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# THE EFFECT OF RIPARIAN FOREST ON THE VOLUME AND CHEMICAL COMPOSITION OF BASEFLOW IN AN AGRICULTURAL WATERSHED

William T. Peterjohn and David L. Correll  
Smithsonian Environmental Research Center  
Box 28, Edgewater, MD 21037, U.S.A.

Abstract--For two years the nutrient, chloride, and hydronium ion concentrations in groundwater leaving agricultural fields and entering an adjacent riparian forest were compared to the chemical concentrations in stream water draining the riparian forest under baseflow conditions. Yearly mean nitrate-N concentrations decreased by approximately 4 mg/l whereas the chloride concentration increased by 3 mg/l due to evapotranspiration. The yearly mean pH increased by approximately one pH unit. The volumes of precipitation and baseflow were used in conjunction with the observed change in the groundwater chloride concentration to estimate an annual water budget for the riparian forest. The water budget, in turn, was used with the chemical compositions of precipitation, groundwater, and baseflow to calculate the change in the chemical load in groundwater moving through the riparian forest. From this study, a riparian forest in a coastal plain agricultural watershed: (a) acted as an important sink for nitrate-N; (b) had a significant effect on the volume of stream flow; and (c) significantly reduced the acidity of the groundwater and precipitation which enters it.

## INTRODUCTION

Concern over the effects of nutrient loss from agricultural lands to receiving waters has led several investigators to study the effectiveness of riparian forests in reducing the nutrient concentrations in agricultural runoff. The approaches taken in studying the role of riparian forests in agricultural settings have been both direct and indirect. The more direct methods have sampled along transects running from the edge of the agricultural fields through the riparian forest (Doyle et al., 1975; Lowrance et al., 1984a; Peterjohn and Correll, 1984) or have attempted chemical budgets (Lowrance et al., 1983; Lowrance et al., 1984b; Peterjohn and Correll, 1984;

Todd et al., 1983). The more indirect methods have compared the nutrient concentrations in stream water from agricultural watersheds with varying amounts of riparian forest or have analyzed the predictive capability of models which include or exclude the presence and/or proximity of riparian forest (McColl, 1978; Schlosser and Karr, 1981a; Yates and Sheridan, 1983; Schlosser and Karr, 1981b; Omernick et al., 1981). All the studies we are aware of, with one exception (Omernick et al., 1981), have reached the same general conclusion that riparian forests effectively reduce the loss of nutrients from agricultural lands to receiving waters. Studies of clear-cut, forested watersheds have also demonstrated the effectiveness of riparian zones as nutrient sinks (Karr and Schlosser, 1978). Although the general results from these studies are surprisingly similar, many questions remain concerning spatial and temporal variability as well as the internal processes responsible for the observed effects.

In this study, groundwater leaving agricultural fields and entering an adjacent riparian forest was sampled monthly for two years. During the same time period, weekly volume integrated stream water samples were also taken. During the week closest to the date of groundwater sampling when only base-flow occurred, nutrient concentrations in stream water leaving the watershed were compared to the concentrations in groundwater entering the riparian forest. Since riparian forest completely surrounds the stream, such a comparison was used to estimate the effect of the riparian forest on the nutrient concentrations in groundwater flowing through it. The purpose of this study was to: (a) document any nutrient concentration changes in groundwater moving through a riparian forest for a two year period; (b) explore the possible implications of any observed changes; and (c) begin to assess the functional role of a riparian forest in an agricultural system.

#### SITE DESCRIPTION

The study site (Fig. 1) is a 16.3 ha agricultural watershed located in the inner mid-Atlantic Coastal Plain (38°53'N, 76°33'W) approximately 20 km south of Annapolis, Maryland. The site contains a shallow, perched aquifer

due to an underlying clay layer with low vertical hydraulic conductivity (Chirlin and Schaffner, 1977). Soils above the aquiclude are a noncalcareous fine sandy loam. The average basin slope is 5.44% and the channel slope is 2.65%. A 10.4 ha area at the higher elevations on the watershed was planted in corn and tobacco. The remaining 5.9 ha of the watershed is composed of hedgerows and a riparian forest which completely surrounds the stream draining the watershed. The dominant tree species in the riparian forest are sweetgum and red maple.

