

# **ATMOSPHERIC SULFUR DEPOSITION**

## **Environmental Impact and Health Effects**

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## CHAPTER 42

# IMPACT OF SULFUR DEPOSITION ON THE QUALITY OF WATER FROM FORESTED WATERSHEDS\*

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### ABSTRACT

Nutrient discharge in streamflow resulting from five manipulative treatments to experimental watersheds was used to evaluate the potential impact of sulfur and associated acid deposition on cation-leaching and content of water. Observed stream discharge of nitrate nitrogen was used to calculate  $H^+$  production due to accelerated nitrification in response to forest harvest. This value or a calculated value for  $H^+$  production following urea fertilization was combined with observed cation discharge, which had been corrected for release from organic matter decomposition, to estimate cation release ratios from the soil exchange complex due to  $H^+$ . These ratios were then used to estimate potential increases in watershed discharge of cations if precipitation acidity were to change from pH 4.3 to pH 4.0, 3.5, or 3.0. The potential increases in annual Ca, Mg, K, and Na discharge were calculated to be less than 0.5 kg/ha at pH 4.0 and less than 2.5 kg/ha at pH 3.5, increases which would be difficult to detect among natural variations in stream water chemistry. Calculations for precipitation at pH 3.0 suggest a potential increase in cation discharge which could be as great as 8.5 kg/ha for individual elements, a change which would be more easily detected.

### INTRODUCTION

We have a difficult task addressing the title of this paper in the emphatic nature in which it is stated. The path of any ion through a forested ecosystem is tortuous at best, and interactions with biotic and abiotic components are numerous and complex. As such it is difficult to relate quality of streamflow to atmospheric inputs of sulfur, hydrogen, or any other element.

As added evidence of the difficulty of our task, we know of no studies which have quantified the impact of precipitation chemistry on quality of streams draining forested watersheds. The reported impacts of atmospheric deposition on chemistry of lakes and streams in Scandinavia and northeastern North America have not been

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accompanied by information about the relative contributions of direct atmospheric inputs vs outputs from terrestrial watersheds. Gorham and McFee (1979) emphasize this lack of quantitative understanding when they state, "There is an urgent need for mass-balance studies to determine the degree to which the acids, heavy metals, nutrients and organic molecules reaching aquatic ecosystems have originated from direct precipitation upon the lake surface, transfer from atmospheric deposition upon the land, or—in some cases—enhanced soil leaching due to acid precipitation."

Gorham and McFee's proposal of enhanced soil leaching is of special interest to our paper since sulfur occurring as sulfate in precipitation is closely associated with hydrogen ion content (Hornbeck et al., 1977). Any increase in sulfate is accompanied by an increase in hydrogen ions, which may in turn accelerate the leaching of basic cations from soil exchange sites and into streams. In this paper we will use results from some experimental watershed studies to indirectly assess the potential impact of increased sulfate and its accompanying acidity upon chemistry of streams draining forested headwaters.

The complexity of sources and pathways for streamflow is a major reason why there have been no direct studies of impacts of atmospheric deposition on stream chemistry. Streamflow from forested watersheds is a combination of four possible sources: base flow, direct channel input, surface storm flow, and subsurface storm flow. These flow components are generated by water moving through different paths, and thus chemical properties are influenced by different factors. Base flow commonly has contact with bedrock and soil for a relatively long period of time, so the chemistry of base flow reflects the chemical composition and weathering characteristics of the geology. Acid precipitation could be expected to increase bedrock weathering rates, but its influence will be diminished as acidity is neutralized on passage through the vegetation canopy and soil profile (Eaton et al., 1973; Hornbeck et al., 1977).

Water entering the stream system through direct channel input is only a small proportion (less than 1%) of the total streamflow; however, its chemistry can be altered by the vegetation canopy. Concentration increases of some nutrients in streamflow during the initial periods of storms have been attributed to leaching from vegetation (e.g., Henderson et al., 1977; Johnson and Henderson, 1979). If acid precipitation accelerates foliar leaching through cuticular erosion and/or altering concentration gradients between internal and external leaf surfaces (Tukey, 1970), then stream chemistry will likewise be changed.

