EFFECTS OF PRECIPITATION AND AIR TEMPERATURE ON NITROGEN DISCHARGES FROM RHODE RIVER WATERSHEDS

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Abstract. We studied discharges of total-N, nitrate, ammonium, and total organic-N from seven contiguous small watersheds on the Atlantic Coastal Plain in Maryland for up to 25 yr. These watersheds have perched aquifers so all groundwater discharges as well as surface runoff were measured at V-notch weirs which included volume-integrating flow-proportional samplers. Interannual variations in annual and seasonal precipitation during this study spanned approximately the range of 160 yr weather records in the region. Annual total-N area yields from the overall watershed varied ninefold, correlations of all N-parameter discharges with precipitation were highly significant, and power function regressions of precipitation vs N-discharge explained from 36 to 59% of the variance. Nitrogen fluxes from a cropland watershed were much higher and more variable with volume of precipitation, while fluxes from a forested watershed were much lower and were primarily composed of organic-N. Correlations of N-fluxes with precipitation were higher in the winter and spring. Annual and seasonal N-concentrations also often increased significantly with precipitation. Variations in seasonal air temperature sometimes explained significant amounts of variance in N-discharges, especially ammonium. A model composed of regressions was used to construct graphical and tabular summaries.

Keywords: ammonium, nitrate nitrogen, organic-N, watershed, weather effects

1. Introduction

Excessive N-discharges to estuaries including Chesapeake Bay are believed to be the key to over-enrichment or eutrophication of these valuable natural resources and diffuse or non-point sources are believed to be the dominant sources of these excessive N-inputs (Boynton *et al.*, 1995); Seitzinger and Sanders, 1997).

A large number of studies have measured the discharge of nitrate, ammonium, and organic-N from various watersheds. The usual focus has either been comparative effects of land use in a small region (e.g. Cooper and Thomsen, 1988; Correll and Dixon, 1980; Hill, 1978; Hirose and Kuramoto, 1981), differences in discharges among widely separated regions (e.g. Beaulac and Reckhow, 1982; Frink, 1991; Malmer and Grip, 1994), or patterns of change in nitrogen concentrations from a single watershed due to a storm event (e.g. Burt and Arkell, 1987; McDiffett *et al.*, 1989; O'Brien *et al.*, 1993). These studies have clearly established that land use, particularly intensive agriculture, has a strong influence on N-discharges. They have also shown that N-discharge fluxes from a given watershed are seasonal,

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peaking in the winter and spring in temperate regions. The evidence seems fairly good that there are also significant differences in N-discharges from a given land use in different regions, perhaps due to geological and climatic differences. It is also clear that during individual storm events concentrations of parameters such as nitrate, ammonium and organic-N span a broad range and usually are not well correlated with the hydrograph.

However, very few studies have analyzed the effects of interannual variations in precipitation and temperature on discharges of N-fractions. Such an analysis requires many years of data from the same watershed. A few studies (e.g. Alexander *et al.*, 1996; Lucey and Goolsby, 1993) have examined the relationship of interannual variations in stream water discharge with nitrate fluxes, but these studies were of larger rivers with more complex land use, waste water outfalls, reservoirs, and water withdrawals. In contrast, our study provides a unique perspective because the watersheds were first and second order streams with relatively simple land use compositions.

In this study we have sampled for up to 25 yr the discharges of nitrate, total ammonium, and total organic-N from seven contiguous small subwatersheds of the Rhode River in Maryland, U.S.A., which differed in land use, but had similar weather, soils, geology, and hydrology. The watersheds were continuously monitored for discharge with V-notch weirs which included volume-integrating flow-proportional samplers. It is our objective to define the effects of various in mean annual, seasonal, and weekly precipitation and air temperature on discharges of N-fractions from forested, cropped, grazed, and mixed land use watersheds on the inner mid-Atlantic Coastal Plain of North America.

2. Methods

2.1. Site Description

The watersheds studied are all subwatersheds of the Rhode River, a tidal tributary to the Chesapeake Bay in Maryland, U.S.A. (38°51′N, 76°32′W). The Rhode River is within the inner Atlantic Coastal Plain. This region characteristically has frequent intense precipitation events, especially in the spring and summer and highly erodible soils. The watershed has sedimentary soils from the Pleistocene Talbot formation at low elevations on the eastern part 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. The soils are fine sandy loams and the mineralogy of the soils is fairly uniform, with a high level of montmorillonite and quartz, intermediate levels of illite and kaolinite, and low levels of gibbsite, chlorite, potassium feldspar, and plagioclase (Correll *et al.*, 1984). Soils have high moisture capacity, but relatively low infiltration rates, so that intense storms generate overland storm flows. However,

TABLE I

Areas (ha) and land use composition (%) of Rhode River study subwatersheds in 1976 (Correll, 1977)

Watershed	Area	Forest	Row crops	Pasture and hay fields	Residential	Old fields
101	226	38	10	27	6	19
102	192	47	18	22	6	7
103	253	63	2	16	5	14
108	150	39	24	20	3	14
109	16.3	36	64	0	0	0
110	6.3	100	0	0	0	0
111	6.1	27	0	73[a]	0	0

[a] Until 1989, when it was planted in pine seedlings.

about 65 to 75% of annual water discharge is via groundwater. bedrock is about 1000 m below the surface, but the Marlboro Clay layer forms an effective aquiclude slightly above sea level throughout the watershed (Chirlin and Schaffner, 1977). Each subwatershed has a perched aquifer so that overland storm flows, interflow, and groundwater discharges all move to the channel draining each subwatershed. The slopes of the watersheds average between five and nine percent. The study watersheds ranged in size from 6.1 to 253 ha and differed in land use (Table I). Three watersheds were drained by first order streams. One (# 110) was completely forested, another (# 109) was primarily row-cropped, and one (# 111) was primarily land rotationally grazed until the spring of 1989, when it was planted with pine seedlings (Correll *et al.*, 1995). The other watersheds were drained by second order streams and had mixed land use. For more detailed descriptions of the site see Correll (1981) and Corell and Dixon (1980).

2.2. Sampling

Discharges of water from each watershed were measured with sharp-crested V-notch weirs, whose foundations were in contact with the Marlboro Clay aquiclude (Correll, 1977). All weirs were 120° notches, except for watershed 111, which was 150°. Each weir had an instrument building and a stilling well. Depths were measured to the nearest 0.3 mm with floats and counterweights and were recorded every 5 min for watersheds 101, 109, 110, and 111; every 15 min for the other watersheds. Prior to the summer of 1974, discharges from watershed 101 were measured with a 90° V-notch weir and recorded on a strip chart (Pluhowski, 1981).

Water samples were composited and volume-integrated for one week intervals, then promptly collected and returned to the laboratory. A Stevens, model 61R, flow meter actuated the sampling of an aliquot once every 154 m^3 of flow on the second order streams and once every 77 m^3 of flow on the first order streams. The water sample was drawn from the stream channel upstream of the weir and was deposited into a plastic container pretreated with 20 mL of 18 N sulfuric acid to prevent biological or enzymic activity during storage. After collection samples were either analyzed immediately or stored at 4 °C.

Rainfall volume and air temperature data were obtained from the Center's weather station, located on watershed 101 (Higman and Correll, 1982; and subsequent data). Rainfall volumes were measured with standard manual rainfall gauges, backed up wih a Belfort weighing gauge. Air temperatures were recorded with maximum/minimum mercury thermometers and a Belfort recording hygrothermograph.

2.3. Sample Analysis

Total Kjeldahl (TKN) was determined by digestion to ammonium with sulfuric acid, Hengar granules, and hydrogen peroxide (Martin, 1972). The ammonium in the digestate was steam distilled and analyzed by Nesslerization (APHA, 1989). Ammonium was also determined in undigested aliquots by oxidation to nitrite with alkaline hypochlorite (Strickland and Parsons, 1972) and analysis of the nitrite by reaction with sulfanilamide (APHA, 1989). Ammonium was the sum of dissolved and acid-extractable particulate ammonium. Total organic-N was calculated by substracting ammonium from TKN. The sum of nitrate and nitrite was measured by reducing nitrate to nitrite with cadmium amalgam, and analyzing nitrite by reaction with sulfanilamide (APHA, 1989).

2.4. Data preparation

Weir discharges and rain volumes were summed and mean daily air temperatures were averaged for watershed weeks, which normally began on Monday; and seasons, which were winter (December, January, February), spring (March, April, May), summer (June, July, August), and fall (September, October, November). Watershed years began with December. Discharge volumes were multiplied by volume-integrated concentrations to obtain weekly fluxes of various N-fractions. Seasonal and annual mean concentrations of N-fractions were calculated by summing weekly fluxes, then dividing by summed water discharges. Mean Rhode River watershed discharge data from the study watersheds (Table I) were weighted by area and are, for convenience, referred to as Rhode River or overall watershed discharges.

When flow was loo low to obtain an integrated sample for analysis, spot samples were analyzed. From five to ten percent of the discharge data for any given weir were missing due to equipment failures. When no significant precipitation occurred during the data gap, these data were estimated by interpolation of data from the same weir. When storm events occurred during the data gap, these data were estimated by correlation with discharge data from the watershed with the most similar nitrogen discharge behavior.

The mean and range of annual and seasonal precipitation which were observed during this study were put into perspective by comparison with a longer-term record. Higman and Correll (1982) summarized data collected from 1967 to 1977 at our research center, from 1857 to 1967 at the U.S. Naval Academy in Annapolis, MD; and from 1817 to 1856 at U.S. Army Fort Severn, on the Severn River near Annapolis for a total record of 160 yr. Gaps in the Naval Academy data were filled with data from Fort Severn. All three sites are on the upper western shore of Chesapeake Bay within 20 km of each other and at the times of data collection were fairly small towns, thus minimizing any ‘heat island’ effects.