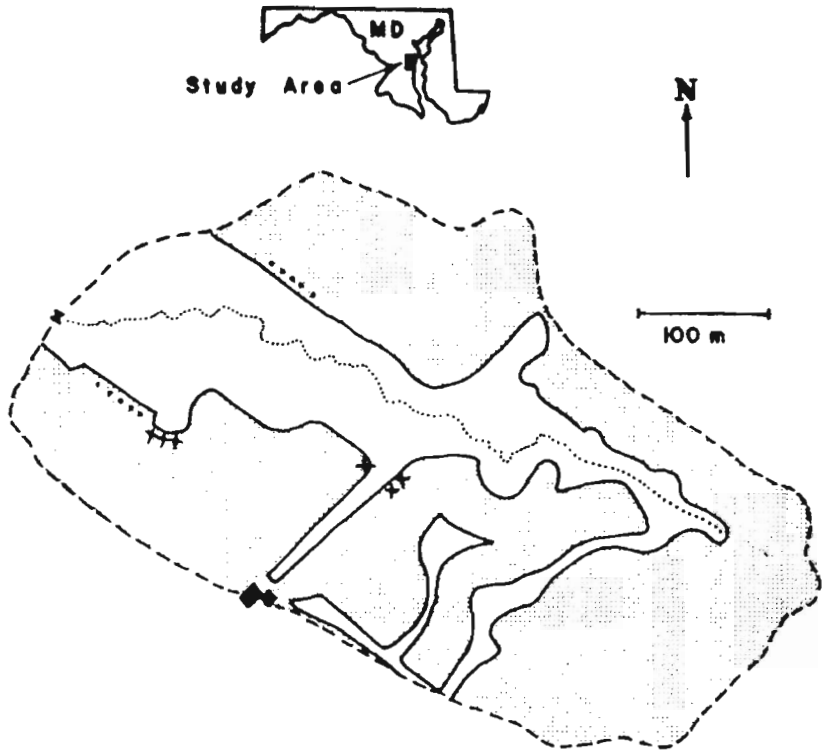


Fig. 1. General location (insert), and map of the watershed. The positions of groundwater wells during Year 1 (X) and Year 2 (.) are shown. Shading indicates cultivated fields. Dotted line indicates stream channel.

## MATERIALS AND METHODS

Sampling - Bulk precipitation was sampled continuously for chemical analysis at the central weather station for the Smithsonian Environmental Research Center (Correll and Ford, 1982) which was located approximately 2.3 km from the study site. Samples were collected after each precipitation event and returned to the laboratory for analysis. The volume of rainfall was measured both at the central weather station and at the study site.

Stream water discharge was measured and weekly volume integrated stream water samples were taken at a 120° sharp-crested V-notch weir. Depending on the amount of flow, either a combination of acidified and unacidified volume integrated samples or unacidified weekly spot samples were taken at the weir. Sulfuric acid was used as a preservative for biologically labile chemical species. Stream water and nutrient discharge from the study site have been measured continuously since 1976. Quickflow and slowflow (baseflow) rates were calculated graphically from the hydrograph (Barnes, 1940). In this study we equate slowflow with subsurface or groundwater flows.

Monthly groundwater samples were taken from wells (piezometers) located at the edge between the cropped fields and riparian forest (Fig. 1). Seven wells in two clusters were sampled during the first study year (see Peterjohn and Correll, 1984). Ten wells in two clusters were sampled during the second year. Clusters of wells were located at different positions each year and well construction differed each year. Wells during the first year were perforated over a narrow length ( 8 cm) and sampled at a discrete depth whereas wells during the second year were perforated over a length of approximately 2 m. Otherwise, well construction and installation have been previously described (Peterjohn and Correll, 1984).

The study years for this paper were March, 1981 through February, 1982 (Year 1) and March, 1984 through February, 1985 (Year 2).

Chemical analysis - Bulk precipitation, stream water, and groundwater samples were analyzed for nitrate-N, sulfate-S, Kjeldahl-N, total-P, chloride, and hydronium ion concentrations. Chloride, sulfate-S, and nitrate-N concentrations were measured with a Dionex Model 16 ion chromatograph after filtration through a prewashed Millipore HA membrane filter (0.45 um nominal pore size). In samples with low nitrate-N concentrations, nitrate-N was determined by re-

duction on cadmium amalgam and colorimetry (APHA, 1976). Since nitrite was seldom present in measurable quantities, nitrite and nitrate are routinely summed and referred to as nitrate-N. Hydronium ion concentration was measured as pH using a pH meter. Kjeldahl-N, which includes ammonium-N and organic amines, was determined by digestion with sulfuric acid, selenium and hydrogen peroxide (Martin, 1972); distillation; and Nesslerization (APHA, 1976). Total-P concentration was measured by reaction with ammonium molybdate and stannous chloride (APHA, 1976) after a perchloric acid digestion (King, 1932).

