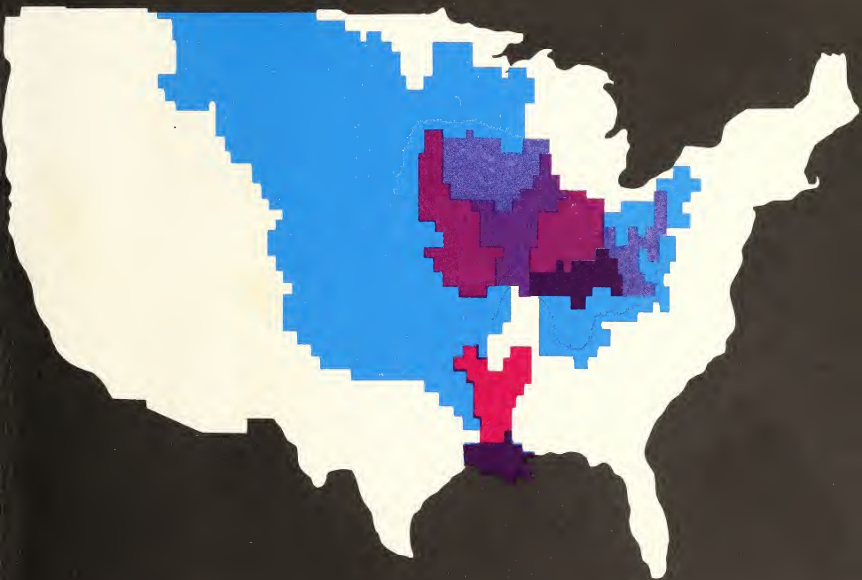


WATERSHED RESEARCH PERSPECTIVES

Edited by

DAVID L. CORRELL



SMITHSONIAN ENVIRONMENTAL RESEARCH CENTER

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Preface

Eight years ago I hosted a watershed research workshop and a two-volume proceedings was published. I expressed surprise that it was really the first watershed research symposium ever to be published. After all, research on mass balance input-outputs or processes which control these processes is of rather obvious practical utility. However, in the last 8 years interest in or at least funding of this type of work has languished. Of the group research efforts represented at the 1977 workshop, the majority no longer are functional entities! One must assume that it has been too difficult to maintain adequate funding for research at this organizational level. Individual scientists cannot handle the problem and must settle for a piece of the pie. This is indeed unfortunate and society will be impoverished by the lack of research findings at the watershed level of integration for this extended period of time.

In planning this workshop I selected five topical themes and then reviewed the published literature and my knowledge of current watershed research programs. I invited all of those scientists identified in this review to attend the workshop and to submit abstracts for possible presentations. Two proposed themes generated little or no response and were dropped. The other three, particularly the role of riparian vegetation, seemed viable and were followed up in the program. The meeting was held at the Smithsonian Environmental Research Center's facility near Edgewater, Maryland in June of 1985.

I sincerely hope, in the next 7 or 8 years, the role of long-term multidisciplinary watershed level research will be acknowledged by our society. Then a third workshop might profitably be held, with a new theme. Perhaps evolution of the theoretical framework of watershed research will have progressed significantly and the ranks of the practitioners will have swelled significantly.

A GLOBAL MODEL OF NUTRIENT CYCLING:
I. INTRODUCTION, MODEL STRUCTURE AND TERRESTRIAL MOBILIZATION
OF NUTRIENTS

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Abstract. This paper presents a terrestrial model of nitrogen cycling in the Mississippi River drainage basin. The model mobilizes total N loadings from terrestrial systems. These loadings then serve as input into models of adjacent aquatic systems. Through the use of nutrient budgets for each of 15 land use categories, the model predicts the amount of total (dissolved plus particulate) N lost from each 0.5 x 0.5 degree grid cell within the basin. We contrast a pre-settlement scenario loading of 0.55 million metric tons/yr (MMT/yr) with a contemporary (1975) land use scenario which mobilized 1.37 MMT/yr for the entire basin. This model serves as our test case for eventual global coverage of nutrient cycling, which will be achieved by studying 10 to 20 of the major world rivers.

INTRODUCTION

The model presented in this and the following paper (Vorosmarty et al., this volume) represents our efforts to date in building a structure which can describe some key aspects of nutrient cycling at the global level. The objectives of our current modelling effort are twofold. First is to characterize natural elemental cycles and their linkages, and second is to identify and quantify changes in these cycles and linkages due to human activity. We use simple mathematical models to represent the global complexities of nutrient cycles, and have developed an approach to identify and quantify those ecological phenomena integral to cycling dynamics.

We identified three system states through which a particular elemental cycle on a particular site could move during its land use history: 1) closed steady state, 2) transient non-steady state and 3) open steady state.

For example, an undisturbed site can be described as a closed, steady state system where inputs closely equal outputs, the internal pool sizes are relatively constant, and fluxes to and from the site are small relative to pool size. With initiation of extensive human land use, the input and output fluxes change, as do the internal pool sizes, resulting in what we call a transient, non-steady state system. With intensification of land use, many ecosystems reach a point where a steady state is again achieved, with inputs equalling outputs and pool sizes close to constant. The difference in the latter system, however, is that it is "open", with large nutrient throughputs, whereas the undisturbed system is relatively closed.

A model also needs a mechanism to tie together adjacent ecosystems or adjacent land uses, to integrate landscapes and their varying nutrient fluxes. We use watersheds as our organizational unit, coupling terrestrial nutrient response with aquatic and riverine nutrient processing in well-bounded units of landscape. River basins by their morphology explicitly define concise sections of the earth's surface within and between which chemical elements move.

As a test case, we selected the Mississippi River basin. Reasons for its selection were: 1) data were plentiful in constructing the initial models; 2) it is typified by both closed and open steady state systems; 3) sufficient validation data exist with which to examine our fundamental methodology and assumptions. Global coverage will

eventually be achieved by studying 10 to 20 of the largest (in terms of area drained) world rivers.

By modelling the closed steady state system we address the first objective of the model: the characterization of natural elemental cycles. We contrast this with a contemporary nutrient cycling scenario in the Mississippi basin, which has intensive land use patterns and can be described by the open steady state system. This and the following paper describe methodologies and results of this initial modelling effort. With later development of a transient, non-steady state model we will add a time component, which will follow the history of land use changes from undisturbed to present. We present here our initial results for total N, with later additions into the model of globally significant nutrients.

MODEL STRUCTURE

Organization of the various components of the model is shown in Figure 1. From global data bases, a study region (i.e., a major world river basin) is selected. From a data set assembled for the study region, land use patterns for the basin are determined. The land use or land cover then determines, in the terrestrial component, the size and nature of nutrient responses due to that land usage. The terrestrial parameters are specific to a study region or vegetation and land use. The terrestrial component thereby produces a nutrient loading for adjacent aquatic systems. Nutrients are then biologically, chemically and physically processed, resulting in a net fraction of nutrients retained or mobilized within the recipient aquatic system (see Vorosmarty et al., this volume). The fraction retained is a

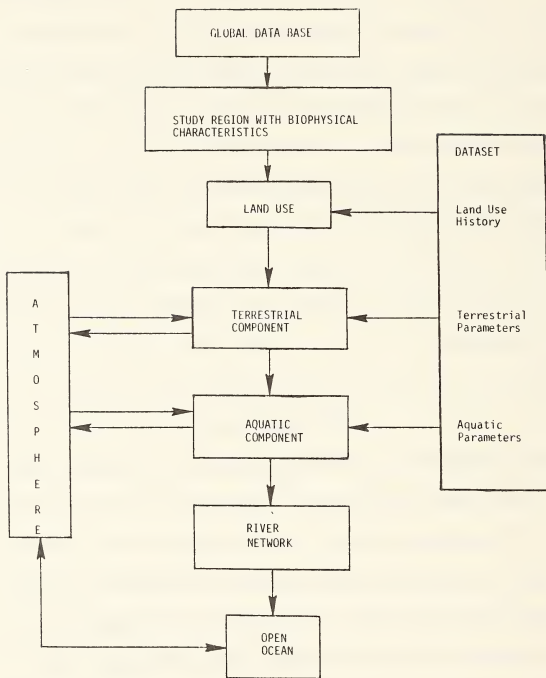


Figure 1. Model macro-structure

function of geographic location and stream geomorphology. Nutrients are moved through the basin's river network, being mobilized and retained throughout. Eventually, the aquatic nutrient load at the river mouth enters the ocean where it not only can be validated against available literature, but will become, in the future, input data for a 12-box model of the open ocean (Bolin et al., 1983).

The study region is divided into 0.5 x 0.5 degree grid cells (1374 in the Mississippi basin), and for each cell the biophysical characteristics are assigned, including vegetation, soil, terrain, subregional drainage units, political boundaries, and specific discharge.

Within the terrestrial component, nitrogen pools and fluxes are described using a simple first order box model adapted from Frissell (1977). The nutrient budget that the model defines can be thought of as a "spread sheet." The fluxes between pools in kg N/ha/yr (see "Methods" for more detailed discussion) represent the line items. The terrestrial model, applied to each 0.5 x 0.5 degree grid cell within a basin, predicts a dissolved and a particulate flux which are combined as a single total N loading for the aquatic system within the grid cell.

The aquatic nitrogen submodel receives the terrestrially-derived nutrients, receives an import of N from the adjacent upriver cell, internally retains or mobilizes a portion of the gross loading, and yields a net downriver export. In summary, nitrogen is mobilized terrestrially, loaded into aquatic systems, and retained throughout the drainage network of the river basin.

METHODS

This section describes the hydrology submodel (the river network of Figure 1), the land use submodel, and the terrestrial submodel. The total N mobilized by this suite of submodels is for non-point sources only. Point source N contribution is generated by a population submodel which is discussed in the following paper (Vorosmarty et al., this volume), as are the details and results of the aquatic submodels.

Hydrology Submodel - The Mississippi basin covers 41% of the conterminous U.S. and includes all or part of 28 states (Figure 2). There are 6 regional basins which the Mississippi River drains: the Ohio, Tennessee, Upper Mississippi, Lower Mississippi, Missouri and the Arkansas-White-Red (Figure 3). These regional basins are the highest level in the drainage hierarchy used by the USGS and the U.S. Water Resources Council (1978) shown in Figure 4. Within the Mississippi basin, there are 35 assessment subregions and 85 planning subregions. We have digitized the Mississippi basin at these first three levels of drainage hierarchy, at 0.5 x 0.5 degree grid cell resolution. As previously mentioned, the level of resolution for the terrestrial model is the grid cell, while for the aquatic model it is the 35 assessment subregional basins. For each of the subregional basins, a single major water course was identified, using the river data of the World Data Bank II (Gorny, 1977). We aggregated the ten-minute river data points to 0.5 degree increments, identifying the grid cells in the basin through which a major water course ran, and defining the direction and order of flow between subbasins. This then defines the major river network for the entire basin, linking subregional watersheds. The network receives and processes terrestrially mobilized nutrients at



Figure 2. The Mississippi River drainage basin (heavy outline) which is composed of 6 regional basins and 35 subregional basins taken from Water Resources Board (1978).

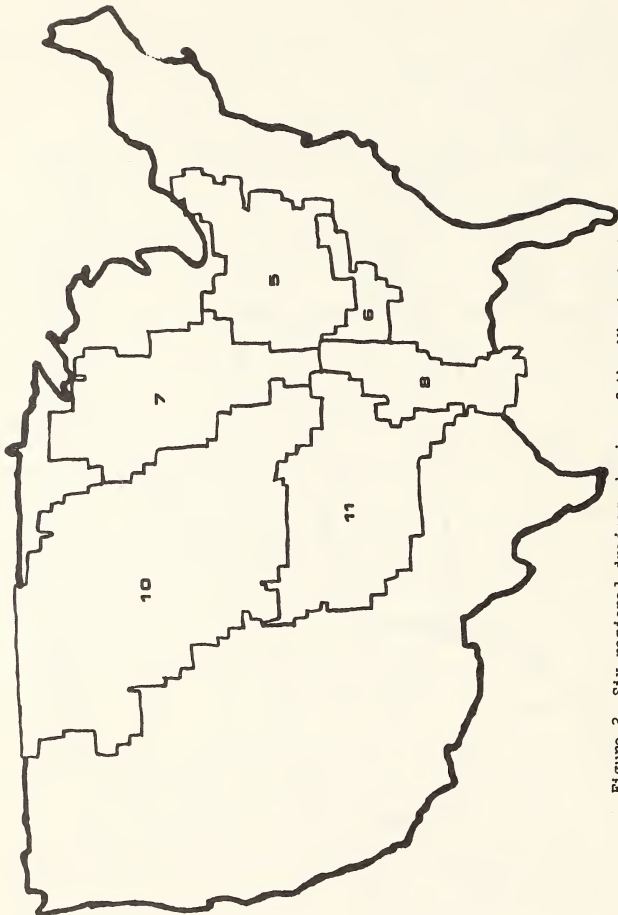


Figure 3. Six regional drainage basins of the Mississippi:

- 5 - Ohio
- 6 - Tennessee
- 7 - Upper Mississippi
- 8 - Lower Mississippi
- 10 - Missouri
- 11 - Arkansas - White - Red

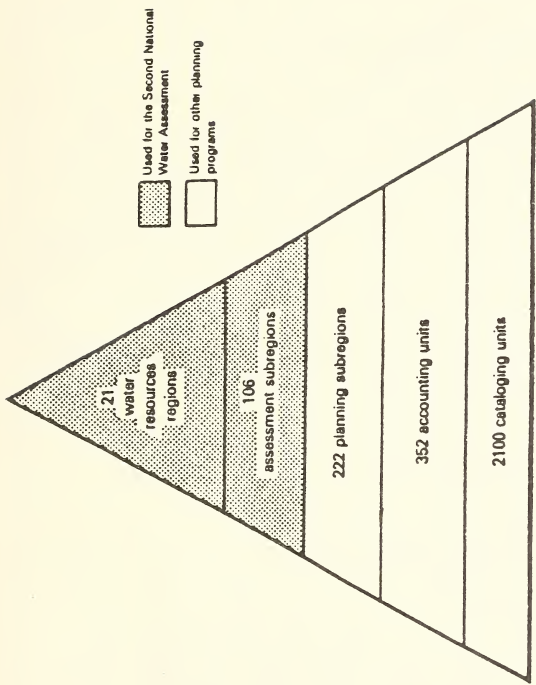


Figure 4. Organizational hierarchy of drainage units for the U.S., taken from Water Resources Council (1978).

each major river grid cell. Contributions of all non-river grid cells within each subbasin are moved to major river cells through an algorithm described by Vorosmarty et al. (this volume).

Land Use Submodel - The land use submodel assigns a land use or land cover to each of the 1374 grid cells of the Mississippi basin, for both the pre-settlement and the contemporary scenarios. To define pre-settlement natural ecosystem patterns, we use the Holdridge Life Zone classification system (Holdridge, 1947), which predicts a life zone or ecosystem type based on climatic parameters. The global data base, developed by Oak Ridge National Laboratory, represents the life zone predicted for every 0.5 x 0.5 degree grid cell on the earth's land surface. It was produced by applying the Holdridge regression relationships to a World Meteorology Organization data set for temperature and precipitation. Figure 5 shows the relationship between these climatic parameters and the 38 predicted life zones.

For the contemporary scenario, land use data were obtained at the state level for the 28 states in the Mississippi basin. Fifteen possible types of land use, as shown in Table 1, were used in the model. Areas in each state of four major categories (forest, cropland, grassland, and other), taken from a comprehensive USDA report on major land use in the U.S. in 1974 by Frey (1979), were supplemented with additional statistical sources detailed below, to produce land area in each of the 15 categories for each state. A summary table with the fifteen categories aggregated into seven significant categories is shown in Table 2. The seven categories do not total 100% area coverage.

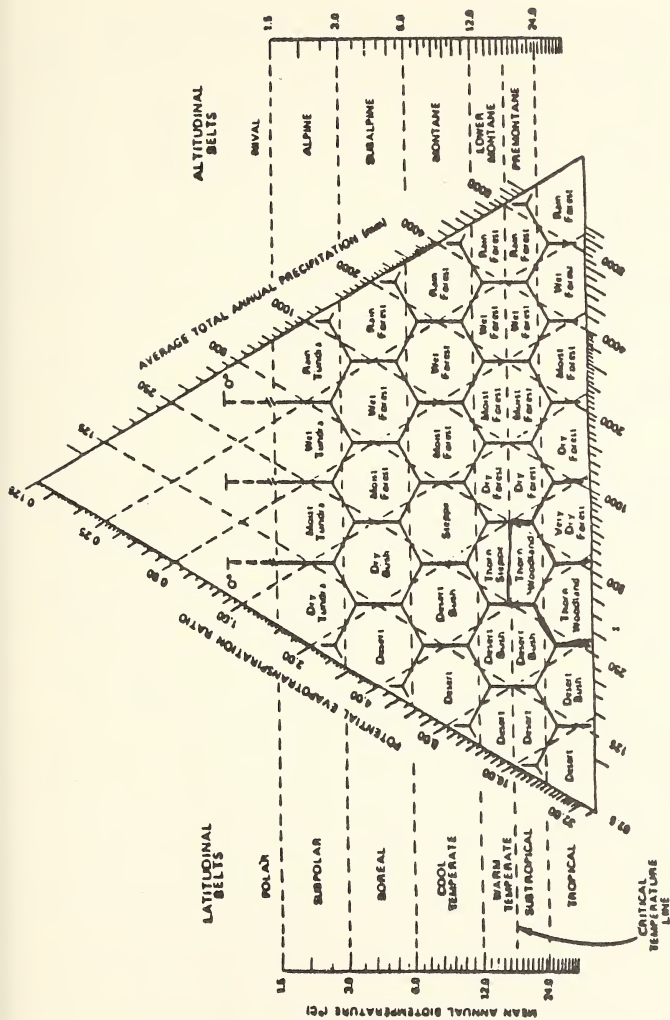


Figure 5. Holdridge Life Zone classification scheme showing the relationships between climatic parameters and predicted ecosystems (adapted from Holdridge, 1977).

Table 1. Categories of land use in Mississippi terrestrial N model.

AGRICULTURE

WHEAT	- fertilized	CORN	- fertilized
"	- unfertilized	"	- unfertilized
SOYBEAN	- fertilized	OTHER	- fertilized
"	- unfertilized	"	- unfertilized
PASTURE	- fertilized		

FORESTRY

HARDWOOD

SOFTWOOD

UNDISTURBED

GRASSLAND

HARDWOOD

SOFTWOOD

OTHER (urban and transportation areas, recreation and wildlife areas, national defense areas, farmsteads, farm roads and lanes)

1. Forest land - Total forest area for each state, taken from Frey (1979), included commercial (capable of producing usable crops of wood, economically available, or not withdrawn from timber utilization) and noncommercial forest land. Forest statistics taken from Forest Service Resource Report for 1977 (USDA, 1982) were used together with state forest area to determine area of forest land cleared. To simplify matters, we assumed that all harvested forest land was clear cut.

Undisturbed forest area, the difference between total forest land area and harvested forest area, consists of both noncommercial forest and unharvested commercial forest. The ratio of areas of undisturbed softwood to hardwood was set by assuming that the ratio of each forest type area by state was the same as in 1962 (USDA, 1965).

2. Cropland - Total area in crops by state was taken from Frey (1979), which included cropland harvested, crop failure, cultivated summer fallow, idle cropland, and cropland used only for pasture. The three

major crop types in the U.S. - corn, soybeans and wheat - cover about 40% of all cropland in the Mississippi drainage basin. Because their nitrogen budgets differ (soybeans fix nitrogen, corn receives more nitrogen fertilizer than wheat), we created three separate categories for these major crop types. A fourth category, containing the remaining 60% of the total cropland, is "other" crops. Areas of corn, soybeans, and wheat, both fertilized and unfertilized, were obtained from U.S. Census of Agriculture (U.S. Dept. of Commerce, 1977). We assumed that 50% of the area planted with other crops is fertilized.

3. Grassland and Pasture - Grasslands were divided into two categories: natural grasslands which occur in areas receiving insufficient rainfall to support forests, and successional grassland which exist where forest is the original vegetation and which must be maintained by either grazing, mowing or burning. To simplify, we assumed that grassland and pasture in any state east of and including Minnesota, Iowa, Missouri, Arkansas and Louisiana are successional and the western states contain only natural grasslands.

Total grassland was taken from Frey (1979), which includes pastures and range land. Area of grassland fertilized was found in USDA (1973). Unfertilized grassland was the difference between total and fertilized. The percentage of grassland fertilized within the Mississippi basin ranges from 9% (Mississippi) to 0.1% (Montana, Wyoming, Colorado, New Mexico) with an average of 1%.

4. Other - The land assigned to the "other" category is from Frey (1979). This category includes urban and transportation areas, recreation and wildlife areas, national defense areas, farmsteads and farm roads and lanes.

STATE	FERTILIZED ROW CROPS	UNFERTILIZED ROW CROPS	HARVESTED FORESTS	GRASSLAND UNFERTILIZED	SOFTWOOD UNDISTURBED	HARDWOOD UNDISTURBED	OTHER
Montana	8.50	8.69	0.03	53.04	20.80	0.42	8.36
Wyoming	2.02	2.36	0.03	73.95	8.77	0.66	12.18
Colorado	7.45	9.04	0.05	44.04	22.43	6.70	10.22
New Mexico	1.51	1.45	0.03	65.01	20.61	1.55	9.80
Texas	11.57	11.03	0.31	56.56	6.87	7.15	5.95
Oklahoma	20.13	15.83	0.23	35.99	4.17	16.70	6.03
Louisiana	9.44	11.62	1.49	7.10	19.18	32.67	17.68
Arkansas	13.70	17.24	1.49	7.10	17.07	36.28	6.50
Missouri	23.45	22.92	0.58	14.05	0.56	27.53	9.97
Iowa	45.05	33.68	0.10	5.75	1.48	6.68	8.46
Minnesota	27.22	19.88	0.43	3.79	12.54	23.30	12.75
Wisconsin	20.62	13.41	0.76	5.94	7.55	34.40	17.22
Illinois	40.33	29.76	0.27	4.96	0.10	10.11	14.26
Mississippi	13.25	15.15	2.09	7.86	20.94	32.76	6.76
Tennessee	16.41	15.25	0.95	6.71	6.65	40.85	12.68
Kentucky	20.27	16.76	0.97	7.65	13.76	32.10	8.18
Virginia	10.44	7.98	1.59	6.73	17.84	43.69	11.28
West Virginia	5.41	5.08	0.92	4.34	4.66	73.11	6.13
Pennsylvania	12.20	8.40	0.45	3.46	3.65	57.18	14.53
New York	11.48	8.39	0.67	5.10	7.67	40.30	26.29
Georgia	11.71	7.51	2.29	4.04	32.95	31.65	9.19
Alabama	9.97	7.89	2.09	7.95	27.36	36.26	7.41
Indiana	41.45	19.48	0.34	6.23	0.65	15.75	15.86
Ohio	30.20	18.23	0.42	6.03	0.96	23.09	20.92
South Dakota	19.58	20.90	0.02	50.63	2.81	0.65	5.26
North Dakota	36.03	32.29	0.01	21.68	0.01	0.91	6.97
Kansas	33.21	27.20	0.04	30.23	0.56	2.55	6.31
Nebraska	28.04	21.48	0.01	44.67	0.52	1.56	4.84

Table 2. Aggregated land use categories and their percentage of area for each state in the Mississippi river basin.

Terrestrial Submodel - The terrestrial submodel, inspired by Frissell's (1977) nutrient budgets of agro-ecosystems, is a simple first order box model (Figure 6). We set most outputs as functions of inputs, and we represented nutrient fluxes as "line items" in a "spreadsheet" approach to the nutrient budget. Our concern is with fluxes at present; treatment of pool sizes is secondary, and will evolve with development of transient non-steady state models. First described is a methodology for assessing inputs of fertilizer, the predominant source of N. Then the budgets of the major land use categories are described which utilize the fertilizer inputs along with other input and output variables. Output variables are set as functions of fertilizer input and include: volatilization, denitrification, leaching of NO₃, runoff of available N and harvest. All other fluxes in both disturbed and undisturbed systems are independent of input.

1. Fertilizer Inputs - Fertilizer application rates (kg N/ha/yr) were derived from combining the total amount of nitrogen used by each state in 1973 (USDA, 1973) with some estimates of average nitrogen application rates in certain states for selected crops, (USDA, 1973). These estimates were for only those states which are principal producers of the crop types investigated. To obtain fertilizer rates for the rest of the crop types and for all the states in the Mississippi basin, we made the following assumptions. We established a ratio of 1:3:7:10 (soybeans, wheat, corn, grassland) for the average fertilizer application rates taken from USDA statistics (1974). The ratio was then applied to the existing crop fertilizer rates to predict rates for the other crops within each state. For the states without any fertilizer estimates, application rates were using rates from the

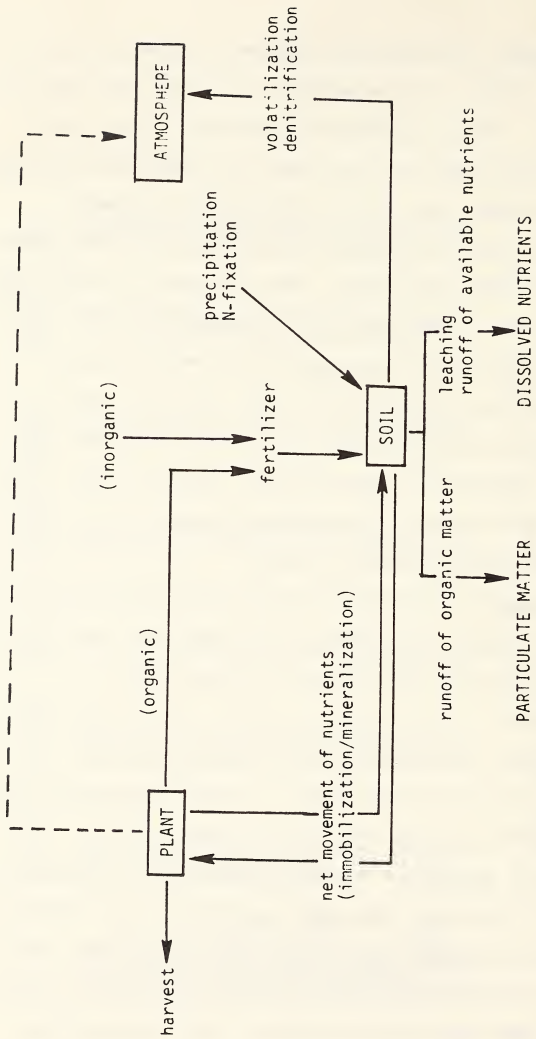


Figure 6. Terrestrial N model (after Frissell 1977) for open and closed steady state systems.

geographically closest state.

2. Nitrogen Budgets - Our aim was to develop standardized "spread sheets" for nitrogen budgets for each of the 15 land use categories. Each budget would be generalized for the category, determined through literature searches of studies of each ecosystem.

a. Forests - We established two types of forest budgets; hardwoods and softwoods, represented by oak-hickory and loblolly systems, respectively. For both forest types, the budget inputs were precipitation and N fixation; the outputs were denitrification, harvest and soluble losses (NO_3 , NH_4 and organic N). Values for the representative hardwood nitrogen budgets were taken from Aubertin and Patric (1974), Henderson and Harris (1975), Mitchell et al. (1975), Monk (1975), and Swank and Douglas (1977). Precipitation input was set at 11 kg N/ha/yr; N fixation at 2 kg N/ha/yr. Dissolved inorganic N loss was 1.5 kg N/ha/yr for undisturbed and 3.5 kg N/ha/yr for disturbed. Particulates were 1.5 kg N/ha/yr for both. Denitrification was set at 2 kg N/ha/yr for undisturbed and 3 kg N/ha/yr for disturbed. Harvest was set at 1400 kg N/ha/yr. Values for the undisturbed and disturbed softwood budgets (Gosz, 1981; Waide and Swank, 1977; Frissell, 1977; Switzer and Nelson, 1972) were 1 kg N/ha/yr for precipitation; 0 for fixation; 0 for undisturbed and 1 for disturbed denitrification; 1 for undisturbed and 3 for disturbed total N (dissolved plus particulate). Softwood harvest was 800 kg N/ha/yr.

b. Grasslands - Nitrogen enters grassland systems through precipitation and fertilizer input; nitrogen is lost through animal tissue, volatilization, denitrification, and runoff of NO_3 , NH_4 , and organic N. As described in the "Land Use" section, grasslands were either Western

natural range land or Eastern cultivated pastures. For cultivated pastures, inputs through wet and dry deposition were 10 kg N/ha/yr. Runoff of organic N was set at 2 kg N/ha/yr (Frissell, 1977). Fertilizer input was derived from USDA data with specific rates for each state as described above ("Fertilizer Inputs"). All outputs, except runoff of N in organic matter, are dependent upon the fertilizer input. It is assumed that as N fertilizer inputs increase, losses through runoff of NO₃ and NH₄, volatilization, denitrification and animal tissue also increase. Data on NO₃ and NH₄ losses in runoff from a number of studies (Kilmer, 1974; Frissell, 1977; Schuman, 1973; Sharpley, 1983) show a range of 3 to 7% of applied fertilizer nitrogen lost as available nitrogen in runoff. Colbourn and Dowdell (1984) and Frissell (1977) estimate losses of N by denitrification to range between 0 and 7% of applied fertilizer nitrogen. In Frissell (1977) 58% and 23% of applied nitrogen are lost through volatilization and animal tissue, respectively, although these losses depend upon grazing intensity. The nitrogen budget for unfertilized natural grasslands is derived from three similar budgets by Woodmansee (1978) for a shortgrass prairie in northern Texas and a tallgrass prairie in central Oklahoma.

c. Cropland - Inputs to cropland ecosystems are precipitation, fertilizer and nitrogen fixation. Outputs are leaching, runoff of available N, runoff of organic N, and harvest.

Fertilizer inputs were determined by state and crop type (see "Fertilizer Inputs"). Precipitation, which includes wet and dry deposition, is assumed to be 10 kg N/ha/yr for all crops. Nitrogen fixation is significant only for soybeans with a value of

123 kg N/ha/yr (Frissell, 1977).

Nitrogen is lost from agricultural systems as NO_3 moves in solution below the plant rooting zone. Legg and Meisinger (1982), reviewing different studies, report leaching of NO_3 ranging from 3 to 95% of input nitrogen. Frissell's (1977) values for corn, wheat and soybeans are 13, 12 and 8% of fertilizer input, respectively. We used 10% for soybeans and 15% for corn and wheat.

Values for runoff of available N (NH_4 , NO_3) were determined by averaging the percentages of fertilizer input represented by runoff, as given in several studies of corn and wheat for the U.S. (Alberts, 1978; Angle, 1984; Burnell, 1975; Klausner, 1974; Menzel, 1978; Olness, 1975; Schuman, 1973). For soybeans, we used Frissell's (1977) value of 2%. For corn we used 1%, for wheat 3%, and other crops 2%. Runoff of organic N, however, is more likely to depend upon topography and management practices than upon fertilizer input. We used Frissell's (1977) values for organic N runoff for all crop types and set them independent of fertilizer input.

In studies of denitrification rates, losses as percentages of applied fertilizer N show ranges of 0 to 20% (Colbourn and Dowdell, 1984), and 2 to 73% (Frissell, 1977). For corn and wheat budgets Frissell (1977) uses 13 and 15%, respectively. We assigned 15% for all crops to our agricultural budgets. Volatilization losses of NH_3 according to Nelson (1982) are normally low for acid or neutral soils. A summary of NH_3 losses as measured in the field show 3 to 50% of surface nitrogen applied evolving as NH_3 (mean = 17%) (Nelson, 1982). Frissell (1977) has no discussion of losses of nitrogen through volatilization and does not include it in his nutrient budgets for

arable ecosystems in the U.S. We set the amount of NH_3 volatilization from all agro-ecosystems to be 10% of the fertilizer nitrogen applied. Nitrogen removed from fields in harvested crops can in part be determined from fertilizer input. Legg and Meisinger (1982) reviewed studies which used ^{15}N to trace nitrogen transformations in corn and wheat agro-ecosystems. Several show that as the amount of fertilizer nitrogen applied to the soil increases, the proportion of the applied nitrogen taken up by the crop decreases because the total amount of nitrogen obtained in the grain levels off at a certain rate of application. In three studies on wheat fertilized with 100 to 112 kg N/ha/yr, 43 to 51% of the ^{15}N applied was recovered in the grain and stover. In five studies on corn fertilized with 55 to 112 kg N/ha/yr, 46 to 67% of the applied N was recovered. Consequently, we assumed that 50% of the applied nitrogen is taken up by the crop. Removal of nitrogen in crops from the system was determined from: 1) the amount of nitrogen taken up from available nitrogen in the soil, and 2) the percentage of crops grown that are actually removed from the field. In Barber and Olson (1968) average nitrogen content in a corn crop is 78, 127, 183 and 200 kg/ha at nitrogen application rates of 0, 84, 169 and 253 kg/ha, respectively. Given this, we assumed that 78 kg N/ha/yr is taken up by the corn from the soil regardless of fertilizer input, and additionally the crop takes up one half of the nitrogen applied as fertilizer. For wheat we used a rate of 40 kg N/ha/yr taken up from the soils, for soybeans 120 kg N/ha/yr and for other crops 50 kg N/ha/yr (all estimated using nitrogen budgets from Frissell, 1977). From Frissell (1977) the percent of crop production removed from the system ranges from 64 to 75% for the four crop types and that which

remains in the soil as crop residue is 25 to 36%. The amount of nitrogen harvested and removed from the field in crops is determined by adding together an amount of nitrogen taken up by the crop from the soil (a constant value which is dependent upon crop type) and one half of the fertilizer input, and then multiplying that value by 0.7, which is the average ratio of crop removal to crop production.

d. Other - At present the "other" category generated by the land use model does not explicitly receive an N budget which describes potential mobilization, except for point source loading generated in the population submodel (see Vorosmarty et al., this volume).

MOBILIZED TERRESTRIAL NITROGEN

We contrast here our pre-settlement scenario with a contemporary (1975) land use pattern in producing terrestrially mobilized total N as potential loading to adjacent aquatic systems. For the entire Mississippi basin, the pre-settlement scenario predicts 0.55 million metric tons (MMT) for a single year. With a contemporary land use pattern, the terrestrial N model predicts a loss of 1.37 MMT/yr total N to aquatic systems. This 150% increase over the pre-settlement loading can be directly attributed to human activity. These values represent the sum of all 1374 grid cells within the basin.

The contemporary scenario shows, however, great differences in accelerated N loss among the six regional basins of the Mississippi drainage. To examine these regional patterns, terrestrial loads for each grid cell within a regional basin were summed for the basin and digitally mapped on a color graphics terminal. Figures 7 - 8 are graphic representations of those maps and show strong regional

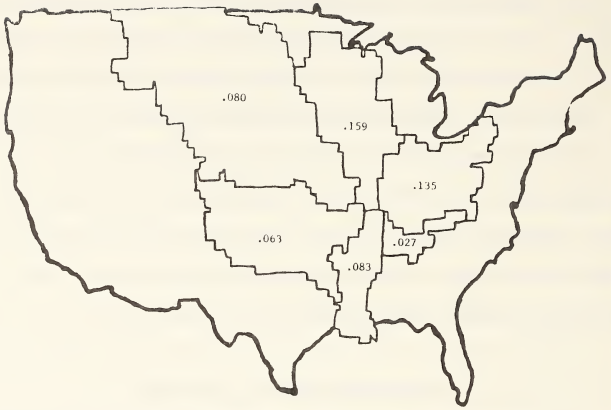


Figure 7. Terrestrially mobilized total N (x 10 kg) summed within each regional basin for the pre-settlement scenario.

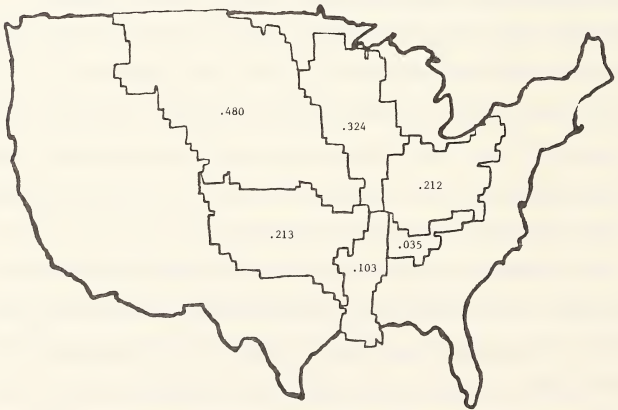


Figure 8. Terrestrially mobilized total N (x 10 kg) summed within each regional basin for the contemporary land use scenario (1975).

contrasts. Figure 7, showing the regional basin loading for the pre-settlement scenario, illustrates the difference in "leakage" rates between eastern hardwoods of regions 7 and 5 and western grasslands of regions 10 and 11. Figure 8 shows a dramatic increase in terrestrial N loading in the western regions with their contemporary agriculture use, but increasingly smaller increases over pre-settlement conditions for basins 7, 5, 6, and 8, respectively. These differences can be seen in Table 3 which shows the increase for each basin in the contemporary scenario over the pre-settlement scenario. Basins 8 and 6 show the smallest increases: 23% and 30%, respectively.

Table 3. Comparison of changes among the six regional basins of the Mississippi for the pre-settlement and the contemporary scenario (1975).

Terrestrially Mobilized Total N Load (MMT/yr)

<u>Drainage Basin</u>	<u>Presettlement</u>	<u>1975</u>	<u>Percent Increase</u>
5	0.135	.212	57.1
6	0.027	.035	29.6
7	0.159	.324	103.4
8	0.083	.103	23.2
10	0.080	.480	500.0
11	0.063	.213	238.1

Basins 5 and 7 show more (57%, 103%), but basins 10 and 11 display the bulk of the total increase in loading for the entire Mississippi basin. An increase of 500% in basin 10 reflects the change from a natural grassland with zero leakage in its nutrient budget to its contemporary

land use. Basin 10, as seen in Figure 2, includes all or part of Montana, Wyoming, North and South Dakota, Nebraska, Iowa, Missouri, Kansas and Colorado. The various percentages of land use within each state are shown in Table 2. In several of these states, over half of the land area is still in natural (unfertilized) grassland (Montana, Wyoming, South Dakota), and several more states still have more than 25% of their land area in grassland (Colorado, Kansas, Nebraska, North Dakota).

However, Iowa, although only partly included in basin 10, has 30% fertilized corn and 11.8% fertilized "other" crops; Missouri has 5% fertilized corn and 13.9% fertilized "other" crops; North Dakota has 22% fertilized "other" crops; Kansas and Nebraska have 16.8 and 13.3% in fertilized wheat, respectively. The shift from natural grassland nutrient budgets to agricultural budgets (corn, wheat, soybean, "other"), even for less than half of the land area in basin 10, causes the 500% increase in mobilized total N. Similarly, for basin 11, changing the pre-settlement scenario of grasslands with zero leakage to contemporary agriculture produces a large (238%) increase in total N mobilized within the basin.

These basins (10 and 11), although exhibiting the largest increases in total N mobilized, do not have the highest loads on an areal basis. Table 4 presents basin loadings on a kg/ha basis, and clearly shows, in the pre-settlement scenario, the regional differences between grasslands and eastern woodlands (<1 kg/ha vs. 3.2 kg/ha).

Table 4. Comparisons of terrestrially mobilized total N on an areal basis among the six regional basins of the Mississippi river drainage.

<u>Drainage Basin</u>	<u>Presettlement (kg/ha)</u>	<u>1975 (kg/ha)</u>
5	3.2	5.0
6	3.2	4.2
7	3.2	4.9
8	3.2	3.9
10	0.6	3.6
11	0.9	3.2

However, in the contemporary scenario it is basin 7 that produces the heaviest loading on a per area basis, despite the 238% and 500% increases in the western basins. This can be confirmed by again referring to Table 2 and Figure 2. Basin 7 includes most of Iowa, Illinois, Wisconsin and Minnesota, and their percent land use in fertilized row crops (Table 3) is higher than those states in basins 10 and 11. The smaller increases in mobilized total N in basins 5, 6, 7 and 8 (vs. 10 and 11) in the contemporary scenario are a result of several statistical factors. Our nutrient budget for the undisturbed hardwood ecosystem has a leakage of total N set at 3 kg/ha, and the undisturbed softwood budget has a leakage rate of 1 kg/ha. The average leakage rate for fertilized crops was roughly 10 to 15 kg/ha. This three- to fivefold increase in total N mobilized per hectare, however, has to be viewed in light of the percentages in each state in the land use categories. Basin 8, with the least change from pre-settlement to contemporary, includes Louisiana which has 51.7% undisturbed forest and 17% "other" land use, and only 9.4% fertilized row crops. Similarly, in basin 8, Arkansas has 53.2% undisturbed forest and 13.7% fertilized

row crops, and Mississippi has virtually the same land usage as Arkansas in all categories.

Contemporary basin 6 also has a high percentage of undisturbed forest systems (both hard- and softwood), with its states having low percentages of fertilized crops. Whereas it was entirely hardwood in the pre-settlement scenario, for 1975 Tennessee has 6.7% undisturbed softwood, Georgia has 33% and Alabama has 27.4%. This shift from pre-settlement hardwood to some contemporary softwood land usage, combined with high percentages in the "other" category, contributes to the smaller increase in total N mobilized.

Finally, while basin 5 contains states with significant percentages of fertilized crops such as Indiana (41.45%), Ohio (30.2%), and Kentucky (20.27%), it also contains states such as West Virginia (5.41% fertilized crops and 73.11% undisturbed hardwood forest), Pennsylvania (12.2% and 57.18%, respectively), and Virginia (10.44% and 43.69%).

While careful examination of the land use composition within each basin explains much of the vast regional differences in the contemporary scenario, we also suspect some overestimation of the arid and semi-arid agricultural lands' contribution.

The total N lost from a terrestrial system or site represents the particulate matter (organic N) and the dissolved inorganic N predicted by a nitrogen budget with state-specific fertilizer input rates. Both the particulate and the dissolved terms are measured flux rates taken from studies on the particular ecosystem. The problem arises in applying a budget taken from studies in eastern regions to the arid regions in the west. As both the particulate and the dissolved fluxes

are influenced by amounts of precipitation, this application of "generic" crop budgets uniformly to the entire basin will result in erroneous estimates of total N mobilized.

To correct this imbalance, we intend to tie the loss rates of the studies used in constructing the budget to the specific discharge for that study location. Then by pro-rating loss rates against specific discharges for the entire basin we will achieve a more representative regional pattern of terrestrial N mobilization.

SUMMARY AND CONCLUSIONS

Our spatially resolved terrestrial model of nitrogen mobilization for the Mississippi has clearly illustrated a major consequence of human activity on the nutrient cycling system. A 150% increase in total N mobilized from non-point sources is predicted over pre-settlement conditions. Of the contemporary loading, 87% (1.197 MMT/yr) is due to agricultural land uses and 0.7% (0.009 MMT/yr) is due to forest harvesting. This clearly characterizes this drainage basin as heavily agricultural. Furthermore, the model illustrates the disproportionate regionality of this change from pre-settlement to contemporary land use. With the study of other major river basins of the world, we hope to examine impacts of other major categories of land usage in those basins where they dominate.

These results of the terrestrial nitrogen model serve as input to the aquatic submodel, which further describes the impact of land use on nutrient cycling. Through the aquatic processing and retention of nutrients of terrestrial origin, the "signal" of contemporary human activity seen at the mouth of major world rivers begins to characterize

the status of regional and global cycles. With further elaborations of these submodels, both the scope and the complexities of global nutrient cycling can be addressed.

ACKNOWLEDGEMENTS

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DISCUSSION: Deferred to next paper.

A GLOBAL MODEL OF NUTRIENT CYCLING:

II. AQUATIC PROCESSING, RETENTION AND DISTRIBUTION
OF NUTRIENTS IN LARGE DRAINAGE BASINS.

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Abstract. This paper describes a simple model which routes terrestrially derived nutrients across large units of landscape with simultaneous aquatic processing. Our methodology has been applied to total nitrogen within the Mississippi River system under pre-settlement and contemporary nutrient loading regimes. The model predicts 1.05 million metric tons (MMT) of total N to pass across the mouth of the river annually, an estimate four percent lower than observed flux. The pre-settlement N flux is lower, 0.43 MMT per year. These results indicate a significant acceleration in continental N loss due to widespread human settlement and industrial agriculture. The Mississippi River has served as a data-rich test case; our model will ultimately be applied at the global level through consideration of other large drainage basins outside the US.

INTRODUCTION

Although the effects of human disturbance on nutrient biogeochemistry are well-documented in a variety of specific environments, a global consideration of such impacts is still a relatively recent scientific undertaking. To maintain both conceptual and computational tractability, global models traditionally have condensed the processes of interest into a form suitable to mathematical analysis. In addition, these models are normally highly aggregated in space. With the expansion of computer speed and storage

potential, the availability of sophisticated geographic information systems (GIS) and well-documented global datasets, it now becomes possible to consider the biosphere with a substantially greater degree of geographic specificity.

We have developed a highly resolved spatial model that tabulates the release of nutrients from land and monitors the subsequent passage of these constituents through large drainage basins. The purpose of this paper is to summarize a strategy for moving nutrients through river networks and for processing them within streams of various size. This paper complements the discussion of Gildea et al. (this volume), which describes a model for quantifying the mobilization of nutrients within large units of landscape.

We have applied the methodology to the Mississippi basin as a test case, the first step in its eventual application at the global level. For the Mississippi, we offer predictions of total nitrogen load flowing past the mouth of the river. We contrast pre-settlement and contemporary conditions and compare model results to published findings.

AQUATIC NUTRIENT TRANSPORT

There are six regional drainage basins within the larger Mississippi River system -- the Ohio, Tennessee, Missouri, Arkansas-White-Red, Upper Mississippi and Lower Mississippi. Within each of the six regional drainages there are from two to eleven subregional drainage basins as defined by the US Water Resources Council (1978). These subregional basins serve as the basic unit of landscape for the aquatic nutrient model, and there are 35 such basins

within the Mississippi. Each subregional basin is defined by a set of 0.5 x 0.5-degree grid cells. Land use in these basins is assigned to the grid cells on the basis of state-level data. The assignment of landscape characteristics is detailed further in Gildea et al. (this volume). Use of subregional drainage basins and the 0.5 x 0.5-degree grid system enables us to simplify the otherwise intractable complexity of the natural landscape, its land use and hydrology which characterizes the Mississippi basin as a whole. Our analysis is based on geographic specificity, and we can identify areas of active nutrient flux within the 3.3 million km² basin.

There are two pathways for aquatic transport through each subregional drainage basin. The first involves a series of smaller "subcatchments," which taken together form a mosaic of landscape within the subregional basin. In each subcatchment, the model collects all non-point source nutrient load, processes it, and funnels the remainder into a mainstem river assigned to the associated subregional basin. Non-point loads are derived from natural and disturbed ecosystems (Gildea et al., this volume) and from human wastes associated with the rural population. We have used an annual per capita loading of 4 kg total N (Metcalf & Eddy, Inc., 1979, Gotaas, 1956) together with population estimates for each subregional basin taken from the US Water Resources Council (1978) and the US Geological Survey (1974) to determine the aggregate waste input.

Since there can be thousands of tributary streams within each subcatchment it would be impossible to treat each explicitly. Instead, we have assigned an implicit stream network based on a simple relationship taken from the geomorphologic literature. This

relationship (derived from the data of Leopold et al., 1964) enables us to calculate the largest stream order capable of draining sub-catchments of various size (in km² area):

$$\text{Order}_{\text{max}} = \frac{\log_{10}(\text{Area} / 2.590) + 0.6760}{0.6776} \quad (1)$$

The maximum order stream is then used as the starting point of a geometric expansion of coalescing streams of smaller order. Each stream of order n-1 is assumed to flow directly into a stream of order n, for all orders n=2 through the maximum. Although there are exceptions to this routing scheme it represents the predominant pattern found in nature (Giusti and Schneider, 1963). We apply the non-point source load evenly to each order and allow the material to pass downward through the subcatchment.

The second major aquatic pathway involves large rivers and impoundments. To each subregional drainage basin we assign one mainstem channel, identified by a series of linked 0.5 x 0.5-degree grid cells containing information on stream size and direction of flow. At its single entry point into a subregional basin, the river accepts water or material from any upriver source. The material is then routed downstream through the basin, grid cell by grid cell, gaining nonpoint loads from the subcatchments and point loads predominantly from sewage. We again use an annual per capita loading of 4 kg total N. Nutrient processing within the large rivers, if any, will modify the exogenous loading. Nutrient load exits the subregional basin at a single point and is passed to the next recipient basin. A dominant feature of the Mississippi River and its tributaries is extensive impoundment, a

phenomenon that dramatically alters the nutrient transport potential of natural rivers (Ward and Stanford, 1983; Ward and Stanford, eds., 1979). We specified 17 large reservoirs in our current model of the Mississippi (Harbeck and Thomas, 1956) and assigned to them a distinct nutrient processing potential as described below.

In summary, the transport model for nutrients in a large drainage basin is straightforward and descriptive. Material is routed and potentially transformed through aquatic ecosystems along a gradient of topography which begins at the highest extremities of the basin and which ends at a single exit point. Our model operates at an annual timestep and tabulates mean annual constituent load throughout the drainage basin. The model is a simple accounting device and does not rely on mechanistic hydraulic routing schemes to perform its calculations.

NUTRIENT PROCESSING

The concept of loading nutrients into river networks and passing them downriver forces consideration of a critical issue. Namely, are rivers passive conduits that carry materials to the sea, or are they active processors of constituents? In their classic text on geomorphology, Leopold et al. (1964) stated that rivers are simply "gutters down which flow the ruins of continents." Aquatic biologists take a substantially different view, and there is ample evidence from diverse disciplines (e.g., lotic system ecology, environmental engineering, fisheries management) to support the existence of active processing (Peterson et al., 1983; Fontaine and Bartell, eds., 1983; Whitehead and Lack, eds., 1982; Newbold et al., 1981; Vannote et

al., 1980; Ward and Stanford, 1979; Metcalf & Eddy, Inc., 1979; Whitton, ed., 1975). We accept the concept of active aquatic processing and have incorporated the phenomenon into our drainage basin model.

Aquatic processing is, in reality, a series of complex biogeochemical reactions. For nitrogen these include plankton/periphyton/macrophyte uptake, bacterial turnover, denitrification and fixation, burial, bedload movement and resuspension, sorption/desorption, and benthic remineralization and subsequent diffusion. We recognize the importance of each process, but for the intended purpose of constructing a model at the global level, substantial simplification is required. Figure 1 schematically depicts this simplification.

AQUATIC NITROGEN PROCESSING SUBMODEL

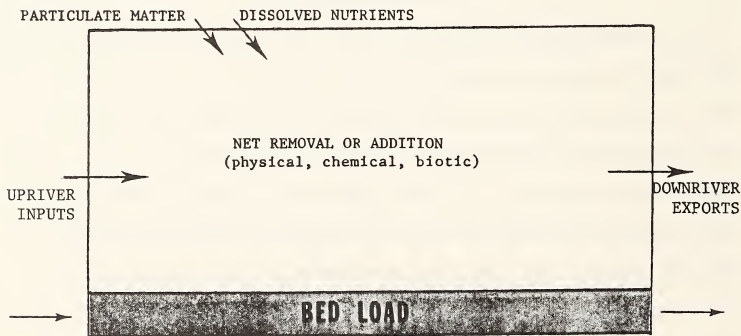


Figure 1. Model treatment of nutrient transport and processing in aquatic ecosystems. The removal or addition term is a distillation of what is in reality a complex amalgam of subprocesses.

We have sought estimates of nutrient processing in rivers that treat the phenomenon as either a net source or a net sink during each yearly timestep. Unfortunately, there is no consensus on the magnitude of net flux, and very few strictly aquatic nutrient budgets have been performed over the year. The work of Mattraw and Elder (1984), Triska et al. (1984), and Meyer et al. (1981) are notable exceptions.

On the basis of the available data, we assigned parameters to the model using a single retention/loss coefficient for each stream order in the subcatchments and for each mainstem river. The coefficient is expressed as a proportion of the total annual nutrient load passing through the river which is physically detained or lost by the aquatic system during the yearly timestep. Thus, for any river reach we have:

$$\frac{dN}{dR} = N_{\text{new}} - kN \quad (2)$$

where N is total annual aquatic nitrogen load in kg, R is river reach (or stream order), N_{new} is annual nitrogen load added to the stream order from point and non-point sources, and k is the retention/loss coefficient. The above equation implies that the system is at steady state during any yearly timestep and that the net aquatic processing is best described by a first-order retention/loss coefficient. In fact an annual net sink varies with year-to-year changes in discharge, and long-term nutrient and organic material storage is disrupted by flooding events (Triska et al., 1984; Webster et al., 1979; Hobbie and Likens, 1973).

RIVERINE RETENTION/LOSS COEFFICIENTS

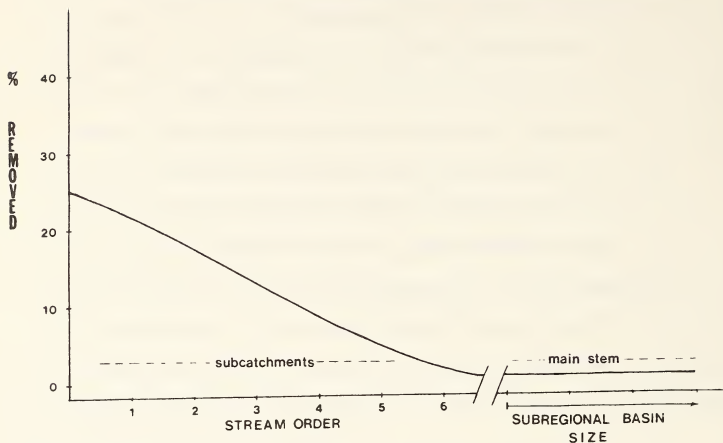


Figure 2. Retention/loss coefficients assigned in the model as a function of stream size. These parameters are expressed as the proportion of annual riverborne nutrient load trapped within or lost from lotic ecosystems.

We apply equation (2) collectively to all streams of a given order. The absolute mass of total N that passes downstream is thus a function of reach-specific loading and reach-specific retention. Figure 2 shows retention coefficients for relatively small subcatchment streams (order less than 6) and mainstem rivers. Currently we assume that all of the total N mobilized from terrestrial sources finds its way into water courses and is potentially processed. The influence of intervening riparian vegetation can be significant (Cluis et al., 1979; Volleweider, 1968; various contributions in this volume) and will be addressed in future refinements of our global model. Deltaic and estuarine nutrient processing is not considered explicitly in the current version of our model.

We also assume retention or loss of total N within large impoundments. Figure 3 shows retention/loss coefficients for reservoirs in our preliminary model based on hydraulic retention time (Serruya, 1975; Soltero et al., 1974; Soltero et al., 1973; Ahlgren, 1967). Given retention/loss coefficients and nutrient loading, N transport through impoundments can be determined using equation (2). The flux of N so calculated is subsequently passed downriver.

RESERVOIR RETENTION/LOSS COEFFICIENTS

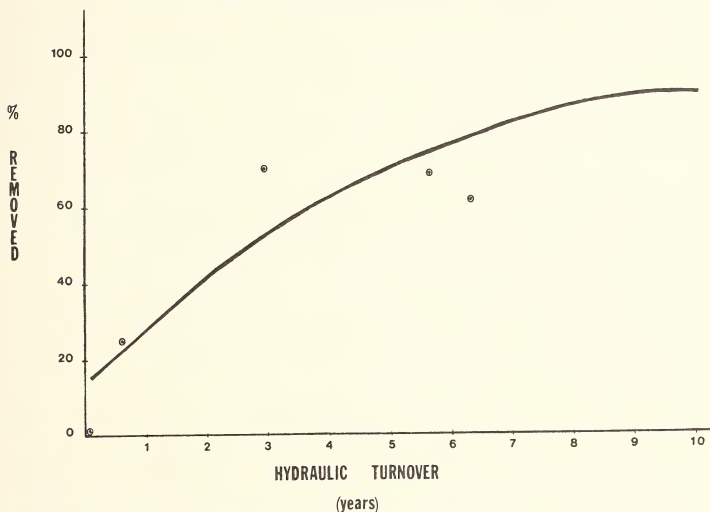


Figure 3. Retention/loss of nutrients in reservoirs is assumed dependent on hydraulic turnover time (volume/inflow). This preliminary parameterization was based on a cursory review of the literature and will be refined as part of our ongoing work.

N LOADS IN THE MISSISSIPPI BASIN

We used the model to contrast contemporary and pre-settlement total N loading throughout the Mississippi drainage. For the pre-settlement basin, vegetation was specified by the Holdridge (1947) life zone system as described by Gildea et al. (this volume). Non-point source loads for particulate and dissolved N were derived from corresponding nutrient budgets as reported in Frissell (1977) and computed by the terrestrial ecosystem model of Gildea et al. Human waste loading and impoundments were absent from the river network. The annual aggregate mass of terrestrial N transferred to aquatic systems in the pre-settlement condition was estimated by Gildea et al. to be 0.547 million metric ton (MMT). For the contemporary setting (ca. 1975), the landscape is characterized by widespread industrial agriculture and numerous large point sources for N. The annual pool of total N mobilized as a result of these activities was estimated to be to 1.610 MMT. According to our calculations, this mass was dominated by land use-related non-point sources, mainly inorganic fertilizer, at a level roughly six times greater than that for human wastes.

Figures 4 and 5 contrast the pre- and post-settlement flux of total N in the six regional drainage basins of the Mississippi as predicted by the coupled terrestrial/aquatic model. The numbers enclosed by parentheses represent the aggregate terrestrial ecosystem loading of total N within each regional drainage basin while the values in brackets show direct human waste loads. Beside each arrow is the cumulative transport of total N out of the basin, which integrates both nutrient loading and subsequent aquatic processing. For the pre-settlement scenario, there are sizable areas of the Mississippi

PRE-SETTLEMENT N LOADING

--Model Prediction

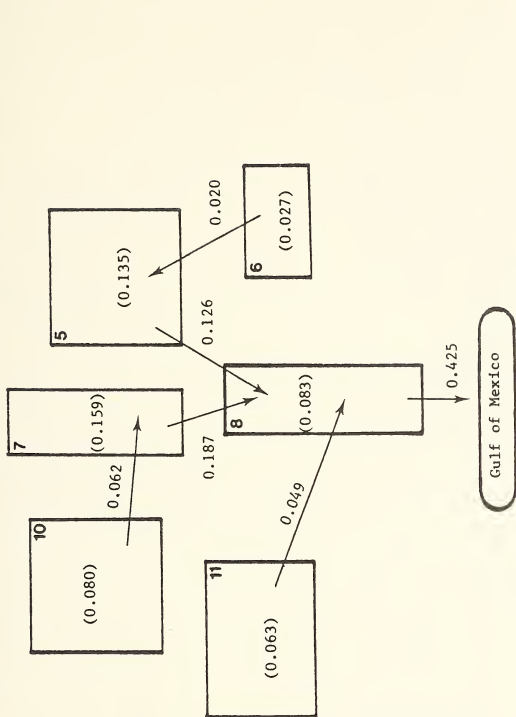


Figure 4. Pre-settlement cumulative total N loads (MMT/year) in rivers exiting the six regional drainage basins of the Mississippi. The transfer of material is denoted by the arrows. The figures in parentheses show terrestrially-derived N from non-point sources (MMT/year). Note that the most significant aquatic N loads are associated with terrestrial mobilization in the Ohio and Upper Mississippi regional basins. (USGS regional basin key is as follows: 5 = Ohio; 6 = Tennessee; 7 = Upper Mississippi; 8 = Lower Mississippi; 10 = Missouri; 11 = Arkansas-White-Red.)