3. Results

3.1. Nitrogen fluxes

3.1.1. *Annual*

Annual fluxes of total-N, nitrate, total organic-N, and total ammonium from the Rhode River watershed increased substantially with precipitation volume (Figure 1). Total-N area yields varied from about one to nine kg N ha^{-1} yr. Linear correlations of N-fluxes with precipitation were all highly significant ($P < 0.0001$) but power function regressions fit the data best (highest R^2) and explained from 36 to 59% of the variance. Organic-N fluxes increased more rapidly and were more correlated with precipitation than nitrate or ammonium fluxes. Annual fluxes from a cropland watershed were much higher, varying with volume of precipitation from 0.33 to 24.4 kg N ha^{-1} yr, also highly significant and volume of precipitation explained from 42 to 64% of the variance. The fluxes of all forms of N from the cropland watershed increased more rapidly with precipitation than was found for the overall Rhode River watershed (Figure 1). In the case of a forested watershed, fluxes of total-N were much lower and varied from 0.07 to 5 kg ha^{-1} yr. Most of the total-N discharged from the forested watershed was organic-N and the organic-N fluxes were similar to those from the overall Rhode River watershed, however the fluxes of ammonium and nitrate were much lower from the forested watershed. Total-N and organic-N fluxes and precipitation volume were highly significantly correlated, but the significance for nitrate and ammonium were much lower (P = 0.05 and 0.15, resp.). For a grazed watershed the relationships between precipitation and N-discharges were much weaker ($R^2 = 0.20$ to 0.32, $P > 0.05$). Total-N fluxes varied from 0.33 to over 5 kg N ha^{-1} yr and were composed of about equal amounts of organic-N and and nitrate with a small amount of ammonium.

Annual temperature variations generally had little relationship with N-fluxes from the watersheds. Usually the combination of precipitation and air temperature explained only a few percent more of the variance in N-discharges than precipitation alone. The exception was for nitrate flux from the grazed lands, where the R^2 for linear regressions improved from 0.19 to 0.29 when air temperature was included.

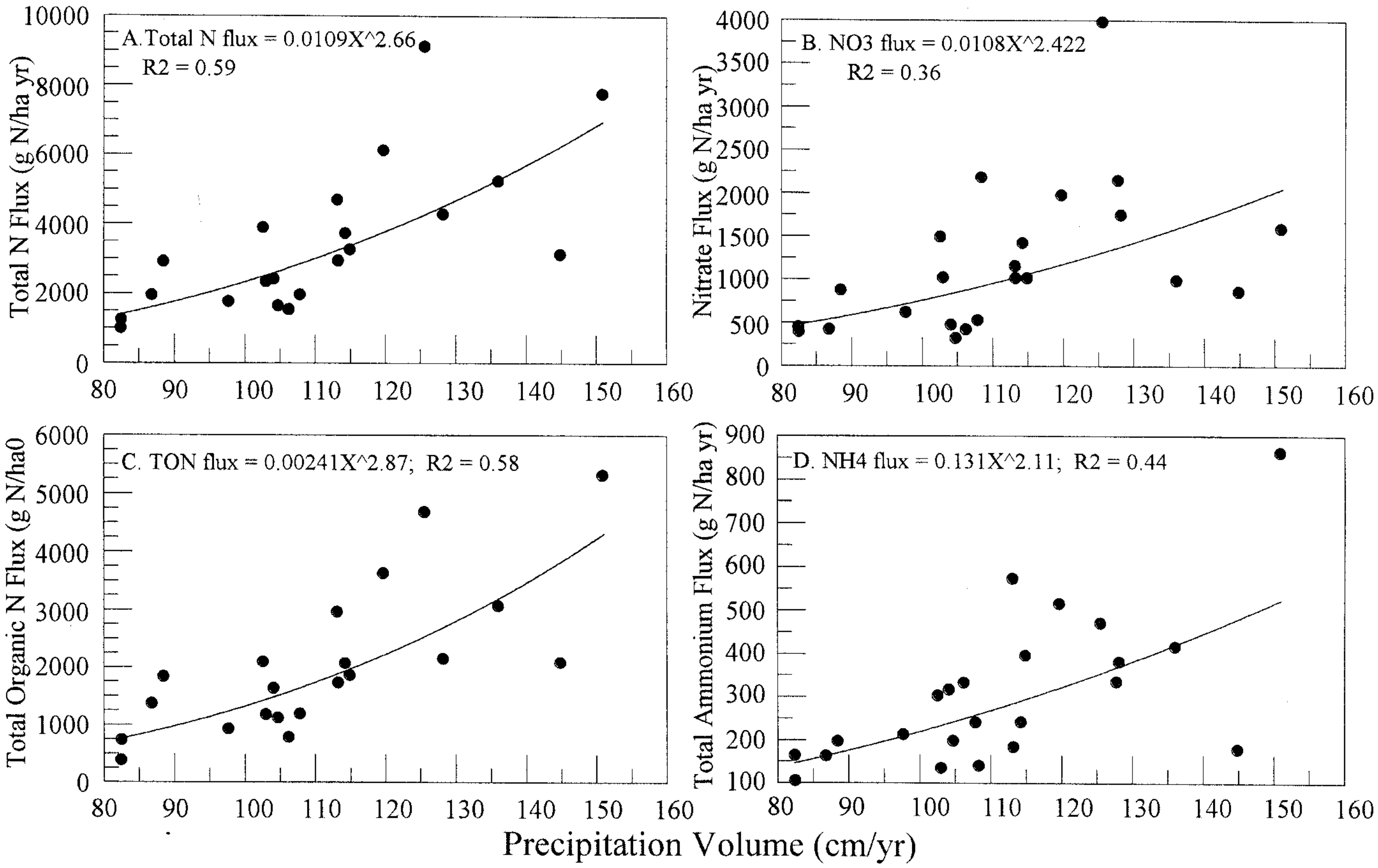

Figure 1. Variations in nitrogen parameter annual fluxes from area-weighted Rhode River watershed with volume of precipitation.

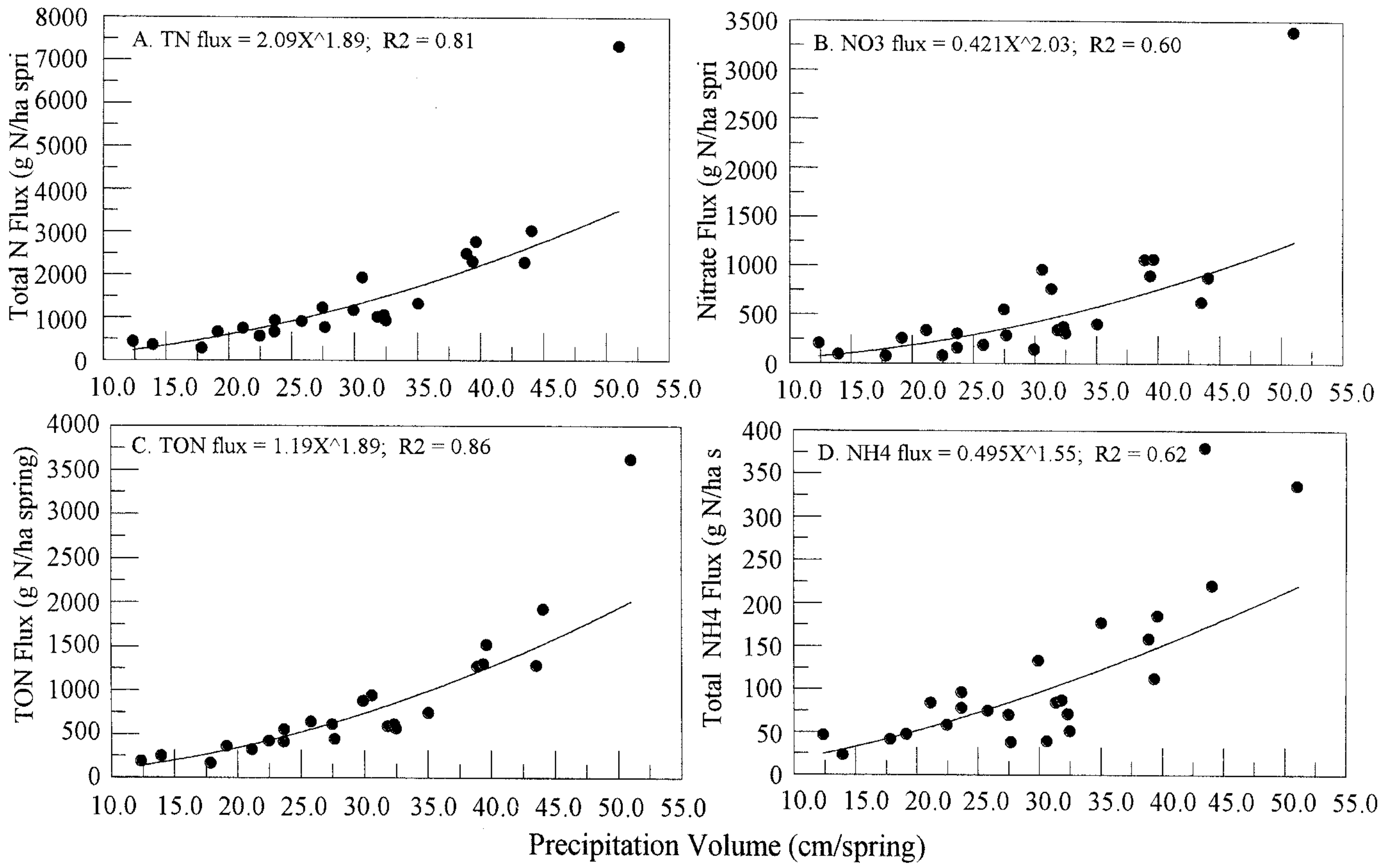

Figure 2. Variations in spring nitrogen fluxes from areas-weighted Rhode River watershed with volume of precipitation.

