

CHAPTER 5

Ion Balances Between Precipitation Inputs and Rhode River Watershed Discharges

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In recent years, environmental scientists in several locations have gradually perceived the importance of chemical fluxes that enter various ecosystems in precipitation. To a considerable extent this concern has resulted from the documentation of steadily increasing acidity in rainfall [1]. This increased flux of hydrogen ions in precipitation is primarily due to increasing concentrations of sulfur and nitrogen oxides in the atmosphere [2]. In such places as Sweden [3,4], the White Mountains of New Hampshire [5-7], the Smoky Mountains of North Carolina [8,9], the Appalachian Mountains of Tennessee [9], the Rocky Mountains in Colorado [10] and the Sangre de Cristo Mountains of New Mexico [11] research reports have documented and summarized both ionic inputs in precipitation and ionic losses in land discharge. Differences between ionic inputs and outputs can then be ascribed to the interactions of vegetation and soils with chemical components in the precipitation. Most of these published studies were conducted in mountainous regions with low human populations and limited land management. None were in the Atlantic Coastal Plain of the United States. An understanding of natural (i.e., unmanaged) systems is theoretically important but of limited value when extrapolated to complex, multiple-land-use systems. The land area of the United States is a mosaic of primarily three land uses: pasture/rangeland (39%), ungrazed forest (21%) and cropland (17%) [12]. Thus understanding the nutrient dynamics of multiple-land-use basins is critically important for wise management of the land.

In the early 1970s the Smithsonian Institution initiated long-term environmental studies of the Rhode River Ecosystem in Maryland with an emphasis on systems analysis (Figure 1). This system is located on the coastal plain and the most abundant land uses on the watershed are forest, cropland and pastureland. The forest is composed of mixed deciduous, broadleaved species typical of the eastern U.S.

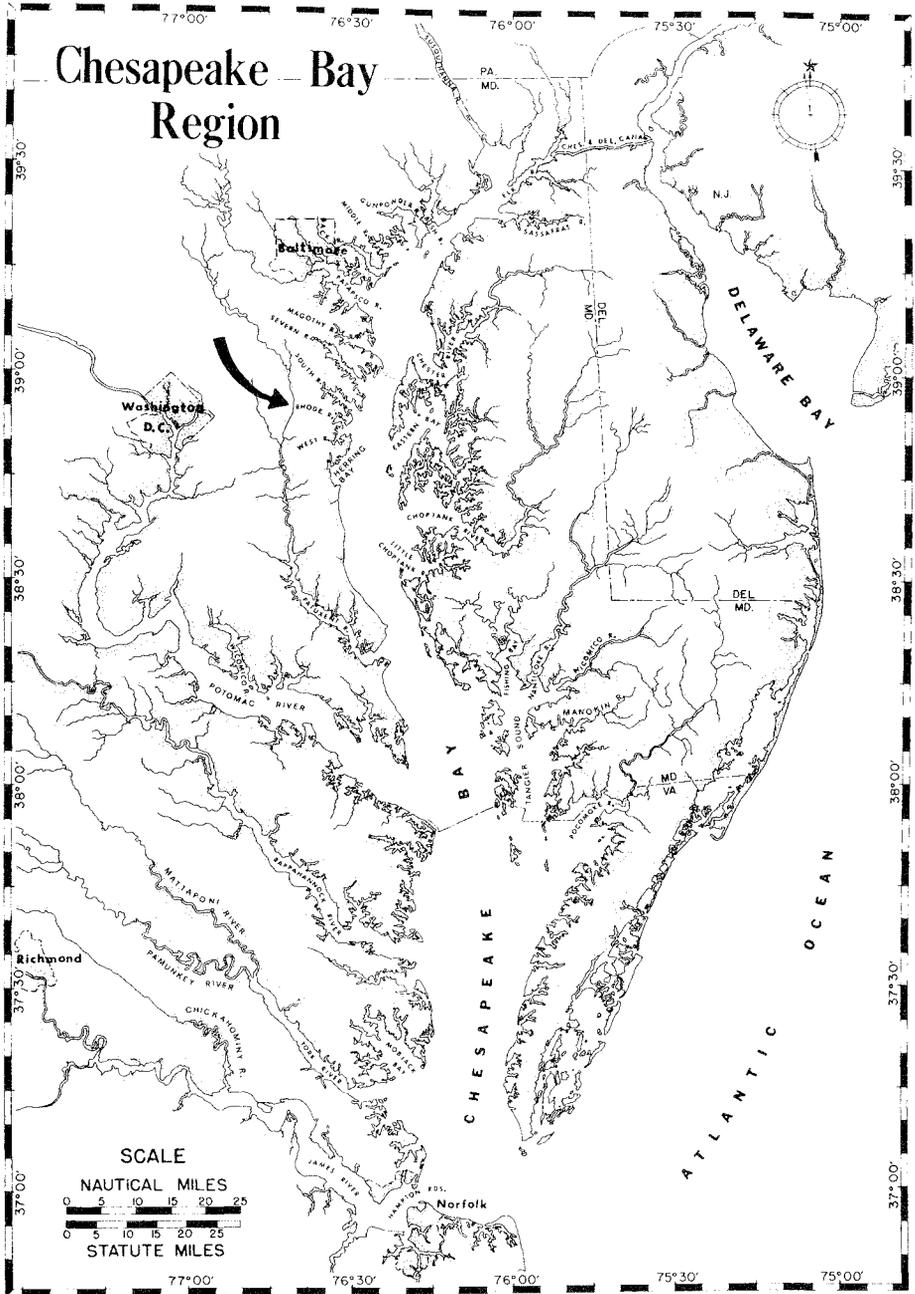


Figure 1. Map of the Chesapeake Bay Region. Location of Rhode River Ecosystem is marked with an arrow.

deciduous forest. Since no calcareous minerals are found in the watershed soils, they are poorly buffered against acid rain inputs. Past research on the Rhode River system has included the effects of nutrients in precipitation on the estuary [13] and the watershed [14,15]. It also has documented changes in the pH of precipitation and stream discharges for 7–10 years.

The objectives of the project reported here were:

1. a comparison of ion inputs from precipitation with outputs in land discharge for a mature forest;
2. assessing how cropland and pasturelands differ in their ion balances due to management practices; and
3. tracing changes in ionic composition as water moves down through the watershed either over the soil/litter surface during storms or through the soils as shallow groundwater.

Available data indicate that the coastal plain region might be especially sensitive to displacement of potassium, magnesium and calcium by hydrogen ions, since these elements are present only in low concentrations in the soils and no calcium-containing minerals occur in the surface soils. Thus, it was anticipated that the data resulting from this study would allow us to test whether important losses of these essential plant nutrients were occurring from the watershed.

In addition to the possible effects of cation displacements, another concern involves the increasing flux of nitrate and sulfate from the atmosphere. Nitrate is a significant source of nitrogen to forests and both sulfate and nitrate can serve as electron acceptors in anoxic soils.

A long-term objective is to understand the impact of management practices such as liming and fertilizing not only on chemical ion balances, but also on plant and animal species that are adapted to a specific set of ion-balance and pH conditions. The ability to predict changes at the ionic level could result in more efficient management and a more stable ecosystem.

SITE DESCRIPTION

The Rhode River Estuary is a tidal tributary to Chesapeake Bay (Figure 1), located approximately 20 km south of Annapolis, MD (38°53' N, 76°35' W). Geologically, the Rhode River watershed is located on the inner mid-Atlantic Coastal Plain. It has sedimentary soils from the Pleistocene Talbot formation at low elevations on the eastern portion of the watershed, Eocene Nanjemoy formation soils at low elevations further west, Miocene Calvert formation soils at intermediate elevations and Pleistocene Sunderland formation soils at the highest elevations. A few outcrops of Pleistocene Wicomico formation soils are also found. The mineralogy of the surface soils in the watershed is fairly uniform with high levels of montmorillonite [$\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$], intermediate levels of illite (interlayered mica and montmorillonite) and kaolinite ($\text{H}_4\text{Al}_2\text{Si}_2\text{O}_9$), and lower levels of plagioclase

($\text{NaAlSi}_3\text{O}_8$), potassium feldspar (KAlSi_3O_8), gibbsite [$\text{Al}(\text{OH})_3$] and chlorite [$(\text{Al}_2\text{Si}_6)\text{Al}_2\text{Mg}_{10}\text{O}_{20}(\text{OH})_{16}$] in the silt and clay fractions. The soils differ locally primarily with respect to the proportions present of sand, silt and clay. Underlying the watershed is an impervious clay layer (the Marlboro Clay) which acts as an effective aquaclude [16]. A layer of glauconitic sands [$\text{K}_{15}(\text{Fe},\text{Mg},\text{Al})_{4-6}(\text{Si},\text{Al})_8\text{O}_{20}(\text{OH})_4$] is found immediately above the Marlboro Clay.

Three small subwatersheds representative of the most abundant land uses on the watershed and in the Atlantic Coastal Plain were selected for study. All three are within the Eocene Nanjemoy formation and have fine sandy loam soils, which have been intensively mapped by the Soil Conservation Service. One study site (watershed) was composed of 6.3 ha of mixed, broadleaved deciduous forest. An area on the upper part (0.6 ha) was farmed until approximately 1940, then abandoned. The remaining 5.7 ha were never clear-cut or farmed [17,18]. The average watershed slope is 8.3%. The mean surface soil pH of the forest site was 4.9 and surface organic matter content was 4.2%. The soils of the lower elevations are from the Keyport series, those at intermediate elevations are from the Howell and Donlonton series, while those at the highest elevations are from the Monmouth, Adelpia and Collington series.

The second study watershed (6.1 ha) was composed of 4.4 ha of perennial cattle pasture and 1.7 ha of grazed riparian forest. Surface soil pH was 5.3 and surface soil organic matter content was 3.5%. Average watershed slope was 10.8%. The soils of the lower elevations are from the Monmouth series, those of the intermediate elevations are from the Howell series and the upper elevation soils are from the Marr and Westphalia series.

The third study watershed (16.3 ha) was composed of 10.4 ha of cornfields under conventional tillage and 5.9 ha of hedgerows and riparian forest. Surface soil pH was 5.6 and surface soil organic matter content was 1.9%. The soils of the lower part are primarily of the Collington series while those of the upper part of the watershed are primarily of the Westphalia series. Average watershed slope is 5.4%.

SAMPLING

Bulk precipitation was sampled continuously at an elevation of 13 m as described previously [13]. Land discharge from the three study watersheds was monitored and sampled at permanent 120° V-notch weirs. The weirs included stilling wells and instrument sheds equipped with depth monitors (Stevens model 7001) which recorded digital data on paper tape every 5 min, and flowmeters (Stevens model 61R) that had been modified to close a sampling switch once every 38,000 L. Each switch closure activated a sampling cycle in which a fixed volume of stream water was pumped from the bottom of the V-notch into sample bottles. Samples were composited for one-week intervals over a one-year study period. One bottle contained sulfuric acid preservative for analysis of biologically labile parameters [19] and another had no preservatives. At times of very low discharge weekly spot samples were taken. If stream stage height was above a predetermined thresh-

old, a custom-built fraction collector was also activated with each flowmeter switch closure. In this case up to 12 discrete bottles without preservative could be taken automatically at flow-spaced intervals. Each switch closure during which the fraction collector was active caused an event mark to be made on the paper punch tape.

