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Effects of Precipitation and Air Temperature on Phosphorus Fluxes from Rhode River Watersheds

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ABSTRACT

We studied fluxes of total P, total phosphate, and total organic P 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 equipped with 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-P area yields from the overall watershed varied 28-fold, correlations of all P-species fluxes with precipitation were highly significant, and power function regressions of precipitation vs. P-flux explained from 42 to 55% of the variance in the latter. Phosphorus 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 primarily composed of organic P. Correlations of P fluxes with precipitation were higher in the spring. Annual and seasonal P concentrations also often increased significantly with precipitation. Variations in seasonal mean air temperature sometimes explained significant amounts of variance in P fluxes, especially phosphate from cropland. A regression model was used to construct graphical and tabular summaries.

A LARGE number of studies have measured the fluxes of phosphate, organic P, and total P from various watersheds. The usual foci have either been comparative effects of land use in a small region (e.g., Cooper and Thomsen, 1988; Correll et al., 1977; Hill, 1981; Hirose and Kuramoto, 1981; Malmer and Grip, 1994), differences in discharges among widely separated regions (e.g., Beaulac and Reckhow, 1982; Dillon and Kirchner, 1975; Frink, 1991), or patterns of change in P concentrations from a single watershed due to a storm event (e.g., Johnson et al., 1976; McDiffett et al., 1989; Prairie and Kalff, 1988). These studies have clearly established that land use, particularly intensive agriculture, has a strong influence on P flux. They have also shown that P fluxes from a given watershed are seasonal, peaking in the spring and summer in temperate regions. The evidence seems fairly good that there are also significant regional differences in P fluxes from a given land use, perhaps due to geological and climatic differences. It is also clear that during individual storm events concentrations of parameters such as total phosphate and total organic P span a broad range and usually reach maxima before the peaks of storm hydrographs.

Very few studies have analyzed the effects of interannual variations in precipitation and temperature on fluxes of P species. Such an analysis requires many years of data from the same watershed. For up to 25 yr we have sampled the fluxes of total phosphate, total organic P, and total P from seven contiguous small subwatersheds of the Rhode River in Maryland. The subwatersheds differed in land use, but had similar weather, soils, geology, and hydrology. The watersheds were continuously monitored for discharge with V-notch weirs that included volume-integrating flow-proportional samplers. Here we report the effects of variations in mean annual, seasonal, and weekly precipitation and air temperature on fluxes of P species from forested, cropped, grazed, and mixed land use watersheds on the inner mid-Atlantic Coastal Plain of North America. Our study provides a unique perspective because of the long-term (25 yr) data records from watersheds drained by first- and second-order streams with relatively simple land use compositions.

METHODS

Site Description

The watersheds studied are all subwatersheds of the Rhode River, a small tidal tributary to the Chesapeake Bay in Maryland (38°51′ N, 76°32′ W). The Rhode River is within the inner Atlantic Coastal Plain. 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). 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). Therefore, each subwatershed has a perched aquifer and overland storm flows, interflow, and groundwater discharges all move to the channel draining each subwatershed. The slopes of the watersheds average between 5 and 9%. The study watersheds ranged in size from 6.1 to 253 ha and differed in land use (Table 1). Three watersheds were drained by first-order streams. One (no. 110) was completely forested, another (no. 109) was primarily row-cropped, and one (no. 111) was primarily rotationally grazed land 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

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and had mixed land use. For more detailed descriptions of the site see Correll (1981) and Correll and Dixon (1980).

Sampling

The study period was from the fall of 1971 through the fall of 1996. 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 7-d 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 sample water was drawn from the stream channel upstream of the weir and was deposited into a plastic container pretreated with 20 mL of 18 *N* of 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). All of the watershed drainage under study was within 4 km of the weather station. Rainfall volumes were measured with standard manual rainfall gauges, and also with a Belfort weighing gauge. Air temperatures were recorded with maximum/minimum mercury thermometers and a Belfort recording hygrothermograph.

Sample Analysis

Total P was determined by digestion to orthophosphate with perchloric acid (King, 1932). The phosphate in the digestate and undigested aliquots was analyzed by reaction with stannous chloride and ammonium molybdate (APHA, 1989). Total phosphate in the undigested, acid-preserved samples was the sum of dissolved and acid-extractable particulate phosphate. Total organic P was calculated by subtracting total phosphate from total P.

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, and February), spring (March, April, and May), summer (June, July, and August), and fall (September, October, and November). Watershed years began with December. Discharge volumes were multiplied by volume-integrated concentrations to obtain weekly fluxes of various P fractions. Seasonal and annual mean concentrations of P fractions were calculated by summing weekly fluxes, then dividing by summed water discharges. Overall area-weighted Rhode River watershed P-flux data were calculated from individual subwatershed discharges (Table 1).

The three small first-order watersheds (nos. 109, 110, and 111) were not equipped until the mid-1970s. Several significant gaps in individual watershed data records resulted from storm damage. Data from any individual weir were only included in the analyses when the weir was operational for a complete season or year. When flow was too low to obtain an integrated sample for analysis, spot samples were analyzed. From 5 to 10% of the flux data for any given weir were missing due to short-term 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 flux data from the watershed with the most similar P-flux behavior.

The mean and range of annual and seasonal precipitation and air temperature, 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 15 km of each other. At the times of data collection they were fairly small towns, thus minimizing any "heat island" effects.

Phosphorus-flux data were regressed against precipitation volumes and mean air temperatures for the relevant periods. Linear, power function, and exponential regressions were determined. The linear regression was used if the coefficient of determination (R^2) for the linear regression was highest or almost as high as either of the other regressions. Often power functions had much higher R^2 values and in some cases exponential regressions had much higher R^2 values. In these cases, the type of regression with the best fit to the data was used. In a few cases, a subjective choice was made by inspecting data plots for best visual fit. An effort was made to use the same type of regression for P fluxes from a given watershed and time for all P species (e.g., watershed 111 in the spring). Since the volume of water discharged was often a power function of precipitation volume and P concentrations often increased with increasing precipitation volume, one would not expect P fluxes to normally be a linear function of precipitation volume.

