ION AND ACID BUDGETS FOR A FORESTED ATLANTIC COASTAL PLAIN WATERSHED AND THEIR IMPLICATIONS FOR THE IMPACTS OF ACID DEPOSITION

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Abstract - We measured the bulk precipitation inputs and stream water outputs of major ions to a 6.3 ha forested watershed from March 1981 through February 1985; and the pH of bulk precipitation and stream water from 1975 through 1984. We calculated charge balances for precipitation and stream water and used the mass balances between inputs and outputs to construct an average annual acid budget for the watershed and to draw inferences about the fate and impacts of acid deposition.

The mean pH of bulk precipitation events was 4.14 (range 3.41-6.11) for 1981-1984 while the mean pH of weekly stream samples was 5.17 (range 4.15-6.37). At the 90% confidence level, the average annual pH of both precipitation and stream water declined significantly between 1975 and 1984 and the pH of stream water was significantly correlated with precipitation pH (r^2 = 0.44, P = 0.06). Both precipitation and stream water had a slight excess of anions over cations, but the discrepancy was only 4.3% for precipitation and 1.5% for stream water. Bulk precipitation was primarily a dilute solution of nitric and sulfuric acids with smaller amounts of ammonium, chloride, and metallic cations, while stream water was primarily a solution of metallic sulfates and chlorides. The differences reflect the nearly complete retention of ammonium, hydronium, and nitrate ions; the partial retention of sulfate; and a net loss of metallic cations from the watershed.

An average of 1102 eq ha^{-1} yr^{-1} of acid was neutralized in the watershed. Of this, 76% entered as hydronium ions in precipitation, 21% was generated by ecosystem processes that retained the ammonium ions in precipitation, and 3% came from dissociation of carbonic acid within the ecosystem. Total acid neutralization evidenced by the mass balances of other ions was 1048 eq ha^{-1} yr^{-1}, of which 42% was from release of metallic cations, 38% from retention of nitrate, 20% from retention of sulfate, and <1% from retention of phosphate.

The watershed ecosystem neutralized 98% of the acidity in bulk precipitation, but the remainder was sufficient to acidify the effluent stream. Because of nitrate retention within the ecosystem, the nitric acid in precipi-

tation was effectively self-neutralizing and did not affect stream chemistry. Sulfuric acid was the acidic pollutant responsible for cation leaching and stream acidification. Natural acid sources (carbonic and organic acid dissociation) contributed less than 3% of the total acid budget. The total loss rate of all metallic cations was not alarming considering the size of soil pools and replenishment from weathering; however, calcium is present in the soil only in trace amounts. If present leaching rates continue with no replacement, 36% of the soil calcium pool would be exhausted in 70 years. Observed levels of acid and dissolved aluminum in the effluent stream are within the ranges that cause adverse changes in aquatic communities.

Existing maps of potential acid deposition impacts do not correctly identify our site as acid susceptible. Such maps should be interpreted with care until more accurate predictions are available.

INTRODUCTION

Much recent research has been directed toward evaluating the impact of atmospheric deposition of nitric and sulfuric acids on terrestrial and aquatic systems (see reviews in ERL, 1983; OTA, 1985). Acid deposition ("acid rain") can be harmful, unimportant, or even beneficial to ecosytems (Likens et al., 1977; Johnson et al., 1982; Linthurst, 1984; Paerl, 1985). For a terrestrial ecosystem and its receiving waters, the impact of acid deposition depends on the geology, soils, and ecology of the system; therefore, assessments must be made for individual systems on a total ecosystem basis (Johnson et al., 1982; OTA, 1985). We are studying the effects of acid deposition at the Smithsonian Institution's Rhode River study site on the western shore of the Chesapeake Bay, where the soils, vegetation, and land uses are typical for the coastal plain of southern Maryland. The impacts of acid deposition on coastal forests are important because the forests are inherently valuable and because terrestrial systems control the impact of acid deposition on ecologically and economically important receiving waters, such as the Chesapeake Bay and its tributaries.

We apply the small watershed technique (Likens et al., 1977) to infer the mechanisms of neutralization of acid deposition by comparing the ionic inputs in precipitation to the ionic outputs in the stream discharge from a small monitored watershed. A complete accounting of all ions is needed because hydronium ion is involved in most biological and geological reactions that pro-

duce or consume other ions (Driscoll and Likens, 1982). We construct an acid budget to evaluate the relative importance of different pathways of acid neutralization, and consider the implications of the budget for the impacts of acid deposition on the forest and on aquatic communities in the receiving waters.

METHODS

Study site - The Rhode River drainage basin is part of the inner mid-Atlantic coastal plain and is located on the western shore of Chesapeake Bay at 38°53'N, 76°35'W (20 km south of Annapolis, Maryland). The mean annual rainfall from a 160-year weather record is 108 cm, and this rainfall is distributed evenly throughout the year (Higman and Correll, 1982). The mean January and July temperatures are 1.6 and 25.2°C, respectively (Higman and Correll, 1982). We monitored the inputs and outputs from a 6.3 ha subwatershed referred to as watershed 110. The average slope is 8.3% and the soils are sandy loams from the Eocene Nanjemoy formation (Correll et al., 1984). Lower elevation soils are from the Keyport series; intermediate elevation soils are from the Howell and Donlonton series; and upper elevation soils are from the Monmouth, Adelphia, and Collington series (Kirby and Matthews, 1973). In the modern soil classification, all these series are ultisols; and the Keyport, Donlonton, and Adelphia series are aquic hapludults while the Howell, Monmouth, and Collington series are typic hapludults (Kirby and Matthews, 1973). The average particle composition of the watershed soils is 46% sand, 39% silt, and 15% clay (Pierce, 1982). For 60 cm soil cores collected in all seasons from different sites on watershed 110, the mean pH was 4.9 and soil organic matter content was 4.2% (Correll, 1982). The watershed is underlain by an impervious clay layer (Marlboro Clay) which forms an effective aquiclude and allows water discharge to be measured by a V-notch wier on the ephemeral stream draining the basin (Correll, 1977; Chirlin and Schaffner, 1977). Bedrock is located hundreds of meters below the aquiclude (Otton, 1955; Correll, 1977) and does not affect the chemistry of surface water.

Whigham (1984) described the vegetation as a mixed species, broadleaf deciduous forest dominated by white, southern red, and black oaks (Quercus alba, Q. falcata, Q. velutina); pignut and mockernut hickories (Carya glabra, C. tomentosa); tulip poplar (Liriodendron tulipifera); and sweetgum (Liquidambar styraciflua). The well developed understory is dominated by dogwood

(Cornus florida) and ironwood (Carpinus caroliniana) in higher parts of the watershed, and by black haw (Viburnum dentatum) and spicebush (Lindera benzoin) in lower areas. Ninety percent (5.7 ha) of the watershed has never been cleared, but was selectively logged prior to 1940. The remaining 10% (0.6 ha) was abandoned from farming in 1940.