Surface storm flow (also termed overland flow) is rainfall which fails to infiltrate the soil. It rarely occurs in undisturbed forested watersheds in the eastern United States except when headwater streams expand during extreme events. At such times, much of the surface flow is actually exfiltrating subsurface storm flow. Subsurface storm flow is made up of precipitation which infiltrates and then moves vertically and laterally downslope to become streamflow. The chemistry of this large proportion of annual streamflow is largely determined by interaction with the cation and anion exchange reactions of the soil.

Results from the gaged watershed studies we will be discussing are an integration of all the above sources of streamflow. Obviously, much research lies ahead if we are to fully understand the impacts of precipitation chemistry upon streamflow.

#### WHAT CAN BE LEARNED FROM PREVIOUS MANIPULATIVE WATERSHED EXPERIMENTS?

Forest cutting and fertilization experiments conducted on experimental catchments may provide a way to approximate the potential impact of acid precipitation

on leaching of cations from soils and into streams. Harvesting and fertilization generally result in increases in stream nutrient discharge. The increases in cation discharge have been attributed to acidity generated during the process of nitrification of ammonium (Likens et al., 1970). Given the cation discharges, if the amount of acidity generated in the studies can be determined, the quantity of cations released can be expressed as a function of the acidity produced. In turn, projections can be made of increased cation leaching which might be expected if sulfate content and precipitation acidity were to increase.

### Harvesting Effects on Acidity

When forests are cut, both soil moisture and soil temperature are affected. Soil moisture increases during summer months because transpiration and interception have been reduced. Soil temperature is elevated due to increased radiation reaching the forest floor in the absence of a shading forest canopy. Increases in both soil moisture and soil temperature are conducive to accelerating the rate of organic matter decomposition. One product of decomposition is the release of the ammonium ion. The ammonium ion then undergoes a two-step oxidation to nitrate (Alexander, 1967):



The first stage is mediated by bacteria in the genus *Nitrosomonas*, while the second reaction is controlled by the genus *Nitrobacter*. Thus, in the conversion of one equivalent of ammonium to one equivalent of nitrate, four equivalents of hydrogen ion are released. It is this increase in acidity which has been thought to partly cause the increase in cation discharge observed after forest cutting (Likens et al., 1970).

### Calculations from Harvesting Studies

#### Hubbard Brook deforestation

In 1965-1966, all vegetation on watershed 2 of the Hubbard Brook Experimental Forest in New Hampshire was felled, and subsequent regrowth was inhibited with herbicides for three successive years (Likens et al., 1970). Streamflow amounts and element concentrations were monitored at weekly intervals and compared with similar values from a control watershed. The changes in element discharge from the deforested watershed are shown in Table 1. An increase of 245.9 kg/ha of nitrogen was discharged over a two-year period due to the deforestation and herbicide application. If this increased nitrogen discharge was the result of accelerated organic matter decomposition in the soil, which had an N concentration of 2.34% (Bormann et al., 1977), then decomposition of organic matter increased by 10,500 kg/ha. Cations are also released during decomposition, and part of the observed increase in nutrient discharge can be attributed to this source, the remainder to displacement by hydrogen ions on the soil exchange. The cation release due to decomposition was calculated by multiplying the amount of decomposition (10,500 kg/ha) by the concentration of the nutrient in soil organic matter. These concentrations were 0.79, 0.08, 0.14, and 0.008% for Ca, Mg, K, and Na, respectively (calculated from Likens et al., 1977, Table 9). Cation release due to decomposition was subtracted from stream discharge values to estimate the amount of each cation lost from the soil exchange (Table 1).