## RESULTS

Concentration and stream flow data were summarized for each month and year. The monthly mean chemical concentrations in the groundwater entering and in the stream water leaving the riparian forest are presented in the Appendix. Yearly mean chemical concentrations in groundwater entering and baseflow leaving the riparian forest for both years are presented in Table 1.

Nitrate concentrations in groundwater flowing through the riparian forest decreased by approximately 5 and 3 mg/l during years 1 and 2, respectively. The observed increase in Kjeldahl-N concentrations for both years was approximately 0.27 mg/l, indicating that the observed change in nitrate-N concentrations was not simply due to conversion into ammonium and organic nitrogen forms. Chloride concentrations were approximately 3 mg/l higher in stream water leaving the riparian forest than in groundwater entering the forest for both years. Chloride concentrations were also approximately 4 mg/l higher during Year 1 than during Year 2 for both the groundwater entering and leaving the riparian forest. The observed changes in chloride concentrations are thought to be due to evapotranspiration. This hypothesis is supported by the following facts: (a) chloride concentrations in groundwater were consistently higher after flux through the riparian forest; (b) Year 1 had below normal rainfall and followed a regional drought whereas Year 2 had slightly above normal rainfall; and (c) chloride is often considered to be an inert tracer. Of particular interest was the observed change in the hydronium ion concentration which suggests that the riparian forest neutralized some of the acidity of the entering groundwater.

Table 1. Yearly mean nutrient concentrations (mg/l) in groundwater entering, and in stream water leaving a riparian forest. Yearly means for bulk precipitation are given in parentheses.

		<u>Year 1</u>		<u>Year 2</u>	
Chloride	In	14.6	(1.43)	10.3	(0.930)
	Out	17.8		13.7	
Nitrate-N	In	6.18	(0.519)	4.47	(0.492)
	Out	0.841		0.915	
Sulfate-S	In	9.22	(1.44)	6.66	(1.61)
	Out	9.95		8.00	
Total-P	In	0.061	(0.0445)	0.090	(0.082)
	Out	0.133		0.149	
Kjeldahl-N	In	0.276	(0.841)	0.112	(0.752)
	Out	0.542		0.381	
pH	In	4.56	(4.01)	4.46	(4.16)
	Out	5.46		5.50	

There were no discernible seasonal patterns in chemical concentrations except for the baseflow concentration of hydronium ions. This does not mean, however, that other seasonal patterns do not exist. The selective nature of the data and the fact that only 2 years were studied are both reasons why seasonality might be obscured. To ensure that the apparent seasonality in pH was not an artifact of the short-term and selective nature of the data, the long-term monthly mean hydronium ion concentrations (expressed as pH) in stream water were plotted (Fig. 2). A dramatic yearly cycle in pH is shown in Fig. 2. The general pattern is one in which the pH is relatively constant from October through April at approximately 5.4 and then begins to increase to a peak in August of approximately 6.4 before the cycle repeats. Neither the groundwater, which had a relatively constant pH of 4.4 in Year 2, nor bulk precipitation entering the riparian forest have seasonal trends which could account for those observed in stream water at the weir. Therefore, processes within the riparian forest must explain the seasonality in stream water pH.