RESULTS

Phosphorus Fluxes

Annual fluxes of total P, total phosphate, and total organic P from the overall Rhode River watershed in-

Table 1. Areas (ha) and land use composition (%) of Rhode River 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*	0	0

* Until 1989, when it was planted with pine seedlings (Correll et al., 1995).

creased substantially with precipitation volume (Fig. 1). Total-P fluxes varied from 0.15 to 4.11 kg P/ha per yr. Linear correlations of P fluxes with precipitation were all highly significant ($P < 0.001$) but power function regressions fit the data better (highest R^2) and explained from 42 to 55% of the variance. Phosphate fluxes from the overall watershed contributed over half of the total-P fluxes, increased more rapidly, and were more highly correlated with precipitation than organic-P fluxes.

Annual total-P fluxes from a cropland watershed (no. 109) were much higher than from the other watersheds, varying with volume of precipitation from 0.14 to 13.3 kg P/ha per yr. Fluxes of all forms of P were highly significantly correlated with volume of precipitation, which explained from 54 to 73% of the variance. The fluxes of all forms of P from the cropland watershed increased more rapidly with precipitation than was found for the overall Rhode River watershed (Fig. 1) and were dominated by phosphate. In the case of a forested watershed (no. 110), fluxes of total P were much lower than from the cropland watershed and varied from 0.013 to 1.18 kg P/ha per yr. The correlations of forest P fluxes with precipitation were all highly significant and volume of precipitation explained from 53 to 60% of the variance. Over half of the total-P flux from the forested watershed was organic P and the organic-P fluxes were similar to those from the overall Rhode River watershed; however, the fluxes of phosphate were much lower from the forested watershed. For a grazed watershed (no. 111) the relationships between precipitation and P fluxes were much weaker and were not statistically significant ($R^2 = 0.20$–0.32). Total-P fluxes from the grazed land varied from 0.071 to 0.44 kg P/ha per yr and were composed of somewhat higher amounts of phosphate than organic P.

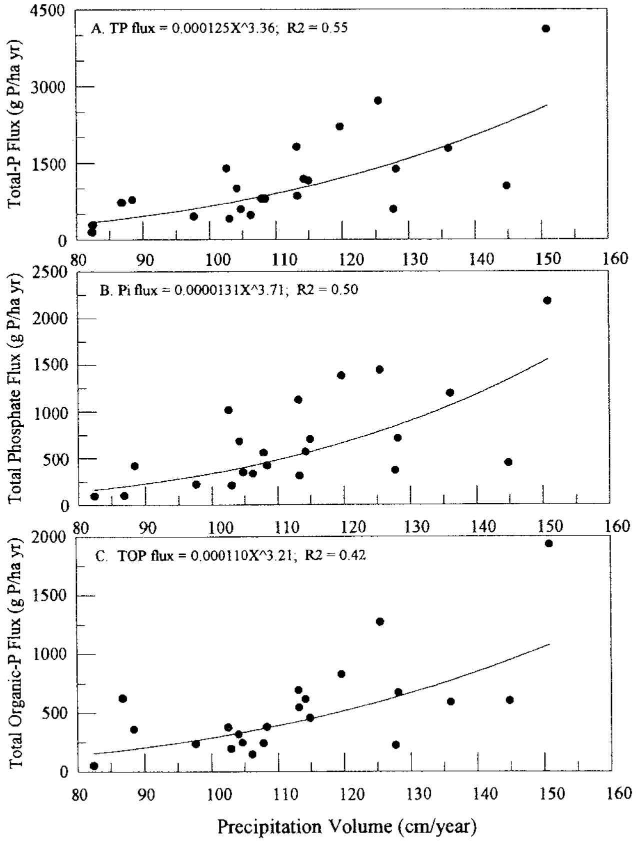

Fig. 1. Variations in annual P fluxes from the Rhode River watershed with volume of annual precipitation.

Annual air temperature variations generally had little relationship with P fluxes from the watersheds. Usually the combination of precipitation and air temperature explained only a few percent more of the variance in P fluxes than precipitation alone. For example, for total-P fluxes from the overall watershed, the R^2 for linear regressions improved from 0.48 to 0.50 when air temperature was included. Including air temperature increased the correlations the most for organic P.

For the overall Rhode River watershed in the winter, fluxes of total P ranged from 0.023 to 0.59 kg P/ha winter. The best regression fits for P flux vs. precipitation volume were usually power functions, the correlations were all highly significant ($P < 0.001$), and volume of precipitation explained 42 to 45% of the variance in P flux. Total phosphate accounted for about 55% of the total-P flux in winter. Cropland winter total-P fluxes ranged from 0.035 to 1.11 kg P/ha winter and were dominated by phosphate, but correlations with precipitation were only marginally significant ($P = 0.06$–0.09). Forest winter fluxes ranged from 0.0009 to 0.11 kg P/ha winter and, in years of above average precipitation, over half was organic P. Forest P-flux correlations with precipitation were only significant for total organic P ($P < 0.05$). Grazing land total-P fluxes ranged from 0.019 to 0.40 kg P/ha winter, were composed of about equal amounts of phosphate and organic P, and all correlations with precipitation were highly significant.

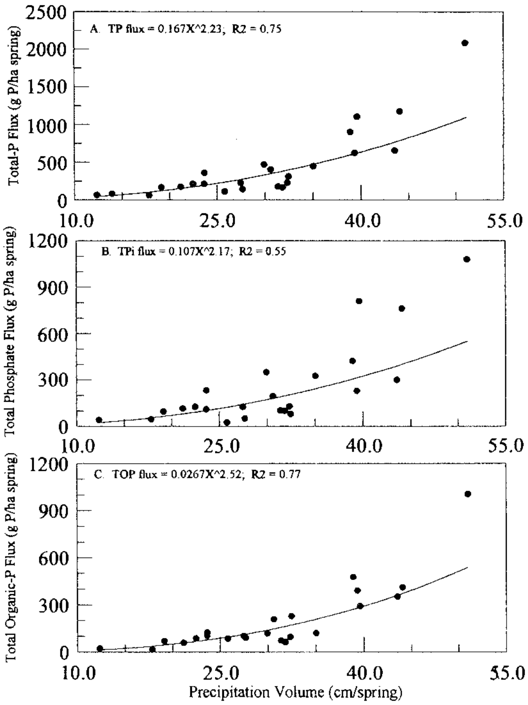

Fig. 2. Variations in spring P fluxes from the Rhode River watershed with volume of spring precipitation.