Transects of surface water collectors and shallow groundwater wells were established on each study watershed. Each transect consisted of several clusters of samplers located from high to low ground along the expected direction of flow. Thus, uphill/downhill comparisons could be made as well as interwatershed comparisons. Each cluster consisted of three replicate wells and three surface collectors, approximately 10 m from each other along a line normal to the transect axis. Surface water collectors were 4-L polyethylene bottles placed into holes in the soil in an inverted position. A slot was cut at ground level and an apron of plastic sheeting sealed to the bottom of the slot was spread uphill a short distance to funnel surface runoff into the bottle. Plastic tubing was sealed into the mouth of the inverted bottle so that samples could be withdrawn without disturbing the samplers. Before withdrawing samples, air was briefly bubbled through the sample to suspend particulates immediately before the sample was withdrawn. Samplers were rinsed out between storm events. Groundwater wells (piezometers) were used to sample shallow groundwater. They consisted of 3.8-cm-i.d. polyvinyl chloride (PVC) pipe perforated with 2.5-mm holes for approximately 8 cm on the lower end. The bottom end of the pipe was capped. Holes were bored with a bucket auger either to the top of the Marlboro Clay or to 6 m depth, whichever came first. The pipes were then inserted and clay was packed around the pipe at the soil surface. The pipe was then cut off approximately 0.4 m above the surface and a loose cap was placed over the top. In most cases another well, which was shallower in depth, was placed in a cluster. Our intent was to test realistically whether lateral, and perhaps vertical variances in soil water and surface runoff water composition were less than differences found between clusters within a given transect or between different transects. Two transects were established on the cropland watershed, one with three clusters of samplers and one with two clusters. Only one transect was used on each of the other two study watersheds, each consisting of only two clusters. Wells were pumped out one day before sample collection.

ANALYSIS OF SAMPLES

Na^+ , K^+ , Ca^{2+} , Mg^{2+} , NO_3^- , NO_2^- , Cl^- and SO_4^{2-} were analyzed with a Dionex Model 16 ion chromatograph after filtration through prewashed Millipore® HA membrane filters (0.45 mm nominal pore size). Nitrite was usually only present in trace amounts. Therefore, nitrate and nitrite were routinely summed and will be referred to as nitrate. Millipore HA-filtered water was also analyzed for total Kjeldahl nitrogen by digestion as described by Martin [20], distillation and Nesslerization. Ammonia was determined by oxidation to nitrite and subsequent coupling to sulfanilamide [21]. Total phosphorus was determined by perchloric acid digestion

and reaction with ammonium molybdate and stannous chloride [22]. Orthophosphate was determined by the same procedure without the digestion and organic phosphorus was calculated as total P minus orthophosphate. Hydrogen ion was determined with an expanded-range pH meter and bicarbonate by titration. Only about 10% of the samples were analyzed for bicarbonate. The rest were estimated from pH data with a regression derived from samples that were analyzed (meq HCO_3^- equals $-0.80 + 0.163\text{pH}$). This regression had an R^2 of 0.82. Approximately 10% of compositional data for other ion parameters were estimated. These were estimated as seasonal averages or by interpolation in most cases. When flowrates were changing rapidly, a few values were estimated as being the same as found at other times under similar flow conditions.

RESULTS

pH of Precipitation and Land Discharge

An essentially continuous data record for bulk precipitation pH at the Rhode River site exists for the last seven years. The mean pH declined over that time period for each season of the year, but the trend is most apparent for the spring season when precipitation results primarily from regional fronts (Figure 2). Yearly variation in pH was apparent and high variance within each season was also found. Mean seasonal pH declined at a rate of 0.12 pH unit per year and the correlation had a R^2 of 0.92. A seven-year record from a slightly earlier period is also available for stream water pH in the streams draining the larger watersheds of the Rhode River site. Between 1972 and 1978, weekly data from five to seven streams were taken and mean seasonal pH was calculated. Dry years such as 1977 had higher mean pH, and summer and fall data were erratic. However, in the winter and spring, when significant runoff occurred, stream pH values seem to have declined about 0.5 units during those years (Figure 3). If one examines the winter and spring stream pH data for the last five years from the mature, forested watershed from which ion balance data were taken in this study (Figure 4), a decline is also apparent. Although perhaps due to chance, the rates of decline in the pH of this forested stream are almost identical to that of bulk precipitation (Figure 2). This stream was not studied earlier.

These pH data illustrate that (1) the Rhode River site is well within the so-called acid rain belt of eastern North America; (2) these coastal plain soils are not able to buffer effectively the acidity of the precipitation; and (3) therefore, the mid-Atlantic Coastal Plain is an area very vulnerable to acid rain.

Hydrologic Data

Summaries of fluxes into the watershed study sites as bulk precipitation and out of the sites as combined surface and groundwater drainage are presented in Table

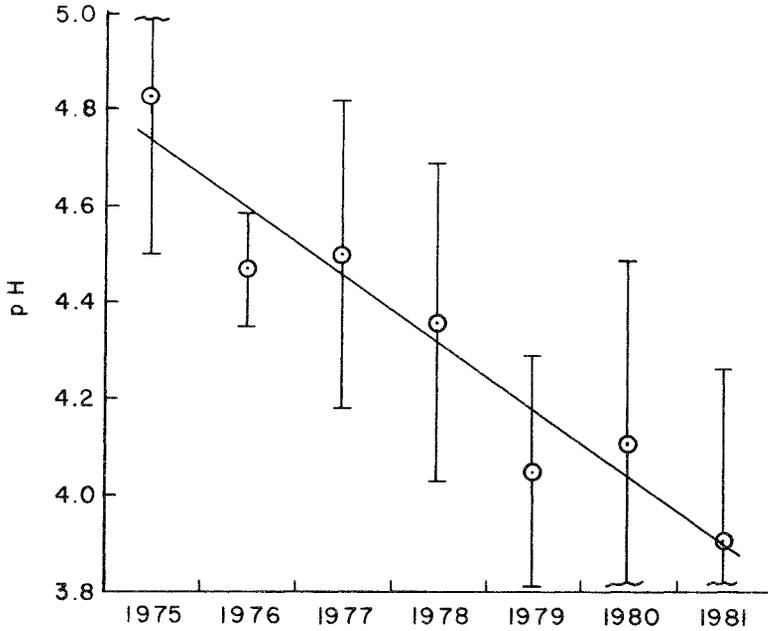


Figure 2. Mean pH of bulk precipitation in the spring at the Rhode River site. Bars are one standard deviation. $R^2 = 0.92$.

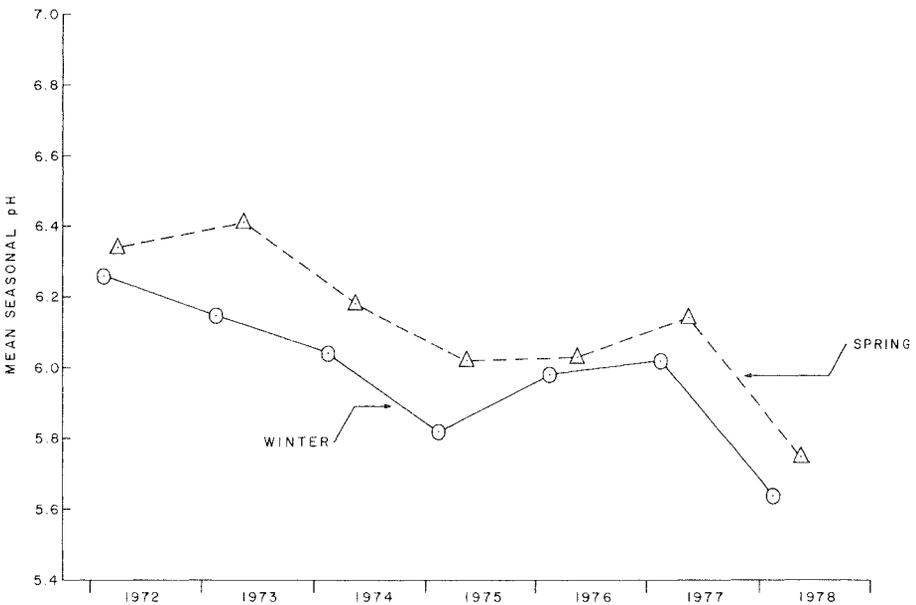


Figure 3. Mean seasonal pH of larger streams draining the Rhode River watershed.

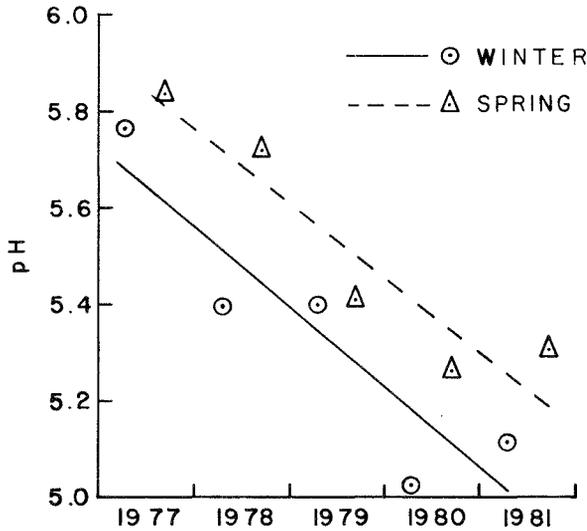


Figure 4. Mean seasonal pH of stream draining mature forest study site watershed. Correlation for spring, -0.94 ; for winter, -0.91 .

I. Precipitation volume during the study period (100.4 cm) was somewhat below the 160-year long-term mean of 108 cm [23]. The winter season had slightly above average precipitation, while all others, especially fall, were below average. During the preceding year, only 87.8 cm of precipitation occurred and during the season immediately before the study period (winter of 1980–1981) only 12.6 cm of precipitation occurred. Thus, following a year of drought, soils were dry and water tables were low when this study was initiated and until late in the study period land discharges were low.

Ion Balances of Mature Forest

Although cation input fluxes were highest in spring ($0.85 \text{ keq}\cdot\text{ha}^{-1}$), and next highest in the summer ($0.48 \text{ keq}\cdot\text{ha}^{-1}$), cation outputs were highest in winter and spring. Less than 15% of the measured cation inputs were discharged during the study period. This low discharge was probably largely due to the dry conditions and should be reversed during the first extended period of wet weather. No discharges at all occurred during the fall, but with increased rains during the winter months discharges steadily increased. Of the annual cation outputs, 40% were during February alone. Hydrogen ions comprised 50% of cation inputs but less than 1% of cation outputs. Organic nitrogen (20%), ammonium (10%), calcium and sodium (6% each), magnesium (5%), and potassium (2%) constituted the remainder of the measured cation inputs.

Table I. Summary of Ion Fluxes (keq-ha⁻¹) in Bulk Precipitation and Land Discharges from Three Study Watersheds Between March 1, 1981, and February 28, 1982.