CONTEMPORARY N LOADING
--Model Prediction

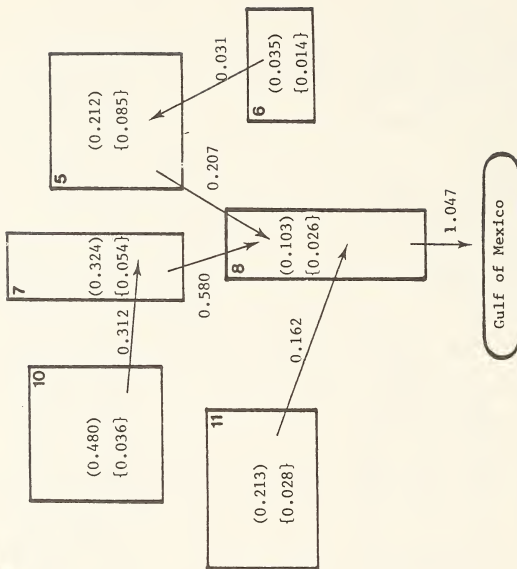


Figure 5. Post-settlement (ca. 1975) cumulative total N loads (MMT/year) in rivers exiting the six regional drainage basins of the Mississippi. The transfer of material is denoted by the arrows. The figures in parentheses are terrestrially-derived N from natural and disturbed ecosystems; those in brackets show N in point and non-point human waste. In comparison to pre-disturbance, all regions show a large relative increase in N loading from all sources and the mass of total N transferred by aquatic systems is corresponding elevated. There has been a more than two-fold increase in the amount of N passing the mouth of the Mississippi basin. (USGS regional basin key is as follows: 5 = Ohio; 6 = Tennessee; 7 = Upper Mississippi; 8 = Lower Mississippi; 10 = Missouri; 11 = Arkansas-White-Red.)

basin that fail to display significant N loading. Significant riverine N loads appear as a consequence of relatively large terrestrial losses in only the Upper Mississippi and Ohio basins with only moderate increases continuing downriver. The annual pre-disturbance load that passes the mouth of the Mississippi was calculated to be 0.425 MMT total N. Twenty-two percent of the terrestrially-derived load was retained or lost in aquatic systems. This demonstrates the importance of aquatic nutrient processing in large basins and argues for a much more comprehensive analysis of linkages between river systems and terrestrially-derived nutrients than currently exists in the literature.

The impact of more than two centuries of human expansion, particularly agriculture, within the basin is dramatic (Figure 5). Except for the Tennessee and Lower Mississippi, all regional basins show a significant increase in non-point terrestrial N loading over pre-settlement conditions. With the dramatic increase in human settlement and its associated waste load, the mass of total N derived from all terrestrial sources is now large relative to the predisturbance state in all basins. Aquatic loads are correspondingly elevated, thereby accelerating nutrient transport across the landscape and within recipient aquatic systems. Transport of total N across the mouth of the Mississippi is predicted to be 1.047 MMT, a two- to three-fold increase over pre-settlement conditions. Thirty-five percent of point and non-point loads are retained or lost in rivers and impoundments.

Geographically-specific output from the contemporary scenario was validated against data for water year 1975 (October 1974 through

September 1975) as reported by the US Geological Survey (Briggs and Ficke, 1977). A map summarizing this information appears in Figure 6, and it is directly comparable to the graphic for our contemporary scenario (Figure 5). There is substantial agreement between predicted and observed datasets, in terms of both the geographic distribution of N load and its absolute magnitude. The greatest differences between predicted and observed aquatic loads occur in waters exiting the Missouri and Ohio basins. Results from these basins suffer from the application of terrestrial nutrient budgets to regions other than those for which they were originally developed. As discussed by Gildea et al. (this volume), this can lead to over- and underestimates of terrestrial loading and the nutrient mass eventually finding its way into recipient aquatic ecosystems will thus be misrepresented. Despite this shortcoming, the model underestimates true N flux past the final downriver station (1.086 MMT) by less than four percent.

Ideally, our prediction that the Mississippi basin has experienced a two- to three-fold increase in total N flux above background level could be compared directly to other documented studies of human disturbance of the N cycle. However, ours is a flux estimate for both dissolved and particulate N species, and there are virtually no adequate datasets or analyses upon which to base a comparison for the particulate fraction (Meybeck, 1982). Van Bennekom and Salomons (1981) do offer estimates based on direct and indirect human waste loads, cautiously citing a three- to four-fold increase in total N flux for all world rivers. Studies of dissolved N also show increases due to human activity. Meybeck (1982) gives a global estimate of a 50% increase for total dissolved N over pre-disturbance conditions. For

CONTEMPORARY N LOADING
--NASQUAN Database

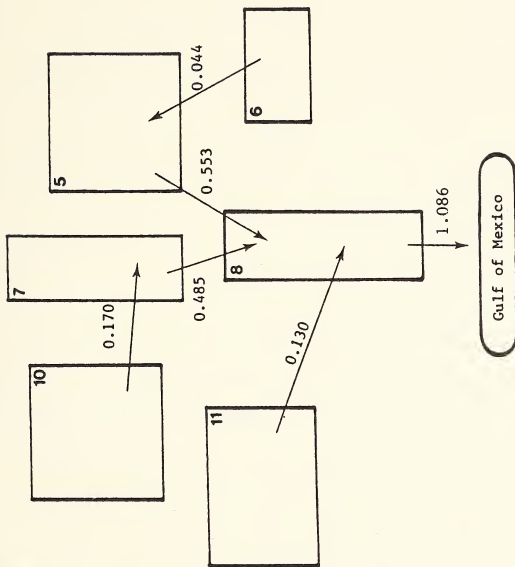


Figure 6. Observed post-settlement cumulative total N loads (MMT/year) in rivers exiting the six regional drainage basins of the Mississippi as given by the U.S. Geological Survey in Briggs and Ficke (1977). The transfer of material is denoted by the arrows. There is substantial agreement between model results and observed N loads exiting the Missouri and Ohio basins, the model predicts transport of total N past the amount of the Mississippi to within 10 percent. (USGS regional basin key is as follows: 5 = Ohio; 6 = Tennessee; 7 = Upper Mississippi; 8 = Lower Mississippi; 10 = Missouri; 11 = Arkansas-White-Red.)

nitrate-N, Meybeck documents common increases in major Western European waterways from 10 to 30 times pre-disturbance. Significant increases in nitrate-N flux were assumed to have already been in place at the turn of the century in the US and Europe (van Bennekom and Salomons, 1981). Inhabited river basins also will show dramatic enrichment in ammonium-N and the phenomenon spans many different regions of the globe (Meybeck, 1982). Our model results seem reasonable in the context of these other studies. An increase in N flux appears an inevitable consequence of human interaction with river networks. The precise rate of increase is a site-specific function of land use, settlement patterns and human modification of waterways.

SUMMARY AND CONCLUSIONS

We have constructed a descriptive model for terrestrial mobilization, material transport and aquatic retention of nutrients in large drainage basins. The contemporary Mississippi basin was chosen as a test case and model predictions for total N flux were compared to results derived from an empirical dataset. Model prediction was less than four percent below measured total N mass exiting the basin. The model was used to contrast pre-settlement and contemporary nutrient flux. We found a two- to three-fold increase in total N load as a result of human disturbance.

Preliminary success for total N in the Mississippi basin encourages application of the methodology to other important nutrient forms (dissolved and particulate N and P, organic and inorganic N and P) and to carbon. We will refine our spatial resolution beyond the level of subregional drainage basin and extend the analysis to other

regions of the world. We will restrict our current research to a consideration of the large drainage basins listed in Table I.

Collectively, the eleven river basins drain a significant portion, about 30%, of the continental surface area which delivers runoff to the world's oceans (Meybeck, 1976; Alekin and Brazhnikova, 1960). They also represent 30% of all water flow (Meybeck, 1982; Alekin and Brazhnikova, 1960) and sediment discharge (Milliman and Meade, 1983) to the oceans. These major rivers are enriched with respect to dissolved N and P flux and constitute 40% or more of the current global total for each nutrient (Meybeck, 1982). When compared to the global anthropogenic load, this subset of rivers is further enriched -- at least 60% and 50% of the added N and P loads, respectively. An analysis of these drainage basins using our model therefore will cover a substantial fraction of the earth's surface subject to active human disturbance of nutrient cycles.

Finally, these basins represent contrasts between non-industrial and industrial agriculture, low and high population density, arid and humid climate and tropical and arctic regions. Such contrasts could be considered a form of paired watershed study. In small catchments this type of research has yielded important insights into the functioning of terrestrial and aquatic ecosystems. We hope to benefit from the comparative approach at the regional and global level.

ACKNOWLEDGEMENTS

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Table I. Characteristics of Eleven Major Rivers

River Basin	Area (a)		Discharge (a)		Sediment (b)		Dissolved (c)	
	km ²	x 10 ⁶	m ³ /sec	10 ⁶ t/yr	Inorganic N Load 10 ⁹ g/yr	Phosphate P Load 10 ⁹ g/yr		
Amazon	6,300		175,000	900	420	65		
Zaire	4,000		39,200	43	120	30		
Mississippi	3,250		18,400	210	640	120(g)		
Nile	3,000		2,800	0	NA	NA		
Parana	2,800		18,000	92	280	40		
Yenisei	2,600		17,200	13	NA	NA		
Yangtze	1,950		22,000	478	190	NA		
Orinoco	950		30,000	210	90	5		
Ganges/Brahmaputra	1,550		30,900	1,670	340	50		
Mekong	800		18,300	160	140	NA		
Rhine	150(d)		2,000(d)	NA	280	15		
Above Total	27.4x10 ³		373.8x10 ³	>3.8x10 ³	>2.5x10 ³	>325		
Contemporary Continental Total	100x10 ³ (e)		1,175x10 ³ (f)	13.5x10 ³	6.5x10 ³ (h)	800		
Share of the World Total by Rivers Listed Above	27%		32%	>28%	>38%	>41%		
Natural Transport (Global)					4.5x10 ³	400		
Anthropogenic Nutrient Source (Global)					2x10 ³ (h)	400		
Fraction of Source Attributable to Rivers Listed Above					>50%(i)	>60%(i)		

- (a) Meybeck (1976).
- (b) Milliman and Meade (1983). The load reported is that delivered to world oceans.
- (c) Data for inorganic N are for sum of nitrate-N, nitrite-N and ammonium-N, as available. Loads calculated using discharge from Meybeck (1976) and concentration from Meybeck (1982).
- (d) van Bennekom et al. (1975).
- (e) Meybeck (1982) and Alekin and Brazhnikova (1960). Area refers to that which delivers discharge to the world's oceans.
- (f) Average of Baumgartner and Reichel (1975) and Alekin and Brazhnikova (1960). Discharge is that flowing into world oceans.
- (g) Based on the ratio of PO₄-P to total dissolved P of 0.4 as given by Meybeck (1982).
- (h) Based on the ratio of dissolved inorganic N to total dissolved N of 0.30 (Meybeck, 1982).
- (i) We assumed that 30% of the natural load is attributable to the eleven major rivers listed above in a pre-disturbance condition. Any additional load was assigned to human disturbance in these basins, and the collective load was then compared to the global total.

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DISCUSSION: Gildea and Vorosmarty Papers

Question (Liljedahl): Could you, without going to different basins, actually make any discrimination between urban and agricultural inputs by looking at the different subregions within the Missouri River basin or the Mississippi River basin? You have a lot of good data right in the Mississippi River basin.

Answer (Gildea): We do have some results from looking at what we call regional checkpoints. This is a standing validation from Charlie's model, and it varies between overestimating the dry agricultural western region as the concentration plot indicated, to our underestimated aquatic loading in the Ohio region. We hypothesized an underestimate of point sources in the Ohio because we really don't have industrial input data. So we do have some regional analyses, but we still have to address industrial point sources, especially if we are going to apply the model to a basin like the Rhine. We have such a good data base in the USGS NASQUAN, there really is a tremendous opportunity to sharpen up the inputs and outputs. The whole process for us was so educational finding out with all that wealth of data where the holes are.

Comment (Vorosmarty): Hopefully, we will be a catalyst for studies of other basins who have rich data sets.

Question (Sidle): I wish you would briefly give us a bit of overview on what went into your retention coefficient. From what I gather, your retention coefficient was a function of stream order and also impoundments, was I missing something else? Or were there actually some more data that went into the development of the retention coefficient?

Answer (Vorosmarty): What I presented was our first parameterization of the model. We have 25% retention in the small rivers decreasing to 0% when you get to large rivers. You also have a turnover time relationship. Those are, in fact, the only two relationships we used. They are lookup functions which will attenuate the loading that traverses that particular type of aquatic system. A first order stream gets 100 units of nitrogen, 75 get sent down river and 25 are retained through burial processes or loss to denitrification processes within that year. These retention coefficients are the result of a literature search of aquatic nutrient budgets. We found very few, but the ones that we were able to find indicated that the small order streams were better retainers of nutrient than large order streams.

Question (Sidle): I can appreciate the problem, but actually you probably had very few if any first order streams given the the grid size you were working with, is that not true?

Answer (Vorosmarty): That is the purpose of the subcatchment. This is an important point. We have these subregional buckets and to each subregional bucket we assign a main stem river. Now you are right, we have a very coarse level of resolution so we can't digitize every primary stream. But what we can do is rely on the geomorphological laws of drainage composition to infer what these streams look like within the subcatchment. That is important because the subcatchment is going to process the terrestrially derived non-

point sources before that material actually gets to the main stem. We don't want to digitize the whole river network explicitly, so we made some assumptions about the size of the stream that you could have and the bifurcation ratio that I was talking about which depends upon the area of the subcatchment.

Question (Meisinger): I was wondering Pat, if you could give us a little bit of your black box in percentage terms to get a better feel for what the outputs are on your terrestrial system. Secondly, the folks at Maryland here have done a similar kind of thing, where they are trying to look at nutrient loadings as a function of agricultural use. They found animals to be very important. I wonder do you have any animal component in your model?

Answer (Gildea): There was a volume of Agroecosystems which was entirely devoted to budgets in agricultural systems. We adapted that approach. They had animal components, but we just had plant, soil, and atmosphere boxes. We made a decision not to introduce animals until we go to systems where there is a lot of grazing. We want to try to develop that under point sources.

In answer to your first question, we used numbers from the Purcell budget. For corn it was 122 kg/ha/yr fertilizer input plus 11 in precipitation and 31 coming out as a combination of particulates, dissolved runoff, and leaching. Crop yield removed 85, 15 were lost by volatilization and denitrification. That was a budget for fertilized corn. We also had budgets for unfertilized corn, fertilized wheat, and unfertilized wheat. We took fertilizer rates from each state on the grids.

Comment (Gilliam): Do you use the same leaching practice over the whole country?

Comment (Gildea): What we are using is the same relationship of leaching to fertilizer input. The leaching rate is different because the fertilizer input rate is different. But we are using the same relationship for corn no matter where.

Comment (Vorosmarty): That is what produces that anomaly in the concentration, and we really do need to refine that.

Comment (Taylor): There are large-scale nutrient movements which are simply a matter of feed and animals being trucked from one place to another. For example, you have a very large influx of nutrient on the Eastern Shore which goes in as grain for chicken farms. I don't see how you can make a reasonable estimate of nitrogen loading without counting the animals. Not in terms of the fecal output, but in terms of the food that is carried in to feed them.

Comment (Gildea): In our generic graph of the planned budget of the undisturbed scenario there is a line item for animal tissue, so we do have the capability of accounting for the animal tissue. Transfers between grid cells such as you mentioned are tricky. We are working on that. We had a long debate about how you deal with hamburgers. If you harvest them in the mid-west and eat them in another place, how do you account for that kind of movement when you have a picture as big as we are looking at? Yes, you are

right, that is a problem.

Question (Correll): I am wondering if in the future of your model development you will use a shorter time step, maybe seasonal and whether or not you will accommodate regional weather patterns that vary from year-to-year such as drought and heavy rain.

Answer (Vorosmarty): I think the next step is to look at how the aquatic systems are driving material through the drainage network. And that does include looking at dry years vs wet years. I think that is going to be an important component in controlling what is coming out of the bottom end of the Mississippi River. I agree with that.

Comment (Correll): If you are a shrimp down off the Gulf Coast you want to know what happens in the spring as well as on an annual basis. It has some very practical applications.

Question (Whigham): In the atmospheric components, I don't remember if you had anything which dealt with evapotranspiration. It may be you are simply going across such a broad climatic zone with more humid conditions in the east and more arid in the western area of your grid system that a correction for evapotranspiration might account for the concentration gradient you had.

Answer (Vorosmarty): No, we only use discharge values. We use published values for the amount of water that flows out, discharge per unit area.

Question (Whigham): That is applied uniformly?

Answer (Vorosmarty): No, each subregion of the basin has its own characteristic specific discharge. Discharge per unit area per year multiplied by the area in that bucket gives you the total flow out of that bucket. That is really the only hydrology we have in there now. Certainly an added degree of sophistication would be to put the hydrologic budget terms, precipitation, evapotranspiration, and runoff into a common framework.

Question (Bragan): I am curious, once the model has been refined and verified on a watershed how will it be applied? What is the long-term expectation of how this model will be used?

Comment (Gildea): Well, our first priority is global, that is just our agenda. Transfer of the Mississippi basin watershed model to other basins such as the Amazon. We started with the Mississippi because we had an intuitive feeling that the intensive agriculture would result in a through put system. But, is that true in the Ganges where there has been a thousand years of agriculture? Where different fertilizer regimes and a different intensity of harvest occur? What's the soil organic matter content? How is it different from what it was 2,000 years ago?

Comment (Vorosmarty): The questions that we will be able to address are large-scale questions, we won't be able to pinpoint what is going on in a particular subcatchment. But on a regional scale we could address questions such as: What is the impact of the large-scale no-till agriculture in the United States?

NUTRIENT FLUX IN A LANDSCAPE:
THE RHODE RIVER WATERSHED AND RECEIVING WATERS

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Abstract--We present here a synthesis of our studies of nitrogen and phosphorus flux through a watershed and its receiving waters during a one year period (March 1981 to March 1982). The 2286 ha watershed consists of 62% forest, 23% cropland, 12% pasture, and 3% freshwater swamp. It drains into the tidal headwaters of the Rhode River, a subestuary of Chesapeake Bay. The 58 ha tidal headwaters consist of 40% subtidal mudflats and creeks, and 60% tidal marsh. We used automated sampling stations to monitor nutrient fluxes between the headwaters and the Rhode River, and nutrient fluxes from eight subwatersheds of differing land use compositions.

Croplands discharged far more nitrogen per hectare in runoff than did forests and pastures. Most of the nitrogen released by the croplands was absorbed by adjacent riparian forests. However, nutrient discharges from these riparian forests still exceeded discharges from pastures and other forests. The ratio of nitrogen to phosphorus leaving all forests was so low that nitrogen rather than phosphorus could limit phytoplankton growth in the receiving waters.

The freshwater swamp was a minor sink for nutrients. The tidal headwaters were a major sink for phosphorus due to sediment accretion in the subtidal area. The headwaters were also a sink for nitrogen in the year of this study, but were a source in other years.

Of the total non-gaseous nitrogen influx to the landscape, 31% was from bulk precipitation and 69% was from farming. Forty-six percent of the total non-gaseous nitrogen influx was removed as farm products, 53% either accumulated in the system or was lost in gaseous forms, and 1% entered the Rhode River. Of the total phosphorus influx to the landscape, 7% was from bulk precipitation and 93% was from farming. Forty-five percent of the total phosphorus influx was removed as farm products, 48% accumulated in the system, and 7% entered the Rhode River.

INTRODUCTION

Hydrologically linked ecosystems interact through the flow of water-borne nutrients. Nutrients discharged from uplands pass through lowlands and through a series of aquatic ecosystems on their way to the sea. Understanding the dynamics of such nutrient flows requires knowledge of the effect of land use on nutrient discharge and of the effects of uphill ecosystems on downhill ecosystems.

Agricultural lands are sources of nutrient discharges from watersheds (Biggar and Correy, 1969; Omernik, 1976). Forests also release nutrients, but at lower rates than agricultural lands (Cooper, 1969; Likens and Bormann, 1974). In contrast, riparian forests (Peterjohn and Correll, 1984), flood plain forests, freshwater swamps (Brinson, 1984; Yarbrow et al., 1984), and tidal marshes (Valiela et al., 1976) can act as nutrient sinks. Whether these systems do trap nutrients may depend on how much nutrient they receive from uphill systems. For example, riparian forests receiving nutrient influxes from adjacent croplands can retain much of the nutrients they receive (Peterjohn and Correll, 1984; Lowrance et al., 1984).

There have been many studies of nutrient flow through specific ecosystems, but few studies of nutrient flows through landscapes containing several ecosystems. In this paper we present a synthesis of our studies of nitrogen and phosphorus flux through a complex landscape containing many different hydrologically linked ecosystems.

STUDY SITE

The Rhode River estuary is located east of Washington, DC on the western shore of Chesapeake Bay. We studied the watershed which drains into a tidal creek at the head of the Rhode River estuary (Fig. 1). The 2286 ha watershed consists of 62% forest, 23% croplands, 12% pasture, and 3% freshwater swamp (Correll, 1977). The soils are fine sandy loams (Kirby and Mathews, 1973). The forests are deciduous and mostly of the tulip poplar association described by Brush (1980). The land we categorized as cropland consists of 53% corn fields, 19% tobacco fields, and 28% residential land plus roads (Correll, 1977). The pastures are grazed primarily by beef cattle (Miklas et.

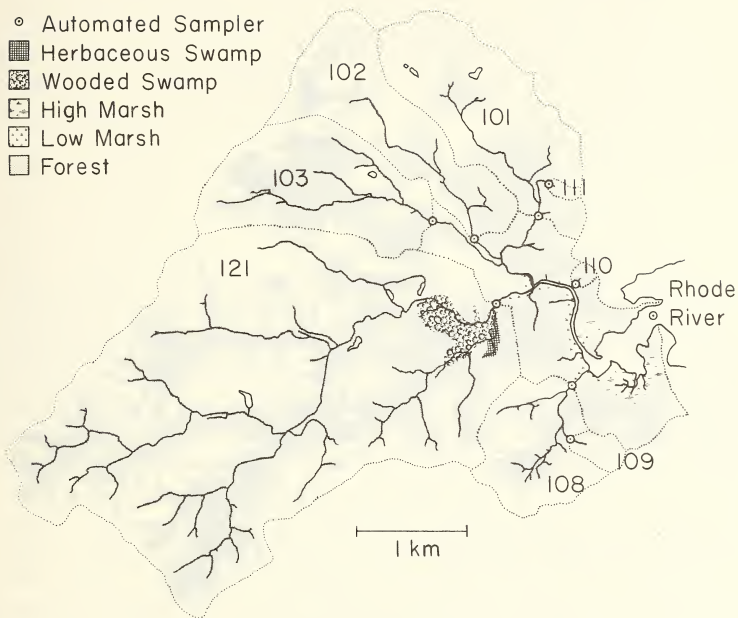


Fig. 1. The eight numbered subwatersheds and tidal headwaters where we measured nutrient fluxes. Dotted lines are watershed boundaries.

al., 1977). The freshwater swamp, Mill Swamp, includes wooded areas of the river birch-sycamore association (Brush, 1980) and an area covered by herbaceous plants and suffrutescent shrubs (Whigham et al., these proceedings).

The tidal creek at the head of the Rhode River estuary, includes 23 ha of subtidal mudflats and creeks and is bordered by 13 ha of tidal low marsh and 22 ha of tidal high marsh. The low marsh is about 30 cm above mean low water and is vegetated primarily by Typha angustifolia. The high marsh is about 42 cm above mean low water and is vegetated by Spartina patens and many other species (Jordan et al., 1983). The mean tidal amplitude is 30 cm, but water level can fluctuate just as much due to weather conditions. The salinity in the estuarine headwaters ranges from 0 to 16 ppt.

METHODS

The watershed's aquifers are isolated from deeper aquifers by an underlying layer of clay, the Marlboro Clay (Chirlin and Schaffner, 1977). Natural drainage divides separate the watershed into several subwatersheds (Fig. 1). We monitored discharges of water and nutrients from eight of these subwatersheds totaling 2057 ha. Water samples and flow measurements were taken continuously by automated sampling stations (Correll, 1977 and 1981). The stations for seven of the subwatersheds employed V-notch weirs for flux measurements. The eighth subwatershed (number 121) was tidally influenced, so a tidal flume, a tide gauge, and an electromagnetic current meter were used for flux measurements. A similar sampling station located in a constricted channel between the headwaters and the rest of the Rhode River (Fig. 1) measured tidal flux in and out of the headwaters (Correll, 1981). The sampling stations automatically collected water samples in volumes proportional to the flows. The tidally influenced stations collected separate ebb and flood samples. The volume-integrated samples were composited for weekly time periods. Samples for nutrient analysis were preserved with 1-3 ml per liter 15 N sulfuric acid. The analytical techniques we used are described by Correll (1981). Nutrient discharges from 229 ha of unmonitored watersheds were estimated from data on the monitored watersheds. Bulk precipitation was sampled and analyzed as described by Correll and Ford (1982). The study period ran from March 1981 to March 1982.

RESULTS

The subwatersheds differ in their percentages of forest, pasture and cropland (Table 1, Fig. 2). We regressed the annual nutrient discharges per hectare against the percentages of cropland and pasture (Table 1 and 2, Fig. 2). Both nitrogen and phosphorus discharges increased significantly as percent cropland increased, but did not vary significantly with percent pasture (Table 2). We used the regression equations to predict nutrient inputs to the freshwater swamp located at the bottom of watershed 121 (Fig. 1), then subtracted the measured discharge from watershed 121 to estimate the net nutrient exchanges in the swamp.

Extrapolating the regression suggests that pure cropland should discharge $7.53 \text{ kg N ha}^{-1} \text{ yr}^{-1}$, but our previous studies of a small watershed containing mostly corn fields (watershed 109, Fig. 1,2) indicated that the corn fields discharged $39 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ (Peterjohn and Correll, 1984). The discrepancy exists because the riparian forest between the corn fields and the stream retains most of the nitrogen it receives from the corn fields. Therefore, a watershed containing both cropland and riparian forest discharges less nitrogen than does the cropland itself. In contrast, extrapolating the regression assumes incorrectly that discharges from a watershed with both cropland and forest will equal the sum of discharges from the cropland and discharges from the forest. Therefore, to estimate nutrient discharges by the croplands

Table 1. Land uses and nutrient discharges for eight Rhode River subwatersheds.

Watershed	Area (ha)	Land use percentages			Discharge ($\text{kg ha}^{-1} \text{ yr}^{-1}$)	
		Crops	Pastures	Forests	Nitrogen	Phosphorus
101	225.9	15.6	27.2	57.2	1.97	0.61
102	191.7	23.8	21.6	54.6	3.41	0.89
103	253.8	6.6	16.5	77.0	1.89	0.72
108	150.4	26.6	20.2	53.2	3.10	1.16
109	16.3	65.6	0	34.4	4.89	1.29
110	6.3	0.9	0	99.1	0.42	0.10
111	6.1	0	73.3	26.7	1.02	0.17
121	1228.8	28.9	8.9	62.3	2.17	0.69

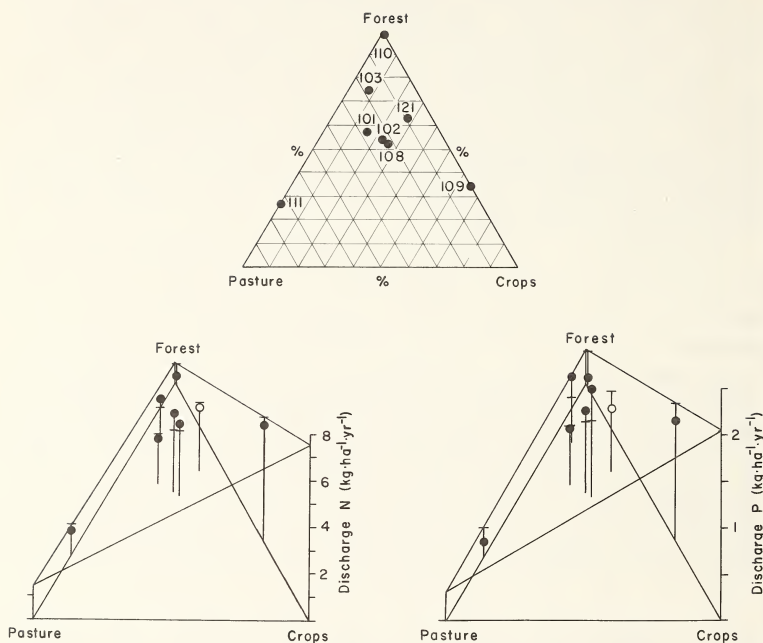


Fig. 2. Upper triangle: land use composition of eight numbered subwatersheds. Corners of triangles are 100% of indicated land use. Lower triangles: total nitrogen and phosphorus discharge plotted against land use percentages. Points represent measured discharges. Plane through points was fit by linear regression. Horizontal dashes indicate discharges predicted by the regression. Watershed 121 (open circle) was not used in the regression.

Table 2. Summary statistics for regression models.

$$\text{Discharge kg N or P ha}^{-1} \text{ yr}^{-1} = A + B(\text{fraction crop}) + C(\text{fraction pasture})$$

Parameter	Nitrogen			Phosphorus		
	Parameter Estimate	Standard Error	p *	Parameter Estimate	Standard Error	p *
A	0.98	0.47	0.108	0.39	0.23	0.161
B	6.55	1.20	0.005	1.66	0.58	0.045
C	0.51	1.11	0.672	-0.07	0.54	0.900
Model:	F = 17.6, p = 0.010, r ² = 0.898			F = 5.46, p = 0.072, r ² = 0.732		

* for null hypothesis that parameter = 0

in our entire watershed, we have assumed that discharges from the corn fields of watershed 109 are representative of discharges by all of the croplands. We estimated the discharges from riparian forests bordering the croplands in our watershed from the regression equations assuming a 2:1 ratio of cropland to riparian forest as in watershed 109.

Data from Correll et al. (1984) suggests that the riparian forest bordering the pasture of watershed 111 (Fig. 1 and 2) does not absorb much of the nutrient input it receives from the pasture. Therefore, we felt it was reasonable to extrapolate the regressions (Fig. 2) to estimate the nutrient discharges from pure pasture. We also estimated discharges from pure forest by extrapolation. The discharges from watershed 110 (Fig. 1 and 2) which is nearly pure forest were lower than we would expect from extrapolation (Fig. 2), but we attribute this to the fact that most of the forest of watershed 110 is older than most of the forests in our watershed (Roberts, 1979).

We calculated nutrient fluxes in the tidal headwaters from our measurements of tidal exchanges between the headwaters and the Rhode River, and from our measurements of nutrient discharges from the watershed into the headwaters. We subtracted nutrient exchanges by the marshes (Jordan et al.,

1983) from net exchanges by the tidal headwaters to estimate nutrient exchanges by the subtidal areas. Figure 3 presents all of the measurements and estimates of between-ecosystem nutrient fluxes in a single flow diagram.

Croplands discharge by far the most nitrogen of any ecosystem in our watershed despite the fact that they cover less area than forests (Fig. 3). Most of the nitrogen leaving the croplands is intercepted by riparian forests. Nevertheless, these riparian forests discharge more nitrogen and phosphorus than other forests or pastures. Pastures, partly due to their small area, contribute very little to the total discharges of either nitrogen or phosphorus from the watershed.

The freshwater swamp acted as a sink for phosphorus and, to a lesser extent, for nitrogen (Fig. 3). Much of the phosphorus retained was trapped during a week when a severe storm caused high sediment discharges by the watershed. Thus, the trapping of phosphorus was probably the result of trapping sediment.

The tidal marshes had very little effect on the net flow of nutrients through the tidal headwaters (Fig. 3). In addition, the net effects of the low and high marshes were opposite and tended to cancel each other. In contrast, the subtidal area trapped large amounts of nutrients (Fig. 3). As with the freshwater swamp, much of the phosphorus trapping followed a severe storm. Net nitrogen flux in the subtidal area varied from year to year. In some years the subtidal area was a source rather than a sink for nitrogen (unpublished data). However, the trapping of phosphorus occurred consistently from year-to-year.

We calculated the total inflows of nutrients to each ecosystem by adding the inputs from bulk precipitation ($13.7 \text{ kg N ha}^{-1} \text{ yr}^{-1}$, $0.449 \text{ kg P ha}^{-1} \text{ yr}^{-1}$), inputs from upstream parts of the watershed, and inputs from farming. We calculated the total outflows by adding nutrient discharge downstream and nutrient removals by farming. Farming inputs to pastures were $52 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ and $10 \text{ kg P ha}^{-1} \text{ yr}^{-1}$ and outputs were $31 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ and $4.5 \text{ kg P ha}^{-1} \text{ yr}^{-1}$ (Correll et al., 1977; Miklas et al., 1977). Farming exchanges for cropland were assumed equal to those for the corn fields of watershed 109, with inputs of $105 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ and $20 \text{ kg P ha}^{-1} \text{ yr}^{-1}$, and outputs of $71 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ and $10 \text{ kg P ha}^{-1} \text{ yr}^{-1}$ (Peterjohn and Correll, 1984). In the case of the tidal marshes, nutrients entering with the flood tide were considered

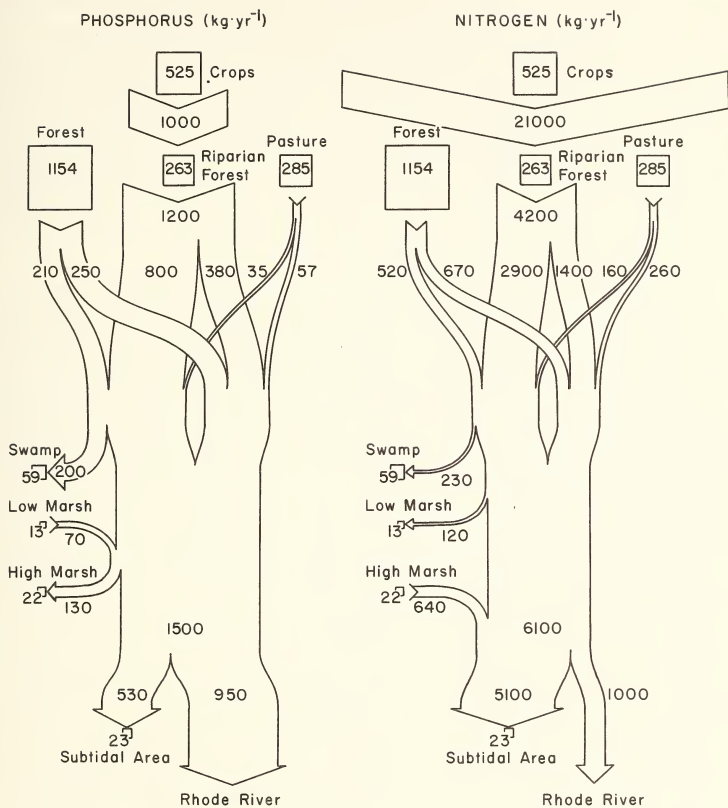


Fig. 3. Net total nitrogen and phosphorus fluxes, kg yr^{-1} , indicated by numbers in arrows. Numbers in boxes are areas in hectares of each ecosystem type. Watershed fluxes are split according to whether they go through the swamp or directly to tidal waters. Fluxes in tidal waters are net tidal exchanges.

part of the inflow, and nutrients leaving with the ebb tide part of the outflow. Our measurements of nitrogen flow refer only to non-gaseous forms.

Inflows of nutrients generally exceed outflows in most of the ecosystems we studied (Fig. 4). This is especially marked for non-gaseous nitrogen flows in the forests. However, phosphorus inflows to the forests are about equal to outflows. In contrast to forests, croplands are more retentive of phosphorus than of nitrogen. In the freshwater swamp and pastures, nitrogen retention is roughly proportional to phosphorus retention. The low and high tidal marshes behaved oppositely to each other, with one retaining a given nutrient while the other released it.

Differences in nitrogen and phosphorus flows result in differences in the N:P ratios of nutrients entering and leaving an ecosystem. For example, the molar N:P ratio of nutrients entering the forests is greater than 40 but the N:P ratio of nutrients discharged from the forests is less than 10 (Fig. 5). In contrast, the trend for croplands is exactly opposite, with the discharged nutrients having a higher N:P ratio. However, the relatively nitrogen rich discharge from croplands enters riparian forest where much of the nitrogen is

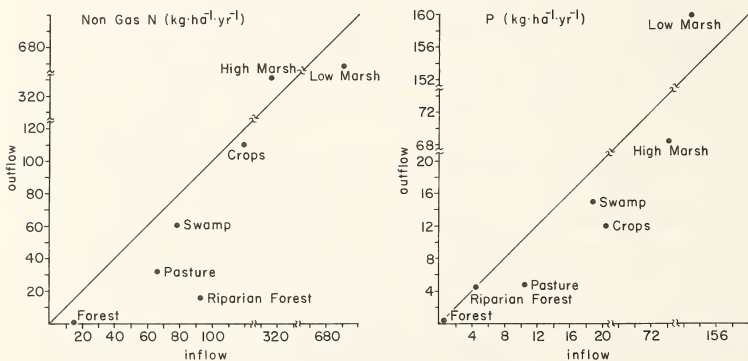


Fig. 4. Total outflow versus total inflow of non-gaseous nitrogen and phosphorus for various ecosystems. The line of equality is shown. Riparian forest refers to forest between croplands and streams.

retained. Consequently, the discharge from the riparian forests is relatively nitrogen poor. By the time the nutrients leave the watershed and enter the tidal waters the N:P ratio has dropped to 10 or less (Fig. 5). At such a low ratio, nitrogen rather than phosphorus would potentially limit phytoplankton growth (Redfield, 1958). The trends are even more pronounced for the N:P ratios of inorganic nutrients, those most readily available for plant growth (Fig. 5).

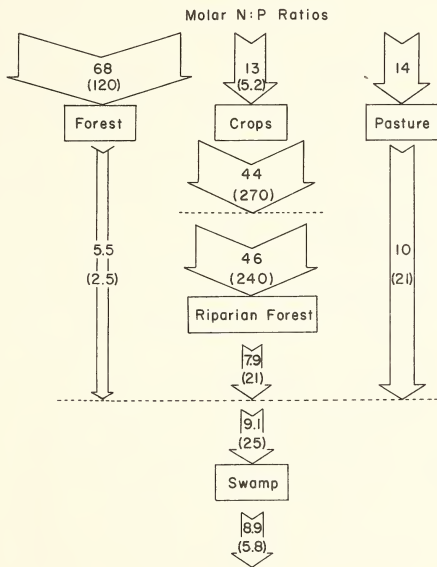


Fig. 5. Molar N:P ratios of nutrients entering ecosystems and of nutrients discharged to the watershed. Nutrients entering a system include inputs from precipitation and from farming as well as from upstream systems. Widths of arrows are proportional to ratios for total nutrients shown without parentheses. Ratios for inorganic nutrients are in parentheses. Most of the discharge from forests, riparian forests, and pastures flows directly to tidal waters without passing through the swamp.

Examining nutrient flux through the entire landscape of watershed plus tidal headwaters, we find that farming provides the largest input of nitrogen and phosphorus (Fig. 6). Bulk precipitation provides less than one tenth of the total input of phosphorus but about a third of the total input of nitrogen. Harvesting of farm products removes slightly less than half of the total inputs of nitrogen and phosphorus. Most of the rest of the inputs accumulate in the landscape or are lost as gaseous forms. Only 1% of the nitrogen and 7% of the phosphorus entering the landscape is discharged to the Rhode River.

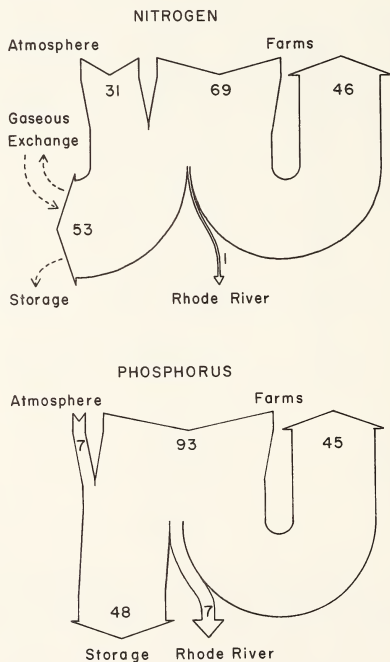


Fig. 6. Non-gaseous nitrogen and phosphorus fluxes through the entire landscape as percentages of the total input.

DISCUSSION

Since our automated stations sample discharges from areas containing more than one type of ecosystem, we had to deduce the behavior of individual ecosystems. Comparing our results to results of studies of single ecosystems, we find both similarities and differences. For example, our multiple regression models indicate that our forests discharge less nitrogen and more phosphorus than do most forests reviewed by Beaulac and Reckhow (1982). Thus, the N:P ratio of nutrients discharged from our forests is relatively low.

Nutrient release by forests is generally thought to be related to age or amount of disturbance. Young or highly disturbed forests release the most nutrients, old forests release less, and intermediate aged forests release the least (Bormann and Likens, 1979). Watershed 110 (Fig. 1), which consists almost entirely of very old forest (Roberts, 1979), discharged much less nitrogen and phosphorus than the average forest in our regression model (Fig. 2). Soil type may also influence phosphorus discharge. Dillon and Kirchner (1975) found that watersheds with soils of sedimentary origin, like ours, discharged more phosphorus than those with soils of igneous origin. Our forests discharge less nitrogen and phosphorus than they receive in precipitation as do most forests (Likens et al., 1977).

Nutrient releases from forests are generally less than releases from croplands. Others have found, as we did, that nutrient discharge from watersheds increases as the percentage of cropland increases (Fig. 2; Likens and Bormann, 1974; Omernik, 1976). However, the amounts of nutrients released by croplands differ greatly even among lands with the same crop. This is partly due to the variety of farming methods. For example, nutrient budgets have been published for corn fields with farming inputs ranging from 0 to 448 kg N ha⁻¹ yr⁻¹ and 0 to 81 kg P ha⁻¹ yr⁻¹, and watershed discharges ranging from 1 to 72 kg N ha⁻¹ yr⁻¹ and 0.02 to 19 kg P ha⁻¹ yr⁻¹ (Beaulac and Reckhow, 1982). The nutrient budgets for the corn field we studied fit within these broad ranges. Frissel (1977) reviewed data from many kinds of arable land and found that, when farming inputs of nitrogen were less than 150 kg N ha⁻¹ yr⁻¹, farming outputs were about 66% of the inputs. In comparison, our corn field returned 68% of the nitrogen investment.

Our regression models indicated that pastures release nutrients at rates more like those of forests than those of croplands (Fig. 2). Similarly, Beaulac and Reckhow (1982) found that pastures exhibited a wide range of nutrient discharges overlapping the range of discharges from forests. However, nitrogen discharge from our pastures is lower than that from most pastures (Beaulac and Reckhow, 1982). This may represent a real difference or it may be an error due to extrapolating our regression model. As we have mentioned, such an extrapolation would underestimate nitrogen discharge by croplands because riparian forests retain most of the nitrogen the croplands release. An earlier study suggested that the riparian forests adjacent to our pastures trap little or no nitrogen (Correll et al., 1984), but further research is needed to confirm this.

Riparian forests bordering croplands are major nitrogen sinks, but it is not clear if they are phosphorus sinks as well. In our watershed 109, measurements of phosphorus concentration in surface and ground water along transects from the corn fields into the riparian forest suggest that the riparian forest traps most of the phosphorus it receives in surface runoff but releases phosphorus in ground water (Peterjohn and Correll, 1984). Discharge of phosphorus from the whole watershed measured at a weir was about equal to the estimated discharge from the corn fields (Peterjohn and Correll, 1984) suggesting that, overall, the riparian forest traps very little phosphorus. Our estimates of between-ecosystem nutrient fluxes (Fig. 3) reflect the weir data although we are uncertain whether the riparian forests are phosphorus sinks. Others have found that riparian forests near croplands are sinks for both nitrogen and phosphorus (Lowrance et al., 1984; Yeats and Sheridan, 1983; Cooper et al., these proceedings).

We found that the fresh water swamp was a sink for $17 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ and $3.8 \text{ kg P ha}^{-1} \text{ yr}^{-1}$. Similarly, Yarbrow et al. (1984) found that a swamp in North Carolina retained $13 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ and $3.1 \text{ kg P ha}^{-1} \text{ yr}^{-1}$. However, that swamp mainly retained dissolved ammonia and phosphate while ours retained nitrate and particulate phosphorus. Mitsch et al. (1979) found that a swamp in Southern Illinois trapped primarily particulate phosphorus, and Brinson et al. (1984) found that a swamp in North Carolina could act as a nitrate sink. Although several studies have shown swamps to be nutrient sinks, Elder et al. (1985) found that a flood plain in Florida was a source of nitrogen, phosphorus and particulate detritus.

The tidal marshes in our landscape were not very important in net nutrient fluxes (Fig. 3). This is due to their small areas and the fact that the marshes import particulate nutrients and export dissolved nutrients, resulting in little net flux (Jordan et al., 1983). Tidal marshes typically export dissolved nutrients, but may either import or export particulate nutrients (Nixon, 1980; Jordan et al., 1983).

The subtidal area was an important sink for phosphorus and nitrogen in the year of this study (Fig. 3). In other years, however, it was a source of nitrogen (unpublished data), so it may not be an important long-term nitrogen sink. The subtidal area is a long-term sink for sediment though (Jordan, Pierce and Correll, in prep.), and accretion of sediment can account for the amount of phosphorus trapped (Jordan et al., 1983).

In conclusion, croplands were the dominant nutrient sources in our landscape although they cover only 23% of the area. Most of the nitrogen released by croplands is retained by adjacent riparian forests. Therefore, the ratio of nitrogen to phosphorus discharged by these riparian forests was relatively low (<10). The N:P ratio of nutrients discharged by other forests was similarly low. As a result, nitrogen rather than phosphorus could limit phytoplankton growth in the receiving waters. Sediment accretion in the subtidal area of the receiving waters was the major sink for phosphorus.

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DISCUSSION: Jordan Paper

Question (Gilliam): How did you obtain your nutrient budgets coming off your agricultural lands? How did you calculate your agricultural land inputs?

Answer: For the cropland and the pastureland we used surveys of the farmers to determine how much nutrients were added in the fertilizer and how much were removed in farm products. For the discharge from croplands we relied on measurements from one particular watershed. There we measured the discharge from the cornfields using surface water collectors and a series of wells arranged in transects from the cornfields into the riparian forest.

Question (Gilliam): How did you get your water flow from the series of wells? How do you know how much went that way?

Answer: We looked at the hydrographs from the stream weir at the bottom of the watershed. You can separate out surface water flow from groundwater flow using a graphical method.

Question (Gilliam): I assume that your losses of phosphorus from the field are as dissolved phosphate?

Answer: Most of the phosphorus moving through that system really is associated with sediment. Some of this gets stopped by the riparian zone so there is some trapping.

Question (Gilliam): Did I misinterpret your data? I thought you said you get very little phosphorus trapped there and much of the nitrogen was trapped.

Answer (Peterjohn): We had quite a bit of trapping of sediment and particulate-associated phosphorus in the surface runoff. However, some dissolved phosphorus is lost in subsurface discharge.

Comment (Jordan): So maybe what you are seeing is a trapping of particulate phosphorus in the riparian zone followed by a slow conversion of some of the phosphorus to dissolved forms which eventually make their way out past the weir.

Comment (Gilliam): I think this is a surprise, Dave. I am just trying to figure out why your observations are so different from ours in North Carolina.

Comment (Correll): The groundwater in the riparian zone quite often goes anoxic in the summer, and I think that has a lot to do with this question. When it is anoxic or alternately anoxic at times you do get more phosphorus released in the groundwater.

Question (Alaback): You said the input of nutrients for the forest came primarily from the atmosphere. I was wondering why, or did you have data on weathering and inputs from soil? Is that an important property?

Answer: It may be quite important. Your saying that there could be weathering going on in the forest's soils, and we think that is happening. This is just of a semantic problem. I don't think that is an input because the material is already there. But, yes that may be an important source of nitrogen for the plant life.

Question (Meisinger): You were a little concerned about being able to measure groundwater flux going directly into the tidal marshes. I am surprised to see your marshes play such a small role. Do you have some idea of how much groundwater is flowing into those marshes directly?

Answer: We think there is a negligible amount of groundwater directly entering the marshes. When you get to the marshes you are in a brackish water area. If you look at the salinity of the water entering the marsh with the flooding tide vs ebbing from the marsh there is no change in salinity. So there is very little direct entry of groundwater into the marshes. What they are receiving is nutrients from tidal water and ultimately from the watershed.

LAND USE AND NUTRIENT YIELDS OF
THE CHOWAN RIVER WATERSHED

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ABSTRACT. The Chowan River watershed is primarily forested, but about 19% is farm land. Agriculture has not increased in area recently, but its impact on water quality may be increasing because of greater mechanization, higher crop yields, more livestock, and extensive farmland drainage and stream channelization. Mass balance models for nitrogen and phosphorus were constructed for cropland, livestock, and swamp forest systems, permitting estimation of nutrient yields from different land uses. Agricultural non-point source nutrients were found to be a major load to downstream systems whereas the swamp forests act to reduce nutrient loads to the river. Satisfactory water quality in the Chowan River depends both on reducing agricultural runoff and on conserving the functions of these swamps.

INTRODUCTION

The Chowan River and its tributaries drain 12,652 km² of southeastern Virginia and northeastern North Carolina (Fig. 1). The region is mostly forested but farmland occupies about 16% and 28% in Virginia and North Carolina, respectively (Table 1). It is sparsely populated (200,000 people in 1970) with most municipalities having less than 10,000 people. The river drains

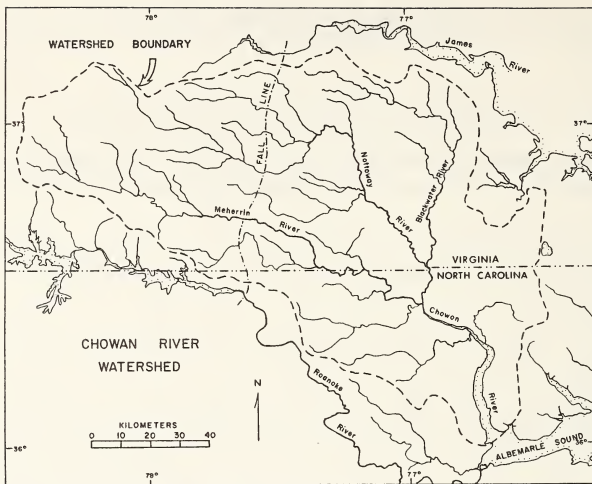


Figure 1. The Chowan River drainage basin in northeastern North Carolina and southeastern Virginia).

both the Piedmont west of the Fall Line (32% of the watershed) and the Coastal Plain (Fig. 1). Piedmont soils tend to be loamy and well-drained, whereas Coastal Plain soils may be poorly or moderately well-drained sands and clays, or low-lying, poorly-drained peaty soils (Humenik, et al., 1980). The climate is hot and humid; normal precipitation is 110 to 125 cm (U.S. Department of Agriculture, Soil Conservation Service 1981a) distributed throughout the year. Seasonally flooded swamp forests border, or formerly bordered, most of the Coastal Plain tributaries; floodplain swamps become 1-4 km wide in the lower 80 km of river where they are subject to frequent inundation by wind tides.

The lower part of the Chowan River is a wide, shallow, eutrophic estuary; except during extreme drought, however, the water is fresh (Kuenzler, et al., 1982). Since the early 1970's the river has frequently had summertime algal blooms (e.g.,

Table 1. Characteristics of the Chowan River watershed (N.C. Dept. Nat. Res. & Comm. Devel. 1982c; U.S. Bureau of Census, Census of Agriculture 1981).

	Virginia	North Carolina	Total Watershed
Watershed area (km ²)	9,215	3,437	12,652
(%)	73	27	100
Land use (% of area)			
Agriculture	16.2	28.2	19
Forest & Wetland	83.2	65.8	79
Urban	0.6	2.0	1
Open water	-	4.0	1
Land artificially drained			
Area (10 ³ ha)	23	101	124
Percent of total land (%)	2.4	31.3	9.7
Percent of farmland (%)	6.2	66.7	23.6

Stanley and Hobbie 1977; Kuenzler et al. 1982; Paerl 1982) resulting in surface scums of blue-green algae, impaired water quality, anoxic bottom waters, and decreased fish catches (N.C. Department of Natural Resources and Community Development 1982c).

Nutrients responsible for accelerated eutrophication come from point sources such as municipal sewage and industrial wastes and non-point sources such as urban runoff and drainage from forested or agricultural land. This study focused primarily on non-point source (NPS) pollution, discharges which arise over an extensive area of land, flow overland before reaching a stream, and enter surface waters intermittently in a diffuse manner (Aamkus 1976).

Non-point sources contribute about 80% of the total-N load and more than 50% of the total-P load to receiving waters in the United States (Novotny and Chesters 1981). Agricultural runoff is a major non-point contributor; it contains fertilizer

nutrients, sediment, and animal waste (Loehr 1977). Its local importance depends on the type of farming, the fertilizer practices, and the drainage intensity of the area (Keeney and Walsh 1972). Natural sources such as precipitation, forested areas, and wetlands are generally considered the background with which natural river and lake systems have developed. The rate of NPS nutrient loss from a tract of land is its nutrient yield.

This study had three aspects. The first was an examination of published data on land use during the past few decades in order to establish the nature and magnitude of changes which might affect nutrient yields. The second was the construction of simple mass balance models for major non-point sources (Cropland, livestock, upland forest) in the watershed to estimate nutrient yields by land use. Details of these first two aspects are in a report by Craig and Kuenzler (1983). Finally, data on forested wetland functioning was used to assess the probable magnitude of nutrient removal by swamps and to provide an original estimate of N and P loading of the lower Chowan River.

METHODS

Agricultural trends, fertilizer useage, and drainage.

Changes during the past thirty years in number and size of farms, types of agricultural land use, plantings and yields of major crops, and livestock numbers in the watershed came primarily from the U. S. Census of Agriculture (Craig and Kuenzler 1983). Trends in fertilizer sales in counties of the watershed came from North Carolina and Virginia agricultural statistics as well as those of the U. S. Bureau of Census (Craig and Kuenzler 1983). Data showing the extent of farmland drainage and stream channelization came from U.S. Census of Agriculture Special Reports: Drainage of Agricultural Lands, and reports of the U. S. Soil Conservation Service (Craig and Kuenzler 1983).

Mass balance models. Mass balance models for N and P were constructed for agricultural cropland, livestock operations, and

swamp forest. Agricultural mass balance models have become common (Frink 1969; Gilliam and Terry 1973; Fried et al. 1976; Frissel 1978; Schueler and Kemp 1979; Correll 1981). The method attempts to identify all inputs, storages, and outputs of a particular nutrient within a defined system, assuming the storage pool (soil system, forest system) is not changing (Frissel 1978). This assumption may not be true, especially for P in agricultural soil. However, the year-to-year fluctuations in the agricultural system tend to be cancelled if long-term values are used.

To calculate the nutrient budgets for agriculture, farming operations were divided into cropland systems and animal systems. Quantities were expressed in kilograms of elemental N or P (not N_2O or P_2O_5) per year for the whole watershed or per unit area (hectare) of different types of land use. The term "yield" is used two ways: (1) the amount of crop harvested from farmland, and (2) the amount of nutrient carried away by runoff from the land. We shall distinguish them by speaking of crop yield or nutrient yield, respectively.

Cropland. The primary sources of nutrient input to the mass balance models for cropland were fertilizer, precipitation, and nitrogen-fixation by legumes. The principal outputs were denitrification, harvested plant biomass, surface runoff, and erosion of soil. To arrive at rates for these processes the following assumptions and calculations were made: (1) The amount of fertilizer applied annually to a specific crop was the average amount recommended by the state's agricultural extension agency. (2) The amounts of N and P in precipitation falling on the watershed were 8.7 and 0.69 kg/ha yr, respectively (Gambell and Fisher 1966; Kuenzler et al. 1977). (3) The N-fixation rates for soybeans and peanuts were 105 and 112 kg/ha yr, respectively (Frissel 1978; J. Baird, personal communication). N-fixation by free-living prokaryotes was omitted. (4) Denitrification was assumed to be 15% of the applied fertilizer N (Frissel 1978). (5) The amount of N and P in harvests was

obtained by multiplying the N and P content of each crop by its average annual crop yield (kg /ha yr) (Romaine 1965). Average crop yields were calculated for years 1972-1980 for all major crops in Virginia and North Carolina (N.C. Crop and Livestock Reporting Service 1972-1981; Virginia Department of Agriculture, Division of Chemistry and Foods, 1972-81). (6) The potential amount of N and P in surface runoff and leaching from soils is the difference between these outputs and inputs. This nutrient yield may be considered the "field edge" rate. (7) Since a major fraction of P applied to acidic soils becomes fixed (Buckman and Brady 1969), we assumed that 75% of the potential P was retained in the soil and 25% remained mobile. Eroded soil materials were not explicitly considered in the models.

Each mass balance model was calculated on an areal basis (kg/ha yr) for each major crop within the basin (Craig and Kuenzler 1983); North Carolina and Virginia were calculated separately. Total inputs, outputs, and excesses were then calculated (10^6 kg/yr) by multiplying areal values by the average area planted with that crop.