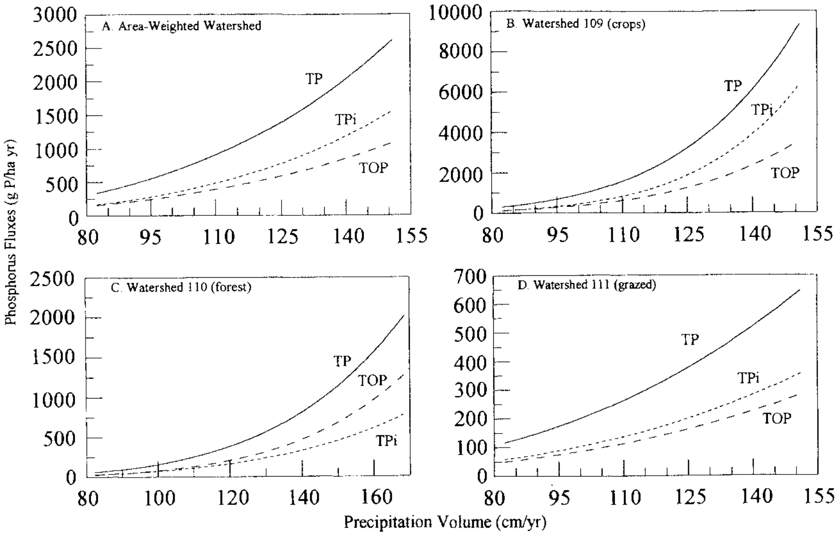

Fig. 3. **Variations in annual watershed P fluxes with volume of annual precipitation. Curves are from regression equations in Table 4A.**

Spring total-P flux from the overall watershed ranged from 0.064 to 2.08 kg P/ha spring (Fig. 2) and about half of this was organic P. The volume of spring precipitation explained from 55 to 77% of the variation in spring fluxes of P species from the overall watershed and all correlations were highly significant ($P < 0.00002$). Total-P fluxes from the cropland watershed in spring ranged from 0.032 to 6.9 kg P/ha spring and were dominated by phosphate. Variations in precipitation explained 69 to 76% of the variance in P fluxes, and all correlations were significant ($P < 0.001$). Total-P fluxes from the forest watershed in spring varied from 0.0086 to 0.72 kg P/ha spring, with organic P becoming more dominant in wetter springs. Precipitation volume explained 65 to 73% of the variance in spring forest P fluxes and all correlations were highly significant ($P < 0.0002$). Total-P fluxes from grazing lands in spring were similar in magnitude to those from forest (range = 0.018–0.99 kg P/ha) and, like the forest, organic P became more dominant in the wetter springs. The best regression fits for grazing land were exponential, variations in precipitation explained 43 to 54% of the variance in P fluxes, and all correlations were significant ($P < 0.01$).

As in the case of the annual data, including air temperature in multiple linear regressions for winter data had little effect except for phosphate fluxes from the grazed watershed 111. In that case, R^2 was increased from 0.58 to 0.68 by including air temperature. For spring data, only the linear regression for total organic-P fluxes from cropland was improved by including air temperature in the regression ($R^2 = 0.48$ and 0.72, respectively).

Phosphorus fluxes from the watersheds had higher ranges in the summer and, in very wet seasons, were higher than those experienced in the spring. Correlations of P fluxes with precipitation were lower in the summer than in the spring, but were usually very highly significant. The best regression fits (highest R^2) were usually exponential in both the summer and fall. For the overall watershed in the summer, total-P fluxes varied from 0.010 to 2.75 kg P/ha summer and consisted of about equal amounts of phosphate and organic P.

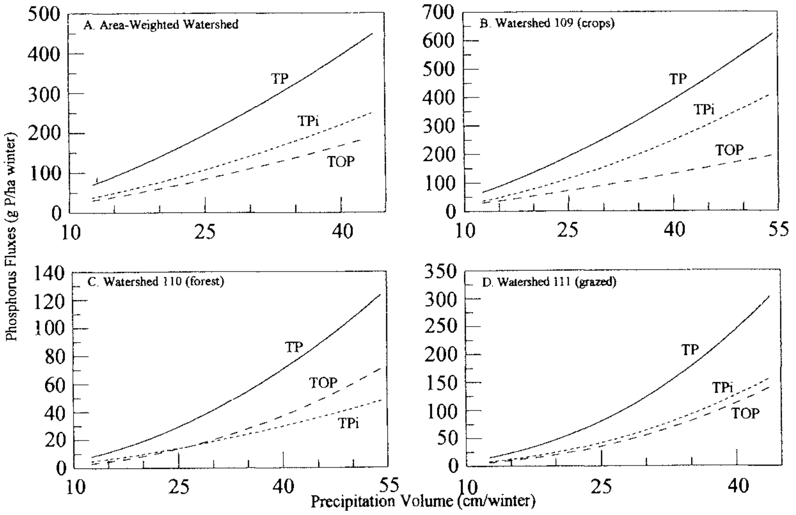

Fig. 4. **Variations in winter watershed P fluxes with volume of winter precipitation. Curves are from regression equations in Table 4B.**

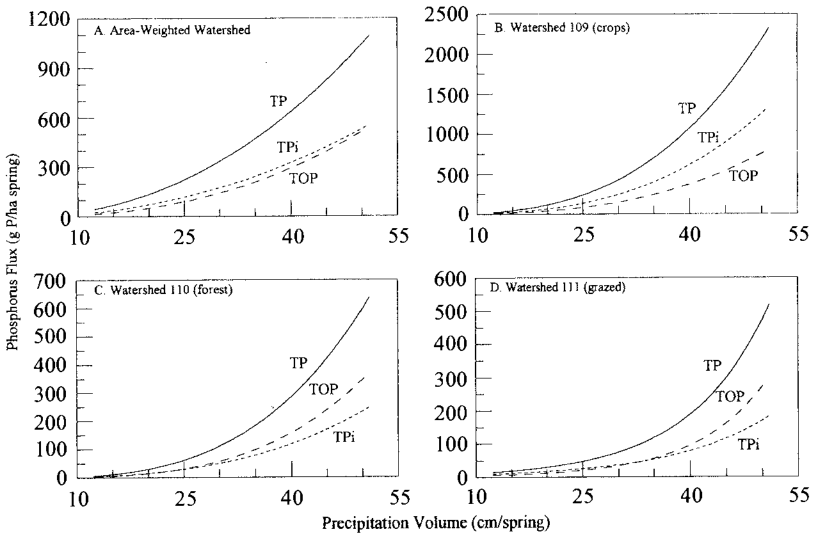

Fig. 5. Variations in spring watershed P fluxes with volume of spring precipitation. Curves are from regression equations in Table 4C.