Season	Vol. (cm)	Na ⁺	K ⁺	Organic N ^a	NH ₄ ⁺	H ⁺	Mg ²⁺	Ca ²⁺	Sum Cations	NO ₃ ⁻	H ₂ PO ₄ ⁻	Organic P ^a	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	Sum Anions
Bulk Precipitation																
Spring	25.4	0.073	0.029	0.23	0.083	0.38	0.030	0.034	0.85	0.10	0.00019	0.0069	0.00	0.11	0.20	0.42
Summer	29.7	0.027	0.00088	0.086	0.051	0.26	0.020	0.028	0.48	0.11	0.0009	0.0008	0.000	0.099	0.21	0.42
Fall	18.8	0.012	0.0017	0.036	0.036	0.16	0.014	0.017	0.28	0.081	0.0011	0.0006	0.000	0.056	0.21	0.35
Winter	26.5	0.019	0.0027	0.026	0.036	0.14	0.021	0.026	0.27	0.15	0.0008	0.0004	0.000	0.055	0.23	0.44
Year	100.4	0.12	0.042	0.38	0.21	0.94	0.085	0.11	1.88	0.45	0.0046	0.0086	0.000	0.32	0.86	1.64
Mature Forest Land Discharge																
Spring	1.46	0.038	0.013	0.0043	0.0008	0.0009	0.031	0.020	0.11	0.0014	0.0001	0.0003	0.0027	0.033	0.085	0.12
Summer	1.44	0.014	0.010	0.0050	0.0013	0.0004	0.014	0.011	0.056	0.0021	0.0017	0.0002	0.0042	0.012	0.038	0.0580
Fall	0.00															
Winter	1.86	0.020	0.0090	0.0044	0.0009	0.0009	0.050	0.032	0.12	0.0044	0.0001	0.0001	0.0052	0.035	0.14	0.18
Year	4.76	0.072	0.033	0.014	0.0030	0.0021	0.095	0.063	0.28	0.0080	0.0019	0.0006	0.0122	0.080	0.27	0.37
Pastureland Discharge																
Spring	3.20	0.064	0.030	0.0073	0.0014	0.0016	0.034	0.037	0.18	0.012	0.0001	0.0002	0.0081	0.058	0.17	0.25
Summer	2.72	0.030	0.015	0.0054	0.0015	0.0004	0.022	0.030	0.10	0.0054	0.0002	0.0003	0.0235	0.025	0.066	0.12
Fall	0.91	0.0074	0.0050	0.0013	0.0005	0.0001	0.013	0.017	0.044	0.0009	0.0001	0.0001	0.0115	0.0093	0.034	0.056
Winter	4.46	0.027	0.010	0.0046	0.0009	0.0020	0.049	0.050	0.14	0.035	0.0001	0.0002	0.0109	0.044	0.30	0.39
Year	11.3	0.13	0.061	0.018	0.0042	0.0041	0.12	0.13	0.47	0.053	0.0004	0.0007	0.054	0.14	0.57	0.82
Cropland Discharge																
Spring	6.93	0.15	0.083	0.041	0.014	0.0012	0.12	0.14	0.55	0.048	0.0036	0.0035	0.051	0.29	0.33	0.72
Summer	4.01	0.074	0.025	0.023	0.0063	0.0010	0.11	0.11	0.35	0.055	0.0009	0.0009	0.024	0.19	0.18	0.45
Fall	0.66	0.0091	0.0051	0.0008	0.0002	0.0002	0.024	0.019	0.058	0.015	0.0000	0.0000	0.0014	0.039	0.058	0.10
Winter	11.6	0.11	0.037	0.022	0.0044	0.0043	0.36	0.29	0.82	0.18	0.0003	0.0003	0.017	0.57	0.78	1.54
Year	23.2	0.35	0.15	0.088	0.024	0.0067	0.61	0.56	1.78	0.28	0.0048	0.0048	0.093	1.08	1.35	2.82

^a It was assumed that all organic N or P was monovalent.

In forest outputs, magnesium was the most-abundant cation (34%), followed by sodium (26%), calcium (22%), potassium (12%), organic N (5%) and ammonium (1%). If chloride can be assumed to be reasonably inert chemically and biologically, the ratio of a given cation to chloride can be used as a tracer for enrichment or depletion due to watershed interactions. The Mg^{2+}/Cl^{-} ratio was enriched the most over precipitation (4.5-fold) followed by potassium (3.1-fold), then calcium and sodium (both 2.4-fold). The ratios of organic N and ammonium ion to chloride in discharge were less than in precipitation. Ratios of potassium and magnesium to chloride were enriched the most over precipitation in the summer (9.6-fold and 5.8-fold, respectively). The highest potassium-to-chloride ratios were observed during a major summer storm event when most of the flow was due to surface runoff (Table II). At that time the K^{+}/Cl^{-} ratio was enriched 20-fold and the Mg^{2+}/Cl^{-} ratio was enriched 10-fold over the monthly average for precipitation. Surface and shallow groundwater flowrates were calculated from the hydrograph by the method of Barnes [24] for all storm events during the study period. A linear regression of K^{+}/Cl^{-} ratios in weekly spring and summer forest discharges vs the ratio of surface to groundwater discharge had a correlation of 0.71 and gave the equation $K^{+}/Cl^{-} = 0.30 + 0.467(\text{surface/groundwater ratio})$.

In general, both the potassium-to-sodium and calcium-to-magnesium ratios in forest runoff were higher in summer. Perhaps this was due to the larger proportion (57%) of land discharge which was surface runoff. The K^{+}/Na^{+} ratio varied more than the Ca^{2+}/Mg^{2+} ratio. Both the K^{+}/Cl^{-} and Na^{+}/Cl^{-} ratios declined in forest discharge in winter. The decline in K^{+}/Cl^{-} was greater, which may indicate a greater role for biota in the release of potassium than sodium.

Anion inputs in bulk precipitation were dominated by sulfate (52%) and nitrate (27%), followed by chloride (20%) and contained less than 1% of combined inorganic and organic phosphates (Table I). Input fluxes were relatively constant from season to season.

Due to drought conditions, anion outputs from the forest study site (Table I) were only 22% of inputs. Sulfate constituted 75% of these outputs and chloride 22%, while nitrate was only 2%. Chloride outputs only exceeded inputs in February, the last month of the study period, when 1.5 cm of discharge occurred and salts stored in the soils due to evapotranspiration during the drought began to be flushed out. Sulfate-to-chloride ratios varied relatively little from season to season or with flowrates during storms and were only enriched over precipitation by 25% for the year.

Ion Balances of Pastureland

Cation discharges from the pasture study site watershed were somewhat larger than from the forest site (Table I), but the volume of water discharged was also greater, due to lower rates of evapotranspiration. During the study period no synthetic fertilizer or lime was applied and the cattle were not fed concentrates.

Table II. Land Discharge Data on Sequential Samples from Two Storms: Mature Forest Watershed

<i>Fraction</i>	<i>Time</i>	<i>Dis-charge</i> ($L\cdot s^{-1}$)	<i>Flow Ratio, Quick/Slow</i>	Na^+ ($meq\cdot L^{-1}$)	Na^+/Cl^-	K^+ ($meq\cdot L^{-1}$)	K^+/Cl^-	K^+/Na^+	Mg^{2+} ($meq\cdot L^{-1}$)	Mg^{2+}/Cl^-	Ca^{2+} ($meq\cdot L^{-1}$)	Ca^{2+}/Cl^-	Ca^{2+}/Mg^{2+}
May 15, 1981, Storm (4.98 cm, peak intensity of 1.55 mm-min ⁻¹)													
1	1500	26	8.8	0.078	0.61	0.066	0.52	0.85	0.132	1.04	0.089	0.70	0.67
2	1530	16	5.2	0.077	0.61	0.074	0.58	0.96	0.154	1.21	0.099	0.78	0.64
3	1830	2.0	0.0	0.139	1.04	0.063	0.47	0.45	0.276	2.06	0.158	1.18	0.57
July 4, 1981, Storm (10.06 cm, peak intensity of 1.30 mm-min ⁻¹)													
1	0935	34	4.6	0.057	1.46	0.065	1.67	1.14	0.057	1.46	0.058	1.49	1.02
2	0950	54	6.7	0.077	1.79	0.077	1.79	1.00	0.074	1.72	0.068	1.58	0.92
3	1040	56	7.5	0.065	1.51	0.074	1.72	1.14	0.085	1.98	0.069	1.60	0.81
4	1100	58	8.2	0.090	1.48	0.077	1.26	0.86	0.085	1.39	0.069	1.13	0.81
5	1115	22	2.9	0.080	1.43	0.080	1.43	1.00	0.097	1.73	0.075	1.34	0.77
6	1700	2.8	0.0	0.117	1.36	0.078	0.91	0.67	0.131	1.52	0.100	1.16	0.76

However, during prior years these types of inputs sometimes occurred and may influence some of the data. Between 22 and 26 cattle were pastured on an 18.9-ha pasture, which included the study watershed site, for the entire study period, except during April through July when no cattle were present. For the entire year of the study an average of 0.91 adult cow equivalents per hectare were pastured. Cation outputs of sodium and calcium (28% each) were highest and magnesium outputs (26%) were almost as high. Potassium (13%), organic nitrogen (4%) and ammonium (1%) constituted the remaining cation discharges measured. These values are rather similar to those for forest discharges, as were the ratios of K^+ , Na^+ , Ca^{2+} and Mg^{2+} to Cl^- . On the average, however, Mg^{2+}/Cl^- ratios were somewhat lower and Ca^{2+}/Cl^- ratios were somewhat higher than for forest discharges. Calcium-to-magnesium ratios in pasture discharges averaged 1.13 for the year with little seasonal difference, while the ratio averaged 0.66 for forest discharges. Compositional data for discharges from two storm events is given in Table III. Potassium-to-chloride ratios peaked in discharges during storm events with a maximum enrichment over summer bulk precipitation of 38-fold during the July storm event. The May storm is a clear example of the changes in K^+ and Na^+ concentrations during a storm event and of how they relate to surface flow and the groundwater (slow flow) recession curve (Figure 5). Generally, Na^+ concentrations seemed to change more than K^+ during storms. Sometimes K^+ concentrations didn't change much at all. Before the May storm (Figure 5), both K^+ and Na^+ concentrations were high, then the concentrations both declined during peak surface flow, but Na^+ declined much more than K^+ . Then, during the hydrograph recession, K^+ concentration fell further while Na^+ began to increase. A few days later, when groundwater flowrates were very low again, Na^+ continued to increase and K^+ began to increase. The K^+/Na^+ ratio was always highly correlated with discharge rate and during the May storm high K^+/Na^+ ratios were found in discharges at the peak of the storm when most was due to surface runoff. The ratio declined steadily with the declining hydrograph. The highest Mg^{2+}/Cl^- ratios were found on the descending part of the hydrograph for the May storm, corresponding to a 4.6-fold enrichment over spring bulk precipitation. Unfortunately, the sampler failed during part of the July storm, so that the falling hydrograph was not analyzed chemically. The spring average K^+/Na^+ ratio for pasture discharges was 0.47 which is only 20% above that for spring bulk precipitation. Both K^+/Na^+ and Ca^{2+}/Mg^{2+} ratios averaged higher in the summer and fall for discharge from pastureland than during the winter and spring. As in the case of forest discharges, this winter decline in K^+/Na^+ ratio was due to a greater decline in the K^+/Cl^- than the Na^+/Cl^- ratio.

Anion outputs from pastureland (Table I) were only 47% of precipitation inputs. Over half of the measured outputs occurred in the winter when the volume of discharges began to increase. As for forest, sulfate constituted 75% and chloride 18% of anion discharges. Nitrate, however, was more significant (7%). Sulfate-to-chloride ratios were highest in winter and lowest in summer. For the year, sulfate-to-chloride in discharges was enriched 55% over precipitation.