3.1.2. *Winter and Spring*

In the winter and spring when most N-discharge usually occurred, correlations between total-N and nitrate discharges from the overall watershed and precipitation were higher than for annual data and all were highly significant. For the overall Rhode River watershed in the winter, the best regression fits were usually linear and volume of precipitation explained 65% of the variance in nitrate and total-N discharge. Nitrate accounted for well half of the total-N discharge in winter. Cropland winter discharges were dominated by nitrate, while forest and grazing land discharges were dominated by organic-N. Spring total-N discharge from the overall watershed ranged from 0.28 to over 7.4 kg N ha^{-1} spring (Figure 2) and over half of this was organic-N. Volume of spring precipitation explained from 60 to 86% of the variation in spring discharges of N-parameters from the overall watershed. Spring cropland discharges were composed of about equal amounts of nitrate and organic-N plus small amounts of ammonium. Variations in precipitation explained 67 to 73% of the variance in total-N, organic-N, and ammonium spring fluxes from cropland, but only 46% for nitrate. Spring forest total-N discharges varied from 0.033 to 2.8 kg N ha^{-1} spring, mostly as organic-N. Precipitation volume explained 78 to 79% of the variance in spring forest discharges of total-N, nitrate, and organic-N, but only 57% for ammonium. Spring total-N discharges from grazing lands were similar in magnitude to those from forest, but were composed of about equal amounts of nitrate and organic-N and were less correlated with precipitation. All correlations were significant ($P < 0.01$, except ammonium flux, $P = 0.05$). The best regression fits for grazing land were exponential.

As in the case of the annual data, including air temperature in multiple linear regressions for winter data had little effect except for the grazed watershed 111. In that case all correlations were improved considerably by including air temperature. For total-N, R^2 increased from 0.55 to 0.79; for nitrate, R^2 increased from 0.43 to 0.69; for organic-N R^2 increased from 0.63 to 0.76; and for total ammonium, R^2 increased from 0.49 to 0.71. For watershed 111 in the winter a multiple regression appears significantly improved over using only precipitation. For spring data, only the linear regression for total ammonium from grazed lands was improved by including air temperature in the regression ($R^2 = 0.23$ and 0.49, resp.), but there was a similar improvement for organic-N flux from cropland ($R^2 = 0.57$ and 0.71, resp.).

3.1.3. *Summer and Fall*

Much less N was usually discharged from the watershed in the summer and fall and the correlations with precipitation were lower in the summer than in the spring. The best regression fits (highest R^2) were usually exponential in the summer, except for grazing lands which were usually linear. In the fall the best regression fits were usually power functions, except for grazing lands, which were usually linear. For the Rhode River watershed total-N fluxes varied from 0.008 to 3.7 kg N ha^{-1} summer or fall and were dominated by organic-N. Precipitation volume explained 42–46%

of the variance in summer N fluxes and 48–64% for fall fluxes and all of these correlations were highly significant ($P < 0.001$). Fall total-N fluxes from cropland ranged from 0.001 to 2.5 kg total-N ha^{-1} fall. Fall correlations of N fluxes from cropland and forest with precipitation were fairly high and significant ($P < 0.005$), but for grazed land were nearly zero.

Summer air temperatures only helped explain N fluxes from the grazed lands, for which the linear correlations with precipitation were quite low. For example, including air temperature improved the R^2 for nitrate from 0.026 to 0.12 and for organic-N from 0.066 to 0.14.

3.1.4. *Statistical Models*

Regression curves for the annual fluxes of N parameter from the watersheds versus precipitation volume (Figure 3) help visualize the patterns of flux for total-N, nitrate, total organic-N, and total ammonium. For the overall watershed, organic-N is dominant at all levels of precipitation, followed by nitrate. For cropland, nitrate is dominant for dry years, but in wetter years organic-N becomes at least equally important, while ammonium is always a minor component. For forest, nitrate and ammonium are about equal and do not increase very rapidly with precipitation, but organic-N increases very rapidly with precipitation and is always dominant. For grazed land, there is an intermediate pattern, with nitrate only a little lower than organic-N at all levels of precipitation. In the winter, in wet years nitrate becomes more important than organic-N for the overall watershed (Figure 4), while in the spring the pattern for the overall watershed (Figure 5) is similar to the annual pattern. In the summer, the regressions curve upward much more steeply with increasing precipitation, except for the grazed watershed (Figure 6) and at high precipitation organic-N dominated the cropland fluxes. In the fall, N-fluxes from cropland were about equally composed of nitrate and organic-N (Figure 7).

These regressions of N-fluxes versus precipitation and long-term rainfall records were used to construct Tables II and III. The regression equations and their coefficients of determination are listed in Table IV and constitute a statistical model of N-fluxes from these watersheds as a function of precipitation. For the overall Rhode River watershed, cropland, forest, and grazed land, annual and seasonal N-discharge fluxes of total-N, nitrate, organic-N, and ammonium were calculated for time periods of low, average, and high precipitation. For convenience we used the mean precipitation, $\pm$ one standard deviation (SD) from the mean, and $\pm$ 2 SD from the mean. Generally, the ranges of precipitation that occurred during this study are bracketed by the $\pm$ 2 SD category.

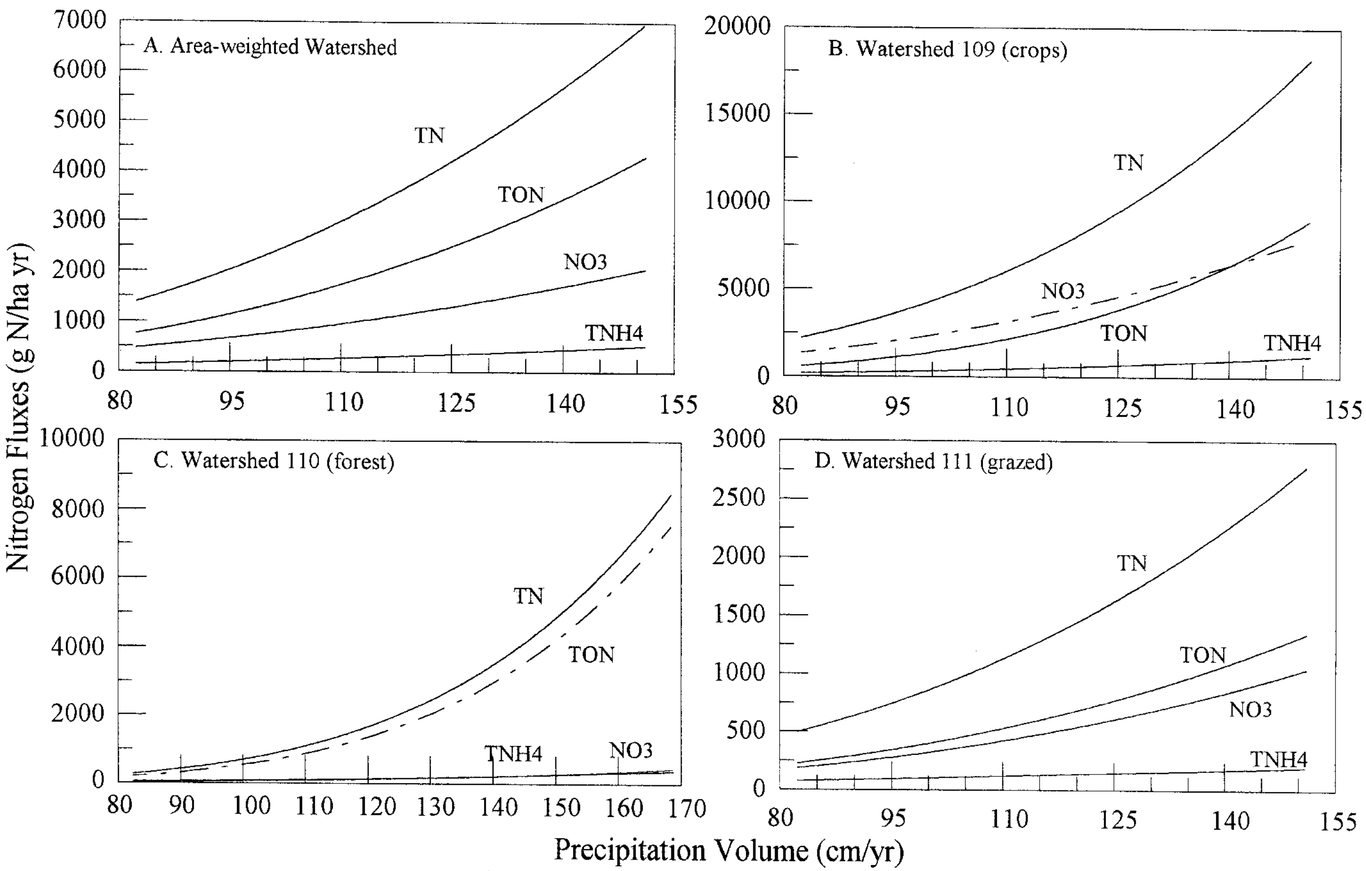

Figure 3. Variations in annual watershed nitrogen fluxes with volume of precipitation. Curves are from regression equations in Table IVA.

