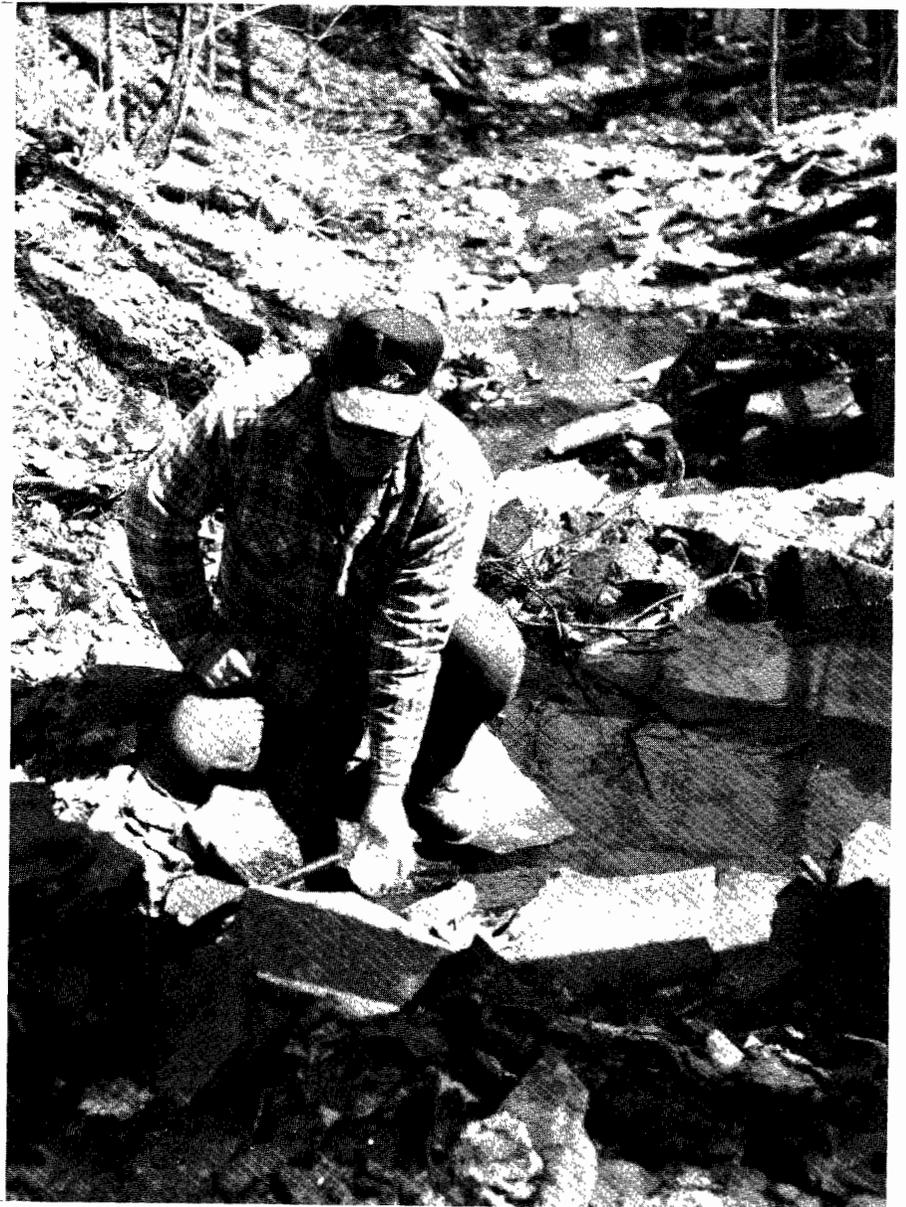




# Input-output Budgets of Selected Nutrients on an Experimental Watershed Near Parsons, West Virginia

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Manuscript received for publication 22 May 1985

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## Abstract

The objectives of this 3-year study were to determine (1) budgets of  $H^+$ ,  $Ca^{++}$ ,  $Cl^-$ ,  $NO_3-N$ ,  $NH_3-N$ , and  $SO_4=$  for a 38.9-ha forested watershed and (2) changes in concentration of these constituents that occur in the tree canopy, the soil and bedrock, and the stream channel. Sampling points were two forest openings for bulk precipitation, 20 throughfall sites, four springs where water first seeps out of the soil, and the main stream at the watershed outlet. The most important conclusion was that sulfate is accumulating in the watershed. Average annual kg/ha of sulfate were: bulk precipitation = 39.9, throughfall = 53.0, and stream = 25.1. Sulfate budgets are compared with published results from five other study sites in the hardwood region of the Eastern United States and with some results from Germany.