Table 1. Changes in element discharge due to deforestation at Hubbard Brook Experimental Forest and the estimation of the proportions arising from organic matter decomposition and the soil exchange complex

Data for the period from June 1, 1966, to May 31, 1968, and based on Likens et al. (1970)

	Increase in streamflow loss (kg/ha)	Release from organic matter (kg/ha)	Loss from soil exchange	
			(kg/ha)	(eq/ha)
NH <sub>4</sub> <sup>+</sup> -N	1.0	Assumed all		
NO <sub>3</sub> <sup>-</sup> -N	244.9	Assumed all		
Ca	147.9	83.1	64.8	3240
Mg	28.5	8.5	20.0	1650
K	55.6	14.7	40.9	1050
Na	21.7	0.8	20.9	910
Al	36.4	?	36.4	4040

The amount of hydrogen ion produced was estimated from the nitrate ion discharge. Increased nitrate-nitrogen discharge was 244.9 kg/ha, or 17,490 equivalents per hectare. If four equivalents of H<sup>+</sup> are produced during the transformation of one equivalent of NH<sub>4</sub><sup>+</sup> to one equivalent of NO<sub>3</sub><sup>-</sup>, then 69,960 equivalents per hectare of H<sup>+</sup> were produced. This is the amount of acidity which presumably produced the loss of cations from the soil exchange complex shown in Table 1.

#### Hubbard Brook strip cut

In October 1970, one-third of the vegetation on watershed 4 (89 ha) of the Hubbard Brook Experimental Forest was cut and harvested. The harvest was accomplished by removing vegetation from 25-m-wide strips running perpendicular to the stream and leaving 50-m uncut strips between those that were cut (additional 25-m strips from the uncut area were harvested in 1972 and 1974). Details of the experiment are given by Hornbeck et al. (1975). Changes in nutrient discharge due to the strip cut during the first two years are presented in Table 2 together with the amount of cation release from organic matter decomposition and estimates of loss from the soil exchange complex. Organic matter decomposition was calculated to be 500 kg/ha. Accelerated nitrate-nitrogen discharge amounted to 11.9 kg/ha (850 equivalents per hectare), which translates to 3400 equivalents per hectare of H<sup>+</sup> produced during the N mineralization and nitrification process.

#### Fernow clear cut

In 1969-1970 a 34-ha watershed on the Fernow Experimental Forest near Parsons, West Virginia, was commercially clear-cut, and water chemistry before and after the cut was compared with that of an adjacent control watershed. Data for the period from the 1970 growing season through the 1971-1972 dormant season were obtained

Table 2. Changes in element discharge due to strip-cutting at Hubbard Brook Experimental Forest

Estimates of the amounts arising from organic matter decomposition and the soil exchange complex are included for the period from the 1970-1971 dormant season through the 1972 growing season and are derived from Hornbeck et al (1975)

	Increase in streamflow loss (kg/ha)	Release from organic matter (kg/ha)	Loss from soil exchange	
			(kg/ha)	(eq/ha)
NO <sub>3</sub> <sup>-</sup> -N	11.9	Assumed all		
Ca	9.8	4.0	4.8	240
Mg	1.4	0.4	1.0	80
K	1.7	0.7	1.0	30
Na	1.1	0.1	1.0	40

from Aubertin and Patric (1974) and are presented in Table 3. Calculations for organic matter decomposition release were similar to those for the Hubbard Brook studies, but on-site concentrations of nutrients in soil organic horizons were not available. Values used were 1.23, 1.42, 0.07, 0.13, and 0.002% for N, Ca, Mg, K, and Na, respectively, and were average values for similar vegetation types in the Appalachian region (Henderson et al., 1978). Organic matter decomposition was calculated to be 195 kg/ha based on an increase in N loss of 2.4 kg/ha (increase in nitrate-nitrogen loss of 3.4 kg/ha and a decrease in ammonium-nitrogen loss of 1.0 kg/ha). Nitrate-nitrogen discharge was 3.4 kg/ha, or 240 equivalents per hectare, which means 960 equivalents per hectare of H<sup>+</sup> was generated during nitrification.