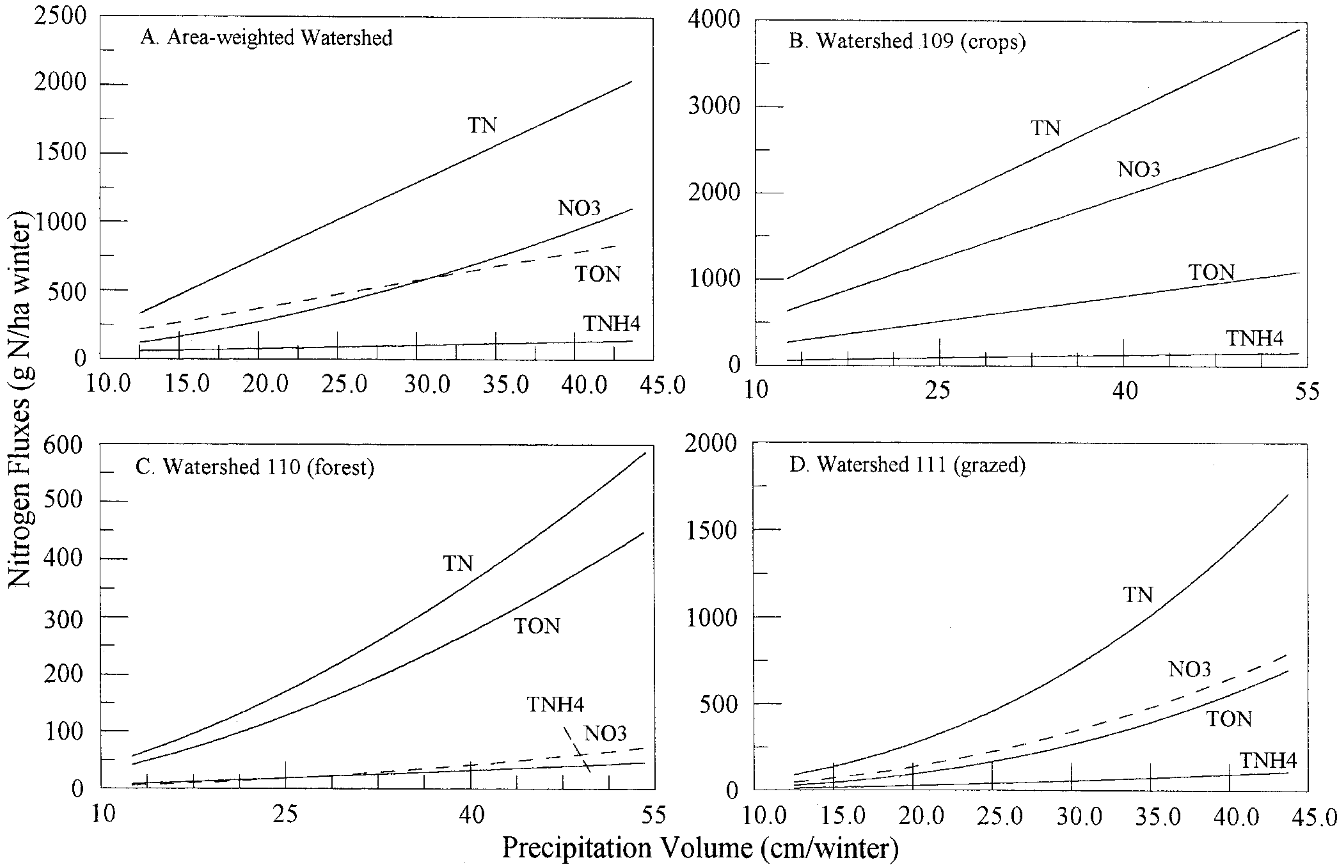

Figure 4. Variations in winter watershed nitrogen fluxes with volume of precipitation. Curves are from regression equations in Table IVB.

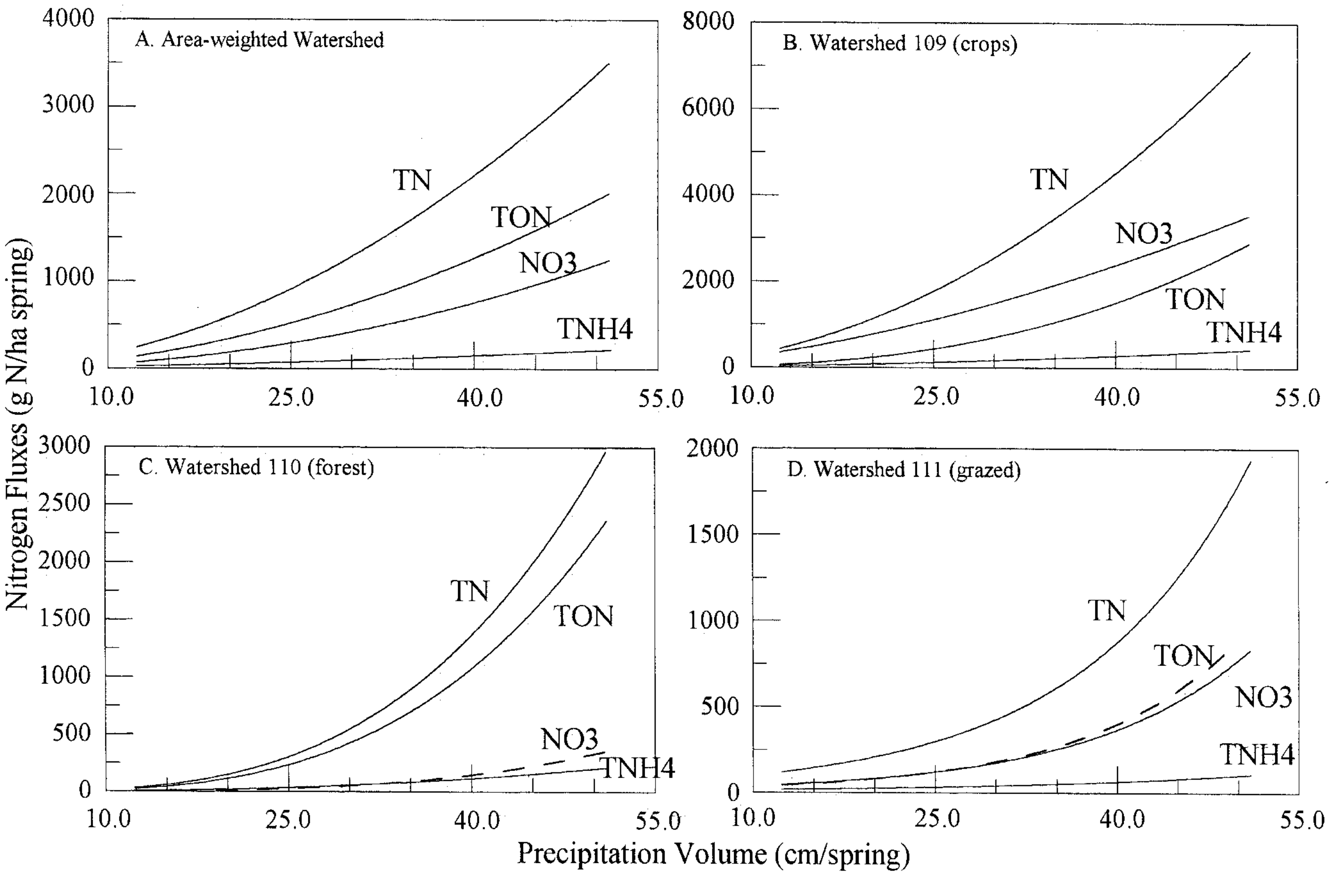

Figure 5. Variations in spring watershed nitrogen fluxes with volume of precipitation. Curves are from regression equations in Table IVC.

