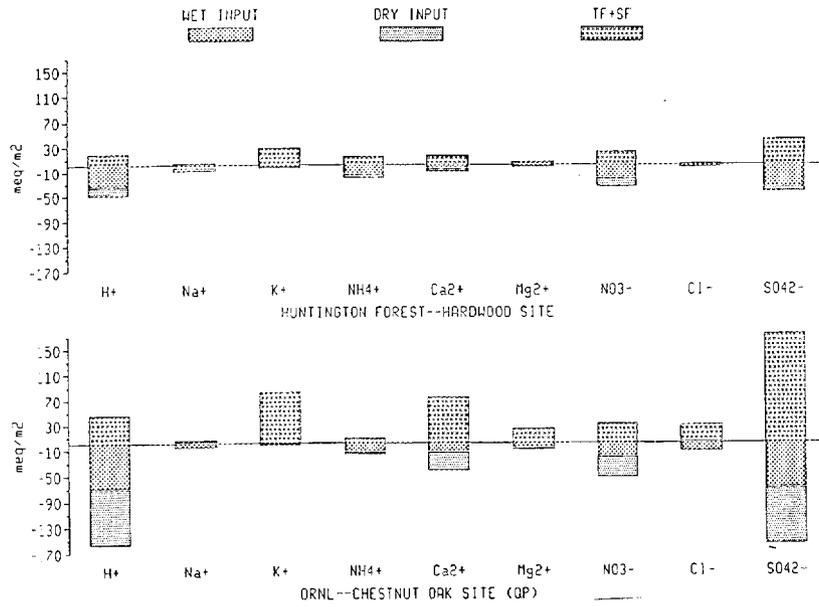


Figure 1. Comparison of inputs between Huntington Forest and Walker Branch, Tennessee (Shepard et al., 1989)¹

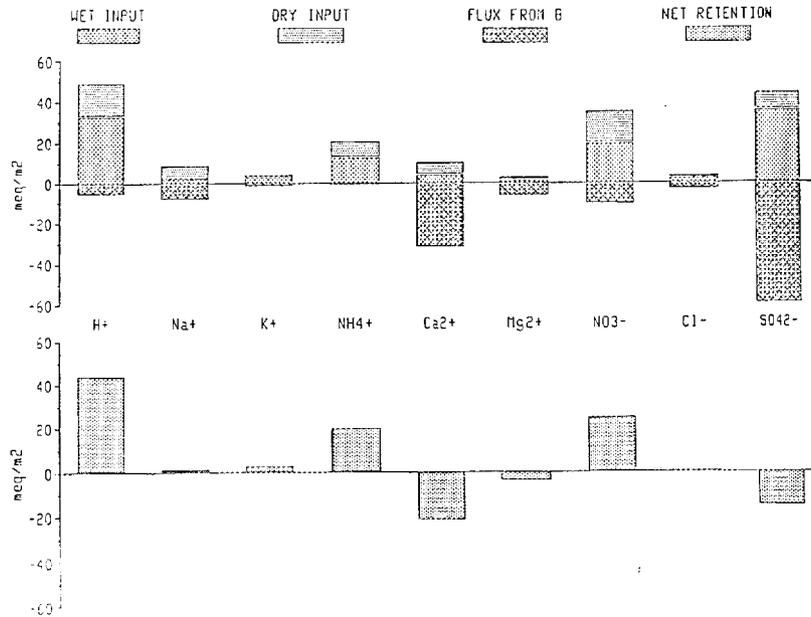


Figure 2. input, outputs, and net retention at Huntington Forest.¹

¹Shepard, J.P., M.J. Mitchell, T.J. Scott, Y.M. Zhang. 1989. Measurements of wet and dry deposition in a northern hardwood forest. Water, Air and Soil Pollution (In Review).

ANNUAL REPORT

THE HOWLAND, MAINE IFS SPRUCE-FIR SITE

Ivan J. Fernandez
Gregory B. Lawrence
S. Michael Goltz

University of Maine
Orono, Maine

OVERVIEW

The study site at Howland, Maine is one of the newest in the EPRI/ORNL IFS program with installation beginning in the 1987 field season. The site is considered a non-funded cooperator. Funding for the nutrient cycling and atmospheric sciences research at the Howland site is from the U.S. Forest Service Forest Response Program where Howland represents the only low elevation, commercial spruce-fir site in the Spruce-Fir Research Cooperative. Meteorological and deposition work at the site is supported through the U.S. Environmental Protection Agency's Mountain Cloud Chemistry Program. The site has been developed as a long-term nutrient cycling study site that will provide information on questions related to the effects of sulfur and nitrogen deposition, as well as concerns regarding forest management and potential climate change. Being a mid-latitude forest located within the regional ecotone between boreal spruce-fir to the north and northern hardwoods to the south, this site offers the potential for being sensitive to shifts in successional patterns and ecosystem function as a result of shifts in climate.

SITE DESCRIPTION

The intensive nutrient cycling study at Howland is located in a low elevation (60 meters), commercial spruce-fir forest owned and operated by International Paper Company. The stand consists of conifers with a minor component of hardwoods as shown in the figure. Balsam fir is losing importance at the site as a result of the natural expression of dominance within these stands, as well as the influence of some spruce budworm infestation during the 1970's. Being on the southern edge of the spruce-fir region there exists a strong presence of hemlock with a few large white pine individuals remaining from the last rotation.