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Precipitation in the central Appalachians is among the most acidic in the United States. Average annual pH is 4.20, but pH readings below 4.0 are common in the summer months (Helvey et al. 1982). The 15-year average pH of streamflow from an undisturbed watershed is 5.85. Thus, major chemical changes occur as water from precipitation passes through the ecosystem. Some scientists believe that acid precipitation will accelerate nutrient leaching from the forest foliage (Tukey 1980) and the soil profile (Hutchinson 1980). The long-term consequences could be a decrease in forest productivity.

We started a study in 1980 to determine changes in the chemistry of precipitation as it filters through an undisturbed watershed on the Fernow Experimental Forest. Our specific objective was to determine the chemical characteristics of bulk precipitation, throughfall, spring water, and streamflow. By establishing current budgets of the common nutrients within the ecosystem, changes in these budgets over time can be determined. Although similar studies have been reported for New England (Likens and others 1977), the southern Appalachians (Swank and Douglass 1977), and eastern Tennessee (Kelly 1979), this is the first nutrient balance study to be reported for the high-precipitation zone of the central Appalachians.

### Study Area and Methodology

The Fernow Experimental Forest, located near Parsons, in north-central West Virginia, is typical of much wooded land in the central Appalachians. Elevations range from 650 to almost 1,000 m, slopes from 10 to 60 percent, with 20 to 30 percent most common. The soils are derived from acid shale and sandstone of the Hampshire series, with Calvin channery silt loam (loamy-skeletal, mixed, mesic typic Dystrichrepts) prevalent. Soil pH averages 4.3, 4.6, and 4.7 for the A, B, and C horizons, respectively (Tomkowski 1983). Soil depth averages about 120 cm.

The study was conducted on watershed 4 (38.9 ha), which has served as a control catchment since the research program began in 1951. Forest vegetation, little disturbed since a high-grading operation in 1909, consists of several hardwood species including yellow-poplar (*Liriodendron tulipifera* L.), sugar maple (*Acer saccharum* Marsh.), black cherry (*Prunus serotina* Ehrh.), white ash (*Fraxinus americana* L.), sweet birch (*Betula lenta* L.), yellow birch (*Betula alleghaniensis* Britt.), red oak (*Quercus rubra* L.), American beech (*Fagus grandifolia* Ehrh.), black locust (*Robinia pseudoacacia* L.), and hickories (*Carya* spp.).

Average basal area, determined from a 100 percent cruise in 1984, was 30.3 m<sup>2</sup>/ha for stems greater than 12.7 cm at breast height. The understory contains reproduction of overstory species along with a scattering of flowering dogwood (*Cornus florida* L.) and other shrubby species. During

the growing season, the forest floor is almost covered with stinging nettles (*Laportea canadensis* (L.) Wedd.), which often reach 120 cm in height.

Annual precipitation averages 150 cm, evenly distributed through the year. Annual streamflow averages 60 cm, but the distribution is strongly seasonal. Seventy-five percent occurs during the dormant season and 25 percent during the growing season. The watershed seems to have very limited buffering capacity because annual stream alkalinity averages less than 2 mg/L as CaCO<sub>3</sub>.

Annual leaf fall biomass averages about 4.2 metric tons/ha (Kochenderfer and Wendel 1982). Litter decomposition, although not measured, seems to be very rapid because the previous year's accumulation virtually disappears by the end of each growing season.

Figure 1 shows the experimental watershed with plotted sampling points. Bulk precipitation was sampled with two