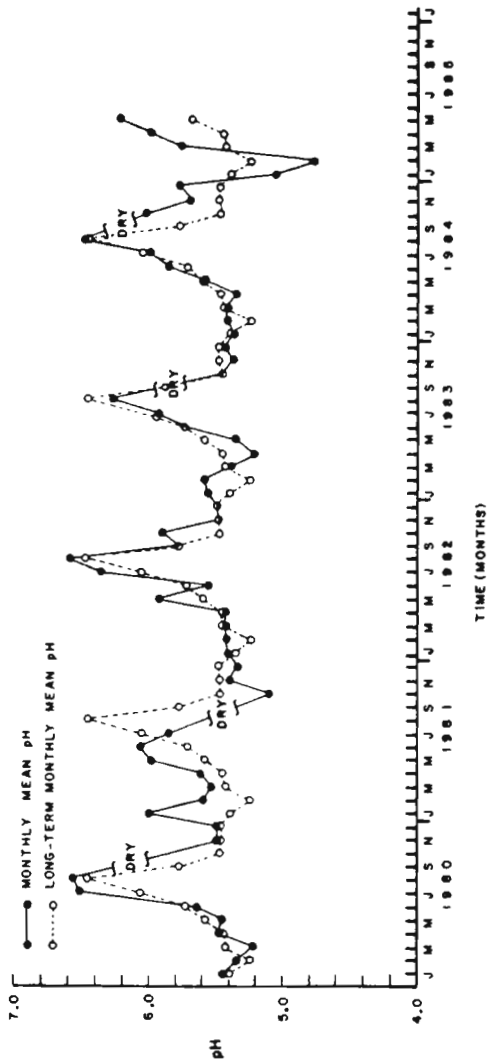


Fig. 2. Monthly and long-term monthly pH values measured at the weir. Mean pH values were determined by averaging hydronium ion concentrations and then converting to pH.

The volume of water leaving the agricultural fields and entering the forest was estimated for each month during the two study years. The procedure for calculating the volume of groundwater entering the riparian forest is given below.

ASSUMING A CHLORIDE BALANCE:

$$(VG * GCL) + (VP * PCL) = (VB * BCL) \quad (1)$$

Where: VG= volume of groundwater  
entering the riparian  
forest

GCL= chloride concentration  
in groundwater

VP= volume of bulk precipitation

PCL= chloride concentration  
in precipitation

VB= volume of baseflow at  
the weir

BCL= chloride concentration in  
baseflow

SOLVE FOR VG

This calculation also assumes that surface runoff inputs and quickflow losses can be ignored or that they are equal and thus cancel each other. Monthly flow estimates calculated using equation 1 were summed and used in conjunction with yearly precipitation values to estimate evapotranspiration (by difference) for both the agricultural fields and riparian forest for each of the two years. The annual water budgets thus constructed are presented in Table 2.

Table 2. Annual water balance for the agricultural fields and riparian forest. All values are l/ha.

		<u>Year 1</u>	<u>Year 2</u>
Agricultural Fields	Precipitation	$1.00 \times 10^7$	$1.09 \times 10^7$
	Subsurface	0	0
	Evapotranspiration	$6.08 \times 10^6$	$6.48 \times 10^6$
	Subsurface	$3.92 \times 10^6$	$4.42 \times 10^6$
Riparian Forest	Precipitation	$1.00 \times 10^7$	$1.09 \times 10^7$
	Subsurface	$7.90 \times 10^6$	$7.79 \times 10^6$
	Evapotranspiration	$1.07 \times 10^7$	$1.18 \times 10^7$
	Subsurface	$6.17 \times 10^6$	$6.94 \times 10^6$

Evapotranspiration was greater in the riparian forest than in the agricultural fields by factors of 1.7 and 1.8 for years 1 and 2, respectively. During Year 1, subsurface input to the riparian forest was equivalent to 69% of precipitation input and evapotranspiration accounted for the loss of approximately 63% of the total water input. During Year 2, subsurface input was 71% of precipitation input and evapotranspiration accounted for the loss of approximately 63% of the total water input. Thus, evapotranspiration in the riparian forest has a considerable influence over the amount of water draining the watershed.

The estimated subsurface flow of water into the riparian forest was multiplied by the nutrient and hydronium ion concentrations in groundwater entering the forest to estimate the monthly subsurface flux of nutrients into the forest. These values were compared with the estimated monthly nutrient and hydronium ion losses in baseflow at the weir to determine the net effect of the riparian forest (addition or removal) on the chemical load in the groundwater flowing through it. Monthly estimates were summed to arrive at yearly values. The annual subsurface fluxes of nutrients and hydronium ions through the riparian forest for both years are presented in Table 3.

Table 3. Annual subsurface nutrient and hydronium ion fluxes in groundwater moving through the riparian forest. All values are kg/ha. Bulk precipitation inputs are given in parentheses.