The nutrient cycling studies are concentrated on two 0.2 ha (40 X 50 meter) plots divided into a 1 sq. meter grid system. The Tower site is so named because adjacent to it is a 26 meter tower with various meteorological and deposition instrumentation. Within each study plot there are 20 funnel-type throughfall collectors, 12 stemflow collectors, 20 litterfall collectors, 6 snowmelt collectors, 36 zero-tension lysimeters, and 18 tension lysimeters with a constant 10 kPa tension created with an electric vacuum pump system. At the Tower site there are three wet-only collectors for event sampling of throughfall and open precipitation. All trees on the site are tagged and numbered with mensurational data presented from 1987 measurements. At twelve locations within each site, quantitative soil pits have been excavated by depth

increments. In addition, soils from face pits have been sampled based on morphological features, and all soil samples collected are being chemically analyzed. Sampling of red spruce and balsam fir foliage occurred during 1987, and sampling of all major vegetative components for all species took place during 1988.

Both on the tower at the Tower site, and in an open orchard approximately two kilometers east of the Tower site, there is a complete meteorological package (solar radiation, air temp., RH, barometric pressure, wind speed/direction, precip. depths, and fog occurrence) and air quality monitors (sulfur dioxide, ozone, filter packs, and wet-only collector). At the Tower site there is also one location with continuous soil temperature and water potential monitoring at six depths in the soil. Intermittent energy budget and flux measurements include water, vapor, sensible heat, soil heat flux, net radiation, ozone and sulfur dioxide.

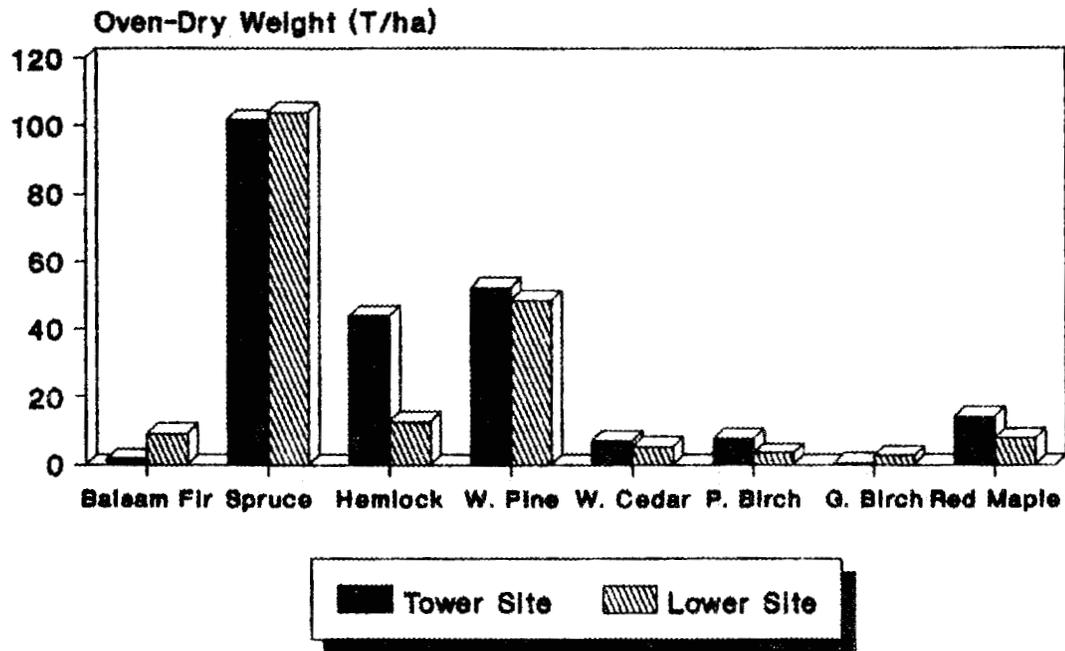
PROGRESS AND FUTURE ACTIVITIES

For the Howland site 1988 represented the first full growing season of data collection for all fluxes in the ecosystem, and quantitative soil pit excavations as well as biomass sampling were completed with chemical analyses of these materials to be carried out during 1989. Monthly foliage samples were collected from red spruce and balsam fir during the 1987 growing season to examine temporal variability of foliar chemistry. Results showed that only N, P, K, and Ca showed distinct temporal patterns. For these four nutrients, Ca showed a continuous increase in concentration for all tissues believed to reflect the accumulation of Ca in maturing vegetative tissues. The pattern for N, P, and K was similar to that of N shown here whereby concentrations rapidly decreased in current year foliage early in the growing season due to dilution and then leveled off. For previous year foliage in both species slight increases in concentration occurred prior to leveling off which was attributed to increased uptake and availability of nutrients in the soil. Comparing the nutrient concentrations in this study to nutritional guidelines for red spruce and balsam fir revealed that both species are below optimum levels or deficient with regards to N and P.

Current vegetation analyses are focused on quantifying biomass nutrient pools and samples of foliage, branches, bark, bolewood, and roots from all species present are being analyzed. Stemflow concentrations were typically greater than throughfall, but stemflow at this site contributes less than one percent of the nutrient and water flux to the forest floor. All solutions will continue to be collected and monitored into the future and data analysis over the next year will concentrate on refining nutrient budget estimates for the site. More intensive work is planned for the Howland site to examine the characteristics of events and their influence on soil solution properties, as well as evaluating the influence of decreased soil moisture on soil solution chemical composition.