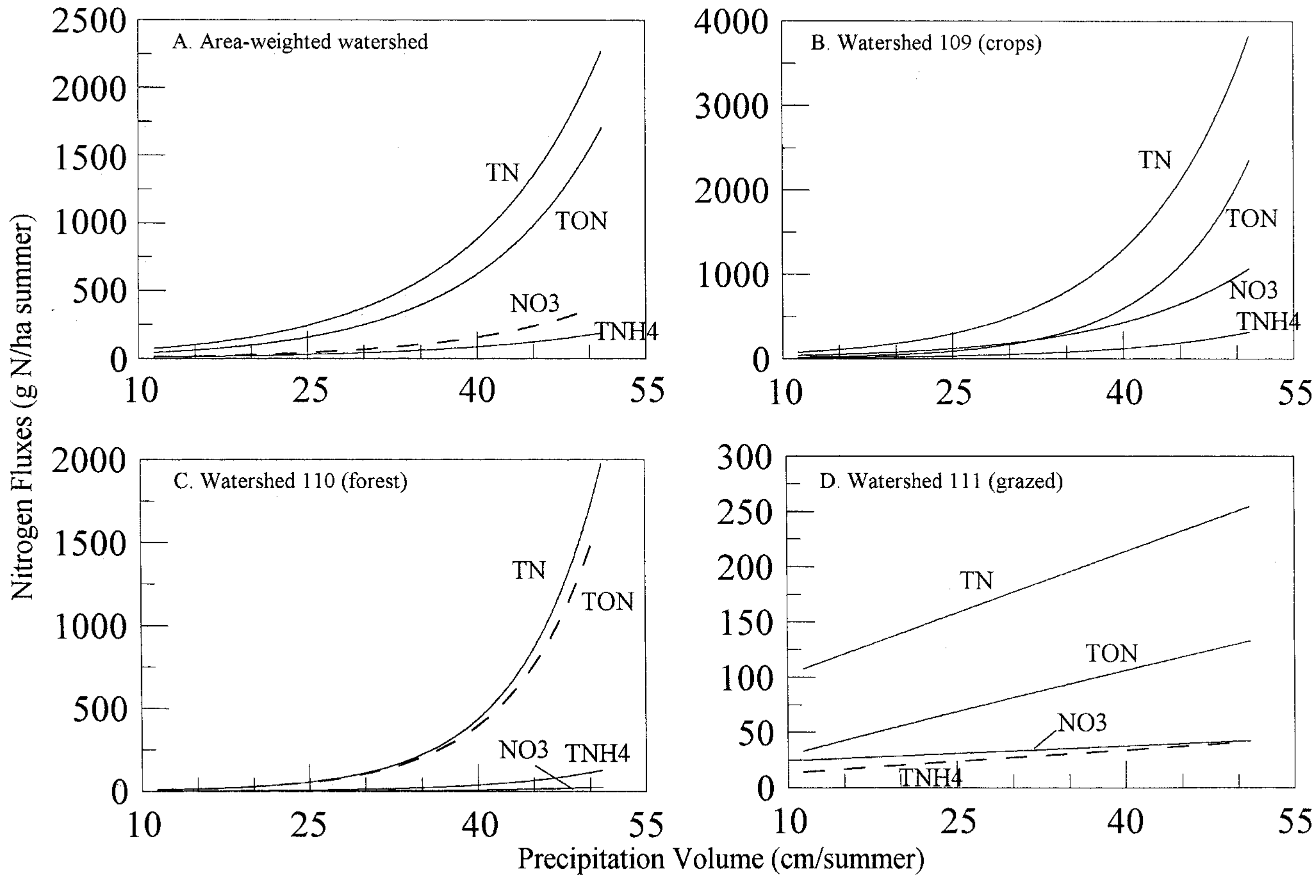

Figure 6. Variations in summer watershed nitrogen fluxes with volume of precipitation. Curves are from regression equations in Table IVD.

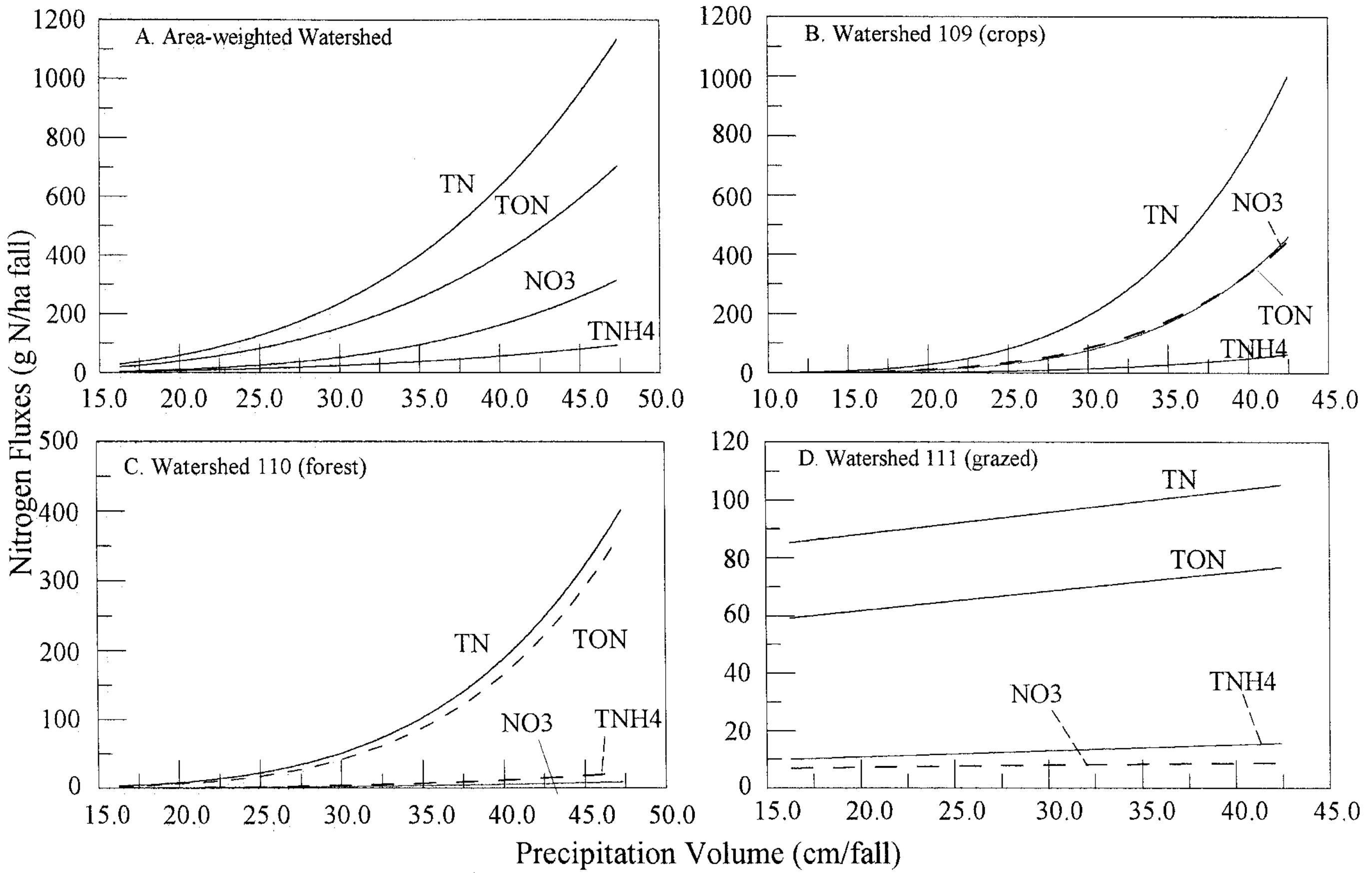

Figure 7. Variations in fall watershed nitrogen fluxes with volume of precipitation. Curves are from regression equations in Table IVE.

TABLE II

Annual nitrogen discharge fluxes (g N ha^{-1} yr) from Rhode River watersheds as a function of precipitation (cm yr^{-1}). Flux values calculated from regressions of nitrogen discharge versus precipitation

Precipitation	Area-Weighted Watershed				Watershed 109 (crops)				Watershed 110 (forest)				Watershed 111 (grazed)			
	TN	NO_3	TON	TNH_4	TN	NO_3	TON	TNH_4	TN	NO_3	TON	TNH_4	TN	NO_3	TON	TNH_4
–2 SD (64.4 cm)	706	258	375	85.9	935	653	194	83.5	83.3	11.7	57.8	22.9	241	92.9	110	51.6
–1 SD (86.2 cm)	1530	522	865	159	2590	1540	723	208	339	35.0	244	53.6	553	213	259	82.0
mean (108.0 cm)	2790	900	1650	256	5680	3000	2000	421	1000	81.5	795	103	1050	406	502	117
+1 SD (129.8 cm)	4560	1400	2800	377	10800	5160	4600	749	2430	162	2020	176	1770	685	862	157
+2 SD (151.6 cm)	6890	2050	4370	523	18600	8160	9280	1220	5120	291	4440	277	2740	1070	1360	201

TABLE III

Seasonal nitrogen discharge fluxes (g N ha^{-1} season) from Rhode River watersheds as a function of precipitation (cm/season). Flux values calculated from regressions of nitrogen discharge versus precipitation

Precipitation	Area-Weighted Watershed				Watershed 109 (crops)				Watershed 110 (forest)				Watershed 111 (grazed)			
	TN	NO_3	TON	TNH_4	TN	NO_3	TON	TNH_4	TN	NO_3	TON	TNH_4	TN	NO_3	TON	TNH_4
A. Winter																
–2 SD (10.22 cm)	206	82.7	169	52.0	842	523	226	53.6	40.9	3.67	29.7	6.55	55.9	29.5	16.6	7.79
–1 SD (17.41 cm)	601	277	316	70.8	1340	874	367	75.6	96.0	9.53	70.4	12.2	197	97.8	65.3	20.40
mean (24.6 cm)	996	395	464	89.7	1840	12220	509	94.4	167	17.7	123	18.3	445	213	159	38.2
+1 SD (31.79 cm)	1390	623	611	108	2350	1570	650	111	252	28.0	187	24.7	815	379	307	60.8
+2 SD (38.98 cm)	1790	896	759	127	2840	1920	792	127	349	40.3	260	31.4	1320	600	519	87.9
B. Spring																
–2 SD (10.94 cm)	192	54.1	109	20.2	337	288	47.3	28.4	21.5	1.33	16.3	4.60	123	48.2	45.9	18.3
–1 SD (19.47 cm)	572	174	325	49.3	1060	734	220	78.0	135	10.9	106	19.2	250	100	100	28.8
mean (28.0 cm)	1140	365	647	86.6	2180	1320	581	147	430	40.7	342	47.3	507	209	220	45.3
+1 SD (36.53 cm)	1880	626	1070	131	3710	2030	1180	234	1000	107	963	91.6	1030	435	480	71.3
+2 SD (45.06 cm)	2790	958	1590	181	5630	2860	2070	338	1960	230	1600	154	2090	906	1050	112

TABLE III

Continued.