Table 3. Changes in element discharge due to a commercial clear cut on the Fernow Experimental Forest

Data represent the period from the 1970 growing season through the 1971-1972 dormant season (Aubertin and Patric, 1974), and estimates of release from organic matter decomposition and loss from the soil exchange complex are also included

	Change in streamflow loss (kg/ha)	Release from organic matter (kg/ha)	Loss from soil exchange	
			(kg/ha)	(eq/ha)
NH <sub>4</sub> <sup>+</sup> -N	-1.0			
NO <sub>3</sub> <sup>-</sup> -N	3.4	2.4		
Ca	3.0	2.8	0.2	10
Mg	1.1	0.1	1.0	80
K	2.2	0.3	1.9	50
Na	0.7	Negligible	0.7	30

### Coweeta clear cut and cable logging

In 1976-1977, roads were built and stabilized on watershed 7 at the Coweeta Hydrologic Station near Franklin, North Carolina, and it was clear-cut and harvested using cable logging. Changes in nutrient discharge the second year after cutting (June 1, 1978, to May 31, 1979) and not including the period of road building are presented in Table 4. Organic matter decomposition and element release were calculated using soil organic horizon nutrient concentrations of 1.25, 1.16, 0.07, 0.17, and 0.002% for N, Ca, Mg, K, and Na, respectively (Henderson et al., 1978). Accelerated organic matter decomposition was calculated to be 100 kg/ha. H<sup>+</sup> production was estimated to be 360 equivalents per hectare based on the observed increase in nitrate-nitrogen discharge of 1.26 kg/ha (90 equivalents per hectare).

Table 4. Changes in element discharge due to clear-cutting and cable logging at the Coweeta Hydrologic Station for the period June 1, 1978, to May 31, 1979

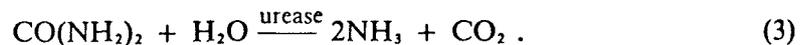
Estimates of release from organic matter decomposition and loss from the soil exchange complex are also included

	Change in streamflow loss (kg/ha)	Release from organic matter (kg/ha)	Loss from soil exchange	
			(kg/ha)	(eq/ha)
NH <sub>4</sub> <sup>+</sup> -N	0.0			
NO <sub>3</sub> <sup>-</sup> -N	1.26	Assumed all		
Ca	*	1.16	*	*
Mg	0.35	0.07	0.28	25
K	0.98	0.17	0.81	20
Na	0.10	< 0.01	0.10	5

\*Calcium loss in streamflow from the clear-cut and cable-logged watershed was 0.25 kg/ha less than that from the control catchment.

### Fernow urea fertilization

When urea is added to soils, it has a pronounced influence on soil reaction. Initially, urease present in the soil breaks down urea as follows (Alexander, 1967):



The ammonia produced then reacts with water:



The result of this reaction causes soil pH to rise shortly after urea is added to soils. Thereafter, the NH<sub>4</sub><sup>+</sup> undergoes nitrification as shown in Eqs. (1) and (2), and H<sup>+</sup> is released, causing soil pH to drop. The net result is that for each equivalent of urea nitrogen applied, an equivalent of OH<sup>-</sup> and four equivalents of H<sup>+</sup> will be generated, and the net acidity produced will be three equivalents. The above analysis assumes

that no NH<sub>3</sub> is lost through volatilization, but, in fact, at least a small volatilization loss can be expected.

In May 1971 an experiment was conducted at the Fernow Experimental Forest in which 260 kg/ha of urea nitrogen was applied to a 30-ha forested watershed. Following the application, streamflow chemistry was monitored closely for a year (Aubertin et al., 1973). The increases in nutrient discharge for this period are shown in Table 5. The 260 kg/ha of urea nitrogen applied is equal to 18,750 equivalents per hectare, yielding a net increase in H<sup>+</sup> of 55,710 equivalents per hectare.

Table 5. Changes in element discharge due to urea fertilization at the Fernow Experimental Forest for the period May 1, 1971, to April 30, 1972

Data are from Aubertin et al., 1973.