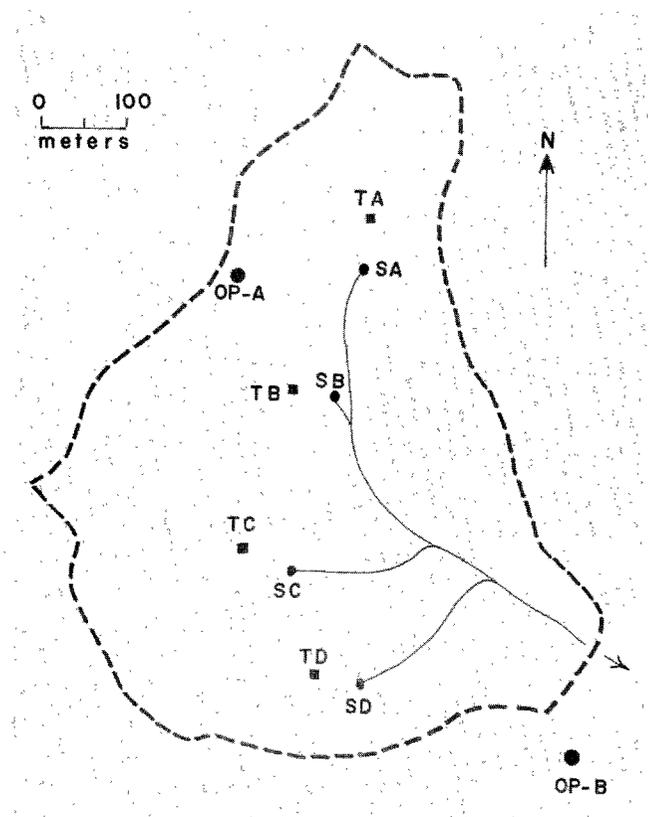


Figure 1.—The experimental watershed with the location of sampling sites. Forest opening sites: OP-A and OP-B; throughfall sampling sites: TA, TB, TC, and TD; and spring water sampling sites: SA, SB, SC, and SD.

gauges in each of two forest openings. In addition to the gauges for collecting samples for chemical analysis, standard and recording precipitation gauges are located in each forest opening. Records from these gauges were used for total amounts and timing of precipitation events. Throughfall was sampled with five randomly located gauges on each of four plots (40 m<sup>2</sup>). Spring water was sampled at the four locations where water first seeps out of the soil. Streamflow was sampled about 10 m above the 120° V-notch weir.

Deep seepage, water leaving the catchment without flowing across the weir blade, is a concern when input-output budgets are computed. Although the amount of deep seepage is impossible to determine, it is not believed to be a serious problem for the experimental watershed. Nutrient input as stemflow, which was not measured, at least partly compensates for unmeasured nutrient losses by deep seepage.

During the snow-free season, gauges for throughfall and bulk precipitation consist of polyethylene funnels, with a diameter of 17 cm, mounted on 2-L polyethylene bottles. A piece of fiberglass was placed across the opening of each funnel to help prevent sample contamination by insects and plant debris. After each throughfall or precipitation sample was collected, the funnels were scrubbed and thoroughly rinsed with distilled water, and a new piece of fiberglass was installed. Also, bottles that had been scrubbed with soapy water, then thoroughly rinsed with distilled water, were installed to sample the next storm.

During the months when snow normally falls (December-February), bulk precipitation and throughfall were sampled with one 120-L container at each throughfall plot and at each open site. A new plastic liner was installed each week after the preceding week's sample was collected.

A test of precipitation catch efficiency was made among the funnels, containers, and standard precipitation gauges located in the two forest openings. There was no significant difference ( $P = 0.05$ ) in the performance of these three collectors.

Grab sampling was used for the spring and stream sites. Chemically clean polyethylene bottles were rinsed 3 times with water at the sampling site prior to sample collection.

During the snow-free season, bulk precipitation, throughfall, spring flow, and streamflow samples were usually collected within 15 hours after each storm. The exceptions were storms that occurred on weekends; those samples were collected the following Monday morning. During the snowy season, samples were collected on Tuesday of each week. Stream and spring samples were collected at frequent intervals during selected storms in order to better define the relationship between flow rate and the concentration of chemical constituents. The sampling interval varied depending on changes in stage.

On rare occasions, a throughfall sample was lost because of animal disturbance or because it was obviously contaminated by insects or plant material. These missing values were estimated by averaging values from the remaining samples.