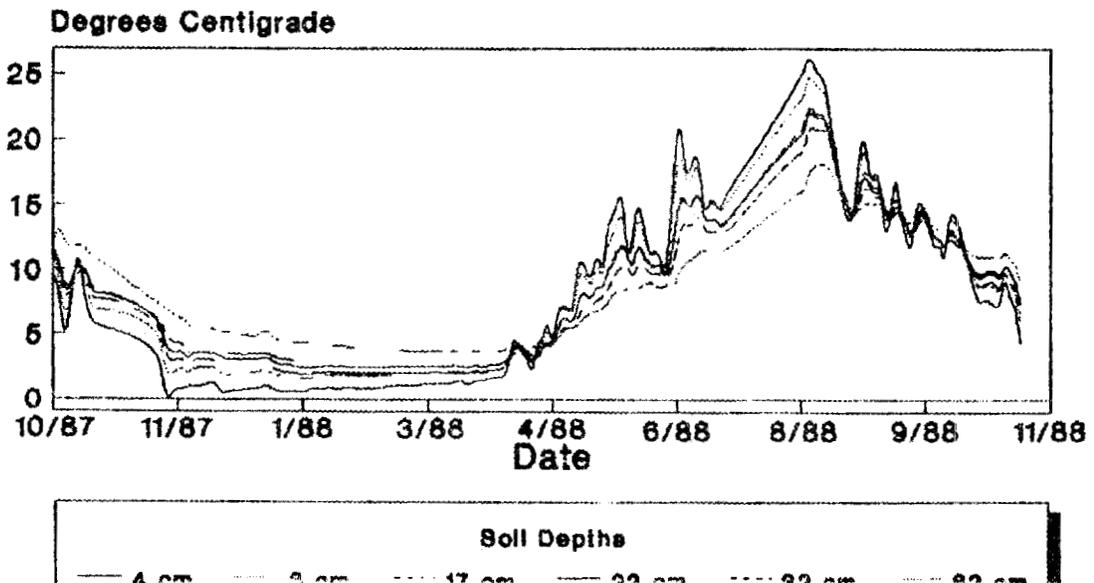
HOWLAND IFS STUDY SITE

Complete Live Tree Biomass

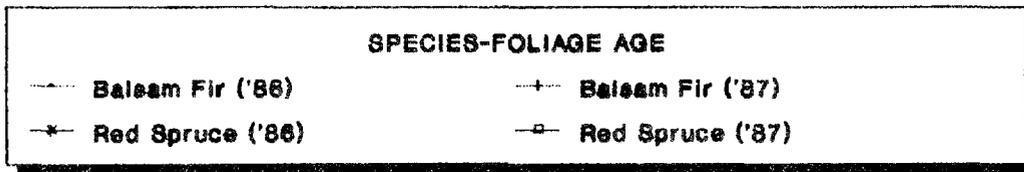
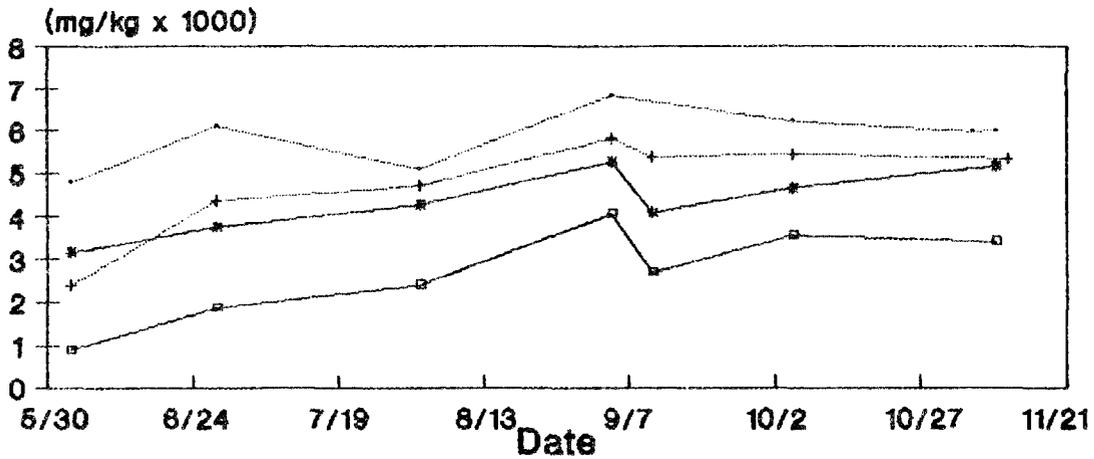