Precipitation volume explained 36 to 39% of the variance in summer fluxes and all of these correlations were significant ($P < 0.01$). Summer total-P fluxes from cropland ranged from 0.0016 to 11.54 kg total P/ha summer. Although correlations with precipitation only explained 19 to 24% of the variance in P fluxes, all were significant ($P < 0.01$). For forest, summer total-P fluxes varied from 0.000 to 0.71 kg P/ha summer and, in very wet summers, were increasingly dominated by organic P. Precipitation volume explained 35 to 36% of the variance in P fluxes, and all correlations were highly significant ($P < 0.0002$). Summer total-P fluxes from grazing lands varied from 0.010 to 0.20 kg P/ha summer and were dominated by phosphate. Correlations with precipitation were low and not significant.

Fall total-P fluxes from the overall watershed varied from 0.0020 to 1.48 kg P/ha fall and phosphate constituted about 60% of the total. Precipitation volume explained 51 to 56% of the variance in P fluxes and all correlations were highly significant ($P < 0.001$). Fall fluxes of total P from cropland ranged from 0.00016 to 0.79 kg P/ha fall and were predominantly composed of phosphate. Variations in precipitation explained 20 to 62% of the variance in P fluxes from cropland and all correlations were significant ($P = 0.001$–0.03). Forest total-P fluxes in the fall ranged from 0.000 to 0.52 kg P/ha fall and were composed of roughly equal amounts of phosphate and organic P except in unusually wet falls, when organic P exceeded phosphate. Total-P fluxes from grazed lands in the fall ranged from 0.0077 to 0.15 kg P/ha fall and were dominated by phosphate. Correlations with precipitation were low and not significant.

Multiple correlations that included summer and fall air temperatures only helped explain a few percent more variance in P-fluxes for most P-species from most watersheds. The largest improvement in correlation by including air temperature was for phosphate flux from cropland in the summer, which improved the R^2 from 0.36 to 0.44.

Statistical Models

Regression curves for the annual fluxes of P-species from the watersheds vs. precipitation volume (Fig. 3)

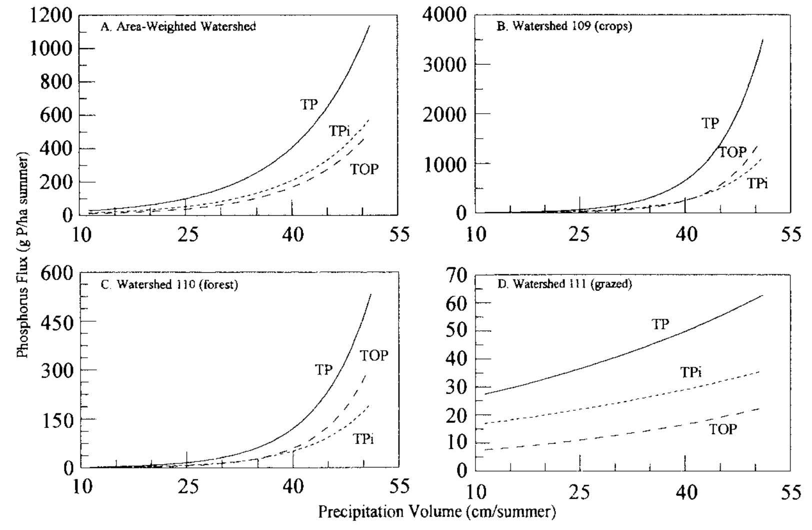

Fig. 6. Variations in summer watershed P fluxes with volume of summer precipitation. Curves are from regression equations in Table 4D.

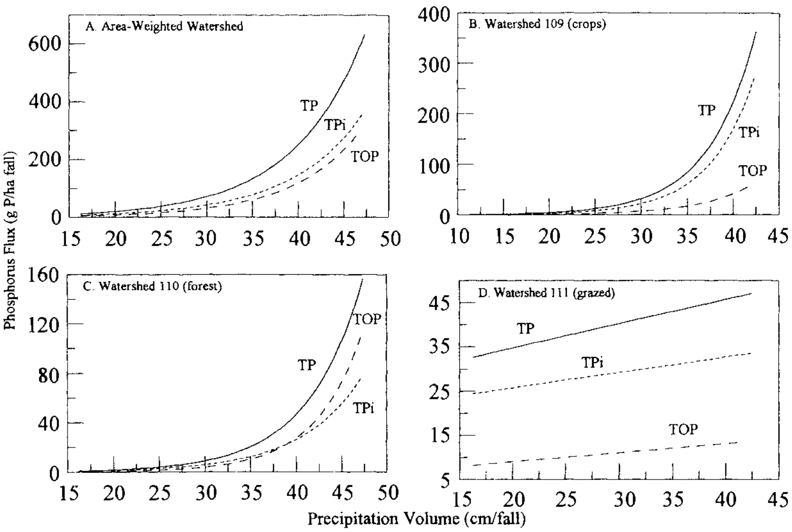

Fig. 7. Variations in fall watershed P fluxes with volume of fall precipitation. Curves are from regression equations in Table 4E.

help visualize the patterns of flux for total P, total phosphate, and total organic P. For the overall watershed and for cropland, phosphate flux exceeds organic-P flux at all levels of precipitation. For forest, phosphate, and organic-P fluxes are about equal in dry years, but organic-P flux increases more rapidly with precipitation. In the winter, for the overall watershed, phosphate fluxes were always somewhat higher than organic P (Fig. 4). Cropland in the winter has a similar pattern, but phosphate fluxes are more dominant. In grazed lands, phosphate and organic-P fluxes are about equal. In the spring the pattern for the overall watershed (Fig. 5) is similar to the annual pattern. The effects of precipitation in wet springs are most evident in the forest watershed, where organic-P fluxes increase disproportionately with precipitation. In the summer, the regressions curve upward much more steeply with increasing precipitation, except for the grazed watershed (Fig. 6). For the cropland in wet summers organic-P fluxes became larger than the phosphate fluxes. In the fall, P fluxes from cropland were once again dominated by phosphate (Fig. 7).