	Increase in streamflow loss	
	(kg/ha)	(eq/ha)
Ca	33.5	1680
Mg	6.7	550
K	3.3	80
Na	2.5	110

**Cations Leached as a Function of H<sup>+</sup> Produced**

Results from the five watershed studies discussed above are summarized in Table 6 with respect to the amount of total cations (Ca, Mg, K, and Na) released in response to the amount of H<sup>+</sup> produced. The cation release associated with an

Table 6. Summary of total cation release, hydrogen production, and the cation release ratio for five manipulated-watershed studies

	H <sup>+</sup> produced (eq/ha)	Total cation release (eq/ha)	Cation release ratio (eq/eq H <sup>+</sup> )
Hubbard Brook			
Deforested	69,960	6,850	0.10
Strip-cut	8,400	390	0.05
Fernow			
Clear-cut	960	170	0.18
Fertilization	55,710	2,420	0.04
Coweeta			
Clear-cut and cable-logged	360	50	0.14

equivalent of  $H^+$  ranges from a low of 0.04 for the urea fertilization to a high of 0.14 for the Fernow clear cut. The value for the urea fertilization may be slightly low due to overestimation of the amount of  $H^+$  actually produced. This overestimation could be due to volatilization of  $NH_3$  and/or uptake and incorporation of  $NH_4^+$  by vegetation and microorganisms prior to nitrification. It is interesting that these diverse treatments on a variety of sites produce ratios which are so similar. Additional data from this and other sites would help to further establish the variability of this ratio. The release of individual cations (Ca, Mg, K, and Na) as a function of  $H^+$  produced for each of the five studies is given in Table 7.

Table 7. Release ratios for individual cations observed in five manipulated- watershed studies

	Cation release ratio (eq/eq $H^+$ )			
	Ca	Mg	K	Na
Hubbard Brook				
Deforested	0.046	0.024	0.015	0.013
Strip-cut	0.029	0.010	0.004	0.005
Fernow				
Clear-cut	0.010	0.083	0.052	0.031
Fertilization	0.030	0.010	0.001	0.002
Coweeta				
Clear-cut and logged	0.0	0.069	0.056	0.014

#### CATION LEACHING POTENTIAL UNDER VARIOUS PRECIPITATION ACIDITY AND SULFUR CONTENTS

The ratios of total and individual cation release to  $H^+$  produced were used to assess leaching potential under different precipitation acidity regimes. To do this it was assumed that annual precipitation amounts to 150 cm and has a weighted average pH of 4.3, which would correspond to a sulfate-sulfur input of 12.0 kg/ha if the  $H^+$  were associated only with sulfate. These conditions are very similar to those found in much of the eastern United States. These baseline precipitation characteristics were used to calculate potential changes in leaching for conditions where precipitation acidity changed to pH values of 4.0, 3.5, and 3.0. Additional  $H^+$  inputs of 750, 3990, and 14,250 equivalents per hectare would be experienced for 150 cm of precipitation at pH 4.0, 3.5, and 3.0, respectively (Table 8). If all of the  $H^+$  were associated with sulfate, these conditions would be associated with sulfate-sulfur inputs of approximately 25, 75, and 240 kg/ha.

Three values for increased leaching are given in Tables 8 and 9—low, high, and median—which were determined using the low, high, and median values for total and individual cation release presented for the study locations in Tables 6 and 7.

Based on the median value (Table 9), cation discharge could be expected to increase by less than 0.5 kg/ha for any nutrient for precipitation at pH 4.0 and by less

Table 8. Potential increases in cation leaching expected under three precipitation acidity regimes

Low, high, and median values are based on corresponding cation release ratios in Table 6

pH	Additional H <sup>+</sup> (eq/ha)	Cation leaching potential (eq/ha)		
		Low	High	Median
4.0	750	30	135	75
3.5	3,990	160	720	400
3.0	14,250	570	2,565	1,425

Table 9. Potential increases in annual discharge of four cations under three precipitation acidity regimes