SOIL TEMPERATURES

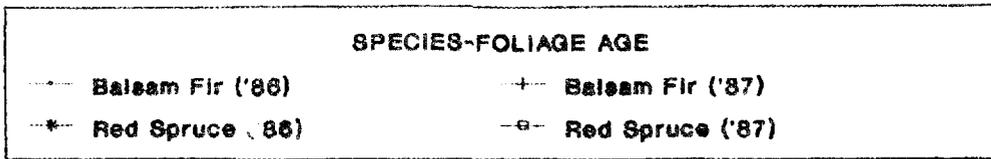
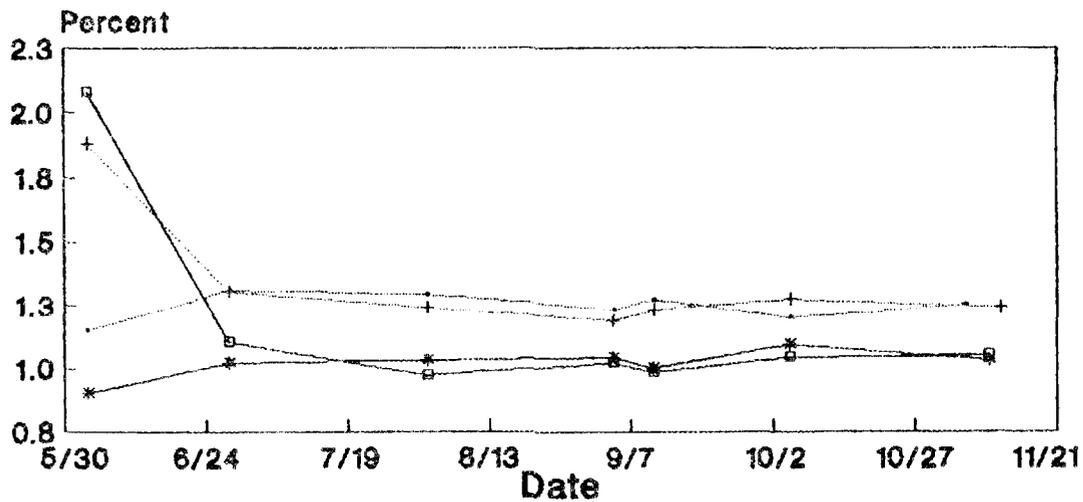
October 1987 - October 1988



1987 Foliar Calcium Variability



1987 Foliar Nitrogen Variability



Integrated Forest Study 6.9
Norway Spruce 1988 Annual Summary

Investigators: Arne O. Stuanes, Ingvald Røsberg, and Magne Huse,
Norwegian Forest Research Institute
Einar Joranger, Norwegian Institute for Air
Research

Nutrient Cycling

During 1988 we have continued routine collection of bulk precipitation, bulk throughfall, and soil solution at all four plots. Stemflow is collected only at two plots. Bulk precipitation and throughfall have been collected at the manipulated plots (A-2) since 1983. A complete sampling program has been carried out at all plots since October 1986. It was difficult to collect samples during the winter 87/88 due to frequent thawing and freezing in the first part and a huge amount of snow in late winter giving a very late snow-free ground. Seasonal and annual fluxes for the period October 1986 to May 1988 have been reported.

The A-2 plots are more dense than the A-4 plots, giving a larger year to year variation. Since 1983 the A-2 plots have shown some years with less SO_4^{2-} throughfall flux than bulk precipitation flux. This holds for the period May to December which is usually free of permanent snow. There is a large amount of lichens in the stands, about 1500 kg per ha in the trees of the A-2 plots. Uptake and buffering by the lichens may explain some of the differences.

Al-speciation was carried out on all the soil solutions in the period April '87 to May '88. As shown in Fig. 1, the total Al (total reactive Al, acid digested) varies seasonally for the O and E horizon, but not for the Bs and BC horizons. The Al concentration leaving the BC horizon is low.

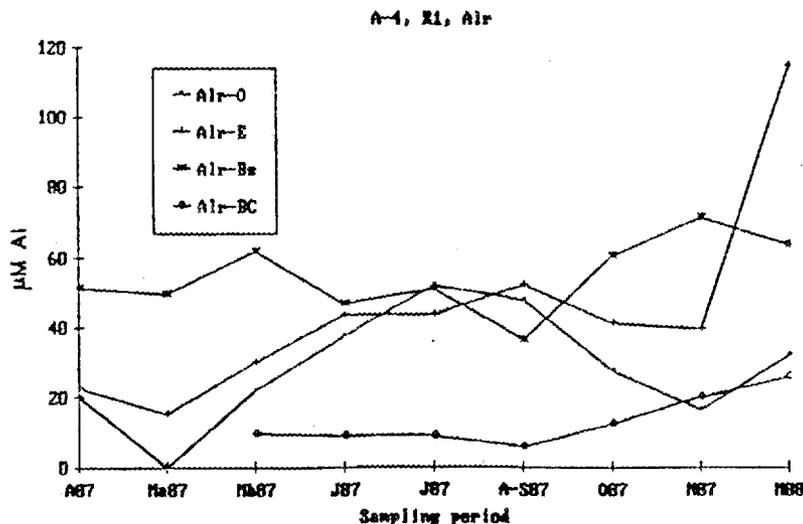


Figure 1. Concentration of total Al in soil solution leaving different soil horizons in the A-4, R1 plot.

Almost all Al is organically complexed (non-labile monomeric Al) in the O and E horizons (Fig. 2), while only a small fraction is in an organic form in the Bs and BC horizons. This is in accordance with the podzolization theory and indicates that most of the Al in the main rooting zone is in a nontoxic organic form. Some of the Al-fractions are sensitive to the moisture condition in the soil. The highest suction that was measured in the soil during the period was -70 kPa.