Livestock. Mass balances for N and P intakes, products, and excreta were determined for livestock of the Chowan basin based on data in Frissel 1978 (Craig and Kuenzler 1983) and an eight-year average for the number of animals in each grouping. The number of broilers in Virginia were for the year 1978 only (U.S. Bureau of Census 1981). Because manure largely goes back onto the land, cropland as well as pasture, we assumed that only five percent of the excreted N and P reached the swamps and streams (Robbins et al. 1972; Frissel 1978).

Upland forest and swamp-forest systems. A mass balance model for upland forest could not be completed for lack of good data on all major inputs and outputs. Annual nutrient outputs of 1.6 kg N/ha and 0.10 kg P/ha, however, were estimated from several reports (Loehr 1974; Schreiber, et al. 1976; Correll et al. 1977; Reckow, et al. 1980; and N.C. Dept. of Natural

Resources and Community Development, 1982a).

The mass balance model for the swamp forest ecosystem used the U.S.D.A. Forest Service (1974, 1976a,b) areas of oak-gum-cypress and elm-ash-cottonwood. The major nutrient inputs to this system came from precipitation and from runoff from cropland, livestock operations, and upland forests. The major outputs were timber harvests, denitrification, P-sedimentation, and outflow of swamp water carrying nutrients to the lower Chowan River. Values for inputs, outputs, and cycles were derived from the following assumptions: (1) Nutrients in precipitation were the same per unit area as for major crops. (2) All of upland forest runoff potentially passed through swamp streams. (3) 76% of cropland runoff potentially passed through swamp streams and carried nutrients into the swamp system. (4) Runoff from livestock operations and pastures yielded only 5% of N and P in excreta; 95% remained on agricultural soil. (5) N-fixation rates were negligible. (6) Denitrification accounted for 94% of nitrate (43% of TN) and ammonium loss and immobilization was 75% of ammonium (17% of TN) (Kuenzler et al. 1977; Brinson et al. 1981). (7) Sedimentation and soil uptake removed 30% of total P input to the swamps (est. from Kuenzler et al. 1980).

RESULTS

Agricultural Changes, 1950-1978. During the past 30 years agricultural land use and practices in the Chowan River watershed have changed markedly. The number of farms decreased from 20,562 in 1950 to 5,403 in 1978 and the percentage of land area devoted to farming decreased from 63% to 41%; average farm size more than doubled, however, in this period from 39.3 to 97.5 ha (Craig and Kuenzler 1983). There was a significant decrease in farm woodland from 1950 to 1978 and a slight decrease in total crop acreage and pastureland, while harvested cropland stayed about the same (Fig. 2). Seven major crops accounted for most of the harvested cropland with corn, soybeans, and peanuts being the dominants (Fig. 3). Decreased plantings of several of the

crops contributed to the dip in total acreage between 1959 and 1969. By 1978 the increase in soybean acreage approximately equaled the decrease in peanuts; corn for silage and cotton had, however, both decreased. Except for tobacco, harvest yields of five major crops all showed modest to marked increases from 1950 to 1978 (Fig. 4). Relatively small changes in livestock numbers took place from 1950-1978, except for number of broiler chickens (Fig. 5) which increased during the past decade from 60 thousand to 14.5 million (B. Young, personal communication). The number of farm machines in the watershed nearly tripled from 1950-1978 (not shown) to a total of approximately 5,500.

Farmland drainage during the past 30 years appears to have increased exponentially from 950 ha in 1940 to 124,035 ha in 1978, or about 13% per year (Craig and Kuenzler 1983). About 31% of total land and 67% of land in farms of the North Carolina portion of the watershed has been drained (Table 1); this rate

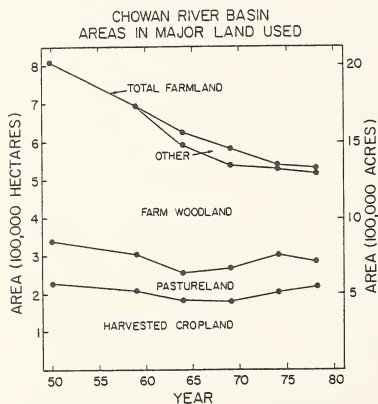


Figure 2. Changes in areas of major agricultural land uses in the Chowan Basin (Craig and Kuenzler 1983).

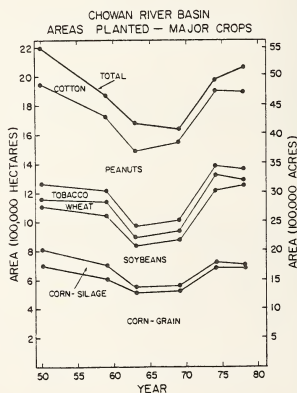


Figure 3. Changes in areas devoted to major crops in the Chowan Basin, 1950-78 (Craig and Kuenzler 1983)

YIELDS OF MAJOR CROPS
CHOWAN RIVER BASIN

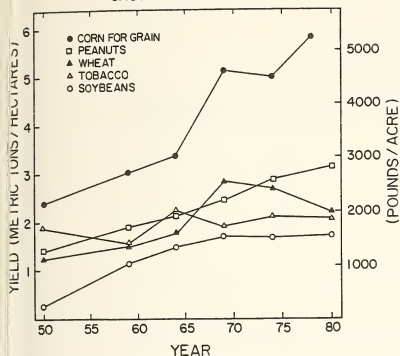


Figure 4. Changes in yields of major crops in the Chowan Basin, 1950-1978 (Craig and Kuenzler 1983)

LIVESTOCK NUMBERS
CHOWAN RIVER BASIN

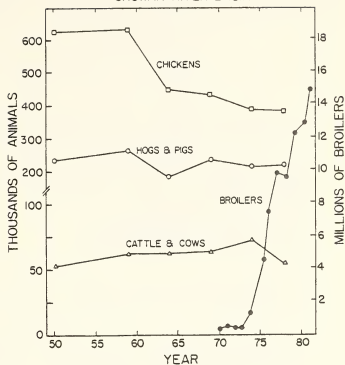


Figure 5. Changes in livestock numbers in the Chowan Basin, 1950-1978 (Craig and Kuenzler 1983)

clearly cannot be sustained. Much less drainage has taken place in Virginia where only 2% of the total land and 6% of farmland is artificially drained. For the total watershed, about 9.7% of the total land and 23.6% of farm land has been drained (Table 1). The Soil Conservation Service (S.C.S.) channelized 100 km of streams (23% of total stream lengths) in draining 45,000 ha of farmland in North Carolina (Craig and Kuenzler 1983). No completed S.C.S. watershed drainage projects were reported in the Virginia watershed.

Changes in forest. Commercial forest area in the Chowan watershed increased from 1964 to 1974 (Table 2). There was an increase in loblolly-shortleaf pine, oak-hickory, oak-gum-cypress, and elm-ash-cottonwood forest, and a small decrease in oak-pine forest. In the North Carolina portion there was a net decrease of 9.1×10^3 ha; all forest types decreased except oak-hickory, but the largest decrease (-21.3×10^3 ha) was in the

Table 2. Percentages of total commercial forest area (905×10^3 ha) by type in 1974 and changes in area (10^3 ha) since 1964 in the Chowan River watershed. (after Craig and Kuenzler 1983).

<u>Forest Type</u>	<u>Percentage of total, 1974</u>		
	<u>Va.</u>	<u>N.C.</u>	<u>Watershed</u>
Loblolly-shortleaf	36	29	34
Oak-pine	17	17	17
Oak-hickory	37	27	35
Oak-gum-cypress	6	24	11
Elm-ash-cottonwood	<u>4</u>	<u>3</u>	<u>3</u>
All types	100	100	100

<u>Forest Type</u>	<u>Changes in area, 1964-1974</u>		
	<u>Va.</u>	<u>N.C.</u>	<u>Net</u>
Loblolly-shortleaf	+94.1	-2.8	+91.3
Oak-pine	+7.0	-18.4	-11.4
Oak-hickory	+19.2	+31.6	+50.8
Oak-gum-cypress	+27.5	-21.3	+6.2
Elm-ash-cottonwood	<u>+17.9</u>	<u>+1.8</u>	<u>+19.7</u>
All types	+165.7	-9.1	+156.6

important oak-gum-cypress forested wetlands. This was a 30% decrease in swamp forest in North Carolina since 1964, and a 24% decrease for the total watershed. In the Virginia portion, each forest type increased from 1964-1974. Bottomland types (oak-gum-cypress and elm-ash-cottonwood) constituted 27% of the commercial forest in North Carolina and 10% in Virginia (Table 2).

Major crop models. Mass balance calculations for N and P for each major crop were based on inputs (fertilizer and precipitation; for legumes, N-fixation was also included) and outputs (N and P harvested in the crop, N lost by denitrification) (Fig. 6). The inputs minus these outputs equal the potential nutrient yield from the land. A single mass balance model combining all inputs, outputs, and yields was constructed by summing the data for each major crop in the basin. Total

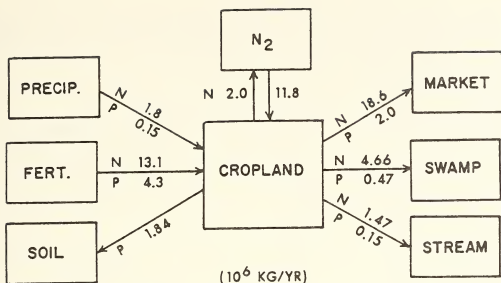


Figure 6. Mass balance model for major crops in the Chowan River watershed (2.1×10^7 ha), 1972-80.

inputs of N and P were 26.7×10^6 kg N/yr and 4.45×10^6 kg P/yr; the outputs to denitrification and to markets were 20.6×10^6 kg N/yr and 2.0×10^6 kg P/yr (Fig. 6). The amounts potentially available in runoff from farmland, then, were about 6.1×10^6 kg N/yr and 2.45×10^6 kg P/yr. The potential amounts, however, do not all reach downstream surface waters. Since only 25% of the soil P was assumed to be mobile, 1.84×10^6 kg P/yr would have been added to the soil compartment (Fig. 6.). Furthermore, most of the runoff in this watershed has access to swamp forests; we assumed that 76% had access to wetlands based on 24% of cropland having been artificially drained; accordingly the proportions of N and P going to swamp and stream systems were in the ratio of 76:24 (Fig. 6).

The amounts of N and P in fertilizer sold in the watershed agreed closely with the amounts recommended by the North Carolina and Virginia agricultural extension services (Table 3A, B). The mean annual areal nutrient yield from the major crops was 29 kg N/ha and 11.3 kg P/ha (Table 3C), or approximately half the amounts of fertilizer presumably applied (Table 3A, B).

Livestock mass balance estimates. Tabulation of nutrient inputs and outputs showed that chickens, including broilers, account for about half of both N and P (Table 4). About two-

Table 3. Assumed fertilizer N and P application rates based on (A) sales or (B) recommendations compared to (C) nutrient yields from croplands of the Chowan River watershed. (kg/ha yr) (A and B after Craig and Kuenzler 1983).

Nutrient	North Carolina	Virginia	Total Watershed (weighted mean)
A. Applied to harvested cropland, 1978-80, based on fertilizer sales.			
Total N	85	41	63
Total P	19.3	20	19.9
B. Applied to major crops, 1972-80, based on state agricultural extension service recommendations.			
Total N	68	59	67
Total P	15	24	20
C. Potential yields from cropland, based on mass balance models (this study; potential P yields assuming no soil fixation).			
Total N	37	25	29
Total P	5.6	15	11.3

thirds of the nutrients in feed becomes manure and therefore is potentially available for loss. Total watershed yields of N and P from livestock were estimated at 5% of the amounts in excreta (Table 4), 0.44×10^6 kg N/yr and 0.10×10^6 kg P/yr, respectively.

Swamp forest model. The mass balance model for the swamp forest ecosystem included N and P inputs from precipitation, upland forest, croplands, and livestock (Fig. 7). Total inputs to the swamp forest were 7.45×10^6 kg N/yr and 0.74×10^6 kg P/yr, respectively, with cropland inputs being dominant. The swamp lost nutrients by denitrification, harvesting of timber, and sedimentation. Denitrification was a significant output (3.0×10^6 kg/yr), comprising 40% of total nitrogen inputs. The sediment compartment inputs exceeded outputs (Fig. 7) because of immobilization of about 0.94×10^6 kg $\text{NH}_4\text{-N}$ /yr and sedimenta-

Table 4. Nitrogen and phosphogus mass balances for livestock of the Chowan River watershed (10^6 kg/yr) (after Craig and Kuenzler 1983).

Type	Nitrogen			Phosphorus		
	Feed	Market	Excreta	Feed	Market	Excreta
Swine	2.44	.81	1.66	.55	.06	.49
Dairy Cattle	.88	.24	.64	.15	.04	.11
Beef Cattle	3.00	.77	2.23	.43	.20	.23
Chickens	<u>8.20</u>	<u>3.97</u>	<u>4.23</u>	<u>2.10</u>	<u>.89</u>	<u>1.21</u>
Totals	14.52	5.79	8.76	3.23	1.19	2.04

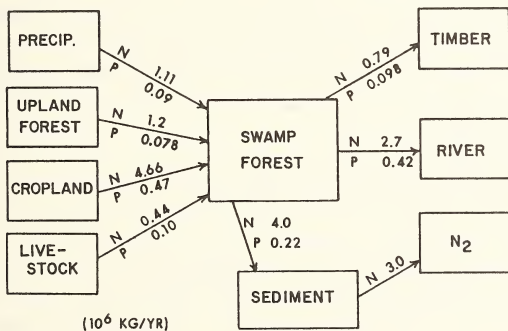


Figure 7. Mass balance model for swamp forest of the Chowan River watershed (1.3×10^5 ha).

tion and fixation of 0.22×10^6 kg P/yr. Removal of N and P by harvesting of timber was also significant (0.79×10^6 kg N/yr; 0.098×10^6 kg P/yr). The nutrients available to the stream after swamp processing were 2.7×10^6 kg N/yr and 0.42×10^6 kg P/yr. The model indicates that the swamp forest can remove 64% of total N inputs and 43% total P inputs.

DISCUSSION

Historical trends. There have been recent land use changes which affect nutrient yields from the watershed. First, substantial increase in the agricultural intensity is reflected by fewer farms, greater mechanization, increased crop yields (Fig. 4), greater livestock numbers (Fig. 5), and extensive farmland drainage and stream channelization, especially in North Carolina (Craig and Kuenzler 1983). Sales of fertilizer peaked in 1976, then dropped again to 1957 amounts (Craig and Kuenzler 1983). Secondly, although total forest area increased by 157,000 ha during 1964-1974 (Table 2), wetland forest in the watershed decreased 24%; North Carolina lost 30%. Not only have swamps been physically converted to other land uses, many have been functionally destroyed by channelization which prevents effective sedimentation and nutrient processing by their floodplains (Kuenzler et al. 1977). Intensive drainage elsewhere in the Southeast has also resulted in higher nutrient concentrations in surface waters and downstream eutrophication (Bedient 1975; Gael and Hopkinson 1979).

Nutrient yields from major crops. The availability of published values of nutrient yield from various land uses permits calculation of loadings to downstream surface waters and allows assessment of the eutrophication potential (Brezonik 1973). Nutrient concentrations in surface and subsurface runoff from agricultural land are highly variable. (Scheuler and Kemp 1979; Reckow et al. 1980; Jacobs and Gilliam 1983; Humenik et al. 1983). This variability results from factors such as topography, intensity and distribution of rainfall, rates of infiltration, soil moisture, type of artificial drainage, the nature and amount of soil N and P, redox potential, crop rotation and tillage, and fertilization rates (Scheuler and Kemp 1979; Engelbrecht and Morgan 1961, Jacobs and Gilliam 1983). Because of variability in agricultural runoff values, the extrapolation of literature values, which are site specific, to other regions

cannot be done very accurately.

Nutrient yields more specific to the Chowan watershed were obtained from mass balance models of crop and livestock systems. Adequate data were available for fertilizer usage, precipitation inputs, and quantities of nutrients in harvested crops; N-fixation and denitrification rates were considered reliable estimates. The inputs minus outputs of N and P equaled the potential yield from agricultural activities.

The rates we used for precipitation inputs may be low; other studies in the Southeast reported rates of 9 to 20 kg N/ha yr (Brezonick 1973; Scheuler and Kemp 1979; Skaggs, et al. 1980). The denitrification rate of 15% of applied nitrogen (Frissel 1978) probably underestimates the rate on poorly-drained soils of the Coastal Plain, and overestimates the rates on well-drained soils. In North Carolina, as much as 60 kg/ha was denitrified on poorly drained soils, whereas none was denitrified on a well-drained soil (Gambrell et al. 1975), or very little where subsurface tile drains had been installed (Jacobs and Gilliam 1983). However, nitrate from well-drained soils markedly decreased as subsurface waters flowed through swamp floodplain soils to a stream; apparently the best system for nitrate removal is a natural stream with riparian vegetation (Jacobs and Gilliam 1983).

Our estimated quantities of N and P removed in harvested crops may also be low depending on the thoroughness of the harvesting procedure. We included only the nutrients in the prime components (bushels of grain for corn, pounds of peanuts, bales of cotton); if more of the crop, for example wheat straw, is removed, these estimates will be low and nutrient yield estimates proportionately higher. When the major crops were ranked by annual nutrient yield per hectare, farmland growing corn for grain or silage, soybeans, and tobacco were the major potential exporters of nutrients from the Chowan watershed (Craig and Kuenzler 1983).

There is a problem in using average rates of N application in fertilizer in a calculation of average N yields because the

relationship is not linear (Frissel 1978). Fields heavily fertilized leach larger percentages of N than those lightly fertilized so that the averages underestimate the amount of N in runoff (Frissel 1978). Although mass balance models represent a composite of average years, they compute the potential for water pollution from fertilizer nutrients over large areas.

Cropland had more potential than other types of land use in this watershed for releasing nutrients to downstream systems. Even if as much as 24% of cropland runoff bypasses the swamp forest system because of agricultural drainage practices, loading of N to the swamp forest ecosystem (4.66×10^6 kg/yr) exceeds any other input by a factor of four (Fig. 7). Even with the additional assumption of field soil retention of 75%, loading of P to the downstream swamps (0.47×10^6 kg P/yr) is four times any other input (Fig. 7).

Phosphorus is quite immobile in mineral soils where abundant iron and aluminum fix it into insoluble forms (Buckman and Brady 1969). It is removed from soils mostly by crop uptake or by erosion (Novotny and Chesters 1981). Eroded soil materials carry large amounts of both P and N, especially during large storm events (Mulholland et al. 1981; Hubbard et al. 1982), but significant amounts of soluble P are also lost from fertilized, cultivated soils (Baldovinos and Thomas 1967; Frissel 1978). Organic soils, when farmed, lose even more (50-87%) of their P as soluble orthophosphate (Skaggs et al. 1980); the amount lost from organic soils varied widely, but averaged 7.64 and 9.54 kg P/ha yr from cropland and pasture, respectively. Although soil types in the watershed are acidic and predominantly mineral, and therefore tend to fix P, some organic soil exists in the bottomlands of streams and along the upper Chowan River (U.S. D.A., Soil Conservation Service 1977). Conversion of these bottomland soils to agriculture may adversely affect water quality because of their inability to retain much phosphorus.

The fact that a major portion of fertilizer P remains fixed in farmland soils may in the short term seem acceptable, preventing immediate eutrophication of receiving waters. The total

P content of farm soils will continue to increase, however, and eventually erosion will remove these enriched soil particles from the land. High correlation coefficients exist between suspended solids and total P content in streams (Kuenzler et al. 1977; Humenik et al. 1983). Although the processes of runoff, erosion, sedimentation, and alluvial soil accumulation are understood, there is serious lack of quantitative data for most watersheds, including the Chowan River. Huge amounts of sediments eroded from the Piedmont may still be present in alluvial valleys (Schubel 1984). The greater the total P content of such sediments, the greater the potential difficulties in the future to restrict phosphorus loadings to downstream lakes and estuaries. Under anaerobic conditions in lake or estuarine bottom sediments, P is released to overlying waters and is available for algal growth (Patrick and Khalid 1974).

Similar arguments hold for P fixed in soils in livestock operations. Erosion rates from grassy pastures are relatively low, and P yields are often low (Reckow et al. 1980), but unvegetated feedlots will yield larger amounts of P per unit area not only because of direct washout of manure, but also because the surface, eroding layer will have accumulated the most phosphorus.

"Field-edge" estimates of N and P yields from croplands (Table 5) are within the total range of values for row-crops and for mixed agriculture summarized by Reckow et al. (1980). Our estimate for N is substantially higher than their upper 95% confidence level, however, probably because our model estimates the potential loss for fields whereas their empirically derived data come from streams, often some distance from the fields. Denitrification and uptake by vegetation can substantially reduce N concentrations as runoff flows laterally through the soil or through wetland systems (Jacobs and Gilliam 1983) so that instream concentrations are less than at the field-edge. Phosphate is also attenuated by sorption onto soil and sediment particles. With such removals, and with dilution by less-rich waters from non-agricultural systems, our models suggest yields

from the entire watershed of 3.4 and 0.46 kg/ha yr of N and P, respectively (Table 5).

Livestock mass balance models. Livestock waste is potentially a major source of NPS pollution. It is one of the largest sources of agricultural waste in the U.S., especially when animals are raised intensively, as in feedlots (Loehr 1977; Environmental Protection Agency 1973). We assumed that only 5% of livestock wastes would enter streams, based largely on the report of Robbins et al (1972). Depending on the management of hog, chicken, and dairy farms, this value may be low, especially for nitrogen since nitrate is quite mobile in soil. If all of

Table 5. Areal yields (kg/ha yr) of total N and total P derived from mass balance models of the Chowan River watershed.

Source	N	P
Major Crops	29	2.9
Watershed	3.4	0.46

the manure in the Chowan watershed (Table 4) were to enter streams directly, the N and P inputs (8.8 kg N/yr and 2.0 kg P/yr) would exceed those in runoff from major crops (Fig. 6). Some North Carolina counties have excessive amounts of livestock waste, especially broiler litter, in relation to area available for its disposal (Humenik et al. 1983). There is a considerable, but unquantified, amount of linkage between our cropland and livestock mass balances; much of the livestock feed is grown within the watershed and much of the manure goes back onto cropland. There was an approximate balance between N in harvested crops (Fig. 6) and N needed for feed (Table 4); there appeared to be too little P in harvested crops for feed for livestock. About half of the animal N and P is produced by chickens; since our calculations for broilers in North Carolina are an 8-year

average, yields would be about 60% higher if more recent numbers were used. If the estimate that 5% of animal waste enters streams proves to be low, the number of broilers in the watershed could be more important to Chowan River water quality than suggested here. Finally, if 95% of P in manure stays in the soil, the buildup for eventual erosion to downstream systems will be even faster than in cropland soils where we assumed only 75% retention.

Upland forest mass balance model. Mature, undisturbed forests yield low concentrations of nutrients and their yields are generally considered background levels (Cooper 1969; Loehr 1974; Tamm et al. 1974; Singer and Rust, 1975; Sopper 1975; Likens et al. 1977; Corbett et al. 1978; Brozka et al. 1981) Soils are generally permeable due to abundant organic matter and vegetative root penetration; there is less runoff than from most other systems. Nutrient inputs are conserved within the system (Cooper 1969) so that undisturbed or properly managed forests retain nutrients efficiently and do not accelerate eutrophication (Brezonik 1973). Timber management and harvesting result in larger nutrient yields primarily because of greater sediment erosion, but even clear-cutting does not increase nutrient yields if nutrients are taken up by rapid growth of new vegetation (Aubertin and Patric 1974; Bormann et al. 1968). Work in North Carolina by Sanderford showed no difference in nutrient content runoff from a pine forest before or after fertilization (Frissel 1978).

Nutrient interactions with the swamp forest. Wetlands usually function as N and P sinks, thereby improving the quality of water that passes through them (van der Valk et al. 1978). Their ability to trap nutrients depends on the frequency, timing, and duration of flooding and the magnitude of the nutrient inputs. Wet, organic-rich soils of forested wetlands have high denitrification potential; flooded organic soils have

been used as treatment systems for nitrate removal from agricultural runoff (Reddy et al. 1980).

As water moves through swamps during flooding, suspended sediments and associated nutrients are deposited on the floodplain (Boto and Patrick 1978). The wetland system traps substantial amounts of suspended sediment (Gagliano and van Beek 1975, Kadlec and Kadlec 1980), including particulate P (Mitsch et al. 1979). Phosphorus undergoes dynamic interactions with swamp soil (Patrick and Khalid 1974); oxic soils rich in iron and aluminum strip inorganic P from solution but release it again when they become reduced. Inorganic P is also removed by bacteria and by plants. Several studies have shown the role of forested wetlands as partial nutrient sinks (Kitchens et al. 1975; Boyt et al. 1976; Tuschall et al. 1981; Ewel and Odum 1978; Nessel 1978; Qualls 1984; Mitsch et al. 1979; Day et al. 1981. Studies in the Coastal Plain of North Carolina support the above findings. Brinson et al. (1981) showed that 75% of ammonium and 94% of nitrate was removed as floodwaters moved through two riverine swamps. The Creeping Swamp forest removed more than 45% of the total P inputs, primarily by sedimentation and uptake by plant biomass (Yarbro 1979).

Our mass balance model for the swamp forest ecosystem, using assumptions based on these studies, suggest that the swamp removes 64% of the total N and 43% of the total P inputs. This amounts to a removal of 37 and 2.4 kg/yr of N and P, respectively, per hectare of swamp. There are, of course, limits to nutrient removal by wetlands. Nichols (1983) showed that the percentage removal of both N and P in wastewater decreased as loading rates to wetlands increased, and decreased over time since loading began. From this we may predict that either increased nutrient concentrations in runoff or decreased area of wetlands will result in higher concentrations leaving swamp forests. Net areal yields from the entire Chowan River watershed, including cropland, livestock, upland forest, and wetlands, generated assuming not only several sources of runoff water but also several sinks for N and P as the runoff moves

into streams and through wetland areas toward the river, were estimated at 3.4 and 0.46 kg/ha yr for total N and total P, respectively (Table 5). Such yields are within the ranges reported for four intensively studied N.C. Coastal Plain agricultural watersheds (Humenik et al. 1983).

Swamp forest ecosystems seem to be vital to water quality of the Chowan River. Wetlands are particularly important in agricultural watersheds subject to NPS pollution problems, and efforts should be made to preserve them (van der Valk et al. 1978). Even a slight increase in the percentage of wetlands reduced the amount of nitrate in the water leaving an agricultural watershed (Jones et al. 1976). Hopkinson and Day (1980) estimated that N and P loading to a eutrophic Louisiana Lake would decrease by 23% and 28%, respectively, if the swamp forest in the agricultural watershed were allowed to have free exchange with the river water.

Swamp forests however, have been physically removed from the North Carolina Chowan watershed at a rate of 3% per year. Channelization of streams functionally removes swamps from the watershed, so the rate of wetland loss (functional plus physical loss) has been significantly greater than 3% per year. Furthermore, drained wetlands release large amounts of nutrients, primarily nitrate, during the first few years, as litter oxidizes (Keeney and Walsh 1972; van der Valk et al. 1978; Kirby-Smith and Barber 1979). Conversion of forested wetlands is very likely a major factor in the increased nutrient load to, and eutrophication of, the Chowan River.

Importance of NPS pollution to the Chowan River. The total nutrient load to the lower Chowan River includes point sources as well as non-point sources. Point source loadings of total N and total P were 0.88×10^6 kg N/yr and 0.17×10^6 kg P/yr (from N.C. Dept. of Natural Resources and Community Development 1982c). The loading from wetland forest (Fig. 7) includes nutrients from upland forest, cropland, and livestock wastes which remains after swamp processing. The loading to streams

from major crops includes nutrients which bypassed the swamps (Fig. 6). Our calculated NPS total-N loading to streams (4.2×10^6 kg N/yr) (Fig. 6, 7) is about one-third higher than the estimate of 3.3×10^6 kg N/yr made by the N. C. Department of Natural Resources and Community (1982c). Our estimate for NPS total-P loading (0.56×10^6 kg P/yr) is twice theirs (0.28×10^6 kg P/yr), suggesting that cropland soils, stream sediments, and wetland soils may be even more retentive of P than assumed in our model. Their estimates of watershed nutrient yields appear to be confirmed by measured Chowan River nutrient concentrations. The loadings to downstream water bodies attributed to wetland forests, however, must not be misinterpreted. Most of the nutrients coming from the wetland forest did not originate there; about 62% came from agricultural operations and 11-17% from upland forest (Fig 8). The swamp forest is an effective sink for nutrients in runoff. Continuing loss of wetland area and functioning capacity can only result in greater loadings of sediments, N, and P to lakes, rivers and estuaries.

Studies in similar watersheds have come to the same conclusion. Kemp (1949) showed that agricultural runoff generated 65% of the nutrient load of nitrogen although agricultural land constituted only 38% of the Potomac River watershed. Agricultural watersheds in Virginia exported more inorganic N, total Kjeldahl N, and total P than a non-agricultural control watershed, and N and P species increased in response to cropping activity (Smolen and Shanholtz, 1980). Mass balance estimates in their study indicated that 10-15% of the fertilizer N and 2-3% of the P was exported in streamwater. Scheuler and Kemp (1979) calculated that agricultural land, although only 52% of the Choptank watershed area, contributed 77% of the total (potential) N load. An extensive study showed that mean concentrations of total P were nearly 10 times greater, and of total N were nearly 5 times greater, in streams draining agricultural land than in streams draining forested land (Omernik 1976). In the Chowan basin, concentrations of inorganic N were 2 to 15 times greater in streams draining

agricultural areas than in streams from upland forested areas; organic N was 1 to 3 times greater; and total P was 1 to 9 times greater (Duda and Klimek, 1979).

Increased agricultural NPS pollution with N and P, along with recent swamp drainage practices, appear to be major factors in promoting algal blooms in the Chowan River. The relative significance of non-point sources of nutrients must be put into perspective with point sources (Brezonik 1973). If non-point sources, including agricultural runoff, are sufficient to accelerate eutrophication of the Chowan River, controlling only point sources would not restore water quality to high standards. Management of NPS pollution is more difficult than point sources because the sources are diffuse, and it will also take longer to alleviate the problem. It is encouraging that state and federal agencies and members of the academic community at North Carolina State University-Raleigh have begun seeking best management practice (BMP) strategies to reduce nutrient loadings from agriculture to the Chowan River (North Carolina Department of Natural Resources and Community Development, Division of Environmental Management 1982c; Humenik, et al. 1983). Farmers are understandably reluctant to adopt BMP's until experience with reduced tillage and fertilization rates demonstrates their cost effectiveness (Humenik et al. 1983). Best management practices on agricultural land, reductions in drainage activities and channelization, and protection of remaining swamp forests are all management techniques which must be initiated along with controls on point sources to return the Chowan River to a more desirable trophic condition.

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DISCUSSION: Kuenzler Paper

Question (Vorosmarty): You mentioned in one of your first slides the denitrification of 94% of the nitrate in stream water. Does that mean in a central channel?

Answer: No, it would not apply to a central channel because these wetlands are flooded periodically in the winter and spring, and nitrate levels are relatively high then. The water is spread out over a wide flood plain system. Nitrate is not usually the dominant form of nitrogen.

Comment (Vorosmarty): What is the state of the hypothesis for ammonium immobilization? Is that a long-term kind of steady state? Or is there some finite capacity to assimilate ammonium?

Answer: These are percentages generated by particular studies on particular swamp systems. They are not going to be universal with every patch of swamp or every stream. I think that there is good evidence where sewage wastes were introduced into wetland systems that the percentage removal of nitrogen and phosphorus decreases the bigger the load or the higher the concentration in the system. That has been occurring in our natural wetland systems, since if you take a large area of wetland that is receiving a certain concentration of nutrients and reduce the area, then you have a heavier load on the area that remains.

MAHANTANGO CREEK WATERSHED - FATE AND TRANSPORT OF WATER AND NUTRIENTS

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ABSTRACT--Results of hydrologic and water chemistry research done on this 7.4 km² subwatershed of the Susquehanna River Basin are integrated and summarized. Data are presented in the context of a hydrologic cross-section that includes forested ridges, farmed valleys, and stream channel and riparian areas. Both surface runoff and groundwater discharge data are included. Almost all groundwater flow resurfaces at the 7.4 km² scale due to the geology and geometry of the watershed. Most surface runoff, not associated with man-made impervious surfaces in the watershed, originates from near-stream areas, i.e., mostly as runoff from the channel catch and adjacent groundwater discharge zones. The NO₃, Cl, NH₄, and P data collected are analyzed in the context of the experimental hydrologic cross-sections researched on this watershed.

The highest NO₃ and Cl concentrations measured in the stream originate from groundwater discharge. In contrast, the highest concentrations of NH₄, soluble P, and orthophosphate are associated with storm flow and surface runoff from nearby groundwater discharge zones. Soluble P and orthophosphate concentrations in subsurface discharge and stream baseflow are an order of magnitude less than that associated with storm flow.

A hydrologically-based cross-section model was developed and generalized to describe the dominant hydrologic processes in the near-stream zone. The behavior of NO₃, NH₄, and soluble P in base and storm flow are presented and explained in the context of this cross-sectional model.

Key words--Phosphorus, nitrogen, hydrology, watershed, groundwater, seepage, runoff, model, Pennsylvania

INTRODUCTION

Watersheds that exhibit zones of seepage occupy major portions of the landscape in many areas of the United States. Seepage refers to the discharge of subsurface water at the soil or land surface. Seep zones not only discharge groundwater and perched water to streams, but they can also be major sources of surface runoff production during storm events. These zones are dynamic and responsive during single storms, rapidly expanding and subsequently shrinking on time scales within the order of a storm event. Such response has very important implications for studying the chemical dynamics. The expanding seep zone represents an increased groundwater discharge that may originate from chemically different or previously unsaturated source zones. In addition, the ratio of surface runoff to groundwater discharge changes substantially and quickly throughout the storm, causing concomitant changes in streamflow chemistry. The chemistry of surface runoff is usually much different than that of groundwater discharge. The changes in hydrologic-chemical interactions need to be much better understood in these types of watersheds, if the chemical dynamics are to be established.

Watersheds that exhibit seep zones have a combination of properties that cause the ground- or perched-water flow downgradient to exceed the subsurface transmission capacity of the subsurface systems, thereby forcing this water to surface as seepage. This phenomenon is usually not watershed wide but local, occurring primarily near the stream channels, rock outcrops, or clay-fragipan outcrops. Watersheds subject to seep zone formation are usually located in regions where substantial percolation occurs, i.e., precipitation exceeds evapotranspiration (ET) over parts of the year or groundwater is a substantial contributor to stream flow. Seep zone formation is most likely to be substantial on those watersheds with geologic, geometric, or geohydrologic properties that restrict the flow transmission capacity of subsurface flow systems. These include decreased downslope groundwater gradients (e.g., decreasing land slope without increased storage), decreased cross-section (e.g., slope break, high water table, or intrusions of aquicludes such as shale layers) or decreased permeability (e.g., downgradient shifts from coarser- to finer-textured soils or geologic deposits). One research watershed that exhibits these properties and seep zones is a 7.4 km² subwatershed of the Mahantango Creek Watershed located in east-central Pennsylvania.

Until very recently, the seepage zones on this watershed were not studied specifically, but instead as part of the hydrologic partial area. The basic premise of the partial area is that most surface runoff occurs from an areally small part of the watershed where precipitation excess (rainfall minus infiltration rate) is being generated. The partial area concept of surface runoff generation (Betson, 1964; Betson and Marius, 1969; and Ragan, 1968) apparently is the dominant hydrologic mechanism generating surface runoff on the Mahantango Creek Watershed (Engman and Rogowski, 1974; Gburek, 1978). In the Mahantango Creek Watershed, this area is generally near the stream (Gburek, 1978; Engman and Rogowski, 1974), or has a direct surface water hydraulic connection to the stream (Engman and Rogowski, 1974). Precipitation excess (surface runoff) obviously occurs from the seep zone which acts as an impervious surface. However, it also can be generated on soils characterized by high antecedent soil moisture contents, low permeabilities, and subsurface water- or air-impeding layers. The seep zones and bordering areas are dominated by soils having these characteristics. In addition, bordering areas that are normally considered noncontributing can generate surface runoff if the storm is sufficiently intense. When subjected to a 10.7 cm rainfall during a 2-hour period (650-year return period storm) about 17% of the watershed area contributed most of the surface runoff and erosion to the stream, yet this 17% was still limited to the alluvial and fragipan soils located closest to the stream (Gburek et al., 1977). The importance of the seep zone contribution to the hydrologic partial area on this watershed has long been recognized (Engman and Rogowski, 1974; Gburek, 1978), but the interrelationship between partial area runoff, seep zone runoff and groundwater (seep) discharge has not been examined, particularly as it affects the chemistry of stream flow.

The objectives of this paper are: 1) to unify in a cross-section approach the past water chemistry and hydrologic research done on this watershed, 2) to examine and expand this concept in terms of recently observed nutrient-hydrologic interaction occurring in the seep zone and in the stream, and (3) to philosophically describe the near-stream cross-section in terms of an interactive groundwater discharge-surface water runoff zone.

WATERSHED PROPERTIES, CHARACTERISTICS, AND INSTRUMENTATION

The 7.4 km² subwatershed of the Mahantango Creek Watershed is located approximately 40 km north of Harrisburg, Pennsylvania, within the Susquehanna River Basin. Land use is about 57% cropland, 35% forest, and 8% permanent pasture. Elevation ranges from about 460 to 240 m, and there are no urban areas or industries within the watershed.

The climate is temperate and humid, with the hydrologic budget given in Table 1. About 65% of the stream flow is estimated to be base flow, of which groundwater discharge is a major component. Potential ET is less than precipitation about seven months of the year, with most groundwater recharge occurring during the dormant months. Subsurface flow moves from ridge tops at the north to the weir in the south (Figure 1).

Geology, topography, and soils on the watershed are typical of the unglaciated, intensely folded and faulted, Valley and Ridge Province of the Appalachian Highlands. The predominantly shale Trimmers Rock Formation (Late Devonian) outcrops at the watershed outlet in a near-horizontal position, and forces most subsurface flow to surface for measurement at the weir. The Catskill Formation (Late Devonian - Early Mississippian), consisting of

Table 1. Hydrologic Budget for the 7.4 km² Subwatershed of the Mahantango Creek Watershed from 1973-79.

Component	Depth, mm/yr
Precipitation ¹	1128
Evapotranspiration ¹	479
Streamflow ¹	649
Surface runoff ²	229
Base flow ²	420
Groundwater recharge ³	217 (473)

¹ Measured except for evapotranspiration which is computed by difference.

² Surface-base flow hydrograph separation.

³ Data from Sharma and Pionke (1983). Value based on analysis of a single bore hydrograph from 1973-79. Parenthetical value computed from the increase in Cl concentration from precipitation to groundwater (4 wells) during 1973-82, and assumes all Cl originates in precipitation.

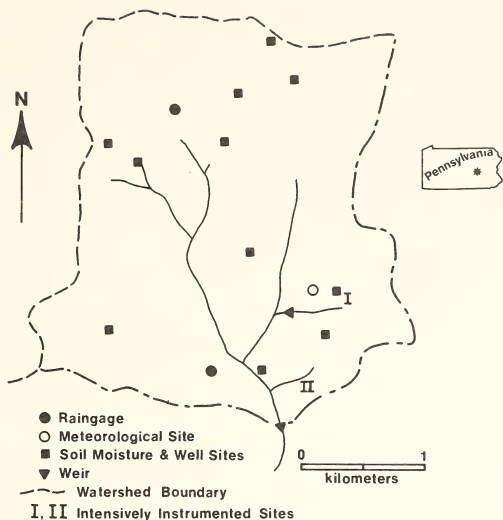


Figure 1. Data Collection and Research Sites - 7.4 km² Mahantango Creek Subwatershed

interbedded shales, siltstones, and sandstones, becomes increasingly coarse-grained from south to north, with siltstone outcropping in midwatershed, and a relatively pure quartz sandstone conglomerate outcropping at the north watershed divide.

The two geologic formations are hydrologically similar based upon specific capacity data (Urban, 1977). However, the rock type extremes, coarse sandstone (9.3×10^{-4} cm/sec) in the north, versus clay shale (1.1×10^{-5} cm/sec) in the south, show pronounced permeability differences.

Soil depth ranges from 1 to 2 m, and a 2- to 10-m thick blanket of periglacial talus covers the mountain slopes. Beneath the soil, a 3- to 10-m mantle of weathered, highly fractured rock exists as a transition zone between bedrock and soil. During the dormant season, perched water tables exist within both the soil and the transition zone.

Soils generally grade from the shallow (Weikert) or coarse-textured (DeKalb) on ridge tops, to the finer-textured, deeper agricultural soils

(Klinesville, Leck Kill, Hartleton, Berks) in the valley. Colluvial soils (Laidig, Meckesville) found on the ridge side slope often contain fragipans at 30 to 100 cm depth. The deepest soils (Albrights, Conyngham, Shelmadine, Basher and Alvira), are located usually adjacent to definable stream channels, and characteristically have high water tables or fragipans.

The general instrumentation network is shown in Figure 1 and has been operational from 10 to 15 years, depending on the particular site. Site II is an intensively and recently instrumented study area that will be described when the data are presented. Site I refers to a cross-section operated from 1969 to 1970, and is described in Rogowski et al. (1974) and Heald and Rogowski (1977). More detailed descriptions of the general data collection network, watershed properties and characteristics are presented by Gburek (1977), Pionke and Urban (1985), Pionke and Weaver (1977), Urban (1977), and Urban and Pionke (1984).

THE HYDROLOGIC CROSS-SECTION

Both past and ongoing research on the Mahantango Creek Watershed has been based philosophically and experimentally on the cross-section. The cross-section is a two-dimensional vertical slice of a soil and/or geologic zone that characterizes water flow through that zone. The cross-section is usually oriented in the plane of maximum hydraulic gradient so that the flow lines parallel the cross-section, and the outlet is usually the defined stream channel. The cross-section approach is particularly useful because it is simple, readily incorporates subsurface flow, and can be focused on the important hydrologic interactions. The cross-section is the tool and model we will use to examine the partial area concept, particularly seepage face development during the storm, the seepage face-surface runoff interaction, and later, the dynamics of selected chemical parameters in the near-stream zone. The cross-sections examined here will be the full geologically-based cross-section for the watershed and the near-stream experimental cross-sections.

Full geologically-based cross-section--The overall groundwater system of the 7.4 km² subwatershed appears to operate in accordance with the cross-section presented in Figure 2 (Pionke and Urban, 1985; Urban and Pionke, 1984). Groundwater flow is from left to right with groundwater recharge being dominant at the ridge top (X) and groundwater discharge being dominant near the stream (X'). Essentially, the watershed can be viewed as having two

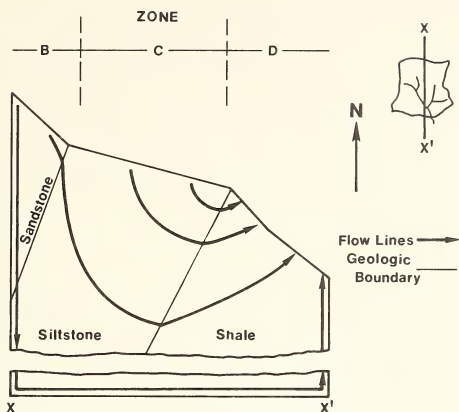


Figure 2. Full Geologically-based Cross-Section Representing the 7.4 km² Mahantango Creek Subwatershed

hydrologic partial areas: 1) groundwater recharge area with the highest rates occurring in zone B and 2) the surface runoff area associated with the groundwater discharge areas in zone D. Hydrologically, zone C is a combination groundwater through-flow and recharge zone connecting zones B and D. However, the cropland dominated C and D zones are the primary sources of NO₃ and Cl in groundwater and stream base flow (Pionke and Urban 1984, 1985). In this chemical sense, these cropland-dominated zones are partial areas. Zone D represents predominantly a mixing and discharge zone where deep (B) and shallow (C) groundwaters converge and then resurface at the stream and adjacent land surface. The reason for the mixing and surfacing of groundwater is that the shale layer in zone D has a very low permeability, particularly near the right lower boundary. A combination of geologic structure, stratigraphy, and geometry of flow favors a groundwater return flow to X' and the lower soil-surface boundary of the cross-section. Superimposed on this geology and geometry are changes in the groundwater table gradient and stored groundwater volume due to seasonal and longer term climatic variability which control the basic position of the groundwater table relative to the land surface. In summary, it is the properties of this full cross-section that establishes the overall control on

the extent and location of seep zones and the groundwater contribution to stream flow. Within this framework, individual or short series of storms appear to generate or expand seep zones temporarily and locally. This effect is basic to establishing the partial area of surface runoff.

Near-stream experimental cross-sections--Two hydrologically based cross-sections were established to study primarily the hydrologic interactions in the near-stream zone. On the scale of the full cross-section (Figure 2), the near-stream cross-sections occupy an extremely short, paper-thin surface layer normal to stream channels located in zone D. Both cross-sections (locations at I and II, Figure 1) are located at the bottom of small hills and drain directly into tributaries rather than the main channel. The two near-stream cross-sections have some similarities in that both contain a groundwater discharge zone, are grassed, are at about the same slope, deal with the shallow zone (3 m or less instrumentation depth), and collect data on soil water content, soil water tension and water-table levels along the cross-section. However, the cross-section at site II is much more intensively and completely instrumented. The main differences are that the site I cross-section is longer (150 vs 39.6 m), located in a fragipan rather than an alluvial soil, located over a fracture trace (flow convergent in 3 dimensions) rather than in a sloping plane (flow convergent in 2 dimensions), and includes some chemical data collected in association with the hydrologic data. Data, site and data network characteristics for cross-sections at sites I (Rogowski et al., 1974; Heald and Rogowski, 1977) and II (Hoover, 1984; 1985) are available.

The research at site I showed that the upper and lower ends of the 150-m cross-section behaved quite differently (Rogowski et al., 1974; Heald and Rogowski, 1977). The near-stream groundwater levels were quickly responsive to, and were controlled by, rainfall events; whereas groundwater responses at the upper end of the 150-m cross-section were delayed 5 to 6 days. Also the greatest rate of soil water accumulation and groundwater recharge occurred concurrently in the lower part of the cross-section, implying that a single process was affecting both the rate of soil moisture accumulation and groundwater recharge. However, at the upper end of the cross-section, the maximum rate of soil water accumulation preceded that of groundwater recharge by about 100 hours. Upon examining the water chemistry, the chemical pattern in both soil and water at the upper end of the cross-section matched that

expected if ET and plant extractions were the dominant processes (Heald and Rogowski, 1977). At the lower end, an inverse relationship between groundwater stage and the NO_3 , Cl, and EC concentrations was observed, implying that dilution by entry of purer waters was the dominant mechanism. These results, and the existence of seepage faces, identified the near-stream zone as hydrologically active, very dynamic, and greatly impacted by groundwater.

The results from the site II cross-section verify, better define, and expand these conclusions. Hoover (1985) determined the water potential distribution for a 39.6-m long cross-section before (Figure 3A, 1200 hr. on

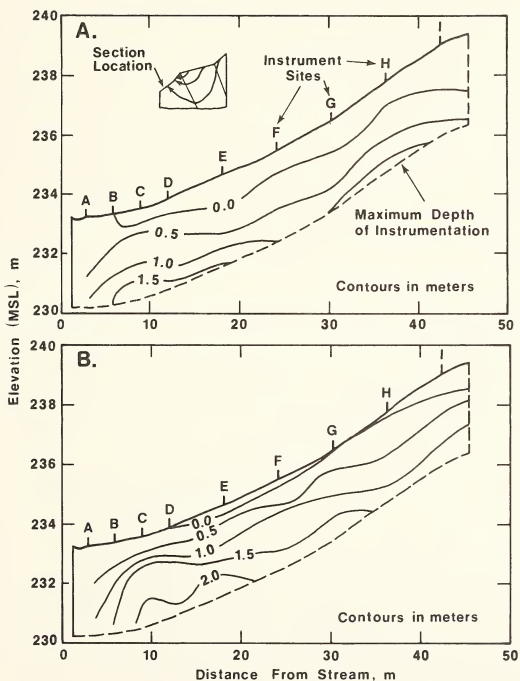


Figure 3. Water Potential in the Site II Cross-Section Before (A) and Soon After (B) the Storm

6/28/83) and following (Figure 3B, 1200 hr. on 6/29/83) a storm that delivered 49 mm of rainfall from about 1430-2030 hr. on 6/28/83. Water potential is defined as the matric potential when ≤ 0 , and the water pressure potential when > 0 . Before the storm (Figure 3A), the water table (water potential = 0.0 m) is roughly parallel to the land surface in most of the upper part of the cross-section. It becomes shallow in the lower part of the cross-section, intersecting the land surface at instrument site B. Because the 0.0-m line designates the upper boundary of the saturated zone (water table), it also defines the upper boundary of the seepage face where it intersects the land surface. The soil located above the 0.0-m line is unsaturated. Following the storm, the water table rises and the seepage face expands considerably (Figure 3B), intersecting the land surface at instrument site D which more than doubles the size of the seepage face. Also, there is little unsaturated soil, because the water table is quite close to the land surface throughout the cross-section. It may even have intersected the land surface sometime earlier during the storm causing seepage and/or surface runoff to occur in the vicinity of F-H. Although not presented here, the system returns more slowly to the pre-storm state of Figure 3A. The soil water and water table status had nearly returned to its pre-storm state by 1200 hr. on 7/1/83 (Hoover, 1985).

Seepage faces also serve as major surface runoff-producing areas during a storm. These faces are dynamic, responding quite quickly to rainfall, which in turn, generates more runoff. Note how much this single storm not only increased the extent of the seepage face, but also reduced the volume of unsaturated soil. Another major storm event following this 49-mm storm, during the season when these water tables are normally close to the surface, could turn most of this cross-section into a surface-runoff generating zone. Also, the subsequent return (reduction in seepage face) to the pre-storm state provides relatively large amounts of soil and groundwater drainage to streams. The quick response and hydrologic instability of the cross-section may be explained with the help of Figure 4. The flow lines are plotted as arrows normal to the total equipotential lines (water potential plus elevation). The flow lines occurring soon after the storm (1200 hr. on 6/29/83), suggest substantial groundwater movement to the land surface. In contrast, before the storm (1200 hr. on 6/28/83), Hoover (1985) observed the flow lines to be

basically parallel and directed toward the bottom left corner of the cross-section which suggests substantial groundwater movement away from the land surface. Because this temporary divergence of flow lines in response to the storm, not only expands the seepage and partial area, but alters flow pathways, the chemistry of the resultant stream flow can be greatly impacted.

Although the two cross-sections are different in several important ways, they provide similar general results. This is encouraging because together they represent the major near-stream soils (fragipan and alluvial soils) and the most common near-stream configurations (sloping plane or fracture trace) associated with the hydrologically active near-stream zones of the Mahantango Creek Watershed.

The behavior of these near-stream cross-sections is largely controlled by the full geologically-based cross-section. The groundwater flow lines, indicating groundwater discharge in portions of zone D (Figure 2), basically extend into the near-stream cross-section. Upward groundwater flows in large part create and support the pre-storm seep zone and relatively high water tables (Figure 3A) that expand in response to a storm (Figure 3B). Also, major flow lines following the storm event exhibit a very strong upward component (Figure 4).

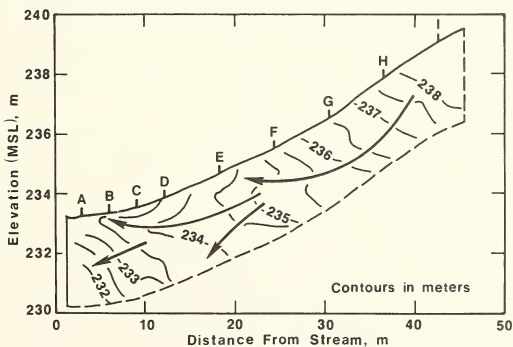


Figure 4. Flow Lines and Total Potential in the Site II Cross-section Soon After the Storm (1200 hr. on 6/29/83)

The implications of these cross-section research results on the chemical dynamics of the watershed system are tremendous. The source of water, its pathway, and residence time, not only control the entry of chemicals into the water enroute, but also control the chemical and biological processes to which those transported chemicals are subjected. Without a good understanding of the hydrodynamics of the system, the chemical dynamics cannot be realistically examined or understood. In the next section, we examine chemical analyses of seepage, partial area runoff, and stream flow in the hydrologic context of the near-stream cross-section.

CHEMICAL RESPONSES TO HYDROLOGIC PROCESSES IN THE NEAR-STREAM ZONE

The chemistry of 1) seep flow and surface runoff from the near-stream zone and 2) precipitation, stream flow, and base flow for a small watershed associated with that near-stream zone will be presented and examined in the context of the cross-section. The focus will be on those agricultural chemicals mostly transported in water phase at this small scale; these are NO_3 , soluble phosphorus (P), and NH_4 . Select data are also presented for Cl and orthophosphate (Ortho P). The role of erosion and sediment on the loss and transport of adsorbed and other sediment-associated P fractions will not be treated here. Past work on the Mahantango Creek Watershed has shown the most critical processes affecting the soluble P-sediment relationship to occur in the stream channel rather than on the adjacent hill slopes. The dominant in-channel processes include adsorption, fixation and dilution of soluble P (Heald and Gburek, 1977; Kunishi et al., 1972; Taylor and Kunishi, 1971). Thus, any study of the soluble P-sediment interaction would need to include the effect of these channel processes which are beyond the scope of this study. However, soluble P behavior can be examined independently of sediment on these small experimental watersheds because the impact of the stream channel is usually small relative to the rest of the watershed. The soluble P concentration in stream flow is highest at the small watershed scale (see Table 1 - Heald and Gburek, 1977), and the soluble P load is usually larger than the adsorbed P load (Kunishi et al., 1972).

Site characteristics, sampling and analytic procedures--The chemical and hydrologic data presented in this section were collected at site II from Brown's

weir, both raingages and the upper (R-3 to -10) and lower (R-1S to -5S) rings (Figure 5). The weir site provided continuous measurement of the stream flow rate and was the source of the frequently sampled storm flows and periodically sampled base flows. The conventional and chemical raingages provided the rainfall depth, intensity, and samples. The rings provided surface runoff and seepage samples with some measure of the water volume produced.

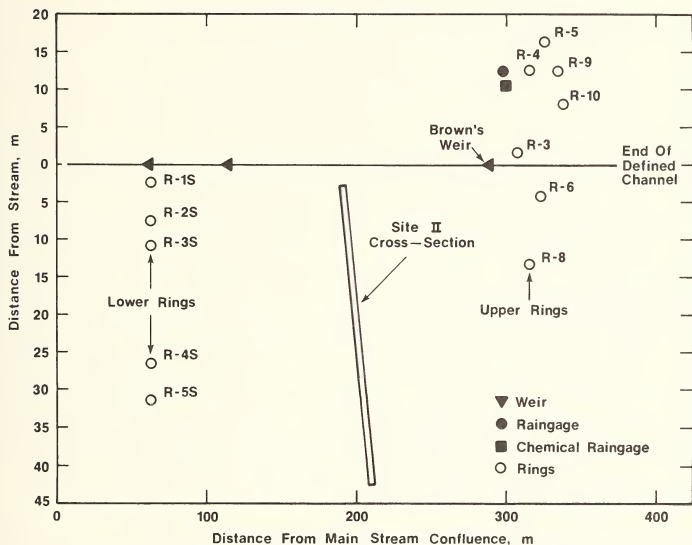


Figure 5. Location of Site II, Including Cross-section, Brown's Weir, Upper and Lower Rings

The rings, which resemble infiltrimeters, are painted circular steel bands (96-cm dia., 15-cm height) with a drainage port cut through the side at 7.5 cm height. They were installed about 1 year earlier by driving them 7.5 cm into the ground until the drainage port was at ground level. The captured water drains by gravity to an interred, covered plastic container. Only one accumulated surface runoff sample was collected from each ring per storm. However, it was discarded if there was a high probability that seepage had contaminated ring runoff during the storm as indicated by either seepage

occurring during sample pickup following the storm or captured water volume exceeding 75% of the total rainfall. Seepage samples were taken periodically, but only during nonstorm periods. Seepage volumes were not corrected for ET loss; however, the seepage flow collection period never exceeded 6 hours.

The weir site consists of a 90° V-notch weir, a continuous stage recorder, and an automated sampler. One raingage is a conventional weighing-recording gage, while the other is a specially designed chemical gage with an open circular steel bore (76 cm dia.) that is rinsed daily with distilled water.

The 9.7-hectare subwatershed defined by Brown's weir is nearly all cropped (corn, wheat, oats, and hay) with a permanent grass strip, surrounding and extending about 15 m out from the defined channel. The field is mostly Hartleton and Berks channery silt loam with slopes ranging from 3 to 15%. The rings and the site II cross-section are located in permanent grass on an alluvial soil (Berks channery silt loam). The permanently grassed area is neither fertilized nor manured. The rings occupy a flatter area with slopes ranging from 4 to 10%. The two ring locations are separated by 250 m distance and 18 m elevation.

Chemical analysis and sample handling procedures are given in Pionke and Urban (1985) except for NH_4 (Schnabel, 1985). Basically, all samples were filtered through a 0.45 μ filter and analyzed for soluble P, Ortho P, NO_3 , NH_4 , and Cl as soon as possible thereafter. Soluble P is that extracted by 0.5 N HCl from the dried residue of this filtrate; Ortho P was determined by specific orthophosphate analysis of the filtrate. All chemical data are expressed on the elemental basis.

Chemistry of surface runoff and seepage from the rings--Surface runoff and seepage samples were taken from both sets of rings from spring through midsummer, 1984. Most of the runoff samples came from the upper rings (R-3 to -10) and most of the seepage samples from the lower rings (R-1S to -5S). The mean quartile values of soluble P, Ortho P, $\text{NO}_3\text{-N}$, $\text{NH}_4\text{-N}$ and Cl are given for the combined data set (Table 2). The quartile is used as a measure of variability because these data were not normally distributed.

Seepage patterns were quite variable over time and space, being generated by major storms and often dissipating within a few days. Seasonal patterns generated in spring may exist for weeks or months, depending on subsequent rainfall. Over the late spring-early summer period, some seepage rates were

Table 2. Mean and Variability of Chemical Concentration in Seep and Surface Runoff Taken from Rings at Two Locations¹

Chemical Parameters ²	Surface Runoff			Seep		
	Mean	Quartile ³	N	Mean	Quartile ³	N
	-----mg/l-----			-----mg/l-----		
soluble P	0.233	.167	41	.034	.025	15
Ortho P	0.161	.090	41	.019	.024	15
NH ₄ -N	0.53	0.48	43	0.15	.13	20
NO ₃ -N	0.32	0.40	43	8.81	8.35	20
Cl	3.05	2.75	44	4.34	3.45	21

¹ Two clusters of rings were used, one located downstream from the other about 250 meters. Both clusters were located near the stream channel. Data collection period for the upper and lower locations were 4/16-8/23/1984 and 5/30-6/24/1984, respectively.