Sampling - Bulk precipitation samples were taken after each rainfall event from a collector on a 13 m tower about 450 m north of the study site. Stream discharge was measured by a 120 degree sharp-crested V-notch weir and recorded every 5 min. Each week, three samples of stream water were taken for chemical analysis. Two of the samples were integrated samples composited over one week from aliquots pumped in proportion to stream flow (Correll and Dixon, 1980). One of the integrated samples was preserved with 2-3 ml of 12 N sulfuric acid per liter to prevent chemical and biological transformations. When the two integrated samples were collected, a third spot sample was taken for analysis of labile chemical species that could not be analyzed in the acid preserved samples.

Chemical analyses - Precipitation and acidified integrated stream samples were filtered through prewashed 0.45 μm Millipore HA membrane filters. Ammonia was analyzed colorimetrically after reaction with hypochlorite (Richards and Kletsch, 1964); orthophosphate by reaction with molybdate and stannous chloride (APHA, 1976); and nitrate plus nitrite by reducing nitrate to nitrite on an amalgamated cadmium column, then coupling the nitrite to sulfanilamide (APHA, 1976). Because nitrite was present only in trace amounts, the sum of nitrite and nitrate is referred to here as simply nitrate. Over the observed pH ranges of both precipitation and stream water, orthophosphate is present in the form of biphosphate ion ($H_2PO_4^-$).

Precipitation and nonacidified integrated stream samples were filtered and analyzed for sulfate and chloride by ion chromatography (Dionex Model 16). This method was also used for calcium and magnesium until December, 1983 and for sodium and potassium until March, 1984. After these dates, metallic cations were determined by atomic absorption spectroscopy on a Perkin-Elmer Model 5000. Sodium and potassium were determined with an acetylene and air flame in the presence of cesium chloride while calcium and magnesium were determined with an acetylene and nitrous oxide flame in the presence of potassium chloride (Perkin-Elmer, 1982a).

The acidities of precipitation and spot stream flow samples were measured with an expanded range pH meter. For spot stream flow samples, total alkalinity, dissolved reactive silica, and total fluoride were also determined. Total alkalinity was measured by potentiometric titration with 0.02 N sulfuric acid to endpoints of pH 4.5 and 4.2 (APHA, 1976). Within the range of observed stream pH, ionized carbonic acid is present primarily as bicarbonate ion, so the measured total alkalinity was interpreted as equivalents of bicarbonate. Bulk precipitation samples were too acid to contain significant amounts of bicarbonate. A portion of spot stream flow sample was filtered through a 0.4 μm Nucleopore filter and dissolved reactive silica determined by the molybdo-silicate method (APHA, 1976) and total fluoride by the SPADNS method (APHA, 1976). Another portion of spot stream sample was filtered through a 0.4 μm Nucleopore filter and acidified to pH 2.0 with ultrapure concentrated nitric acid for analysis of aluminum, iron, and manganese. Total dissolved aluminum was determined by atomic absorption spectroscopy on a temperature stabilized platform in the Zeeman graphite furnace in the presence of magnesium nitrate (Perkin-Elmer 1982b). Iron and manganese were determined by atomic absorption spectroscopy with an acetylene and air flame in the presence of calcium chloride.

Time spans of measurements - Eleven variables were measured continuously in both bulk precipitation and stream discharge from March 2, 1981, through February 25, 1985: volume of water (Table 1); pH (Table 2); and the concentrations of sodium, potassium, calcium, magnesium, ammonium, nitrate, biphospate, chloride, and sulfate (Table 3). There were 181 precipitation events during the four-year study. Stream flow was ephemeral so only 150 weekly samples were taken over the 208-week period. Approximately 10% of the compositional data were missing because of equipment malfunctions or faulty analyses. These missing values were estimated by interpolation, by extrapolation of previous or succeeding values, or by comparison to measurements taken at other, similar watersheds in the Rhode River drainage.

Bicarbonate, fluoride, aluminum, iron, manganese and dissolved silica were not measured over the entire four-year study period (Table 4). Alkalinity was measured between October 1981 and May 1982 and between November 1984 and May 1985. Aluminum was measured from February 1984 through May 1985 and fluoride, silica, iron, and manganese were measured from June 1984 through May 1985. Twelve weeks of data beyond the February 25 ending date of the study were used

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Table 1. Volumes of precipitation and stream discharge (cm)

	Annual volume					Average seasonal volume			
	1981	1982	1983	1984	Mean	Mar- May	June- Aug	Sep- Nov	Dec- Feb
Precipitation	102.2	115.0	138.4	109.5	116.3	34.1	30.3	24.0	27.9
Stream discharge	4.8	8.8	34.5	21.0	17.3	10.4	2.3	0.3	4.3
% runoff		4.7%	7.7%	25.0%	19.1%	14.8%	30.4%	7.5%	1.3% 15.4%

Note: Seasons defined as four 13-week periods starting approximately March 1, June 1, September 1, and December 1.

Table 2. pH of bulk precipitation and stream water

						Seasonal statistics			
	Annual statistics					Mar.- May	June- Aug.	Sep.- Nov.	Dec.- Feb.
	1981	1982	1983	1984	Mean				
Bulk precipitation									
Mean*	4.01	4.30	4.11	4.17	4.14	4.13	4.06	4.15	4.23
Median	3.99	4.28	4.12	4.17	4.16	4.18	4.00	4.17	4.25
Min.	3.41	3.81	3.44	3.53	3.41	3.41	3.44	3.53	3.60
5th %	3.62	3.97	3.50	3.59	3.64	3.70	3.52	3.60	3.70
95th %	4.68	4.92	4.89	4.95	4.82	4.92	4.84	4.89	4.69
Max.	4.85	4.93	4.92	6.11	6.11	4.93	6.11	4.92	4.74
Stream water									
Mean*	5.36	5.33	5.13	5.14	5.17	5.17	5.40	5.14	5.08
Median	5.41	5.36	5.19	5.21	5.30	5.22	5.51	5.20	5.19
Min.	4.15	4.88	4.85	4.36	4.15	4.15	5.23	4.85	4.85
5th %	4.30	5.04	4.85	4.91	4.89	4.57	5.23	†	4.88
95th %	5.82	5.91	5.52	6.12	5.32	5.84	6.32	†	5.74
Max.	5.90	6.02	5.88	6.37	6.37	6.02	6.37	5.76	5.90

*Calculated as the negative logarithm of the volume-weighted mean hydronium ion concentration.

†Equal to min. or max. because of small sample size.

Table 3. Fluxes of ten ions in precipitation and stream water

Ion	Annual flux (eq ha^{-1} yr^{-1})					Average seasonal flux (eq ha^{-1} season^{-1})			
	1981	1982	1983	1984	Mean	Mar.- May	June- Aug.	Sep.- Nov.	Dec.- Feb.