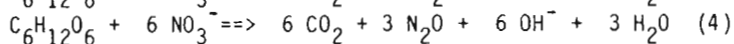
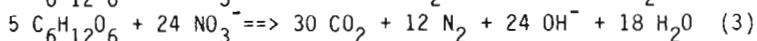
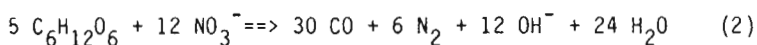
		<u>Year 1</u>		<u>Year 2</u>	
Nitrate-N	In	50.7	(5.23)	43.4	(5.19)
	Out	7.54		5.58	
	In-Out	43.2		37.8	
Sulfate-S	In	69.9	(14.5)	55.8	(17.0)
	Out	58.2		58.5	
	In-Out	11.7		-2.70	
Kjeldahl-N	In	1.79	(8.46)	2.07	(8.07)
	Out	3.16		2.94	
	In-Out	-1.37		-0.870	
Total-P	In	0.351	(0.449)	0.622	(0.884)
	Out	0.711		1.04	
	In-Out	-0.360		-0.417	
Hydronium Ion	In	...	(0.981)	0.250	(0.744)
	Out	0.021		0.021	
	In-Out	...		0.229	

Inputs, outputs, and the net addition or removal of nutrients to the groundwater were similar (less than a factor of 2 difference) for each study year except for sulfate-S which had a net removal of approximately 12 kg/ha during Year 1 compared to a slight (2.7 kg/ha) addition during Year 2. Nitrate-N and hydronium ion data indicated a net removal from the groundwater as it flowed through the riparian forest whereas Kjeldahl-N and total-P data indicated a net addition of these nutrients to the groundwater for both years. If the chemical influx from bulk precipitation was also considered, then the riparian forest would appear to be a sink for nutrients and hydronium ions. A complete chemical budget for the riparian forest, however, would also have to include the influx and output of nutrients in surface runoff and quickflow.

#### DISCUSSION

The internal processes occurring in the riparian forest, which account for the observed changes in the chemistry of the groundwater moving through

it, cannot be directly assessed by this study. We can, however, explore some implications of our data if certain simplifying assumptions are made concerning the internal processes at work in the riparian forest. Denitrification has been considered to be a significant pathway of nitrogen loss from riparian forests (Cooper et al., 1986; Lowrance et al., 1984b). Assuming that the observed change in nitrate-N in groundwater (Table 3) was due solely to denitrification, one can calculate the amount of organic matter that would be required to account for the observed loss. Three formulas for the process of denitrification were assumed:



Each formula assumes different end products which might result under a gradient of redox conditions. Formula 2 is conservative in the sense that it will give the maximum value for the amount of organic matter required by denitrification whereas formula 4 will give the lowest value of the three formulas. The amount of organic matter required would have been 231 kg/ha for formula 2, 116 kg/ha for formula 3, and 92.4 kg/ha for formula 4 during Year 1. During Year 2 the amount of organic matter required would have been 202 kg/ha given formula 2, 101 kg/ha given formula 3, and 81 kg/ha given formula 4. The actual amount of organic matter required was no doubt some weighted average of the values given above with the weighting factors being determined by the various redox potentials encountered by the groundwater moving through the riparian forest. Whether or not such values are excessive is difficult to evaluate because the source of organic matter for denitrification is uncertain. Such values, however, are small in comparison to forest above-ground production which in general is on the order of tens of thousands of  $\text{kg/ha}^{-1} \text{ yr}^{-1}$  in temperate deciduous forests (Cole and Rapp, 1981).

Another question that can be addressed is whether the production of hydroxide ions by denitrification could account for the observed change in groundwater pH, assuming that the observed change in nitrate-N in groundwater was due solely to denitrification. Regardless of which formula is

assumed the amount of hydroxide ions produced would be the same. During Year 1, 3080 moles/ha of hydroxide ions would have been produced whereas 2700 moles/ha of hydroxide ions would have been produced during Year 2. These values are quite large when compared to the estimated input of 250 moles/ha of hydronium ions into the riparian forest in groundwater flow during Year 2. In fact, the estimated amount of hydroxide ion production could have also neutralized the hydronium ion input from bulk precipitation (744 moles/ha) during that same year. It is interesting to note that even if the observed change in the groundwater  $\text{NO}_3\text{-N}$  was due solely to uptake by vegetation, the amount of hydroxide ions produced would have been the same since  $\text{NO}_3$  uptake results in the release of hydroxide ions on a 1:1 equivalent basis (Driscoll and Likens, 1982). Thus, denitrification and or uptake by vegetation might be significant in controlling the acidity in stream water draining the watershed.