Collected samples were transported about 12 km to the laboratory where they were composited by plots and subsequently analyzed for various chemical constituents. During the first year of the study (May 1980-April 1981), the samples were analyzed for pH, specific conductance, and the concentration of sulfate. Samples collected after May 1981, were analyzed for pH, specific conductance, nitrate nitrogen (NO<sub>3</sub>-N), sulfate (SO<sub>4</sub><sup>=</sup>), chloride (Cl<sup>-</sup>), calcium (Ca<sup>++</sup>), and ammonia nitrogen (NH<sub>3</sub>-N). pH was determined with a Corning<sup>1</sup> 10 meter and specific conductance with a temperature compensating Markson meter. Anions were measured with a Dionex 10 ion chromatograph, except that the Hach Chemical Company (1977) method was used for sulfate between May 1980 and May 1, 1981. Calcium was measured with a 503 Perkin Elmer Atomic adsorption Spectrophotometer. Ammonia nitrogen (NH<sub>3</sub>-N) was measured by the Hach Chemical Company (1977) method using a Bausch and Lomb spectrometer with digital readout for color comparisons.

pH and specific conductance were measured within 24 hours, anions within 7 days, and cations (including NH<sub>3</sub>-N) within 30 days after sample collection. Each sample for anion analysis was injected through an individual 0.2- $\mu$ m filter, but samples were not filtered prior to the other analyses. No preservatives were used because of the short time between sample collection and analysis. All samples were refrigerated at 4°C until they were analyzed.

## Data Analysis

Each chemical constituent was averaged by dates for each sampling site before input-output budgets were computed. Chemical inputs were computed by first converting depth of measured precipitation and throughfall for each event to volume per hectare. Next, the concentration of each ion was multiplied by the computed volume to give kg/ha of that ion for that event. Finally, the kg/ha values per event were accumulated for growing season (May 1–October 31), dormant season (November 1–April 30), and hydrologic year (May 1–April 30).

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The intensive sampling during storms showed only minor and inconsistent changes in the concentration of measured constituents as flow rate increased. Therefore, chemical outputs were computed by first determining the volume of streamflow represented by each collected stream sample. This volume was defined as the measured flow occurring midway between the time of the previous sample and the current sample and between the current sample and the next sample. This outflow volume, in L/ha, was multiplied, in turn, by the concentration of each chemical constituent. Finally, the individual output values were accumulated by the same time periods as the input values.

## Results

Output budgets at the springs could not be computed because flow rates were not measured. A total of 87 storms in the growing season and 72 in the dormant season was sampled during the 3-year study. Table 1 shows average concentration of each measured chemical constituent by season and the standard error ( $S\bar{x}$ ) of each mean. Several conclusions can be drawn from the table:

- During the growing season, hydrogen ion concentration decreases dramatically from bulk precipitation to throughfall and to springs and streams. Throughfall contains about 38 percent fewer hydrogen ions than bulk precipitation. Of the hydrogen ions in throughfall, 85

percent are neutralized in the soil and bedrock, and about 8 percent are neutralized in the open stream channel.

- Specific conductance of throughfall is greater than conductance of bulk precipitation during both seasons, presumably because of nutrients added by the forest canopy. Average conductivity and the variability between samples are much less for streamflow than for the other sampling sites.
- The neutralization capacity of the tree canopy is much less during the dormant than during the growing season. However, the soil and bedrock continue to neutralize incoming acids, and the pH of streamflow during both seasons averaged 5.85.
- Water is enriched in the canopy and soil with respect to most ions and slightly diluted in the stream channel. Exceptions are  $SO_4^{=}$  and  $NH_3-N$ , which are greatly enriched in the canopy but are diluted within the soil and bedrock.
- Concentration of  $SO_4^{=}$ ,  $Ca^{++}$ , and  $NH_3-N$  in bulk precipitation is higher during the growing than during the dormant season. However, there is no significant difference ( $P = 0.05$ ) in the streamflow concentration of these nutrients between seasons.