Bulk precipitation

Hydronium	1004	581	1077	741	851	253	266	169	163
Ammonium	221	194	223	326	241	97	72	34	38
Sodium	132	178	311	232	213	71	38	43	61
Calcium	114	181	145	161	150	60	31	26	34
Magnesium	91	141	111	90	108	38	15	21	33
Potassium	45	69	42	81	59	18	13	10	18
Sulfate	908	799	1030	1050	947	288	278	182	199
Nitrate	374	372	538	360	411	132	103	79	97
Chloride	410	258	378	273	330	112	61	66	90
Biphosphate	5	6	8	17	9	4	3	1	1

Stream water

Hydronium	2	4	26	15	12	7	<1	<1	4
Ammonium	3	4	15	9	8	4	2	<1	2
Sodium	77	147	479	334	259	144	39	7	69
Calcium	63	132	418	333	237	126	31	5	75
Magnesium	95	201	616	383	324	182	40	7	94
Potassium	33	72	233	97	109	69	15	4	21
Sulfate	271	414	1375	899	740	412	82	21	226
Nitrate	5	8	32	13	14	10	1	<1	3
Chloride	81	106	380	233	200	106	25	6	62
Biphosphate	1	4	9	6	5	3	1	<1	<1

Note: Ion fluxes calculated weekly as flow times concentration, then summed to give total annual, average annual, and average seasonal fluxes.

for these six chemicals to maximize available data and to ensure that all chemicals were sampled over at least one complete annual cycle.

RESULTS

Water balance - The average annual rainfall for the four years from March 1981 through February 1985 was 116 cm (Table 1); slightly above the 108 cm average calculated from a 160-year weather record, but quite close to the mean of 117

Table 4. Additional constituents of stream water[+]

| | | Volume-weighted mean concentration | | Average annual flux[*] (moles (eq | |
	N[**]	moles/l	eq/l[†]	ha^{-1} yr^{-1})	ha^{-1} yr^{-1})[†]
Cations					
Aluminum	54	4.67	14.0	8	24
Iron	35	3.96	7.91	7	14
Manganese	35	1.75	3.51	3	6
Anions					
Bicarbonate	36	16.9	16.9	29	29
Fluoride	37	10.8	10.8	19	19
Non-ionic					
Silica	37	521		901	

[+]Constituents measured for only part of the March 1981 through February 1985 study period.

[**]Number of concentration measurements made.

[*]Assuming annual stream discharge of 17.3 cm (Table 1).

[†]Assuming ionic forms of Al^{3+}, Fe^{2+}, and Mn^{2+}.

cm reported for 1967 through 1977 (Higman and Correll, 1982). Annual precipitation ranged from 102 cm in 1981 to 138 cm in 1983. Average annual stream flow was 17.3 cm (range 4.8 to 34.5) or 15% of the average annual precipitation (range 5% to 25%). The runoff percentage seems low compared to 1974-76 measurements of seven other Rhode River watersheds, which discharged 20% to 34% of precipitation inputs (Chirlin and Schaffner, 1977), but the lower water yield for watershed 110 can be attributed to the fact that watershed 110 is completely forested while 38% to 69% of the other seven watersheds are devoted

to less retentive land uses such as row crops, residences, and pastures (Correll, 1977).

Acidity of precipitation and discharge - Between March 1981 and February 1985, the average pH of precipitation was 4.14 and that of stream discharge 5.17, a difference of 1.03 pH units (Table 2). The annual averages of both precipitation pH and stream pH have declined between 1975 and 1984 (Fig. 1A). We used linear regressions of pH against time to estimate average rates of pH decline of 0.04 pH units/yr for precipitation and 0.08 pH units/yr for stream water. The regressions also indicated that the declines in precipitation pH and stream pH were statistically significant at the 90% confidence level (Fig. 1A). The pH of discharge was significantly correlated with precipitation pH at the 90% confidence level (Fig. 1B).

Charge balance - The calculation of charge balances for the precipitation and stream water solutions provides a simple check on the chemical analyses. In any solution, the equivalents of dissolved cations must equal the equivalents of dissolved anions, so a major departure from equality would indicate systematic errors in the chemical analyses or failure to measure an important ion. Only for stream water in 1981 is the absolute value of the charge imbalance greater than 7% of the total anion flux (Table 5). This was the first year that many of the chemical analyses were done in our laboratory, so there probably were larger analytical errors in 1981. However, only 9.3% of the four-year anion discharge in stream water occurred in 1981 (a drought year) so that errors in that year were relatively unimportant to the four-year averages. In fact, the four-year charge imbalance was only -1.5% for stream water and -4.3% for bulk precipitation. These figures are quite good in comparison to similar studies. For ten years of data, Likens et al. (1977) reported imbalances of +4.6% for bulk precipitation and -1.4% for stream water and considered any annual imbalance within $\pm 10\%$ to be very good.

The annual averages suggest a slight excess of anions over cations in both precipitation and stream water. The median value of Σ cations - Σ anions for 181 precipitation events is -1.56 eq/ha, which is at the borderline of being significantly different from zero at the 90% confidence level (S_{179} = -1782, P = 0.011) by the centered signed rank test (SAS, 1982). However, the median value of -0.002 eq/ha for 150 weekly samples was not statistically different from zero (S_{149} = -214, P = 0.7).

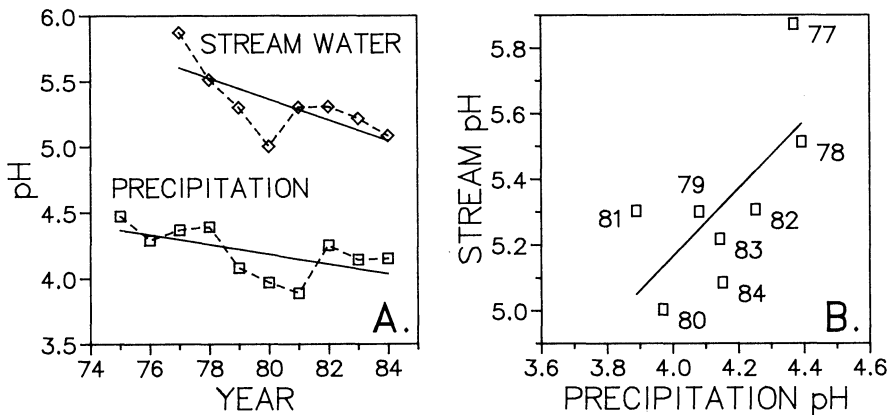Mass balance - In an average year, there were net gains of hydronium, ammoni-