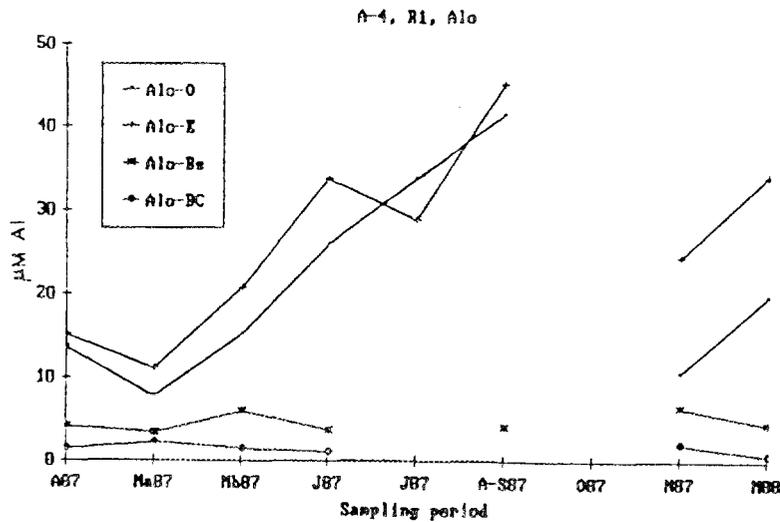


Figure 2. Concentration of organically complexed Al in soil solution leaving different soil horizons in the A-4, R1 plot.

Atmospheric Deposition

The standard meteorologic and gas measurements have been done since April 1986. Wet-only collectors and plates for coarse particles have been in place since June 1987. Only concentrations have been reported for the period May 86 to April 87 and also seasonal and annual fluxes have been reported for the period May 87 to April 88.

We have put a lot of effort into producing values for the coarse particle deposition. This summer and fall we had some very good events. These measurements have indicated that the coarse particles make a great contribution to the total dry deposition. However, we need measurements over a longer period before we make that conclusion.

Bulk and wet-only throughfall for the growing season are very similar, but differ for the dormant season due to too few samples of wet-only throughfall. The wet-only samplers do not work within the forest during snow conditions. The wet-only throughfall flux of NO_3^- is much less than the bulk throughfall flux. We have only two wet-only collectors for throughfall, but they are supplemented by 10 manually operated "wet-only" collectors. Increasing the number of collectors does not change the difference. One possibility is that the 10 "wet-only" collectors are placed in a denser part of the stand than the 20 bulk collectors, but we do not think that this can explain the difference. Neither can the large amounts of lichens explain it since it should influence the wet-only and bulk throughfall in the same way. We have to look further into this.

Annual/Status Report for the Florida Slash Pine IFS Site.

Submitted by: H.L. Gholz, Dept. of Forestry, Peter Nkedi-Kizza, Dept. of Soil Science, and Dr. Eric Allen, Dept. of Environ. Eng. Sci., Univ. of Florida, Gainesville, FL 32611, 904-392-4851, BITNET HLG @ UFFSC

DEPOSITION

Sampling for wetfall (deposition, throughfall and stemflow) was begun slightly later than originally planned on May 2, 1988. Since that time we have monitored over 95% of the wetfall volume. Data for the "growing season" (May 2 - Oct. 31, 1988) have been summarized.

Petri plates at the top of the tower for coarse particle collection were first exposed on 20 April, 1988 and collection has proceeded covering the main dry periods since that time. Filter packs for obtaining air concentration data for fine particles, aerosols and gasses were installed on Sept. 20, 1988. Standard meteorological data have been collected since mid-1986 on this site, but measurements of the standard deviation of the mean hourly wind direction sufficiently accurate to drive the Hicks deposition velocity model have only been collected since Feb. 1989. The use of alternative estimation techniques for Vd's (including the use of literature values) and the potential errors involved in using somewhat cruder wind direction data available since July 1988, will be explored once we have a longer record of filter pack analyses and appropriate wind direction data. Based on a few weeks of calculated Vd's, values for slash pine as predicted by the model are about half those of Lorenz and Murphy (1985) as obtained for a loblolly pine plantation in South Carolina using a concentration gradient/ resistance modeling approach. We will also determine the relative sensitivity of the estimated Vd's to seasonal LAI and stomatal conductance data now available for this site, as well as to the wind direction variable. Unfortunately, analyses for ions other than SO₄, NO₃, Cl and HPO₄ from the Teflon filters were begun only for samples collected since October 1988.

In summary, we will put together a June 1988 - May 1989 data set for deposition for the EPRI synthesis volume, available in July. The dryfall portion will, however, be based on a number of assumptions of currently unknown impact. For example, if filter pack analyses indicate that there is little seasonality to the concentration data, we could extrapolate using averages for the periods we have data for. But if the deposition model is very sensitive to the wind direction term, we still may not be able to use our earlier meteorological data.

NUTRIENT CYCLING

A. Vegetation.

An analysis of the variation in stem and canopy biomass and LAI from 1986 - 1988 has recently been completed, based on the destructive analysis of 140 trees on a related study. Nutrient analyses of all the tissues from these trees will be completed in April (canopies were subsampled by vertical strata). Litterfall has been collected since mid-1986 and nutrient analysis is completed.