Precipitation	Area-Weighted Watershed				Watershed 109 (crops)				Watershed 110 (forest)				Watershed 111 (grazed)			
	TN	NO_3	TON	TNH_4	TN	NO_3	TON	TNH_4	TN	NO_3	TON	TNH_4	TN	NO_3	TON	TNH_4
C. Summer																
–2 SD (8.40 cm)	66.1	13.2	39.3	10.6	66.6	34.2	13.6	8.93	7.09	0.498	7.64	1.54	96.7	23.6	25.1	12.7
–1 SD (19.9 cm)	206	39.5	132	26.8	245	104	71.6	28.2	43.3	1.76	43.1	6.38	139	28.8	55.8	20.6
mean (31.4 cm)	644	118	444	67.8	902	314	378	88.9	265	6.23	243	26.5	182	33.9	85.1	28.4
+1 SD (42.9 cm)	2010	352	1490	171	3320	951	1990	280	1620	22.0	1370	110	225	39.0	114	36.2
+2 SD (54.4 cm)	6270	1050	5020	432	12200	2880	10500	884	9900	77.9	7750	458	267	44.1	141	44.0
D. Fall																
–2 SD (6.64 cm)	1.29	0.13	0.92	0.22	0.15	0.030	0.062	0.016	0.052	0.023	0.030	0.016	77.9	5.62	52.7	4.77
–1 SD (15.57 cm)	24.4	3.80	16.4	3.07	8.52	2.47	3.65	0.882	2.54	0.298	1.79	0.366	84.7	6.88	58.7	9.85
mean (24.5 cm)	117	23.2	75.9	12.3	73.7	25.9	32.0	6.11	19.9	1.17	15.7	1.95	91.5	7.66	64.7	11.7
+1 SD (33.43 cm)	341	80.1	217	32.0	324	130	142	23.0	82.0	2.98	69.5	6.14	98.3	8.25	70.7	13.6
+2 SD (42.36 cm)	771	206	483	66.3	999	441	441	63.3	241	6.07	216	14.7	105	8.73	76.7	15.5

TABLE IV

Regressions of nitrogen fluxes (g N ha^{-1} time period) from Rhode River watersheds with precipitation volumes (X = cm time^{-1} period)

A. Annual											
1. Area-weighted mean watershed						2. Watershed 109 (crops)					
TN	=	$0.0109X^{2.66}$	R^2	=	0.59	TN	=	$0.000455X^{3.49}$	R^2	=	0.61
NO_3	=	$0.0108X^{2.42}$	R^2	=	0.36	NO_3	=	$0.00301X^{2.95}$	R^2	=	0.42
TON	=	$0.0241X^{2.87}$	R^2	=	0.58	TON	=	$0.00000129X^{4.52}$	R^2	=	0.64
TNH_4	=	$0.0131X^{2.11}$	R^2	=	0.44	TNH_4	=	$0.000182X^{3.13}$	R^2	=	0.61
3. Watershed 110 (forest)						4. Watershed 111 (grazed)					
TN	=	$0.000000166X^{4.81}$	R^2	=	0.66	TN	=	$0.00176X^{2.84}$	R^2	=	0.32
NO_3	=	$0.00000193X^{3.75}$	R^2	=	0.40	NO_3	=	$0.000650X^{2.85}$	R^2	=	0.21
TON	=	$0.0000000396X^{5.07}$	R^2	=	0.69	TON	=	$0.000528X^{2.94}$	R^2	=	0.32
TNH_4	=	$0.000125X^{2.91}$	R^2	=	0.31	TNH_4	=	$0.0686X^{1.59}$	R^2	=	0.20
B. Winter											
1. Area-weighted mean watershed						2. Watershed 109 (crops)					
TN	=	$54.9X - 355$	R^2	=	0.65	TN	=	$69.7X + 130$	R^2	=	0.48
NO_3	=	$1.32X^{1.78}$	R^2	=	0.60	NO_3	=	$48.7X + 25.7$	R^2	=	0.40
TON	=	$20.5X - 40.5$	R^2	=	0.48	TON	=	$19.7X + 24.2$	R^2	=	0.36
TNH_4	=	$2.62X + 25.2$	R^2	=	0.24	TNH_4	=	$12.0X^{0.644}$	R^2	=	0.11
3. Watershed 110 (forest)						4. Watershed 111 (grazed)					
TN	=	$0.993X^{1.60}$	R^2	=	0.30	TN	=	$0.232X^{2.36}$	R^2	=	0.56
NO_3	=	$0.0573X^{1.79}$	R^2	=	0.28	NO_3	=	$0.158X^{2.25}$	R^2	=	0.40
TON	=	$0.688X^{1.62}$	R^2	=	0.31	TON	=	$0.0423X^{2.57}$	R^2	=	0.67
TNH_4	=	$0.432X^{1.17}$	R^2	=	0.14	TNH_4	=	$0.116X^{1.81}$	R^2	=	0.45
C. Spring season											
1. Area-weighted mean watershed						2. Watershed 109 (crops)					
TN	=	$2.09X^{1.89}$	R^2	=	0.81	TN	=	$2.88X^{1.99}$	R^2	=	0.67
NO_3	=	$0.421X^{2.03}$	R^2	=	0.60	NO_3	=	$5.98X^{1.62}$	R^2	=	0.46
TON	=	$1.19X^{1.89}$	R^2	=	0.86	TON	=	$0.0795X^{2.57}$	R^2	=	0.73
TNH_4	=	$0.495X^{1.55}$	R^2	=	0.62	TNH_4	=	$0.432X^{1.75}$	R^2	=	0.68
3. Watershed 110 (forest)						4. Watershed 111 (grazed)					
TN	=	$0.0104X^{3.19}$	R^2	=	0.79	TN	=	$49.5e^{0.0718X}$	R^2	=	0.49
NO_3	=	$0.000220X^{3.64}$	R^2	=	0.78	NO_3	=	$18.8e^{0.0743X}$	R^2	=	0.39
TON	=	$0.00701X^{3.24}$	R^2	=	0.79	TON	=	$16.8e^{0.0793X}$	R^2	=	0.54
TNH_4	=	$0.0122X^{2.48}$	R^2	=	0.57	TNH_4	=	$10.2e^{0.0460X}$	R^2	=	0.28

TABLE IV

Continued.

D. Summer season											
1. Area-weighted mean watershed						2. Watershed 109 (crops)					
TN	=	$28.8e^{0.0855X}$	R^2	=	0.43	TN	=	$25.7e^{0.0979X}$	R^2	=	0.17
NO_3	=	$0.421X^{2.03}$	R^2	=	0.60	NO_3	=	$5.98X^{1.62}$	R^2	=	0.46
TON	=	$16.2e^{0.0911X}$	R^2	=	0.43	TON	=	$4.02e^{0.125X}$	R^2	=	0.17
TNH_4	=	$5.40e^{0.0696X}$	R^2	=	0.40	TNH_4	=	$3.86e^{0.0863X}$	R^2	=	0.15
3. Watershed 110 (crops)						4. Watershed 111 (grazed)					
TN	=	$1.89e^{0.136X}$	R^2	=	0.42	TN	=	3.71X + 65.5	R^2	=	0.10
NO_3	=	$0.198e^{0.0949X}$	R^2	=	0.19	NO_3	=	08445X + 19.9	R^2	=	0.026
TON	=	$2.16e^{0.130X}$	R^2	=	0.31	TON	=	$3.51X^{0.925}$	R^2	=	0.11
TNH_4	=	$0.543e^{0.107X}$	R^2	=	0.41	TNH_4	=	0.679X + 7.04	R^2	=	0.26
E. Fall season											
1. Area-weighted mean watershed						2. Watershed 109 (crops)					
TN	=	$0.00188X^{3.45}$	R^2	=	0.60	TN	=	$0.0000180X^{4.76}$	R^2	=	0.65
NO_3	=	$0.0000664X^{3.99}$	R^2	=	0.64	NO_3	=	$0.00000160X^{5.19}$	R^2	=	0.62
TON	=	$0.00153X^{3.38}$	R^2	=	0.55	TON	=	$0.00000710X^{4.79}$	R^2	=	0.66
TNH_4	=	$0.000671X^{3.07}$	R^2	=	0.48	TNH_4	=	$0.00000715X^{4.27}$	R^2	=	0.52
3. Watershed 110 (forest)						4. Watershed 111 (grazed)					
TN	=	$0.00000953X^{4.55}$	R^2	=	0.47	TN	=	0.764X + 72.8	R^2	=	0.0050
NO_3	=	$0.0000769X^{3.01}$	R^2	=	0.29	NO_3	=	$3.58X^{0.238}$	R^2	=	0.0034
TON	=	$0.00000348X^{4.79}$	R^2	=	0.48	TON	=	0.670X + 48.3	R^2	=	0.0072
TNH_4	=	$0.0000146X^{3.69}$	R^2	=	0.32	TNH_4	=	0.212X + 6.55	R^2	=	0.017

3.2. Nitrogen Concentrations

3.2.1. *Total Nitrogen*

Mean annual total-N concentration in Rhode River discharges correlated positively with the volume discharged ($R^2 = 0.30$, $P = 0.01$) and with the volume of precipitation ($R^2 = 0.17$, $P = 0.06$). When examined on a seasonal basis this positive correlation of total-N concentration with watershed discharge was strongest in the spring and winter ($P < 0.01$), but was essentially absent in the summer and fall. The correlations of seasonal total-N concentrations with volume of precipitation were similar but somewhat lower. Total-N concentrations discharged generally had very low correlations with mean seasonal air temperature and multiple correlations with precipitation volume and air temperature were only slightly higher than with precipitation alone. For example, Rhode River watershed spring total-

N concentrations had correlations with precipitation alone and with precipitation and air temperature of R = 0.736 and 0.750, resp. Multiple correlation between weekly total-N concentrations discharged from the overall Rhode River watershed and mean weekly precipitation and air temperature were fairly low. For example, a statistical model based on multiple correlations, [TN conc. (μg N L^{-1}) = 272 + 19.4 (mean air temp over the prior 4 weeks) + 17.6 ($Prcp_0$) + 8.8 ($Prcp_{-1}$) +4.4 ($Prcp_{-2}$) + 2.2 ($Prcp_{-3}$)], had a multiple correlation of 0.280. The subscripts indicate the number of weeks that the precipitation data were lagged. The air temperature variables accounted for most of the overall correlation.