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Fig. 1. Trends in average annual pH. Average pH was calculated as in Table 2 over water years extending from December thorough November. (A) shows time plots of pH and linear regressions of pH against time. The regression for precipitation was Y = -0.0372 X + 4.37 (r^2 = 0.36, $F_{1,8}$ = 4.41, P = 0.069), where Y is average annual pH and X is the year number (0 for 1975, 9 for 1984). For stream pH, the regression for eight years of data was Y = -0.0794 X + 5.76 (r^2 = 0.52, $F_{1,6}$ = 6.53, P = 0.043). (B) shows the correlation of stream pH with precipitation pH. The regression equation was Y = 1.04 X + 1.04 (r^2 = 0.44, $F_{1,6}$ = 5.51, P = 0.063), where Y is stream pH and X is precipitation pH.

um, nitrate, chloride, sulfate, and phosphate ions by the watershed and net losses of silica and of bicarbonate, fluoride, and metallic ions (Table 6, Fig. 2). The total ionic input of 3319 eq ha^{-1} yr^{-1} exceeds the total output of 1999 eq ha^{-1} yr^{-1}, so overall, the ecosystem retains about 40% of ions input. The primary cations in precipitation were hydronium and ammonium while the primary anions were nitrate and sulfate. In stream discharge, the major cations were metallic cations and the major anions were sulfate and chloride. Bulk precipitation is primarily a dilute solution of nitric and sulfuric acids while stream flow is a solution of metallic sulfates and chlorides. The acid

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Table 5. Charge balances for precipitation and stream water (eq ha^{-1} yr^{-1})

	Bulk Precipitation					Stream Water					
	1981	1982	1983	1984	Mean	1981	1982	1983	1984	Mean	Mean*
Σcations	1606	1334	1911	1632	1623	272	560	1786	1172	948	992
Σanions	1696	1435	1954	1700	1696	357	532	1796	1150	959	1007
Σall ions	3302	2769	3865	3332	3319	629	1092	3583	2322	1907	1999
Imbalance[†]	-90	-91	-43	-68	-73	-85	+28	-10	+22	-11	-15
% imbalance[+]	-5.3	-6.3	-2.2	-4.0	-4.3	-24	+5.3	+0.6	+1.9	-1.1	-1.5

*Includes ions in Table 3. Other columns include only ions in Table 2.

[†]Σcations - Σanions.

[+]Charge imbalance as a percentage of total anion flux.

in precipitation is mostly neutralized in the ecosystem and replaced by metallic cations. Most of nitrogen (ammonium and nitrate) in precipitation is removed in the ecosystem. Some of the sulfate in precipitation is retained, but sulfate still has a proportionately larger anionic role in discharge than in precipitation, and sulfate is the mobile anion balancing most of the metallic cations leaving the ecosystem.

Acid budget - Measurements of the pH and volume of precipitation and stream flow yield a direct measurement of the input and output of acidic ions to the ecosystem, and by difference, the acidity neutralized within the system. However, such a simple analysis ignores acidity generated within the ecosystem and yields no useful inferences about the relative magnitudes of external and internal acid sources or the processes by which acidity is neutralized. The mass balance data for all major ions (Table 6) permit the construction of a more complete and informative acid budget. All chemical reactions must proceed so that mass and charge balance are preserved, so reactions that consume hydronium ion must either consume a balancing anion or produce some other cation to replace the hydronium ion. Similarly, processes producing hydronium ions must simultaneously produce a balancing anion or consume some other cation in exchange for the hydronium ion produced. Therefore, the measured mass balance of any ion can be combined with assumptions of how many hydronium ions

Table 6. Mass balances (input fluxes - output fluxes)

Ion	Annual balance (eq ha^{-1} yr^{-1})					Mean seasonal balance (eq ha^{-1} season^{-1})			
	1981	1982	1983	1984	Mean	Mar.- May	June- Aug.	Sep.- Nov.	Dec.- Feb.
Hydronium	1002	577	1052	726	839	246	265	169	159
Ammonium	218	189	208	317	233	93	70	34	36
Sodium	54	31	-168	-102	-46	-74	0	37	-9
Calcium	51	49	-272	-172	-86	-67	0	21	-41
Magnesium	-4	-59	-504	-293	-215	-144	-25	15	-62
Potassium	13	-3	-191	-16	-49	-50	-3	7	-3
Sulfate	637	385	-345	151	207	-124	197	162	-29
Nitrate	369	363	506	347	396	122	102	79	94
Chloride	329	152	-2	40	130	6	36	61	28
Biphosphate	4	2	-1	11	4	1	2	1	1
Aluminum(3+)					-24*				
Iron(2+)					-14*				
Manganese(2+)					-6*				
Bicarbonate					-29*				
Fluoride					-19*				

*Assumes that the unmeasured precipitation input is zero.

are produced or consumed in ecosystem reactions involving that ion to calcu-
late the net production or consumption of acidity implied by the observed mass
balance.

We based our acid budget on the following assumptions about the produc-
tion or consumption of acidity in different ecosystem reactions. Further dis-
cussions of these assumptions may be found in Driscoll and Likens (1982) and
Johnson et al. (1982).

1. Plant uptake of one equivalent of a cation (such as NH_4^+ or M^+, where
M^+ is any metallic ion) is accompanied by the release of one equivalent of
hydronium ion. Similarly, plants exchange one equivalent of hydroxide ion for
each equivalent of nitrate, phosphate, or sulfate assimilated.

2. Metallic cations lost from the ecosystem can be displaced from soil
exchange sites, displaced from living or dead biomass, or produced in chemical
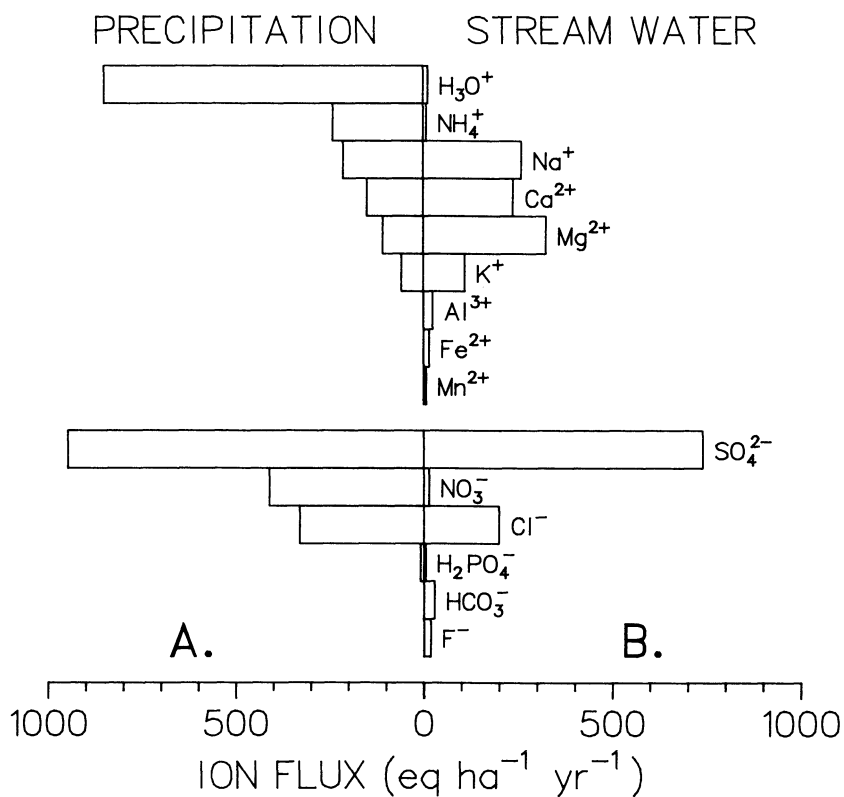weathering of soil minerals. All three processes consume one hydronium ion