² Data were only used when available for both NO₃-N and NH₄-N or soluble P and Ortho P combinations. If data was available for only one of a pair, then that data was not included.

³ 75% minus the 25% value.

measured. The most complete data set is for 6/18/84 when three rings at the upper location were seeping the following amounts in cm/day: R-3 = 12.5; R-4 = 5.5; R-9 = .89. This was the maximum rate and areal extent of seepage observed.

In a general comparison of the seepage versus surface runoff, the concentration of soluble and Ortho P in the surface runoff exceeds those in seepage by about 8 times. Similarly, the NH₄-N concentration was about 4 times higher in surface runoff than in seepage. These observations are consistent with those expected if the highest P and NH₄-N concentrations are presumed to originate in washoff from soil and plant surfaces. In contrast, the NO₃-N and Cl concentrations were higher in seepage than in surface runoff. Although the Cl concentration showed a relatively small difference, the NO₃-N concentration in seepage was about 28 times greater. The higher concentrations of Cl and NO₃-N in seepage would be expected theoretically because these chemicals are readily soluble and not adsorbed. Also higher Cl

and $\text{NO}_3\text{-N}$ concentrations have been observed in groundwater and base flow than in surface runoff on the watershed (Pionke and Urban, 1985; Gburek and Heald, 1970). The variability for all the chemical parameters was large, being least for the soluble and Ortho P in surface runoff and most for the $\text{NO}_3\text{-N}$ in surface runoff and seepage.

A more complete interpretation of these results requires an understanding of the hydrodynamics of the near-stream system. The major P response is to the P status of the surface runoff zone and the hydrologic state of the near-stream system which controls the extent of surface runoff. Because the washoff of P is primarily a surface-associated phenomenon, and all rings are located on the same type surface, i.e., unfertilized permanent pasture growing on the same soil types, the hydrologic state becomes the most important variable affecting the soluble P concentrations and load delivered to the receiving stream. This is because it affects the ratio of surface runoff to groundwater discharge and the volume of surface runoff. The less variability in P concentration in surface runoff from ring to ring, irrespective of location is consistent with this conclusion. The $\text{NH}_4\text{-N}$ response, being greatest for surface runoff, is interpreted the same way except it appears to be subject to greater variability, perhaps because of its greater biological and chemical instability. In contrast, much Cl and most $\text{NO}_3\text{-N}$ response is due to the dominance of seepage. The occurrence and extent of seepage may be more important than the particular origin of that seepage. Evidence for this is that the $\text{NO}_3\text{-N}$ concentration observed in seepage reasonably approximates the $\text{NO}_3\text{-N}$ concentrations: 1) observed in stream base flow at Brown's weir over a 2-year period and 2) computed for agricultural groundwaters of the larger watershed (6.8 mg/l) based on a hydrologic and nitrogen mass balance (Pionke and Urban, 1984).

Chemistry of the stream hydrograph--The chemistry of a stream hydrograph was compared to that of rainfall, ring runoff, ring seepage, and pre- and post-storm base flow. The storm studied began at 1200 on 6/24/84, producing 40.6 mm of rainfall with a maximum 15-minute intensity of 44 mm/hr. The pre- and post-storm base flow samples were taken at 0955 on 6/22/84 and at 1015 on 6/27/84, respectively. All samples were taken at or above the Brown weir site, except for ring seepage which was only available from the lower ring location (Figure 5). The seep zone, which had been quite extensive and active at the

upper ring location on 6/18/84 (see seepage rates given in previous section) shrank to where it was now close to the stream and inside the upper ring sampling zone.

The hydrologic and chemical data are presented in Figures 6 and 7. Figure 6 presents the rainfall distribution, hydrograph and the primarily groundwater-associated chemical parameters (EC, $\text{NO}_3\text{-N}$). Chloride data were not collected for the hydrographs. Figure 7 presents the primarily surface runoff-associated chemical parameters ($\text{NH}_4\text{-N}$, soluble P). The Ortho P results are excluded because they follow the same pattern as soluble P except at somewhat lower concentrations. For this particular event, the mean Ortho P

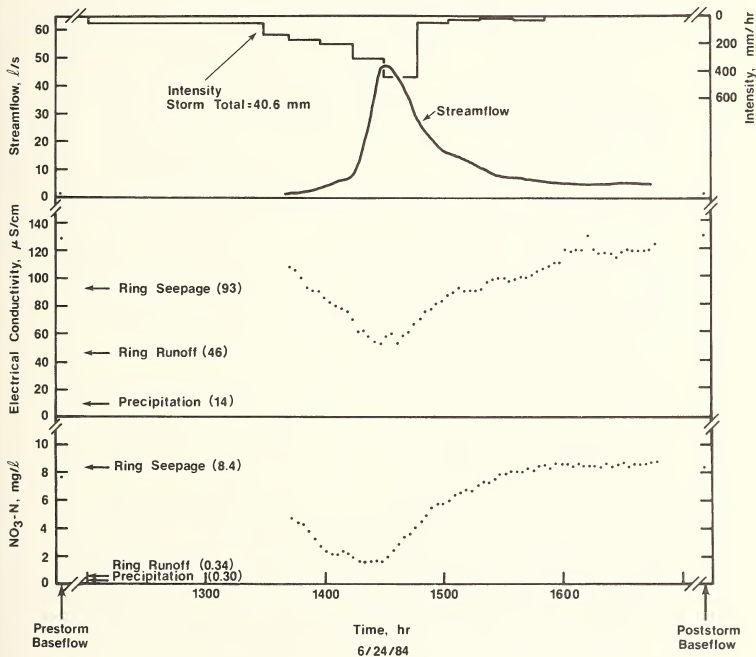


Figure 6. Effect of Hydrologic Source on the Electrical Conductivity and NO_3 Concentration in Storm Flow

concentration expressed as a percentage of mean soluble P concentration is lowest for ring runoff, (60%) and highest for ring seepage, precipitation, and base flow (range of 85 to 100%).

The EC and $\text{NO}_3\text{-N}$ responses to the storm are similar (Figure 6). The concentration patterns of both are the inverse of the flow rate, being lowest when the flow rate is highest. The incremental reduction in EC and $\text{NO}_3\text{-N}$ concentrations per unit increase in flow rate is greatest when the hydrograph begins to rise and becomes less as the storm progresses to the peak flow rate, suggesting that the greatest dilution occurs earliest in the storm. Eventually, the EC and $\text{NO}_3\text{-N}$ concentrations return to pre-storm base flow levels at storm's end. However, the corresponding flow rate remains much higher (about 5 l/s), greatly exceeding the post- (0.85 l/s) and pre-storm (0.68 l/s) base flow rates. This suggests that the same basic chemical regime controls the chemistry of ring seepage, low base flows, and these high relatively stable flows. On another Mahantango Creek subwatershed, Gburek and Heald (1970) observed similar $\text{NO}_3\text{-N}$ patterns with somewhat higher concentrations occurring on the tail of the hydrograph than in pre-storm base flow, while Gburek (1978) observed the same general pattern in EC. Also note on Figure 6 that the $\text{NO}_3\text{-N}$ and EC concentrations in post- and pre-storm base flow generally correspond to the ring seepage concentrations, whereas the peak-flow associated concentrations correspond to ring runoff and precipitation concentrations. The $\text{NO}_3\text{-N}$ concentrations observed in the base flow and ring seepage from this dominantly agricultural watershed closely approximate that computed (6.8 mg/l) for farmland groundwaters in this watershed (Pionke and Urban, 1984).

In contrast to EC and $\text{NO}_3\text{-N}$, the $\text{NH}_4\text{-N}$ and soluble P concentrations were highest at the high flow rates (Figure 7). Heald and Gburek (1977) observed this same soluble P response at another Mahantango Creek subwatershed. Soluble P was determined from two composites rather than from each individual sample. For both $\text{NH}_4\text{-N}$ and soluble P, storm flow concentrations were at least 10 times greater than base flow concentrations, and best matched the concentrations observed in ring runoff. $\text{NH}_4\text{-N}$ and soluble P concentrations in ring seepage, rainfall, and base flow were generally quite low. According to Heald and Gburek (1977), high soluble P concentrations observed in stream flow at the higher flow rates are not

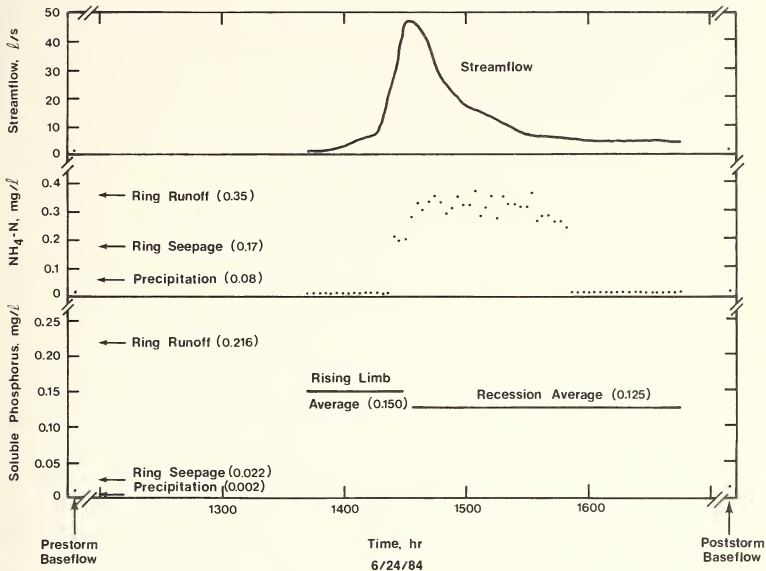


Figure 7. Effect of Hydrologic Source on the NH₄ and Soluble Phosphorus Concentration in the Storm Flow

associated with high sediment concentrations. Here, the ring runoff samples that contained the high soluble P concentrations were devoid of sediment. This high soluble P concentration could result from plant washoff and P desorption from the surface soil layer. Gburek and Broyan (1974), Gburek and Heald (1974) and Heald and Gburek (1977) presented evidence to suggest that plant washoff may be a major source of soluble P. Gburek and Broyan (1974) determined the average soluble P in plant washoff to be $.120 \pm .040$ mg/l. Although somewhat low compared to the ring runoff average (.216 mg/l) for this storm, this value does fall well within the range observed for ring runoff (Table 2).

In the context of the near-stream cross-section, the above results can be interpreted as follows. When subjected to a storm, the hydrologic source area is not stable, but evolves from: 1) base-flow dominated to 2) rainfall-diluted base flow, to 3) surface-runoff dominated flow, to 4) a progressively base-flow dominated flow which then drains back to 5) normal base flow. Earlier Mahantango Creek Watershed studies (Gburek, 1978; Gburek and Pionke, 1983) in which EC and pH patterns associated with storm hydrographs were analyzed, provide a mathematical basis for this breakdown. Note that the system is sufficiently dynamic so that steps may be bypassed or become extreme. For example, a small rainstorm may never reach the surface runoff stage, or a very large intense storm may cause massive surface runoff generated from a large area which may overwhelm the system. However, the storm of 6/24/84 appears to go through all of the above steps. The evidence for step 2, (rainfall-diluted base flow) is that the decrease in $\text{NO}_3\text{-N}$ and EC concentration in stream flow per increase in flow rate is greatest at the beginning of the storm. Our interpretation is that this period is dominated by dilution due to direct interception of rainfall by the stream in large amounts relative to the small volume of stream flow. During this period, stream chemistry is dominated by rainfall and base flow quality. As the storm continues, this initial contributing area expands due to formation of near-stream seep or saturated zones. Surface runoff from these zones, although less pure than rainfall, is considerably purer than base flow. Thus, the concentrations of $\text{NO}_3\text{-N}$ and EC in stream flow continue to be reduced substantially, but less efficiently, relative to the increasing flow rate. The very low NH_4 concentrations suggest that surface runoff is not yet a dominant process. Step 3, (the surface-runoff dominated flow) is evident at the peak flow rate. The $\text{NO}_3\text{-N}$ and EC concentrations in stream flow are at their lowest and approach the concentrations of ring runoff. This suggests little base flow impact on stream flow quality. At the same time, the $\text{NH}_4\text{-N}$ concentration is approaching the peak value which corresponds to the concentrations in ring runoff. The soluble P concentration for the rising limb of the hydrograph is quite high, with the dominant hydrologic source apparently being surface runoff. The quality of surface runoff controls the quality of stream flow. Step 4, (the period dominated by a high base flow) begins with an increasing ground and soil water contribution as evidenced

by much higher $\text{NO}_3\text{-N}$ and EC concentrations on the falling, compared to the rising, limb of the hydrograph for the same flow rates. Surface runoff progressively decreases until the hydrograph gets fairly flat. Although the flow rate is about 10 times that of the pre-storm base flow, the $\text{NO}_3\text{-N}$, EC and $\text{NH}_4\text{-N}$ concentrations in stream flow match the ring seepage, pre-storm and post-storm base flow concentrations. The quality of seepage and groundwater discharge control the quality of stream flow. Step 5 entails the drainage of the expanded seep zones and elevated groundwater tables in the near-stream zone until they are much reduced, and a stable base flow condition is again achieved.

CONCLUSIONS

For the Mahantango Creek and similar type watersheds, surface runoff and groundwater discharge occur mainly near the stream. In fact, the groundwater position relative to the land surface exerts a major control on the location and extent of these surface runoff zones. The long-term groundwater position near the stream is in turn controlled by climatic or seasonal fluctuations superimposed on the geology and geometry of the watershed. Thus, the groundwater state can change in response to a sustained wet or dry period, thereby potentially expanding or contracting groundwater discharge zones and potential zones of surface runoff. Within controls imposed by the long-term water table fluctuations, single or a short series of storm events can cause quick substantial changes in the near-stream surface runoff and groundwater discharge zones, even though the regional water table is not substantially affected. The result of this response is that storm outflow from these types of watersheds is a continually changing mixture of rainfall, surface runoff, and groundwater discharge, each being chemically quite different. Moreover, the seepage and surface runoff zone, expanding in response to a larger storm event, may intersect chemically different areas, thereby causing chemical shifts within each specific hydrologic component. These hydrodynamic and associated chemical responses, expressed earlier as data and in specific near-stream cross-section models, are generalized in the near-stream cross-section schematic of Figure 8A-C.

Before the storm (Figure 8A), stream flow (base flow in this case) is primarily groundwater discharge high in NO_3 and EC, but low in soluble P,

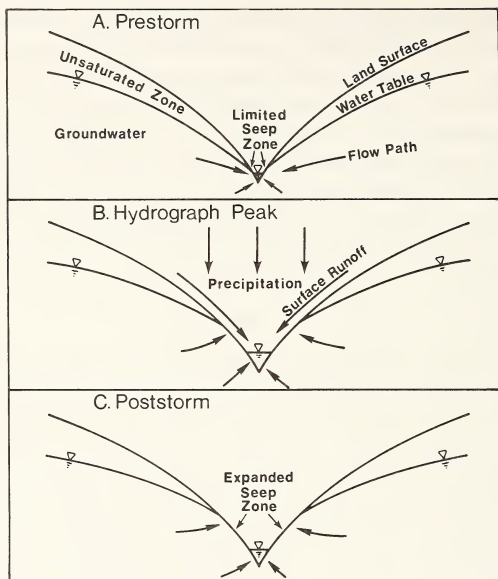


Figure 8. Generalized Near-stream Cross-section Model

orthophosphate, and NH_4 . Once the storm begins, three hydrologic processes are initiated that impact the stream flow volume and quality. In sequence these are: direct rainfall entry in the stream, surface runoff, and additional base flow. Initially, precipitation falls on the flowing stream and adjacent active seep zones. This impact on stream flow quality can be substantial, causing sharp decreases in NO_3 , EC, and pH of stream flow, but little change in NH_4 , soluble P, orthophosphate, and the flow rate. As the storm continues, surface runoff begins from adjacent channel banks and flood plain, which soon swamps out the previously dominating effect of direct interception. The surface runoff zone may expand beyond the seep zone to include traditionally less wet, but related soils that are characterized by low infiltration rates. Simultaneously, due to local recharge of the shallow water table, some groundwater flow pathways

are shifting upward to the land surface, causing a more rapid expansion of the seep and runoff generating zone. The NO_3 and EC concentrations in stream flow now decrease rapidly to a minimum, while the NH_4 , soluble P, and orthophosphate reach their maximums as peak surface runoff rates are approached (Figure 8B). Although surface runoff may still dominate stream flow quantity and quality for some time following the peak flow rate, the slow down or cessation of rainfall causes the surface runoff zone to contract, while the expanded seep zone remains enlarged or continues to expand. Thus, the EC and NO_3 concentrations in stream flow begin to increase sharply, reflecting the growing dominance of groundwater discharge from the expanded seep zone. When surface runoff ceases (Figure 8C), the orthophosphate, soluble P, NH_4 , NO_3 , and EC concentrations are at pre-storm levels because groundwater discharge is again the dominant stream flow source. However, the stream flow rate is much greater because of the extended seep zones and elevated groundwater tables. Groundwater, still draining into the near-stream zone from upslope, continues to support the extended seep zone and the higher groundwater discharge for several days until the near-stream system eventually drains back to the pre-storm condition (Figure 8A).

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DISCUSSION: Pionke Paper

Question (Sidle): How far up the drainage did you have groundwater installations, and what slopes are found there?

Answer: The slopes where we have that midstream cross section ranged between 3 and 10%. The groundwater wells extended up the side slope maybe a fourth or third of the way.

Question (Sidle): I agree with the cross section concept, but would you not feel that on a microscale the process you have described in an overall cross section may be happening in more upland reaches in the watershed? In fact, it may be happening in draws that are not necessarily channels, where you may get these areas of fairly quick saturation. What you end up with is almost like a mosaic of pockets throughout the watershed rather than just restricted to the main channels.

Answer: I think the concept applies on that lower part or the bottom of this watershed because that is where the water table is the highest on the average. Now you do have perched zones existing and you have incisions as you get up to the top of the watershed where there are small areas where indeed you get this effect. As I showed in one of the first slides on the subject

of partial area designation we had partial areas running well up into the top part of the watershed in the stream channels. So, yes you get the effect in the upper areas, but it is most dramatic as you get down to the bottom.

Question (Vorosmarty): You said the baseflow concentration of ammonium is very low, is that true for nitrate?

Answer: The nitrate concentration in baseflow is high, about 8 parts per million.

Question (Vorosmarty): Do you know what nitrate concentration levels are before they get to the seepage?

Answer: The concentration before it gets to the seep is 6.8. Now this isn't a bona fide seep like a pipe, but this is coming up through the soil surface.

BIOMASS, STRUCTURE, AND NUTRIENTS OF RIPARIAN VEGETATION ON A
SMALL WATERSHED ON CHICHAGOF ISLAND, SOUTHEAST ALASKA

BY

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Abstract--Baseline information on riparian vegetation biomass and nutrients were developed in this study to compare the unique climate and geology and its effects on ecosystem processing in southeast Alaska with other more intensively studied regions. A first order stream was chosen in northern southeast Alaska to study the following topics: (1) biomass and nutrient pools of riparian and upland forest types, (2) changes in community structure and composition across the riparian-upland gradient and (3) the role of understory vegetation in ecosystem nutrient dynamics.

Picea sitchensis dominated overstory biomass in the riparian zone (42% of total) and Tsuga heterophylla dominated the overstory in the upland area. Tsuga mertensiana was second in importance in both areas. Live tree biomass was 325 mt/ha for the whole study area, 397 mt/ha in the upland forest, and 217 mt/ha in the riparian area. A wide range of tree age and size classes were found for all conifer species, suggesting an uneven-aged open structure. Snag density was highest in the upland forest zone, but both zones had representations of a wide range in snag dimensions and decay classes.

Understory plant productivity varied widely. Highest productivity was found in the most open areas. Understory biomass density varied from 29 g/m² under dense Tsuga heterophylla or T. mertensiana canopies to 280 g/m² in openings adjacent to the stream. Herbs were most abundant within 10m of the active stream channel, 16 to 70 g/m² versus 3 to 7 g/m² in the upland zone. In the forest uplands, understory biomass density was greatest on well decomposed logs or root mounds. The number of understory species unique to the riparian zone as were four times greater than those unique to the forest

upland zone.

Nutrient pools for understory species were greatest for shrubs and least for bryophytes. Largest differences between lifeforms were in macronutrients in the upland forest zone. Shrubs accumulated 86% of understory nitrogen in upland forest compared to 50% in the riparian zone. Smaller total nutrient pools were measured for herbs and shrubs in the riparian zone. Overall understory nutrient pools were a significant fraction of aboveground nutrient capital, especially in relation to their standing biomass for both upland and riparian zones.

INTRODUCTION

The importance of stream ecosystems to maintenance of fisheries productivity in southeast Alaska is widely recognized. Most research has focused on physical characteristics and processes within the stream channel itself; not on the stream as a component in the riparian ecosystem. Interactions between surrounding upland forest and the stream have implications to many aspects of ecosystem structure and function. In small streams, riparian vegetation contributes a major portion of the allochthonous energy input to microbes and stream invertebrates which form the foundation for aquatic food webs (Cummins 1980, Sidle 1985). The amount, structure, and distribution of riparian plant species are also integrally related to nutrient retention, hillslope stability, and historical fluvial events that characterize stream ecosystems (Swanson and Lienkaemper 1980, Swanson et al. 1982). The amount and distribution of coarse woody debris also plays a key role in stream-forest interactions (Bilby and Likens 1980, Meehan et al. 1977, Swanson et al. 1976, Harmon et al. 1985).

Understory vegetation plays an important role in forest-stream interactions. In many forest systems, detrital inputs from understory vegetation have higher nutrient availabilities and balance than inputs from dominant overstory trees and can significantly improve soil conditions (Scott 1955, Tappeiner and John 1973, Turner et al. 1978, Turner and Long 1975). Composition and productivity of riparian vegetation is also important for wildlife (Thomas et al. 1979, Cline and Phillips 1983). In many regions, riparian vegetation has been found to be floristically unique, and can be used to identify flooding regimes, geomorphic surfaces, and other attributes of

stream systems (Osterkamp and Hupp 1984, Teversham and Slaymaker 1976).

Baseline information on riparian ecosystems in southeast Alaska were developed in this study so that the effects of the unique climate and geology of this region on riparian vegetation could be compared with that of other, more intensively studied regions. For this study, a first order stream in the northern part of southeast Alaska was selected to examine (1) biomass and nutrient pools of riparian and upland forest types, (2) changes in community structure and composition across the riparian-upland gradient and (3) the role of understory vegetation in ecosystem nutrient dynamics.

STUDY AREA

Southeast Alaska is a large region of steep glacially scoured mountain slopes, fjords, bogs, and fog enshrouded coniferous forests. Despite its high latitude (54 - 59 degrees N), the region enjoys a cool wet maritime climate. The region differs from most of the Pacific Northwest by having heavy year around precipitation, generally 200-600 cm per year, and a cool growing season. Peak precipitation generally occurs from September through November. Soils are strongly acid and are derived from a wide variety of igneous, metamorphic, and sedimentary parent materials (Brew et al. 1966). Most upland forest soils are classified as spodosols (Stevens 1965). Paludification and heavy organic matter accumulation is common throughout the region (Neiland 1971).

Previous research on vegetation in the region has concentrated on successional dynamics and plant overstory - understory relationships (Alaback 1982a, 1982b, Harris 1974), and the interaction between forest and bog (Neiland 1971). In contrast the nature of riparian vegetation in southeast Alaska has been little studied. This study was initiated to obtain baseline information on riparian vegetation in the region. The study site is on a small tributary to Trap Creek on the northeast side of Chichagof Island in northern southeast Alaska and has been the subject of numerous physical and biological studies oriented towards the stream ecosystem (see Sidle 1985 (this volume)).

The study stream (Jellybean Creek) is in a moderately incised v-shaped drainage surrounded by an uneven-aged old-growth Tsuga-Picea forest with

dominant trees generally greater than 200-400 yr of age, which typifies much of the low elevation forest in the region (Alaback 1984). Site productivity is average to below average for the region. Bedrock is composed of Silurian graywacke and argillite and Devonian limestone (Lanphere et al. 1965) overlain by glacial or marine till, leading to poor soil development and extensive bog and subalpine vegetation. The drainage is in a U-shaped valley with an overall aspect north to northeast. The study site is a first order stream draining roughly 30-40 hectares, including some upland bogs. Measurements were taken approximately 1 to 2 km from the headwaters. Overall stream gradient is 5-7%

Peak flow for Jellybean Creek is in Fall when highest rainfall intensity generally occurs (Anderson 1955, Sidle and Campbell 1985). Terrace development is minimal; most terraces and floodplains are discontinuous and rarely flood. As for many small streams in mountainous areas, hillslope erosional processes are of greater importance than deposition by sediment by flooding events in shaping geomorphic substrates and drainage patterns in the study area (Swanson et al. 1982, Swanston 1980).

METHODS

Overstory measurements--The tree stratum was sampled by establishing a slope corrected plot .25 ha (50m x 50m) in area, including both riparian and upland forest zones. String was used to define a 5m x 5m grid over the plot. Within this plot, all trees and snags > 5 cm in diameter at breast height were tallied and mapped for diameter and species; and for snags, decay class and height were recorded. It was also noted whether trees could cast foliage directly into the riparian floodplain. Riparian trees were generally less than 10 meters from the stream. Height diameter relationships were developed using regression analysis for all tree species on a sample of 10-20 trees each on nearby riparian areas. On each vegetation plot percent overstory canopy was estimated with a spherical densiometer taking measurements in each cardinal direction (Strickler 1959).

Understory measurements--During late August 1982, understory vegetation was sampled. Plant percent cover and size class (used for biomass estimation) were recorded for all species occurring within 1-m squared microplots distributed on a grid of 4-50 meter transects, 10 plots per transect (n=40)

within the 0.25 macroplot. This vegetation sampling followed methods of Alaback (1982a). Geomorphic substrate and distance from the stream were recorded for each plot. Vertical canopy cover was visually estimated for shrubs and understory trees within each of 11 strata ranging from zero to two meters in height above mean ground level. Dominant vegetation types, and individual shrub species were mapped in each 5m x 5m grid cell.

Nutrient sampling and analysis--Four transects were run in each of three contrasting environments within the drainage: the west side of the north slope, the east side of the south slope, and the active channel area. Three plots were sampled on each transect (a total of 12 for each environment) for the thirteen most common tree seedling, shrub, herb, fern, and moss species. Samples were collected in plastic bags, separated by species and by annual twig, stem and foliage components, and were air dried within 1 wk of sample collection. Vegetative tissue was redried at 60 degrees C, ground and digested in H_2SO_4 with a Se catalyst. Total N and P were measured with an autoanalyzer.

Data Analyses--Tree species composition, dominance, basal area, and component biomass was calculated using equations developed for the Pacific Northwest (Gholz et al. 1979, 1982) and local tree volume equations (Bones 1968). Understory biomass was calculated using equations developed for dominant shrub, fern, herb, and moss species in southeast Alaska (Alaback 1985). Estimates of productivity for shrubs and trees did not include increments of older woody tissue, only annual growth of leaves and twigs. In other regions where shrub woody increment has been measured, it contributed another 20-40% to estimates of shrub productivity (Whittaker 1961, 1962, Yarie 1980). Nutrient pools were estimated using nutrient concentration data for each species or species group for each of the defined strata (riparian zone, north and south slopes) and applying these to biomass estimates for each of the 40 plots. Nutrient uptake was defined as the nutrient pool of annual woody and foliar increment. Comparisons were made using Tukeys procedure for multiple comparisons, and t-tests for single paired comparisons (Steele and Torrie 1980). Nutrient concentration data for trees was taken from seedlings, and was compared with other studies of the same tree species (Grier 1976).

RESULTS AND DISCUSSION

Distribution of Riparian Vegetation--Jellybean Creek has relatively little terrace or floodplain development. In the study area most of the drainage has a steep cross sectional profile (Figure 1). In the upper (northern) portion of the study area, the stream is in a v-notch, and in the lower portion it has a small terrace to the east. Throughout the area, distinct breaks in the slope delimit the riparian vegetation zone. These slope breaks defined the riparian zone for overstory trees. For understory vegetation moist banks just above the stream where shrub foliage could directly fall into the stream were defined as the riparian zone. Soils adjacent to the stream had less organic accumulation than the forest soils, and tended to be moist, but moderately well drained. Heavy accumulation of organic duff and humus (> 15 cm) was common throughout the drainage, especially in the most stable (and oldest) forested areas.

Tree biomass and stand structure--Total aboveground tree biomass for the drainage was $325 \text{ mt}\cdot\text{ha}^{-1}$. The riparian zone had an average of only 217

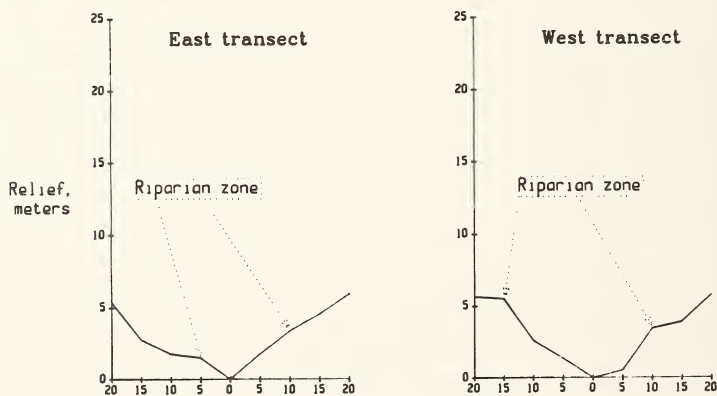


Figure 1. Cross section profiles of the two sides of the study area.

Table 1. Tree biomass and density in riparian and upland forest zones. All values are given on a per hectare basis.

Species	Tree density	Basal area m^2	Mean dbh cm	Foliage	Branches	Biomass ($Kg \cdot ha^{-1}$)	Stem bark	Total
A. Upland forest zone								
<u>Picea sitchensis</u>	180.0	13.3	26.2	4412	19772	50589	5616	80398
<u>Tsuga heterophylla</u>	653.0	22.2	17.4	7011	26613	77031	8556	188413
<u>Tsuga mertensiana</u>	100.0	18.6	41.2	6454	35490	77799	8647	128390
Total	933.0	54.1	84.8	17877	81875	205419	22819	397201
B. Riparian zone								
<u>Alnus rubra</u>	10.0	0.9	34.5	301	1180	3370	374	5225
<u>Picea sitchensis</u>	70.0	61.0	34.2	22656	17157	52903	5882	91437
<u>Tsuga heterophylla</u>	360.0	8.6	14.9	2634	8880	28097	3120	42731
<u>Tsuga mertensiana</u>	170.0	11.7	21.9	4003	21030	47391	5267	77690
Total	610.0	82.2	105.5	29594	48247	131761	14643	217083
C. Average for drainage								
<u>Alnus rubra</u>	4.0	0.4	13.8	120	472	1348	150	2090
<u>Picea sitchensis</u>	136.0	32.4	29.4	11710	18726	51514	5722	84813
<u>Tsuga heterophylla</u>	535.8	16.8	16.4	5260	19520	57457	6382	130140
<u>Tsuga mertensiana</u>	128.0	15.9	33.5	5474	29706	65636	7295	108110
Total	803.8	65.4	93.1	22564	68424	175955	19549	325153

mt·ha⁻¹, and the upland 397 mt·ha⁻¹ (Table 1). This is less biomass than has been reported for most mature coniferous forests in the Northwest, but exceeds that of most eastern and midwestern sites. For example, a highly productive second-growth Picea-Tsuga forest on the Oregon coast was 951 mt·ha⁻¹ (Grier 1976), a series of old-growth Pseudotsuga sites in the western Cascades were 492 mt to 976 mt·ha⁻¹ (Grier and Logan 1977), 304 mt

to 205 mt·ha⁻¹ was measured in lower site second-growth Pseudotsuga forests in the Washington and British Columbia (Turner and Long 1975, Webb 1977) and 609 to 345 mt·ha⁻¹ was measured in Tsuga mertensiana subalpine forests in coastal British Columbia (Yarie 1980). Other studies in southeast Alaska place the study site in the lower half to lower third of biomass densities reported (Alaback 1982b).

The riparian zone differed in overstory composition from the surrounding upland forest. The highest stem density but lowest biomass of Tsuga heterophylla, the climax tree species in the region, was found in the riparian zone. Picea sitchensis had the highest basal area and biomass of any species in the riparian zone (42%). Picea is considered typical of the riparian zone along the northern Pacific coast, preferring moist sites with high amounts of mineralizable nitrogen both along rivers and along the coast (Cordes 1972, Fonda 1974, McKee et al. 1982, Taylor 1935). As is typical in the Northwest, Alnus was most common adjacent to the stream channel (Campbell and Franklin 1979, Swanson et al. 1982). Its occurrence in this drainage was minor, due perhaps to the small size of the stream and the minimal terrace and floodplain development along the stream.

One distinctive feature of Jellybean Creek watershed was the high biomass and basal area of Tsuga mertensiana, a species usually associated with high elevations and subalpine environments. In this region, it appears to prefer cool drainages, and poorly drained sites (Neiland 1971) as well as the typical high elevation sites. In the riparian zone of our study site it comprised 36% of the aboveground tree biomass, in the uplands Tsuga mertensiana was 32% of the aboveground tree biomass.

Tree size class distributions also showed contrasts between the riparian and adjacent upland forests (Figure 2). In both areas, a wide range in diameter sizes existed for all species except Alnus, a seral shade intolerant species. Tsuga heterophylla dominated the seedling and small to medium

Live trees

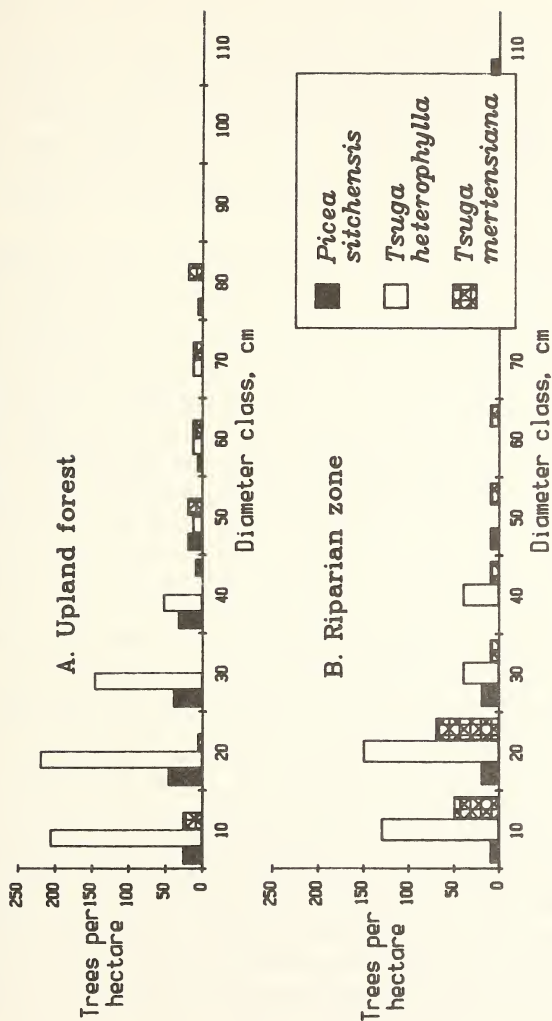


Figure 2. Live tree size class distribution in riparian and upland areas.

size classes (< 50 cm) in both areas. In the riparian zone, Tsuga mertensiana was also common in the 10 - 30 cm size ranges. In the largest size classes, there was a more equitable distribution of Tsuga and Picea species. Tsuga heterophylla greater than 40 cm were only found in the upland forests, whereas Tsuga mertensiana 40-80 cm were found in both zones. Only in the riparian zone were Picea greater than 80 cm found. Thus, in both zones, successful recruitment of Tsuga and Picea is occurring, suggesting an open, multi-aged stand structure. The largest Picea exceed 100 cm in diameter, and are estimated to be over 300 yr old.

The north and south sides of the drainage had large differences in terms of overstory canopy density and biomass. Averaging percent canopy cover over 5 meter intervals across the drainage, the south side of the drainage had greater canopy density (Figure 3). The north side had highly variable canopy density, with large gaps in the canopy and a more uneven slope in several places. The canopy opening created by the stream had less effect on canopy density and understory biomass than the large gaps on the north side of the drainage. The canopy openings on the north side of the stream were more effective in increasing light penetration because of the southern exposure, which generally resulted in increased understory productivity.

Snags--Recent interest in coarse woody debris in forest ecosystems, especially in riparian systems, has focused attention not only on the standing biomass but also on sources of snags and logs in these systems (Harmon et al. 1985). At our study site the riparian zone had less snag density than the upland region (Figure 4). This conforms with preliminary work done with Pseudotsuga in the Pacific Northwest (Cline and Phillips 1983). Using a simple structural decay classification system similar to that used for Pseudotsuga in the Northwest, snags were tallied by decay condition (Thomas et al. 1979, Fogel et al. 1974). The highest density of small recent snags, usually created by overtopping and by crown competition, was found in the upland forest, probably owing to the high density of small Tsuga in that area. Both zones had a wide range of size classes for each decay condition, providing for optimal wildlife habitat (Cline et al. 1980, Cline and Phillips 1983, Thomas et al. 1979). Snag density was higher than that reported for either Picea-Tsuga or Pseudotsuga forests in the Pacific Northwest, probably owing to a higher dominance by smaller, but more numerous and shade

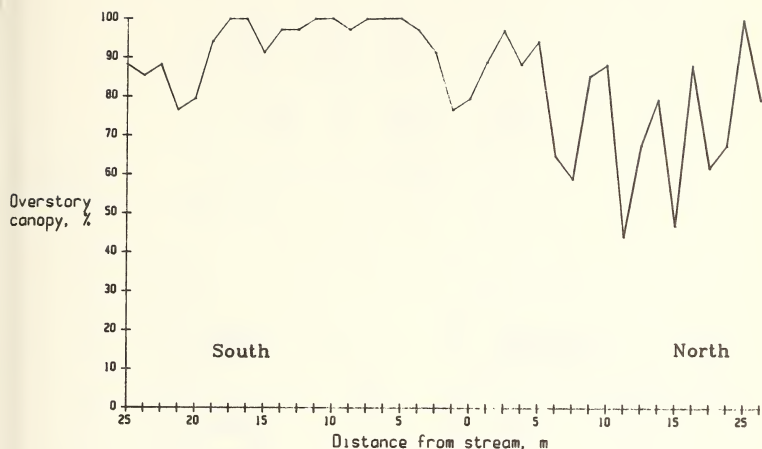


Figure 3. Variation in overstory cover across Jellybean Creek drainage.

tolerant *Tsuga* species in Alaska and perhaps a lower decay rate (Cline et al. 1980, Cline and Phillips 1979, Graham and Cromack 1982).

Understory vegetation biomass--A high degree of variability in understory biomass was found in relation to distance from the stream. This observation was consistent with other studies of coniferous mountain streams (e.g. Campbell and Franklin 1979). In general, shrub biomass was highest on the north side of the drainage, averaging 150-200 g/m² (Figure 5a). *Vaccinium alaskaense* and *V. ovalifolium* were the dominants on this south facing slope, forming almost continuous canopy coverage, sometimes 1.5 to 2 meters high. Shrub biomass was high adjacent to the stream, probably resulting from the canopy opening created not only by the stream channel but also by instability of the adjacent slopes. *Vaccinium* and *Rubus* growth and reproduction are particularly sensitive to changes in overstory canopy

Snags

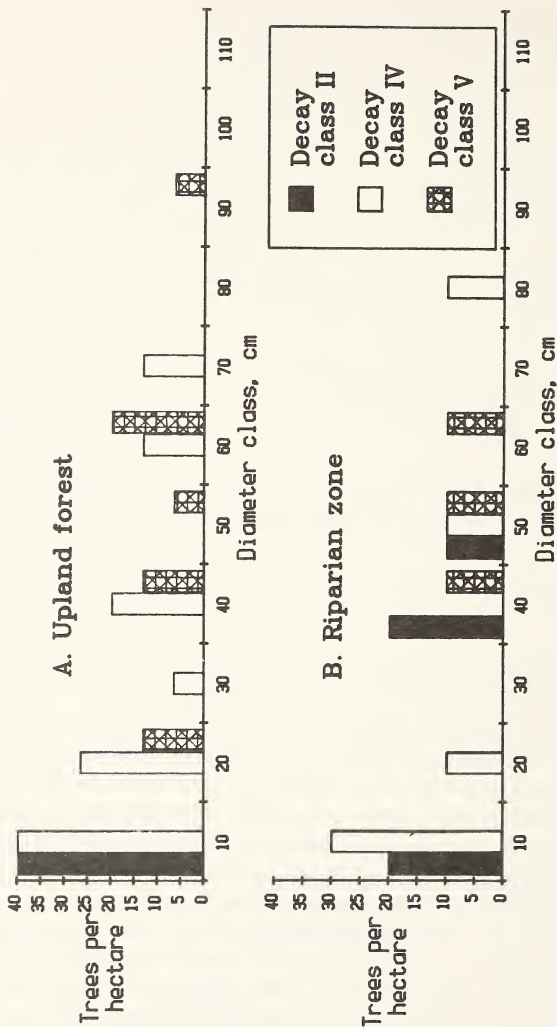


Figure 4. Size class distribution of standing dead trees in riparian and upland areas.

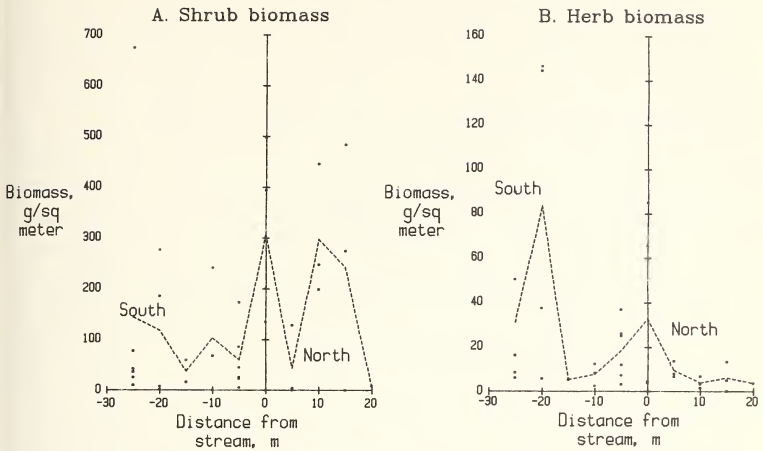


Figure 5. Variation in understory biomass across Jellybean Creek drainage.

density, reaching highest productivity levels in open areas (Alaback 1982a).

Herb biomass and productivity showed an inverse relationship to that of shrubs in most parts of the drainage (Figure 5b). Peak herb biomass generally occurred in seepages and wet microsites where *Lysichiton* and other large foliaceous species dominated the vegetation. A large seepage on the south side of the drainage was responsible for most of the peak in herb biomass. The second largest peak in herb biomass corresponded with that of the shrubs within 10 meters of the stream channel on the south side. Although direct overstory canopy cover was poorly related to understory productivity near the stream, much of the understory vegetation was adjacent to the large opening caused by the stream, and thus could have been influenced by diffuse radiation coming in from these adjacent gaps in the canopy. Decline in herb biomass on the north slope was probably influenced by shrub competition, especially the nearly impenetrable understory canopy of *Vaccinium* foliage on many parts of the slope.

Bryophyte biomass density was also greatest from about 5 to 10 meters from the stream. Here bryophyte biomass density averaged 700-1000 kg/ha, as compared to 370 to 450 kg/ha in dense forested sections and 500 kg/ha within 5 meters of the stream. Dominants were Rhytidiadelphus loreus and Hylocomium splendens.

Overall biomass of understory vegetation in the drainage was 2232 kg/ha for the upland areas, and 843 kg/ha for the riparian zone. This compares with 500 to 700 kg/ha for dense upland Tsuga dominated forests, and 1400 to 6000 kg/ha for open upland Picea-Tsuga forests in the region (Alaback 1982a). The study site had about double the understory biomass reported for the more productive Pseudotsuga and Tsuga forests in the Northwest (Cole et al. 1967, Grier and Logan 1977, Leslie et al. 1984) and about the same as coastal high elevation Tsuga mertensiana forests in British Columbia (Yarie 1980), and towards the high end for riparian vegetation studied in the western Cascades (Campbell and Franklin 1979). The highest proportion of herb biomass to total understory biomass was found within 10 meters of the stream, 18% versus 2.3% in the upland forest. This implies that the riparian zone may have a better balance of forage for wildlife such as Sitka black-tailed deer, which require a diversity of easily digestible herbaceous food rather than heavy woody species (Hanley and McKendrick 1985, Wallmo and Schoen 1980).

Understory species composition

The riparian zone was considerably more diverse and floristically unique than adjacent uplands. Sixty-three plant species were found in the study area; 23 unique to the riparian area and 8 unique to the upland forest (Table 2). The relatively unique flora of the riparian zone appears to be a function of edaphic factors combined with microclimatic restraints, such as a lack of light or low temperature. In open areas, many shrubby species generally thought of as indicators of the riparian zone such Oplopanax and Ribes flourished. In more heavily shaded sections of the stream these species were often absent.

The majority of species endemic to the riparian zone occur on wet microsites within 5 meters of the stream channel. Almost all of these species are herbs, and generally species that have been found to indicate more nutrient rich, productive habitats (Taylor 1932, Taylor 1935). Common exam-

TABLE 2. Understory biomass in relation to substrate, and vegetation zone. Values are grams m^{-2} . Only those species with biomass greater than $0.01 g m^{-2}$ in any given substrate are listed.

Species	----- Upland forest -----		----- Riparian zone -----	
	logs	duff root mound wet microsite	logs root mound wet microsite	logs root mound wet microsite
A. Trees and shrubs				
<u>Menziesia ferruginea</u>	22.26	0.37	-	-
<u>Oplopanax horridum</u>	3.24	-	43.32	47.39
<u>Picea sitchensis</u>	0.17	-	0.11	-
<u>Rubus spectabilis</u>	22.08	-	1.37	11.95
<u>Tsuga heterophylla</u>	2.77	0.05	5.07	0.05
<u>Tsuga mertensiana</u>	21.28	-	-	11.09
<u>Vaccinium alaskaense</u>	196.31	4.39	137.82	49.31
<u>V. parvifolium</u>	0.02	0.02	-	-
wood	174.61	-	136.58	80.65
foliage	67.69	1.30	5.62	20.65
twigs	25.83	3.53	2.17	7.40
Total	268.13	4.83	144.37	108.70
B. Herbs				
<u>Circaea alpina</u>	-	-	-	3.19
<u>Coptis asplenifolia</u>	1.71	2.31	0.23	2.53
<u>Cornus canadensis</u>	2.87	2.89	1.68	1.54
<u>Galium triflorum</u>	-	-	-	0.03
<u>Heracleum lanatum</u>	-	-	-	1.24
<u>Listera cordata</u>	-	-	-	1.00
<u>Lysichiton americanum</u>	-	-	-	0.03
<u>Lycopodium annotinum</u>	0.07	-	-	49.96
<u>Maianthemum dilatata</u>	0.07	-	40.65	0.00
<u>Moneses uniflora</u>	-	0.34	0.09	0.61
<u>Prenanthes alata</u>	-	-	-	0.00
<u>Ranunculus pacificus</u>	-	-	-	0.16
<u>Rubus pedatus</u>	2.67	2.01	0.98	0.44
<u>Stellaria crispa</u>	-	-	-	0.10
<u>S. roseus</u>	-	-	-	0.07
<u>S. streptopoides</u>	0.05	0.14	-	0.06

TABLE 2. Understory biomass in relation to substrate, and vegetation zone. (Continued)

Species	----- Upland forest -----		----- Riparian zone -----	
	logs	duff	logs	logs
<i>Tiarella trifoliata</i>	0.37	-	7.97	2.2
<i>S. amplexifolius</i>	-	-	-	-
<i>Viola glabella</i>	0.85	-	0.25	-
Total	8.66	7.69	57.58	2.6
C. Ferns				
<i>Athyrium filix-femina</i>	0.41	-	0.15	2.34
<i>Blechnum spicant</i>	1.10	1.56	1.64	-
<i>Dryopteris austriaca</i>	0.14	-	-	-
Total	1.65	1.56	1.79	2.34
D. Bryophytes, lichens				
<i>Conocephalum conicum</i>	-	-	0.04	-
<i>Dicranum fuscescens</i>	7.87	7.52	-	16.26
<i>Stokesiella oreganum</i>	0.63	-	2.34	3.77
<i>Hookeria lucens</i>	-	-	0.18	-
<i>Hyponomychia enteromorpha</i>	-	-	-	-
<i>Hylacomium splendens</i>	27.71	5.07	6.95	15.08
<i>Jungermanniales spp.</i>	0.03	-	0.02	-
<i>Lobaria spp.</i>	0.01	-	-	-
<i>Marchantia polymorpha</i>	-	-	0.04	-
<i>Plagiomnium insigne</i>	-	-	-	-
<i>Peltigera canina</i>	0.06	0.05	-	-
<i>Plagiothecium undulatum</i>	0.25	0.18	0.18	-
<i>Pleuroziopsis ruthenica</i>	-	-	-	-
<i>Polytrichum commune</i>	-	-	-	-
<i>Porella navicularis</i>	-	-	-	-
<i>Rhizomnium glabrescens</i>	0.81	1.34	2.45	7.05
<i>Rhytidiadelphus loreus</i>	28.35	1.31	8.17	3.40
<i>Sphagnum squarrosum</i>	-	-	5.40	2.65
<i>S. girgenzonii</i>	12.08	8.09	20.64	1.17
Total	77.80	23.56	28.11	32.51
Total understory	356.24	37.64	145.75	70.27
			225.39	0.39

ples include graminoides such as Bromus sitchensis and Carex as well as mesophytic herbs such as Circaea, Viola, and Heracleum. Bryophyte flora in the stream is also floristically unique including a host of species adapted to growing in the stream or the splash zone, and the edge of the stream. Pleuroziopsis ruthenica and Plagiomnium insigne are examples of such mosses. Many of these understory species are also characteristic of mesophytic riparian herb communities in the western Cascades (in addition to many other species not found in Alaska) (Campbell and Franklin 1979).

Understory rooting substrates--Forests and riparian vegetation in southeast Alaska is highly fragmented and forms a mosaic pattern across the landscape. For this study, four basic substrates in the upland forest and in the riparian zone were recognized: well decayed logs, duff, root mound, and wet microsite. Substrates in the duff category generally had the highest tree density and the least understory vegetation, although one hemi-saprophytic species (Moneses uniflora) was unique to the substrate (Table 2). Well decayed logs and forest floor were the most common substrate in the forest uplands, with the greatest diversity and biomass density. Root mounds included well decayed stumps which formed a mound of organic material covered by mosses. Many shrubs and tree seedlings were rooted on these mounds. Wet microsities were primarily distinguished by the presence of Lysichiton, and poorly drained anaerobic soil conditions. In the riparian zone, endemic species occurred on all but the well decayed logs substrate, but the majority were in the narrow belt of wet microsities adjacent to the stream.

Understory nutrients--Nutrient pools for the understory generally reflected differences in biomass distribution between the upland forest and the riparian zone (Figure 6). In the upland forest, 86% of the understory N pool was in shrubs compared to only 50% in the riparian zone. Tree seedling and shrub biomass were highly variable, leading to insignificant differences between zones for the macronutrient pools other than N ($P=.95$). For all other lifeforms differences in nutrient pools between zones were highly significant ($P < .05$) between zones. Relatively little phosphorus was stored by any species, generally 0.5 to 1 kg/ha.

Macronutrient pools were greater for herbs than for shrubs in the riparian zone. Herbs contributed about the same amount of nitrogen as did

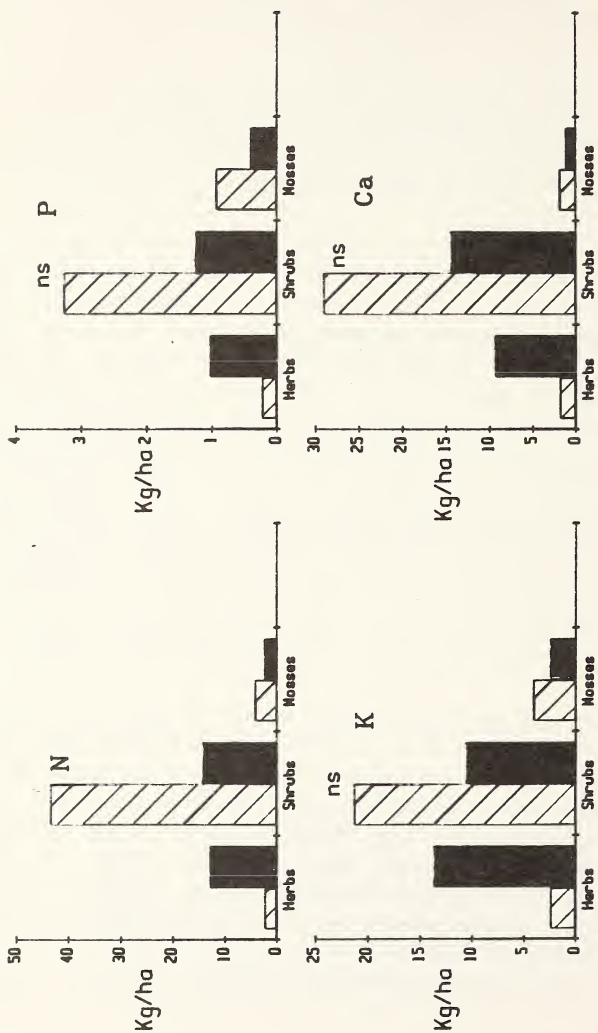


Figure 6. Macronutrient pools for understory vegetation in upland (hatched bars) and riparian (shaded bars) areas. All bars are significantly different at $P = .95$ except when marked with "ns".

Table 3. Understory productivity and annual nutrient uptake. All values in $\text{kg}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$. Standard errors of the mean are in parentheses.

Lifeform	Productivity	N	P	K	Ca	Mg
A. Upland forest						
Mosses	180.2(12.4)	1.1	0.24	1.2	2.9	0.7
Ferns	30.6(14.3)	0.2	0.02	0.2	0.1	0.1
Herbs	114.6(38.0)	2.1	0.20	2.1	1.9	0.5
Shrubs*	585.0(83)	13.2	1.19	6.9	9.4	2.2
Total						
	910.4(147)	16.6	1.65	10.4	14.3	3.6
B. Riparian zone						
Mosses	127.4(26.0)	0.8	0.13	0.8	0.4	0.5
Ferns	20.5(9.7)	0.6	0.60	0.7	0.3	0.2
Herbs	560.9(128.1)	10.1	0.96	13.4	9.2	2.2
Shrubs*	172.2(51)	3.7	0.30	2.4	3.3	0.8
Total						
	881(214.8)	15.2	1.99	17.3	13.2	3.7

* Does not include growth of woody stems, only annual growth of twigs and leaves. Based on studies of similar shrub species, this would add another 20-40% to shrub uptake (e.g. Whittaker 1962).

shrubs. Much of this difference in pattern between the zones was due to the abundance and richness of nutrient concentrations in the large fleshy herb, Lysichiton, which was most common in poorly drained sections of the riparian zone. In addition, the riparian zone had a high diversity of herbaceous plant species adjacent to the stream, many of which, such as grasses and sedges, are known to prefer nutrient rich environments. In the riparian zone, the most abundant macronutrients were N, Ca, and K. In the upland N was also the most abundant, but Ca and K were within 1-2 kg/ha of each other.

Other studies have reported similar macronutrient values for understory

vegetation. Tappeiner and John (1973) working in dense Corylus understories in the Midwest for example, reported 31 kg/ha for nitrogen, 5 kg/ha for P and 30 kg/ha for Ca. Turner et al. (1978) and Yarie (1980) also reported Table 3. Understory productivity and annual nutrient uptake. All values in $\text{kg}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$. Standard errors of the mean are in parentheses. similar levels for understories in low site Pseudotsuga stands in Washington and for coastal forests in British Columbia.

Manganese had the largest micronutrient pool in the understory, from about 0.3 kg/ha in riparian mosses to 2.5 kg/ha for shrubs in the upland forest region (Figure 7). More micronutrients were stored by shrubs growing in the upland forest than in the riparian zone. As with the macronutrients more micronutrients were generally stored by herbs in the riparian than the upland forest zone. Bryophytes were about the same in both areas. Copper was the least abundant element measured, from 0.002 kg/ha to 0.012 kg/ha. Herb accumulation of zinc and manganese exceeded that of the shrubs in the riparian zone, 1 and 0.023 kg/ha respectively. All micronutrient pools were significantly different ($P < .05$) between zones except for Zn in shrubs.

Annual uptake of nutrients by the understory ranged from 16.6 kg/ha/yr for nitrogen to 1.65 kg/ha/yr for phosphorus (Table 3). Total productivity of the understory was 778 kg/ha/yr in the upland forest, and 763 kg/ha/yr in the riparian zone. The three nutrients taken up in greatest quantity were N at 16.6, K at 17.3 and Ca at 14.34 kg/ha/yr. This productivity is almost ten times that reported for high site old-growth Pseudotsuga forests in the western Cascades (Grier and Logan 1977) and about the same as the more open of the sites studied in coastal British Columbia (Yarie 1980).