3.2.2. *Nitrate*

Mean annual nitrate concentration in discharges from Rhode River watershed increased with volume of discharge (R = 0.24, P = 0.28) and precipitation (R = 0.38, P = 0.008). The correlation of nitrate concentration from Rhode River watershed with volume of precipitation was highest in the winter and spring ($P < 0.001$) and almost zero in the summer and fall (Figure 8). The correlation of nitrate concentration with volume of discharge was highest for the forested watershed in the spring (R^2 = 0.50, P = 0.002). Only in the fall for the grazed watershed was the correlation between nitrate concentration and air temperature notable (R = 0.416 vs –0.110 for precipitation; multiple R = 0.419). Correlations of weekly time series of nitrate concentrations discharged from the overall Rhode River watershed with precipitation were low and positive, while those with air temperature were higher and negative. A statistical model, [Nitrate conc. (μg N L^{-1}) = 185 – 3.88 (mean of prior 4 weeks of air temperature) + 4.66 ($Prcp_0$) + 2.33 ($Prcp_{-1}$) + 1.17 ($Prcp_{-2}$) + 0.58 ($Prcp_{-3}$)], where subscripts are weeks of lag, had a multiple correlation of 0.333.

3.2.3. *Total Organic Nitrogen*

Mean annual organic-N concentration in Rhode River discharges was positively correlated with watershed discharge (R = 0.449, P = 0.04). On a seasonal basis it is clear that the highest correlation with watershed discharge was in the spring (R = 0.496, P = 0.02). When one examines the three first-order watersheds, which have the most divergent land use compositions, in the spring organic-N concentrations increased more rapidly with volume of precipitation and had higher correlations with volume of precipitation in the row-cropped watershed (# 109; R^2 = 0.73, P = 0.00001) than in the grazed or forested watersheds. Spring Rhode River watershed linear correlations of organic-N concentration with precipitation (R = 0.619) were improved somewhat by adding air temperature (multiple R = 0.683).

3.2.4. *Total Ammonium*

Total ammonium concentration in discharges from Rhode River watershed was usually negatively correlated with volume of discharge and this relationship was most evident in the winter (slope of linear regression = –0.38, R^2 = 0.19, P = 0.03).

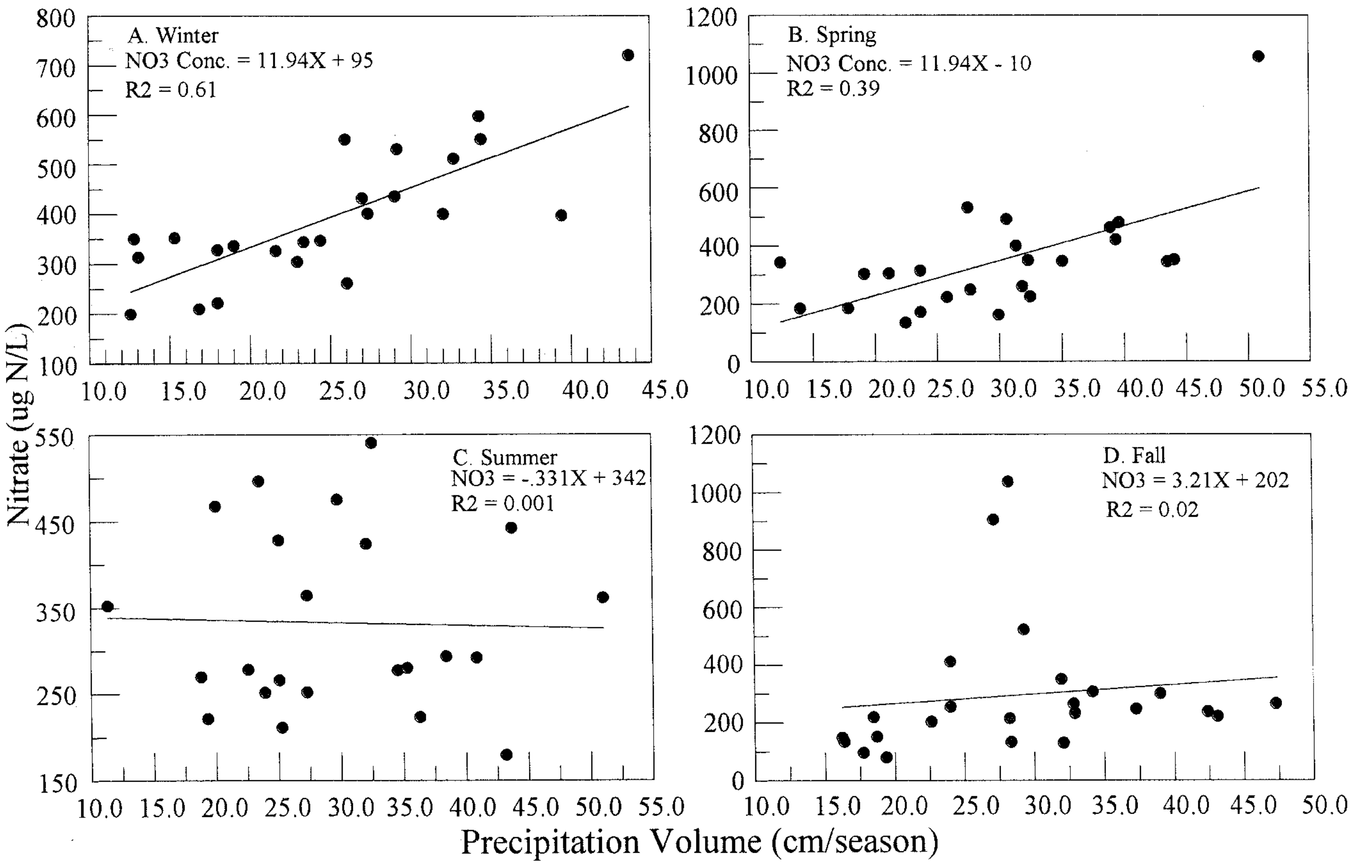

Figure 8. Variations in concentration of nitrate discharged from area-weighted Rhode River watersheds with volume of precipitation.

In the summer and fall, only the grazed watershed ammonium concentrations were correlated with discharge volume (R = –0.61, P = 0.007; and R = –0.48, P = 0.04; resp.). Spring Rhode River ammonium concentration correlations with precipitation (R = 0.316) were increased by including air temperature (multiple R = 0.377). The correlations between summer air temperature and ammonium concentrations were higher than with precipitation for the Rhode River watershed (R = 0.399 vs –0.150), cropped watershed (# 109; R = 0.351 vs 0.024), and grazed watershed (# 111; R = –0.366 vs –0.314).

4. Discussion

4.1. ANNUAL FLUXES

Annual discharge fluxes of total-N, nitrate, total organic-N, and total ammonium clearly were strongly influenced by the volume of precipitation as well as by land use (Figure 1–7). Annual total-N fluxes from the overall Rhode River watershed varied by almost an order of magnitude, but the combination of variation in precipitation and land use gave a range of 0.07 to 24.3 kg N ha^{-1} yr. (350-fold range).

Annual precipitation varied almost two-fold during the period of study, exceeding one standard deviation below the mean and almost two standard deviations above the mean for the long-term records. The fact that the range of observed low annual precipitation does not extend to minus two SD below the mean needs to be kept in mind. The predictions of N-fluxes from regressions for years with very low precipitation are extrapolated beyond the measured discharge data (Table II, Figure 3).

There were distinctly different patterns of variation in N-flux with precipitation for different land uses. Total-N annual flux from forested watershed 110 was highly correlated with precipitation and increased very rapidly, almost entirely due to organic-N (Figure 3C). The forested watershed was completely vegetated with deciduous hardwood forest, mostly old-growth, and had very little human disturbance in the last 50 yr other than atmospheric deposition (Vaithiyanathan and Correll, 1992). Thus, forested watershed # 110 provides a good measure of how effectively natural vegetation in this region can retain N over a broad range of weather conditions. The fairly high fluxes of organic-N in years of high precipitation probably reflect the steep slopes and highly erodible soils characteristic of these inner Coastal Plain landscapes. Nitrogen discharges from this forested watershed, on average, were similar to other forested watersheds (Table V).

Total-N annual flux from grazed land (watershed 111) was much less correlated and increased less rapidly with precipitation, and was composed of roughly equal amounts of nitrate and organic-N (Figure 3D). Nitrate flux from this watershed also had some temperature dependence. Were these characteristics typical of grazed

TABLE V

Comparison of Rhode River watershed nitrogen discharge fluxes with other temperature watersheds. All fluxes are in kg N ha^{-1} yr.