PRECIPITATION   STREAM WATER

Ion	
H_3O^+	
NH_4^+	
Na^+	
Ca^{2+}	
Mg^{2+}	
K^+	
Al^{3+}	
Fe^{2+}	
Mn^{2+}	
SO_4^{2-}	
NO_3^-	
Cl^-	
$H_2PO_4^-$	
HCO_3^-	
F^-	

A.   B.

1000   500   0   500   1000

ION FLUX $\left(eq\ ha^{-1}\ yr^{-1} \right)$

Fig. 2. Average annual ion fluxes in precipitation (A) and stream water (B).

for each ionic equivalent of metal lost.

　　3. Oxidation reactions produce hydronium ions while reduction reactions consume hydronium ions. The reduction of one mole of sulfate to sulfide consumes two moles of hydronium ions, or one equivalent of hydronium per ionic equivalent of sulfate. Similarly, the oxidation of sulfide to sulfate produces one equivalent of hydronium ion per ionic equivalent of sulfate. Reduction of one equivalent of nitrate to nitrous oxide or nitrogen (denitrification) consumes one equivalent of hydronium ion. Oxidation of one equivalent

of ammonium to nitrate (nitrification) produces two equivalents of hydronium ion, but if the resulting nitrate is taken up by plants or denitrified, one equivalent of hydronium ion is consumed in the second process and the net reaction produces one equivalent of hydronium ion.

4. Immobilization of ions in the soil can give apparent neutralization of hydronium ions. For example, if ammonium ion is adsorbed to the soil particles, then the hydronium ion associated with the ammonia molecule is also immobilized. Similarly, sulfate ions may be adsorbed in soils high in sesquioxides, such as gibbsite ($Al[OH]_3$), hematite (Fe_2O_3), or limonite ($Fe_2O_3 \cdot H_2O$). Although this adsorbtion is not a true neutralization, it also immobilizes the associated hydronium ions (or other cations) that were paired with the sulfate in precipitation so that those cations do not appear in the ecosystem output (Johnson et al., 1982; OTA, 1985).

5. Carbonic acid in the soil solution can dissociate to produce one equivalent each of hydronium and bicarbonate ion.

6. Chloride and fluoride enter and leave the ecosystem as neutral salts and do not participate in reactions producing or consuming hydronium ions.

Fig. 3 presents a schematic acid budget based on the above assumptions. We emphasize that this is not a rigid mechanistic diagram, but simply a visual accounting system for hydronium ion. Arrows leading toward the central box represent retentions of ions by the ecosystem, while arrows leading away from the box represent losses of ions. Fig. 4A presents the same budget as a histogram that focuses attention on the total amounts of production and consumption of acidity. Of the total acidity neutralized in the system, 76% enters as hydronium ions in precipitation, 21% is produced internally by retention of ammonium ions in precipitation, and 3% is produced internally by dissociation of carbonic acid. Approximately equal amounts of acidity are neutralized by the release of metallic cations (42%) and the retention of nitrate (38%). Retention of sulfate provides a smaller, but still important percentage of acid neutralization (20%). There is a slight excess of acid inputs (1102 eq ha^{-1} yr^{-1}) over neutralization (1048 eq ha^{-1} yr^{-1}) so the budget does not balance exactly; however, the 4.8% discrepancy is quite small given that these two numbers are derived from several thousand individual flow measurements and chemical analyses. Similar levels of excess of acid production have been reported for other acid budgets (4.5% excess acid, Driscoll and Likens, 1982; 6% excess acid, Hemond and Eshleman, 1984).
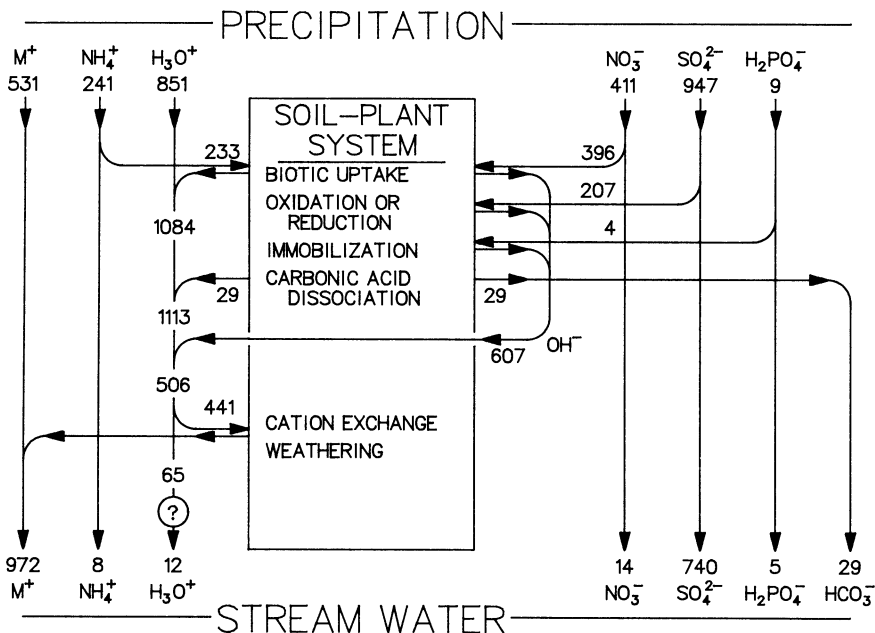
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Fig. 3. Schematic acid budget. Numbers are average annual ion or acid fluxes in eq/ha from Tables 3, 4, and 6. The question mark represents the 5% of the total acid input of 1113 eq ha^{-1} yr^{-1} that is not accounted for by the above acid sinks, yet does not appear in the stream water.