To make a rough estimation of the relative contribution of the overstory to vegetation nutrient pools, nutrient concentration data from litterfall in nearby southeast Alaska streams (Sidle 1985) and data from studies in the Northwest on the same tree species (Grier 1976) were applied to the biomass data. In the upland forest total nitrogen accumulation of foliage was estimated to be about 178 kg/ha, and about 300 kg/ha in the riparian zone. Understory nutrient pools for macronutrients were 3-7% of that for the overstory, and assuming productivity in the range of low-site Pseudotsuga, understory nutrient uptake was 10% or more that of trees. Similar contributions of understory vegetation to ecosystem nutrient pools and litterfall in other regions has resulted in substantial changes in

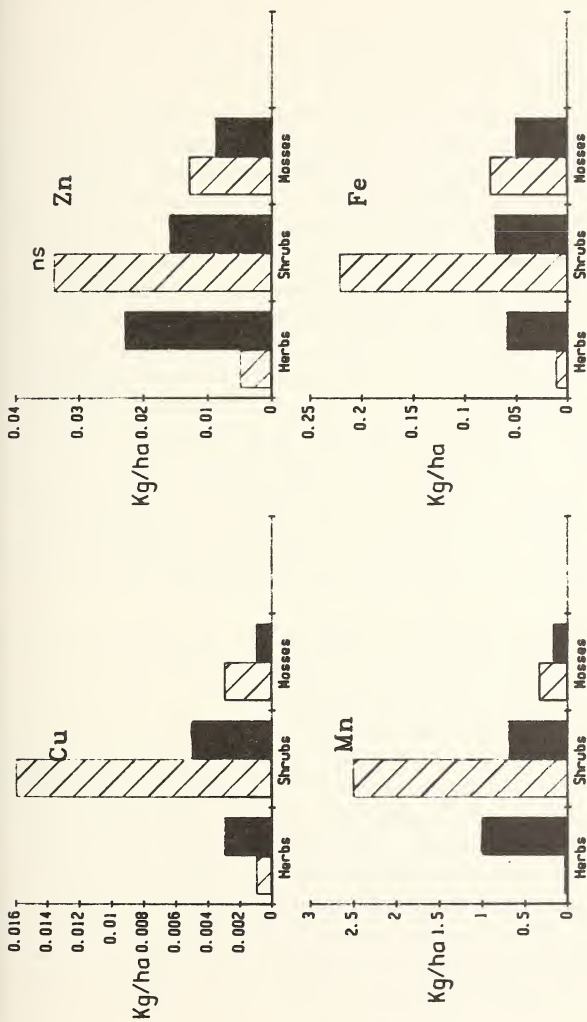


Figure 7. Micronutrient pools for understory vegetation in upland (hatched bars) and riparian (shaded bars). All bars are significantly different at $P = 0.05$ except when marked with "ns".

litter residence time and decomposition rates (Smith 1955, Tappeiner and Alm 1975, Yarie 1980).

SUMMARY AND MANAGEMENT IMPLICATIONS

As suggested by preliminary data from this study changes in composition and productivity of understory, especially herbs in the riparian zone and shrubs in the uplands, could have significant effects on cycling of nutrients in southeast Alaska. Levels of nutrients in the understory are similar to those reported for other regions having a woody shrub understory. If soil nutrient availability is low in this region of high annual rainfall and low growing season temperatures, the relative importance of the understory to the nutrient budget may be greater than for many other forest regions. In those regions in which the contribution of the understory to litterfall, soil formation, and nutrient dynamics has been documented, it was found to be significant (Tappeiner and Alm 1975, Yarie 1980). Typical old-growth forests in southeast Alaska have open canopies and high understory productivity (Alaback 1982a). Intensively managed forests will have only minimal nutrient inputs from understory vegetation due to reduced productivity. Increased rates of nutrient uptake by overstory trees in relation to nutrient mineralization may exacerbate the problem of reduced nutrient availability over the long-term (Kimmins 1977, Sollins et al. 1980).

Further work on decomposition, mineralization, and uptake of nutrients in the below ground system is needed to address key questions of how the understory contributes to ecosystem nutrient cycling. Unlike overstory trees, many understory species store a disproportionate quantity of nutrients and biomass below ground. Tappeiner and John (1973) for example reports 30-40% of Corylus biomass is stored underground as compared with 10-15% in overstory trees. Preliminary data on root to shoot ratios for the dominant clonal understory species in southeast Alaska also suggests about a third of total biomass is belowground for shrubs, and for herbs may be even higher (Alaback and Tappeiner, unpublished data). In Sweden, contributions of fine root turnover of ericaceous understory species was found to be important to nutrient dynamics in that system. Similar studies are needed in the cool wet environments of southeast Alaska to see if the same degree of

below ground activity is present and how it is effected by changes in community structure, productivity, and species composition.

The riparian zone is one of the most floristically unique and diverse habitats in the forests of southeast Alaska. Information on how management or natural disturbances effect the structure and nutrient dynamics of this zone are needed to compare with our undisturbed old-growth study site. Changes in species composition and structure between the riparian and upland forest zones significantly effect estimates of nutrient accumulation and uptake, and will have to be considered in future comparative nutrient cycling studies in the coastal Alaska region.

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DISCUSSION: Alaback Paper

Comment (Correll): I have a comment that maybe the other authors in this session could bear in mind. The riparian zone was defined as the area on either side of the stream from which significant amounts of leaf litter falls into the stream. I found this definition interesting. Maybe each of you could come up with your definition of how you used the term when you give your paper within this session. I don't know a good definition of riparian zone. Maybe we as a group could agree upon a definition of what a riparian zone is before the meeting is over.

Question (Whigham): How much perturbation can that riparian zone take before it is going to fall apart? In a managerial situation is it a hydrobuffer area or is it very prone to degrading quickly?

Answer: I think it really depends exactly on where you are. Some people argue that it can handle a lot of perturbation. A lot of the efforts in recent years by land management organizations to clean streams of organic debris for example are not very beneficial. If they are going to fall apart let them fall apart because of the beneficial effects of having that debris in the stream. A lot of people are for riparian zoning. In some cases riparian zoning is successional zoning. The riparian zone never really is stable.

Question (Fail): You mentioned that the upland area had a biomass roughly double the low riparian zone. Why is that? It would seem to me you wouldn't have a very high biomass.

Answer: Well, the tree density is much higher in the upland zone, the riparian zone has a lot of seeps and a lot of open areas where there isn't any tree regeneration at all.

RIPARIAN AREAS AS A CONTROL OF NONPOINT POLLUTANTS

J. R. Cooper, J. W. Gilliam, and T. C. Jacobs^{1/}

Abstract-The role of riparian areas in treating N, P, and sediment leaving the cultivated field was investigated. Four watersheds in two research projects on the Coastal Plain of North Carolina were studied.

One watershed with predominantly well drained soils in the cultivated fields lost an average of $35 \text{ kg ha}^{-1} \text{ yr}^{-1}$ of $\text{NO}_3\text{-N}$ past the field edge. But, only 5 and $8 \text{ kg ha}^{-1} \text{ yr}^{-1}$ of $\text{NO}_3\text{-N}$ and total N were lost in drainage water leaving the watershed. In natural drainage areas the low Eh and high organic matter content in the riparian area removed $\text{NO}_3\text{-N}$ from subsurface water by denitrification. Riparian strips as narrow as 16 m were effective in removing $\text{NO}_3\text{-N}$. Improved drainage systems that bypassed the riparian areas allowed more $\text{NO}_3\text{-N}$ to move into the stream. Denitrification in the cultivated fields with poor drainage lost little $\text{NO}_3\text{-N}$ at the field edge. The potential for $\text{NO}_3\text{-N}$ treatment of agricultural water in large flood plain swamps downstream was not needed because of treatment in riparian areas upstream.

The distribution and accumulation of sediment during the last 20 to 25 years were measured in two watersheds using the ^{137}Cs method. In Cypress Creek watershed 15 to 50 cm of sediment accumulated at the forest edge but only 5 cm were deposited on the flood plain swamp. More than 80% of the ^{137}Cs sediments deposited within the watershed was located in riparian areas above the flood plain swamp and about 50% of the ^{137}Cs sediment in riparian areas within 100 m of the exit location from the cultivated fields. Throughout the watershed, riparian vegetation controlled the erosion-deposition status of the ground surface. About 88% of the sediment leaving the agricultural fields during the last 20 years remained in the watershed. This watershed is thought to be representative of many head-water watersheds on the southeastern Coastal Plain where flow is intermittent and wide riparian areas are present.

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Most riparian areas below the cultivated field have been enriched in P. Extractable P concentrations decreased with distance through the riparian area. Assimilation and sediment reactions were assumed to have decreased P availability, but total P concentrations increased with distance into the riparian areas in part from the selective sorting of sediment particles. Equilibrium P concentrations (EPC) decreased in value from $110 \mu\text{g L}^{-1}$ in the cultivated field to $30 \mu\text{g L}^{-1}$ in the flood plain swamp. EPC values on the flood plain swamp were 2 to 3 times higher than ortho-P concentrations in the water during high stages of flow. EPC values on the flood plain swamp were more in equilibrium with ortho-P concentrations in base flow and isolated pools. The flood plain swamp has been a sink for total P but may be acting as a source for ortho-P.

Key Words: Riparian Areas, $\text{NO}_3\text{-N}$, P, Sediment, Nonpoint pollutants, ^{137}Cs .

INTRODUCTION

Nonpoint pollution from agriculture has received increased attention for its contribution to water quality degradation. It has been reported that more N leaves the cultivated fields than can be accounted for in the receiving streams (Gambrell et al., 1974; Thomas and Crutchfield, 1974). Similarly the amount of soil eroded from cultivated fields is much higher than sediment yield downstream (Johnson and Moldenhauer, 1970). Because of the high affinity of P for soil particles, P movement is strongly related to the erosion and transport of sediment. Very low amounts of the P added in a watershed as fertilizer pass through the streams as soluble P (Gburek and Heald, 1974).

In the southeastern Coastal Plain, the distance from the cultivated field to a major perennial stream may range from a few meters to several kilometers. The path of water leaving the cultivated field as surface runoff or as shallow ground water often flows through riparian areas of hardwood forest. The distribution of the bottomland forest is directly related to the unsuitability of the land for mechanized agriculture. Soil wetness, flooding potential, and slope restrictions in the drainageways

make the land undesirable for mechanized agriculture. These riparian areas provide an opportunity for water treatment before a major perennial stream is reached.

There is some controversy as to the importance of riparian areas with respect to water quality. Riparian vegetation has been reported to maintain stability of the channel and the quality of the water in both intermittent and continual flow systems (Karr and Schlosser, 1978). Filtering capabilities for P have been observed in flood plain swamps in the southeast (Brinson et al., 1981; Kitchens et al., 1975; Kuenzler et al., 1980). Similarly streamside forests have been observed to be effective in retaining N and P (Lowrance et al., 1983). However, Omernik et al. (1981) concluded that the forest buffer zones have reached the saturation point and had no significant long term effect on nutrient concentrations downstream.

This paper deals with those riparian areas that are positioned between cultivated fields and perennial streams. The definition of riparian area has been extended to include such areas as ephemeral streams, man-made ditches, and seeps at footslopes. Plant communities in these areas are the first to come in contact with surface and subsurface water leaving the fields. The more typical riparian areas such as intermittent streams and flood plain swamps are also addressed. The objective of this research was to observe the effect of the riparian area on the fate of nonpoint pollutants leaving the field domain and to relate this to water quality downstream.

METHODS AND MATERIALS

Watersheds - The watersheds in this research are located on the Middle (MCP) and Lower (LCP) Coastal Plain of North Carolina (Figure 1). All four watersheds have intermittent flow and are representative of the topography and cultural practices of the region. The MCP is moderately dissected with gently sloping uplands of well drained to moderately well drained soils. Soils and sediments in the riparian areas range from well drained at the forest edge to poorly drained in the flood plain swamps. The slopes of the

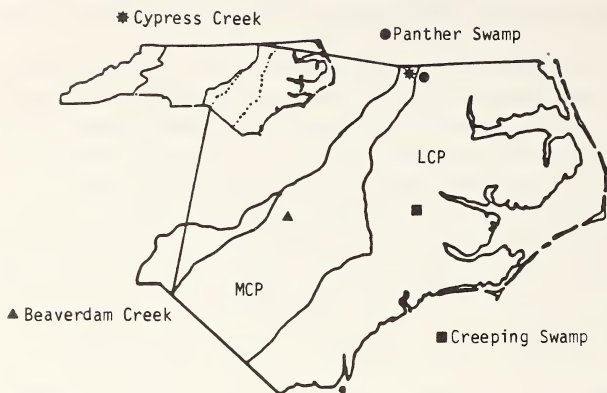


Figure 1. Watershed locations on the Coastal Plain of North Carolina.

adjacent valley walls are gentle to steep: up to 15 to 20%. A swamp is common in most bottomlands where the water table is at or above the ground surface during much of the year. The LCP is less dissected than the MCP. The broad upland plains often have high water tables and poorly drained soils close to the field edge. Similar to the MCP the main stream channels at the lower end of a watershed can have gentle to steep valley walls surrounding the flood plains and swamps below (Daniels et al., 1984).

Nitrogen - Beaverdam Creek watershed, located on the MCP, has 1299 ha and Creeping Swamp watershed, located on the LCP, has 6998 ha. These two watersheds were studied for the movement of N from the cultivated fields into the streams (Jacobs and Gilliam, 1983). In a 3 year study, shallow ground water movement of N from cultivated fields through the riparian areas and into the adjacent stream was monitored by well transects. Each transect location consisted of a series of wells ranging in depths from

0.4 to 4.5 m below the ground surface. Wells were sampled monthly or after rainfall events significant enough to raise the water table. Nitrogen movement in surface runoff was also measured by collecting samples during rising stages in the drainageways after each rainfall event.

Surface water samples were taken throughout the watersheds to monitor movement of N. Nitrate-N, $\text{NH}_4\text{-N}$, TKN, and Cl were determined in both well and surface water samples. The Eh in the riparian areas was also monitored by platinum electrodes. The drainage model, DRAINMOD (Skaggs, 1978), was used to partition drainage flow between surface and subsurface flow. Flow values were used in conjunction with nutrient concentrations to determine $\text{NO}_3\text{-N}$ losses from the field in surface and subsurface flow. Elevational transects of flood plain swamps were used to estimate the area of inundation with a given flow elevation at the stream gage. The streams in all four watersheds were gaged by the USGS and areas inundated at a given stage were computed by them.

Sediment - In a later study Cypress Creek (MCP) and Panther Swamp (LCP) watersheds were used to study the distribution of sediment and P from agricultural fields. Both watersheds have approximately 50% of the land in cultivation and 50% in forest. Cypress Creek watershed is approximately 1860 ha with about 11% in bottomland forest. Both watersheds were previously used in a 208 Best Management Practices (BMP) study. The distribution and accumulation of sediment was determined using $^{137}\text{-Cs}$ analysis by gamma ray emission in conjunction with soil and sediment mapping. Traverses running perpendicular to the drainageway were used to describe the soil and sediment profiles at various landscape positions.

Cesium-137 analysis by gamma ray emission was used to distinguish sediment deposited during the last 20 years from older sediments. The $^{137}\text{-Cs}$ from nuclear fallout was used as a tracer of sediment movement in the last 20 to 25 years. The high affinity of $^{137}\text{-Cs}$ for soil particles restricts movement in the soil profile. Therefore the major mode of watershed movement for $^{137}\text{-Cs}$ was by concomitant movement of the soil particle (Ritchie et al., 1974).

Morphological descriptions were used as an aid in interpreting the sedimentation history of a profile. Soils and sediments were sampled in 5 cm increments to a 40 cm depth. The layer of highest accumulation of ^{137}Cs was assumed to be the surface present during the 1963-1964 peak fallout period. The riparian areas were divided into depositional categories using landscape position and hydrologic behavior as the main criteria (Figure 2).

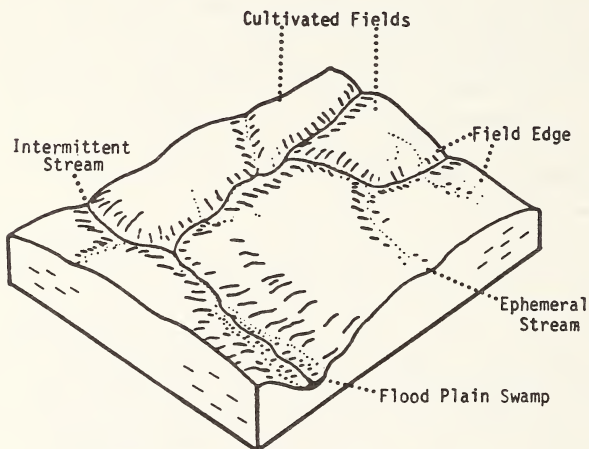


Figure 2. Block diagram showing depositional sites defined in Cypress Creek watershed.

Using areal estimations of each depositional category for the entire watershed, ^{137}Cs sediment depths, bulk density, and percent organic matter, the total mass of sediment on each depositional category was estimated.

The sediment delivery ratio was calculated for Cypress Creek watershed using 3 years of annual yield data from the 208 BMP study. The average annual yield was assumed to be the same for the last 20 years corresponding to the ^{137}Cs sediment period.

Phosphorus - Following the sediment survey, the redistribution of P in the 137-Cs sediment was studied using the same landscape categories. Sediments were sampled at 0 to 3 and 3 to 10 cm layers, air dried, and passed through a 2 mm sieve. Less intensively, soils and sediments were also sampled in 5 cm increments to a 40 cm depth. Total P (Nelson and Summers, 1972), 0.01M CaCl₂ extractable P, dilute double acid extractable P, pH, and the equilibrium phosphorus concentration (EPC) (Taylor and Kunishi, 1971) were run on the samples. The EPC of soil and sediment was determined by equilibrating samples with a 0.01 M CaCl₂ solution containing 0, 50, and 100 µg L⁻¹ ortho-P for 1 hour. Changes in P content in solution were graphed against initial water concentration to determine the water concentration where no net change in P occurred.

Using the sediment mass data and the average total P present on a depositional surface, the distribution of P in Cypress Creek watershed was calculated. This distribution represented the movement of P in the last 20 years.

RESULTS AND DISCUSSION

Nitrogen - The average amount of NO₃-N leaving the agricultural fields in surface and subsurface waters in Beaverdam Creek watershed is approximately 35 kg ha⁻¹ yr⁻¹. An example of the range of values measured is given

Table 1. Movement of N off cultivated fields and out of watershed.

Drainage Type	Field		Watershed*		
	Subsurface	Surface	NO ₃ -N	TKN	Total N
	NO ₃ -N		NO ₃ -N		
	kg ha ⁻¹		yr ⁻¹		
Beaverdam Creek	-----		-----		
Natural	21.4	2.2	5.1	3.2	8.3
Tile + V-Ditch	67.2	1.4			
Creeping Swamp					
V-Ditch	<0.1	1.6	1.6	6.2	7.8

* Losses for watershed are on a cultivated field basis.

in Table 1. The amount of $\text{NO}_3\text{-N}$ leaving the watershed in drainage water past the gaging station is approximately $5 \text{ kg ha}^{-1} \text{ yr}^{-1}$ (Table 1). This value has been corrected for the 52% of the watershed that is forested by assuming that each hectare of forest contributed $0.08 \text{ kg ha}^{-1} \text{ yr}^{-1}$ of $\text{NO}_3\text{-N}$ and $0.70 \text{ kg ha}^{-1} \text{ yr}^{-1}$ of TKN. Thus the amounts are presented on a hectare of cultivated field basis.

Movement of $\text{NO}_3\text{-N}$ from the cultivated fields in drainage water is approximately $30 \text{ kg ha}^{-1} \text{ yr}^{-1}$ higher than the amounts leaving the watershed in the drainage waters. The losses of $\text{NH}_4\text{-N}$ are less than $0.3 \text{ kg ha}^{-1} \text{ yr}^{-1}$ for both watersheds studied. Ammonium-N does not appear to be a significant form of N moving through the watersheds. There is a significant amount of organic N lost from both watersheds. However, there is little indication that the loss in $\text{NO}_3\text{-N}$ in Beaverdam Creek, between the field edge and the watershed boundary, is a result of conversion of $\text{NO}_3\text{-N}$ to organic N in the drainage water. The large loss of N between the field edge and the watershed boundary could be denitrification, or assimilation into biomass or organic material deposited within the watershed. Each of these will be discussed.

The upland soils in Beaverdam Creek watershed are well- to somewhat poorly drained. Improved drainage is not necessary in well to moderately well drained soils. In the wetter soils V-ditches and V-ditches with tile lines are often used. There is little effect of type of field drainage on the $\text{NO}_3\text{-N}$ content of water leaving the field, but a large effect is seen on the amount of N entering the stream (Table 2). The difference in field concentrations presented in Beaverdam Creek watershed is a result of differing cultural practices rather than the system drainage design. However, the type of drainage system has a large effect upon the $\text{NO}_3\text{-N}$ concentrations in water entering the surface waters. In Beaverdam Creek the natural drainage system has a yearly average of 0.2 mg L^{-1} of $\text{NO}_3\text{-N}$ moving into the stream. This value is much lower than the 5.4 mg L^{-1} of $\text{NO}_3\text{-N}$ which was measured in the improved drainage system.

The difference in $\text{NO}_3\text{-N}$ moving into the surface waters is related to the movement of subsurface water across the riparian area. Under natural conditions, surface water has to move through the poorly drained soils and sediments of the riparian area to reach the stream. The low oxidation-reduction potential (Eh values of 274 to 136 mV) and the high organic

matter contents (2 to 46%) provide an environment conducive to denitrification. Removal of $\text{NO}_3\text{-N}$ through assimilation by the riparian vegetation

Table 2. Mean $\text{NO}_3\text{-N}$ concentration across the well transects and surface water.

Location	$\text{NO}_3\text{-N}$ ---mg L ⁻¹ ---	$\text{NO}_3\text{-N/C1}$
Beaverdam Creek (MCP)		
Natural Drainage		
* Field	7.6 ± 1.5 ^{††}	0.68
* Field Edge	5.9 ± 3.7	0.55
+* Stream Edge	0.2 ± 0.5	0.03
Stream (10 m downstream)	0.9 ± 0.8	0.14
Improved (V-Ditch + Tile)		
* Field	16.2 ± 3.3	1.12
Tile Line	10.2 ± 3.5	.
V-ditch (in field)	6.5 ± 2.2	.
V-ditch (300 m downstream)	5.4 ± 3.1	0.62
Creeping Swamp		
Improved (V-ditch)		
* Field	1.9 ± 1.0	0.11
*Adjacent to V-ditch	0.3 ± 0.5	0.06
V-ditch (in field)	0.5 ± 0.8	0.14

[†]Riparian Vegetation, Buffer Strip 16 m wide before stream is met.

* Well $\text{NO}_3\text{-N}$ mean.

^{††} Standard Deviation.

is believed to account for a low percentage of the N removal because of the high amount of N moving through the small areas. The number of plants available to utilize the N cannot account for much of the $\text{NO}_3\text{-N}$ loss observed. Further support of N removal by denitrification is seen in the decrease in the $\text{NO}_3\text{-N}$ to C1 ratio upon crossing the riparian strip. Decreases in the $\text{NO}_3\text{-N}$ to C1 ratio from 0.55 at the field edge to 0.03 in the riparian strip suggest that a large amount of $\text{NO}_3\text{-N}$ is being lost as it passes through the riparian strip. Beyond the riparian area, the slightly higher $\text{NO}_3\text{-N}$ concentrations observed in the stream result from upstream inputs from cultivated fields with little to no riparian area between field and stream.

Buffer strips as narrow as 16 m are effective in removing a large percentage of the $\text{NO}_3\text{-N}$ from the water moving from the field. But under improved drainage agricultural water either bypasses the riparian area or has minimal time and area of contact, permitting a greater amount of $\text{NO}_3\text{-N}$ to enter the surface water.

Even with improved drainage some removal of N is seen as the ground water moves from the field into the surface waters. The tile line effluent concentration for $\text{NO}_3\text{-N}$ is lower than that in the shallow ground water drained by the tile line. Most of the shallow ground water movement is restricted to lateral flow with little deep seepage loss of N from the field. We suggest that low $\text{NO}_3\text{-N}$ in the tile effluent is from denitrification near the entry point of the tile line. Some removal of $\text{NO}_3\text{-N}$ may also occur as water moves laterally from the ditch banks into the V-ditch. Here the combination of organic debris and saturated conditions at the soil-water interface provide an environment suitable for denitrification. Organic debris and sediments in the bottom of the ditches may also provide some denitrification potential but residence time becomes the determining factor. During the low flows in summer, residence time, temperature, and contact of the water with the bottom sediments provide optimal conditions for the removal of $\text{NO}_3\text{-N}$ from the V-ditch water. The net result is that the concentration of $\text{NO}_3\text{-N}$ in water draining through the improved V-ditch is lower than the concentration of water entering the tile line or the $\text{NO}_3\text{-N}$ concentrations in the field ground water. However, the concentration

in the V-ditch drainage is considerably higher than the concentration of $\text{NO}_3\text{-N}$ in the natural drainage water.

In Creeping Swamp watershed, LCP, N movement from the field is limited mainly to surface runoff because of dense clay layers at a 0.5 m depth that restricts subsurface flow. The soils in the watershed are poorly drained and $\text{NO}_3\text{-N}$ movement off the cultivated fields even by V-ditch is not a problem. Denitrification in the field is probably the major removal mechanism as fertilization and other cultural practices are similar to those on the MCP.

In Creeping Swamp, the large flood plain swamp provides a great potential for removing $\text{NO}_3\text{-N}$ from water draining the cultivated fields. But, this potential is largely unused because only small amounts of $\text{NO}_3\text{-N}$ enter the swamp in the drainage waters. The large swamp areas in much of the North Carolina Coastal Plain are believed to have a small effect on the $\text{NO}_3\text{-N}$ concentration in drainage waters because of the very effective removal by the riparian areas adjacent to the agricultural fields.

Sediment -This section will concentrate on the results obtained from Cypress Creek watershed. In this watershed the uplands provide the necessary slopes (2 to 7%) and slope lengths to move measurable amounts of eroded soil off the cultivated fields and into the wooded bottomlands. Dense ecotonal vegetation at the forest edge provides a barrier to sediment movement into the forest. The thickest 137-Cs sediment deposits are observed at the forest edge (Table 3). Sediment deposits as deep as 0.5 m usually overlay a buried A horizon. A good correlation between the soil descriptions and the 137-Cs counts is found. Sand and aggregates are the predominant particle sizes at the forest edge. Forest edge deposits are most often part of an ephemeral stream drainage that originates in the cultivated field. The ephemeral streams are defined as first order in the watersheds and are located in the uppermost part of the drainage system. Surface flow is limited to periods during or shortly after a rainfall event. Annual plowing obscures the smaller, rill type, drainageways in the field, but the larger ephemeral streams have been left as field boundaries. Not all forest edge deposits are a result of the natural drainage system. Plowing and row direction often reroute field runoff onto the sideslopes. With no drainage path to follow, sediment is quickly deposited on the wide

smooth surfaces. Largest sediment accumulations are observed at these locations.

Table 3. 137-Cs activity with soil and sediment profile descriptions.

	Undisturbed Forest	Cultivated Field	Wooded Bottomland
	----- nCi m ⁻² -----		
Depth (cm)			
0	70.6	16.3	1.0
10	33.6	16.9	2.7
	6.6	17.3	4.3
20	1.7	16.8	7.0
	1.0	3.1	13.6
30	1.3	5.2	57.8
	1.1	1.7	14.4
40	0.9	1.2	2.3
Total	116.8	78.5	103.1

Vegetation at the forest edge often has first contact with agricultural runoff. Successive additions of sediment are sometimes stabilized by the forest edge vegetation producing an additional landform barrier^d to runoff. Some deposits at the forest edge are probably very transitory and during future rainfall events may be entrained and redeposited further downstream.

Inside the closed canopy of the forest the runoff path becomes less obstructed by floor debris and vegetation. The lack of forest floor vegetation is due to light restrictions imposed by the canopy trees. Where trees have been selectively cut, understory and floor vegetation is thick. Downstream the intermittent streams, second and third order, are reached. Flow in this category is dependent upon the location of the water table throughout the year. In the upper reaches of the smaller streams, no channel is dominant and water moves mainly by sheet flow. Low flow volumes on wide flat areas often provide an environment conducive to deposition rather than scouring. In the larger intermittent streams a well defined channel and flood plain are characteristic. The higher flow volumes and more erosive power of the water have cut a single dominant stream channel. Sand

and organic debris are the main depositional material in the major second order stream channels.

A subcategory of the intermittent streams is the upper basins. These sites are often a result of man's activity in the watershed such as farm roads crossing the drainageway. Whether it be a graded road structure or just rutting of the surface by tires, upstream ponding promotes deposition. Although these areas are small in extent and account for only a small percentage of the sediment deposition, they are academically interesting. Deposition at these sites ranges from 15 to 20 cm. Like the first order streams silt sized particles appear to be selectively deposited on these surfaces. Silt makes up to 80% of the particle size analysis (PSA) in many of these deposits. In locations where the upper basins are close to the field edge, sand makes up a large percentage of the PSA. Generally these areas are located in the upper region of the second order streams, where flow volumes are low and downcutting is shallow. Below the upper basins, flow is usually confined to stream channels.

The last landscape position identified before the perennial stream is reached is the flood plain swamp. Forest litter, tree roots, and perennial plants provide stability to the swamp surface. In many parts of the swamp, single channel flow has been converted into smaller channel and sheet flow which are more favorable to deposition. The 0 to 3 cm layer was sampled for chemical analysis because it defined a discrete layer of sediment and organic litter at various stages of decomposition. This mixture suggests a trapping mechanism for sediment. However, the accumulation of ^{137}Cs sediment on the flood plain swamp is less than 5 cm. Areas close to the main channel and depressions have accumulations up to 15 cm but these areas make up a small portion of the flood plain.

During the summer and fall, water flow through the flood plain swamp is mainly by subsurface flow in the deeper sediments. Lateral flow from the adjacent uplands has to cross the flood plain environment either on the surface or subsurface allowing for potential deposition and reaction to occur before the main channel is reached.

The total mass of sediment on each depositional site was determined for Cypress Creek watershed (Table 4). The study area was assumed to be repre-

sentative of the erosion and deposition of the entire watershed. Values presented are the medium estimations with high and low values being $\pm 30\%$ of the value presented. About 80% of the sediment deposited within the watershed is deposited in riparian areas above the flood plain swamp. Including 137-Cs deposited in intermittent streams along with ephemeral and forest edge deposits, over 50% of the sediment is deposited within 100 meters of the exit location from the field.

Table 4. 137-Cs sediment depth of accumulation, total weight distribution, and percent distribution in Cypress Creek watershed.

Location	*Sed. Accum. cm	+Total Weight Mg	Sed. Distrib. %	Silt ----- % -----	Clay -----
Forest Edge	15-50	2800	19	19	6
First Order Stream	5-20	2800	19	57	11
Higher Order Streams	5-15	5900	40	45	15
Flood plain Swamp	0- 5	3300	22	38	24
Total		14800	100		

*Redistribution of sediment in the last 20 years.

+Megagrams or metric tons.

Although water treatment capabilities have been reported for flood plain swamps, no data exist on sediment deposition rates. Sediment accumulations reported here for the flood plain swamp are less than 0.25 cm per year in Cypress Creek watershed. Sediment additions probably occur sometime during the high flow stages in winter. This is in contrast to the sediments at the forest edge that are deposited or eroded only in large runoff events throughout the year. Annual leaf fall aids in the quick incorporation of the thin sediment additions into the juvenile soil profile. Lack of good morphological differences causes difficulty in separating the 137-Cs sediments from older sediments.

Even with the thin sediment accumulations, over 20% of the 137-Cs sediment deposited in the watershed is deposited on the flood plain swamp. The much larger surface area available for deposition is more important than the depth of accumulation. The low sediment accumulations on the flood plain swamp are a result of the large riparian areas present upstream. Sediment from much of the uplands would have to travel at least 2 to 3 km through riparian areas to reach the swamp. Lateral additions of sediment and nutrients from adjacent fields are probably a more significant contributor to the flood plain swamp than the more distant uplands.

Using annual yield data from Humenik et al. (1983), a sediment delivery ratio (SDR) of 12% is estimated (Table 5). This value may be an underestimation of past erosion before the 208 BMP study since it does not include deposition within the field or at the edge. This low SDR value may be characteristic of many of the headland watersheds which have large riparian areas.

Table 5. Annual loss of sediment and nutrients in drainage water.

Watershed	Area ha	TN ----- kg ha ⁻¹	NO ₃ -N	ORG-N kg ha ⁻¹	TP -----	Sed.	Flow m ³ ha ⁻¹
Cypress Creek MCP	1858	2.1	0.12	1.42	0.21	56	3521
Panther Swamp LCP	2815	7.2	3.14	3.46	0.95	428	6083

From Humenik et al., 1983.

A second study area, Panther Swamp watershed, is located on the border between the MCP and the LCP and has characteristics of both. Panther Swamp was less intensively studied than Cypress Creek watershed. On the broad uplands little to no sediment movement could be detected for the 137-Cs period. Because of improved drainage in parts of the upland regions, cultivated fields are maintained to the channel edge. This allows a direct input of runoff into the stream. No estimate was made of the ephemeral

stream and forest edge deposits. The broad uplands make up about 60% of the 2815 ha in Panther Swamp watershed. The low slopes, 0 to 2%, do not produce measurable amounts of sediment at these sites. Erosion from the cultivated fields is not a problem.

Upper basins, second order streams, and small swamps are often located in the drainageways just off-field. As in Cypress Creek watershed, some of these areas are results of farm road placements but many others are due to poor natural drainage. Shallow channels are often cut through these areas in an attempt to improve drainage. In contrast to Cypress Creek watershed, second order streams are in much closer contact with the cultivated fields with less riparian vegetation between.

Downstream the increased volume of flow produces more downcutting into the lower Coastal Plain surface. The higher order streams, 3rd and 4th order, have well defined channels and large flood plain surfaces. The stream channel is 1 to 1.5 m deep and 2 to 3 m wide. Steep valley walls separate the flood plain from the uplands. At the base of the steep slopes, seep areas are observed forming small swamps. Flood plain swamps are small in size and scattered along the main stream valley. The flood plains are deeply dissected by the main channels allowing for good drainage. Flood plain swamps are often separated from the stream by a levee. Although the height of the levee is usually less than 15 cm, the width often separates the flood plain swamps from the main channel.

Deposition of 137-Cs sediment on the lower flood plain, 4th order stream, is 10 to 15 cm in depth. The series of buried A horizons is evidence of the past deposition on this surface. Below the 137-Cs sediments a buried surface that may have once behaved similar to a flood plain swamp is located.

Highway crossings appear to have a major influence on the location of the larger flood plain swamps in the Panther Swamp watershed. The decrease in cross sectional area available for water flow produces a damming effect. This effect is probably very important for maintaining the swamp environment in the drier parts of the year. When upstream channel flow comes into the influence of the road dam, flow is divided into smaller channel and sheet flow. Sediment accumulations of 10 to 20 cm are observed in these

areas. Near a bridge and downstream, a deep channel is usually cut in response to the concentration of flow.

Other activities in the watershed appear to influence riparian vegetation and the sediment distribution. The removal of bottomland forest for power line crossings allows a dense cover of grasses and brush to replace the trees. Although not measured, field observations suggest that these areas provide a better obstacle to sediment movement than the mature forest. Power line crossings appear to be most effective in the upper areas of a watershed where water flow volumes are low and channels are not well defined. A major factor not directly controlled by man is the activity of beavers. The beaver dams produce a stilling basin and promote deposition. Diffuse water flow through the structure lowers the hydraulic head without the resultant downstream erosion seen below bridges and culverts. Upstream ponding eventually kills the bottomland trees. With the removal of the dam structure, the beaver pool sediment will probably be readily available to downstream transport.

Phosphorus - Table 6 presents the average concentrations of extractable P and total P present over all sampled sites within a depositional category. The variability within a depositional category is very high as is evident from the standard deviations. The variability is due mainly to the different cultural practices in the fields and the different amounts and types of sediment and P coming off the fields. However, the same general trends are seen along the lines of sampling points leading from the field down into the drainageway. The total P concentrations increase with distance to the flood plain swamp. With the exception of the forest edge, all riparian areas below the cultivated field are enriched with respect to total P. In contrast to the total P behavior, extractable P concentrations decrease with movement through riparian areas. The dilute CaCl_2 extractable P was used to estimate the P that is readily available to runoff water. Once deposited in a riparian area, P and other sediment associated nutrients are available for assimilation and fixation reactions by plants and sediment. This decreases the availability to future runoff or erosion events. In areas of thick deposits, the availability of P to future runoff may be decreased by burying. This may allow enough time for the P to

Table 6. Extractable[‡] and total P by depositional position.

Location [†]	Cypress Creek Watershed		Panther Swamp Watershed	
	Ext. P	Total P	Ext. P	Total P
	----- $\mu\text{g P cm}^{-3}$ soil -----			
Cult. Field	2.24 \pm 1.32*	206 \pm 35	1.05 \pm 0.45	246 \pm 46
Forest Edge	0.13 \pm 0.04	172 \pm 113	-	-
First Order Stream	0.88 \pm 0.84	405 \pm 225	-	-
Intermittent Streams [‡]	0.63 \pm 0.56	597 \pm 200	0.72 \pm 0.45	567 \pm 244
Flood Plain Swamp	0.18 \pm 0.05	382 \pm 65	0.39 \pm 0.25	579 \pm 52

[‡]0.01 M CaCl₂ extractable P.

[†]0-5 cm depth for cultivated field, 0-3 cm depth for the other locations.

*Standard Deviation.

[‡]2nd, 3rd and 4th order streams.

undergo reactions in the soil and become less available before a future erosion event.

The dense growth present at the forest edge is an expression of the light availability rather than increased fertility. Deposits at the forest edge have the lowest extractable and total P values. This is partly a result of the selective sorting for sand at this location (Table 3). The deposited clay at many forest edge sites may be low in P, having less contact with P enriched water than sediments deposited farther downstream. The clay may also have originated from the B horizons in the soil and may be naturally low in P. Overall, most forest edge deposits are low in P and provide a potential sink for P leaving the field in future runoff events.

Clay and silt increase in the sediment downstream. The highest clay contents are observed in the flood plain swamp. The total P distribution

present in the 137-Cs sediments on each depositional category is presented in Table 7. Phosphorus appears to be much more mobile through the

Table 7. Total P distribution in 137-Cs sediments in Cypress Creek watershed.

Location	Total† P kg	P Distrib. %
Forest Edge	500	6
First Order Stream	1000	13
Intermittent‡ Streams	3000	37
Flood plain Swamp	3500	44
Total	8000	100

†Total P present in the 137-Cs sediments.

‡2nd, 3rd, and 4th order streams.

watershed than sediment. In contrast to the sediment distribution, most of the total P has been moved into the lower parts of the watershed. Over 40% of the total P in the 137-Cs sediments is deposited on the flood plain swamp. Expressed on an enrichment of clay basis or a surface area basis, the flood plain swamp values are lower than those of the riparian areas upstream. The low P values per surface area result from the shallow accumulation of sediment on the surface. The low clay enrichment suggests that some of the sediment deposited on the flood plain swamp is coming from soils and sediments that are low in P or that P is being flushed out of the watershed. Whether this is due to gully erosion in the cultivated field or erosion in the forest or streambank, the sediments of the flood plain swamp are a sink for total P. Although the amount of sediment deposition is low, the amount of P deposited is high because of the high percent clay in the sediments and the large area available for deposition.

Using the annual yield data of Humenik et al. (1983), about 0.21 kg ha⁻¹ yr⁻¹ of total P were removed from the Cypress Creek watershed in

the drainage waters. For the 137-Cs period, 7800 kg of P was removed from the watershed in 20 years. This is approximately the same amount of P found in the 137-Cs sediments deposited within the watershed boundaries. From this estimation, half of the P that has left the cultivated fields in the last 20 years is present in the sediments of the riparian areas. This is probably an underestimation of the P in the riparian area since P that has leached downward out of the 137-Cs sediments and P in the standing biomass are not considered in the estimate.

Table 8. Equilibrium phosphorus concentration by depositional position.

Location [†]	Watershed			
	Cypress Creek		Panther Swamp	
	Sediment	Water	Sediment	Water
	----- μg P L ⁻¹ solution -----			
Cult. Field	107 ± 42*	-	79 ± 33	-
Forest Edge	9 ± 3	-	-	-
First Order Stream	63 ± 55	-	-	-
Intermittent Streams	31 ± 19	10 - 20	33 ± 23	10 - 20
Flood Plain Swamp	36 ± 16	10 - 20	35 ± 27	10 - 15

[†]0-5 cm depth for Cult. Field and 0-3 cm for others.
 *Standard deviation.

The equilibrium phosphorus concentration, EPC, of the surface sediments (Table 8) estimates the concentration of ortho-P in the surface water that the sediments can maintain. Throughout the watershed the EPC of the sediments follows a trend similar to the extractable P. Highest EPC values are observed in the field and decrease with movement through the riparian areas. Lowest EPC values are measured on the flood plains and flood plain swamps.

The surface water concentrations of ortho-P average 10 to 20 $\mu\text{g L}^{-1}$ during the high flow stages of winter and early spring. With respect to the surface water concentrations during high flow, only the forest edge deposits appear to be sinks for runoff P (Table 8). All other depositional sites appear to be potential sources of ortho-P to the water. The EPC of the flood plain swamp is almost twice as high as the water concentration measured in the overlying water. But during summer and fall when flow is intermittent the ortho-P concentrations of flows and pools are 30 to 40 $\mu\text{g L}^{-1}$. The EPC of the 3 to 10 cm sediments are not significantly lower than the surface 0 to 3 cm with values averaging 27 $\mu\text{g L}^{-1}$.

In the winter, the soils and sediment of the flood plain and flood plain swamps may be a source of ortho-P when inundated. Contact time on the flood plains may be considerably longer than that in the stream channel. The drying of the sediment in laboratory analysis may have increased the availability of ortho-P in the poorly drained sediments. Although the sediments in the flood plain swamp never become as dry as in laboratory preparation, seasonal wetting and drying to different degrees do occur in the riparian areas. In an incubation study no significant release of ortho-P was observed when dry sediments were rewetted and anaerobic conditions were established. The small pH increases in incubation of 0.5 to 1 units suggest that the system is not controlled by Fe.

The effect of channelization on sediment and nutrient movement can be related to the lower region of the Panther Swamp watershed. The last 5 km of intermittent stream, 3rd and 4th order, have a wide channel cut deep into the flood plain. Although this is a natural channel, much of the flow is carried through it allowing for minimal contact with the flood plain or flood plain swamps. Higher annual yields for sediment, N, and P were reported by Humenik et al. (1983) for Panther Swamp (Table 5). Cypress Creek watershed has more than 6 times the area in flood plain swamp than Panther Swamp watershed. The importance of contact and size of the flood plain swamp may be evident in the amount of nutrients and sediment leaving the watersheds; however, effects of geomorphology, geology, soil types, and cultural practices must not be overlooked.

CONCLUSIONS

The effect of geomorphology and riparian vegetation on the water movement, deposition-erosion, and nutrient dynamics cannot be easily separated from each other. Each factor is interdependent on the other for the environment produced. Although unintentional, the land use pattern throughout the Atlantic Coastal Plain is fortunate from a water quality aspect since riparian areas in the bottomlands allow for the treatment of agricultural pollutants.

Riparian areas behave as chemical filters for $\text{NO}_3\text{-N}$. Much of the $\text{NO}_3\text{-N}$ treatment is subsurface denitrification in riparian areas near the field edge. The combination of poorly drained soils along with microbial and plant activity provide an environment conducive to denitrification.

The width of riparian vegetation needed for N treatment is uncertain but strips as thin as 16 m are effective in removing $\text{NO}_3\text{-N}$ from subsurface waters. Continued treatment by $\text{NO}_3\text{-N}$ removal occurs downstream but contact time and type of stream environment govern the treatment rate. The flood plain swamp provides the environment and contact time necessary for N treatment of water. However, the potential for N treatment is often not utilized because of treatment in riparian areas upstream.

The dominant effect of riparian areas with respect to sediment and P is by the control of sediment deposition. Wherever the unit power of the flowing water is decreased, sedimentation is promoted. The flood plain swamp provides an environment conducive to deposition of sediment and sediment associated nutrients. As in the case with N, the potential of the flood plain swamp for deposition may not be utilized because of deposition and water treatment in riparian areas upstream. Although the flood plain swamp has only thin accumulations of sediment, the large area available for deposition makes it important in sediment trapping. Silt and clay which have passed through the riparian areas upstream may be deposited in the flood plain swamps. These size fractions carry most of the sediment associated nutrients from the uplands.

The greatest losses of N, P, and sediment occur during the winter and early spring. The combination of bare fields, low evapotranspiration rate, and high volume of water flow allow more sediment and nutrients to be moved through the watershed. It is during this time that the plants and microbes

in the riparian area are least active. Lower temperatures less favorable to denitrification and dormant or dead plants provide less uptake of water and nutrients. However, it is during the high flow period that the flood plains and flood plain swamps are inundated and most active in deposition.

Riparian areas can act both as sinks and sources of sediment and nutrients. At present, the flood plains and flood plain swamps appear to be and to have been sinks for total P. However, these areas also appear not to be in equilibrium with the surface water during high flow stages and may be contributing ortho-P to the overlying water. Some of these areas that once served as sinks may have become saturated and are no longer improving downstream water quality on a long term basis (Omernik et al., 1981).

The critical agricultural areas in a watershed are the cultivated land in close contact with a perennial stream. The degree of contact between the cultivated field and the stream is related to width of riparian area through which the agricultural drainage must flow. Improved drainage either in the field or in the riparian area increases the contact between the cultivated field and the stream by bypassing the riparian areas. If the riparian areas can be protected by vegetation, then the contact between field and stream can be decreased. Both ephemeral streams and manmade ditches should be considered for their potential treatment of runoff and potential role as riparian areas.

Development or clearing of riparian areas will increase downstream inputs. Not only are the water treatment capabilities of the riparian areas lost, but these areas may become a source of nonpoint pollutants. Drainage of the areas decreases the $\text{NO}_3\text{-N}$ treatment capabilities. Channelization decreases residence time and contact time with the plants and sediments allowing a more direct delivery of sediment and nutrients downstream (Kuenzler et al., 1977). Clearing and development in riparian areas that have served as sinks for sediment and sediment associated nutrients may initiate erosion and the export of sediment deposited over many years. Selective cutting in riparian areas may maintain the successional stage of the riparian areas and maintain nutrient filtering (Lowrance et al., 1983). This may also provide more floor vegetation for the control of sediment movement in areas with thick canopies.

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DISCUSSION: Cooper Paper

Question (Correll): I noticed in your cesium-137 data that in the cases which were most clearly surface soils in the riparian forest the concentration of cesium was lower than in the plowed zones of the field. I wonder how that would happen? How did that most shallow zone of the soil in the riparian forest have a lower activity than the source?

Answer: Generally, that example I showed was at the edge of the forest where we had thick accumulations, generally dominated by sand. The cesium is more attached to the clay, the smaller particles which were being flushed through those areas and down into the second order streams and down into the flood plain swamps. The phosphorus and the other absorbed nutrients are transported along with the cesium.

Question (Correll): Were those cesium concentrations per mineral weight?

Answer: The cesium concentrations were on a surface area basin, volume of soil. We did that because when you go from the uplands into the bottomlands you are going from a mineral soil down to one of those soils that has mineral and organic layers. Some over here are organic, some over here are mineral. So your bulk densities can vary widely, and we had to express it on a volume basis.

Question (Pionke): When comparing these watersheds we are talking about streams that were not incised and those that were incised. I may have missed something, but it looks like you were comparing watersheds at two different scales that might be two quite different systems. In the sense that we talk about a relatively shallow channel upstream vs a deeper cut down stream. You are also talking about a system that is collecting a totally different source and distribution of groundwater return. When comparing the concentrations in these two streams with different channel systems, how did you eliminate some of these alternative things that are associated with different streams.

Answer: I really don't think that you can separate any of it. I was trying to point out some of the manmade features that separated flow from the riparian areas where they had been channelized through these swamp areas so that the flow could pass through rather quickly. Also the cutting of deeper channels where you had faster flow had lowered the water table. Also this situation we had where a deep channel had cut naturally through the flood plain so that the flow through the channel wasn't in contact with the flood plain except during high flow. You really can't ever compare two watersheds. Not really. We don't control anything out there. We are just looking at what is going on.

Question (Kuenzler): I have heard that if farm soils are receiving heavy loadings of fertilizer that the total phosphorus content of the soils should increase. If this is true and some soil is eroding away and being deposited then the phosphorus content of the sediments should increase from bottom up.

Answer: I think it would if you were trapping more clay, but the clay is being flushed out of the system. If you could trap more of that you might see that, yes sir.

Question (Pionke): First, did you analyze that zone with the denitrification potential? Second, did you have a sense of what the groundwater system was like?

Answer: Some incubation studies were done to measure the denitrification potential in these different areas. We have a very good handle on the water movement in those areas. These losses were estimated from a drainage model by Dr. Scagg at NC State, which estimated the movement of subsurface and surface water from these fields.

Comment (Gilliam): We have a good situation for denitrification and we get a lot. The ditches always have a much lower nitrate nitrogen concentration than the soil water just 2 or 3 meters into the fields.

Question (Correll): In general, how important is surface runoff during storms, and do you have any information on what happens to nitrate in surface runoff?

Answer: We did measure the surface runoff with continuing stage bottles to estimate how much was flowing from the field.

Question (Correll): In the creek channel? Or where?

Answer: In the drainage ways leading from the fields and also in the streams throughout the watershed. We also had on that graph subsurface and surface losses for the natural system which was 21 kg/ha subsurface and for surface it was about 2. So most of the nitrate loss was subsurface.

Question (Correll): Was most of the volume moving subsurface though?

Answer: Yes.

Question (Peterjohn): How did you calculate or estimate the mass of water moving from the edge of the field through the riparian forest? Did you use groundwater table slopes and Darcey's law, or did you do something else?

Answer (Gilliam): We measured the head each time period and we used a hydrologic model which has been very extensively tested and had been adopted by Soil Conservation Services as their model for groundwater movement. So that is an estimate. We had nutrient concentrations and then we simply used Drain Pond to get our surface distribution. We had infiltration measurements and a lot of other soil properties. We used these and then combined that with Drain Pond to get surface runoff and subsurface flow.

Question (Peterjohn): Did you have to make measurements from a hydrologic point of view at the site itself? Was it done in the field?

Answer: In the field. The calculations, as it turns out, are not that different. Even with one order of magnitude difference in conductivities you don't get that much difference. We did use Rain Water, which I think is a tremendous tool for this kind of thing. It has been proven to give fairly accurate predictions of where the water table is going to be for long periods of time.

ABOVE AND BELOWGROUND BIOMASS, PRODUCTION, AND ELEMENT ACCUMULATION
IN RIPARIAN FORESTS OF AN AGRICULTURAL WATERSHED

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Abstract - Plant biomass, production, and element accumulation were assessed in Georgia upper coastal plain riparian forests situated adjacent to agricultural uplands to test the hypothesis that riparian forests intercept mineral nutrients lost from upland agricultural areas.

Dominant overstory species within these forests were Acer rubrum, Liriodendron tulipifera, Magnolia virginiana, Nyssa sylvatica, and Pinus elliottii. The number of woody species at each site ranged from 16 to 36. Basal areas ranged from 24 to 54 cm²/m² and total woody stem density ranged from 4 to 18 stems/m².

Mean woody plant aboveground standing stock of biomass over six sites was 193,877 kg/ha and net primary production was 10,246 kg/ha/yr. Mean belowground biomass for two sites was 25,919 kg/ha (17% of total biomass) and fine root production was 2,841 kg/ha/yr. Trees within a riparian forest situated adjacent to, and receiving nutrients from, an upland pigpen had aboveground production rates 1½ times the average rate over all sites. Aboveground growth rates of individuals of select species within this and other forest sites lying adjacent to cropped lands (forest "test" sites) were significantly higher than rates for the same species in other sites where the riparian forest zone was separated from the cropped uplands by an intervening grass zone (forest "reference" sites). Fine root production in a test site was also 1½ times the rate found on a reference site.

Comparison of forest plant tissue nutrient concentrations from test sites with tissue nutrient concentrations from reference sites shows that forest plants lying adjacent to upland croplands or pigpen areas have higher wood and leaf nutrient concentrations than forest woody plants lying adjacent to little used pasture or grass areas. Mean N, P, K, Ca, and Mg wood concentrations over all sites were 8499, 588, 3161, 5952, and 923 ppm, respectively. Mean leaf concentrations were 21,548, 1250, 9369, 10,266, and 3809 ppm, respectively.

Higher and statistically different overall aboveground woody tissue ash, nitrogen, and leaf phosphorus concentrations were noted in Site 2, the pigpen test site. Significantly higher concentrations of N, P, and K were noted in above and belowground tissues, as well, within select species in test sites as compared to reference sites.

Woody plant aboveground standing stocks of N, P, K, Ca, and Mg averaged 1590, 114, 576, 1233, and 189 kg/ha respectively, over five sites, with substantially higher levels of tissue nutrients in plants from Site 2, the pigpen site. Belowground standing stocks of N, P, K, Ca, and Mg averaged 145, 16.5, 79, 36, and 19 kg/ha, respectively, over two sites.

Significantly higher accretion rates of nutrients were noted for the forest lying adjacent to the pigpen when compared to the other four sites. Mean annual aboveground nutrient accretion rates for woody plants over five sites for N, P, K, and Ca were 52, 3.8, 19, and 40 kg/ha, respectively, but at Site 2 the rates were 98, 6.9, 37, and 80 kg/ha, respectively. Mean belowground nutrient uptake rates for fine roots over two sites were 48, 4.2, 32, 3.9 kg/ha, for N, P, K, and Ca, respectively. Root uptake rates were 1.3-2.2 times greater in a test site compared to a reference site.

Fine root decomposition rates were higher in a test site compared to a reference site.

Key Words-agricultural ecosystem, agricultural watershed, bottomland forests, forests, forest production, forest nutrients, nutrient cycling, nutrient filters, riparian forests, root biomass, root decomposition, root production, tissue nutrients

INTRODUCTION

Although farmlands possess all the characteristics outlined by Odum (1969) as defining ecosystems, agriculture has only recently been considered from an ecosystem perspective by the scientific community. A conceptual basis for such consideration is provided by Azzi (1956), Major (1969), Odum (1969), De Soet (1974), Harper (1974), Cox and Atkins (1975), Loucks (1977), and Lotspeich (1980). Loucks (1977) lists six properties which distinguish agricultural systems from other ecosystems: 1) maximum productivity is the dominant goal, 2) monocultures, 3) perturbation, 4) addition of nutrients,

5) exports of biomass and nutrients, and 6) heavy nutrient leaching losses. Since agricultural systems are managed for crop export, the increased nutrient output requires increased nutrient input. These periodic nutrient inputs tend to generate excesses of nutrients at times that are added (leaked) to other systems as wastes (Loucks, 1977).

The Tifton Agricultural Ecosystem Project, was concerned with the transfer of nutrients within an agricultural ecosystem, and especially with the fates of unutilized nutrients added to (and "leaking" out of) upland agricultural areas. Among the several possibilities of these fates, this report is concerned with nutrients which may be lost from uplands, transferred to lowland vegetation, and subsequently taken up and accumulated in forest biomass.

Several studies (Aubertin and Patric, 1974; McColl, 1978; Asmussen et al., 1979; Nutter et al., 1979; Hirose and Kuramoto, 1981; Caporali et al., 1981; Cooley, 1982) have provided evidence of the ability of forested watersheds or forested buffer strips along streams to reduce nutrient levels in stream waters. Schlosser and Karr (1981) found that when riparian vegetation is maintained in areas of extensive agriculture, stream suspended solid levels are lower, and they suggested that efforts to improve water quality in agricultural watersheds should emphasize maintenance of riparian vegetation.

Recently hydrologic and nutrient budget data from the Tifton Study have been discussed in the literature (Lowrance et al., 1983; 1984a,b,c; 1985) and have offered evidence that nutrients are hydrologically transported from upland agricultural areas to lowland (riparian) forests. Further, the data have given support to the hypothesis that riparian forests may act as "nutrient filters" in agricultural environments.

This report focuses on the riparian vegetation within an agricultural watershed and in particular, combines the separate studies of the above and belowground forest biomass and tissue nutrient data in an attempt to provide a synthesis of the role of the riparian forest vegetation as a nutrient filter in an agricultural environment.

MATERIALS AND METHODS

Study area - The vegetation investigation of the Tifton Study was carried out at six riparian forest sites within the watershed located along the Heard Creek tributary (USDA Watershed N) of the Little River in south

central Georgia near the town of Tifton, Georgia (Figure 1). About 45% of the area is devoted to row crops, 15% to pasture, 25% to roads, residences, and pine forests, and the remainder (about 30%) is composed of riparian forests (Lowrance et al., 1983).

The watershed is underlain by an impermeable clay layer, the Hawthorne Formation (Rawls and Asmussen, 1973), which directs the subsurface movement of the 1200 mm of annual rainfall laterally towards lowland streams. Because of this aquiclude, all nutrients in streamflow either originate in or pass through, the riparian forest zone.

Within the 1568 ha Heard Creek watershed six sites were chosen for study. Three (Sites 2,4,5) were considered "test" sites (Figure 2) because the riparian forests were located directly adjacent to upland agricultural areas. The Site 2 forest was situated adjacent to an upland pigpen and Sites 4 and 5 were adjacent to croplands.

Three other sites (1,3,6) were considered "reference" sites because the riparian forests were separated from upland crop areas by pine forests (Site 1) or grassfields (Site 3) or both (Site 6).

A semi-permanent 10 m x 10 m grid system was laid out within each forest oriented such that rows of 100 m² quadrats paralleled the stream and columns were perpendicular to it. All samples were referenced as to their position within the grid.

Aboveground vegetation - The aboveground vegetation study consisted of three major components: community structure, production estimation, and tissue nutrient concentration determination. Data from the three components were merged to form estimates of annual nutrient accumulation and nutrient pools.

Community structure of woody species and diameter at breast height (DBH) for individual stems were determined for each site with the sampling stratified into tree (>9.9 cm DBH), sapling (>1.1 cm - 9.9 cm DBH), and shrub layers (<1.1cm DBH). Within each site 50-60% of all 10 m x 10 m quadrats were sampled, the community structure determined, and importance values (equal to 200) calculated based on relative density and relative dominance according to methods outlined by Oosting (1956) and Phillips (1959). Nomenclature follows that of Radford, Ahles, and Bell (1968).

Biomass and production estimates for each site were determined by semi-destructive sampling methods described by Reiners (1972), Whittaker (1966),

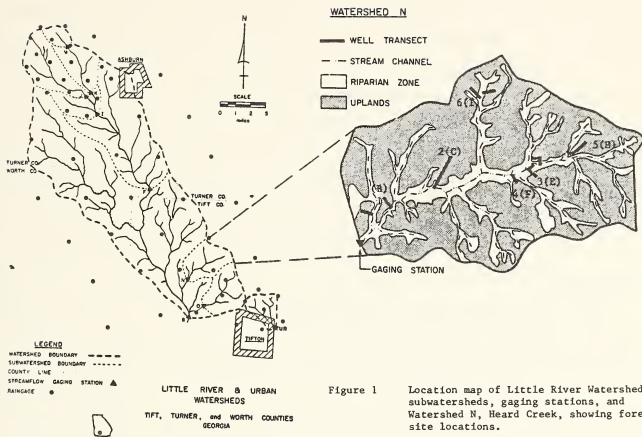


Figure 1. Location map of Little River Watersheds.