Table III. Land Discharge Data on Sequential Samples from Two Storms: Pastureland Watershed

<i>Fraction</i>	<i>Time</i>	<i>Dis-charge</i>	<i>Flow Ratio, Quick/Slow</i>	<i>Na⁺</i>	<i>Na⁺/Cl⁻</i>	<i>K⁺</i>	<i>K⁺/Cl⁻</i>	<i>K⁺/Na⁺</i>	<i>Mg²⁺</i>	<i>Mg²⁺/Cl⁻</i>	<i>Ca²⁺</i>	<i>Ca²⁺/Cl⁻</i>	<i>Ca²⁺/Mg²⁺</i>
		<i>(L-s⁻¹)</i>		<i>(meq-L⁻¹)</i>		<i>(meq-L⁻¹)</i>			<i>(meq-L⁻¹)</i>		<i>(meq-L⁻¹)</i>		
May 15, 1981, Storm													
1	1500	17	19	0.027	0.31	0.069	0.79	2.56	0.056	0.64	0.055	0.63	0.98
2	1515	16	15	0.026	0.09	0.068	0.25	2.62	0.081	0.30	0.085	0.31	1.05
3	1530	3.0	2.3	0.077	0.66	0.064	0.55	0.83					
4	1615	0.90	0	0.105	0.81	0.053	0.41	0.50	0.134	1.04	0.127	0.98	0.95
5	1730	0.70	0	0.101	0.83	0.042	0.35	0.42	0.147	1.21	0.158	1.31	1.07
6	1930	0.60	0	0.098	0.93	0.038	0.36	0.39	0.134	1.28	0.143	1.36	1.07
7	2400	0.45	0	0.105	0.89	0.035	0.30	0.33	0.149	1.26	0.153	1.30	1.03
July 4, 1981, Storm													
1	0830	0.75	0	0.070	1.84	0.113	2.97	1.61	0.041	1.08	0.063	1.66	1.54
2	0950	13	4.9	0.039	1.95	0.040	2.00	1.03	0.022	1.10	0.031	1.55	1.41
3	1005	13	4.9	0.069	2.88	0.083	3.46	1.20	0.022	0.92	0.024	1.00	1.09
4	1020	4.3	1.1	0.080	2.58	0.091	2.94	1.14	0.033	1.06	0.042	1.35	1.27
5	1035	8.6	3.4	0.063	2.10	0.081	2.70	1.29	0.026	0.87	0.035	1.17	1.35

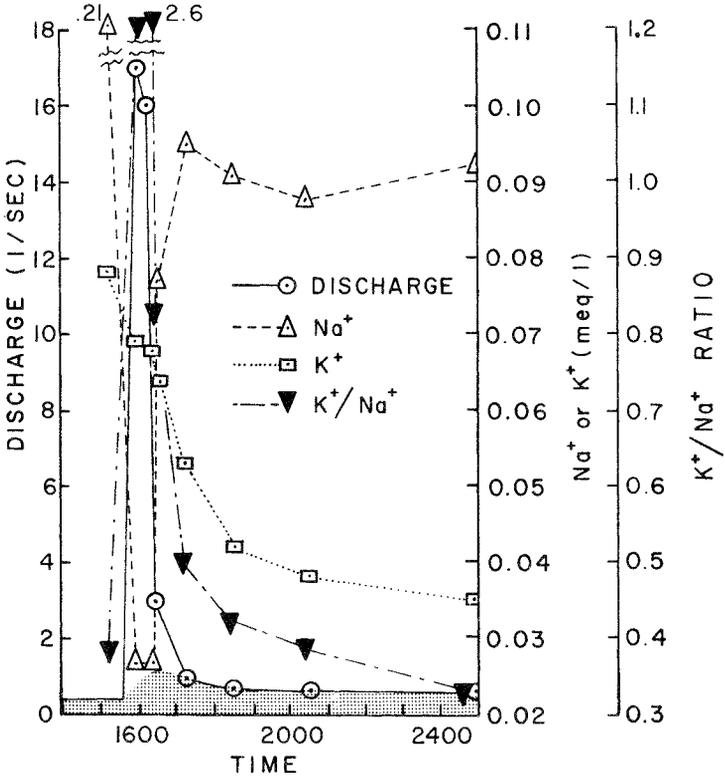


Figure 5. Changes in surface runoff (quick flow) and groundwater (slow flow) discharge rates and concentrations of K^+ and Na^+ in the stream draining the pastureland study site occurring during the May 15, 1981, storm event. Groundwater discharge is shaded and surface runoff discharge is the difference between the total discharge and the shaded area.

Ion Balances of Cropland

Cation discharges from the cropland study site (Table I) were much higher than from the other two sites. The largest cation discharges were in the winter (46% of the total for the year) and 28% of the total cation discharges occurred in February. Almost five times more volume of water than the forest site was discharged, helping to explain the greater ion yields. Higher ion discharges were also partially due to the management input loadings. Those occurred in April and May for all but the organic N, which was applied in July. Management loadings were estimated to be (1) 19 keq-ha⁻¹ of Ca²⁺ and 2.7 keq-ha⁻¹ of Mg²⁺ from applications of limestone and (2) 0.15 keq-ha⁻¹ of K⁺, 3.3 keq-ha⁻¹ of organic N, 2.2 keq-ha⁻¹ of ammonium, 1.1 keq-ha⁻¹ of NO₃⁻ and 0.40 keq-ha⁻¹ of H₂PO₄⁻ in farm fertilizer. Analysis of granular fertilizer indicated the additional presence

of significant amounts of other ions. Approximately $0.45 \text{ keq}\cdot\text{ha}^{-1}$ of Cl^- and $1.0 \text{ keq}\cdot\text{ha}^{-1}$ of SO_4^{2-} were added in granular fertilizers. Other agricultural chemicals may also have contained significant amounts of chloride, since more chloride ($1.08 \text{ keq}\cdot\text{ha}^{-1}$) was measured in discharges than in precipitation plus fertilizer ($0.77 \text{ keq}\cdot\text{ha}^{-1}$). Cation outputs were greatest for magnesium (34%) followed by calcium (31%), sodium (20%), potassium (80%), organic N (5%), ammonium (1%) and traces of H^+ . Ratios of cations to chloride were not a very useful tracer for enrichment, since a large amount of chloride inputs was in the form of agricultural chemicals, which are applied at different times and in differing ratios to other ions of interest. Compared with cation inputs from precipitation and management, very little ammonium, organic N or hydrogen ion was discharged. The average ratio of calcium to magnesium in cropland discharges (0.92) was intermediate between that from forest (0.66) and pastureland (1.08); however, the seasonal pattern differed being highest in the spring (1.2) and lowest in winter, reaching 0.66 in December. The highest values observed (1.8–1.9) were in samples from the second peak in the July storm event (Table IV), but even these were well below the ratio of 7.0 applied as limestone. Ratios of K^+/Na^+ were similar to those found for discharges from pastureland (Table I). Management inputs of potassium were in mid-April and K^+ discharge was highest in spring, but the K^+/Na^+ ratio was highest in the fall and at times of high storm discharge (Table IV, Figures 6 and 7). The K^+/Na^+ ratio was lowest in June (0.28) and February (0.32).

Anion outputs from cropland were composed of sulfate (48%), chloride (38%), nitrate (10%), bicarbonate (3%) and traces (0.3%) of phosphates. Of the anion discharge, 55% occurred during winter. Despite large management inputs, sulfate was a lower proportion of total cropland anion discharges than for forest or pastureland.

Intrawatershed Ion Patterns

Forest

Data on the ionic composition of groundwater in the upper part of the watershed and both surface runoff and groundwater in the lower part of the forested watershed are summarized in Table V. At the lower elevation all cations except sodium were in higher concentrations in groundwater and of these the largest was a 12-fold increase in ammonium ion. Hydrogen ion and bicarbonate data were not tabulated since they were not routinely determined for these samples. However, five sets of pH measurements of groundwater taken from August 1981 to February 1982 show an average increase from 5.1 at the upper position to 6.2 at the lower position. Total measured groundwater anions decreased going down the elevational gradient. Of these nitrate and sulfate concentrations declined 7- and 5-fold, respectively, whereas chloride and phosphate concentrations increased 1.4- and 38-fold, respectively. Groundwater ratios of K^+/Na^+ and $\text{Ca}^{2+}/\text{Mg}^{2+}$ increased along the elevational gradient primarily because of a concomitant decline in the Na^+/Cl^-

Table IV. Land Discharge Data on Sequential Samples: Cropland Watershed (July 4, 1981, Storm Only)

<i>Fraction</i>	<i>Time</i>	<i>Dis-charge</i> ($L \cdot s^{-1}$)	<i>Flow Ratio, Quick/Slow</i>	Na^+ ($meq \cdot L^{-1}$)	Na^+/Cl^-	K^+ ($meq \cdot L^{-1}$)	K^+/Cl^-	K^+/Na^+	Mg^{2+} ($meq \cdot L^{-1}$)	Mg^{2+}/Cl^-	Ca^{2+} ($meq \cdot L^{-1}$)	Ca^{2+}/Cl^-	Ca^{2+}/Mg^{2+}
1	0650	62	0	0.074	0.52	0.077	0.54	1.04	0.105	0.74	0.142	1.00	1.35
2	0740	80	0	0.096	0.60	0.076	0.48	0.79	0.123	0.77	0.160	1.00	1.30
3	0850	46	0	0.116	0.50	0.074	0.32	0.64	0.149	0.64	0.167	0.72	1.12
4	0930	130	0.34	0.062	0.65	0.058	0.61	0.94	0.085	0.89	0.122	1.28	1.44
5	0945	440	1.8	0.053	0.96	0.056	1.02	1.06	0.057	1.04	0.084	1.53	1.47
6	0950	540	2.2	0.054	1.06	0.066	1.29	1.22	0.071	1.39	0.095	1.86	1.34
7	1000	530	1.7	0.041	0.75	0.061	1.11	1.49	0.052	0.95	0.078	1.42	1.50
8	1010	450	1.5	0.039	0.65	0.066	1.10	1.69	0.053	0.88	0.069	1.15	1.30
9	1030	120	0.21	0.066	0.85	0.074	0.95	1.12	0.058	0.74	0.080	1.03	1.38
10	1100	160	0.37	0.077	0.73	0.071	0.68	0.92	0.077	0.73	0.141	1.34	1.83
11	1115	240	0.51	0.043	0.61	0.060	0.86	1.40	0.073	1.04	0.138	1.97	1.89
12	1140	170	0.26	0.059	0.83	0.075	1.06	1.27	0.067	0.94	0.085	1.20	1.27

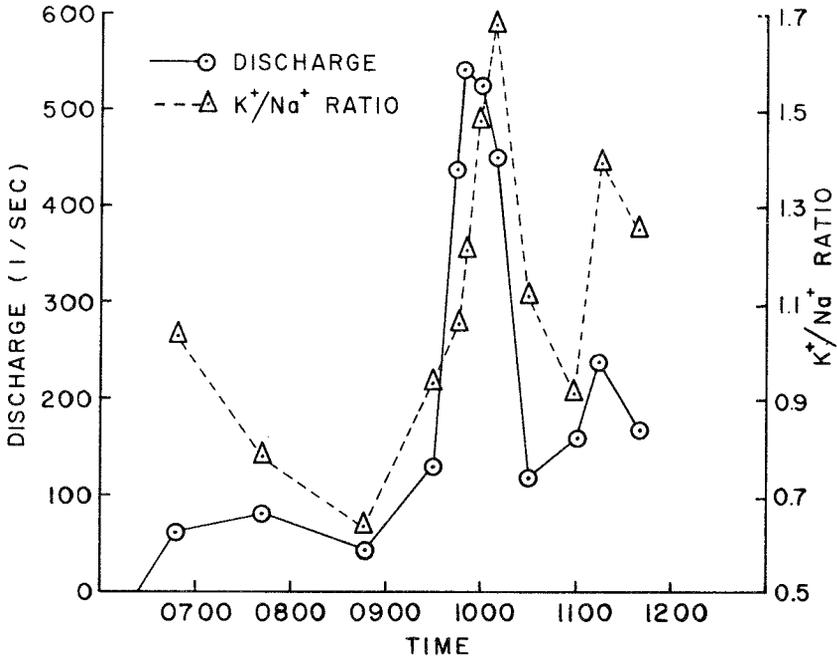


Figure 6. Changes in the hydrograph and K^+/Na^+ ratios for the stream draining the cropland site during the July 4, 1981, storm event, subsequent to being dry.

ratio and increase in Ca^{2+}/Cl^- ratio. Changes in groundwater ion concentrations along the hydrologic gradient appear to be controlled by the combined effects of pH and redox potential. Low redox potentials would account for the lowered concentrations of NO_3^- (via denitrification) and SO_4^{2-} (via reduction to H_2S) and also the increased concentration of NH_4^+ (via a shutdown in nitrification). Higher pH values could explain the higher concentrations of $H_2PO_4^-$ due to reduced binding by Fe, Mn and Al compounds in the deeper subsoils.