DISCUSSION

Acid budget - The low pH and high concentrations of sulfate and nitrate in bulk precipitation confirm that the Rhode River site is receiving significant acid deposition. The average annual pH of 4.14 puts the site in the zone of most acidic rainfall (pH $\leq$ 4.2) within the acid rain belt of the eastern U.S. (OTA, 1985). The forested watershed studied here presently neutralizes over 98% of the total acidity in bulk precipitation, but the unneutralized portion does have an effect on stream pH, as demonstrated by the parallel declines in the pH of precipitation and stream water and by the correlation of stream pH
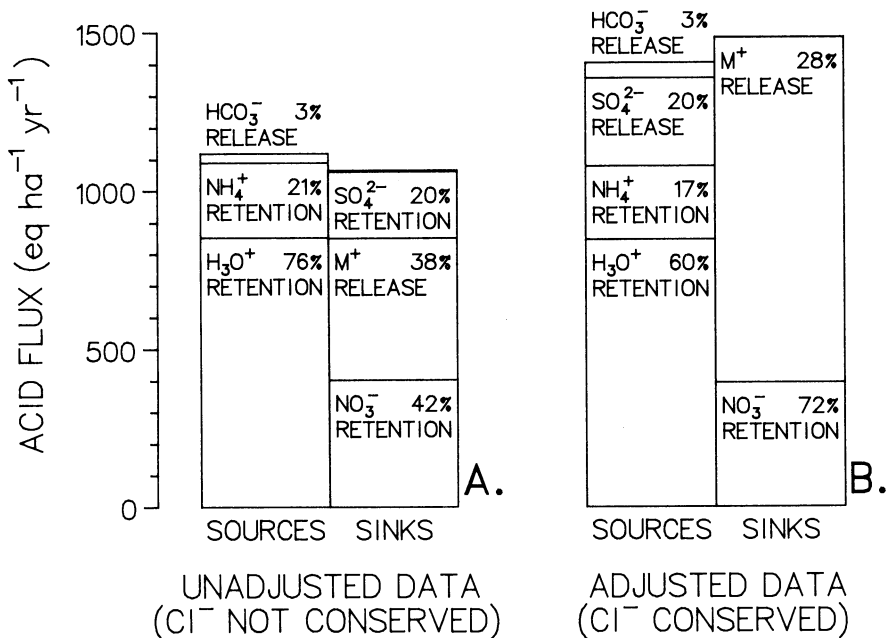
Fig. 4. Net production and net neutralization of acidity. (A) is the unad-
justed acid budget while (B) includes an adjustment that balances the chloride
budget (see discussion).

with precipitation pH (Fig. 1). One encouraging aspect of the pH trends is
the upswing in both precipitation and stream pH after 1980-1981. An earlier
analysis of data from 1975 to 1981 (Correll et al., 1984) indicated very steep
rates of pH decline. If those trends had continued, the average pH of bulk
precipitation and stream water for 1984 would have been 3.63 and 4.57--much
less then the actual values of 4.17 and 5.14. The data still indicate signifi-
cant drops in pH, but the rates of decline are less alarming than previously
indicated.

Hydronium ions in precipitation and those generated by retention of am-
monium ions in precipitation by the ecosystem together contribute 97% of the
total acid budget of the watershed (Fig. 4A). Carbonic and organic acids,

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which are the important natural sources of acidity to unpolluted forests
(Cronan et al., 1978; Johnson et al., 1983), are almost completely overshad-
owed by the anthropogenic acids in precipitation. The dissociation of car-
bonic acid, as evidenced by the efflux of bicarbonate in stream water, contri-
butes less than 3% of the acid budget. Similarly, organic acids do not appear
to dissociate to produce significant amounts of hydronium ions within the wa-
tershed. If this process was important, the charge balance should give an
apparent anion deficit because organic anions were not included (Driscoll and
Likens, 1982; Johnson et al., 1983). Instead, there was a small anion excess
(Table 5).

Sulfuric, rather than nitric acid, is the acidic airborne pollutant with
the greater potential to impact forested watersheds and effluent streams in
the Rhode River. This conclusion follows because 97% of the deposited nitrate
is retained in the ecosystem by plant uptake and denitrification, resulting in
the neutralization of one equivalent of hydronium ion for each equivalent of
nitrate retained. From a watershed perspective, the input of nitric acid is
essentially self-neutralizing and does not affect the chemistry of stream wa-
ter. However, if nitrate retention occurs in deeper soil layers, the nitric
acid might still have important effects on the vegetation and soils before
reaching the retention zone, including physiological stresses on plants and
transport of nutrient cations below the rooting zone. Sulfate provides 73% of
total anion flux in stream water and chloride provides 20%, while anions of
other acids (nitrate, bicarbonate, and organic anions) are only 4.2% of total
anion efflux. These percentages suggest that atmospheric sulfuric acid is the
dominant source of cation leaching and stream acidity (Cronan et al., 1978;
Johnson et al., 1983).

Hemond and Eshelman (1984) also reported 97% nitrate retention for two
watersheds in central Massachusetts and asked whether high levels of nitrate
removal are the norm for the eastern U.S., rather than more modest levels of
14-44% nitrate removal in earlier reports from Hubbard Brook, New Hampshire
and the Integrated Lake-Watershed Acidification Study in the Adirondack Moun-
tains of New York (see references in Hemond and Eshelman, 1984). Our study
does not answer this question, but is an example of a site in a different phys-
iographic province where nitrate retention is almost complete. Thus, our
study supports the importance of nitrate retention as a buffering process in
the eastern U.S., and lends further weight to the proposals of Hemond and

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Eshelman (1984) that consistently low nitrate concentrations in surface water may indicate a high capacity for terrestrial ecosystems to neutralize nitric acid pollution and that more detailed studies of the mechanisms of nitrate retention may help clarify the modifying effects of forest nutrition and land use on acid deposition. Clearly nitrate retention should not be ignored in regional modeling efforts (e.g., Bischoff et al., 1984) nor in geochemical analyses of watershed weathering (e.g., Katz et al., 1986).

Forest impacts - Acid deposition can affect forests directly by injuring plant tissues or indirectly by changing soil nutrient pools. The sulfate and nitrate in acid deposition are important plant nutrients that may fertilize forests limited by these nutrients (Likens et al., 1977). More negatively, acid deposition can remove essential nutrient cations from ecosystems and mobilize soil aluminum, which can be directly toxic to plant roots and interfere with uptake of essential metallic cations (Ulrich et al., 1980; Hutterman and Ulrich, 1984). The possible effects include reduced growth or regeneration, increased mortality, and changes in species composition. The potential for direct acid damage to plants has been verified in laboratory studies and the harmful effects of cation deficiencies on plants are well known, but to date, no field studies have unequivocally demonstrated deleterious effects of acid deposition on U.S. forests (Evans, 1982; Linthurst, 1984; OTA, 1985). Many studies have attempted to evaluate the importance of cation leaching, but have generally concluded that cation loss rates from acid deposition are not alarming because the loss rates are small relative to soil pools (Johnson et al., 1983). Also, the soil pools are constantly replenished by cations released from parent materials in chemical weathering reactions that are actually accelerated by increased acidity.