Low, high, and median values are based on corresponding values in Table 7

	Leaching potential for individual cations (kg/ha)			
	Ca	Mg	K	Na
At pH 4.0:				
Low	0.0	0.1	<0.1	<0.1
High	0.7	0.8	1.6	0.5
Median	0.4	0.2	0.4	0.2
At pH 3.5:				
Low	0.0	0.5	0.2	0.2
High	3.7	4.0	8.7	2.8
Median	2.3	1.2	2.3	1.2
At pH 3.0:				
Low	0.0	1.7	0.6	0.7
High	13.1	14.4	31.2	10.2
Median	8.3	4.2	8.4	4.3

than 2.5 kg/ha for rain at pH 3.5. For some watersheds, changes of this magnitude would be difficult to detect among the natural variations in water chemistry. The increases for pH 3.0 are larger and would be more easily detected. Leaching increases based on the high value are much more pronounced and could more easily be detected, especially for the pH 3.5 and 3.0 situations.

In Table 1, data on aluminum discharge were included. In the Adirondacks of New York, Schofield (1976) has suggested that high Al concentrations in lakes are at least partly responsible for increased fish mortality. It is postulated that Al is leached from soils by infiltrating snowmelt which is very acid. The data from the Hubbard Brook deforestation study show that 0.06 equivalent of Al per equivalent of H<sup>+</sup>

produced was released to streamflow. Using the same assumptions as above, increased Al leaching of 0.4, 2.2, and 7.7 kg/ha could be expected at pH values of 4.0, 3.5, and 3.0, respectively.

In this paper we have attempted to reanalyze manipulative watershed experiments in order to arrive at some possible estimates of the potential effects of acid precipitation on cation leaching. Our calculations have assumed that the  $H^+$  produced as the result of the various treatments interacted exclusively with cations on the soil exchange with subsequent discharge of cations in streamflow. In fact, some of the  $H^+$  has reacted with primary and secondary minerals, causing increased weathering rates and associated cation discharge. While the net effect on water quality is the same, we do not really know the proportions of discharge coming from these different sources.

The harvesting studies reveal the influence of organic matter decomposition on cation discharge. Sulfur deposition and acid precipitation may retard decomposition and thus in part counteract the increases due to leaching and weathering.

#### REFERENCES

- Alexander, M. 1967. *Introduction to Soil Microbiology*. John Wiley and Sons, Inc., New York.
- Aubertin, G. M., and J. H. Patric. 1974. Water quality after clearcutting a small watershed in West Virginia. *J. Environ. Qual.* 3:243-249.
- Aubertin, G. M., D. W. Smith, and J. H. Patric. 1973. Quantity and quality of streamflow after urea fertilization on a forested watershed: first-year results. Pp. 88-100 in *Forest Fertilization, Symposium Proceedings*. U.S.D.A. Forest Service Gen. Tech. Rep. NE-3.
- Bormann, F. H., G. E. Likens, and J. M. Melillo. 1977. Nitrogen budget for an aging Northern hardwood forest ecosystem. *Science* 196:981-983.
- Eaton, J. S., G. E. Likens, and F. H. Bormann. 1973. Throughfall and stem-flow chemistry in a Northern hardwood forest. *J. Ecol.* 61:495-508.
- Gorham, E., and W. W. McFee. 1979. Effects of acid deposition upon outputs from terrestrial to aquatic ecosystems. In *NATO Adv. Res. Institute, Ecological Effects of Acid Rain*. University of Toronto.
- Henderson, G. S., W. F. Harris, D. E. Todd, Jr., and T. Grizzard. 1977. Quantity and chemistry of throughfall as influenced by forest-type and season. *J. Ecol.* 65:365-374.
- Henderson, G. S., W. T. Swank, J. B. Waide, and C. C. Grier. 1978. Nutrient budgets of Appalachian and Cascade region watershed: a comparison. *For. Sci.* 24:385-397.
- Hornbeck, James W., Gene E. Likens, and John S. Eaton. 1977. Seasonal patterns of acidity of precipitation and their implications for forest stream ecosystems. *Water, Air, Soil Pollut.* 7:355-365.
- Hornbeck, J. W., G. E. Likens, R. S. Pierce, and F. H. Bormann. 1975. Strip cutting as a means of protecting site and streamflow quality when clear-cutting Northern hardwoods. Pp. 208-229 in Bernier, B., and C. H. Winget (eds.), *Forest Soils and Forest Land Management*. Les Presses de l'Université Laval, Quebec, Quebec, Canada.
- Johnson, D. W., and G. S. Henderson. 1979. Sulfate absorption and sulfur fractions in a highly weathered soil under a mixed deciduous forest. *Soil Sci.* 128: 34-40.