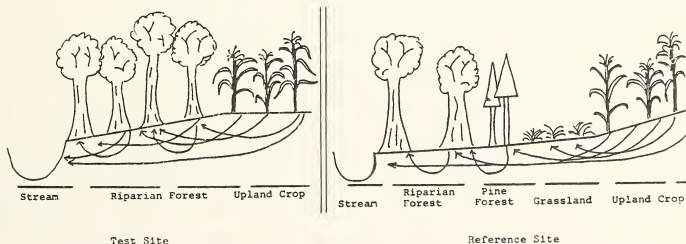


Figure 2. Site schematic indicating relationship between uplands and riparian forest zones for test and reference sites.

Whittaker and Woodwell (1969), and Schlesinger (1978). Samples were obtained from the principal species at each site and all samples were referenced to the grid system. Within sites 2 through 6, tree cores and 267 tree limbs of various sizes ranging from about 1 cm to 6 cm diameter at the base were harvested from 140 trees of predominate species and of a range of tree diameters. Tree heights of these 140 trees were determined by use of an inclinometer, and the number of limbs within three size classes were visually tallied. Wood and leaves were air-dried for one month at about 37°C, then oven-dried at 60°C to constant weight, the dry weights recorded, and the diameter at limb base measured. Tree cores were dried, aged, then wood density determined by measuring dry weight per unit volume.

The method of tree biomass and production estimation is based on parabolic volume calculations described by Reiners (1972), Whittaker (1966), and Schlesinger (1978). This method was used to calculate volumes of the 140 trees for which height, diameter, and wood density were recorded, and from which limb samples were harvested. Log (base 10) volumes calculated by this method were regressed against log DBH values, and the resulting regression equation was used to estimate bole volumes. Bole biomass was calculated by multiplying volume by wood density, then separate log-log regression equations were calculated for the 267 harvested tree limbs and the resulting estimated biomass added to the estimated bole biomass. Equations were generated from these operations to estimate component, whole tree, and shrub biomasses, and DBH information on all measured trees and shrubs within each forest were entered into them. The result was an estimate of total above-ground forest wood and leaf biomass for each site. Production was estimated by dividing estimated whole tree biomasses by the average age of each forest.

Tissue nutrient concentrations for whole trees were determined from limb samples used for biomass estimation. Nutrient concentrations for shrub and sapling plants (up to about 6 cm DBH) were determined from a mix of finely ground branch and bole wood tissue and from dried leaf tissue for each sampled individual. Wood and leaf samples were ground to powder and tissue N, P, K, Ca, and Mg in terms of parts per million (ppm) of dry tissue were determined for 1300 samples. Tissue N was determined by the micro-Dumas technique (Gustin, 1960; Bremner and Tabatabai, 1980) in a Coleman Model 29 nitrogen analyzer. Cations and P were analyzed by using plasma emission spectrophotometry (Isaac and Kerber, 1980).

Standing stocks (pools) and accretion rates of N, P, K, Ca, and Mg were calculated by multiplying mean tissue nutrient concentrations expressed as percentages and sorted by site and species, by the calculated summed or mean biomass and production estimates also sorted by site and species.

Production estimates and tissue nutrient concentration data were subjected to statistical tests using the F-test at the 95% probability level and the Duncan's multiple range test (Duncan, 1975). Differences were tested between sites without regard to species and between sites for four "test" species. The four test species used were Acer rubrum L., Liriodendron tulipifera L., Magnolia virginiana L., and Nyssa sylvatica Marshall.

Belowground vegetation - Site 4, a test site, and Site 6, a reference site, were selected for the belowground vegetation investigation. This investigation also consisted of three major components: biomass and production estimation, tissue nutrient concentration determinations, and estimation of decomposition rates.

Biomass of large roots including crown, tap, and large support laterals was estimated using regression equations developed by Harris et al. (1973) and McGinty (1976), and inserting DBH data (≥ 2.5 cm) obtained from this study (Fail, 1983) as the independent variable. Biomass of lateral roots beyond 60 cm radius of tree trunks was estimated by excavating ten soil pits per site of dimensions 30 cm x 30 cm.

Fine root (≤ 5 mm diameter) biomass was estimated by use of 4.5 cm diameter steel corers inserted down to a depth of 30 cm, and the biomass determined for three levels: 0-10 cm, 11-20 cm, 21-30 cm. Sampling was random along permanently marked rows 0.6 m wide and 30 m long in each site. Soil cores were washed to remove soil, and living and dead roots were separated on the basis of texture and visual appearance and the living root fraction oven-dried at 55°C to constant weight, ground to powder, and N, P, K, Ca, and Mg concentrations were determined according to methods outlined by Allen et al. (1974) and Jones (1977).

Fine root production was estimated by the soil block technique described in detail by Hamzah et al. (1983). Production estimation was restricted to fine roots. Nine soil blocks of dimensions 20 cm x 5 cm x 10 cm were removed from each row within the two sites by using a steel corer. The blocks were then covered with 4 mm nylon mesh netting and returned to their original

locations. Any root growth into the blocks over five 85 day sampling periods (June 1980-August 1981) represented root production. After each core collection, the soil was analyzed for nutrient composition to determine if there was any increase of soil nutrients from decomposition of detached roots within the blocks that might favor root production.

Decomposition estimates were made on both a seasonal (Site 6 only) and cumulative basis (Sites 4 and 6). For the cumulative estimates, which is the basis for the data in this paper, forty-five perforated aluminum tubes (4.5 cm x 15 cm) were randomly driven into the ground along each of two rows paralleling the stream channel and located at 3 (row 1) and 18 (row 2) meters from the channel. The rows were located 25 m and 10 m, respectively, from the cropped field boundary at the test site (4) and 217 m and 202 m, respectively, from the cropped field boundary at the reference site (6). Nine of these tubes were immediately recovered. Samples were pooled by rows, washed, and dried to estimate root biomass, and nutrient contents of root tissue were determined for each pool of samples. There was no separation of live and dead roots for the decomposition study. After 89, 165, 250, and 343 days, nine tubes per row per site were collected and similarly treated.

Tissue pools of nutrients were calculated by multiplying biomasses within tubes and blocks by their determined nutrient concentrations expressed as percentages.

Nutrient analyses of tissue followed standard methods according to Allen et al. (1974) for determination of tissue Kjeldahl nitrogen, and methods of Jones (1977) for determination of tissue P, K, Ca, and Mg.

Statistical differences between sites were determined using the F-test and the Duncan's Multiple Range Test (Duncan, 1975).

RESULTS AND DISCUSSION

Community structure - The species composition of the forests of this study is similar to that found by Harper (1906) in a monograph describing riparian forest community structure in central Georgia. Five species - Pinus elliottii Engel. (slash pine), Acer rubrum L. (red maple), Liriodendron tulipifera L. (yellow poplar), Magnolia virginiana L., and Nyssa sylvatica Marshall (black gum) - make up 83% of the overall basal area of all sites. The last four of these species, termed "test" species, are used for site comparisons

of biomass and nutrient data. The importance of these test species in each site is summarized in Table 1. Test species importance varies widely among sites and a summary of species importance indicates degrees of both differences and similarities between sites which are considerations of some importance in community structural assessment in general (Monk, 1968) and nutrient cycling studies in particular. Determination of species composition is essential in comparisons of nutrient cycling data between different sites.

The ages of the forests range from 22 years to 35 years and the mean is about 27 (Table 2). Site woody plant density ranges from 4 to 18 individuals per m^2 and basal areas range from $20 \text{ cm}^2/m^2$ to $50 \text{ cm}^2/m^2$ (Table 2).

Biomass and production - Odum (1962) has noted that, "...the only way man can have both a productive and a stable environment is to insure that a good mixture of early and mature successional stages is maintained with interchanges of energy and materials." The cropland-riparian forest agricultural system in the south central Georgia coastal plain is an example of a closely integrated mixture of young successional cropland lying adjacent to more mature riparian forest communities. This section of the investigation is concerned with relationships between early and mature successional stages, particularly the possible effect of upland agricultural activity on lowland forest production.

Aboveground woody biomass and primary production estimates for sites 1 through 6 are given in Table 3a. Mean aboveground wood biomass is estimated at about 190,000 kg/ha which is within ranges cited for other temperate forests (Ovington, 1965; Dabel and Day, 1972; Reiners, 1972; Johnson and Bell, 1976; Rolfe et al., 1978; Schlesinger, 1978; Reynolds et al., 1978; Brown et al., 1978).

Belowground and total biomass estimates were made for Site 4, a test site, and Site 6, a reference site (Table 3b). The mean root biomass for the two sites is about 26,000 kg/ha, but the reference site has an estimated 50% more root biomass than the test site, and that site also has substantially more aboveground biomass as well (Tables 3a and 3b). Root biomass accounts for about 17% of the total biomass at both sites, and although in the low range of literature estimates (Santantonio et al., 1977; King and Schnell, 1972), seems reasonable because the same estimation approach was used by Harris et al. (1973) for a Liriodendron tulipifera forest in Tennessee, and that is

Table 1. Summary of test species (Acer rubrum, Liriodendron tulipifera, Magnolia virginiana, and Nyssa sylvatica) importance values (out of total = 200) by site (Fail, 1983).

Species	Site						Mean
	1	2	3	4	5	6	
<u>A. rubrum</u>	19.8	19.6	6.8	68.5	4.7	4.5	20.6
<u>L. tulipifera</u>	1.6	19.5	30.7	49.8	10.5	23.1	22.5
<u>M. virginiana</u>	2.1	13.0	9.9	19.1	14.7	1.9	10.1
<u>N. sylvatica</u>	10.3	46.7	14.4	0.6	22.4	6.6	16.8
% of Total Importance Value	17	49	31	69	26	18	35

Table 2. Select riparian forest stand characteristics, by site (Fail, 1983).

Site	Mean stand age (trees/saplings ≥ 3.0 cm DBH) (±S.E.)	Total number of woody Species	Density stems/m ²	Basal area cm ² /m ²
1 (reference)	27.8 (2.6)	36	17.8	31.4
2 (test)	35.2 (2.6)	21	4.2	54.1
3 (reference)	28.8 (2.6)	35	13.2	38.2
4 (test)	22.0 (2.4)	16	11.0	19.6
5 (test)	23.7 (3.2)	22	11.4	28.7
6 (reference)	27.4 (1.6)	25	6.0	24.5
Mean, (±S.E.)	27.4 (1.9)	25.8 (3.3)	10.6 (2.0)	32.8 (5.0)

Table 3a. Woody plant aboveground biomass and production estimates, by site.

Site	Wood biomass kg/ha	Leaf biomass kg/ha/yr	Wood production kg/ha/yr	Total production kg/ha/yr
1 (ref)	153,378	4,740	5,000	9,740
2 (test)	397,463	4,090	11,230	15,324
3 (ref)	197,816	4,080	6,750	10,831
4 (test)	92,076	2,340	4,150	6,494
5 (test)	160,060	3,810	6,800	10,610
6 (ref)	162,496	2,640	5,830	8,474
Mean, (\pm S.E.)	193,882(43,048)	3,617(380)	6,627(1,011)	10,246(1,215)

Table 3b. Distributions of forest woody plant biomass for Site 4 (test) and Site 6 (reference), kg/ha. Values in parenthesis indicate per cent of total biomass.

	Site 4 (test)	Site 6 (reference)
Aboveground biomass	94,416 (82.2%)	165,136 (83.9%)
Wood	92,076 (80.2%)	162,496 (82.6%)
Leaves	2,340 (2.0%)	2,640 (1.3%)
Belowground biomass	20,345 (17.8%)	31,592 (16.1%)
Stump roots	11,275	17,122
Lateral roots	9,075	14,470
Total woody plant biomass	114,761	196,728
Root/Shoot ratio	0.2	0.2

an important species in these forests as well. Also the same proportion of stump and lateral roots (each about 50% of root biomass, Table 3b) was noted in this and at least two other studies (Harris et al., 1973; McGinty, 1976)

The low proportion of roots to shoots (Table 3b) has been suggested to be a type of plant response to high fertility environments (Head, 1973; Roger and Vyvgan, 1934) and to wet or mesic sites (Monk, 1966).

Biomass production is an important ecosystem attribute because it is closely interrelated with the fate of incoming nutrients. That is, plant biomass could reasonably be expected to increase at a relatively faster rate when the nutrient environment is relatively richer. Mean net primary production (not including standing dead vegetation or aboveground decomposition) for six sites is about 10,000 kg/ha/yr, but is 50% greater at Site 2 (Table 3a). That is the site considered to be most heavily impacted by upland nutrient losses due to the presence of a constantly occupied adjacent pigpen. The estimates, in general, are within ranges reported by other investigators for riparian and lowland forests (Reiners, 1972; Conner and Day, 1976; Johnson and Bell, 1976; Brinson et al., 1978, Schlesinger, 1978; Brown, 1981; Brown and Peterson, 1983).

Aboveground production was also calculated for individual stems without regard to area for the four test species. Higher and statistically significant individual stem production rates were noted for all the test species in various of the test sites (2,4, and 5). Data for one of the species, Liriodendron tulipifera, are presented in Table 4a, and at Test Site 2 the average individual had a net annual biomass increase of nearly 9,000 grams which is significantly different from the other sites.

Belowground production of fine roots was estimated by the soil block technique developed by Hamzah et al. (1983). Five sample periods over one year's duration provided an overall estimate of annual fine root production within the top 10 cm of soil of 3517 kg/ha for Site 4 (test) and 2176 kg/ha for Site 6 (reference). Data were also analyzed for within-site effects along three rows of fixed distances from the cropped uplands (Table 4b). At the reference site production was about the same for the three rows, but at the test site fine root production was over three times higher in the row closest to the adjacent cropland, an effect possibly attributable to nutrient subsidies from upland croplands.

Table 4a. Mean annual aboveground net primary production per individual (> 1.1 cm DBH) by site for *Liriodendron tulipifera*, gms/individual/year, (\pm S.E.). Site NPP significantly higher at $p \leq .05$ denoted by "a"

Site	n	NPP/Individual
1 (reference)	75	1,786 (679)
2 (test)	27	8,898 (1511) ^a
3 (reference)	114	6,825 (1007)
4 (test)	30	5,988 (2050)
5 (test)	14	4,044 (2688)
6 (reference)	76	5,905 (775)

Table 4b. Fine root (≤ 5 mm diameter) production within the top 10 cm of the soil horizon by row (distances from cropped field boundary), gm/m². Production estimate is based on four 80-85 day sequential sampling periods.

Site	Row	Distance from cropped field boundary (m)	n	Annual production 11Jun80-10Jun81
4 (test)	1	25	9	158.3
	2	18	9	379.9
	3	8	<u>9</u>	513.8
			27	Site mean = 351.7
6 (reference)	1	217	9	204.7
	2	210	9	236.4
	3	200	<u>9</u>	211.7
			27	Site mean = 217.6

Tissue nutrient concentrations - If plants growing in riparian forests situated adjacent to agricultural areas were, as hypothesized, absorbing nutrients exported from these uplands, then one might reason that their tissues would contain higher concentrations of these nutrients than plants in riparian forests separated from the uplands by some intervening vegetation such as a grass field. Lowrance et al. (1983, 1984a,b,c, 1985) have previously determined that nutrients are moving in hydrologic pathways from the upland fields to the riparian forest zones. Hendrickson (1981) and Herrick (1981) in studies of nitrogen cycling and soil cations on the same sites as this and Lowrance's investigation, found, respectively, higher soil concentrations of $\text{NH}_4\text{-N}$ and soil pools of cations in test sites (2,4,5) than in reference sites (3,6). The evidence indicates, then, that the plant environment in test site riparian zones is a relatively nutrient rich one.

Tissue dry ash is the total fraction of tissue remaining after burning at 450°C and is representative of the total nutrient content less carbohydrates, sulfur, and nitrogen, thus the proportion of tissue ash might serve as an index reflective of the state of the nutrient environment. High ash fractions in plant tissues might be expected in plants growing in nutrient rich environments. Aboveground tissue ash concentrations are presented in Table 5a along with tissue concentrations of N, P, K, Ca, and Mg. The data is for all woody species by site and species effects are ignored. Site 2, the forest adjacent to the upland pigpen, had significantly higher ash concentrations in both wood (3.0%) and leaves (7.0%). Since Site 2 also had the largest standing stock of biomass it would appear that forest plants subjected to high nutrient input loads may both add large amounts of biomass and at the same time concentrate nutrients to a greater degree than forest plants not receiving such subsidies.

The trend observed for dry ash occurs for specific nutrients as well (Table 5a). Site 2, without regard to species, has higher concentrations of N, P, K, and Ca. The other test sites indicate no clear differences in overall tissue nutrient concentrations, but when species effects are taken into consideration, as in Table 5b, for Liriodendron tulipifera, significantly higher concentrations of P and Ca are noted for samples of wood and leaves from test sites (2,4,5) for that species. Although not shown, significant differences in tissue nutrient concentrations were found for various of the other test species as well (Fail, 1983) and included all 5 of the previously mentioned elements.

Table 5a. Mean aboveground tissue nutrient and ash concentration of all woody species by site, ppm dry weight, (\pm S.E.). Site concentrations significantly higher by t-test at the 0.01 level of probability from others for the same tissue and nutrient, denoted by "a"; "b"=.05 level.

Site component	Tissue	Nutrient concentration, ppm, (\pm S.E.)					
		N	P	K	Ca	Mg	Ash
2	Wood	10086(326) ^a	741(47) _a	3932(254)	6968(385)	952(65)	30687(1540) ^b
	Leaves	25742(996) ^a	1578(119) _a	12237(1063)	12307(802)	4069(381)	69820(4275) _a
3	Wood	7947(151)	491(23)	3148(115)	4421(177)	956(25)	22283(659)
	Leaves	20140(366)	1218(32)	11988(528)	8372(206)	4086(197)	58805(4630)
4	Wood	4899(245)	666(52)	3287(151)	6375(353)	964(48)	26593(1299)
	Leaves	21920(734)	1331(60)	7079(288)	10253(619)	4077(242)	52502(2152)
5	Wood	8525(152)	532(29)	3121(155)	5008(241)	788(33)	22483(801)
	Leaves	20483(572)	1204(51)	9481(411)	9129(374)	2881(144)	52583(1717)
6	Wood	8042(216)	512(57)	2320(129)	6991(380)	954(76)	24755(1388)
	Leaves	19460(936)	922(89)	6061(409)	11271(889)	3934(432)	53925(4864)
Mean	Wood	8449(412)	588(49)	3161(257)	5952(526)	923(33)	25360(1547)
	Leaves	21548(1122)	1250(106)	9369(1250)	10266(709)	3809(224)	57527(3276)

Table 5b. Mean aboveground tissue nutrient concentrations by site for *Liriodendron tulipifera*, ppm dry weight, (\pm S.E.). Site nutrient concentrations significantly higher at $p < .05$ than others for the same tissue and nutrient denoted by "a, b".

Site	Tissue	N	P	K	Ca	Mg
2	Wood	8550(250)	807(121) ^b	5593(611)	7899(570)	1341(95)
	Leaves	28924(1543)	1458(93)	18778(2146)	17481(1249) _a	6937(246)
3	Wood	7559(303)	457(68)	4149(350)	6919(424)	1275(92)
	Leaves	22985(191)	1294(132)	12503(2124)	12549(808)	6514(402)
4	Wood	8802(787)	1268(170) ^a	4430(522)	6855(520)	1251(146)
	Leaves	28698(1499)	1470(85)	7264(1293)	19837(1407) _a	6823(1187)
5	Wood	8687(397)	472(82)	3022(384)	6945(655)	1246(82)
	Leaves	27285(884)	1140(144)	9132(1340)	18247(1241) _a	6110(390)
6	Wood	9002(455)	508(115)	3028(261)	7255(439)	1509(152)
	Leaves	24868(1056)	1044(153)	8080(439)	13880(1127)	7071(181)

Belowground tissue nutrient concentrations for two sites (4 and 6) indicate trends similar to those of aboveground tissues. Significantly higher concentrations of N, P, and K were noted in root tissues at three soil depths without regard to species (Table 6a), and, specifically, significantly higher concentrations of N and P were found in the root tissues of Liriodendron tulipifera (Table 6b).

Forest tissue nutrient standing stocks and accumulation rates - Ovington (1968) in a paper discussing nutrient distributions in ecosystems found that generally (but not always) forests growing in areas of nutrient impoverishment have lower concentrations of nutrients in their tissues. Similarly, forest trees growing in rich nutrient areas generally show higher levels of tissue nutrients than trees of forests located in more nutrient poor areas. Tissue nutrient pool data of Whittaker et al. (1979) and Schlesinger (1978) from forests growing in relatively nutrient poor areas and data from Johnson and Risser (1974) from forests growing in nutrient rich areas offer support for Ovington's observation.

Results of this study indicate support for Ovington's observation as well. Data from Lowrance (1981, 1983, 1984a,b,c, 1985), Hendrickson (1981), and Herrick (1981), at Tifton, have demonstrated that the riparian forests of this study exist in nutrient rich environments and that differences exist in soil contents of nutrients between test sites (2,4,5) and reference sites (3 and 6). The apparently rich nutrient environment found by investigators of this study is paralleled in the vegetation. The mean standing stocks over all sites (Table 7) fall within ranges given by Ovington (1968) for high producing temperate woodlands. The Site 2 forest, below the pigpen, has about twice the mean aboveground nutrient pools of N, P, K, Ca, and Mg.

Root tissue nutrient pools were variable between the test and reference sites (Table 7). Although root tissue nutrient concentrations were higher at the test site (4) (Tables 6a and b), the greater root biomass at the reference site (6) resulted in higher estimated belowground pools of N, Ca, and Mg at that site.

The proportion of estimated nutrient pools belowground ranged from 5% to 20% of the total pools with slightly higher proportions noted in the test site (Table 7). The estimated belowground fractions of the total biomass are lower

Table 6a. Mean (\pm S.E.) nutrient concentrations (mg/gm dry tissue) by soil depth in living fine root biomass (diameter \leq 5 mm) in 1980. Significant differences detected with F-test. NSD = no significant difference. Note, ppm = 1000 x (mg/gm) (Hamzah, 1983).

Depth (cm)	Element (mg/g)	Site		p<F
		4(test)	6(reference)	
0-5 (n=54)	N	12.58 (.40)	11.03 (.50)	.01
	P	1.49 (.01)	0.69 (.02)	.01
	K	6.42 (.30)	4.21 (.20)	.01
	Ca	1.18 (.10)	1.27 (.10)	NSD
	Mg	0.70 (.06)	0.64 (.06)	NSD
6-10 (n=15)	N	10.73 (.90)	8.79 (1.0)	.01
	P	1.55 (.16)	0.73 (.11)	.01
	K	6.32 (.61)	4.25 (.68)	.01
	Ca	1.26 (.29)	0.60 (.12)	NSD
	Mg	0.72 (.11)	0.94 (.14)	NSD
11-15 (n=15)	N	10.48 (1.0)	8.36 (1.0)	.01
	P	1.36 (.19)	0.60 (.08)	.01
	K	6.83 (2.1)	3.13 (.40)	.01
	Ca	1.50 (.50)	1.55 (.20)	NSD
	Mg	0.62 (.15)	0.92 (.19)	.05

Table 6b. Mean (\pm S.E.) nutrient concentrations (mg/gm, dry tissue) in roots of *Liriodendron tulipifera* at sites 4 and 6. Samples were collected in July 1981. Significant difference between sites detected by t-test: **p \leq .01 *p \leq .05. Note, ppm = 1000 x (mg/gm) (Hamzah, 1983).

Element (mg/gm)	Site	Lateral Roots			Crown Roots (n = 2)
		<5 mm (n=3)	5-25 mm(n=6)	>25 mm (n=4)	
N	4 (test)	8.54 (0.60)	5.45 (0.30)	5.32 (0.30)	6.11 (0.02)**
	6 (reference)	8.52 (1.0)	5.33 (0.70)	4.64 (0.40)	2.09 (0.03)
P	4 (test)	1.41 (0.23)	1.13 (0.27)*	1.05 (0.21)*	0.59 (0.12)
	6 (reference)	0.76 (0.09)	0.42 (0.03)	0.40 (0.03)	0.32 (0.08)
K	4 (test)	7.27 (2.39)	4.53 (0.38)	4.24 (0.55)	2.44 (0.22)
	6 (reference)	5.82 (1.45)	4.11 (0.46)	2.92 (0.32)	1.60 (0.17)
Ca	4 (test)	2.62 (0.89)	0.91 (0.32)	1.37 (0.75)	0.35 (0.20)
	6 (reference)	1.02 (0.15)	1.61 (0.79)	1.35 (0.46)	1.12 (0.54)
Mg	4 (test)	0.41 (0.16)	0.51 (0.19)	0.78 (0.24)	0.59 (0.10)
	6 (reference)	0.79 (0.32)	0.84 (0.18)	0.71 (0.24)	0.64 (0.49)

Table 7. Nutrient standing stocks, kg/ha, by site for riparian forest woody plant tissue. Data includes all woody species.

Site	Component	Nutrient Standing Stock (kg/ha)				
		N	P	K	Ca	Mg
2 (test)	Wood	3440.0	244.0	1290.0	2850.0	372.0
	Leaves	96.8	5.7	47.5	46.4	17.0
	Total	3536.8	249.7	1337.5	2896.4	389.0
3 (ref)	Wood	1445.0	103.0	543.0	1043.0	175.0
	Leaves	69.7	5.0	36.8	29.9	14.0
	Total	1514.7	108.0	579.8	1072.9	189.0
4 (test)	Wood	768.0	91.0	335.0	573.0	105.0
	Leaves	52.7	3.0	15.1	29.3	10.9
	Subtotal	820.7	94.0	350.1	602.3	115.9
	Roots	132.5	20.6	88.0	28.4	13.1
	Total	953.2	114.6	438.1	630.7	129.0
5 (test)	Wood	889.0	47.0	277.0	603.0	100.0
	Leaves	49.5	2.6	21.3	21.7	8.3
	Total	938.5	49.6	298.3	624.7	108.3
6 (ref)	Wood	1097.0	66.0	302.0	949.0	133.0
	Leaves	40.0	2.2	13.1	18.2	8.1
	Subtotal	1137.0	68.1	315.1	967.2	141.1
	Roots	158.1	12.2	70.0	44.1	24.6
	Total	1295.1	80.3	385.1	1011.3	165.7
Mean (\pm S.E.)	Wood	1527.8(492)	110.0(35)	594.4(191)	1203.0(422)	177.0(51)
Mean (\pm S.E.)	Leaves	61.7(10)	3.7(0.4)	26.8(6.6)	28.5(4.9)	11.7(1.7)
Mean, Roots		145.3	16.4	79.0	36.2	18.8

than those found at both Hubbard Brook Forest in New Hampshire (Whittaker et al., 1979) and Coweeta Forest in North Carolina (McGinty, 1976). Forty to sixty-five per cent of the total plant nutrients within hardwood and pine stands in Coweeta were estimated to be located in the roots (McGinty, 1976). The low belowground proportion of biomass found in this investigation may be due to errors of estimation or could be a response to a relatively rich nutrient environment as suggested by Head (1973) and Roger and Vyvgan (1934) or due to a relatively wet soil environment (Monk, 1966), or all three.

Accretion rates of nutrients (Table 8) are estimates of the annual quantities of nutrients sequestered in plant biomass. The mean annual aboveground accretion rates over five sites were estimated to be 51.8, 3.8, 18.6, 40.3, and 5.9 kg/ha, respectively, of N, P, K, Ca, and Mg (Table 8). The rates at Site 2, below the pigpen, were about double those of the other sites, and such high rates may be plant responses to high influxes of nutrients from the upland pigpen. Note that the aboveground accretion estimates do not include estimates of annual decomposition or of standing dead wood.

Leaf stocks of nutrients (Table 7) are important from a cycling viewpoint. The estimated average of 3146 kg/ha of leaves within each site of this study contain an estimated 62, 4, 27, 28, and 12 kg/ha, respectively, of N, P, K, Ca, and Mg. Unlike wood accretion of nutrients, they do not represent nutrients in long term storage. Rather, they are cycled annually; but, taken together with the annual amounts of nutrients withdrawn and stored in wood biomass, the total amount of nutrients withdrawn periodically from soil, water, and gas circulation is substantial.

Belowground fine root accretion rates of tissue nutrients (Table 8) include gross estimates, and after subtracting decomposition rates, net accretion estimates. Both the gross and net accretion rates are $1\frac{1}{2}$ to 2 times greater at the test site (4) than at the reference site (6) in spite of the greater estimated biomass of the reference site.

Nutrient accretion data, then, for both above and belowground components of the riparian vegetation (Table 8, Fig. 3) offer evidence of higher rates in forest sites lying adjacent to upland agricultural areas, and the effect may be lowland plant responses to inputs of nutrients lost from the upland areas.

Fine root decomposition and root net nutrient accumulation rates - Root decomposition processes are little understood (Clark and Paul, 1970; Lewis, 1970), difficult to measure, and literature estimates are few. Cox

Table 8. Annual above and belowground (fine roots, ≤ 5 mm diameter, top 10 cm soil) nutrient accretion rates by site for riparian woody plants, kg/ha.

Site	Nutrient	Above-ground accretion	Fine root production	Gross below-ground accretion	%Below-ground decomposition loss	Net below-ground accretion
2 (test)	N	97.6	-	-	-	-
	P	6.9	-	-	-	-
	K	36.6	-	-	-	-
	Ca	80.0	-	-	-	-
	Mg	10.6	-	-	-	-
3 (ref)	N	49.8	-	-	-	-
	P	3.6	-	-	-	-
	K	18.7	-	-	-	-
	Ca	36.0	-	-	-	-
	Mg	6.0	-	-	-	-
4 (test)			3517			
	N	34.6	-	63.7	54.4	29.1
	P	4.1	-	5.7	78.6	1.2
	K	15.1	-	43.8	95	2.2
	Ca	25.9	-	4.4	55.8	1.9
	Mg	4.7	-	2.3	48.5	1.2
				Mean	78.1	
5 (test)	N	36.9	-	-	-	-
	P	1.9	-	-	-	-
	K	11.4	-	-	-	-
	Ca	25.1	-	-	-	-
	Mg	4.2	-	-	-	-
6 (ref)			2176			
	N	40.0	-	31.8	53.8	14.7
	P	2.4	-	2.8	75.1	0.7
	K	11.0	-	20.1	95	1.0
	Ca	34.6	-	3.4	40.0	2.0
	Mg	4.2	-	1.5	38.3	0.9
				Mean	60.0	
Mean			2846			
	N	51.8	-	47.7	54.1	21.9
	P	3.8	-	4.2	76.8	0.9
	K	18.6	-	31.9	95	1.6
	Mg	5.9	-	1.9	43.4	1.1

(1971) in a study of root production and turnover in a Liriodendron tulipifera forest found high decomposition rates and quick turnover times for fine roots, and that is apparently the situation observed in this study.

Cumulative fine root decomposition was estimated for test Site 4 and reference Site 6 by the use of 45 perforated aluminum tubes, serially sampled over a 343 day period. The method allows aeration and movement of water throughout the core, and the roots within the core are not removed either from the ground or their spatial orientation, resulting in minimal disturbance effects. The problem with the method is that live roots are massively killed, and such perturbation is probably not observed in nature.

Annual loss rates (Table 8) of both fine root biomass and nutrient pools are similar for the two sites. An estimated 60% of the fine root biomass was lost at both sites (Hamzah, 1983), and an average of 78% of the belowground fine root nutrient pools were lost from the test site and 60% from the reference site (Table 8). Nutrient loss rates were similar at both sites for N, P, and K, but higher at the test site for Ca and Mg. At these rates, the time estimated to completely decompose standing fine root biomass is about 1.4 years at the test site and about 1.6 years at the reference site. Even though nutrient loss rates are apparently higher at the test site, the net accretion rate (Table 8 and Figure 3) at the test site is higher than at the reference site. It may be that the longer turnover time and lower decomposition rate at the reference site is a general strategy of nutrient conservation at relatively nutrient poorer sites (Hamzah, 1983).

Error - Ecosystem studies are characterized by the merging of independently sampled data sets and the resulting possible accumulation of large error terms, particularly within data sets joined by multiplicative operations. Freese (1962), for example, has noted that the variance of two data sets joined by multiplicative operations, such as estimating pools of nutrients from tissue nutrient concentration and biomass data, is calculated by multiplying the product of their respective means by the sum of their variances and divided by their squared means. Resulting error terms are large but the calculated error applies to all sites within the study so relative comparisons are possible.

In addition to errors associated with estimations, errors emerging from investigation methods are present in both the above and belowground parts of this study. The most serious aboveground methodological error arises due to the use of nutrient data derived largely from branches for whole tree nutrient

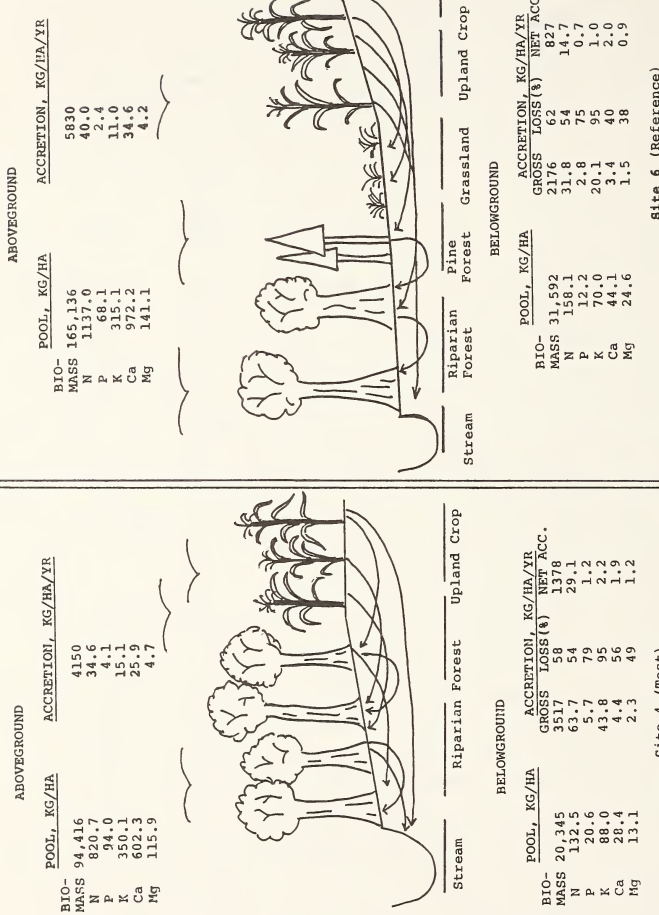


Figure 3. Site schematic indicating above and belowground vegetation nutrient pools and accretion rates for N, P, K, Ca, and Mg.

pool estimations. The exact magnitude of this error is not known but an estimate can be made from literature sources giving tissue nutrient concentrations and woody plant biomass proportions for similar species and for relatively nearby forests. Using these sources (Henderson, 1971; Johnson and Risser, 1974; Day and Monk, 1977; Schlesinger, 1978; Rolfe et al., 1978; and Whittaker et al., 1979) and combining corrections for possible overestimations of tissue nutrient concentrations with proportions of aboveground plant tissue devoted either to boles or branches, indicate that the calculated aboveground pools and accretion rates were possibly overestimated by about 23%. The error may not be as great as this and/or may be offset by non-destructive biomass estimation procedures.

Principal errors within the belowground investigation arise from the obvious problems of below ground level work. No whole trees were excavated to develop biomass estimating regression equations based on local forest species. Instead, equations developed in Tennessee (Harris et al., 1973) and North Carolina (McGinty, 1976) were used. Regression equations for biomass are species related and root biomass is affected by many site factors, particularly soil fertility (Head, 1973), aeration (Aldrich-Blake, 1929), and water availability (Monk, 1966). Thus even though the equations of McGinty (1976) were developed for a species - Liriodendron tulipifera - that is of high importance in the Tifton study, nevertheless, site environmental differences could make differences in the relationships of tree diameter to belowground biomass.

Production estimates of fine roots might also be overestimated because of greater nutrient availability due to decomposition of detached roots, and Hamzah (1983) during this study, found higher soil nutrient concentrations inside of soil blocks than outside of them.

Both root tissue nutrient concentration and decomposition data are affected, to a largely unknown extent, by unavoidable inclusion of soil particles and organic material adhering to root tissue used for analyses and estimations (Hamzah, 1983).

Finally, decomposition rates are estimated by severing living roots with aluminum tubes and measuring biomass loss over time. Such perturbation does not simulate natural root death and may not reflect real world root decomposition losses.

CONCLUSIONS

This paper is an attempt to synthesize results obtained from two separate investigations within the Tifton, Georgia, Agroecosystem Study. Data from above and belowground components of riparian forests located within agricultural environments have been merged to provide overall estimates of biomass accumulation and production, tissue nutrient concentrations, and tissue nutrient pools and accretion rates. The data have been used to test the hypothesis that vegetation in riparian forests located adjacent to upland agricultural areas are acting as nutrient filters by intercepting nutrients lost from uplands and incorporating them into forest biomass. The hypothesis has been tested by comparing production and tissue nutrient contents of plants in riparian forests located directly adjacent to upland agricultural areas (test sites) with such data from forests located adjacent to grassland buffer zones (reference sites).

The general results and conclusions of this synthesis are:

1) Test site (Sites 2,4,5) forest species showed statistical evidence of higher aboveground growth rates than the same species in reference sites (Sites 3 and 6). Fine root production without regard to species was higher in Site 4, a test site than in Site 6, a reference site. The test site production rate was estimated to be 3517 kg/ha/yr and the reference site rate was estimated to be 2176 kg/ha/yr. Within Site 4 fine root production was three times greater in plants located in a row 8-10 m from the adjacent upland cropped field than root production of plants located in a row 25 m away from the field. Fine root production was essentially the same within rows of the reference site.

2) Aboveground tissue concentrations of nutrients were higher in test site plants, in general, than in reference site plants. Significantly higher concentrations of N and P were noted in the aboveground tissue of select species within Test Site 2. Belowground tissues indicated a similar trend. Concentrations of N, P, and K were significantly greater in root tissue from Test Site 4 compared to Reference Site 6.

3) Aboveground nutrient accretion rates in Site 2, the forest located adjacent to an upland pigpen, were about double those from all other sites. Such a high rate may be due to high nutrient inputs from the upland pigpen. Belowground gross nutrient accretion rates in Test Site 4, were about twice those estimated for Reference Site 6.

4) Belowground fine root decomposition rates were higher at the test site than at the reference site. Annually it is estimated that over 70% of fine root tissue nutrients are returned to soil, water, and gas cycles, though that estimate may be higher than is actually the case due to perturbations caused by the method of measurement.

The two investigations which make up this synthesis appear to offer independent support for the hypothesis that riparian forests may act as nutrient filters in agricultural environments by uptake of applied nutrients which are lost from upland agricultural areas. It is supported also by nutrient budgets from Lowrance et al. (1983; 1984a,b,c; 1985) and by soil nutrient and soil process data of Herrick (1981) and Hendrickson (1981).

In light of the apparent ability of riparian forests to act in the capacity of nutrient filtration mechanisms within stream watersheds, forest management takes on special significance. It has been suggested (Vitousek and Reiners, 1975; Lowrance et al., 1983, 1984c) that select harvest of "mature" trees within forests is a method of perpetuating vigorous vegetative uptake of soil nutrients. Odum (1969) has hypothesized that nutrient conservation increases over successional time, and in discussing the effect of nutrient subsidies on ecosystems (fish ponds, for example) notes: "...the system is pushed back, in successional terms to a younger or 'bloom' state." Agricultural lands receive regular pulses (subsidies) of nutrients, some of which can, apparently, move into lowland forest areas. Constant, pulsed, and annually increasing inputs of nutrients may keep riparian forests in a "bloom" state, and the forest may respond by high and vigorous growth and nutrient uptake rates for a considerable period of time; much longer, perhaps, than the age generally considered as forest maturity. Thus, it may be ecologically worth more in the long term to let the forests remain untouched, which suggests that long term ecological research on agricultural systems and the riparian forests often associated with them, should be implemented, and indeed, is long overdue.

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DISCUSSION: Fail Paper

Question (Kuenzler): I wonder whether your above ground accretion rates included leaves?

Answer: No, that is not an accretion.

Question (Pionke): What was the mortality that was found in the long-term studies of productivity in this forest? This is an important component of productivity over the long-term. Why not get information from standing dead trees and logs?

Answer: It was a mistake, but I didn't measure it.

Comment (Alaback): You apparently had low nutrient pools in the foliage. Is that typical for a forest in that region?

Answer: Well, I think it is more a function of the small pools of biomass estimated for leaves. Typically the nutrient concentration was quite high for leaves, but the pools were low by literature standards.

CONTROLLED AGRICULTURAL DRAINAGE: AN ALTERNATIVE
TO RIPARIAN VEGETATION

J. W. Gilliam, R. W. Skaggs and C.W. Doty¹

Abstract-Drainage system design and management can be utilized to minimize offsite water quality effects of improved agricultural drainage. Improvement of subsurface drainage can cause a 10-fold increase in $\text{NO}_3\text{-N}$ efflux. This increase can be partially offset by using controlled drainage which can reduce the $\text{NO}_3\text{-N}$ efflux by as much as 50% in some situations. However, controlled drainage may slightly increase the phosphorus efflux, because of increased loss of water through surface runoff.

The design of controlled drainage systems must be site specific. This paper describes the effects of controls placed in collector tile lines, field collector ditches and large channelized streams on nutrient efflux.

INTRODUCTION

Riparian areas bordering agricultural fields in the North Carolina Coastal Plain are effective for improving the quality of drainage water from agricultural fields. When surface drainage water passes over these areas, much of the sediment and P are removed before the drainage water reaches a major stream (Cooper et al., 1985). When subsurface flow moves through a riparian zone, much of the nitrate is removed by denitrification (Jacobs and Gilliam, 1985); but it is not always practical or possible to pass agricultural drainage water over or through riparian areas. Design and management of the drainage system can influence the nutrient content of drainage water as well as time distribution of the outflows from essentially all land where improved drainage is necessary for agricultural production.

In this paper, drainage system design refers to whether a field is largely surface or subsurface drained as well as spacing and depth of improved subsurface drainage system. Controlled drainage refers to restricting the flow of subsurface drains by the use of some mechanical structure.

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CHARACTERISTICS OF IMPROVED AGRICULTURAL DRAINAGE SYSTEMS

Several drainage system designs can be utilized to satisfy the drainage requirements for agriculture. In the North Carolina Coastal Plain and along much of the Atlantic Coast, conventional agricultural drainage systems are designed primarily to remove surface water. Open ditches are dug about 100 m apart and the land surface is sloped toward the ditches to facilitate surface drainage to the ditches. In most soils, the ditches are too far apart to provide good subsurface drainage. When rainfall occurs, the water table often rises to the surface causing much of the drainage water to leave the field as surface runoff. These drainage conditions are not sufficient for economically viable yield on many soils (Skaggs and Tabrizi, 1983).

An alternative drainage system involves the use of more closely spaced drains to provide good subsurface drainage. Although open ditches can be used, buried tubes are normally installed at intervals that depend on the soil properties, climatological factors and crop to be grown. The utilization of this drainage system is becoming much more common in poorly drained Coastal Plain soils because of increased yields as compared to systems with primarily surface drainage. Tube drainage systems at proper spacings also offer more management opportunities for efficient water use and water quality improvement.

There are significant differences in the outflow rates from a field that is surface-drained than from one with good subsurface drainage. The peak outflow from a surface drained field is greater than from a similar field with good subsurface drainage. Subsurface drains remove excess water from the soil profile over a long period of time compared to surface runoff events. This lowers the water table which provides more storage for infiltration from subsequent rainfall thereby reducing surface runoff.

An example of the effect of good subsurface drainage on outflow rates is shown in Fig. 1 (Gilliam and Skaggs, 1985). The outflow rates plotted were measured on adjacent 36 ha watersheds near Belhaven, North Carolina for a 32 mm rainfall event in Feb. 1985. The watersheds are essentially flat (slopes less than 2%) and each watershed is composed

of the same shallow organic and mineral soils. The only known difference is that one watershed has a conventional drainage system with open ditches 100 m apart while the other watershed has two additional tile lines, equally spaced between each pair of ditches, providing good subsurface drainage. The peak flow rate from the watershed with good subsurface drainage was about half of that measured for the watershed with poor subsurface drainage. The flow event was extended over a longer period of time for the watershed with good subsurface drainage. The total outflow was about the same for both watersheds, but good subsurface drainage reduced the peak flow rate.

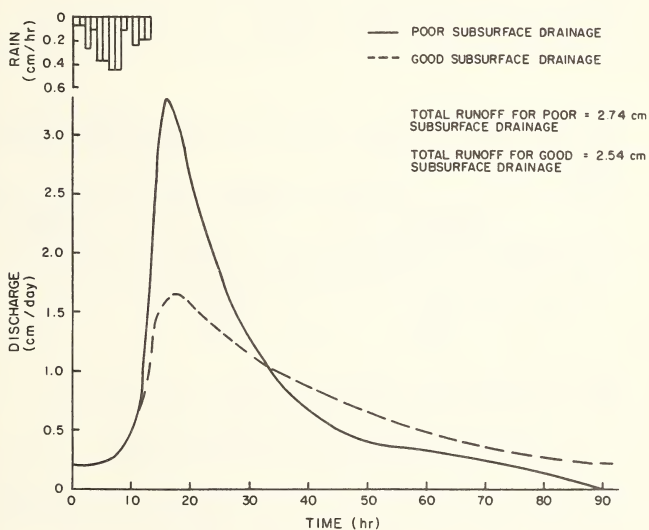


Figure 1. The effect of improved subsurface drainage on peak discharge rates.

Simulation modeling studies (Skaggs and Tabrizi, 1981) on a similar soil showed that annual surface runoff could be reduced by a factor of three (from 57 cm to 19 cm) by reducing the drain spacing from 100 m to 15 m. Annual subsurface drainage was increased by a similar amount. The results of these studies show clearly that the drainage system design

significantly affects the amount and rate of surface runoff--on both an annual basis as well as for single storm events. Changes in rate and distribution of runoff implies an effect on erosion and pollutant movement carried in the surface and subsurface drainage waters from these poorly drained soils.

The proportion of the drainage water which leaves agricultural fields via surface or subsurface drainage has a large influence upon the potential pollutants carried by the water (Baker and Johnson, 1976; Bengtson et al., 1982; Gilliam and Skaggs, 1985). Surface runoff carries more sediments, pesticides and phosphorus than subsurface flows. But the higher proportion of subsurface flow is accompanied by a greater loss of nitrate-nitrogen and generally a greater loss of total N. The effects on N and P losses are illustrated by data in Table 1 from the Coastal Plain of North Carolina.

Table 1. Effect of type of drainage on N and P efflux in drainage water from three similarly cropped soils in the North Carolina Coastal Plain.

Nutrient	Drainage Type		
	Poor Subsurface	Intermediate	Good Subsurface
	----- kg ha ⁻¹ yr ⁻¹ -----		
NO ₃ -N	4.1	17.6	36.3
Total-N	15.2	22.4	47.2
Total-P	0.60	0.33	0.24

The three fields from which the data in Table 1 were collected were in a corn-soybean rotation and cultural practices were very similar. The field with poor subsurface drainage contained ditches spaced approximately 100 m apart, but the internal conductivity was so poor that most drainage water was removed via surface runoff. The intermediate field had a similar drainage system but this field had a sand layer present at a depth of approximately 1 m. This sand layer improved the drainage to the open ditches, but this field was still not as well drained as one with two equally spaced drain tubes installed parallel to the open ditches. In the field with good subsurface drainage nearly all drainage water reached the open ditches via subsurface flow. The large effect that the type of drainage has upon nutrient outflows (Table 1) has significant implications for the design and management of drainage systems.

Approximately half the drainage water from agricultural land in North Carolina occurs during the period December through March (Fig. 2). In many cropping systems, drainage during this period is not agriculturally critical, so drainage water can be managed to minimize nutrient outflows without influencing agricultural production. Our initial experiments on controlled drainage were designed to control water only during the winter, but we now know that controlled drainage throughout the year offers potential for increased agricultural production as well as providing environmental benefits.

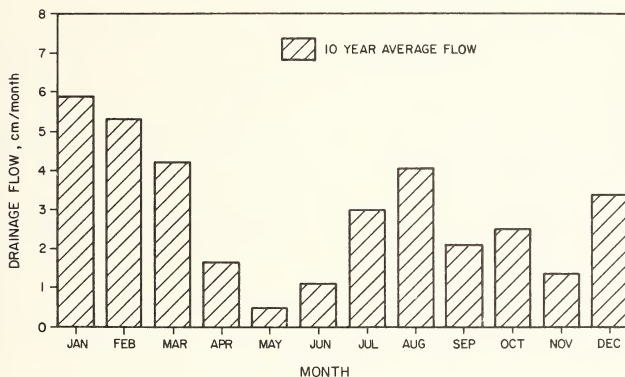


Figure 2. Average monthly discharge as predicted by DRAINMOD (Skaggs, 1978) for a cropped Goldsboro soil in North Carolina.

CONTROLLED DRAINAGE FROM AGRICULTURAL FIELDS

Moderately well drained soils - It must be emphasized that to be most effective the drainage system design must be site specific and effective controlled drainage design systems are also site specific. For moderately well drained soils of the Middle Coastal Plain, control structures in collector ditches from relatively large areas generally are not feasible because slopes are too great. Installation of control structures in main

tile outlets is possible and the effect that control structures can have upon $\text{NO}_3\text{-N}$ outflows from the tile outlets is shown in Fig. 3. The reduction due to drainage control in the total amount of $\text{NO}_3\text{-N}$ loss through the tile lines is a result of decrease in the amount of water passing through the tile lines and not due to any reduction in $\text{NO}_3\text{-N}$ concentration. We found no evidence that controlled drainage increased the amount of N lost to denitrification in these fields so it is assumed that approximately equal quantities of $\text{NO}_3\text{-N}$ left the controlled and uncontrolled fields in drainage water. However, in the uncontrolled fields, approximately $35 \text{ kg ha}^{-1} \text{ yr}^{-1}$ of $\text{NO}_3\text{-N}$ was added directly to surface waters through tile drainage. The drainage water from the controlled fields would have to enter surface water in different areas. Other experiments have shown that much of the $\text{NO}_3\text{-N}$ is removed from drainage water when the subsurface water enters surface water through ditch banks or riparian areas (Jacobs and Gilliam, 1985; Cooper et al., 1985). Thus the controlled drainage in these moderately well drained soils probably prevented a large percentage of the $\text{NO}_3\text{-N}$ from entering surface water as compared to uncontrolled drainage. This control system would seem to have potential water quality benefits anywhere that improved subsurface drainage systems are used.

Poorly drained soils - In poorly drained and very poorly drained flat soils of the Lower Coastal Plain, flashboard risers in collection ditches have been used to control water tables in fields up to 40 ha in size. These poorly drained soils have enough organic matter in the top 2 m of the profile to cause reducing conditions below the water table (Fig. 4). Nitrate which moves into the saturated zone is quickly reduced through denitrification (Gambrell et al., 1975). This is shown in Fig. 4 where the nitrate-nitrogen concentrations are $< 0.05 \text{ mg L}^{-1}$ below 1 m. Water passing through this zone on the way to an outlet has essentially all of the $\text{NO}_3\text{-N}$ removed from it.

Because of the higher water table maintained with controlled drainage, surface runoff will be increased. Since surface runoff contains a higher concentration of P than subsurface flow, an increase in P losses would be

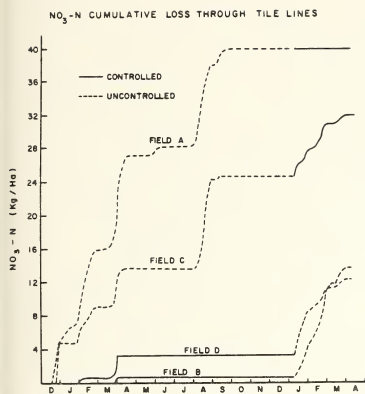


Fig. 3. The effect of controlled drainage on nitrate loss through tile drainage lines (Gilliam et al. 1979).

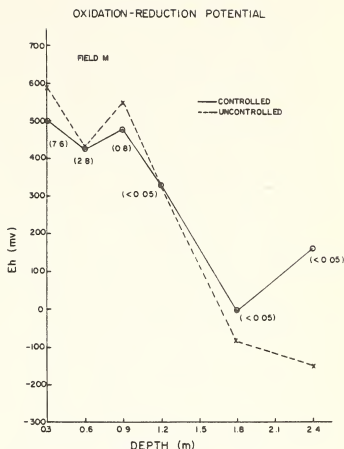


Fig. 4. Oxidation-reduction potential with depth in a poorly drained high water table soil. Numbers in parenthesis are average $\text{NO}_3\text{-N}$ concentrations (mg L^{-1}) in soil water at each depth (Gilliam et al. 1984).

expected under controlled drainage. The data in Table 1 are a good indication of the potential effects of controlled drainage on N and P effluxes from a naturally poorly drained lower Coastal Plain soil with a good subsurface drainage system installed on it. The good subsurface drainage represents the conditions which exist under no control and the poor subsurface drainage represents maximum control throughout the year. It would be expected that actual control conditions would be between these two extremes with regard to N and P losses to surface water.

Deal et al. (1985) used nutrient losses measured in several experiments under different types of drainage (Gambrell et al., 1974; Gilliam et al., 1979; Skaggs et al., 1980) in conjunction with the water management

model DRAINMOD (Skaggs, 1978) to predict surface runoff, subsurface drainage, and nutrient losses for six soils for hypothetical field drainage conditions. The soils modeled were poorly drained to very poorly drained and all had a high water table (< 1 m) during much of the year unless improved drainage systems were installed. For each nutrient loss simulation, a 20 year long period of climatological data was used with DRAINMOD. During the period used (1950-1969), the average annual precipitation was 120 cm with a range of 86 to 159 cm. Water and nutrient losses for each soil were simulated for four combinations of surface-subsurface drainage with and without drainage control. Controlled drainage consisted of raising the control structures to within 30 cm of the surface from 1 December to 11 March each year. The control structures were then lowered to 1 m to allow tile drainage to proceed. Lowering the control structures in March was necessary for land preparation and planting. The controls remained at 1 m until 16 June to allow establishment of the crop and then were raised to within 45 cm of the surface. The structures remained at 45 cm until 1 September when they were lowered again to 1 m to facilitate harvesting and remained there until 1 December when the schedule was repeated. Data are reported as annual averages.

It can be observed from the data given in Table 2 for two soils that controlled drainage was predicted to significantly reduce $\text{NO}_3\text{-N}$ efflux, particularly under good subsurface drainage conditions. Drainage control was predicted to have some effect on soils with poor subsurface drainage but this effect was relatively small. We wish to emphasize that $\text{NO}_3\text{-N}$ reductions under controlled drainage in fields with good subsurface drainage cannot be extrapolated to soils with poor subsurface drainage.

In general, mechanical control of the water level also decreased the total efflux of total Kjeldahl N (TKN). Even though surface loss increased with controlled drainage, the subsurface efflux decreased by a greater amount so that a net decrease in total TKN occurred with controlled drainage.

The negative side of controlled drainage from an environmental viewpoint is that total P efflux in drainage water was increased (Table 2). The increase in P efflux was much less than the decrease in N efflux but is a factor which must be considered in management of agricultural drainage water.

Because the simulations considered no deep seepage of drainage water, the effect of controlled drainage in reducing nutrient effluxes are minimized. It is known that controlled drainage usually increases deep or lateral seepage. The water which leaves the field via this mechanism is expected to contain a very low concentration of both N and P because of denitrification and P fixation by the subsoils. We have measured as much as a 50% reduction in flow in collection ditches from controlled drainage fields as compared to uncontrolled fields of similar soils (Gilliam et al., 1979). Controls in these fields reduced the nutrient efflux more than those predicted by the modeling techniques employed to generate the data in Table 2. However, we would not expect controlled drainage to reduce outflows in drainage ditches by 50% so we predicted no deep seepage in generating data for Table 2. We currently are conducting field experiments to obtain data to allow us to better predict the effects of deep seepage under controlled drainage upon water and nutrient effluxes.

Table 2. Prediction of annual nutrient efflux under various drainage designs under condition of no deep seepage. (From Deal et al., 1985)

Soil	Drainage Practice *	NO ₃ -N		TKN		P	
		Uncon**	Con***	Uncon	Con	Uncon	Con
		----- kg ha ⁻¹ yr ⁻¹ -----					
Portsmouth	A	43.9	33.9	6.4	5.7	0.06	0.07
	B	43.5	29.7	6.3	5.4	0.10	0.18
	C	13.0	8.3	5.4	4.7	0.23	0.33
	D	12.0	8.0	5.0	4.1	0.14	0.24
Wasda	A	31.5	24.5	5.7	5.4	0.11	0.12
	B	31.2	21.4	6.1	5.8	0.20	0.31
	C	2.5	1.9	6.9	7.2	0.57	0.67
	D	2.1	1.6	5.4	5.6	0.37	0.51

*A = poor surface drainage-good subsurface drainage; B = good surface drainage-good subsurface drainage; C = good surface drainage-poor subsurface drainage; D = poor surface drainage-poor subsurface drainage.

**Uncontrolled drainage

***Controlled drainage

CONTROLLED DRAINAGE FROM WATERSHED SCALE AREAS

Under Public Law 566-Drainage Projects, many streams draining agricultural watersheds have been channelized. When Public Law 566 was initiated, only the agricultural benefits of channelization were generally recognized. Since that time offsite effects resulting from increased nutrient effluxes have been discussed (O'Rear, 1975) as well as onsite effects on wildlife (Tiner, 1984). When most drainage projects were designed, no management of the drainage water was envisioned. Furthermore, most critics of the drainage projects assume that no management is possible.

The Conetoe Drainage District in North Carolina was instrumental in improving the drainage of 26,000 ha of land in 1967. It is a good example of a channelization project. Several thousand ha of cropland that once were flooded several times a year are now protected against flooding. Although flooding is no longer a major problem in the District, overdrainage in some areas and lack of sufficient water for irrigation are problems. We initiated a cooperative research project among USDA-ARS, NC-ARS and USDA-SCS in 1979 to evaluate the effects of controlling the drainage in one channelized stream in this watershed on water utilization for agricultural production of row crops. Another important objective was to determine the effect of controlled drainage on quality of the water leaving the watershed.