The exact nature of the processes controlling the seasonal pattern in stream pH is unknown, but they are probably biological since the pH peaks in late summer (Fig. 2). It has been suggested that instream processes, such as algal photosynthesis in the weir pond, were responsible for the seasonality in stream pH. Algal photosynthesis in the weir pond seems an unlikely explanation, however, since a series of 18 pH measurements from the weir to the origin of the stream revealed that the pH was highest in the shaded upper reaches and, in general, decreased as the water flowed toward the weir. Although the processes responsible for the observed trend in stream water pH are unknown, it is clear that knowledge of these is essential to our basic understanding of how this riparian forest functions and might be managed.

From this study, a riparian forest in a coastal plain agricultural watershed: (a) acts as an important sink for nitrate-N; (b) has a significant effect on the volume of stream flow; and (c) reduces the acidity of the groundwater flowing through it. Considering the above effects and the present concern over the acidification and eutrophication of receiving waters, the protection and establishment of riparian forest "buffer strips" should be seriously considered as a management practice on agricultural watersheds.

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## APPENDIX

Table A1. Mean<sup>a</sup> dissolved nutrient concentrations in shallow groundwater leaving cropland and entering adjacent riparian forest from March 1981 through February 1982.

Month	No. of Wells Sampled	No. of Samplings per Month	Concentration (mg/l)					pH <sup>b</sup>
			Chloride	Nitrate-N	Sulfate-S	Kjeldahl-N	Total-P	
Mar	4	1	15.6	5.65	12.2	0.523	0.008	...
Apr	14	2	13.8	4.54	7.45	0.522	0.059	...
May	7	1	13.0	5.12	7.40	0.259	0.046	...
June	7	1	15.5	5.92	6.75	0.317	0.029	...
July	13	2	13.2	6.10	6.75	0.201	0.039	...
Aug	6	1	15.9	4.84	7.57	0.236	0.089	5.38
Sept	7	1	13.8	5.55	8.28	0.330	0.056	4.60
Oct	7	1	15.1	5.88	9.44	0.206	0.042	4.74
Nov	7	1	14.9	6.58	11.8	0.150	0.151	4.32
Dec	7	1	14.1	6.47	10.3	0.172	0.113	4.44
Jan	7	1	14.9	8.18	10.5	0.202	0.053	4.56
Feb	6	1	15.1	9.31	12.2	0.197	0.052	4.49
Yearly Mean <sup>c</sup>			14.6	6.18	9.22	0.276	0.061	4.56

a means are weighted averages using the number of wells sampled as the weighting factor.

b ... indicates missing data. Mean pH values were determined by averaging hydronium ion concentrations and then converting to pH.

c yearly means are arithmetic averages of monthly means.

Table A2. Mean<sup>a</sup> dissolved nutrient concentrations in shallow groundwater leaving cropland and entering adjacent riparian forest from March 1984 through February 1985.

Month	No. of Wells Sampled	No. of Samplings per Month	Concentration (mg/l)					pH <sup>b</sup>
			Chloride	Nitrate-N	Sulfate-S	Kjeldahl-N	Total-P	
Mar	10	1	10.7	3.78	8.76	0.045	0.080	4.68
Apr	10	1	9.25	4.01	7.39	0.153	0.098	4.47
May	10	1	12.8	11.2	7.18	0.342	0.012	4.50
June	10	1	12.1	4.83	6.52	0.116	0.106	4.48
July	10	1	10.7	2.69	4.04	0.068	0.136	4.31
Aug	10	1	9.28	3.63	5.16	0.121	0.092	4.44
Sept	10	1	10.0	3.02	9.66	0.186	0.152	4.39
Oct	10	1	7.64	3.28	4.53	0.052	0.022	4.38
Nov	10	1	9.25	3.58	6.14	0.018	0.091	4.50
Dec	10	1	10.6	4.52	7.04	0.100	0.100	4.53
Jan	10	1	10.8	4.65	6.84	0.050	0.098	4.41
Feb	10	1	10.1	4.46	6.60	0.090	0.092	4.49
Yearly Mean <sup>c</sup>			10.3	4.47	6.66	0.112	0.090	4.46

a means are weighted averages using the number of wells sampled as the weighting factor.

b mean values for pH were determined by averaging hydronium ion concentrations and then converting to pH.

c yearly means are arithmetic averages of monthly means.