Preliminary analysis of particulate dryfall and subsequent crown wash versus canopy leaching via the "throughfall regression model" is completed, and indicates little dry deposition and little canopy leaching (net canopy effect).

We anticipate constructing a complete nutrient budget for the tree strata by the end of May, which would include an analysis of spatial variation over the 60 ha study site, as well as an analysis of three year's fluctuations in both nutrition and biomass distribution.

Forest floor sampling was conducted in December 1988, with 8 samples each from 17 plots collected and separated into pine needles, understory foliage, wood plus bark, and other, by layer. Understory surveys of the 17 plots were completed in the Fall 1988, and data will be applied to existing biomass regression equations to estimate understory biomass distribution. Statistical and chemical analyses of both of these sample and data sets are underway.

Although not a direct part of the IFS research, estimates of fine and coarse root biomass, production and respiration for similar stands were made under a previous project (previously published) and were synthesized into a simulation model of belowground dynamics in a recently accepted paper (Ewel and Gholz 1989). More recent versions of this model are being applied to the current site to estimate the magnitude of root processes. Surface (0 - 20cm depth) fine roots were sampled in December of 1986 and 87 to help calibrate the model for this new stand, and extensive

sampling of root respiration, soil CO₂ evolution, and root carbohydrate storage are being conducted to help test its applicability and predictions. Also, bimonthly samples of all tree tissues (above- and below-ground) are being analyzed for nutrient concentrations.

B. Soil

Solutions leaching through the forest floor into 10 tension-free lysimeters in an intensive sampling site adjacent to the IFS tower plot have been collected on an event basis (n = 22) since May 1988 and have been analyzed for anions, pH and volume. 36 tensiometers were installed in the fall 1988, and have been manually monitored since January 1989. They were fitted with pressure transducers and computerized in mid-February 1989; since then water potentials have been read and logged every 15 minutes. There are four tensiometer "stations" on this plot, with 10 sensors from 5 to 130 cm depth (matching horizon changes) at each. A fifth station is being considered for a tracer study.

Soil solution samplers were installed in May 1988, with an automated vacuum pump and collection system. Routine sampling was begun in association with the tensiometer monitoring. Concentrations of dissolved ions are very low. If they stay relatively constant over time, it may allow us to extrapolate with some confidence from measurements through May back to the unmeasured time period from May through December 1988 for purposes of the EPRI synthesis.

Analysis of soil variation over the 60 ha study site was completed last year and assembled into a recent paper (Gaston et al. 1989). Sampling in the vicinity of the IFS tower and intensive soil plots was more intensive, and samples from the various horizons from these locations were composited to produce the "modal" profile samples distributed to the IFS/ ORNL "Task Leaders" for various analyses. We received data at the annual meeting for bulk soil characterization and sulfate absorption and total S; according to Bob Newton, mineral weathering is near zero (100% quartz in the sand fraction). 28 soil core samples were submitted for analysis to a Univ. of Florida lab for hydraulic conductivity and moisture release curves.

C. Modeling

A key variable for making estimates of soil water and ion fluxes is, of course, transpiration. This is especially critical at the Florida site, as it is dominated by highly layered, coarse soils and a fluctuating water table. We are proceeding with a detailed model of the fluxes through each of the soil horizons, including effects of root distributions and the fluctuations in the water table. The full development of this model and its validation will take at least the rest of 1989. In the meantime, we are using several approaches to estimate the total amount of water transpired from the soil over short periods (matching our rainfall event intervals). For example, we have recently produced an empirical transpiration model based on meteorological parameters only which can account for over 80% of the variation observed in canopy/small chamber measurements of transpiration (obtained on a related NSF project). This model is being used with the monthly leaf area index changes, measured incoming PAR and light absorption by the canopies, precipitation, interception and VPD to estimate whole-canopy transpiration on an hourly basis. Although powerful, more process-oriented models are also under development on this project, as well as some alternative indirect models (e.g., based on Priestly-Taylor type estimation of PET).

CONCLUSIONS

A full July 1988 - June 1989 report should be available in July with: (1) actual volume and chemistry data for wet deposition, throughfall, stemflow on a rainfall event, growing season and annual basis, (2) extrapolated data for dry deposition on an event, growing season and annual basis, (3) actual data for vegetation (tree and understory) and forest floor standing crops and nutrient pools, canopy leaching (event, seasonal and annual basis), and annual net aboveground nutrient uptake over a three year period (it will be possible to estimate seasonal values as well for some years), (4) soil water flux (model estimates) on an hourly, daily and longer basis, and (5) extrapolated leaching of ions from the soil within and beyond the root zone on a seasonal and annual basis.

References

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Gaston, L., P. Nkedi-Kizza, G. Sawka and P.S.C. Rao. Spatial variability of morphological properties at a Florida flatwoods site. SSSAJ (in press).

1989 Integrated Forest Study Site Report
WHITEFACE MOUNTAIN, NEW YORK
 Atmospheric Deposition and Nutrient Cycling

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Erik K. Miller and Arthur H. Johnson, University of Pennsylvania

Jeanne A. Panek and John A. Kadlecck, ASRC, SUNY-Albany

This summary describes results from ecosystem monitoring at approximately 1000-m elevation on Whiteface Mountain, New York during the period 1 June 1986 through 31 May 1988.