The study area is a 3.2 km section of a channelized stream (Mitchell Creek) which drains about 3200 ha above the study area and 700 ha in the study area. Six lines of wells were installed perpendicular to the creek on each side to measure water table elevations as well as quality of ground water moving toward the creek. A fabric dam (Fig. 5) was installed in April to control the water level in the creek. The fabric dam is capable of controlling the water level at any desired level between 2.45 and 11.75 m above MSL.



Fig. 5. Fabridam structure used for water control in a channelized stream.

This project has attracted much attention primarily because of the positive effect of the control upon water table and crop yields (Doty et al., 1984). Controlled drainage has also had an apparent positive effect on some parameters of quality of the drainage water leaving the study area. The effect of the control upon concentrations of N and P are given in Table 3. The largest effect of control was on the $\text{NO}_3\text{-N}$ concentration. During the previous three years before control, $\text{NO}_3\text{-N}$ concentration in the stream increased as it flowed through the stream reach affected by the control structure (control section). It is believed that this increase is

a result of the more intensive agricultural development and cultural practices of the area draining into the creek in the control section as compared to the upstream area. Nearly all of the area draining into the control section is under cultivation, whereas a significant percentage of the upstream area contains unmanaged forest.

Table 3. Effect of controlled drainage in a channelized stream on nutrient concentrations. Concentrations are averages of weekly samples.

	Year				
	Before Control			After Control	
	79-80	80-81	81-82	82-83	83-84
	NO ₃ -N in Control Section (mg L ⁻¹)				
Entry	2.6	2.2	1.9	2.9	4.2
Exit	3.0	2.6	2.7	1.5	3.2
% Change	+15	+18	+42	-48	-23
	Total N in Control Section (mg L ⁻¹)				
Entry	3.7	2.6	2.5	3.2	4.7
Exit	3.7	3.0	3.4	2.0	3.6
% Change	0	+23	+36	-37	-23
	Total P in Control Section (mg L ⁻¹)				
Entry	.03	.02	.01	.07	.02
Exit	.04	.06	.13	.04	.04
% Change	+33	+200	+1200	-43	+100

After the fabridam was installed, there was a decrease in NO₃-N concentration as the water moved through the controlled area of the stream. It is unfortunate that we do not have an accurate measure of flow as the stream entered and left the control area so that total nutrient fluxes could be computed as well as flow weighed concentrations. We expended much effort to measure flows but were unsuccessful due to variable resistance to flow caused by the extensive weed growth in the creek.

Three factors are believed to contribute to the decrease in $\text{NO}_3\text{-N}$ after the fabric dam was installed. One factor is an increase in denitrification in the more poorly drained soils toward the outer edge of the drainage area influenced by the control. The effect of control on the water table in the fields adjacent to the creek is shown in Fig. 6. Also shown are the average $\text{NO}_3\text{-N}$ concentrations in the ground water in a transect below the fields. The $\text{NO}_3\text{-N}$ concentrations at the outer edge of the drainage area were always lower, presumably because of more denitrification in these more poorly drained sections. Even though the water table control influenced the water table less at the outer edge, it is in this region that slight changes in water table elevation can result in significantly more denitrification. The average $\text{NO}_3\text{-N}$ in the wells immediately adjacent to the stream was 9.2 mg L^{-1} (95 samples) before control and 5.0 mg L^{-1} (177 samples) after control.

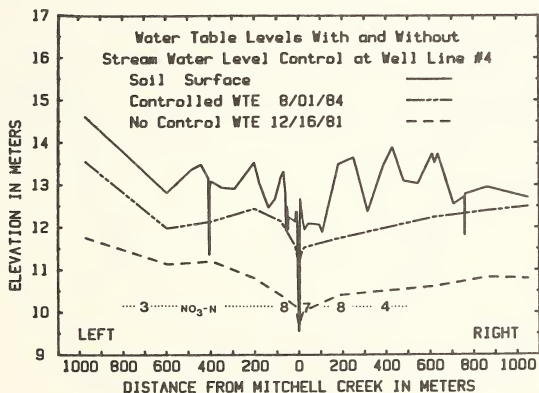


Fig. 6. Water table levels with and without control in a channelized stream. The numbers across the lower portion of the figure are average $\text{NO}_3\text{-N}$ concentrations (mg L^{-1}) in the shallow ground water.

There is a further reduction in the $\text{NO}_3\text{-N}$ concentration because of denitrification as the water flows from the field into the ditch. This is illustrated in Fig. 7 for a lateral ditch which flowed into the main channelized stream. The ground water in the fields on either side of the ditch which drained into the ditch contained 5-8 mg L^{-1} and 8-10 mg L^{-1} of $\text{NO}_3\text{-N}$. The ditch water concentration was approximately 2.5 mg L^{-1} . Numerous samples taken in the ground water within 1 m of the ditch bank contained from zero to the same $\text{NO}_3\text{-N}$ concentrations as that in the field. Oxidation-reduction potential measurements taken in this area showed that much of the area was highly reduced so conditions for denitrification were favorable. These conditions exist whether water table control is used or not but it is believed that the higher the water table, the greater the probability that drainage water will pass through an area adjacent to the ditch which is conducive to denitrification.

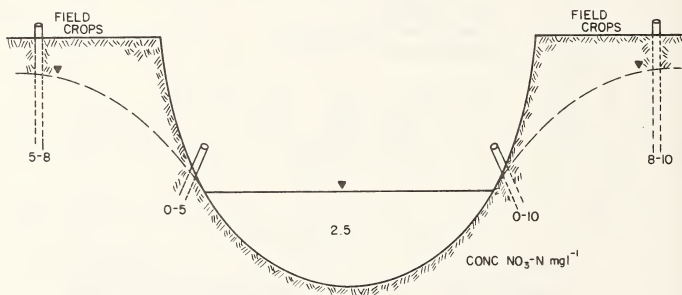


Fig. 7. Nitrate-nitrogen concentrations in a lateral ditch which drains into the channelized stream, in ground water in fields on either side of the ditch and in water within 1 m of the ditch bank.

The third factor believed responsible for the decrease in $\text{NO}_3\text{-N}$ in the control section is denitrification in the ditch itself. As mentioned above, the ditch contained a large growth of weeds. Even during periods of moderate flow, stagnant areas could be seen in the channelized stream. The effect that the reducing conditions measured in these areas, as well as the generally reducing conditions below the stream bed, have on $\text{NO}_3\text{-N}$ concentration in a profile of the stream water is shown in Fig. 8. The concentration of $\text{NO}_3\text{-N}$ in the bulk solution was 2.6-2.7 mg L^{-1} . It is apparent that $\text{NO}_3\text{-N}$ concentration is not uniform across the stream. The generally lower concentration in the bottom sample (as close to the bottom as possible to sample) is a result of the highly reducing conditions and near zero $\text{NO}_3\text{-N}$ concentration below the stream bed. The lower concentrations on the right hand side of the stream were measured in a relatively stagnant pool of water. Again, these processes occur whether the stream level is controlled or not; but the residence time of water in the control section is greater during periods of control. For example, the cross-sectional areas taken on Mitchell Creek show that when the depth of water in the creek is increased from 0.5 to 2.5 m, the wetted perimeter of the water interface in contact with the soil surface increases three-fold. This increases the probability for denitrification to occur.

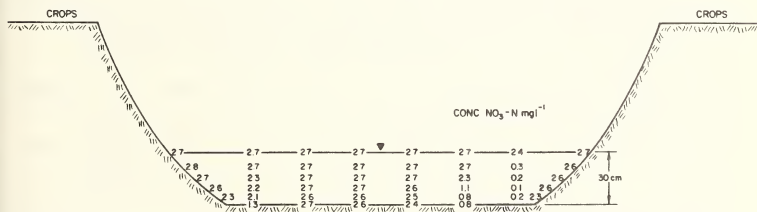


Fig. 8. Nitrate-nitrogen concentrations in a cross section of the channelized stream. Numbers are averages of three samples taken over a 24-hour period.

The effect of control on total N concentration was nearly the same as for $\text{NO}_3\text{-N}$ because $\text{NO}_3\text{-N}$ makes up a large percentage of the total N. Most of the difference between total N and $\text{NO}_3\text{-N}$ is organic N because $\text{NH}_4\text{-N}$ concentration is usually $< 0.1 \text{ mg L}^{-1}$.

There was an inconsistent effect of watershed drainage control on P concentration in the control section. Processes responsible for the nitrogen decreases are not effective for removal of P. Actually the P levels measured in this stream are about as low as can be expected for drainage water from agricultural watersheds in the Atlantic Coastal Plain. The low P levels are probably a result of the high hydraulic conductivity in deep sands adjacent to the ditch. Most water entering the channel enters by subsurface flow which contains little P.

SUMMARY

The utilization of controlled subsurface drainage offers potential for reducing offsite nutrient inputs as a result of improved agricultural drainage. Management can also be used to distribute the drainage flow over a longer period of time to reduce peak outflow rates. It can reduce the nitrogen content, particularly $\text{NO}_3\text{-N}$, of the drainage water. Drainage control systems which increase surface runoff do tend to slightly increase the P content of the drainage water.

Water management techniques to improve the quality of agricultural drainage water are very attractive to those concerned with agricultural production because it offers the potential for increased crop yields. Several controlled drainage systems have recently been installed in Eastern North Carolina with the anticipation of increased crop yields. These systems have also been recognized by regulatory agencies and SCS as a Best Management Practice in North Carolina and cost sharing is available in nutrient sensitive watersheds.

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DISCUSSION: Gilliam Paper

Comment (Correll): I wonder whether or not you have enough organic matter in those soils to carry out more denitrification or is that becoming a limiting factor when you flood the soils? Are those agricultural soils too poor in organic matter and especially the subsoils to drive denitrification further?

Answer: That is very definitely true, and is the reason I have said, I didn't think we increased the denitrification close to the main channel. Those subsoils do not have enough organic carbon to become reduced, and there is no indication we would ever get denitrification in that system where we have the Fabridams. Now that isn't true in poorly drained soil where we are controlling it on the field basis.

Question (Vorosmarty): I was wondering what proportion of denitrification was in the form in N_2O losses?

Answer: In most of these poorly drained fields we measured from 10 to 20 kg ha/yr coming off as N_2O .

Question (Vorosmarty): So about half of the loss would be N_2O ?

Answer: Maybe a third. We have measured some fields where we get much higher. In some of the organic soils we have measured 50-60 kg ha/yr where we have low pH's, pH 4.5 - 4.8. But most agricultural fields where I talked about using control drainage we measured from 10 to 20 kg ha/yr coming off as N_2O .

Comment (Pionke): I noticed you were recommending this to farmers and there were large numbers of farmers involved. Under the conditions of a raised water table you had considerably higher phosphorus concentrations. This raises a lot of questions. The discharge of that watershed may contain increased trace metals or pesticides. What I am saying is that there may be some negative aspects to the reduction process.

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

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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.

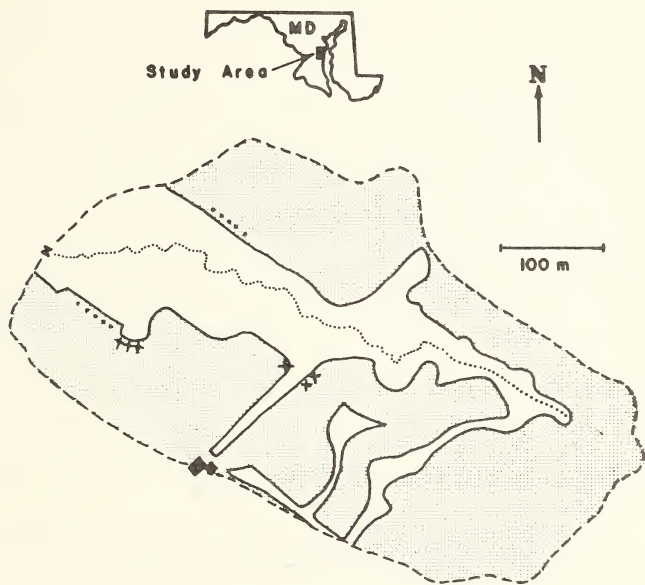


Fig. 1. General location (insert), and map of the watershed. The positions of groundwater wells during Year 1 (X) and Year 2 (.) are shown. Shading indicates cultivated fields. Dotted line indicates stream channel.

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.

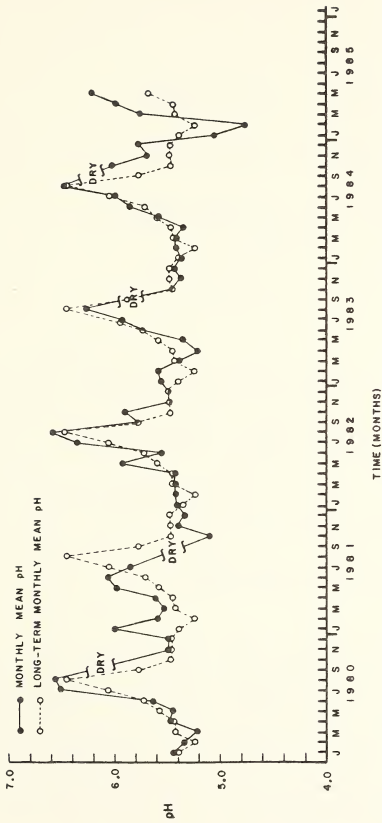


Fig. 2. Monthly and long-term monthly pH values measured at the weir. Mean pH values were determined by averaging hydronium ion concentrations and then converting to pH.

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	1.00×10^7	1.09×10^7
	Subsurface	0	0
	Evapotranspiration	6.08×10^6	6.48×10^6
	Subsurface	3.92×10^6	4.42×10^6
Riparian Forest	Precipitation	1.00×10^7	1.09×10^7
	Subsurface	7.90×10^6	7.79×10^6
	Evapotranspiration	1.07×10^7	1.18×10^7
	Subsurface	6.17×10^6	6.94×10^6

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.

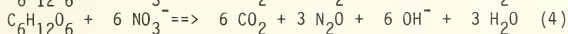
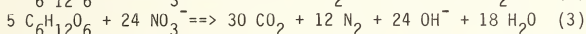
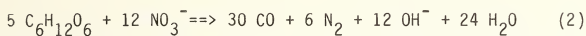
		<u>Year 1</u>		<u>Year 2</u>	
Nitrate-N	In	50.7	(5.23)	43.4	(5.19)
	Out	7.54		5.58	
	In-Out	43.2		37.8	
Sulfate-S	In	69.9	(14.5)	55.8	(17.0)
	Out	58.2		58.5	
	In-Out	11.7		-2.70	
Kjeldahl-N	In	1.79	(8.46)	2.07	(8.07)
	Out	3.16		2.94	
	In-Out	-1.37		-0.870	
Total-P	In	0.351	(0.449)	0.622	(0.884)
	Out	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 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^a 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 ^b
			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 ^c			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^a 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 ^b
			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 ^c			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.^a

Month	Concentration (mg/l)					pH ^b
	Chloride	Nitrate-N	Sulfate-S	Kjeldahl-N	Total-P	
Mar	17.4	0.654	9.63	0.257	0.032	5.07
Apr ^c	18.5	0.566	7.53	0.556	0.136	5.99
May	16.4	1.02	6.71	0.190	0.142	...
June	19.2 ^e	1.01 ^e	...	0.944 ^e	0.442 ^e	6.41
July ^c	20.1	1.06	8.81	1.88	0.251	6.35
Aug	----- Dry -----					
Sept	----- Dry -----					
Oct	22.7	0.056	11.5	0.204	0.080	5.36
Nov	10.9	0.900 ^e	14.2	0.324 ^e	0.041 ^e	5.39
Dec	15.2	0.380 ^e	10.2	0.288 ^e	0.095 ^e	5.46
Jan	18.2	0.496 ^e	10.4	0.422 ^e	0.053 ^e	5.39
Feb	19.7 ^e	2.27 ^e	10.6 ^e	0.354 ^e	0.057 ^e	5.33
Yearly Mean ^f	17.8	0.841	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. ^a

Month	Concentration (mg/l)					pH ^b
	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 ^C	8.81	0.428 ^C	0.103 ^C	5.48
May	14.6	0.008 ^C	4.08	0.747 ^C	0.285 ^C	5.89
June	15.7	1.37 ^C	19.8	0.617 ^C	0.182 ^C	6.05
July	14.0	1.93 ^C	4.75	0.463 ^C	0.138 ^C	6.59
Aug	15.3	1.06 ^C	4.60	0.530 ^C	0.188 ^C	6.70
Sept	-----		Dry	-----		
Oct	10.7	1.15 ^C	6.36	0.520 ^C	0.263 ^C	6.06
Nov	15.0	0.046 ^C	8.11	0.199 ^C	0.057 ^C	5.58
Dec	14.3	0.102 ^C	6.63	0.114 ^C	0.206 ^C	5.97
Jan	16.1	0.566 ^C	9.97	0.167 ^C	0.034 ^C	4.72
Feb	10.4	1.43 ^C	4.93	0.282 ^C	0.109 ^C	5.70
Yearly Mean ^d	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 CO₂ 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.

NITRATE CONCENTRATIONS IN A SMALL STREAM AS AFFECTED BY CHEMICAL
AND HYDROLOGIC INTERACTIONS IN THE RIPARIAN ZONE

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ABSTRACT

Nitrate concentration of groundwater decreased by more than 50% during transit through 16 m of the riparian zone near a small stream in Pennsylvania. Depth to the water table and denitrification measured for soil/sediment samples collected from the stream channel suggest that biological processes caused this reduction in nitrate concentration. Potential denitrification was measurable in samples collected to the depth at which a rock-soil interface was encountered and was not restricted to areas of sediment accumulation. The reduction in nitrate concentration in the riparian zone of the stream indicates that processes occurring within the riparian zone should not be ignored when projections are made concerning the impact of land management changes on stream water quality.

INTRODUCTION

A schematic, typical of a watershed in the Ridge and Valley physiographic province of Pennsylvania is shown in Fig. 1. Nitrogen is transported from upland source areas on the watershed to the stream by 1) overland flow, 2) interflow and 3) groundwater flow. A number of control points exist enroute from field boundary to watershed outlet which affect changes in the composition and concentration of stream flow. Biological processes which alter the nitrogen composition of the soil solution and groundwater are thought to occur primarily within two regions of the watershed: 1) the root zone, and 2) the riparian zone. The degree to which these processes alter the nitrogen concentration of solutions flowing to a stream depends on the quantity of biomass and the kinetics of biological processes, which define the intensity of solution concentration changes; and on the morphology and hydrology of the watershed which together govern the extent of the near-stream zone and the contact time between solution, roots and microbes. Watersheds with steep slopes and layered soils may route most of the subsurface flow

through a zone largely explored by roots, and if a perched water table develops, this zone may also support denitrification along the entire flow pathway. In contrast, gently sloping watersheds with deep uniform soils may have a small interactive zone near the stream and therefore exert less control over stream N concentrations.

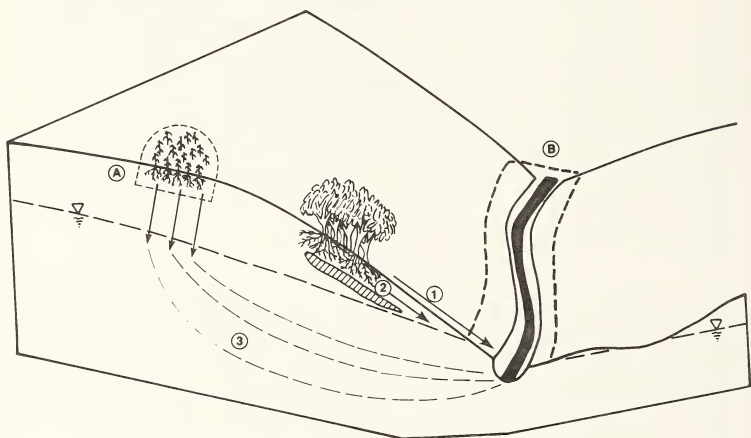


FIG. 1. Watershed schematic depicting nitrogen transport in 1) surface runoff, 2) interflow, and 3) groundwater from an upland source area (A) through the riparian zone (B).

This paper will report research results concerning changes in the nitrate concentration of solutions in the riparian zone of a watershed in central Pennsylvania. Data showing the magnitude of nitrate reductions as solutions flow through the riparian zone will be presented, as will laboratory data of denitrification for sediments collected from the stream channel.

METHODS AND MATERIALS

The research reported here was conducted on a subwatershed of the Mahantango Creek Watershed in central Pennsylvania (II of Fig. 2). The subwatershed is drained by 288 m of first-order stream, of which approximately

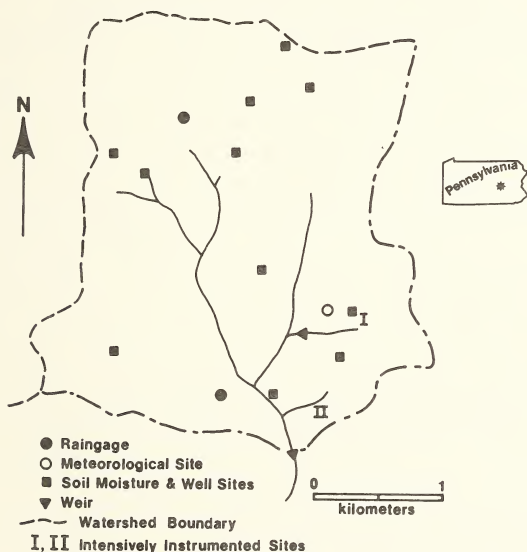


FIG. 2. Location of research site (II) within the Mahantango Creek Watershed in central Pennsylvania.

the upper 50 m is ephemeral. The soils of the subwatershed are loamy-skeletal, mixed, mesic, Typic Dystrochrepts, developed from brown and gray shales and sandstone. Soil slopes generally range from 3 to 30 percent, with some slopes greater than 50 percent. Seven year averages for rainfall, ET, surface runoff and base flow for the Mahantango Creek Watershed may be found in Pionke et al. (1985).

A schematic of the instrumentation in the riparian zone of the subwatershed is presented in Fig. 3. The watershed was instrumented to measure the quantity and quality of rainfall, runoff, seepage and stream flow. In addition, the elevation of the local water table and composition of soil solution in the near-stream zone were determined. Rainfall was measured at the site in a standard recording rain gauge and its composition was determined in samples collected in a 50 cm diameter container which was rinsed daily. Stream flow was measured over weirs at three locations on the first-order stream and at the outlet of the main research watershed. Grab samples were collected for chemical analysis at six locations along the stream three times weekly during the months of April through October and once weekly during the rest of the year. Surface runoff and seepage upwards through the soil surface were collected at 5 locations by driving a 96 cm diameter steel ring approximately 10 cm into the soil. Runoff and seepage were gravity fed through an outlet in the ring into sampling containers. Twenty-four piezometers were installed to determine the depth of the local water table in the vicinity of the stream. The piezometers were installed to a depth where bedrock was encountered (approximately 1 meter). Suction lysimeters were also installed along a transect normal to the stream at the soil-bedrock interface. The depth to the water table was measured weekly. Samples of the soil solution were extracted with lysimeters on a weekly basis during the months of April to October. Water samples were analyzed for $\text{NO}_3\text{-N}$, $\text{NH}_4\text{-N}$ and TKN following the procedures of Technicon Industrial Systems (1977a,b) and Schuman et al. (1973).

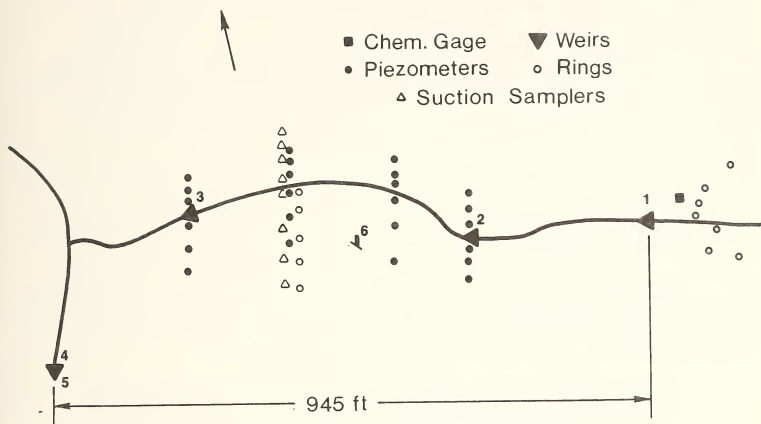


FIG. 3. Instrumentation within the riparian zone of the stream draining the research site, II of Fig. 2. The instrumentation was located in a band approximately 30 m wide on either side of the stream.

Additionally, the denitrification potential of stream sediments were determined following the procedure of Swank and Caskey (1982). Stream sediment samples were collected at 1 m intervals along a 20 m section of the stream to the depth at which fractured rock was encountered, approximately 0.6 m.

RESULTS AND DISCUSSION

Stream Flow Composition

All the data presented in this paper were collected during the calendar year 1984. The data in Table 1 give a general description of discharge over the course of the year at the watershed outlet (position 5 of Fig. 3) and at the outlet of the small subwatershed (position 3). A mass of nitrogen equivalent to 36 kg/ha was exported from the main watershed. Fifty-three percent of the watershed is cropped, and the measured nitrogen, occurring primarily during the months of November through May, is approximately 50 percent of the total fertilizer nitrogen applied to the fields. Stream flow discharge from the main watershed is equivalent to approximately 50 percent of rainfall and, as with nitrogen discharge, occurs primarily during the period when evapotranspiration (ET) is low. The discharge data for the subwatershed in Table 1 is not scaled by area because the exact extent of the drainage basin is not known. The patterns of discharge, however, are similar for both watersheds, with discharge in the smaller watershed being more responsive to rainfall.

TABLE 1. Cumulative Discharge and Nitrate-N Export Density during 1984 at Positions 3 and 5 of Fig. 3.

Month	Rainfall	<u>Position 5</u>		<u>Position 3</u>	
		Stream flow	Nitrate-N	Stream flow	Nitrate-N
	(mm)	(mm)	(kg/ha)	(ha-cm)	(kg)
Jan.	33.78	31.02	1.51	0.13	14.40
Feb.	164.08	153.96	8.38	1.27	106.07
Mar.	264.67	215.27	11.78	2.16	229.25
Apr.	382.52	349.61	19.16	3.84	456.25
May	545.59	432.98	24.40	4.51	534.71
June	719.07	512.76	31.13	5.87	716.82
July	794.51	539.21	32.75	6.24	764.20
Aug.	865.89	547.38	33.07	6.28	767.85
Sept.	894.08	550.93	33.15	6.29	768.31
Oct.	955.80	552.66	33.24	6.30	768.69
Nov.	1087.12	581.30	35.45	6.32	770.36
Dec.	1158.24	622.91	39.32	7.27	926.97

A comparison of nitrate concentration and stream discharge (Fig. 4) shows no discernible pattern between nitrate concentration and the maximum discharge rate for that day. Data such as these have been reported for watersheds in the Northeast by Ritter and Harris (1984) and for watersheds on the Coastal Plain by Campbell (1978). While no relationship is apparent between discharge and nitrate concentration when the values are lumped, a relationship comes into focus when they are plotted against time (Fig. 5). During periods of low flow the concentration of nitrate decreases and following rainfall, when discharge increases, the concentration of nitrate increases.

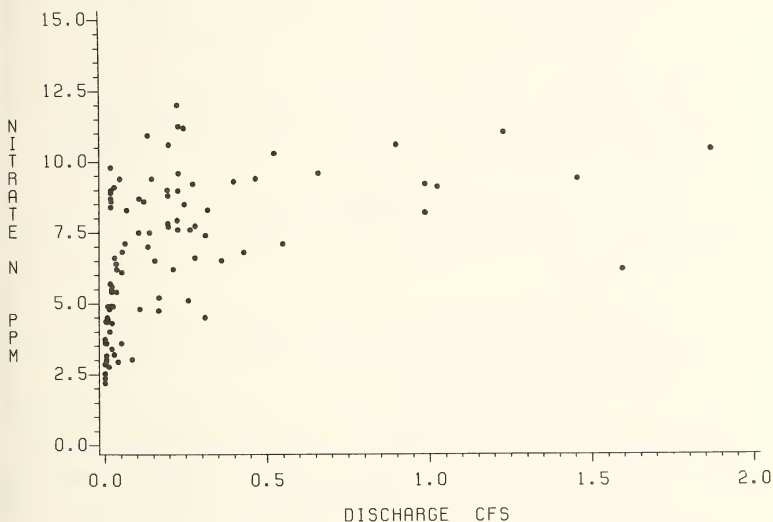


FIG. 4. Relationship between Nitrate-N concentration and stream discharge at location 3 (A Fig. 3) for the year 1984.

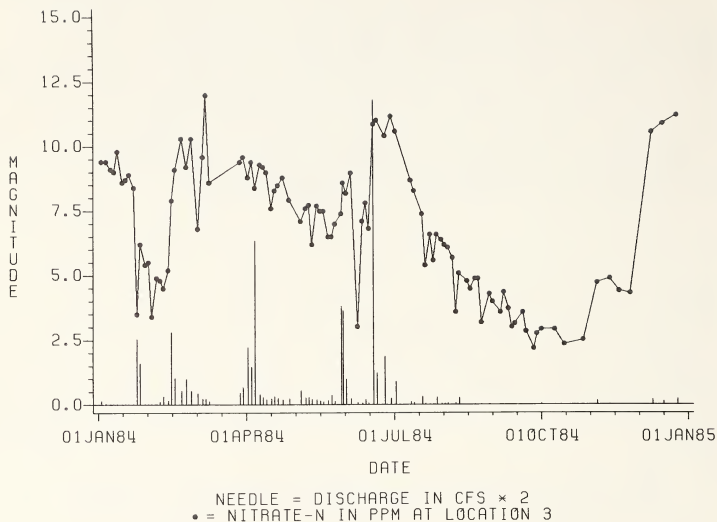


FIG. 5. Nitrate-N concentration and daily maximum discharge during 1984 at position 3. Discharge has been multiplied by 2 to aid visual comparison.

A similar but more consistent pattern is seen when nitrate concentration and precipitation are plotted over the course of the year (Fig. 6). The pattern in Figs. 5 and 6 consists of cycles of increasing nitrate concentration subsequent to storm events, followed by decreasing concentration as discharge decreases and presumably the water table drops. The measured increase in nitrate concentration lags rainfall and persists for days. This pattern of increasing concentration with increasing flow could result from the local water table rising into previously unsaturated zones and flushing nitrate which had accumulated during periods when the water table was

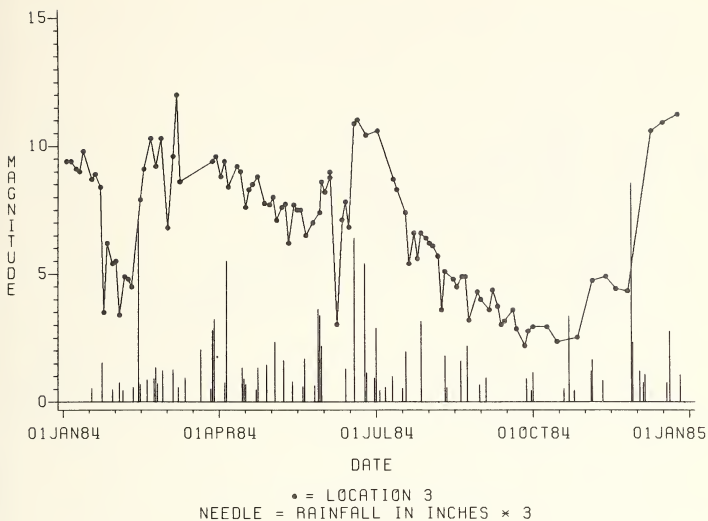


FIG. 6. Nitrate-N concentration and precipitation during 1984 at position 3. Precipitation has been multiplied by 3 to aid visual comparison

relatively deeper. Alternatively, the travel time of solutions through the near-stream zone is shortened during periods of higher flow reducing the possibility that nitrogen transformations would decrease the nitrate concentration.

The pattern of nitrate concentration with time measured at position 1 (Fig. 3) is repeated at all downstream positions. While the pattern is similar, the magnitude of nitrate concentration is variable. For example, nitrate concentration at position 3 ranges 2-3 ppm greater than that measured at position 2 (Fig. 7). This change in concentration is measured at positions

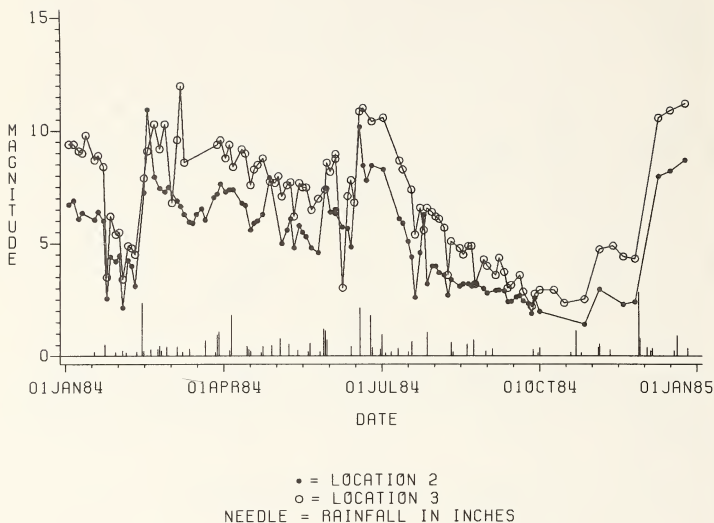


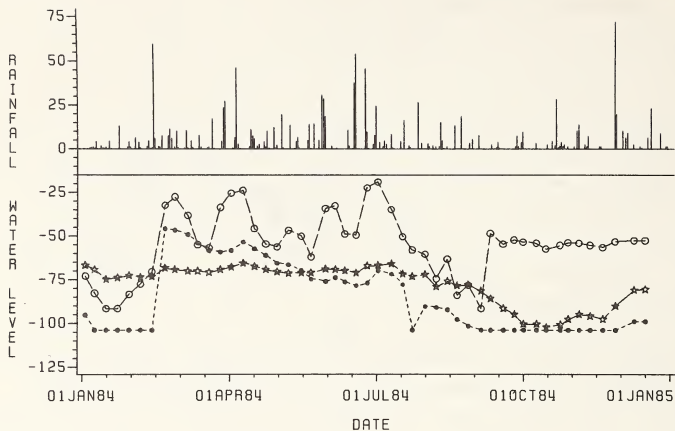
FIG. 7. Nitrate-N concentration and precipitation at positions 2 and 3 during 1984.

approximately 83 m apart. Reports of denitrification in stream sediments in recent literature (Hill, 1983; Kaplan et al. 1979; Swank and Caskey, 1982), plus denitrification measured at this site, reported later, suggest that nitrate concentration should decrease at downstream positions. That the concentration at position 3 is greater than at position 2 may in part be explained by the mixing of streamflow and spring discharge between positions 2 and 3. The nitrate-N concentration of the spring is consistently greater than 10 ppm, either originating from a source different from that of upstream flow, or being less altered during transit through the riparian zone.

Nitrate in the Riparian Zone

The development of seepage faces adjacent to the stream and seep zones at more distant positions is a common phenomenon in the Ridge and Valley Province which is illustrated in Fig. 8. The data in Fig. 8 were obtained from the series of piezometers located normal to the stream near position 3 (Fig. 3). The piezometers were installed to a depth at which the interface between soil and fractured rock was encountered (approximately 1 meter) and are used here to indicate the depth of the local water table. As was expected, depth to the water table was responsive to rainfall. This was especially true of piezometer 8 which is located 9 meters from the stream at a slight break in slope. The piezometer most distant from the stream was least responsive, with the nearest piezometer being intermediate. The water table was measured to be at the surface only at piezometer 8. Water table elevation at piezometers 7 and 9 changed less than at piezometer 8, and the changes lagged rainfall more than at piezometer 8. The water table elevation was recorded at weekly intervals. Measurement times rarely coincided with heavy rainfall, yet the water table was measured to be within 6 inches of the soil surface on one occasion. This is important for a number of reasons. It illustrates the rise and fall of the water table which could act to flush previously unsaturated soil or mineralized nitrogen and demonstrates that in these watersheds, the water table is near the surface for an extended distance away from the stream. Conditions in this near-stream zone are, therefore, sufficient for denitrification to occur, reducing the nitrate concentration of solutions moving to the stream through the riparian zone.

If denitrification is occurring in the riparian zone, the concentration of nitrate in solution will decrease with time, and in a flowing system nitrate will decrease as the solution moves down gradient (towards the stream). The suction lysimeter data in Table 2 illustrates that the nitrate concentration of ground water decreases as the stream is approached. Lysimeters 1-4 and 5-8 are located on opposite sides of the stream. Lysimeters 1 and 5 are nearest the stream, while 4 and 8 are farthest from the stream. The entire riparian zone is wooded on side 5-8, while a grassed strip runs



RAINFALL IN MM, DEPTH TO WATER TABLE IN CM
 • = PIEZ #7
 ○ = PIEZ #8
 ★ = PIEZ #9

FIG. 8. Water table elevation and precipitation during 1984, 3, 9, and 18 m from the stream, piezometers 9, 8, and 7, respectively. Horizontal 1 m at -15 cm corresponds to the land surface.

parallel the stream on side 1-4 for a width of approximately 30 meters. Accordingly, lysimeters 1-3 are located in the grassed strip and lysimeter 4 is in the wooded area just beyond. The nitrate concentration in the riparian zone is random, with no pattern of decreasing or increasing concentration as the stream is approached during May. From June through September, however, the nitrate concentration of solutions collected with the lysimeters was consistently less for the lysimeters nearer the stream. The nitrate concentration of ground water 2.5 m from the stream was less than half that 18.5 m from the stream. The greatest reduction in nitrate concentration was

TABLE 2. Nitrate-N Concentration in Ground Water within the Riparian Zone

	Lysimeter [#]							
	4	3	2	1	5	6	7	8
	Distance from stream (m)							
Date	27.0	18.0	9.0	2.5	2.5	7.0	12.5	18.5
May	15.1	15.3	15.9	13.6	2.0	0.8	1.1	4.9
June	22.3	17.0	16.1	8.7	0.4	1.2	1.3	5.6
July	23.7	19.4	18.2	6.8	0.1	0.9	1.3	2.5
Aug.	-	21.8	14.9	8.2	-	-	-	-
Sept.	-	22.6	16.6	11.5	-	-	-	-

[#]Lysimeters 1-4 are on the grassed side of the stream, while lysimeters 5-8 are on the wooded side of the stream.

measured between the two lysimeters nearest the stream (lysimeters 1 and 2). These lysimeters were located at positions in the riparian zone where the water table was generally nearest the land surface and consequently, at a position where denitrification is most likely. Ammonium concentrations of all lysimeter samples were measured to be less than 0.2 ppm and TKN concentrations were generally less than 1 ppm and exhibited no pattern with respect to distance from the stream. The reduction in nitrate concentration does not appear to result from storage of nitrogen in another form, but rather reflects a loss of nitrogen from solution.

A further confirmation of changes in nitrate concentration as solutions move towards the stream was found in the nitrate concentration of seepage samples. Samples which were known to be seepage were collected on 3 occasions from the rings designated on Fig. 3. The average nitrate concentration measured for the seepage was 11.6 ppm. On each of the occasions, the highest nitrate concentration was measured in the sample collected farthest from the stream. These three samples are insufficient to make generalizations, but this limited sampling suggests that solution nitrate concentrations are decreased during flow through the riparian zone.

Perhaps the most striking feature of the data in Table 2 is the 2 to 3-fold greater nitrate concentrations measured in lysimeters 1-4 compared with lysimeters 5-8. The grassed strip had been wooded until approximately 6 years ago, and the higher nitrate concentrations measured on this side of stream might be explained by the nitrogen mineralized from the decaying tree roots. The fact that lysimeter 4 is located up gradient in the wooded area and has nitrate concentrations of similar magnitude as from lysimeters 1-3 requires that another explanation be found for this phenomenon. An inviting explanation is that the upland sources of the water flowing to the stream on either side are different, with different paths to the stream and perhaps different surface management practices. However, insufficient subsurface exploration of the area has been performed to substantiate the previous speculation. The water table elevation data do, however, provide an explanation. The piezometer data demonstrates that the lysimeters on the grassed side of the stream were positioned below the water table and the samples collected with these lysimeters were indeed ground water. In contrast, the water table on the wooded side of the stream was frequently below the position of the lysimeters (data not shown) and these samples were soil solution from a wooded area, which is expected to have a low nitrate concentration.

To this point, a chemical component has been sought to explain the observed pattern of nitrate concentration in stream flow. However, a similar pattern was also observed in the electrical conductivity (EC) of stream flow. Since electrical conductivity is a measure of total salinity, the possibility that the observed patterns are purely hydrologic phenomena must be explored. To that end, the measured pattern of EC was compared to EC estimated from nitrate concentrations for 4 storm periods. Electrical conductivity was estimated with a simple relationship developed by the Soil Salinity Laboratory Staff (1954). The best fit linear regression lines of measured to estimated conductivity for the storms are given in Table 3. The slopes of the regression lines ranged from 0.8 to 1.14, providing evidence that the great majority of the rise and fall of EC subsequent to storms was accounted for by changes in nitrate concentration. If the observed patterns were the result of hydrologic processes, then all salts would be affected similarly and only a

TABLE 3. Regression Equations for Electrical Conductivity
 Estimated from Changes in Nitrate Concentration
 against Measured Electrical Conductivity

Storm	Equation	Corr Coeff
1	Est. EC = 19.1 + 0.80 Mea. EC	$r^2 = 0.97$
2	Est. EC = 24.4 + 0.81 Mea. EC	$r^2 = 0.98$
3	Est. EC = -22.9 + 1.14 Mea. EC	$r^2 = 0.94$
4	Est. EC = - 1.49 + 1.01 Mea. EC	$r^2 = 1.00$

small fraction of the measured changes in EC would have been accounted for by changes in nitrate concentration. Since much of the measured change in EC was attributable to nitrate concentrations, it seems that the observed patterns of nitrate in the riparian zone are the result of chemical or biologic processes.

Denitrification in the Stream Channel

The decrease in nitrate concentration in solutions collected nearer the stream in both the lysimeters and in seepage suggests that denitrification may be occurring in the riparian zone. Soil/sediment samples collected from the stream channel were therefore incubated under an argon atmosphere as a measure of potential denitrification. The soil/sediment samples were collected from the stream bottom to a depth at which rock was encountered (usually less than 0.5 m) and into the stream bank approximately 0.2 m above the free water surface in the stream for a distance of 0.6 m. The samples were collected at 1 meter intervals along the stream and segmented with depth prior to incubation. No attempt was made to sample from areas of sediment accumulation only. The position in the stream bank from which the samples were taken is within a zone which seeps during much of the year. The measured rate of denitrification was quite variable with a mean rate of 52.6 ng N/g/s (Table 4). There was little difference in mean denitrification rates between channel bank

TABLE 4. Denitrification Rates of Stream Channel Samples as Measured by Nitrous Oxide Evolution. Denitrification Rates on a Mass Basis in ng N/g/s and on an Areal Basis in mg N/m²/s

	Mean	CV	
All Samples	52.6	229.61	
Bottom Samples			
Depth (cm)	Mean	CV	Mean
	mass basis		areal basis
0-7.5	72.7	105.64	0.0031
7.5-15	38.8	137.63	0.0021
15-30	10.0	118.51	0.0014
30-60	07.5	63.79	0.0022
All Depths	45.5	137.93	0.0088
Bank Samples			
Depth (cm)	Mean	CV	Mean
0-7.5	36.9	78.57	0.0029
7.5-15	43.3	93.95	0.0034
15-30	35.1	80.75	0.0067
30-60	38.5	213.64	0.0130
All Depths	37.3	260.68	0.0260

and bottom samples. The major difference between the bank and bottom samples is that the bank samples had a relatively uniform rate of denitrification with distance into the bank, while the rate of denitrification decreased with depth into the stream bottom. The larger value for the 30-60 cm depth into the bank results from a single large value. When this is removed from consideration, there is little difference in mean denitrification rate between the bank and channel samples. On an areal basis, the potential denitrification rate into the stream bottom equalled approximately 0.01 mg N/m²/s which is considerably greater than that reported by other researchers (Hill, 1983; Sain et al., 1977; Wyer and Hill, 1984). Given that denitrification was measured in samples collected to the rock interface in the stream bottom, and was undiminished with distance into the stream bank suggests that denitrification

may occur in much of the near-stream zone through which solutions travel enroute to the stream. While the rate of denitrification at the 30-60 cm depth in the stream bottom was approximately 10% of that for the surface 7.5 centimeters, when calculated on a mass basis, the rate on an area basis was about 30% of that at the surface. This difference results from the greater mass of soil between 30-60 cm as compared to the surface 7.5 cm and indicates that, although the denitrification rate on a mass basis for a given position in the soil may be low. If the solution is in contact with this soil for a longer time, even the lower rate will result in significantly reduced nitrate concentrations.

Further evidence of denitrification in ground water discharging into the stream can be found by examining the concentration of nitrate in the samples collected for incubation (Table 5). If denitrification were altering the composition of solutions flowing to the stream, then the nitrate concentration would decrease as the surface of the stream channel is approached. The nitrate values for the bottom samples support this contention. The greater concentration in the upper 5 cm is the result of a high nitrate spring discharging into the stream approximately 25 m upstream of the sample

TABLE 5. Nitrate Concentration of Solutions with Depth into the Stream Channel

Depth	Channel Bottom	Channel Bank
(cm)	----- nitrate-nitrogen (mg/l) -----	
0-5	7.26	6.44
5-10	3.21	7.51
10-15	1.72	7.24
15-30	2.77	6.56
30-45	7.64	9.79
45-60	16.90	12.80

collection area. The mixing of this higher nitrate water with the solution discharging into the stream results in a greater concentration at the solution sediment interface of the stream.

The magnitude of nitrate reductions in ground water in the riparian zone of a small stream demonstrates that accurate predictions of stream water quality resulting from changing management practices cannot be made without considering processes which occur between field boundary and stream. The measureable denitrification rates at depth into the channel bottom and bank further suggest that when assessing the denitrification potential in stream channels it is important to sample more than just the surface few centimeters of areas where sediment accumulates.

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DISCUSSION: Schnabel Paper

Question (Correll): I don't have a good feel for the vegetation along the stream. You mentioned some patches of woods and, in Pionke's paper yesterday, I got the impression a lot of the channel is not vegetated or is only vegetated with grass. Could you give us a better description of the vegetation along that channel at various places?

Answer: I would sure like to, but I am only doing it in a general way. It is pretty common for there just to be a grass strip on either side of the channel. There is no submerged aquatic vegetation in the stream itself and it is rare for there to be any floating.

Comment (Correll): I got the impression that there was some woody vegetation some places, though.

Answer: Yes, there is. Woody vegetation again is pretty common. In fact, it is common along the main channel and in the lower reaches of the tributary. When you look at the tributary topography along the upper region it is more gently sloped and as you come to the confluence of streams the channel is more deeply incised. That deeply incised channel, where the slopes are relatively steep, is wooded and right in the stream channel there is some brush.

Question (Correll): Are there alder in the streams?

Answer: I think a very low proportion, there is some.

Comment (Pionke): The interesting thing about his site is that it is instrumented the same way on both sides. One side is grass like most of the watershed, but the other side is woods. Kind of a nice comparison. It appears as if it is not necessary to have woody vegetation in this riparian zone. There

is some question as to whether clear cutting has an effect. Just having the water table near the surface moving through an area which is checkered with roots and is organically rich appears to be sufficient to drop nitrogen concentrations.

Question (Kelly): I would like you to go back and expand a little bit on the observation you are reporting on the difference in nitrate concentration in the grass part vs the woody part. If I understand you correctly, you said you attribute this difference to sampling in the water table in grass and above the water table in the trees.

Answer: I am saying that on the one side of the stream I was measuring a solution that was representative of the root zone in the forest area. On the grass side of the stream, I was measuring solutions that were representative of the ground water. If I had been able to bore through the fracture rock material into the ground water on the woody side of the stream the results would have been considerably different.

SEASONAL PATTERNS OF ALLOCHTHONOUS DEBRIS IN THREE
RIPARIAN ZONES OF A COASTAL ALASKA DRAINAGE

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Abstract--Forest streams in coastal Alaska are largely dependent on allochthonous debris from riparian vegetation for a source of energy. To characterize the quantity, nutrient content, and seasonal patterns of detrital inputs into forest streams, allochthonous material was collected in 0.51-m^2 traps during a 26-month period at three riparian communities dominated by the following vegetation types: (1) red alder (*Alnus rubra*); (2) old-growth western hemlock-Sitka spruce (*Tsuga heterophylla-Picea sitchensis*); and (3) *Vaccinium* spp. Although average daily allochthonous inputs were highest from the old-growth area ($1.14\text{ g m}^{-2}\text{da}^{-1}$), only about half as much N was added to the old-growth stream reach ($8.5\text{ mg N m}^{-2}\text{da}^{-1}$) compared to the alder reach ($15.3\text{ mg N m}^{-2}\text{da}^{-1}$). The *Vaccinium* spp riparian zone, located in a more open forest than the old-growth zone, contributed the lowest amounts of allochthonous biomass ($0.57\text{ g m}^{-2}\text{da}^{-1}$), nitrogen ($4.6\text{ mg N m}^{-2}\text{da}^{-1}$), and phosphorus ($0.31\text{ mg P m}^{-2}\text{da}^{-1}$), to the stream. Allochthonous debris from the alder zone was dominated by deciduous leaves and had lower average C:N (30:1) and C:P (720:1) ratios than the other two areas, indicating that it was a better food source for biological consumers. All three riparian zones had their highest allochthonous rates during autumn, with peak inputs of 2.9, 2.2, and $1.0\text{ g m}^{-2}\text{da}^{-1}$ for the alder, old-growth, and *Vaccinium* spp areas, respectively. Vegetation type was more important than stream size or stream position in determining the amount, timing, and nature of allochthonous inputs.

INTRODUCTION

Allochthonous detritus is a major source of energy for aquatic ecosystems in small forest streams (Russell-Hunter, 1970; Fisher and Likens, 1973). After entering the stream, detritus is processed into finer particles by macroinvertebrates, flowing water, and abrasive action of sediment (Anderson et al., 1978; Bilby and Likens, 1979; Cummins et al., 1980). Initial particle size and resistance to breakdown affect the rate of detritus processing (Boling et al., 1975). Detritus becomes increasingly susceptible to microbial attack as it is physically broken into smaller pieces (Triska and Sedell, 1975). The fiber content of detritus affects its resistance to breakdown. Woody material is high in refractory components (cellulose and lignin) and, thus, decomposes and releases nutrients more slowly than other less refractory components such as deciduous foliage (Anderson et al., 1978).

Water quality also affects the rate of detritus processing. Wider temperature fluctuations and warmer average temperatures increase the abundance and diversity of macroinvertebrate populations and thus accelerate detritus processing (Hynes et al., 1974; Vannote et al., 1980). Nutrient enrichment of water, especially with N and P, increases decomposition rates of detritus in certain streams (Kaushik and Hynes, 1971; Hynes et al., 1974). The low temperatures and nutrient concentrations of pristine forest streams in coastal Alaska would limit biological processing of detritus.

Input rates and processing of detritus frequently occur in generalized patterns related to stream order. The River Continuum Concept, for example, postulates that upstream reaches receive greater inputs of coarse detritus per unit stream area than do downstream reaches and are, therefore, less efficient in processing detritus (Vannote et al., 1980). Local in-stream conditions and riparian vegetation can override these generalized patterns. Conners and Naiman (1984) found that composition of allochthonous detritus in four streams in eastern Quebec was more strongly determined by physical and vegetative characteristics of the riparian zone than by stream size. Large organic debris in streams can also influence the rate and spatial sequence by which smaller organics are processed. Naiman and Sedell (1978) found that smaller forest streams are more

efficient in processing allochthonous detritus than are larger streams partly because large organic debris dams in upstream reaches entrap fine detritus and retain it for decomposition and processing by macroinvertebrates. The overall ability of the stream to retain and process fine detritus appears to be related to the amount and orientation of large organic debris, the interaction of mineral substrate and organics, and the microvelocity profile along the stream bottom.

Allochthonous detritus can influence water quality as well as energy relationships in forest streams. Upon entering the stream, detritus is quickly leached of its soluble nutrients. This leachate is rapidly utilized by stream microbes and exerts a biochemical oxygen demand in stream water (Ponce, 1974; Triska and Sedell, 1975). Following initial leaching, however, organic detritus (especially deciduous leaves) can act as sink for nutrients in streams while being processed (Hynes et al., 1974; Sollins et al., 1985). Litterfall during low flow conditions has been linked to undesirable color, taste, and odor characteristics of water (Slack and Feltz, 1968; Taylor et al., 1983).

Composition and input rates of allochthonous detritus vary widely in different forest riparian communities. Some studies report input rates and composition of allochthonous detritus by measuring: (1) litterfall, and (2) lateral movement from the streambank. Lateral movement is a significant transport process in streams with steep banks or gradients (Fisher and Likens, 1973; Sedell et al., 1974). Approximately 65% of the litterfall in a small forest stream in western Oregon consisted of Douglas-fir and western hemlock needles (Sedell et al., 1974). Estimates of allochthonous detritus inputs from litterfall and lateral movement into this Oregon stream were 1.0 and $1.5 \text{ g m}^{-2}\text{da}^{-1}$, respectively. Litterfall inputs of N in this same stream amounted to $1.35 \text{ g m}^{-2}\text{yr}^{-1}$ (Triska et al., 1984). Iversen et al. (1982) estimated average allochthonous inputs in an old-growth beech forest headwater stream to be $2.0 \text{ g m}^{-2}\text{da}^{-1}$; leaves made up 71% of the inputs. Average litterfall into a small boreal forest stream in Quebec was estimated to be $1.2 \text{ g m}^{-2}\text{da}^{-1}$; litterfall into a nearby second-order stream with dense riparian stands of alder and paper birch averaged $0.72 \text{ g m}^{-2}\text{da}^{-1}$ (Connors and Naiman, 1984). None of these data on allochthonous inputs

from other regions are directly applicable to riparian communities and climatological conditions of coastal Alaska (Alaback, 1982; Alaback and Sidle, 1985). The objectives of this study were, therefore, to characterize and compare the quantity, quality, and seasonal patterns of allochthonous debris from three different riparian communities typical of small forest streams in coastal Alaska.

STUDY AREA

This study was conducted along three reaches of Bambi Creek located within the Trap Creek watershed on northeast Chichagof Island, Alaska (Fig. 1). Bambi Creek is approximately 2570 m long and drains an area of 154 ha ranging in elevation from 5 to 614 m above sea level. Three riparian communities along Bambi Creek were selected for investigation: (1) a red alder (Alnus rubra)-dominated zone near the mouth of Bambi Creek (Fig. 2); (2) a dense old-growth western hemlock-Sitka spruce (Tsuga heterophylla-Picea sitchensis) zone (Fig. 3) located about 300 m upstream of the alder zone, and (3) a Vaccinium spp-dominated zone (Fig. 4) in a more open old-growth stand located along a steeper (6 to 13%), first-order tributary. The lower portion of Bambi Creek that flows through the dense old-growth and alder study areas is a gentle (1 to 2% gradient), second-order reach with many riffle-pool sequences. Large organic debris plays an important role in regulating stream energy and provides sites for storage of sediment and fine organics in the middle to lower stream reaches.

Old-growth western hemlock-Sitka spruce is the dominant overstory at lower elevations. Understory vegetation in the rather broad floodplain of the alder riparian zone was dominated by skunk cabbage (Lysichiton americanum) and, to a lesser extent, devilsclub (Oplopanax horridus). Scattered spruce and hemlock occur along the periphery of the alder riparian zone and merge into an old-growth hemlock-spruce forest above the stream terrace. The stream channel through the old-growth riparian zone was more deeply incised and, thus, the adjacent riparian zone was not subject to frequent flooding. Understory vegetation in the old-growth zone was dominated by Vaccinium spp, devilsclub, and salmonberry (Rubus spectabilis) under relatively dense canopies of hemlock and spruce. A

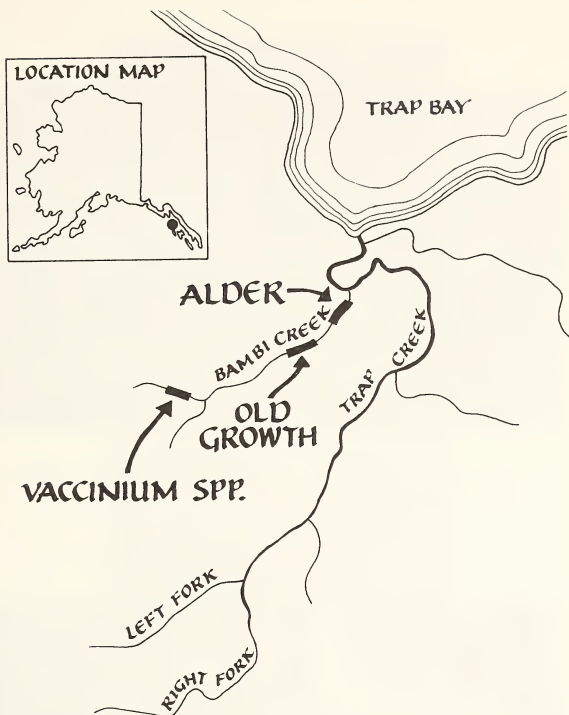


Figure 1. General locations of the alder, old-growth, and Vaccinium spp riparian zones studied in the Trap Creek drainage.

less dense, primarily hemlock, stand surrounded the higher elevation Vaccinium spp riparian zone. Overstory and understory vegetation in the Vaccinium spp area was similar to that in a nearby area described by Alaback and Sidle (1985).

The northern maritime climate of the area, typical of coastal Alaska, is characterized by cool summers, wet autumns, and relatively mild winters with intermittent snowpacks at lower elevations. Average annual precipitation at nearby Tenakee Springs (sea level) is 1670 mm of which approx-



Figure 2. Red alder-dominated riparian zone with a rather broad floodplain grading into a hemlock-spruce forest.



Figure 3. Riparian zone dominated by a dense old-growth western hemlock-Sitka spruce stand.

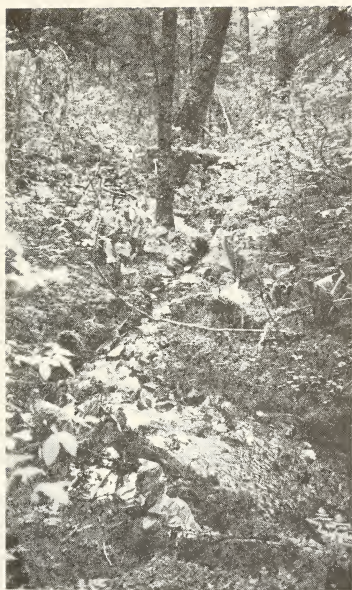


Figure 4. Vaccinium spp-dominated riparian zone in a more open old-growth stand.

imately 40% occurs as rain during autumn. Precipitation is believed to be significantly higher at Trap Bay because of orographic influences and exposure. Major stormflows normally occur during autumn. Maximum flow in Bambi Creek in the past 5 yr was $2.25 \text{ m}^3\text{sec}^{-1}$, which occurred during the peak of an intense autumn storm (Sidle and Campbell, 1985); low flows are typically $< 0.3 \text{ m}^3\text{sec}^{-1}$.