These regressions of P fluxes vs. precipitation and long-term rainfall records were used to construct Tables 2 and 3. The regression equations and their coefficients of determination are listed in Table 4 and constitute a statistical model of P fluxes from these watersheds as a function of precipitation. For the overall Rhode River watershed, cropland, forest, and grazed land; annual and seasonal P fluxes of total P, phosphate, and organic P were calculated for time periods of low, average, and high precipitation. For convenience we used precipitation levels equal to the mean precipitation, ± one standard deviation (SD) from the mean, and ± 2 SD from the mean. Generally, the ranges of precipitation that occurred during this study are bracketed by the ± 2 SD category.

Phosphorus Concentrations

Mean annual total-P concentration in Rhode River discharges correlated positively with the volume of precipitation ($R^2 = 0.19$, $P = 0.04$). When examined on a seasonal basis this positive correlation of total-P concentration with Rhode River precipitation volume was highest in the spring ($R^2 = 0.45$; $P = 0.0003$; Fig. 8), but was essentially absent in the summer and fall. Mean annual total-P concentrations from cropland had higher correlations with volume of precipitation and were highly significant ($R^2 = 0.51$; $P = 0.001$). Annual total-P concentrations from forest had lower but significant correlations with precipitation ($R^2 = 0.35$; $P = 0.02$). For grazing land, the correlation of annual total-P concentrations with precipitation was not significant.

As was the case for the overall watershed, total-P concentrations discharged from the cropland, forest, and grazing land were most correlated with precipitation in the spring and all were significant ($P < 0.01$; Fig. 9). Correlations of total-P concentration with precipitation for these subwatersheds were not significant in the summer, but in the fall forest total-P concentrations were significantly correlated with precipitation ($R^2 = 0.22$; $P < 0.05$). Also, while in most cases total-P concentrations were more highly correlated with volume of precipitation than volume of watershed discharge, this was not the case in the fall. Correlations in the fall for crop-

Table 2. Annual P area yield fluxes (g P/ha per yr) from Rhode River watersheds as a function of precipitation (cm/yr). Flux values calculated from regressions of P vs. precipitation.

	Area-weighted watershed			Watershed 109 (crops)			Watershed 110 (forest)			Watershed 111 (grazed)		
Precipitation	TP	TPi	TOP	TP	TPi	TOP	TP	TPi	TOP	TP	TPi	TOP
−2 SD (64.4 cm)	150	67.3	70.5	75.7	27.5	31.3	18.1	9.36	7.12	58.7	27.7	24.8
−1 SD (86.2 cm)	398	199	180	393	182	159	75.2	35.7	34.2	134	66.5	57.4
Mean (108.0 cm)	850	458	370	1410	787	557	226	100	115	255	131	110
+1 SD (129.8 cm)	1580	907	668	3970	2590	1550	557	234	309	430	228	187
+2 SD (151.6 cm)	2650	1610	1100	9550	7110	3690	1190	476	712	668	364	292

Table 3. Seasonal P area yield fluxes (g P/ha season) from Rhode River watersheds as a function of precipitation (cm/season). Flux values calculated from regressions of P vs. precipitation.

	Area-weighted watershed			Watershed 109 (crops)			Watershed 110 (forest)			Watershed 111 (grazed)		
Precipitation	TP	TPi	TOP	TP	TPi	TOP	TP	TPi	TOP	TP	TPi	TOP
A. Winter												
−2 SD (10.22 cm)	52.0	27.9	22.5	48.9	25.8	22.6	5.57	3.54	2.07	9.48	5.04	3.86
−1 SD (17.41 cm)	115	62.8	49.3	110	62.8	45.1	15.0	8.17	6.41	33.5	17.8	14.3
Mean (24.6 cm)	193	106	82.0	186	112	70.7	28.6	14.1	13.3	76.0	40.4	33.5
+1 SD (31.79 cm)	282	157	120	275	172	98.7	46.0	21.0	23.0	140	74.1	63.0
+2 SD (38.98 cm)	382	214	161	374	241	129	67.2	29.0	35.4	226	120	104
B. Spring												
−2 SD (10.94 cm)	34.7	19.2	11.1	17.5	9.96	6.32	4.09	2.32	1.64	12.9	8.49	4.59
−1 SD (19.47 cm)	125	67.2	47.4	109	62.7	38.8	27.2	13.3	12.5	28.4	16.3	11.1
Mean (28.0 cm)	282	148	118	347	200	122	90.0	40.0	44.8	62.2	31.4	27.0
+1 SD (36.53 cm)	510	263	231	809	466	282	216	89.6	114	136	60.5	65.7
+2 SD (45.06 cm)	814	415	393	1580	911	546	431	169	239	299	116	159
C. Summer												
−2 SD (8.40 cm)	21.4	11.7	7.53	5.47	3.85	1.30	1.73	1.07	0.494	25.8	16.1	7.01
−1 SD (19.9 cm)	62.3	33.4	23.3	31.1	17.8	8.79	8.09	4.36	2.81	32.8	20.0	9.61
Mean (31.4 cm)	182	95.4	72.1	176	82.1	59.3	37.8	17.7	15.9	41.7	24.7	13.2
+1 SD (42.9 cm)	530	273	223	1000	379	400	176	72.2	90.4	53.0	30.6	18.0
+2 SD (54.4 cm)	1550	781	690	5690	1750	2700	823	294	513	67.3	38.0	24.7
D. Fall												
−2 SD (6.64 cm)	3.60	2.15	1.24	0.337	0.189	0.103	0.197	0.188	0.0409	27.4	21.1	5.61
−1 SD (15.57 cm)	11.2	6.63	4.22	1.92	1.17	0.516	0.852	0.705	0.233	32.3	24.2	8.07
Mean (24.5 cm)	34.8	20.4	28.7	11.0	7.23	2.58	3.69	2.64	1.33	37.2	27.3	9.91
+1 SD (33.43 cm)	108	62.9	48.8	62.6	44.7	12.8	15.9	9.92	7.59	42.1	30.4	11.7
+2 SD (42.36 cm)	336	194	166	357	276	64.1	69.0	37.2	43.3	47.0	33.5	13.6

Table 4. Regressions of P fluxes (g P/ha time period) from Rhode River watersheds with precipitation volumes (X = cm/time period).