We do not have measurements to examine possible physiological effects of acid deposition on our forests or to evaluate the effects of nitrate and sulfate fertilization; however, the loss rate of calcium from our system is unusually alarming. Currently, 441 eq/ha of metallic cations are annually leached from the forested watershed. This rate is lower than cation leaching rates reported for other sites in the eastern U.S. (e.g. 1270 eq ha^{-1} yr^{-1} at Hubbard Brook, Likens et al., 1977; approximately 1200 eq ha^{-1} yr^{-1} in central Massachusetts, Hemond and Eshelman, 1984; 890-2300 eq ha^{-1} yr^{-1} in eastern Tennessee, Johnson et al., 1982), but must be evaluated in comparison to the

Table 7. Cation loss rates

	1976 Soil pool [*] (keq/ha)	Measured fluxes[†]		
		Average annual loss		
		(keq/ha)	%	Percent loss in 70 years	Years to 100 %
Ion					
Potassium	16.0	0.049	0.31%	22%	324
Calcium	16.9	0.086	0.51%	36%	197
Magnesium	510	0.215	0.04%	3%	2372

[*]Amounts of total Ca^{2+} and exchangeable K^+ and Mg^{2+} in the upper 60 cm of soil (from Correll et al., 1984).

[†]Average annual loss rate (Table 6) as a flux and as a percentage of the soil pool. Also gives the percentage of surface soil pool lost in 70 years and the time required to exhaust the pool if current losses continue with no replacement.

the amounts of exchangeable cations in the surface soil of our study site (Table 7). The comparison is difficult to interpret for potassium and magnesium because there are large amounts of these elements in the soil minerals (Pierce, 1982) which can be weathered to replenish available potassium and magnesium at some unknown rate. However, there are no significant sources of calcium in the soil minerals (Pierce, 1982), so Table 7 may give the true net loss from the ecosystem. At the current rate of loss, the calcium pool in the soil would be depleted in 197 years, and 36% would be lost in a single human lifetime of about 70 years.

Coastal plain soils in southern Maryland generally have only trace levels of calcium (Foss et al., 1969; Kirby and Matthews, 1973; J. W. Pierce, personal communication), so that acid-mediated leaching of calcium may be a particularly significant loss to the terrestrial ecosystems of the region. However, our analysis of calcium loss rates must be interpreted with two important caveats. First, our estimate of the forest calcium pool does not include the calcium in vegetation, which may be 1 to 5% calcium in dry weight (Baker, 1983). Given that forests maintain a large standing crop of biomass, the vegetation pool could easily equal or exceed the measured soil pool in Table 7. For example, Likens et al. (1977) reported that the standing stock of plant

biomass and forest floor litter in their northern hardwood forests contained 43 keq/ha of calcium. Second, we do not know the rate of leaching by carbonic and organic acids under the natural weathering regime that existed prior to the advent of acid deposition in the twentieth century; so we can not quantify the extent to which acid deposition has increased the natural leaching rates. However, the fact that stream pH has dropped in response to acid deposition indicates that the acid load has increased above natural levels and strongly suggests a corresponding increase in cation leaching rates. Cronan et al. (1978) concluded that leaching rates are accelerated as the pH of precipitation drops below 4.5.

Stream impacts - More than 98% of the total acidity in bulk precipitation was neutralized within the forested watershed, but the remainder decreased the pH of the stream. Because the forests cannot completely buffer the streams from acid deposition, aquatic ecosystems are also vulnerable to damage. The average pH of 5.17 in the effluent stream represents a level of acidity that can have direct toxic effects on fish, invertebrates, and other aquatic organisms and can alter the community compositions and trophic structures of aquatic ecosystems (Haines, 1981; Schindler et al., 1985). Acid deposition can also raise the level of dissolved aluminum in streams. Although the net output of 24 eq ha^{-1} yr^{-1} of dissolved aluminum from watershed 110 corresponds to only 2% of the total acidity neutralized, this small flux elevates the dissolved aluminum concentration in the stream to potentially dangerous levels. The average dissolved aluminum concentration was 4.67 µM, and maximum values near 9.3 µM were recorded for two weeks in March and April, 1984. These values are less than the aluminum concentration reported for low order streams in New England (e.g. 26 µM, Johnson, 1979; 67 µM, Cronan and Schofield, 1979), but similar levels of pH and dissolved aluminum have been shown to induce mortality or sublethal growth reductions (Cronan and Schofield, 1979; Driscoll et al., 1980; Hall et al., 1985). Furthermore, the highest values of acid and dissolved aluminum concentrations for our stream have been recorded in the spring, when many economically important anadramous fish species of the Chesapeake Bay enter the streams to spawn. Juvenile fish are even more susceptible to the deleterious effects of low pH than are adults (Haines, 1981; Schindler, 1985), so the unusually high spring acidities may effectively prevent reproduction and may be partly responsible for recent precipitous declines in the Chesapeake Bay populations of many economically important anadra-

mous fish species, such as striped bass (Morone saxatilis), white perch (M. americana), yellow perch (Perca flavescens), American shad (Alosa sapidissima), and others (Correll et al., submitted). Of course, the stream draining watershed 110 is not representative of coastal plain streams because few watersheds are completely forested and land use can have important effects on stream acidity. Preliminary comparisons of watershed 110 to nearby watersheds dominated by crops and pastures suggests that average stream acidity is higher, but more stable in the forested system. However, the cropland and pasture streams reach more acidic extremes during episodic acid surges that may be especially dangerous to aquatic organisms (Correll et al., 1984, Correll et al., submitted).

Chloride balanced acid budget - One aspect of our ion mass balances is troubling and may have important implications for the acid budget and inferences about the sources and sinks of acidity in the watershed. Of the total average ionic influx of 3319 eq ha^{-1} yr^{-1}, only 1999 eq ha^{-1} yr^{-1} was recovered in the effluent stream; so about 40% of the total ionic influx was retained in the watershed. The total retention is difficult to interpret because some ions (nitrate, ammonium, hydronium) are almost completely retained through various biogeochemical reactions, while there is a net loss from the ecosystem of other ions (calcium, magnesium, bicarbonate). However, chloride is generally regarded as a conservative tracer that is neither retained in biogeochemical reactions nor generated by weathering, so that recovery of chloride in the stream water should equal the input in precipitation over the long term (Todd, 1964; Burton et al., 1977; Vitousek, 1977; Lowrance et al., 1985). Therefore, the observed recovery in stream output of only 61% of the four-year chloride input is disturbing.