Inputs

Atmospheric inputs during this study were lower than expected based on other high-elevation studies in the northeastern United States (Table 1). Gross water input was lower by 50% or more than other reports for high-elevation forests (Table 1). Ion deposition rates were more comparable with Hubbard Brook than Mt. Moosilauke or Camels Hump. We feel this difference is in part due to micro-site variations particular to our study site and in part due to overestimations of deposition amounts by previous investigators.

Table 1. Comparison of annual water and ion deposition estimates for the northeastern U.S.

Location	Moosilauke NH	Green Mts. VT	Whiteface NY	Hubbard Brook NH
Elevation	1220 m	1110 m	1025 m	700 m
Annual Water Deposition	264 cm	380 cm	131 cm	132 cm
Ion Deposition	-----($\text{kg ha}^{-1} \text{ yr}^{-1}$)-----			
H ⁺	3.90	3.89	1.27	0.98
NH ₄ -N	16.0	nm	6.34	2.3
Na ⁺	7.5	nm	0.76	1.59
K ⁺	5.4	nm	1.39	0.89
SO ₄ -S	56.8	85.8	17.6	12.8
NO ₃ -N	28.2	37.5	15.9	4.5

Data from Mt. Moosilauke, Lovett et al. (1982); Green Mountains, Sherbatskoy and Bliss (1984); Hubbard Brook, Likens and et al. (1977). nm = not measured.

Estimating Cloud Water Deposition

Several independent methods for estimating cloud water deposition to the IFS site at Whiteface Mountain, NY indicate a range of possible values for the average deposition velocity. There is general agreement between the deposition velocities estimated by growing season water balance (0.025 cm/hr), canopy balance for sulfate (0.0185 cm/hr) and an adaptation of the Lovett Model for a two component canopy on a steep slope (0.242 cm/hr). Our best estimate of cloud water deposition to the IFS site on Whiteface, approximately 16 cm per year, is much lower than published estimates for only slightly higher elevation stands in the northeastern US (Lovett et al., 1982). This is consistent with a strong elevational gradient for immersion times determined for the IFS stands (6-20% of the year) and the summit of Whiteface (50%, R.MacDonald, ASRC unpublished data).

Cloud water provides 13% of water input to the forest and up to 40-60% of H, NO₃ SO₄ and NH₄ deposition (Table 1). This deposition pathway is responsible for 47% of the total anion loading of the ecosystem. For approximately 10% of the year the forest canopy is exposed to cloud water solutions of pH 3.8 as compared to the average rainfall solution pH of 4.2. The additional exposure to acidity this forest receives during cloud immersion may contribute to increased foliar leaching and reduced winter hardiness in red spruce .

Spatial Variability of Throughfall Flux

Accurate measurement of throughfall water and ion flux is critical to the IFS because throughfall fluxes are used to validate and calibrate both dry and cloud water deposition models. The characterization of net canopy effects (NCE) for nitrogen species and nutrient cations is a primary goal of the project. Throughfall water flux is the fundamental measurement driving soil-solution flux estimates at all sites regardless of the way leaching is modeled.

We investigated spatial variability in throughfall water and ion fluxes in the fir-spruce-birch forest at Whiteface Mountain, NY to obtain a better understanding of the accuracy of those measurements. Event throughfall was sampled from a large number of collectors in a dense sampling grid (25 collectors spaced 5 meters apart in a 0.09 ha plot) to quantify the performance of fewer collectors in low density sampling plots used in routine throughfall monitoring (5 collectors in 0.09 ha). Most IFS sites have used a small number of samplers (2 to 5) for their long term sampling program. The collectors used were standard NADP polyethylene buckets with 658 cm² collection area.

In the mixed conifer-hardwood forest at Whiteface, ion concentrations were often more variable than water deposition (Table 2). Variability in ion deposition is increasingly controlled by the variation in water deposition as precipitation volumes increase. The great variation in ion concentration and water deposition present in events with volumes just a few multiples of the canopy storage capacity makes accurate determination of through-canopy ion fluxes impractical for these events.

Table 2. Coefficients of Variation in Throughfall Water Amount and Ion Concentration for Events Sampled in 1985

Event #	DEP (cm)	Water	H	Na	NH4	K	Cl	NO3	SO4	
<----- Coefficient of Variation ----->										
2	3.08	0.14	0.33	0.73	0.62	0.78	0.81	0.36	0.43	
3	0.50	0.34	0.27	0.41	0.66	0.46	0.55	0.38	0.38	
4	0.94	0.21	0.40	1.70	0.76	0.72	0.81	0.40	0.55	
6	3.01	0.40	0.26	0.61	0.27	0.67	0.58	0.36	0.33	
7	1.48	0.18	0.69	0.67	0.85	0.57	0.67	0.75	0.75	
8	0.73	0.23	0.36	----- no analysis -----						
9	0.94	0.41	0.31	0.38	0.73	0.52	0.34	0.31	0.22	

We have found that for 11 out of 17 events sampled, the probability of 5 randomly located collectors having a mean within 20% of the high-density sampling grid mean was greater than 90% (data not shown). The 6 events showing the greatest variability tended to be low water deposition events (< 1cm), less than a few multiples of the canopy storage capacity. When depositions to individual collectors are summed over the course of 8 or 9 events with a total deposition representative of a month of continuous sampling, variability is greatly reduced. Five samplers had a 98% probability of predicting the high-density grid mean to within 10.2% in 1985 and 6.5% in 1987. Three randomly located collectors had only 90% probability of predicting the high-density grid mean to within 19.8% in 1985 and 6.13% in 1987.