A. Annual

1. Area-weighted mean watershed
TP = $0.000125X^{3.36}$ $R^2 = 0.55$
TPi = $0.0000131X^{3.71}$ $R^2 = 0.50$
TOP = $0.000110X^{3.21}$ $R^2 = 0.42$

2. Watershed 109 (crops)
TP = $0.00000000456X^{5.65}$ $R^2 = 0.66$
TPi = $0.0000000005X^{6.49}$ $R^2 = 0.73$
TOP = $0.00000000263X^{5.57}$ $R^2 = 0.54$

3. Watershed 110 (forest)
TP = $0.0000000258X^{4.89}$ $R^2 = 0.60$
TPi = $0.0000000466X^{4.59}$ $R^2 = 0.53$
TOP = $0.00000000132X^{5.38}$ $R^2 = 0.60$

4. Watershed 111 (grazed)
TP = $0.000428X^{2.84}$ $R^2 = 0.24$
TPi = $0.0000993X^{3.01}$ $R^2 = 0.27$
TOP = $0.000153X^{2.88}$ $R^2 = 0.19$

B. Winter season

1. Area-weighted mean watershed
TP = $1.63X^{1.49}$ $R^2 = 0.45$
TPi = $0.816X^{1.52}$ $R^2 = 0.43$
TOP = $0.740X^{1.47}$ $R^2 = 0.42$

2. Watershed 109 (crops)
TP = $1.43X^{1.52}$ $R^2 = 0.27$
TPi = $0.532X^{1.67}$ $R^2 = 0.30$
TOP = $1.10X^{1.30}$ $R^2 = 0.20$

3. Watershed 110 (forest)
TP = $0.0739X^{1.86}$ $R^2 = 0.31$
TPi = $0.0921X^{1.57}$ $R^2 = 0.21$
TTOP = $0.0150X^{2.12}$ $R^2 = 0.37$

4. Watershed 111 (grazed)
TP = $0.0384X^{2.37}$ $R^2 = 0.68$
TPi = $0.0204X^{2.37}$ $R^2 = 0.67$
TOP = $0.0127X^{2.46}$ $R^2 = 0.60$

C. Spring season

1. Area-weighted mean watershed
TP = $0.167X^{2.23}$ $R^2 = 0.75$
TPi = $0.107X^{2.17}$ $R^2 = 0.55$
TOP = $0.0267X^{2.52}$ $R^2 = 0.77$

2. Watershed 109 (crops)
TP = $0.00868X^{3.18}$ $R^2 = 0.76$
TPi = $0.00483X^{3.19}$ $R^2 = 0.69$
TOP = $0.00337X^{3.15}$ $R^2 = 0.69$

3. Watershed 110 (forest)
TP = $0.00156X^{3.29}$ $R^2 = 0.73$
TPi = $0.00165X^{3.03}$ $R^2 = 0.65$
TOP = $0.000361X^{3.52}$ $R^2 = 0.73$

4. Watershed 111 (grazed)
TP = $4.72e^{(0.0921X)}$ $R^2 = 0.53$
TPi = $3.67e^{(0.0767X)}$ $R^2 = 0.43$
TOP = $1.47e^{(0.104X)}$ $R^2 = 0.54$

D. Summer season

1. Area-weighted mean watershed
TP = $9.77e^{(0.0931X)}$ $R^2 = 0.39$
TPi = $5.41e^{(0.0914X)}$ $R^2 = 0.36$
TOP = $3.30e^{(0.0982X)}$ $R^2 = 0.37$

2. Watershed 109 (crops)
TP = $1.54e^{(0.151X)}$ $R^2 = 0.24$
TPi = $1.26e^{(0.133X)}$ $R^2 = 0.22$
TOP = $0.32e^{(0.166X)}$ $R^2 = 0.19$

3. Watershed 110 (forest)
TP = $0.562e^{(0.134X)}$ $R^2 = 0.36$
TPi = $0.385e^{(0.122X)}$ $R^2 = 0.35$
TOP = $0.139e^{(0.151X)}$ $R^2 = 0.36$

4. Watershed 111 (grazed)
TP = $21.7e^{(0.0208X)}$ $R^2 = 0.06$
TPi = $13.8e^{(0.0186X)}$ $R^2 = 0.05$
TOP = $5.57e^{(0.0274X)}$ $R^2 = 0.05$

E. Fall season

1. Area-weighted mean watershed
TP = $1.55e^{(0.127X)}$ $R^2 = 0.36$
TPi = $0.932e^{(0.126X)}$ $R^2 = 0.56$
TOP = $0.500e^{(0.137X)}$ $R^2 = 0.51$

2. Watershed 109 (crops)
TP = $0.0923e^{(0.195X)}$ $R^2 = 0.58$
TPi = $0.0488e^{(0.204X)}$ $R^2 = 0.62$
TOP = $0.0313e^{(0.180X)}$ $R^2 = 0.20$

3. Watershed 110 (forest)
TP = $0.0663e^{(0.164X)}$ $R^2 = 0.52$
TPi = $0.0704e^{(0.148X)}$ $R^2 = 0.56$
TOP = $0.0112e^{(0.195X)}$ $R^2 = 0.57$

4. Watershed 111 (grazed)
TP = $0.550X + 23.7$ $R^2 = 0.01$
TPi = $0.347X + 18.8$ $R^2 = 0.01$
TOP = $0.206X + 4.86$ $R^2 = 0.03$

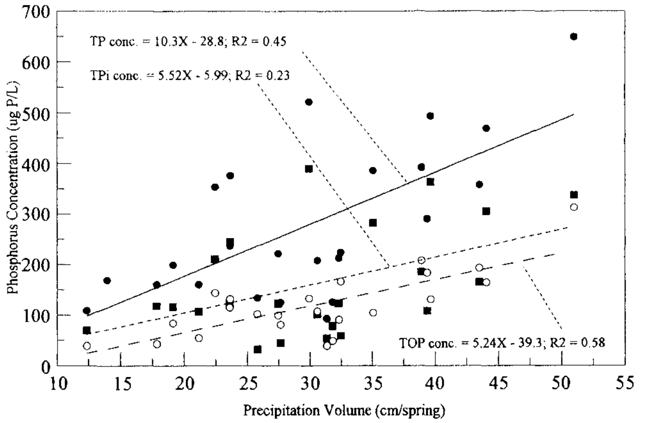

Fig. 8. Variations in spring P concentrations from the Rhode River watershed with volume of spring precipitation. Solid circles are data for TP, solid squares for TPi, and open circles for TOP concentrations.

land, forest, and grazed land with volume of watershed discharge were all more significant ($R^2 = 0.30, 0.37, 0.26$, respectively; $P = 0.01$, 0.007, and 0.09, respectively).