Surface runoff contained lower concentrations of sodium and higher concentrations of potassium, ammonium, organic nitrogen and nitrate than the groundwater at the lower elevation. The K^+/Na^+ ratio in surface runoff averaged 3.45 during the study year and 5.36 during the spring. Respectively, these ratios were 9.8 and 22 times higher than found in groundwater, and 9.9 and 14 times higher than found in bulk precipitation. Concentrations of nitrate in surface runoff were lower and sulfate higher than those measured in bulk precipitation.

Pastureland

The most noticeable differences in groundwater data between the pasture study site (Table VI) and the forest site are the somewhat lower concentration of cations

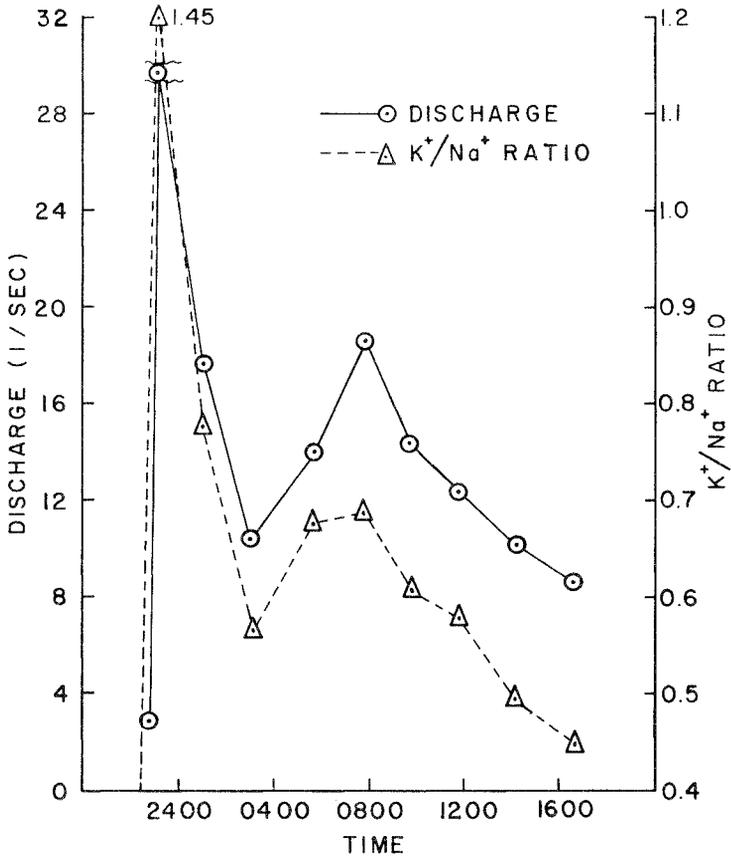


Figure 7. Changes in the hydrograph and K^+/Na^+ ratios on the stream draining the cropland study site during the February 2-3, 1982, storm event.

measured at the lower elevations and the reversal of the gradient patterns found for phosphate, magnesium, calcium and chloride concentrations.

Groundwater at the lower elevation had 3.2-fold higher ammonium concentrations and 3.8-, 4.5-, 2.6-, 1.2-, 1.3- and 1.2-fold lower concentrations, respectively for phosphate, calcium, magnesium, chloride, sodium and sulfate. Five sets of groundwater samples for the higher position and three for the lower also showed a decline in average pH from 6.3 to 5.5. Less anoxic conditions in groundwater at the lower elevation probably account for the smaller decline in SO_4^{2-} and increase in NH_4^+ concentrations when compared to the forest. The decline of pH with elevation in the pasture could also explain the reversed pattern of phosphate concentrations.

Surface runoff for the year contained higher concentrations of all cations and anions, except for NO_3^- and SO_4^{2-} when compared to the groundwater at the

Table V. Summary of Ionic Composition (meq-L⁻¹) of Surface Runoff and Shallow Groundwaters: Mature Forest Watershed

		<i>Na⁺</i>	<i>K⁺</i>	<i>Organic N</i>	<i>NH₄⁺</i>	<i>Mg²⁺</i>	<i>Ca²⁺</i>	<i>Sum of Cations</i>	<i>NO₃⁻</i>	<i>Total P^a</i>	<i>Cl⁻</i>	<i>SO₄²⁻</i>	<i>Sum of Anions</i>
Watershed Elevation of 15 m													
Groundwater	Spring	0.240	0.050	0.008	0.003	0.213	0.141	0.655	0.010	0.000	0.123	0.580	0.714
	Summer	0.240	0.043	0.010	0.004	0.112	0.098	0.507	0.016	0.000	0.164	0.606	0.786
	Fall	0.166	0.037	0.002	0.001	0.110	0.091	0.408	0.015	0.002	0.108	0.612	0.738
	Winter	0.122	0.028	0.003	0.001	0.131	0.096	0.381	0.014	0.000	0.128	0.736	0.878
	Year	0.192	0.039	0.006	0.002	0.141	0.107	0.488	0.014	0.001	0.131	0.636	0.781
Watershed Elevation of 5 m													
Surface Runoff	Spring	0.061	0.327	0.114	0.003	0.122	0.135	0.762	0.008	0.007	0.322	0.099	0.436
	Summer	0.103	0.275	0.219	0.061	0.143	0.177	0.978	0.043	0.020	0.117	0.186	0.365
	Fall	0.069	0.199	0.131	0.146	0.194	0.296	1.035	0.026	0.050	0.239	0.205	0.520
	Year	0.077	0.266	0.155	0.070	0.153	0.202	0.924	0.026	0.026	0.226	0.163	0.440
Groundwater	Spring	0.256	0.063	0.020	0.023	0.232	0.298	0.893	0.002	0.020	0.165	0.169	0.355
	Summer	0.215	0.081	0.023	0.017	0.169	0.277	0.782	0.000	0.024	0.209	0.098	0.330
	Fall	0.160	0.071	0.008	0.031	0.205	0.264	0.739	0.000	0.067	0.191	0.100	0.358
	Winter	0.116	0.049	0.008	0.026	0.244	0.317	0.760	0.004	0.043	0.171	0.115	0.339
	Year	0.187	0.066	0.015	0.024	0.212	0.289	0.793	0.002	0.038	0.186	0.120	0.346

^a Most phosphorus was orthophosphate.

Table VI. Summary of Ionic Composition (meq-L⁻¹) of Surface Runoff and Shallow Groundwaters: Pastureland Watershed

		<i>Na</i> ⁺	<i>K</i> ⁺	<i>Organic N</i>	<i>NH</i> ₄ ⁺	<i>Mg</i> ²⁺	<i>Ca</i> ²⁺	<i>Sum of Cations</i>	<i>NO</i> ₃ ⁻	<i>Total P</i> ^a	<i>Cl</i> ⁻	<i>SO</i> ₄ ²⁻	<i>Sum of Anions</i>
Watershed Elevation of 22 m													
Groundwater	Summer	0.189	0.052	0.021	0.004	0.133	0.336	0.736	0.033	0.022	0.108	0.425	0.589
	Fall	0.142	0.043	0.014	0.007	0.264	0.486	0.956	0.010	0.045	0.159	0.472	0.686
	Winter	0.129	0.040	0.013	0.007	0.287	0.539	1.01	0.024	0.046	0.117	0.548	0.735
	Year	0.153	0.045	0.016	0.006	0.228	0.454	0.902	0.022	0.038	0.128	0.482	0.704
Watershed Elevation of 7.5 m													
Surface Runoff	Spring	0.452	0.033	0.102	0.034	0.217	0.100	0.937	0.018	0.004	0.936	0.192	1.15
	Summer	0.199	0.309	0.137	0.023	0.132	0.200	1.00	0.037	0.015	0.087	0.182	0.321
	Fall	0.048	0.481	0.151	0.014	0.166	0.392	1.25	0.003	0.035	0.128	0.120	0.286
	Year	0.233	0.274	0.130	0.023	0.172	0.231	1.06	0.019	0.018	0.384	0.165	0.586
Groundwater	Spring	0.192	0.075	0.026	0.032	0.081	0.074	0.479	0.100	0.001	0.118	0.311	0.440
	Summer	0.131	0.052	0.028	0.030	0.067	0.098	0.406	0.024	0.001	0.093	0.373	0.491
	Fall	0.072	0.035	0.005	0.013	0.089	0.103	0.316	0.038	0.001	0.089	0.458	0.585
	Winter	0.072	0.026	0.008	0.003	0.111	0.123	0.343	0.022	0.000	0.110	0.532	0.665
	Year	0.116	0.047	0.017	0.019	0.087	0.100	0.386	0.023	0.001	0.103	0.418	0.545

^a Most phosphorus was orthophosphate.

same elevation. Nitrate concentration was only 82% and sulfate 39% as high as in groundwater. Seasonal variations in the concentrations of surface runoff were particularly high for Na^+ , K^+ and Cl^- , each having more than a 0.4-meq range in concentration. The dominant cations and anions were sodium and chloride during the spring, potassium and sulfate during the summer, and potassium and chloride during the fall. Compared to the forest, ion concentrations in pastureland runoff were very similar differing substantially only in sodium (three times higher) and ammonium (threefold decrease). Potassium-to-chloride and potassium-to-sodium ratios were greater than one in the surface runoff and less than one in the groundwater for all seasons except spring. In spring, surface runoff contained a very low concentration of potassium resulting in K^+/Na^+ and K^+/Cl^- ratios of less than one and less than the groundwater ratios.

Cropland

Data from the two transects on the cropland site were averaged and are presented in Table VII. Groundwater concentrations underwent little seasonal variation at either elevation. The only seasonal pattern was a steady, twofold decline in sodium concentrations from spring to winter, which was a pattern common to all watersheds in this study. Groundwater leaving the cultivated portion of the cropland each season contained high calcium, magnesium, sulfate and nitrate concentrations. After traversing 50–100 m of riparian forest, nitrate, magnesium and calcium concentrations were reduced 94, 33 and 37%, respectively, whereas ammonium ion increased fivefold. Five sets of groundwater samples also showed an average increase in pH from 4.8 to 5.3 between the bottom of the cropland and the stream bank. The large reductions in nitrate and smaller concomitant increases in ammonium and pH indicate that low redox potentials and high levels of denitrification probably occurred in the riparian zone soils.