We considered several hypotheses to explain the fate of this missing chloride: temporary storage in the soil during periods of high evapotranspiration (Correll et al., 1984), storage in aggrading forest biomass (Likens et al., 1977), a net gain in ground water storage over the four-year period, and possible errors in stream flow measurement. Since three of the four study years had above average annual rainfall we discarded the hypothesis of soil storage. Our best estimate of net wood production (12800 kg ha^{-1} yr^{-1}, Peterjohn and Correll, 1984) could explain a retention of only 36 eq ha^{-1} yr^{-1} of chloride if the concentration of chloride in wood is about 0.01% of dry weight (Epstein, 1972; D. L. Correll, unpublished). We discarded the hypothesis of

storage in ground water because a net gain of about 60 cm of ground water would be required to store the missing chloride at the concentration observed at the end of the study. Precipitation and discharge characteristics in November-January 1980 were very similar to the same period in 1985, so the amounts of stored ground water should also be similar, not increased by 60 cm. Our measurements of stream discharge are accurate to $\pm$3-5% (Chirlin and Correll, 1977), but more serious, systematic hydrological errors could result if drainage divides were incorrectly mapped, if the topography of the aquiclude layer differs from surface topography, or if there were holes in the aquiclude allowing unmeasured losses to deep aquifers. We compared the winter 1978 water yields of several Rhode River watersheds after the watersheds were fully recharged by a long period of heavy precipitation. Watershed 110 should have had an unusually low water yield if it has a break in the aquiclude while the other watersheds do not, but the observed 40 cm of runoff was not noticeably different from eight other watersheds, which yielded between 35 and 45 cm. We also compared the seasonal outputs of chloride to the seasonal inputs. If there was a leak in the aquiclude, greater absolute amounts of chloride should be unaccounted for during periods of highest rainfall and discharge, because these would be the periods of greater absolute leakage. Instead we observed more absolute chloride retention during periods of lowest precipitation and discharge.

None of the hypotheses explained the observed chloride retention. The retention may be due to analytical errors or other storage mechanisms that we have not considered, but other investigators have also reported unexplained net retentions of chloride in input-output analyses of ecosystems (Likens et al., 1977; J. W. Gilliam, personal communication). The Hubbard Brook study (Likens et al., 1977) reported chloride retentions of 57 eq ha^{-1} yr^{-1} (about 29% of inputs) and substantial releases of chloride after deforestation, suggesting some internal reservoir in the forest system. These results cast doubt on the common assumption that chloride is a conservative tracer in ecosystem studies.

Because we were unable to explain the observed chloride retentions, we also calculated a revised acid budget after applying an adjustment that balanced the chloride budget (Fig. 4B). All output fluxes were multiplied by 1.650, the ratio of average annual chloride input to chloride output (Table 2). This adjustment, which makes the output flux of chloride equal to the

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chloride input, assumes that there is some unmeasured loss of water from the system and the lost water is chemically identical to stream water. The adjustment hardly changes net retentions of hydronium ion, nitrate ion, or ammonium ion because the output fluxes are so small that multiplication by 1.650 is inconsequential. However, the net loss of metallic cations is increased from 441 eq ha^{-1} yr^{-1} to 1071 eq ha^{-1} yr^{-1} and the sulfate balance is changed from a net retention of 207 eq ha^{-1} yr^{-1} to a net production of 273 eq ha^{-1} yr^{-1}. Because sulfate retention is a symptom of internal acid neutralization while sulfate production is evidence of acid production, the change in sulfate balance gives the major difference between the original budget and the chloride-balanced budget: an increase in the sum of acid sources from 1102 to 1381 eq ha^{-1} yr^{-1}. The budget remains reasonably well balanced because an increase in metallic cation loss approximately offsets the combined effect of 273 eq ha^{-1} yr^{-1} of new acid associated with sulfate production, and the loss of 207 eq ha^{-1} yr^{-1} of acid sink associated with sulfate retention in the unadjusted budget.

It is difficult to independently resolve which of the two budgets in Fig. 4 is more reasonable for the forested watershed. The adjusted value of metallic cation loss is closer to values reported at other sites in the eastern U.S. (see previous discussion of forest impacts), but the lower value of the unadjusted budget is certainly plausible. Nor can we predict from independent information whether the watershed should produce or retain sulfate. Highly weathered soils are typically high in the sesquioxide compounds that can retain sulfate (Johnson et al., 1979) and our soils are highly weathered (Kirby and Matthews, 1973), so sulfate retention seems possible. However, the soils in some areas of the Rhode River watershed contain pyrite (iron sulfide, Otton, 1955), which could be oxidized to produce sulfate, so sulfate production is also possible. Also, sulfate can enter the system by dry deposition on the forest canopy, a process that is poorly measured by bulk precipitation (Johnson et al., 1979). This unmeasured component of sulfate input, if significant, would give an apparent sulfate production in our analysis (Hemond and Eshelman, 1984). Since we have no clear evidence of important hydrological errors, we favor the unadjusted budget (Fig. 4A). Acceptance of the adjusted budget would not change our discussion of the impacts of acid deposition on forests and streams, except in the area of cation loss. With the larger cation loss rates of the adjusted budget, the annual loss of all metallic cations

would be 2.4 times greater than implied by the unadjusted budget, while the annual loss of calcium alone would be 240 eq ha^{-1} yr^{-1}, 2.8 times the unadjusted value. At this rate of depletion, 99% of the soil calcium pool would be leached away in a 70 year human lifetime.

Comparison to regional assessments - Much attention is currently focused on identifying areas where terrestrial and aquatic resources are susceptible to damage by acid deposition. For example, contractors for the Office of Technology Assessment (1985) have produced maps of regions where soils and surface waters are susceptible to acidification. These maps do not place the Rhode River area within a susceptible region, yet our site specific data indicate that adverse effects of acid deposition have been underway for several years. Other recent work suggests that acid deposition may be a major factor in the recent decline of anadromous fish populations throughout the Chesapeake Bay (Correll et al., submitted). These population declines would represent a major regional impact of acid deposition that has been missed in existing efforts to map sensitive resources. Our results suggest that further refinement is needed in identifying acid sensitive areas and that existing maps may underestimate the extent of susceptible areas.

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DISCUSSION: Weller Paper

Question (Alaback): I was wondering how confident you are with your estimates of plant uptake and what components you were considering in making that a condition?

Answer: We really haven't tried to partition the amount of plant uptake. Nitrate could be going to plants, or it could be going to microbes. We know what the total amount is because we have data on what is coming in and what is going out. But, we can't really partition it between those two pathways.

Question (Pionke): Generally you have a low pH stream, water coming into the stream, I guess it is around 4 or 5.

Answer: The average is about 5.2.

Question (Pionke): You seem to be finding a lot of silicate discharged, but not much aluminum. I guess you are ascribing that to mineral weathering. Do you hope to resolve the high silicic acid and low aluminum in your discharges?

Answer: That is a dilemma we have. We saw this large discharge of silica of about 943 moles of silicic acid/year, so there is evidence weathering processes are going on. But, we couldn't take a set of chemical reactions and put them together in such a way that all constraints were met.

Question (Pionke): Do you have any organic analyses?

Answer: If you had a lot of organic anions one major symptom of that would be in your charge balance. You would see a deficit of anions. Instead, we see an excess of anions. That would seem to argue against that hypothesis.

WATERSHED
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PERSPECTIVES

Edited by
DAVID L. CORRELL

Published for
SMITHSONIAN ENVIRONMENTAL
RESEARCH CENTER
BOX 28
EDGEWATER MD 21037

by the
SMITHSONIAN INSTITUTION PRESS
WASHINGTON DC 20560