Total-P concentrations discharged were generally correlated with interannual variations in mean annual and seasonal air temperature and multiple correlations with precipitation volume and air temperature were often higher than with precipitation alone. In some cases (winter from cropland, summer from overall and grazed watersheds, fall from all but forest), correlations with temperature were higher than with precipitation.

Multiple correlations between weekly total-P concentrations discharged from the overall Rhode River watershed and mean weekly precipitation and air temperature were fairly low but highly significant ($P < 0.0001$). A multiple correlation, [TP conc. (μg P/L) = 14.6 + 8.81(air temp.) + 27.0 (precip. in cm)], had a multiple R of 0.386.

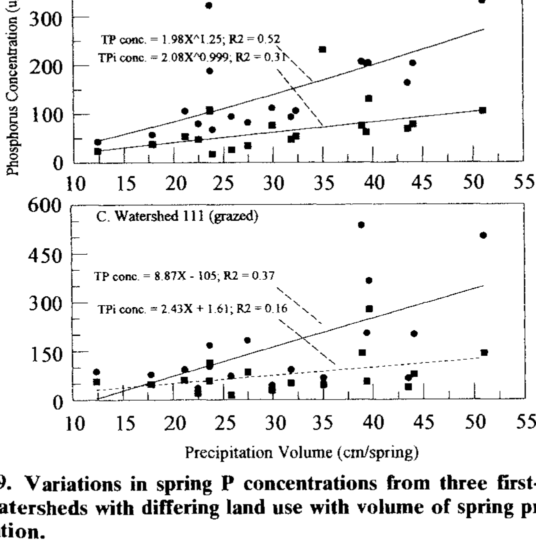

Fig. 9. Variations in spring P concentrations from three first-order watersheds with differing land use with volume of spring precipitation.

As was the case for total P, mean annual total phosphate concentration in discharges from Rhode River watershed increased with volume of precipitation ($R^2 = 0.17$, $P = 0.06$). The correlation of phosphate concentration from Rhode River watershed with volume of precipitation was highest in the spring ($R^2 = 0.23$; $P = 0.02$; Fig. 8) and almost zero in the summer and fall. The correlation of phosphate concentration with volume of precipitation was high for the cropland watershed in the spring ($R^2 = 0.61$, $P = 0.0004$; Fig. 9).

Phosphate concentrations had higher correlations with air temperature than was the case for total P. Annual mean phosphate concentrations from the overall watershed and the cropland had significant positive correlations with both air temperature and precipitation (multiple $R^2 = 0.29, 0.54$, respectively). Multiple correlation of overall watershed spring phosphate concentrations with air temperature and precipitation improved the R^2 from 0.23 for precipitation to 0.36 for both.

Correlations of weekly time series of total phosphate concentrations discharged from the overall Rhode River watershed with mean weekly precipitation and air temperature were low but highly significant. The equation, TPi conc. = −0.60 + 5.46(air temp.) + 10.3(precip.), had a multiple R of 0.402.

Mean annual total organic-P concentration in Rhode River discharges was not significantly correlated with volume of precipitation ($R^2 = 0.08$, $P = 0.25$). On a seasonal basis, it is clear that the highest correlation of total organic-P concentration with precipitation was in the spring ($R^2 = 0.58$, $P = 0.00003$; Fig. 8) and correlations for other seasons were not significant. However, while multiple correlations of weekly organic-P concentrations with mean weekly precipitation and air temperature were low, they were highly significant. The equation, TOP conc. = −13.8 + 3.45(air temp.) + 16.1(precip.), had a multiple R of 0.314.

DISCUSSION

Annual Fluxes

Annual fluxes of total-P, total phosphate, and total organic-P clearly were strongly influenced by the volume of precipitation as well as by land use (Fig. 1–7). Annual total-P fluxes from the overall Rhode River watershed varied 28-fold, but the combination of variations in precipitation and land use among subwatersheds gave a range of 0.013 to 13.3 kg P/ha per yr (three orders of magnitude).

Annual precipitation varied almost twofold during the period of study, exceeding 1 SD below the mean and almost 2 SD above the mean for the long-term records. There were no significant time trends in annual or seasonal precipitation volume during the period of study. Note that the range of observed low annual precipitation does not extend to minus 2 SD below the mean. Therefore, the predictions of P fluxes from regressions for years with very low precipitation are extrapolated beyond the measured flux data (Table 2, Fig. 3).

There were distinctly different patterns of variation in P-flux with precipitation for different land uses. Organic P constituted a higher proportion of the total-P flux in very wet years for forest but constituted a lower proportion of total P those years for cropland (Table 2, Fig. 3). The forested watershed was completely vegetated with deciduous hardwood forest, mostly old growth, and had been subjected to very little human disturbance in the last 50 yr other than atmospheric deposition (Vaithiyanathan and Correll, 1992). Thus, it provides a good example of how effectively natural forest vegetation in this inner Coastal Plain region can retain P over a broad range of weather conditions. The fairly high fluxes of organic P in years of high precipitation probably reflect the steep slopes and highly erodible soil characteristics of these inner Coastal Plain landscapes. Erosion rates are much higher in this part of the Coastal Plain than in the much sandier outer Coastal Plain. This reflects the rather low infiltration rates of the fine sandy loam soils in this region. During intense rain storms most of the discharge, even from forest, is overland flow (Correll et al., 1984). Phosphorus fluxes from the forested watershed, on average, were higher than other forested watersheds (Table 5A).

Compared to fluxes from other Rhode River subwatersheds, annual fluxes of total P from grazed watershed no. 111 was much less correlated, increased less rapidly with precipitation, and was composed of roughly equal amounts of phosphate and organic P over the entire range of precipitation (Fig. 3D). Watershed 111 was subjected to low intensity rotational grazing, rather than the high intensity pasture management sometimes practiced in the humid eastern USA, in which mineral fertilizers and feed supplements are imported from outside the watershed to sustain high livestock populations. There were no bare spots in the vegetative cover of the grazed watershed and sheet erosion rates were extremely low. Fluxes of P species from watershed 111 were in the expected range for such grazing lands (Table 5B; Correll, 1996).