To summarize, five collectors performed at least twice as well as three collectors for quantifying seasonal water and major ion fluxes. Five collectors did not adequately characterize extremely low water deposition events and would not be adequate for assessing NCE or cloud water contributions. However, when events are summed to monthly or seasonal values the variability inherent in low volume events is overshadowed by the more uniform behavior of the canopy in large volume events. For two growing seasons five collectors had a 90% probability of yielding a seasonal mean deposition within 10% of the high density mean. We have demonstrated the confidence we have in the adequacy of our five permanent collectors to accurately estimate throughfall fluxes to the nutrient cycling study plots at Whiteface.

Soil Solution Chemistry

In general, solution chemistry is hydrogen and sulfate ion dominated. Ammonium, nitrate and base cation concentrations are fairly low in precipitation and throughfall but increase in the forest floor and mineral soil horizons. Calcium becomes an increasingly large component of solution chemistry in the forest floor and mineral soil.

Ion Concentrations on Whiteface Mountain

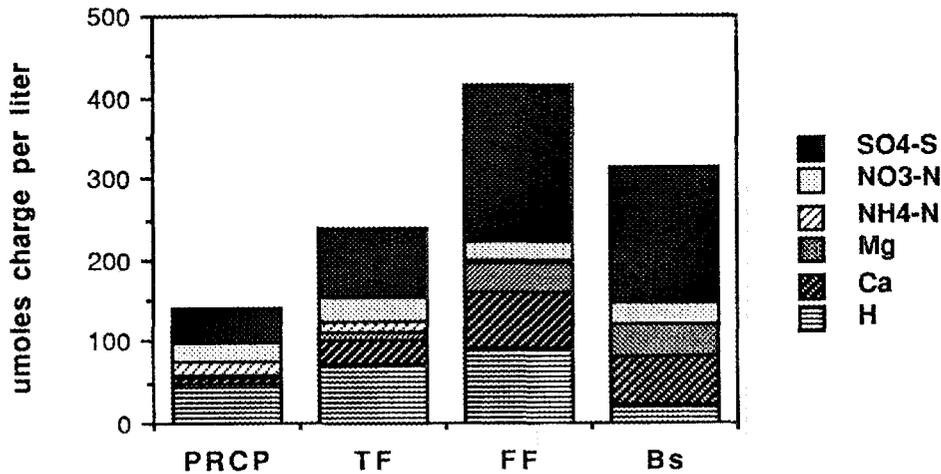


Figure 1. Ion concentrations in precipitation (PRCP), throughfall (TF), forest floor soil water (FF) and Bs horizon mineral soil water (Bs). Values are volume-weighted mean concentrations from samples collected from 1 June 1986 through 31 May 1988.

Aluminum in Soil Solution

During the monitoring period 1 June 1986 through 31 September 1987 the concentration of total solution aluminum in monthly integrated samples remained below the 250 micromole per liter Al^{3+} (Table 3) toxicity threshold suggested for red spruce seedlings.

Table 3. Total aluminum concentration range and quartile values.

Horizon	Total Aluminium ($\mu\text{moles l}^{-1}$)				
	MIN	25%	50%	75%	MAX
O	3.3	40.8	74.1	103.8	207.6
A	5.9	29.7	44.5	70.4	126
B	7.4	29.7	40.1	51.9	146.6

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APPENDIX. IFS PROJECT PUBLICATION LIST

SUMMARY LISTING OF PUBLICATIONS
FROM EPRI
INTEGRATED FOREST STUDY*Open Literature

- Binkley, D. 1987. Use of the terms "base cation" and "base saturation" should be discouraged. Soil Sci. Soc. Am. J. 51:1090-91.
- Binkley, D. 1986. Reduction in soil acidity in a loblolly pine stand with interval burning. Soil Sci. Soc. Am. J. 50:1590-94.
- Binkley, D., and D. Richter. 1987. Nutrient cycles and H⁺ budgets of forest ecosystems. Adv. Ecol. Res. 16:1-51.
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- * Van Miegroet, H. 1986. Role of N status and N transformations in the H⁺ budget, cation loss, and S retention mechanisms in adjacent Douglas-fir and red alder forests in western Washington. Ph.D. Thesis, University of Washington, Seattle.
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- * Autry, A., J. W. Fitzgerald, and P. Caldwell. Sulfur retention mechanisms in forest soils. Can. J. For. Res. (submitted)
- * Bondietti, E. A. Site descriptions for the Integrated Forest Study. ORNL/TM (in press)
- * Burke, M. K., and D. J. Raynal. Phenology of fine root production in a northern hardwood forest. (In preparation)
- * Burke, M. K., and D. J. Raynal. Fine root production and turnover in a northern hardwood forest. (In preparation)

- * Burke, M. K., and D. J. Raynal. The influence of nitrogen on fine root production and carbon allocation in sugar maple.
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- Hanson, P. J. 1988. Drying air streams for CO₂ analysis: A semipermeable membrane technique. Plant Cell Environ. (submitted)
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