**Table 1.—Simple averages and standard errors of measured chemical parameters by season and sampling sites**

Site	H <sup>+</sup> μeq/L	Conductivity μs/cm	Cl <sup>-</sup>	NO <sub>3</sub> -N	SO <sub>4</sub> <sup>=</sup>	Ca <sup>++</sup>	NH <sub>3</sub> -N	pH
----- mg/L -----								
GROWING SEASON (May 1—Oct. 31)								
Bulk	64.6	34.8	0.07	0.45	3.90	1.06	0.72	4.19
S $\bar{x}$	4.7	1.9	.01	.06	.22	.10	.04	—
Throughfall	40.1	40.7	.11	.58	6.03	1.97	1.47	4.40
S $\bar{x}$	3.7	2.1	.01	.05	.31	.16	.10	—
Springs	6.0	26.3	.11	1.37	3.33	1.86	.19	5.22
S $\bar{x}$	.2	.3	.01	.04	.08	.03	.03	—
Stream	1.4	22.2	.07	1.05	3.59	1.60	.16	5.85
S $\bar{x}$	.1	.2	.01	.02	.07	.02	.03	—
DORMANT SEASON								
Bulk	66.2	32.8	0.03	0.52	2.85	0.44	0.53	4.18
S $\bar{x}$	4.8	2.2	.01	.07	.21	.05	.05	—
Throughfall	76.0	44.6	.06	.86	4.26	1.06	.92	4.12
S $\bar{x}$	4.7	2.5	.01	.07	.26	.09	.09	—
Springs	5.1	25.8	.08	1.34	3.19	1.79	.10	5.29
S $\bar{x}$	.2	.4	.01	.03	.08	.05	.01	—
Stream	1.5	22.4	.06	1.06	3.48	1.63	.11	5.84
S $\bar{x}$	.1	.3	.01	.03	.10	.05	.01	—

- Concentration of most ions differ very little from the time water appears at springs until it exits the watershed. An exception is NO<sub>3</sub>-N, which decreases in concentration from about 1.35 mg/L at the springs to 1.05 mg/L at the watershed outlet.

Budgets of the measured ions are presented in Table 2. As suggested by Shaffer and Galloway (1982) these relationships can be divided into the following classes: input > output, input < output, and input = output. The ions falling into each of these categories are as follows:

greater than the loss as streamflow (9.3 kg/ha). Total nitrogen budgets could not be computed because organic nitrogen was not measured.

#### input < output (Ca<sup>++</sup>)

Calcium input as precipitation averaged about 4 kg/ha/yr less than the loss in streamflow during the 2 years of record. An enrichment occurred in the canopy, and throughfall contained almost double the calcium measured in bulk precipitation samples.

**Table 2.—Annual budgets of measured nutrients**

Year <sup>a</sup>	Site	Cl <sup>-</sup>	NO <sub>3</sub> -N	SO <sub>4</sub> <sup>=</sup>	Ca <sup>++</sup>	NH <sub>3</sub> -N	H <sup>+</sup>	NO <sub>3</sub> -N + NH <sub>3</sub> -N	Water depth
									cm
									kg/ha
1980-81	Bulk	—	—	38.6	—	—	0.84	—	107.1
	Throughfall	—	—	47.2	—	—	.63	—	97.3
	Stream	—	—	19.9	—	—	.01	—	57.2
1981-82	Bulk	0.9	7.2	48.5	7.4	8.5	0.95	15.7	160.0
	Throughfall	1.0	8.8	65.0	15.7	15.2	.75	24.0	139.2
	Stream	.7	10.5	31.5	13.7	.8	.02	11.3	83.4
1982-83	Bulk	0.3	4.9	32.6	8.3	6.8	0.68	11.7	140.2
	Throughfall	.6	6.1	46.9	14.2	12.8	.53	18.9	124.0
	Stream	.3	6.6	23.9	10.9	.6	.01	7.2	69.0
Average for period of record	Bulk	0.6	6.0	39.9	7.9	7.7	0.82	13.7	135.8
	Throughfall	.8	7.5	53.0	15.0	14.0	.64	21.5	120.2
	Stream	.5	8.6	25.1	12.3	.7	.01	9.3	69.9

<sup>a</sup>The hydrologic year begins May 1st and ends the following April 30th.

#### input > output

##### (H<sup>+</sup>, SO<sub>4</sub><sup>=</sup>, NH<sub>3</sub>-N, Total inorganic N)

Input of hydrogen ions was 0.8, 1.0, and 0.7 kg/ha for the first, second, and third year of the study, respectively. Losses in streamflow were only 0.01 kg/ha for each year. Therefore, as pointed out earlier, this watershed effectively neutralizes acid received in precipitation. Annual sulfate input averaged 40 kg/ha during the 3 years of record and ranged from 32.6 to 48.5 kg/ha. During the 3 years of study, sulfate in throughfall averaged 33 percent more than the amount measured in bulk precipitation samples. The sulfate export by streamflow averaged 14.8 kg/ha less than the input as bulk precipitation and 27.9 kg/ha less than throughfall.