Surface runoff leaving the fields had higher concentrations of K^+ , organic N, NH_4^+ and total P than groundwater had leaving the cultivated fields. Surface water that had traversed the riparian forest had higher concentrations of K^+ , organic N, NO_3^- and total P than did groundwater at the same location. Transit through the riparian forest caused average yearly reductions in all ion concentrations, except total P. However, substantial declines (greater than a 2-fold reduction) occurred only for the nitrate (6-fold) and ammonium (6.4-fold) ions. Seasonal variations in concentrations were often greater than twofold at both elevations, and the direction and magnitude of the riparian forest's effect on the water flowing through it also varied. Compared to surface runoff concentrations in the forest and pasture study sites, surface water leaving the cropland contained substantially higher levels of Mg^{2+} , NO_3^- , and SO_4^{2-} and slightly higher levels of Ca^{2+} and Cl^- . After passing through the riparian zone, surface runoff concentrations were lower than those in the forested watershed for all ions except NO_3^- and SO_4^{2-} . As was typical in the other two watersheds K^+/Cl^- and K^+/Na^+ ratios were higher for surface runoff than for groundwater.

Table VII. Summary of Ionic Composition (meq-L⁻¹) of Surface Runoff and Shallow Groundwaters: Cropland Watershed

		<i>Na⁺</i>	<i>K⁺</i>	<i>Organic N</i>	<i>NH₄⁺</i>	<i>Mg²⁺</i>	<i>Ca²⁺</i>	<i>Sum of Cations</i>	<i>NO₃⁻</i>	<i>Total P^a</i>	<i>Cl⁻</i>	<i>SO₄²⁻</i>	<i>Sum of Anions</i>
At Bottom of Cropland													
Surface Runoff	Spring	0.047	0.151	0.105	0.259	0.134	0.200	0.896	0.266	0.008	0.223	0.332	0.829
	Summer	0.067	0.204	0.194	0.084	0.358	0.454	1.36	0.749	0.004	0.197	0.569	1.52
	Fall	0.044	0.183	0.056	0.059	0.131	0.157	0.630	0.114	0.004	0.327	0.282	0.725
	Year	0.053	0.180	0.118	0.134	0.207	0.270	0.962	0.376	0.005	0.249	0.394	1.02
Groundwater	Spring	0.192	0.076	0.019	0.006	0.467	0.352	1.11	0.400	0.005	0.334	0.459	1.20
	Summer	0.172	0.069	0.010	0.007	0.343	0.273	0.874	0.470	0.002	0.364	0.418	1.25
	Fall	0.138	0.060	0.010	0.006	0.344	0.274	0.832	0.504	0.006	0.376	0.556	1.44
	Winter	0.092	0.030	0.011	0.002	0.441	0.338	0.914	0.646	0.003	0.384	0.649	1.68
Year	0.148	0.067	0.013	0.005	0.399	0.310	0.942	0.506	0.003	0.365	0.522	1.40	
After Transit of Riparian Forest													
Surface Runoff	Spring	0.056	0.136	0.084	0.029	0.131	0.124	0.560	0.053	0.008	0.176	0.188	0.425
	Summer	0.055	0.079	0.051	0.012	0.129	0.151	0.478	0.074	0.006	0.102	0.243	0.424
	Fall	0.109 ^b	0.168	0.038	0.049	0.339	0.319	1.02	0.024	0.013	0.674	0.867	1.58
	Year	0.055	0.108	0.067	0.021	0.130	0.137	0.518	0.063	0.007	0.139	0.216	0.425
Groundwater	Spring	0.178	0.073	0.028	0.017	0.285	0.214	0.795	0.014	0.003	0.361	0.461	0.838
	Summer	0.158	0.072	0.023	0.035	0.270	0.161	0.719	0.016	0.007	0.375	0.408	0.806
	Fall	0.126	0.066	0.012	0.031	0.256	0.207	0.698	0.054	0.007	0.396	0.521	0.978
	Winter	0.082	0.032	0.010	0.020	0.260	0.200	0.604	0.039	0.003	0.376	0.602	1.02
Year	0.136	0.061	0.018	0.026	0.267	0.195	0.703	0.031	0.005	0.376	0.498	0.910	

^a Most of total phosphate was orthophosphate.

^b Only one set of samples were collected and these data were not included in the yearly average.

DISCUSSION

Ion Imbalances

One of the most interesting aspects of our data is the lack of ion balances in most instances. These discrepancies are of two types. One is the mass imbalance between ion inputs and ion outputs for a given study site. The second is the imbalance between cations and anions at a given time and place. These imbalances lead to a whole range of new hypotheses to test in future studies.

Mass Balance Imbalances

When inputs from bulk precipitation (Table I) and management of cropland (see Results, Ion Balances of Cropland section) are compared with measured outputs from the three study sites for the entire study year, a net ion gain is apparent. This is true for ions assumed to be biologically inert such as Na^+ and Cl^- as well as for total cations and anions. As mentioned earlier, this seems to be clearly due to the effects of drought. In the forest site the volume of discharge was less than 5% of precipitation. Since transpiration is higher in a forest, drought effects on ion balances are most pronounced for the forest site. Another indication that drought is the main reason for the imbalance is data taken in February, when discharge volumes were relatively high. This was the only month in which ion discharges exceeded ion inputs for all three systems. It is not clear yet how long collection of input/output ion data must continue before a reasonable mass balance is achieved. Since 1980 was also a relatively dry year, ion outputs will hopefully exceed inputs after the next period of high precipitation and thorough flushing of the soils.

Cation/Anion Imbalances

Cations and anions in bulk precipitation appear relatively well balanced for the year (Table I). However, the balance is not as good for seasonal data. Organic N in bulk precipitation included both particulate and dissolved components and was, therefore, an overestimate of dissolved or easily soluble organic amines. This is particularly troublesome in spring due to tree pollen.

All seasonal and annual watershed discharges (Table I) had significantly more measured anions than cations. The reasons include the fact that we didn't determine Fe^{2+} , Mn^{2+} or Al^{3+} (listed in order of probable importance). Although these ions were not measured routinely in this study, some data are available. Discharges of dissolved iron from four larger, mixed-land-use watersheds in 1972 were not highly different and averaged 0.0073, 0.0061, 0.0098 and 0.023 $\text{keq}\cdot\text{ha}^{-1}$ in the spring, summer, fall and winter, respectively, for an annual iron discharge of 0.046 $\text{keq}\cdot\text{ha}^{-1}$. Year-to-year variation due to weather and variation due to differences in land use composition have not been determined. Unpublished data on manganese in stream waters indicates levels about 5–10% of those for iron. Dissolved aluminum levels in streams, including those draining the present study

sites, are usually less than 0.01 meq-L^{-1} , corresponding to less than $0.002 \text{ keq-ha}^{-1}$ of Al^{3+} discharge during the study year. The addition of these cations might have given an approximate cation/anion balance for the forest site discharges, but probably not for the managed sites.

The patterns of cation/anion balances for surface and groundwater (Tables V to VII) are more informative. In forest groundwater, for example, sulfate levels are greatly reduced at the lower elevation, suggesting biological reduction to sulfide, which was not measured in this study. In this case the sum of measured cations was more than double the sum of measured anions. This seems to make sense, but the discrepancy is about as great for surface runoff, collected at the same times. Sulfate concentrations in surface runoff were low, but always higher than those in bulk precipitation. The reduction of sulfate to sulfide in storm runoff is not very plausible, and at this time we have no suggestions of quantitatively important anions that were not measured, other than bicarbonate. Although bicarbonate was not routinely measured in these samples, in a few cases it was. In one set of surface runoff samples from pastureland, the sum of cations averaged 1.25 meq-L^{-1} and anions summed to 1.12 meq-L^{-1} . Of these anions, bicarbonate was 0.83 meq-L^{-1} or 74% of the sum. It seems that these surface runoff waters exchange their H^+ for alkaline earth cations and rapidly become neutralized since they are poorly buffered. The imbalance patterns in the groundwaters and surface waters of the pastureland site paralleled that of the forest site, except that sulfate groundwater concentrations were only slightly lower at the lower elevation. In the case of the cropland site cations anions are more nearly balanced in surface runoff (Table VII) and bicarbonate concentrations when measured were low. Groundwater at the bottom of the cropland was fairly acid (pH 4–5), probably due to the effects of nitrification. Thus, hydrogen ion would also have constituted a significant cation in the balance in addition to Fe^{2+} , Mn^{2+} and Al^{3+} .

Overview of Ion Flux Patterns in the Forest

To synthesize the dynamics of the ion flux through the forest system, simplifying schematic diagrams were drawn to illustrate important patterns of ion change (Figures 8 to 13). The spring season and a July storm were selected because they represent the most complete data available for the forest. In all of these diagrams the width of the pathway is proportional to the magnitude of the parameter measured. The percentage of total seasonal discharge occurring as quick flow (surface runoff) and slow flow (groundwater discharge) is also presented along with actual concentrations positioned relative to where the samples were taken within the system.

Average spring K^+ concentrations in surface runoff (Figure 8) were 30-fold higher than in bulk precipitation. Groundwater K^+ concentrations were 5- and 5.7-fold higher than in bulk precipitation at the upper and lower elevations, respectively. Thus, the increase in K^+ in groundwater seemed to occur primarily during infiltration. The Cl^- concentration pattern was similar qualitatively (Figure 9) to that for K^+ concentrations. Thus, much of the increase in these two ion concentra-

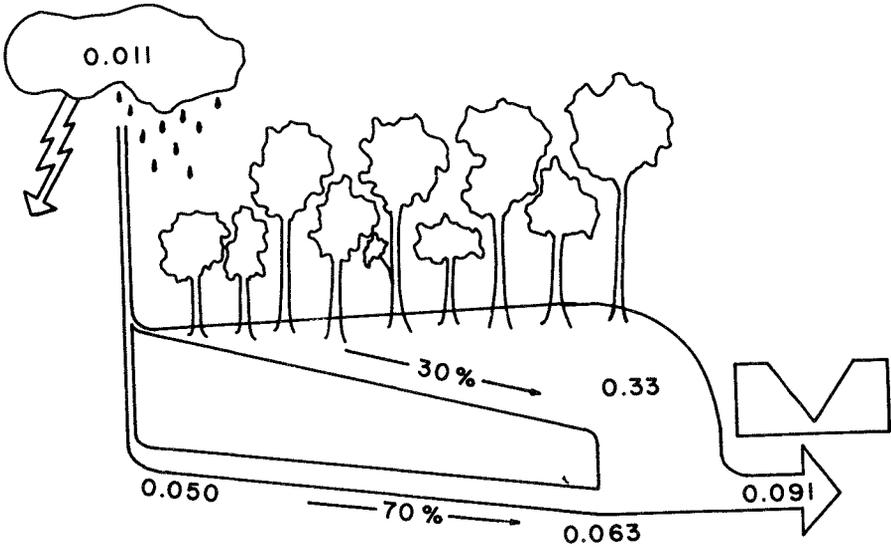


Figure 8. Diagram of average spring K^+ concentration changes (meq-L^{-1}) along different pathways through the forest study site from bulk precipitation inputs to stream outputs at the weir. Percentages given are the portions of total flow occurring as groundwater and surface runoff. Path width is proportional to the average concentration.