- Likens, G. E., F. H. Bormann, N. M. Johnson, D. W. Fisher, and R. S. Pierce. 1970. Effects of forest cutting and herbicide treatment on nutrient budgets in the Hubbard Brook watershed-ecosystem. *Ecol. Monogr.* 40:23-47.
- Likens, G. E., G. H. Bormann, R. S. Pierce, J. S. Eaton, and N. M. Johnson. 1977. *Biogeochemistry of a Forested Ecosystem*. Springer-Verlag, New York.
- Schofield, C. L. 1976. Acid precipitation: effects on fish. *Ambio* 5:228-230.
- Tukey, H. B., Jr. 1970. The leaching of substances from plants. *Annu. Rev. Plant Physiol.* 21:305-323.

## DISCUSSION

*Bill Graustein, Yale University:* I'd like to comment on your last point, on aluminum. One thing that makes it very difficult to make such predictions about aluminum is the great difference between one watershed and another. I think that perhaps if we contrast Hubbard Brook and Coweeta we might be able to make my point fairly clearly. Hubbard Brook currently shows a fairly low rate of weathering in the horizon, but I think this is partially because of the unusual hydrology of the area, where the B<sub>2</sub> horizon is essentially impermeable to water. The Hubbard Brook watershed must have been a site of very rapid weathering in former times, because the A<sub>2</sub> horizon contained nothing but quartz; all the other minerals had been removed. Over a long period of time the only thing that's available for neutralizing acid precipitation is rock weathering. Changes in biomass are virtually nil, so an acid runoff essentially means a weathering rate that's slower than the rate of acid input. In a place like Coweeta, however, where there is much deeper percolation and development of saprolite, there are abundant mineral surfaces available for weathering. These weathering reactions remove hydrogen or increase bicarbonate in solution as great as the pH. Aluminum runoff is a problem from Hubbard Brook only because the pH is so low that aluminum can become soluble. If weathering reactions proceed, they'll raise the pH of the solution, and aluminum will precipitate. Extrapolating aluminum leaching measurements from a watershed that's already so acidic that aluminum will remain in solution to one which does not have a large buffering capacity but has a large reaction capacity to raise pH and therefore reduce aluminum mobility, I think, is a little bit hazardous.

*G. S. Henderson:* Oh, I agree, this whole thing is a little bit hazardous. I should point out, though, that the aluminum data that I used here came just from the Hubbard Brook study. Your points are still well taken, though, and obviously the whole picture of aluminum is tremendously complex, with the change in solubility as a function of pH.

*George Sehmel, Pacific Northwest Laboratory:* Can you determine how much each of the cations is leached as a function of depth?

*G. S. Henderson:* Good question. I don't think that on the short term that we've been studying this type of thing. We can detect in soils these changes due to natural changes in acidity. Certainly over long periods of time, you can analyze soil and find differing zones of cation movement, either loss or addition. One of the best examples of this sort of thing I've found is in many of the mollisols; in that you have secondary calcium carbonate accumulations in the B horizon, and this material has come from the overlying horizons. You can see these zones of differential movement of cations, but I have never looked at differential cation concentrations in different soil profiles and tried to relate them to different levels of acidification or leaching rates at this point.