The cropland watershed (Fig. 3B; Table 2), in exceptionally wet (but observed) years, exported 15 times more phosphate per ha than forest and 20 times more phosphate than grazed land. Thirty-six percent of the 16 ha cropland 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. In a 1-yr study, this riparian forest has been shown to remove about 80% of the total P and 74% of the particulate phosphate entering it from the fields in overland storm flows during all seasons (Peterjohn and Correll, 1984). Fluxes of P species from this watershed would probably have been higher in the absence of this buffer. In 1991, a year of just slightly below average precipitation, six other Maryland Coastal Plain watersheds and five other Piedmont watersheds with similar overall land use composition had average total-P fluxes of 0.59 and 0.47 kg P/ha per yr, respectively (Table 5B; Jordan et al., 1997a, b). That year the Rhode River cropland watershed had a flux of 1.25 kg P/ha per yr and our statistical model (Table 2) predicts a flux of 1.41 kg P/ha per yr for a year with average precipitation. Thus, this cropland watershed had higher annual fluxes of total P than many others in the region, despite its well-buffered riparian zone. This probably reflects the high P content and extreme erodability of soils in the Rhode River area. One might conclude from these data that the cropland watershed was a highly disturbed ecosystem, unable to efficiently retain P, while the low-

Table 5. Comparison of Rhode River watershed P area yield fluxes with other temperate watersheds. All fluxes are in kg P/ha per yr.

Watershed and location	Years	Total-P	Total phosphate	Total organic-P	Reference
		A. Forested			
Puruwai, New Zealand (native podocarp/mixed hardwoods)	2	0.12	–	–	Cooper and Thomsen (1988)
Coastal Plain of MD & DEL USA, #s 301, 307 (native hardwoods/pine)	1	0.044	0.009	0.035	Jordan et al. (1997a)
Piedmont of MD, USA, #401 (native hardwoods)	1	0.37	0.09	0.28	Jordan et al. (1997b)
Rhode River, MD, USA, #110 (old growth deciduous hardwoods)	19	0.43	0.19	0.24	This paper
		B. Cropland			
Coastal Plain, GA, USA, #s F, I, J, K, M (34.3% crops)	3	0.78	–	–	Lowrance and Leonard (1988)
Coastal Plain of MD, DEL, USA, #s 304, 305, 306, 308, 309, 310 (57.8% crops)	1	0.59	0.34	0.25	Jordan et al. (1997a)
Piedmont of MD, USA, #s 403, 404, 405, 408, 409, 410 (62.4% crops)	1	0.47	0.16	0.31	Jordan et al. (1997b)
Rhode River, MD, USA, #109 (64% crops)	19	2.54	1.40	1.14	This paper
		C. Pasture			
Purutaka, New Zealand (continuously grazed, 30 kg mineral P fertilizer/yr)	1	1.67	–	–	Cooper and Thomsen (1988)
Oklahoma, USA, #R-6 (rotationally grazed, no mineral fertilizer)	1	0.20	–	–	Olness et al. (1980)
Oklahoma, USA, #R-8 (continuously grazed, no mineral fertilizer)	1	0.76	–	–	Olness et al. (1980)
Rhode River, MD, USA, #111 (rotationally grazed, no mineral fertilizer)	16	0.40	0.20	0.20	This paper

intensity grazed watershed was less disturbed, but still behaved quite differently from mature native forest.

How do these P fluxes compare with other P fluxes in the Rhode River landscape? Atmospheric deposition of P (0.20 and 0.21 g of phosphate-P and TOP/ha per yr, respectively) is rather low compared with agricultural application rates (Jordan et al., 1995). For the overall Rhode River watershed this atmospheric deposition amounts to 0.94 kg P/yr and can be compared with an overall watershed flux of about 1750 kg P/yr to the tidal headwaters of the river, of which about 950 kg P/yr actually reaches the main tidal basin of the Rhode River (Correll et al., 1992).

Seasonal Fluxes

In the winter seasons of our 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 P-species increased with volume of precipitation and the best regression fits (highest R^2) were usually power functions. The regression slope for the overall Rhode River watershed in winter was lower for organic-P than for phosphate (Fig. 4a). In extremely wet winters, cropland discharged 8.3 and 2.0 times more phosphate per ha than forest and grazed lands, respectively (Table 3A).

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. Fluxes of P species were highly correlated with volume of precipitation and increased substantially with increasing precipitation (Fig. 5). They also had higher correlations with power functions. In extremely wet springs, phosphate fluxes from cropland were 5.4 and 7.9 times higher than from forest and grazed lands, respectively (Table 3B). Therefore, even a moderate proportion of cropland can dominate the release of phosphate in the winter and spring from this landscape.

In exceptionally wet summers, our statistical model predicts the highest seasonal fluxes of all P species from the overall watershed, cropland, and forest; but not for the grazed lands (Table 3; Fig. 6). Observed summer precipitation during the study ranged from almost 2 SD below the mean to almost 2 SD above the mean. These high P fluxes in very wet summers may reflect the importance of intense thunder storms/tropical storms and the high erosion rates from croplands and forests associated with these storms. In a summer of average precipitation, all P fluxes from all watersheds were lower than in the spring.

Fall P fluxes were uniformly low even in exceptionally wet years, but did increase with volume of precipitation (Fig. 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., >1 SD below the mean) in Table 3D should be viewed with caution.

Phosphorus Concentrations

The observed changes in P fluxes with precipitation were not solely due to changes in water discharge. Sometimes P concentrations were significantly correlated with volume of precipitation. For example, the mean concentration of total-P discharged in the spring from the Rhode River watershed ranged from 105 to 847 μg P/L and volume of precipitation explained 45% of this variation (Fig. 8). Since the volume of water discharged from a watershed is obviously somewhat correlated with volume of precipitation and nutrient fluxes are the product of the volume and composition of water discharged, one would expect lower correlations between P concentrations and precipitation volumes than between P 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. Observed mean spring concentrations of total P from the cropland watershed ranged from 89 to 2480 μg P/L, a 28-fold range, and variations in precipitation explained 75% of the variance (Fig. 9a). The relationship of P concentrations to seasonal and annual precipitation volume is different than what is found on a short-term or storm event temporal scale. During individual storm events, P concentrations often reach a maximum near peak stream discharge (e.g., McDiffet et al., 1989). This maximum is due, in part, to the much higher concentrations of P species in overland flows than in groundwater. We believe that the higher P concentrations found in high rainfall seasons or years is due to higher proportions and absolute amounts of overland flows, which carry more eroded soil particles from surface soils to the stream.

The significant positive correlations of phosphate concentrations with interannual variations in air temperature may have been due to increased rates of organic-P mineralization in the soils in warmer years or seasons. The surface layer of soils may have accumulated more phosphate, which could then be carried to the streams by erosion during storm events.

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