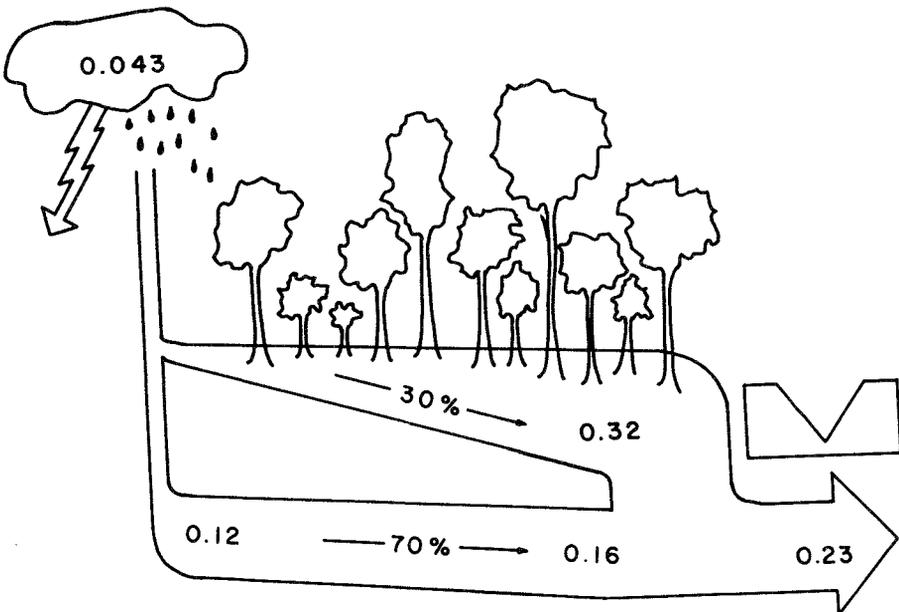


Figure 9. Diagram of average spring Cl^- concentrations (meq-L^{-1}) at the forest site. Otherwise as in Figure 8.

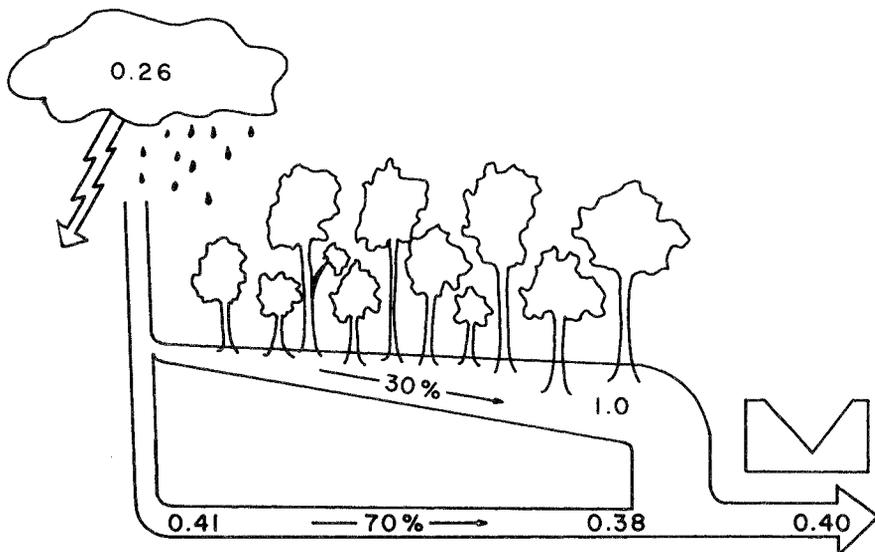


Figure 10. Diagram of average spring K^+/Cl^- ratios of the forest site. Otherwise as in Figure 8.

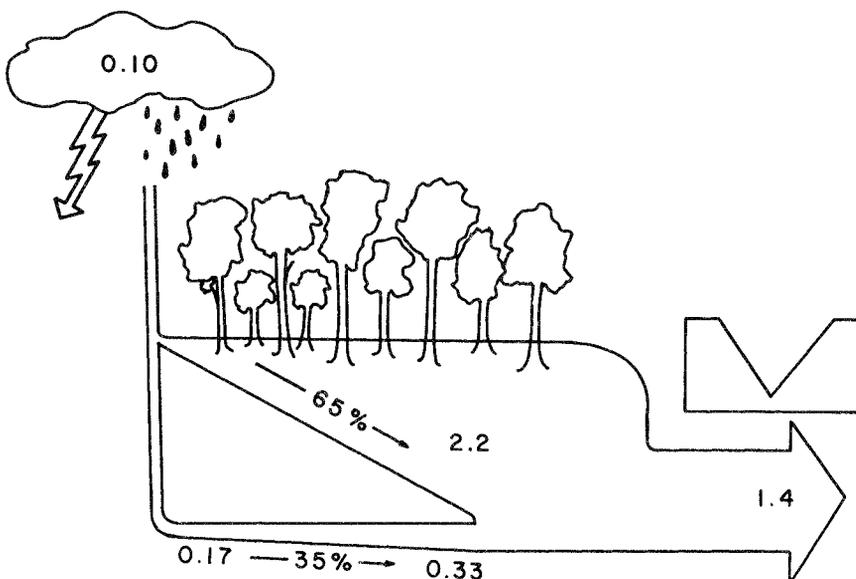


Figure 11. Diagram of K^+/Cl^- ratios during the July 4, 1981, storm week at the forest study site. Otherwise as in Figure 8.

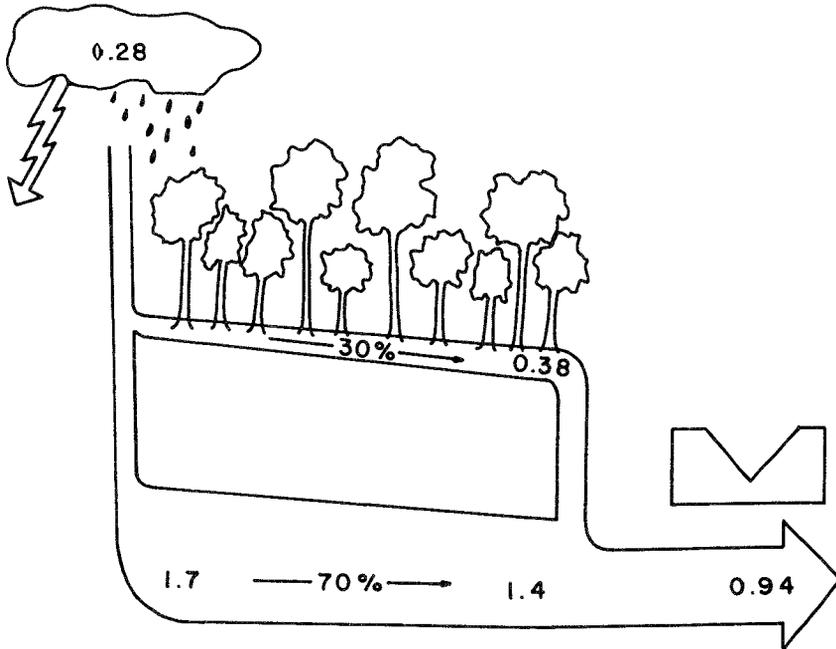


Figure 12. Diagram of average spring $\text{Mg}^{2+}/\text{Cl}^-$ ratios at the forest site. Otherwise as in Figure 8.

tions in surface runoff was probably due to the solution from plant and litter surfaces of dry salts deposited between storms. This deposition was probably both from dryfall impaction and evapotranspiration from surface and near surface materials. Increases in the concentrations of these ions as they move down the hydrologic gradient in groundwater are probably due primarily to the concentrating effects of evapotranspiration. When the ratio of K^+ to Cl^- is diagrammed (Figure 10), the effects of evapotranspiration are minimized and a more easily interpreted pattern is evident. It is reassuring that, although all data in the diagram were obtained independently, they balance reasonably well mathematically. This balance is a check on the adequacy of the hydrograph separations into surface and groundwater discharges and also the transect approach to sampling.

An example of the K^+/Cl^- pattern for a storm event (Figure 11) is given for the July 4, 1981, storm week. In this week 65% of total volume of discharge was surface flow with a K^+/Cl^- ratio of 2.2 while 35% was groundwater flow with a ratio of 0.33 at the lower elevation. The pattern for $\text{Mg}^{2+}/\text{Cl}^-$ ratios in the spring (Figure 12) is sharply contrasting to that for K^+/Cl^- ratios. Surface water ratios were not much higher than in bulk precipitation but groundwater ratios were much higher. An intermediate pattern was observed for the $\text{Mg}^{2+}/\text{Cl}^-$ ratio during the May 15, 1981, storm week (Figure 13). The ratio in surface runoff was enhanced 2.6-fold over bulk precipitation that week and 1.7-fold over

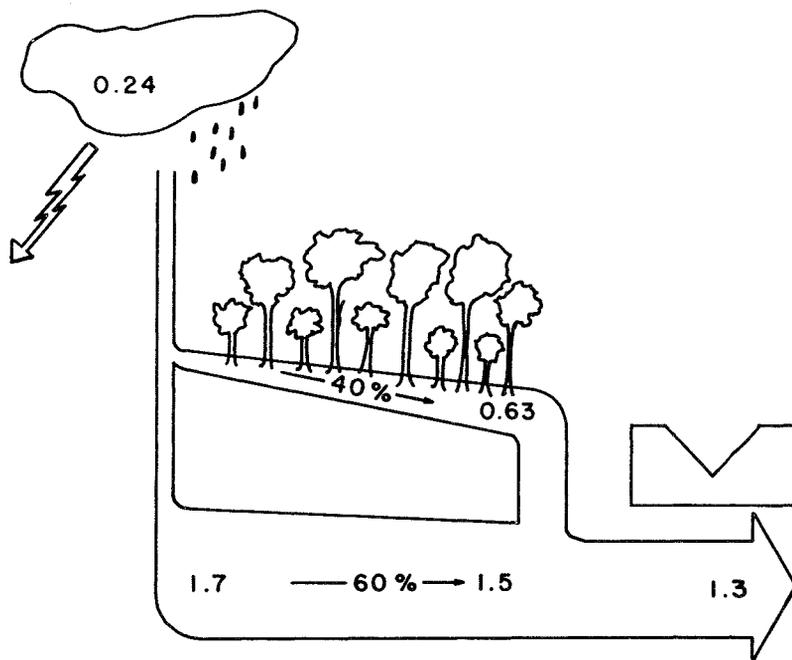


Figure 13. Diagram of Mg^{2+}/Cl^{-} ratios during the May 15, 1981, storm week at the forest study site. Otherwise as in Figure 8.

the average for spring surface runoff, but groundwater ratios were essentially the same. Patterns for Na^{+}/Cl^{-} and Ca^{2+}/Cl^{-} ratios were very similar to those for Mg^{2+}/Cl^{-} .