The annual input of NH<sub>3</sub>-N averaged 7.7 kg/ha during the 2 years of complete record. Almost double this amount was delivered to the forest floor as throughfall (14 kg/ha), but water flowing from the drainage contained almost no nitrogen as NH<sub>3</sub>-N.

When NO<sub>3</sub>-N and NH<sub>3</sub>-N are combined, the annual input of inorganic nitrogen as precipitation (13.7 kg/ha) is slightly

#### input = output (Cl<sup>-</sup>, NO<sub>3</sub>-N)

Input and losses of chloride are expected to roughly balance over the long term because chloride is not involved significantly in biological processes (Shaffer and Galloway 1982). A slight enrichment of NO<sub>3</sub>-N occurs in the forest canopy and a greater enrichment occurs within the soil and bedrock. However, NO<sub>3</sub>-N export by the stream differed only slightly from the input in bulk precipitation.

## Discussion

One concern of all studies involving precipitation and throughfall sampling is the difficulty (or impossibility) of computing error terms for estimated values. The problem is even greater when collected samples are analyzed for the concentration of various ions from which nutrients budgets are computed. Because of these problems, the uncertainty of estimated values is rarely mentioned in research papers that present nutrient budgets.

Potential sources of error include: (1) the accuracy of estimated volumes of precipitation, throughfall, and streamflow, (2) the representativeness of precipitation, throughfall, and streamflow samples with respect to the chemical characteristics of the respective populations, (3) the accuracy of chemical determinations in the laboratory, and (4) computation errors.

The study design used here for volumes of precipitation and throughfall meets the recommendations of Helvey and Patric (1965) for numbers of samplers needed to ensure that estimates are within  $\pm 5$  percent of true values for a given storm. Since many storms were sampled in this study, the errors should tend to cancel out and annual values should be more accurate than individual storm values. Streamflow measurements with the 120° V-notch weir have an accuracy of  $\pm 5$  percent (Hornbeck 1965). As stated earlier, the volume and chemical characteristics of deep seepage is impossible to quantify accurately, but nutrient losses by this pathway are partly compensated by the unmeasured inputs by stemflow. Quality control in the laboratory and double checking of all computations minimizes these sources of error.

Although it is impossible to know for sure, we believe that the values in Tables 1 and 2 are within 10 percent of actual values.

The input-output relationships of  $\text{SO}_4^{=}$  and  $\text{Ca}^{++}$  (Table 2) raise an important question: Is the enrichment of throughfall caused by ions being leached from plant surfaces, the washoff of dry depositions that accumulated between storms, or a combination of these processes. In other words, when computing input-output budgets, is bulk precipitation or throughfall the proper input value?

If leaching is the dominant process in throughfall enrichment, bulk precipitation would be the proper input value because leaching simply cycles the nutrients between the canopy and soil. Without leaching, these nutrients would reach the forest floor with leaf fall. If washoff is the dominant process, throughfall is the proper input term because throughfall would include dry deposition. Bulk precipitation gauges, although open to the atmosphere at all times, are inefficient dry deposition collectors. For example, the National Atmospheric Deposition Program no longer uses buckets on a routine basis for estimating dry deposition because buckets do not accurately simulate the surfaces of vegetation.

The answer to the question is important because, as with calcium, leaching would mean a net loss of these ions to the ecosystem, while washoff indicates a net gain. A net watershed accumulation of sulfate is indicated whether leaching or washoff is the dominant process. However, the magnitude of the accumulation is almost double if washoff is dominant. Others who have addressed this question concluded that the dominant process varies between ions. Leaching is the dom-

inant process for throughfall enrichment of potassium because potassium is an extremely mobile ion (Mayer and Ulrich 1980; Johnson et al. 1982). Washoff is believed to be the dominant process for throughfall enrichment of most other ions (Eaton et al. 1973; Mayer and Ulrich 1980). Smith (1981) stated that forest trees can be extremely efficient at trapping sulfur compounds in their foliage because leaf surface area is about 5 times greater than the ground surface.

Perhaps the most important finding of this research is that annual sulfate input exceeds annual streamflow losses. Shaffer and Galloway (1982) succinctly evaluated the implications of sulfate accumulation: "Sulfate adsorption capacity of soils is finite; as these sites become saturated, sulfate output will rise until input and output are equal, resulting in a major increase in total anion concentration. Simultaneously, there is currently a net export of base cations from the watersheds; at current loss rates and in the absence of significant primary weathering, we estimate depletion of the base cation pool within 50–200 years. As sulfate output increases, this time period will shorten accordingly."