Table A3. Nutrient concentrations during baseflow in stream water leaving an agricultural watershed from March 1981 through February 1982.<sup>a</sup>

Month	Concentration (mg/l)					pH <sup>b</sup>
	Chloride	Nitrate-N	Sulfate-S	Kjeldahl-N	Total-P	
Mar	17.4	0.054	9.63	0.257	0.032	5.07
Apr <sup>c</sup>	18.5	0.056	7.53	0.556	0.136	5.99
May	16.4	0.056	6.71	0.190	0.142	...
June <sup>c</sup>	19.2 <sup>e</sup>	0.056 <sup>e</sup>	...	0.944 <sup>e</sup>	0.442 <sup>e</sup>	6.41
July <sup>c</sup>	20.1	0.056	8.81	1.88	0.251	6.35
Aug	----- Dry -----					
Sept	----- Dry -----					
Oct	22.7	0.056 <sup>e</sup>	11.5	0.204	0.080	5.36
Nov	10.9	0.056 <sup>e</sup>	14.2	0.324 <sup>e</sup>	0.041 <sup>e</sup>	5.39
Dec	15.2	0.056 <sup>e</sup>	10.2	0.288 <sup>e</sup>	0.095 <sup>e</sup>	5.46
Jan	18.2	0.436 <sup>e</sup>	10.4	0.422 <sup>e</sup>	0.053 <sup>e</sup>	5.39
Feb	19.7 <sup>e</sup>	0.436 <sup>e</sup>	10.6 <sup>e</sup>	0.354 <sup>e</sup>	0.057 <sup>e</sup>	5.33
Yearly Mean <sup>f</sup>	17.8	0.241	9.95	0.542	0.133	5.46

a samples were taken from the week closest to groundwater sampling dates when only or mostly baseflow occurred.

b mean values for pH were determined by averaging hydronium ion concentrations and then converting to pH.

c two weeks for this time period were averaged together. For April both values were weekly spot samples. For July one sample was a weekly volume integrated and one was a weekly spot.

d ... indicates missing data.

e indicates a weekly volume integrated sample. Otherwise, a weekly spot sample was used.

f arithmetic average of monthly means.

Table A4. Nutrient concentrations during baseflow in stream water leaving an agricultural watershed from March 1984 through February 1985.<sup>a</sup>

Month	Concentration (mg/l)					pH <sup>b</sup>
	Chloride	Nitrate-N	Sulfate-S	Kjeldahl-N	Total-P	
Mar	12.5	2.13	10.0	0.120	0.077	5.45
Apr	12.3	0.274 <sup>c</sup>	8.81	0.428 <sup>c</sup>	0.103 <sup>c</sup>	5.48
May	14.6	0.008 <sup>c</sup>	4.08	0.747 <sup>c</sup>	0.285 <sup>c</sup>	5.89
June	15.7	1.37 <sup>c</sup>	19.8	0.617 <sup>c</sup>	0.182 <sup>c</sup>	6.05
July	14.0	1.93 <sup>c</sup>	4.75	0.463 <sup>c</sup>	0.138 <sup>c</sup>	6.59
Aug	15.3	1.06 <sup>c</sup>	4.60	0.530 <sup>c</sup>	0.188 <sup>c</sup>	6.70
Sept	-----		Dry	-----		
Oct	10.7	1.15 <sup>c</sup>	6.36	0.520 <sup>c</sup>	0.263 <sup>c</sup>	6.06
Nov	15.0	0.046 <sup>c</sup>	8.11	0.199 <sup>c</sup>	0.057 <sup>c</sup>	5.58
Dec	14.3	0.102 <sup>c</sup>	6.63	0.114 <sup>c</sup>	0.206 <sup>c</sup>	5.97
Jan	16.1	0.566 <sup>c</sup>	9.97	0.167 <sup>c</sup>	0.034 <sup>c</sup>	4.72
Feb	10.4	1.43 <sup>c</sup>	4.93	0.282 <sup>c</sup>	0.109 <sup>c</sup>	5.70
Yearly Mean <sup>d</sup>	13.7	0.915	8.00	0.381	0.149	5.50

a samples were taken from the week closest to groundwater sampling dates when only or mostly baseflow occurred.

b mean values for pH were determined by averaging hydronium ion concentrations and then converting to pH.

c indicates a weekly volume integrated sample. Otherwise, a weekly spot sample was used.

d arithmetic average of monthly means.

DISCUSSION: Peterjohn Paper

Question (Kelly): Have you considered the possibility of CO<sub>2</sub> gas as a possible explanation for your pH calculation?

Answer: No, I haven't. I am looking for some good ideas to explain the seasonality, and I am not sure what is controlling the riparian pH.