Nitrate Overview in the Cropland/Riparian System

Although nitrate fluxes into the watershed as bulk precipitation are high, they are small in comparison to inputs to cropland as fertilizer. Much of this fertilizer is applied as nitrate and ammonium. Nitrification in the surface soils oxidizes some of this to nitrate. Much of the fertilizer is also applied as organic N, often as urea. This material is also slowly mineralized and eventually yields significant nitrate discharges. Considering these large management inputs of nitrogen to croplands and the high concentrations of nitrate measured in both surface and groundwater leaving the cropland, the riparian forest seems to be carrying out an ecologically important role in the prevention of serious overenrichment of receiving waters with nitrate. The concentration pattern for nitrate during the spring in the cropland/riparian forest system (Figure 14) illustrates this beneficial role of the streamside forests. Nitrate concentrations were greatly reduced in both surface

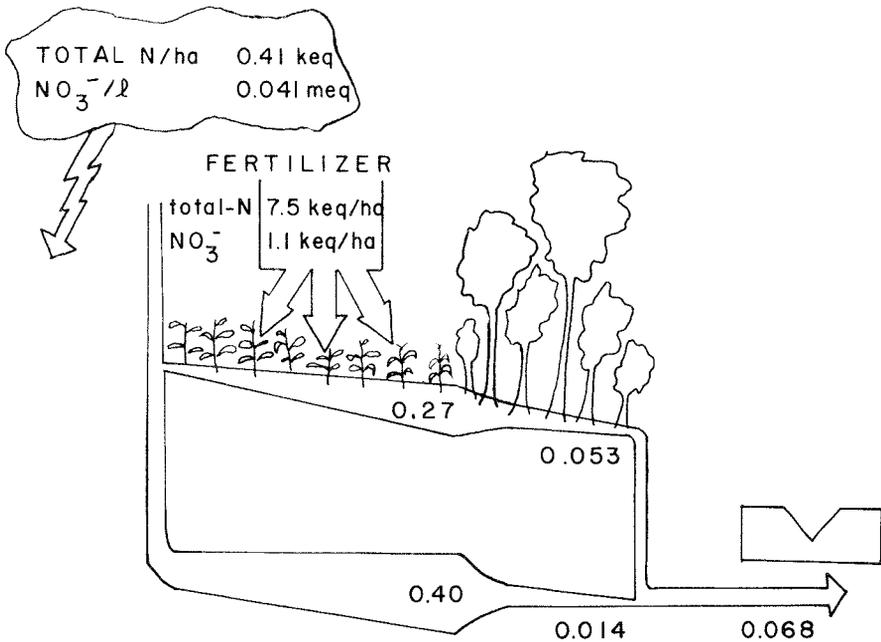


Figure 14. Diagram of average spring nitrate concentration pattern at the cropland study site, including the riparian forest. Spring fertilizer inputs were proportional relative to spring bulk precipitation inputs per hectare. Otherwise as in Figure 8.

and groundwaters during their transit of the forest. A similar pattern was observed for the other seasons. Note that the mean nitrate concentration observed at the weir was higher than the average concentration measured as surface runoff or groundwater. We believe this is due to areas within the riparian forest where conditions are not favorable for significant denitrification.

Comparisons with Other Studies

Bulk precipitation and forest discharge data from this study are compared with data from two other study sites in Table VIII. Hydrogen ion inputs were about equal at the Hubbard Brook site in New Hampshire but Na^+ and Cl^- input fluxes were about half of those at Rhode River. Acidity of precipitation at the Como Creek site in Colorado was much less, Na^+ flux intermediate when compared to the other two sites, and Cl^- was not measured. Ion ratios in bulk precipitation for K^+ and Mg^{2+} were about the same at Rhode River and Hubbard Brook, while $\text{Ca}^{2+}/\text{Cl}^-$ ratios were higher at Hubbard Brook. At Como Creek, the K^+/Na^+ ratio was somewhat higher, $\text{Mg}^{2+}/\text{Na}^+$ lower, and $\text{Ca}^{2+}/\text{Na}^+$ was much higher. When ion ratios in bulk precipitation are compared with the same ratios in land discharges (Table VIII), it is apparent that while the K^+/Na^+ ratio declined at

Table VIII. Comparisons of Ion Fluxes Between Selected Mature Forest Sites on Noncalcareous Soils (Units are $\text{keq}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$ or Ratio of Equivalents)

<i>Site</i>	H^+	Na^+	Cl^-	K^+/Na^+	K^+/Cl^-	Mg^{2+}/Na^+	Mg^{2+}/Cl^-	Ca^{2+}/Na^+	Ca^{2+}/Cl^-
Annual Bulk Precipitation Inputs									
Rhode River	0.94	0.12	0.32	0.35	0.13	0.70	0.27	0.88	0.33
Hubbard Brook [5,6]	0.92	0.067	0.17	0.34	0.13	0.63	0.25	1.5	0.60
Como Creek [10]	0.11	0.086	a	0.48	a	0.43	a	2.3	a
Land Discharge Outputs									
Rhode River	0.0021	0.072	0.080	0.45	0.41	1.3	1.2	0.87	0.79
Hubbard Brook [5,6]	0.012	0.28	0.12	0.14	0.31	0.82	1.9	1.7	3.9
Como Creek [10]	0.00018	0.069	a	0.12	a	0.78	a	1.7	a

^a Chloride was not measured in the Como Creek study.

the other two sites, it increased at the Rhode River site. The K^+/Cl^- ratio is more useful for comparison since sodium itself probably is being displaced from these systems. This ratio increased 2.4-fold at Hubbard Brook and 3.2-fold at Rhode River. The Mg^{2+}/Na^+ ratio increased in land discharges at all three sites and the Mg^{2+}/Cl^- ratio increased more than the K^+/Cl^- ratio at both Rhode River and Hubbard Brook. The Ca^{2+}/Na^+ ratio was relatively constant, except at Como Creek, where it declined. The Ca^{2+}/Cl^- ratio more than doubled in forest land discharges at Rhode River and increased over sixfold at Hubbard Brook. Thus, based on ion ratios to chloride, both the Hubbard Brook and Rhode River systems appear to be displacing K^+ , Ca^{2+} and Mg^{2+} . Judging from sodium ratios, Como Creek is displacing less K^+ and Ca^{2+} . If true, this might be explained by the differences in H^+ inputs (Table VIII).

Anticipated Biological and Ecological Effects

If K^+ , Mg^{2+} and Ca^{2+} are being displaced from the plant/soil system by H^+ in precipitation, one would like to have a temporal perspective of how rapidly this process will deplete the system of these essential plant nutrients. Especially for the forest system, how much is the annual net outward flux as compared to the available nutrient pool? To calculate a first approximation we assumed that the annual forest land discharge of these ions would, on the average, equal the product of the precipitation loading measured in this study and the proportional increase in discharges over bulk precipitation in the ion's ratio to Cl^- . For example, K^+/Cl^- ratios in forest discharges were 3.1-fold higher than in bulk precipitation (Table I). Therefore, average annual K^+ output was estimated to be 3.1 times 0.042 (the annual K^+ loading from precipitation) or 0.13 $keq\text{-ha}^{-1}\text{-y}^{-1}$. As a check on this calculation one would expect that H^+ fluxes into the system should approximately equal the sum of estimated annual outputs of Na^+ , K^+ , Mg^{2+} and Ca^{2+} . These are 0.288, 0.130, 0.382 and 0.264 $keq\text{-ha}^{-1}\text{-y}^{-1}$ for Na^+ , K^+ , Mg^{2+} and Ca^{2+} , respectively. The net estimated output of these ions by this method is 1.06 $keq\text{-ha}^{-1}\text{-y}^{-1}$. This is not very different from the bulk precipitation inputs of 0.94 $keq\text{-ha}^{-1}\text{-y}^{-1}$ of hydrogen ion. Thus, it seems reasonable to use these as an approximate rate of loss on an "average" year.

In a forest system most of the nutrient mass is usually stored in woody plant biomass and forests on the Rhode River site are no exception. The real issue, however, is how much of these plant nutrient elements are found in the soil. Relevant data on the composition of the soils of the forest study site is summarized in Table IX. Exchangeable potassium and magnesium were extracted with 1 *N* ammonium acetate. Total calcium and exchangeable potassium and magnesium were then determined by digestion with nitric acid, addition of lanthanum nitrate and atomic absorption spectroscopy. Appropriate controls, standards and spiked samples were also analyzed in order to correct for matrix effects. From these data (Table IX) it is apparent that there is a fairly large pool of exchangeable magnesium in the surface soils. However, the pools of potassium and calcium in

Table IX. Pools of Potassium, Magnesium and Calcium in Surface Litter and Surface Soils of Mature Forest Site at Rhode River in 1976

Zone	Dry wt. ($kg\cdot m^{-2}$)	Exchangeable K^+		Exchangeable Mg^{2+}		Total Ca^{2+}	
		$mg\cdot g^{-1}$	$keq\cdot ha^{-1}$	$mg\cdot g^{-1}$	$keq\cdot ha^{-1}$	$mg\cdot g^{-1}$	$keq\cdot ha^{-1}$
Leaf litter	1.14	0.25	0.073	2.8	2.66	1.5	0.86
Soil							
0–3 cm	24.8	0.25	1.59	2.1	43.4	0.08	0.99
3–5 cm	27.4	0.24	1.69	1.8	41.1	0.07	0.96
5–8 cm	39.8	0.16	1.63	1.5	49.8	0.06	1.19
8–12 cm	61.1	0.17	2.79	1.4	74.8	0.05	1.60
12–18 cm	93.9	0.17	4.09	1.7	133	0.10	4.70
18–24 cm	94.4	0.17	4.11	2.1	165	0.14	6.61
Sum	342		16.0		510		16.9

surface litter and the first few centimeters of soil, in which root hairs are most active for nutrient uptake, are rather small. They are much larger than the estimated annual flux rate, but could conceivably be completely depleted in a few years or decades, depending on the depth zone one considers. Indeed, this is a conservative estimate, because the rate of H^+ input and hence of cation output has been increasing over the past seven years (Figure 2). Also, much of the nutrient pool currently observed in the soil may really be either part of the root and microbial biomass in the soil or have been recently displaced from above ground and litter pools.

Plants require more calcium than any other mineral element and moderate levels of potassium for growth. Depletion of the available supply of these elements from forest systems is a matter of considerable concern, especially when surface soils do not contain these nutrients in the parent soil minerals. Native forest species have been selected over time for their ability to compete effectively for these ions and to keep them tightly recycled. Also, some species require more of a given element to survive. With hydrogen ion inputs from precipitation increasing rapidly, many plant species may no longer be able to successfully compete for these elements. Thus, the gradual loss of key elements such as calcium may, over time, bring about significant shifts in the species composition of forests [25]. In the case of calcium and potassium, the shorter-term effects anticipated include decreased sexual reproduction, a decline in general vegetative physiological vigor, and a consequent increase in the incidence of disease and insect attack [26,27].

CONCLUSIONS

The results from this study confirm others which have found a trend of increasing acidity in rainfall and important regional differences in its effects. It is also relatively

clear that at the Rhode River site, increased hydrogen ion inputs are displacing the essential plant nutrients of Mg^{2+} , Ca^{2+} and K^+ . Although displacement rates are apparently low, available pools in forested areas could be depleted in a few decades and cause ecologically significant effects.

Ion losses appeared to be proportional to the magnitude of disturbance associated with the three land uses studied. Thus total cation and anion outputs were lowest from the forest site, similar but higher for the pastureland, and significantly greater in the cropland discharge than in either of the other two. Concentrations at the weirs closely approximated the discharge-weighted concentrations of surface and groundwater, indicating that analysis of these different flow pathways through a watershed is an important key to understanding the origins of the final output concentrations.

The functional importance of the riparian forest in reducing nitrate concentrations in discharge from an agricultural watershed was clearly shown and raises interesting questions as to the generality of this result. Other questions raised by this study are the importance of Fe, Mn, and Al ions in intrawatershed patterns of ion change and what measures should be taken to best compensate for K^+ , Mg^{2+} and Ca^{2+} losses. Most importantly, however, this study shows how the concentrations of various chemical components in stream waters are partially controlled by the complex interplay of chemical factors (such as pH), physical/biological factors (such as the redox potential), climatic factors (such as droughts and intense storms) and anthropogenic factors (such as land use and acid rain). All of these factors when taken separately are not perfectly understood, let alone when they are allowed to interact. Thus, future research along these lines is both needed and essential to achieve a better understanding of multiple land use systems.

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