There is no evidence of accelerated cation leaching from the Fernow watershed because calcium losses are approximately balanced by input at the forest floor (throughfall). Although there has been no significant change in pH of streamflow from the experimental watershed during the past 15 years (Helvey et al. 1982), some fishery biologists believe that other streams in the central Appalachians are becoming more acidic because of increased acid deposition (Zurbuch 1984).

Since sulfate budgets are extremely important to the chemical stability of watersheds, Table 3 compares the sulfate budget for this study site with published budgets from other watersheds in the Eastern United States where mixed hardwoods are the dominant forest types. The input values are remarkably uniform considering the wide geographical area covered by the studies. The north-south range is from New Hampshire to North Carolina. The slightly lower deposition reported by Shaffer and Galloway (1982) could be caused by a combination of lower annual precipitation amounts and slightly lower concentrations of  $\text{SO}_4^{=}$ .

Although the  $\text{SO}_4^{=}$  deposition values in Table 2 are greater than would be expected in the absence of atmospheric pollution, they are much less than reported sulfate deposition in certain parts of Europe. For example, sulfate input at three study sites in the Federal Republic of Germany was 69 kg/ha on bare soil, 141–153 kg/ha for throughfall in a birch forest, and 240–258 kg/ha for throughfall in a spruce forest (Mayer and Ulrich 1978).

Sulfate losses in streamflow (Table 3) range from 53.8 kg/ha at Hubbard Brook (Likens and others 1977) to only 9 kg/ha in the Blue Ridge Mountains of Virginia (Shaffer and Galloway 1982). Undoubtedly, this range is caused by the great diversity in soil types and parent material.

**Table 3.—Input and output budgets of SO<sub>4</sub><sup>=</sup> on catchments in the Eastern United States**

Authors	Bulk precipitation	Throughfall	Streamflow
	----- kg/ha -----		
This study	39.9	53.0	25.1
Shaffer and Galloway (1982) <sup>a</sup>	26.8	—	9.0
Likens et al. (1977)	38.4	—	53.8
Lindberg et al. (1979)	39.6	96.0	—
Kelly (1979)	33.9	42.0	—
Swank and Douglass (1977) <sup>b</sup>	36.8	—	9.1

<sup>a</sup>Computed from sulfate concentration and water volume data presented by authors.

<sup>b</sup>These are the averages for seven control watersheds at the Coweeta Hydrologic Laboratory.

More research is needed on the sulfate adsorption capacity of the common soil types in the Eastern United States where sulfate deposition is greatest. By knowing the sulfate adsorption capacity of a given site, we can predict from current sulfate deposition rates the number of years required to reach that capacity. A start toward a better understanding of sulfate adsorption capacity of several soils has been made. Johnson and others (1980) concluded that watershed sulfur accumulation in soils from five sites in the Eastern United States is due to inorganic sulfate adsorption. Fitzgerald and others (1983) and Swank and others (1984) suggest that microbial conversion of sulfate to organic sulfur forms is an additional important process influencing sulfate accumulation and mobility in forest ecosystems at the Coweeta Hydrologic Laboratory. These authors also suggest that microbial processes may be important at other locations and that further research into this question is warranted.

## Conclusions

The control watershed at the Fernow Experimental Forest is currently effective in neutralizing the acids received in precipitation. The accumulation of sulfate within the ecosystem could cause watershed acidification and cation depletion in future years. Research is in progress to better understand the internal cycling of sulfate within the soil profile. Future research will attempt to define sulfate adsorption capacity of the major soil types on the Experimental Forest.

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A control watershed at the Fernow Experimental Watershed effectively neutralizes acids received in precipitation. However, sulfate input by precipitation greatly exceeds sulfate losses as streamflow and watershed acidification is a real concern.

ODC 116.1 (754)

Keywords: Central Appalachians; acid precipitation; nutrient cycling; sulfate budgets

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**Headquarters of the Northeastern Forest Experiment Station are in Broomall, Pa. Field laboratories are maintained at:**

- **Amherst, Massachusetts, in cooperation with the University of Massachusetts.**
  - **Berea, Kentucky, in cooperation with Berea College.**
  - **Burlington, Vermont, in cooperation with the University of Vermont.**
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