Watershed and Location	Yr	Total-N	Nitrate-N	Ammonium-N	Organic-N	References
A. Forested						
Puruwai, New Zealand	2	3.7	2.8	0.06	0.77	Cooper and Thomsen (1988)
(native podacarp/mixed hardwoods)						
Coastal Plain of MD and	1	1.3	0.06	0.23	1.0	Jordan *et al*. (1997a)
DEL, U.S.A. #s 301, 307 (native hardwood/pine)						
Piedmont of MD, U.S.A.	1	4.8	3.5	0.20	1.1	Jordan *et al*. (1997b)
# 401 (native hardwoods)						
Rhode River, MD, U.S.A.	19	1.8	0.14	0.16	1.5	this paper
# 110 (old growth deciduous hardwoods)						
B. Cropland						
Coastal Plain of GA,	3	4.2	1.5	0.11	2.6	Lowrance and Leonard (1988)
U.S.A., #s F, J. K, I, M (34.3% crops)						
Coastal Plain of MD,	1	11.2	8.0	0.69	2.6	Jordan *et al*. (1997a)
DEL, U.S.A., #s 304, 305, 306, 308, 309, 310 (57.8% crops)						
Piedmont of MD, U.S.A.,	1	16.2	14.1	0.30	1.8	Jordan *et al*. (1997b)
#s 403, 404, 405, 408, 409, 410 (62.4% crops)						
Rhode River, MD. U.S.A.	19	7.3	3.8	0.51	3.0	this paper
# 109 (64% crops)						

TABLE VI

Continued.

Watershed and Location	Yr	Total-N	Nitrate-N	Ammonium-N	Organic-N	References
C. pasture (no mineral N fertilizer)						
Purutaka, New Zealand (continuously grazed)	1	12.0	1.2	0.48	10.3	Cooper and Thomsen (1988)
Oklahoma, U.S.A. # R-6, (rotationally grazed)	2	1.9	0.32	0.20	1.4	Olness *et al*. (1975, 1980)
Oklahoma, U.S.A., # R-8 (continuously grazed)	2	7.4	1.1	0.30	6.0	Olness *et al*. (1975, 1980)
Rhode River, MD, U.S.A. #111 (rotationally grazed)	16	1.6	0.67	0.14	0.74	this paper

lands or merely idiosyncrasies of this one first order watershed? The fact that most of this watershed was pasture combined with its southern aspect may make it more sensitive to solar insolation effects such as warming and drying of surface soils and this may not be typical of grazed lands in this region. Watershed 110 also had a southern aspect, but the forest vegetation may have made it less sensitive to solar insolation effects. Watershed 111 was subjected to low intensity rotational grazing, rather than the high intensity management sometimes practiced in the humid eastern United States, in which mineral fertilizers and feed supplements are imported from outside the watershed in order to sustain high livestock populations. Nitrogen parameter fluxes from watershed 111 were in the expected range for such grazing lands (Table V; Correll, 1996).

The cropland watershed (Figure 3B; Table II), in exceptionally wet (but observed) years, exported 28 times more nitrate per ha than forest and 7.6 times more nitrate than grazed land. Thirty six percent of this 16 ha watershed was vegetated with deciduous hardwood riparian forest, while the rest was in continuous corn production. The riparian forest formed a continuous buffer around the first order stream draining the watershed and has been shown to remove most of the nitrate entering it from the fields in overland storm flows and groundwater during all seasons (Peterjohn and Correll, 1984; Correll and Weller, 1989). It has also been shown to remove significant amounts of ammonium and particulate organic-N from overland storm flows (Peterjohn and Correll, 1984). Fluxes of N-parameters, especially nitrate, from this watershed would probably have been much higher in the absence of this buffer. In 1991, a year of just slightly below average precipitation, six other Maryland Coastal Plain and six Maryland Piedmont watersheds with similar overall land use composition had average total-N fluxes of 11.2 and 16.2 kg N ha^{-1} yr, respectively (Table V; Jordan *et al.*, 1997a, b). That yr the Rhode River cropland watershed had a flux of 5.53 kg N ha^{-1} yr and our statistical model (Table II) predicts a flux of 5.68 kg N ha^{-1} yr for a yr with average precipitation. Thus, this cropland watershed had lower annual fluxes of total-N than many others in the region, perhaps because of its well buffered riparian zone. One might conclude from these data that the cropland watershed was a highly disturbed ecosystem, unable to efficiently retain N. The low-intensity grazed watershed was less disturbed, but still behaved quite differently from mature native forest.

4.2. Seasonal Fluxes

In the winter season of the study years, precipitation extended from almost 2 SD below the mean to well over 2 SD above the mean of long-term precipitation. Winter fluxes of N-parameters increased with volume of precipitation, but the relationship was usually fairly linear. The regression slope for the overall Rhode River watershed in winter was lowest for total ammonium and highest for nitrate (Figure 4). In extremely wet winters cropland discharged 40 and 3.2 times more nitrate per ha than forest and grazed lands, respectively (Table III). In the spring season, precipitation volumes during the period of study ranged from nearly 2 SD below the mean to over 2 SD above the mean. Nitrogen parameter fluxes were highly correlated with volume of precipitation and increased substantially (Figure 5). Power functions explained more of the variance than linear functions. In extremely wet springs nitrate fluxes from cropland were 12 and 14 times higher than from forest and grazed lands, respectively (Table IIIB). Therefore, even a modest proportion of cropland in this landscape can dominate the release of nitrate in the winter and spring.

Our statistical model predicts the highest seasonal fluxes of all N-parameters from the overall watershed and the cropland watershed in exceptionally wet summers, but for forest the nitrate flux in the summer is lower than in the spring and for grazed land all fluxes are lower in the summer than in the winter or spring (Table III, Figure 6). Summer precipitation during the study ranged from almost 2 SD below the mean to almost 2 SD above the mean. The high N-fluxes in very wet years may reflect the importance of tropical storms in the summers and the high erosion rates from croplands and forests associated with intense summer storms. In a summer of average precipitation all N-fluxes from all watersheds were lower than in the spring. Fall N-fluxes were uniformly very low even in exceptionally wet years, but did increase with volume of precipitation (Figure 7). No fall seasons observed were more than 1 SD below the mean and only one fall was more than 2 SD above the mean. Thus predictions for exceptionally dry years (i.e. > 1SD below the mean) in Table IIID should be viewed with caution.

The regressions we derived from the relationships of N-fluxes with precipitation and air temperature do not explain all of the variance in the data. The fact that many of the regressions of N-flux versus precipitation are highly significant reflects the large number of data points and strongly indicates that there is a relationship. However, this should not be misinterpreted. There are other independent variables which could cause N-fluxes to be increased or decreased. A few examples should help to illustrate this point. On cropland watershed 109, if the crop fertilizer is applied just prior to a large storm, more N-discharge than expected will occur that spring. If the precipitation in a given spring is composed of a few, very large storms instead of many small storms, more N-discharge than expected will occur from all of the watersheds that spring. There are many such possible explanations of residual variances in N-discharges. However, our statistical models can be used to predict annual and seasonal N-fluxes from Rhode River watersheds and other similar watersheds in this region with a fair degree of reliability.

4.3. NITROGEN CONCENTRATIONS

The observed changes in N-fluxes with precipitation were not solely due to changes in water discharge. Sometimes N-concentrations were significantly correlated with volume of precipitation. For example, the mean concentration of nitrate discharged in the winter from the Rhode River watershed ranged from 199 to 720 μg N L^{-1}

and volume of precipitation explained 61% of this variation (Figure 8). Since the volume of water discharged from a watershed is obviously somewhat correlated with volume of precipitation and since nutrient fluxes are the product of the volume and composition of water discharges, one would expect lower correlations between N-concentrations and precipitation volumes than between N-fluxes and precipitation volumes. That is what we found. However, water discharge is not as highly correlated with precipitation volume as one might suppose. For example, Rhode River water discharge and precipitation volume had coefficients of determination of 0.68, 0.51, 0.76, 0.56, and 0.53 for annual, winter, spring, summer, and fall, respectively. Correlations between N-concentrations and volume of water discharged were sometimes more interesting than for precipitation. Thus, for example, mean annual concentration of total-N discharged from the overall watershed correlated highly with water discharge in the spring, moderately in the winter and not at all in the summer and fall. Observed mean spring concentrations of total-N from the overall watershed increased with higher precipitation from 728 to 2290 μg N L^{-1}, over three-fold. The relationship of nitrate concentrations to seasonal and annual precipitation volume is different from what is found on short-term or storm event temporal scales. During individual storm events nitrate concentration often reaches a minimum at peak stream discharge (e.g. Correll *et al.*, 1987; McDiffet *et al.*, 1989). This minimum is due, in part, to the lower concentration of nitrate in overland flows than in groundwater. We believe that the higher nitrate concentrations found in high rainfall seasons or years is due to more efficient leaching of nitrate from surface soils by more frequent precipitation events and the more efficient transport of groundwater nitrate to the stream, especially in the riparian buffer zone (Correll and Weller, 1989).

Only in the spring were organic-N concentrations discharged from the overall watershed correlated with precipitation. For the cropland and forested watersheds precipitation explained 73 and 54%, respectively, of the variation in spring organic-N concentrations. For the cropland, observed mean spring organic-N concentrations increased from 314 to 2388 μg N L^{-1} (7.6 fold). Similarly observed mean spring organic-N concentrations from forest increased from 155 to 1095 μg N L^{-1} (7.1 fold).

Total ammonium concentrations were unique in that they often declined with precipitation and water discharge. Total ammonium concentrations from the overll watershed increased with precipitation in the spring, but decreased in the winter and summer, while in the fall there was very little correlation. Ammonium concentrations often had more correlation with interannual variations in mean summer temperatures than with precipitation or water discharge. The correlation with temperature was positive for the overall watershed and cropped watershed, but negative for the grazed watershed. One would like to think that these results were brought about by unusually warm summer temperatures causing higher rates of organic-N mineralization in the soils, but why not in the grazed land?

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