The Trap Bay drainage basin was carved during retreat of Pleistocene ice. At lower elevations, surficial bedrock is composed of Silurian graywacke and argillite and Devonian limestone (Lanphere et al., 1965). Soils are primarily spodosols with relatively thick (20 - 60 cm) organic hori-

zons. Numerous muskegs (bogs), interspersed at lower elevations, play an important role in attenuating stormflow peaks (Campbell and Sidle, 1985).

METHODS

Nine sites within a 230-m stream reach were randomly selected for collection of allochthonous debris in each of the three riparian zones (alder, old growth, and Vaccinium spp). Wood frame traps 15 cm deep with catchment areas of 0.51 m² (90 cm by 57 cm) were constructed to collect allochthonous debris. Hardware cloth supported by lathing was attached to the underside of the traps. The inside of the trap was lined with washed muslin. The muslin was tacked to the lathing to facilitate detritus removal.

Traps were suspended over the stream at each of the 27 sampling locations (Fig. 5). The elevation of the traps was between stormflow stage and the top of the stream bank or terrace if possible. Thus, the allochthonous inputs included litterfall and detritus blowing laterally into the traps. Lateral movement into the stream occurring immediately at the streambank was generally not sampled by this method with the exception



Figure 5. Detritus trap installed over Bambi Creek in the alder riparian reach.

of several traps near undercut banks in the more deeply incised old-growth stream reach. Lateral bank movement of detritus in the alder reach is not expected to be very high because of the broad, gently sloping floodplain and shallow banks. Some lateral movement of detritus was sampled in the steeper *Vaccinium* spp reach because the traps often spanned from bank to bank in this narrow headwater stream.

Allochthonous debris was collected from the traps at about 1-month intervals during the summer and autumn months from October 1981 to December 1983. During winter and spring, a number of traps were either destroyed by ice and water action or frozen into the stream. Because of these problems, as well as access limitations, samples were not collected on a routine basis during the winter and early spring; however, input rates for these periods were low.

Once collected, all allochthonous debris was transported to the laboratory, oven-dried at 60 °C, and sieved and weighed into the following size classes: > 16 mm; 4-16 mm; 1-4 mm; and < 1 mm. Size classes were selected to correspond with those used in biological studies of detritus processing (e.g., Naiman and Sedell, 1978). Within each size class, organic material was sorted and qualitatively proportioned and classified into the following components: deciduous leaves, needles, wood fragments, woody stems and twigs, bark, cones, and other organics. Wood fragments, woody stems and twigs, and bark were combined for chemical analyses because of their highly refractory nature and called "woody material." "Other organics" consisted primarily of finely processed (< 1 mm) debris with lesser amounts of small vegetation (e.g., mosses) and aggregated organic matter, all generally < 4 mm.

Detritus components (i.e., woody material, cones, needles, leaves, and other organics) were composited from individual samples collected during different seasons for each riparian zone. These detritus components were redried, ground, and digested in H₂SO₄ with a Se catalyst (Isaac and Johnson, 1976). Total N and P were then measured in the diluted digest with a Technicon Auto Analyzer.^{1/} Carbon content was estimated from loss on ignition, assuming 58% of the volatilized fraction was C.

^{1/}Trade names do not constitute endorsement by the USDA Forest Service.

RESULTS AND DISCUSSION

Allochthonous Biomass- Average input of allochthonous debris from the three riparian zones during the 26-month sampling period was $0.85 \text{ g m}^{-2}\text{da}^{-1}$. Daily inputs from the alder, old growth, and Vaccinium spp dominated riparian zones averaged 0.84, 1.14, and $0.57 \text{ g m}^{-2}\text{da}^{-1}$, respectively (Table 1). The alder riparian zone had the highest percentage of total allochthonous inputs in the $> 16 \text{ mm}$ size fraction, while the Vaccinium spp zone had the highest percentage of inputs in the $< 1 \text{ mm}$ fraction. Allochthonous material in the alder-dominated zone was nearly half deciduous leaves, with lesser amounts of woody material (wood fragments, stems, twigs, and bark) and conifer needles (Fig. 6). The more refractory components (woody material, cones, and needles) comprised 80% of the allochthonous debris in the old-growth riparian zone, compared to only 63% and 47% of the debris in the Vaccinium spp and alder zones, respectively. Approximately half of the "other organic" inputs in the Vaccinium spp zone consisted of finely processed ($< 1 \text{ mm}$) debris.

Table 1. Average daily inputs ($\text{g m}^{-2}\text{da}^{-1}$) of different size fractions of allochthonous debris from the three riparian areas sampled over a 26-month period.

Riparian zone	Fraction size (mm)				Total
	> 16	4 - 16	1 - 4	< 1	
Alder	0.47	0.15	0.18	0.04	0.84
Old-growth	0.34	0.23	0.49	0.08	1.14
<u>Vaccinium</u> spp	0.11	0.15	0.24	0.07	0.57

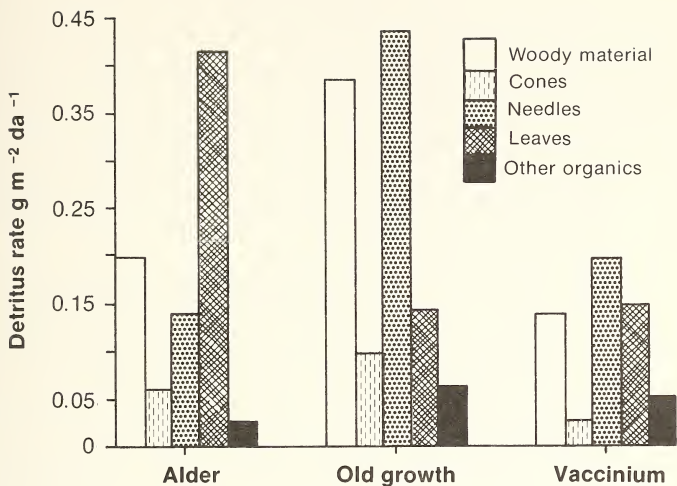


Figure 6. Average daily inputs of various detritus components in the alder, old-growth, and Vaccinium spp areas.

Nutrient Relationships- The nutrient content of allochthonous debris influences the rate of detritus decomposition by stream organisms. Higher concentrations of N and P in detritus and relatively lower C:N and C:P ratios have been associated with better food sources for decomposers in freshwater streams of the Pacific Northwest (Triska et al. 1975; Triska and Buckley 1978).

Nitrogen concentrations were higher in all detrital constituents collected in the alder riparian zone than in either the old-growth or Vaccinium spp zones (Table 2). Leaves had the highest N levels in all areas, ranging from 2.50% in the alder zone to 1.83% in the Vaccinium spp zone. Levels of N in woody material from the alder zone were about five times higher than from the other two areas. Because of the refractory

Table 2. Nitrogen and phosphorus levels in composited samples of detritus components from three riparian zones.

Detritus constituent	Riparian zone											
	Alder				Old-growth				Vaccinium spp			
	%N	%P	C:N	C:P	%N	%P	C:N	C:P	%N	%P	C:N	C:P
Woody material	1.23	0.06	46.5	938	0.24	0.04	241.4	1481	0.22	0.03	263.4	1975
Cones	1.50	0.10	37.8	567	0.72	0.07	80.2	546	1.12	0.07	--	--
Needles	1.02	0.09	54.3	593	0.77	0.07	72.6	811	0.50	0.05	111.4	1092
Leaves	2.50	0.07	21.9	781	2.37	0.09	23.6	612	1.83	0.07	30.5	820
Other organics	0.69	0.11	20.8	123	0.28	0.08	44.7	152	0.67	0.09	43.7	296
Average composition	1.82	0.08	29.7	721	0.76	0.06	69.5	844	0.83	0.06	66.1	980

nature of this woody material, the associated N would be slowly released to the stream system. Average daily inputs of N over the 26-month period were almost twice as high in the alder zone as in the old-growth zone and almost four times greater in the alder zone than in the Vaccinium spp zone (Table 3). Nitrogen inputs from leaves alone in the alder zone ($10.35 \text{ mg N m}^{-2} \text{ da}^{-1}$) were higher than from all sources combined in either of the other two riparian areas. More than half of the N inputs in the old-growth zone were highly refractory (i.e., woody material, cones, and needles).

Table 3. Average daily allochthonous inputs ($\text{mg m}^{-2} \text{ da}^{-1}$) of N and P from three riparian zones.

Detritus constituent	Riparian zone					
	Alder		Old-growth		Vaccinium spp	
	N	P	N	P	N	P
Woody material	2.42	0.12	0.92	0.15	0.30	0.04
Cones	0.90	0.06	0.69	0.07	0.29	0.02
Needles	1.42	0.13	3.35	0.30	0.98	0.10
Leaves	10.35	0.29	3.37	0.13	2.69	0.10
Other organics	0.18	0.03	0.17	0.05	0.34	0.05
Total	15.27	0.63	8.50	0.70	4.60	0.31

Phosphorus, an essential element for cell metabolism in microbes, ranges in concentration from 0.03% to 0.11% in various components of allochthonous debris (Table 2). Although variations in P levels among the different detritus components were smaller than for N, woody material

consistently had the lowest P concentrations (0.03% to 0.06%). Average daily inputs of P during the 26-month sampling period were similar in the alder zone ($0.63 \text{ mg P m}^{-2}\text{da}^{-1}$) to those in the old-growth zone ($0.70 \text{ mg P m}^{-2}\text{da}^{-1}$); P inputs in the Vaccinium spp zone were less than half of these values ($0.31 \text{ mg P m}^{-2}\text{da}^{-1}$) (Table 3). About 75% of the P inputs in the old-growth zone were contained in highly refractory components (woody material, cones, and needles), while almost half of the P inputs in the alder zone were contributed by leaves, a less refractory component. Phosphorus inputs in the Vaccinium spp zone were equally split between highly refractory and less refractory debris.

Average C:N and C:P ratios in detritus from the three riparian zones ranged from 30 to 70:1 and 720 to 980:1, respectively (Table 2). Narrower C:N and C:P ratios in detritus imply that less biological conditioning is required and thus the material is a better quality food source (Triska et al., 1975). Alexander (1961) suggests that terrestrial organic residues with C:N ratios wider than 30:1 favor N immobilization, and residues with ratios narrower than 20:1 favor N mineralization. Russell-Hunter (1970) indicates that optimal secondary productivity in freshwater streams corresponds to C:N ratios in substrate between 17:1 and 11:1. Less information is available on the importance of C:P ratios to decomposition; Alexander (1961) indicates C:P ratios wider than 300:1 favor immobilization of P, while those narrower than 200:1 favor mineralization.

Deciduous leaves from all three riparian zones had the lowest C:N ratios of all allochthonous debris (Table 2). Alder leaves had a lower C:N ratio ($\sim 22:1$) than Vaccinium spp foliage ($\sim 30:1$). These ratios are similar to those found in decaying alder leaves sampled in two riparian communities in the Oregon Cascades (Triska et al., 1975). Woody material from the Vaccinium spp and old-growth areas had the widest C:N ratios (240 to 260:1); C:N ratio of alder woody debris (46:1) was much lower. Woody material also had the widest C:P ratios, especially in the Vaccinium spp and old-growth zones (Table 2). These values were somewhat higher than those reported by Triska et al. (1975) for similar allochthonous debris in the Cascade Range in Oregon. The average C:N ratio of detritus from the alder zone (30:1) indicated that it was a better food source than allochthonous debris from the Vaccinium spp and

old-growth areas (C:N ratios of 66 to 70:1). The average C:P ratio of detritus in the alder area was slightly lower than in either the old-growth or *Vaccinium* spp areas (Table 2), largely because of the higher P levels in woody material and cones in the alder area.

Seasonal Trends- The seasonal distribution of allochthonous detritus is different for the three riparian areas sampled (Fig. 7). An average daily rate was calculated for all sampling periods during the 26-month study. To express these data on a calendar-year basis, rates for individual days of the years sampled were averaged.

Allochthonous debris in the alder reach peaked from early September to mid-October, which corresponds to inputs of deciduous foliage (Fig. 7a). During this period deciduous leaves (largely alder) contributed 1.68 to 2.18 $\text{g m}^{-2}\text{da}^{-1}$ of allochthonous biomass and constituted 72% to 83% of the peak autumn inputs. Coniferous needles and cones comprised only 4% and 3%, respectively, of autumn inputs. The more refractory woody material made up a large portion of the remaining autumn biomass although the proportion of woody material in individual samples was quite variable. Total allochthonous biomass dropped to a relatively constant level (0.44 to 0.53 $\text{g m}^{-2}\text{da}^{-1}$) during the winter, spring, and summer (Fig. 7a). Nearly 80% of the summer allochthonous debris was needles and leaves, in approximately equal quantities. Winter and spring inputs were more refractory, consisting largely of woody material, needles, and cones in decreasing order of abundance. This suggests the importance of wind, ice, and snow as factors influencing breakage and transport of refractory debris.

Input rates of allochthonous debris in the old-growth riparian zone were high ($> 1.5 \text{ g m}^{-2}\text{da}^{-1}$) during most of autumn (Fig. 7b). The peak rate during this period (2.2 $\text{g m}^{-2}\text{da}^{-1}$) was lower than the seasonal peak observed for the alder zone. The composition of autumn allochthonous detritus was variable among sampling periods. Major components of autumn allochthonous detritus were: woody material (largely stems and twigs $> 4 \text{ mm}$), 37%; hemlock and spruce needles, 23%; deciduous leaves, 22%; and cones, 11%. Winter and spring allochthonous debris in the old-growth riparian area was dominated by conifer needles and, to a lesser extent, woody material. Average input rates during winter and

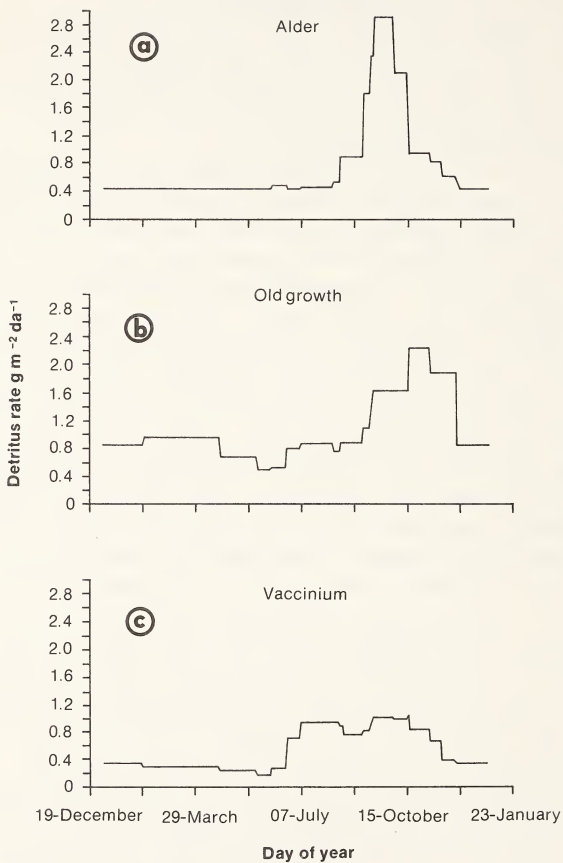


Figure 7. Seasonal distribution of allochthonous debris in the three riparian zones.

spring months in the old-growth area ($0.86 \text{ g m}^{-2}\text{da}^{-1}$) were almost twice as high as in the alder area ($0.44 \text{ g m}^{-2}\text{da}^{-1}$).

Rates of allochthonous debris inputs into the Vaccinium spp-dominated stream reach were lower than in either the old-growth or alder zones during the entire year except for a period between early July and mid-August (Fig. 7c). This small peak during midsummer was dominated by hemlock needles. These needle inputs, although not much higher than corresponding needlefall in the old-growth area, constituted approximately 60% of the midsummer allochthonous biomass in the Vaccinium spp zone. Deciduous leaves contributed slightly more than half of the midautumn peak of allochthonous debris in the Vaccinium spp zone. During winter and spring, total allochthonous rates were $< 0.35 \text{ g m}^{-2}\text{da}^{-1}$ in the Vaccinium spp area.

SUMMARY AND CONCLUSIONS

Although the old-growth riparian zone had the highest total detrital inputs, only about half as much N was added to the old-growth stream reach compared to the alder reach. Average daily allochthonous biomass and N in the Vaccinium spp zone were about half the levels measured in the old-growth zone. Inputs to the old-growth riparian area and, to a lesser extent, to the Vaccinium spp area were dominated by needles, woody debris, and cones. Because of the high C:N ratios and refractory nature of these detritus components, they would be very slowly processed in the stream. In contrast, allochthonous debris in the alder reach was dominated by deciduous leaves with lower C:N ratios, indicating a better food source for biological processors.

Leaves shed in autumn in the alder zone contributed largely to the highest seasonal input of detritus at any of the sites. Based on the N levels in detritus constituents from the alder zone, peak autumn inputs of N were approximately $63 \text{ mg N m}^{-2}\text{da}^{-1}$, of which 85% was from leaves. After an initial period of leaching, this N-rich detritus should be readily utilized by biological consumers. The major autumn inputs of allochthonous debris in the old-growth zone were from a variety of sources and contributed only $17 \text{ mg N m}^{-2}\text{da}^{-1}$ to the stream system. Although the highest autumn detritus inputs in the Vaccinium spp zone were less

than half those in the old-growth zone, N inputs in the Vaccinium spp zone were more than twice as high during autumn.

In small forest stream systems typical of coastal Alaska, size and biomass of allochthonous debris appear more related to riparian vegetation than to stream size or stream position.

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DISCUSSION: Sidle Paper

Question (Correll): How important are these litter inputs that you are measuring relative to surface wash off during storm events of finely suspended organic matter from the surface of the watershed into the stream?

Answer: We don't really feel that the contribution of surface wash off is that great because of the very high infiltration capacity in the riparian zone. We tend to believe that most of the streams are fed by subsurface water even at higher flows. Very few times do you have overland flow in the riparian zone.

Question (Correll): Even with those slopes? They look like they are pretty good slopes.

Answer: Yes, especially from the fact that areas least susceptible to overland flow are the steeper slopes.

MODIFICATION OF RUNOFF FROM UPLAND WATERSHEDS -
THE INFLUENCE OF A DIVERSE RIPARIAN ECOSYSTEM

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Abstract - Both forested and herbaceous wetlands modify surface and subsurface water, but there is little information on how water is modified as it moves through different habitats within wetlands. Nutrient flux studies of the Rhode River system have shown that a diverse wetland (Mill Swamp) has a significant impact on nutrient runoff from upland watersheds. In this paper we present data to demonstrate how water quality parameters change as surface and subsurface water moves through different habitats within Mill Swamp.

Mill Swamp can be divided into three habitats: (1) a floodplain forest that has been hydrologically modified and floods regularly, (2) a floodplain forest that rarely floods, and (3) a wetland that is primarily dominated by herbaceous vegetation.

While there are seasonal changes in all surface water quality parameters, few changes occur as surface water moves through the two forested habitats. In contrast, all parameters change temporally and spatially as surface water moves into and through the herbaceous habitat. Ammonium and phosphate concentrations decrease during spring and winter months and increase during summer months. Nutrient changes in the herbaceous habitat are especially pronounced during summer months when periods of anoxia occur in the water column. Nitrate-nitrite and pH also decrease as surface water moves through the herbaceous habitat. There are also changes in nutrient concentrations in subsurface water, especially nitrate-nitrite and total Kjeldahl nitrogen, in the forested area that rarely floods.

After two years of data collection, it appears that surface water chemistry is primarily controlled by changes that occur as water moves through the herbaceous portion of Mill Swamp. Changes in groundwater chemistry appear to be associated with forested areas which are not regularly flooded with surface

water and where the watertable elevation fluctuates widely during the year.

INTRODUCTION

Swamps and riparian forests are habitats in which nutrients in surface water and groundwater are modified (Brinson et al., 1984; Kitchens et al., 1975; Lowrance et al., 1984). Changes in nutrient concentrations may be associated with biological processes (Brinson et al., 1984; Peterjohn and Correll, 1986), physical processes such as sedimentation (Cooper et al., 1986), or biological uptake (Fail et al., 1986; Kitchens et al. 1975). Except for a few studies of nutrient changes along transects (Peterjohn and Correll, 1984 and 1986; Lowrance et al., 1983 and 1984; Fail et al., 1986; Todd et al., 1983), there have been few investigations of nutrient changes as water moves through different habitats within riparian or swamp forest ecosystems.

This paper presents preliminary results of studies designed to quantify the fluxes of nutrients through a diverse wetland, hereafter referred to as Mill Swamp. Mill Swamp is part of the Rhode River upland-estuarine system ($38^{\circ} 51'N$, $76^{\circ} 32'W$) that is located near Annapolis, Maryland. Jordan et al. (1986) have shown that Mill Swamp has a significant impact on runoff from the largest watershed that drains into the Rhode River, a subestuary of Chesapeake Bay. However, data from that monitoring study could not be used to determine where within Mill Swamp nutrient changes were occurring.

Mill Swamp (Fig. 1A) can be divided into three habitats based on hydrology and vegetation. West of MD Route 468, the forested wetland is inundated when the quantity of water flowing into it is greater than the amount of water that can pass through two culverts under the road (Fig. 1B). Hydrologically, this portion of Mill Swamp is now more similar to a regularly flooded floodplain forest (Mitsch and Rust, 1984) than to alluvial swamp forests as described by Brinson et al. (1984) and Yarbrow (1983). East of the road is a forested habitat that rarely floods and an area dominated by herbaceous vegetation (Fig. 1A). Flooding of the forested area has been almost completely eliminated because of flow restrictions through the culverts under the road. However, one part of the forested area does flood during high flow conditions when the herbaceous area is completely inundated (Fig. 1B). Under low flow conditions, standing water occurs only in the downstream end of the herbaceous

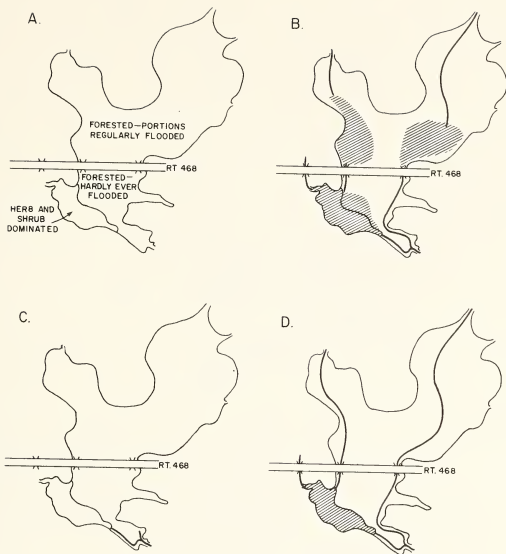


Fig. 1. Diagrammatic representation of Mill Swamp under different hydrologic conditions. Part A shows the 3 major habitats within Mill Swamp. Streams are designated as thicker solid lines and flooded areas are represented by the shaded areas. Flow conditions shown in B, C, and D are described in the text.

habitat (Fig. 1C). Under extremely dry conditions, such as those occurring in the summer of 1985, there is no water in any of the stream channels except tidal water which flows into the stream channels at sampling sites 4 and 5 (Fig. 2) during flood tide. Under normal flow conditions (Fig. 1D) water flows in all streams and the surface of most of the herbaceous area is flooded. There are few historical data to determine how long the herb dominated area has been in existence, but an aerial photograph of the Rhode River area shows that it was present in 1921.

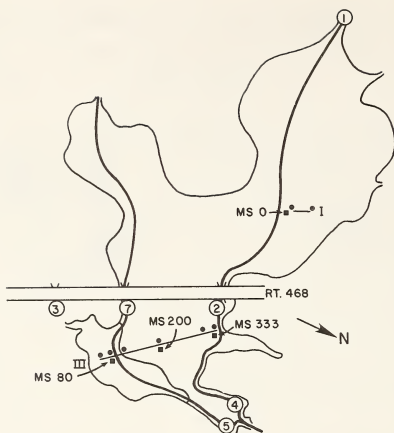


Fig. 2. Sampling sites in Mill Swamp. Surface water collection sites are designated as circled numbers. Subsurface water transects are indicated in roman numerals and sampling stations along the transects are shown as solid circles. Groundwater monitoring stations are indicated with a MS followed by the distance (m) from the origin of the transect.

The canopy of the two forested habitats is dominated by Fraxinus americana, Acer rubrum, Ulmus americana, and Betula nigra. The understory is dense and dominated by Cornus amomum and Viburnum dentatum. The herbaceous area can be divided into four vegetation zones based on species dominance: (1) Typha latifolia and Saururus cernuus, (2) Carex sp. and Leersia oryzoides, (3) Leersia oryzoides and Saururus cernuus, (4) Hibiscus palustris and Saururus cernuus.

MATERIALS AND METHODS

Surface water - Surface water collection sites were chosen to determine if nutrient concentrations changed as water moved into and through each of the three habitats (Fig. 2). Site 1, located upstream of Mill Swamp, was chosen

to be representative of water that entered the system. Sites 2 and 7, located at culverts going under the road, were chosen to represent water that had passed through the frequently flooded portion of Mill Swamp. Water flowing past Site 2 remains in the stream channel and flows through the forested area east of the road without coming into contact with the surface of the forested wetland. Water flowing past Site 7 enters the herb dominated area where it mixes with water that flows past Site 3. Site 3 samples water from a small subwatershed before it enters the herb dominated portion of Mill Swamp. Sites 4 and 5 sample water that has flowed through the forested and herb dominated areas east of the road. Sites 4 and 5 can be tidally influenced under low flow conditions in Mill Swamp and when extreme high tides occur in the Rhode River.

Samples are collected bimonthly in acid washed polyethylene bottles. They are returned to the laboratory, acidified with 36 N sulfuric acid, filtered (0.45 micron), and refrigerated prior to analysis as described below. A separate sample is collected in nonacidified polyethylene bottles, and returned to the laboratory for pH measurements.

Subsurface water - Water levels are monitored at four locations using digital recorders that take readings at 15 minute intervals (Fig. 2). One recorder (MS 0) is located in the frequently flooded area about 200m west of the road. The other three recorders were located east of the road. MS 80 is in the herbaceous wetland and MS 333 on the bank of the stream flowing through the forested area that hardly ever floods (Fig. 2). MS 200 is in a portion of the forested area that is inundated under high flow conditions (Fig. 1B and 2).

Subsurface water is sampled from clusters of wells distributed along the two transects shown in Fig. 2. The transects are perpendicular to the direction of stream flow and each ground water well symbol in Fig. 2 represents a cluster of 3 wells. Transect I is 40 meters long and has clusters of wells, hereafter referred to as Sites 0 and 40, at both ends. Wells at Site 0 are approximately 5-10 meters from the stream channel. Transect III is 333 meters long and has five clusters of wells. Two clusters, Sites 60 and 80, are in the herb and shrub dominated area (Figs. 1 and 2). The site 80 cluster is close to water level recorder MS 80 (Fig. 2). Another cluster of wells, Site 200, is near water level recorder MS 200 (Fig. 2). Two sets of clusters (Sites 300 and 333) are near water level recorder MS 333. Site 333 wells are on the levee of the creek that flows through the forested area east of the

road (Fig. 2). Wells are constructed from PVC pipes that are capped on the bottom and have holes drilled in a band around the pipe to sample water from 15 to 30 cm below the substrate surface.

Subsurface water samples are collected monthly. The wells are pumped dry with a vacuum pump the day before samples are collected. On the sampling day, water that has percolated into the wells is pumped into a glass collecting jar, transferred to acid washed polyethylene bottles, and returned to the laboratory for analyses as described below.

Analytical procedures - The filtered portion of each surface water sample is analyzed for orthophosphate (PO_4), ammonia-N (NH_4), and nitrate plus nitrite-N hereafter referred to as nitrate (NO_3). Orthophosphate is measured colorimetrically using the stannous chloride technique (American Public Health Association 1976). The level of NH_4 was analyzed by oxidizing ammonia and labile amino compounds to nitrite which is then measured colorimetrically (Richards and Kletsch, 1964). Nitrate is reduced to nitrite with amalgamated cadmium and analyzed as above (American Public Health Association, 1976).

The nonfiltered portion of each sample is used to measure total phosphorus (TP), total Kjeldahl nitrogen (TKN), and organic matter (OM). Total phosphorus is digested with perchloric acid (King, 1932) and then measured using the stannous chloride technique (American Public Health Association, 1976). The TKN method measures both NH_4 and organic nitrogen, but does not include nitrate or nitrite nitrogen. The samples are digested to ammonia salts using sulfuric acid and hydrogen peroxide with hengar boiling chips as catalysts (Martin, 1972). The ammonia is then distilled and measured by Nesslerization (American Public Health Association, 1976).

Organic carbon is measured by drying samples at $60^{\circ}C$ then digesting with 67% sulfuric acid and potassium dichromate in a water bath at $100^{\circ}C$ for three hours (Maciolek, 1962). This is done in the presence of mercuric sulfate to complex halides (Dobbs and Williams, 1963). The excess dichromate is then measured colorimetrically and chemical oxygen demand (COD) is determined (Gandy and Rananathan, 1964). COD is multiplied by 3.4 to convert to Calories (g-cal/liter). Acidity is measured with a Cole-Parmer Model 5800-00 pH meter.

Subsurface water collected from wells along transects described above is analyzed using the same techniques as with surface water with two exceptions: the water is not acidified and all analyses are performed on filtered samples.

RESULTS

Surface water - Analysis of variance and discriminant analysis (Ray, 1982) were applied to log transformed data to test for site, season (month), and year differences. ANOVA was also used to test for two-way interactions, but three-way interactions could not be considered because samples were not replicated at each site. Site relationships from the canonical discriminant analysis are shown in Fig. 3. The first two canonical variables were significant ($P < .0001$ and $P < .003$, respectively) and separated sampling sites into the forested (Sites 1, 2, 4) and herbaceous (Sites 3, 5, 7) parts of Mill Swamp.

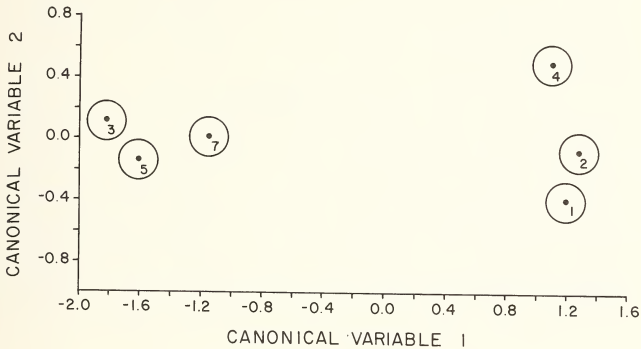


Fig. 3. Results of canonical discriminant analysis of surface water quality data. Sampling locations are shown on Fig. 2. The circles around each station are 95% confidence limits.

pH, TP, PO_4 , TKN, and NO_3 had the highest F values and had significant impacts in discriminating between sites (Table 1). pH had the highest canonical correlation coefficient on the first axis and was the variable most responsible for separation of sites into the forested and herbaceous areas. Total Kjeldahl nitrogen had the highest canonical correlation coefficient on the second

axis (Table 1). The discriminant analysis not only separated the sites into two groups, but the sites were all significantly different from each other at the 95% confidence level. ANOVA also separated the sites into two groups, but produced results that were more readily interpretable.

There were significant site ($P > .0001$) and seasonal ($P > .0001$) effects for all variables. Significant year differences were found only for NO_3 and OM. Season \times site and site \times year interactions were significant ($P > .005$) for all variables. Season \times year interactions were significant for only PO_4 , NO_3 , and pH. Sites, given in parentheses, in Table 2 are arranged in the sequence generated by the ANOVA and are from the highest means on the left to the lowest on the right. Means, expressed as antilogs, not significantly different at the $P > .05$ level share the same superscript. While no two variables are arranged in the same left to right sequence, it is possible to discern general relationships between sites.

ANOVA also divided the sites into two groups. Sites 1, 2, and 4 are not significantly different for any of the variables (Table 2) suggesting that nutrient concentrations change little as water moves through the forested portions of Mill Swamp. Sites 3, 5, and 7 are ranked closest to each other for all but 2 of the variables. Site 5 is significantly different from either Site 3 or 7 for 4 of the variables (Table 2). This suggests that surface water nutrient composition changes as it moves through the herbaceous portion of Mill Swamp. Mean pH, PO_4 , TP, TKN, and OM concentrations increase while NO_3 decreases as water moves through the herbaceous portion of Mill Swamp (Table 2).

Based on results of the ANOVA and discriminant analyses, we have chosen to describe temporal variations by combining sites into two groups: the forested area (Sites 1, 2, and 4) and the herbaceous area (Sites 3, 5, and 7). Figures 4 and 5 suggest that temporal patterns are more pronounced in water that flows through the herbaceous portion of Mill Swamp. Seasonal (monthly) differences and seasonal interactions are also obvious in Figs. 4 and 5. Phosphate concentrations increase in the summer months and decline in the colder months (Fig. 4). There appears to be an inter-annual shift in the time when the increases and declines occur, but the general pattern has held during each of the three years that we have been sampling surface water. Organic matter concentrations (Fig. 5) also increase during the summer, but unlike phosphate, there are no differences between the herbaceous and forested areas

Table 1. Results of canonical discriminant analysis of surface and subsurface water. Variables used in the analysis are listed along with their standardized canonical coefficients, F, and P values.

VARIABLE	CANONICAL VARIABLE 1	CANONICAL VARIABLE 2	F	P
<u>SURFACE WATER</u>				
pH	1.52	0.55	71.81	0.0001
TP	0.48	0.47	4.31	0.0008
PO ₄	0.05	-0.61	5.68	0.0001
TKN	-0.23	1.04	4.97	0.0002
NO ₃	-0.13	0.30	2.47	0.0327
NH ₄	0.03	-0.57	1.81	0.1105
OM	-0.25	0.52	4.16	0.0011
<u>SUBSURFACE WATER</u>				
pH	1.28	-0.86	79.61	0.0001
TP	-0.59	-0.07	4.21	0.0004
PO ₄	0.26	0.12	5.97	0.0001
TKN	0.30	-0.09	31.09	0.0001
NO ₃	-0.29	-0.92	26.39	0.0001
NH ₄	-0.04	0.22	26.99	0.0001
OM	0.08	0.64	25.18	0.0001

during the remainder of the year.

Subsurface water - In addition to seasonal patterns of surface flooding and fluctuations in the groundwater table, there are distinct intra- and interhabitat differences (Fig. 6). Groundwater levels are lowest in late summer and fall and highest in the winter and spring. West of the road (MS 0 in Fig. 6), watertable heights are always elevated above those measured east of the road. There was also less depression of the groundwater at that site during dry periods such as the one between June and September of 1984. Figure 6 suggests that the area west of the road has received large amounts of sediment because the surface elevation at the monitoring site is more than 2 meters above surface elevations of the three recorders east of the road.

Table 2. Results of ANOVA for surface water variables. Sites are given in parentheses. Means for each site are antilogs as the ANOVA was performed on log transformed data. Means that share the same superscript are not different based on Tukey's Studentized Range Tests. Values are parts per billion for all variables except OM and pH. OM units are g-cal/l. Site locations are given in Fig. 2.

VARIABLE	SITES AND MEANS					
TP	a 199 (1)	a 189 (4)	a 186 (2)	b 113 (5)	b 105 (7)	b 91 (3)
PO ₄	a 139 (1)	a 127 (2)	a 122 (4)	ab 65 (5)	b 61 (7)	c 46 (3)
TKN	a 339 (4)	abc 316 (2)	ab 287 (1)	ab 286 (7)	ab 280 (5)	b 262 (3)
NO ₃	a 276 (7)	ab 210 (4)	ab 193 (2)	ab 184 (1)	b 115 (3)	75 (5)
NH ₄	a 73 (1)	a 64 (2)	ab 61 (4)	b 47 (7)	c 28 (5)	c 27 (3)
OM	a 49 (5)	ab 48 (4)	ab 48 (3)	ab 44 (7)	ab 41 (2)	b 40 (1)
pH	a 6.71 (2)	a 6.71 (4)	a 6.64 (1)	b 5.86 (7)	bc 5.75 (5)	c 5.67 (3)

Substrates in the portion of Mill Swamp west of the road are almost always waterlogged.

The herbaceous habitat is also waterlogged for long periods of time as shown by the watertable data in Fig. 6 (MS 80). In the forested area east of the road (MS 200 and MS 333 in Fig. 2), the groundwater is almost always below the surface, especially near the stream channel (MS 333 in Fig. 2) during the growing season months. As noted earlier, MS 200 is flooded under high flow conditions (Fig. 1B) when water spreads into the forested area from the herba-

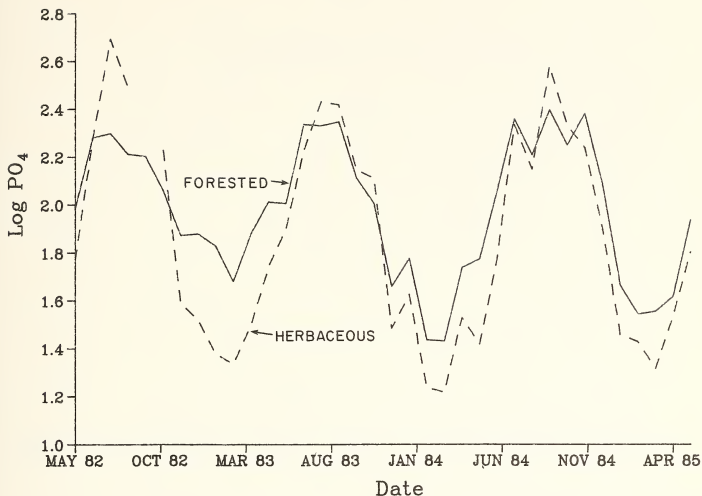


Fig. 4. Seasonal patterns of phosphate concentrations in surface water in the forested and herbaceous portions of Mill Swamp.

ceous area. Watertable fluctuations in the forested areas suggest that substrate conditions alternate between aerobic and anaerobic at MS 200 and that conditions are almost always aerobic at MS 333.

Site relationships for subsurface water were analyzed by discriminant analysis (Fig. 7). The first four canonical variables were highly significant ($P > .0001$), but the first two variables had much higher F values (15.27 and 7.33) for the first and second variables compared to 4.16 and 3.55 for the third and fourth. Sites 0 and 300 were separated by the first canonical variable which was most influenced by pH (Table 1). The second canonical variable separated the sites further (Fig. 7) with pH, NO_3 , and OM having the highest canonical coefficients (Table 1). Sites 300 and 333 have about the same position on the second canonical axis as do Sites 0 and 80. A second grouping is formed by Sites 40, 60, and 200. These two groupings coincide with a gra-

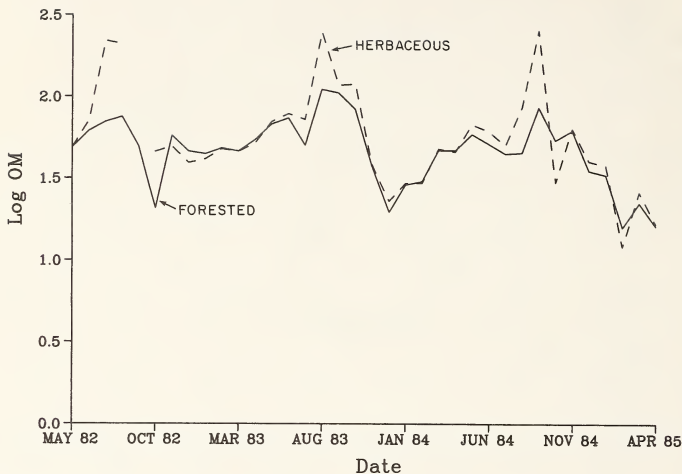


Fig. 5. Seasonal patterns of organic matter concentrations in surface water in the forested and herbaceous portions of Mill Swamp.

dient of decreased flooding and increased fluctuations in the groundwater table. Sites 0 and 80, are in areas where surface flooding is most frequent and groundwater is near the surface for longer periods of time. Those well clusters correspond to the locations of groundwater monitors MS 0 and MS 80 (Fig. 2). Wells at Sites 40, 60, and 200 are at slightly higher elevations and flood less frequently and the groundwater table fluctuations are probably more similar to those found at recorder site MS 200 (Fig. 2). Wells at Sites 300 and 333 are in areas that rarely flood and the watertable is almost always below the wetland surface (Fig. 6).

ANOVA and Tukey's Studentized Range Tests comparisons of water quality data from the wells are shown in Table 3. The ANOVA model was based on main effects due to site, season, and year. All two- and three-way comparisons were made with replicates being the set of 3 wells at each site. Similar to

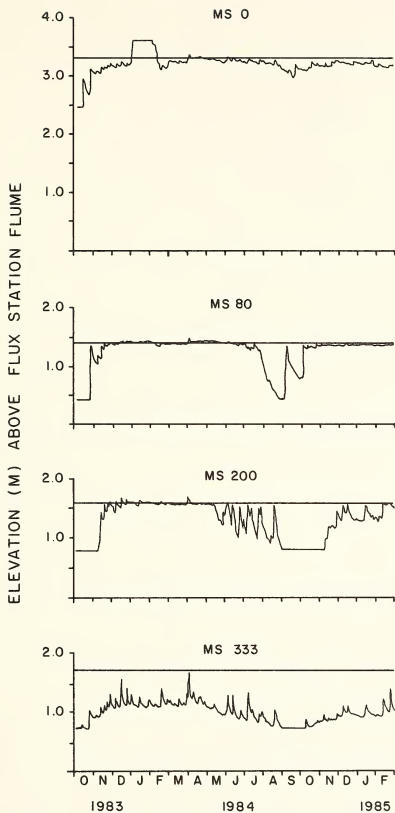


Fig. 6. Subsurface water elevations at the four monitoring stations shown in Fig. 2. All data are shown as elevation (m) above the base of the flux station that is used to continuously monitor water flux through Mill Swamp. The solid horizontal line on each graph represents the elevation of the surface relative to the base of the water flux monitoring station.

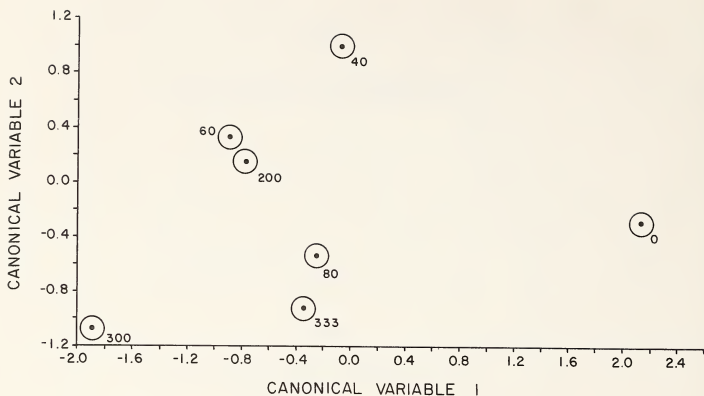


Fig. 7. Results of canonical discriminant analysis of subsurface water quality data. Wells 0 and 40 are on Transect I while the other wells are on Transect III (Fig. 2). Circles around each station are 95% confidence limits.

surface water data, none of the variables have the same left to right alignment of sites and none of the variables have the same statistical between site relationships. There were significant Site ($P > .0001$) effects for all variables. Significant seasonal and yearly differences occurred for all variables except PO_4 (season) and TP (year). Two-way interactions were significant in all variables except TKN and NH_4 .

Comparison of Table 3 and Fig. 7 show slightly different site relationships. Sites 0 and 40 are almost always statistically similar and Sites 60, 80, and 200 form a second group (Table 3). The discriminant analysis grouped Site 0 with 80 and Sites 40 and 60 with 200. Sites 300 and 333 form a separate group in both the ANOVA (Table 3) and discriminant analysis (Fig. 7). Phosphate and NO_3 concentrations are highest in areas that flood less frequently and where groundwater fluctuations are greatest. Organic matter, TKN, and NH_4 show the opposite pattern (Table 3).

We have chosen to demonstrate temporal variations and interactions by combining the well data into 3 groups. Group 1 combines data from wells 0 and

Table 3. Results of ANOVA for subsurface water variables. Sites are given in parentheses. Means for each site are antilogs as the ANOVA was performed on log transformed data. Means that share the same superscript are not different based on Tukey's Studentized Range Tests. Values are parts per billion for all variables except OM and pH. OM units are g-cal/l. Site locations are given in Fig. 2.

VARIABLE	SITES AND MEANS						
TP	a 49 (333)	ab 33 (40)	b 29 (200)	b 28 (300)	b 21 (60)	b 21 (80)	b 20 (0)
PO ₄	a 43 (333)	ab 24 (300)	bc 22 (40)	bcd 20 (200)	cde 13 (80)	de 12 (60)	e 11 (0)
TKN	684 (0)	450 (40)	a 262 (60)	a 257 (80)	ab 213 (200)	bc 155 (333)	c 138 (300)
NO ₃	a 495 (300)	ab 240 (333)	b 236 (80)	c 92 (60)	cd 65 (200)	d 38 (0)	14 (40)
NH ₄	285 (0)	148 (40)	a 66 (80)	ab 59 (200)	ab 57 (60)	b 38 (333)	b 35 (300)
OM	a 64 (0)	a 54 (40)	b 34 (60)	bc 31 (200)	bc 30 (80)	cd 24 (333)	d 22 (300)
pH	6.34 (0)	a 5.81 (333)	a 5.75 (80)	bc 5.68 (40)	bc 5.49 (60)	bcd 5.44 (200)	cd 5.39 (300)

80 which are in areas that flood most frequently. Group 2 combines data from wells in locations that are hydrologically intermediate (40, 60, and 200). Group 3 combines data from the driest locations (300 and 333). Organic matter and NH₄ concentrations are higher in the summer months in wells that are in areas where the groundwater is near the surface (Figs. 8 and 9). The pattern was similar in 1983 and 1985, but was not as obvious in 1984. Nitrate (Fig. 10) and phosphate (Fig. 11) are clearly highest in areas which flood less.

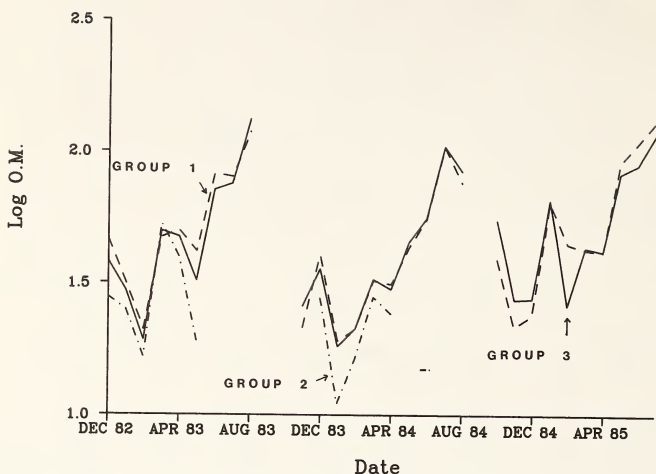


Fig. 8. Seasonal patterns of organic matter in subsurface water. Values are means for data combined into three groups as discussed in the text.

Both parameters show clear seasonal differences. Similar to NH_4 and OM, there are clear annual patterns, but with less obvious seasonality in 1984.

DISCUSSION

Results of this study demonstrate within wetland differences in surface and subsurface water quality parameters. Surface water changes occur primarily in the herbaceous area. We cannot yet completely evaluate within habitat patterns for subsurface water because we only have enough data from groundwater wells along transects I and III. Three other transects are now being sampled, but we have very few data because of the dry conditions that have persisted since the summer of 1984. Data from transects I and III, however, do demonstrate between habitat differences that are related to drawdown of the watertable. The watertable is most often near the surface in the forested area west of the road. As the results for both surface and subsurface

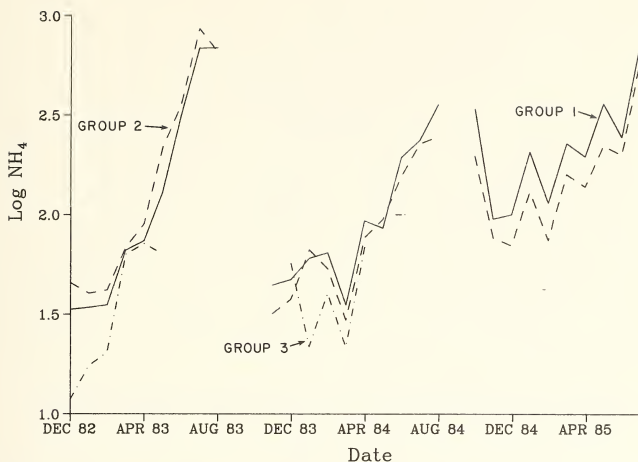


Fig. 9. Seasonal patterns of ammonia in subsurface water. Values are means for data combined into three groups as discussed in the text.

water are preliminary and we have not yet conducted experimental manipulations in Mill Swamp, explanation of the patterns can only be inferred from results of other studies.

Surface water - We have not detected any impact of either of the forested portions of Mill Swamp upon any of the surface water quality parameters. East of the road, surface water in the forested area is almost always contained within the stream corridor and we have not recorded any surface flooding events during the 3 years that we have been collecting data from the recorder at MS 333 (Fig. 2). The stream is completely shaded during the growing season, supports no macrophytes, and contains very few riffle and pool habitats. These conditions are all thought to be important if significant nutrient processing is to occur in streams. West of the road, because the stream channels are small and very shallow, surface flooding occurs more frequently. During the period that watertable data have been collected at MS 0, (Fig. 2) the wetland surface has flooded on numerous occasions. In 1984, a comparatively wet

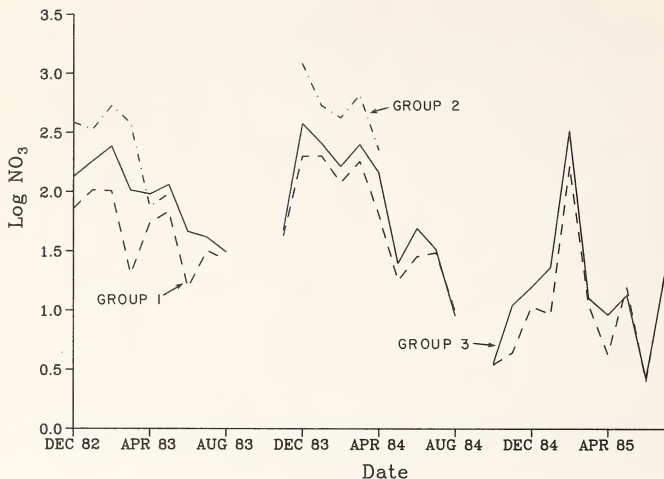


Fig. 10. Seasonal patterns of nitrate in subsurface water. Values are means for data combined into three groups as discussed in the text.

year in the winter and spring, the surface was flooded for several months (Fig. 6). We believe that any significant changes in surface water would be restricted to flooding conditions, especially in the late winter and spring when the water contains large amounts of sediment. We combined watertable data and surface water quality data to compare periods of time when the area west of the road flooded to a comparable time when the area did not flood. Data from that comparison show that greater changes in nutrient concentrations occur between Sites 1 and 2 during periods of flooding (Table 4). Concentration changes between Sites 1 and 2 were more pronounced for NH_4 , TP, PO_4 and NO_3 during the period of flooding from December, 1983 through February, 1984 than they were during the same time period in 1984 and 1985 when surface water was restricted to channel flow. All of the variables except NO_3 declined between Site 1 and Site 2. During the second time period, nitrate concentrations increased between the two sites.

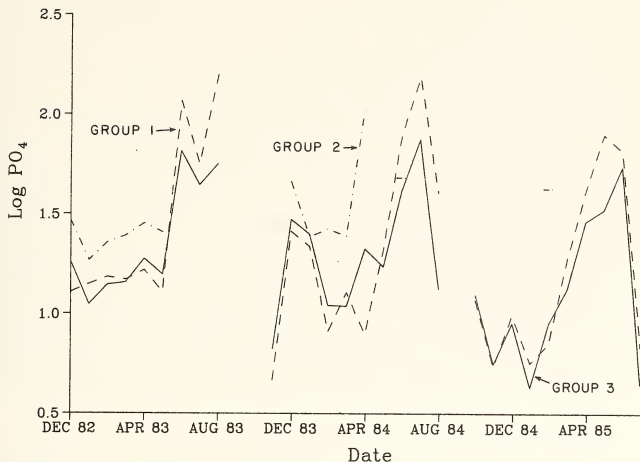


Fig. 11. Seasonal patterns of phosphate in subsurface water. Values are means for data combined into three groups as discussed in the text.

Although we have not conducted any detailed studies of water quality changes during flooding events, data from a study of litter decomposition also demonstrates that nutrient interactions between flooding water and surface litter occur in the area west of the road. The decomposition study was conducted in several upland and wetland habitats to compare changes in the nutrient status of litter and rates of decomposition (Whigham and O'Neill, Unpublished). Litter bags accumulated large amounts of sediment in the riparian forest studied by Peterjohn and Correll (1986), but the amount of sediment that accumulated in the litter bags in the flooded portion of Mill Swamp was an order of magnitude higher (Fig. 12). The amount of phosphorus contained in the litter bags in Mill Swamp was much greater than the amount of phosphorus contained in litter bags at any of the other sites (Fig. 13). Nitrogen followed the same pattern. These findings support the results shown in Table 4 and those of Cooper et al. (1986) who found that larger sediment particles are deposited in riparian forests while finer sediments that contain high

phosphorus levels are transported further downstream and deposited in swamps and/or floodplain areas.

Nutrient transformations in the herbaceous area are most likely caused by interactions between the water and wetland vegetation, litter, and microbes. The importance of the litter zone and its microbial community has been demonstrated in estuarine wetlands (Wolaver and Zieman, 1984; Jordan and Whigham, 1985), and freshwater tidal wetlands (Whigham and Simpson, 1978). The importance of the litter-microbial community in altering water quality has been demonstrated by including it into the development of wastewater management systems that use overland flow systems to treat sewage effluent (Smith and Schroeder, 1985). Nutrient retention can be further augmented by the physical presence of macrophytes which cause water velocity to decline and sediment deposition to be increased (Burton, 1982). Perennial emergent macrophytes

Table 4. Changes in concentrations between Sites 1 and 2 (Fig. 2) during a period of continuous flooding (12/83-2/84) and the same time period a year later (12/84-2/85) when surface flow was restricted to stream channels. Values are antilogs of means that were based on log transformations. All values are parts per billion except for OM which is g-cal/l.

VARIABLE	SAMPLE SITE	FLOODED	NOT FLOODED
TP	1	145	126
	2	110	118
PO ₄	1	85	85
	2	59	66
TKN	1	195	240
	2	195	229
NO ₃	1	427	170
	2	363	186
NH ₄	1	79	93
	2	62	83
OM	1	25	30
	2	27	31

probably have a greater influence on subsurface water as they have been shown to alter the chemistry of interstitial water through the assimilation of nutrients from the substrate and the translocation of large amounts of material from belowground structures (Jayne and Carpenter, In press; Klopatek, 1975; Shaver and Melillo, 1984).

Annual species of vascular plants, in contrast, probably have a large impact on water quality during the growing season. Annuals that occur in the herbaeous portion of Mill Swamp (Polygonum arifolium, Polygonum saggitatum, Impatiens capensis) cannot tolerate anaerobic conditions and their root systems develop in the narrow aerobic zone at the wetland surface. As the plant canopy develops, lower leaves of the annuals senesce and adventitious roots develop at the nodes (Whigham, personal observation). By the middle of the growing season, the annuals have formed a dense mat of adventitious roots

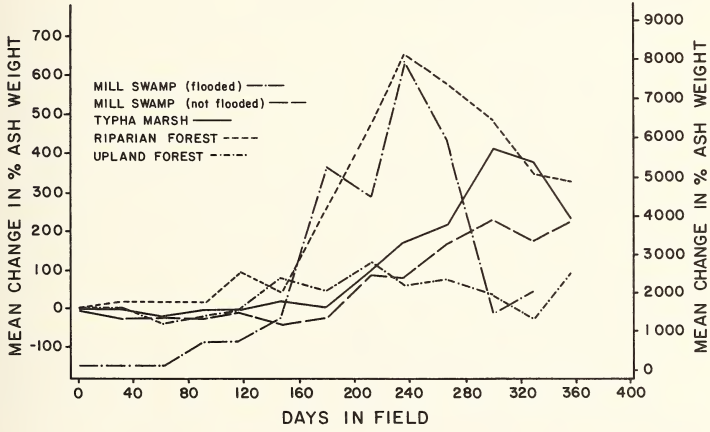


Fig. 12. Changes in the ash content, expressed as a percentage of the original, in leaf litter for several vegetation types on the Rhode River watershed. Site designations are as shown on the figure. The scale for the flooded portion of Mill Swamp is on the right.

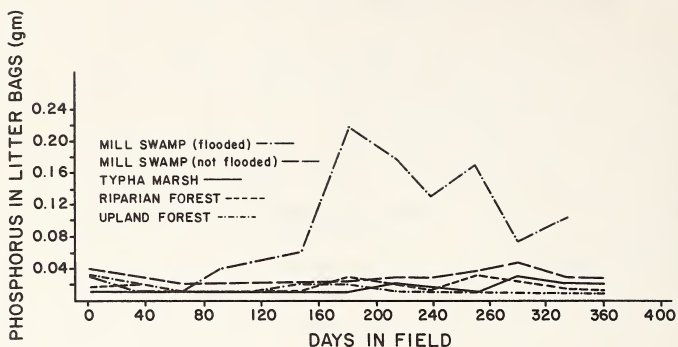


Fig. 13. Temporal changes in the amount (gm) of phosphorus in litter bags. Site designations are as shown on the figure.

on the wetland surface. The root mat is bathed by surface water and we believe that it plays an important role by assimilating nutrients from the surface water. Nutrient retention at other times of the year is most likely controlled by interactions between the water and the litter-microbial community. These interactions are most important in the spring, prior to emergence of the vascular plants, when bacterial growths and algal mats are present on the litter (Whigham, personal observation; Whigham et al. 1980). The litter-microbial community interactions are also important in the fall following dieback of the vascular plants.

Each summer there are increases in phosphate concentrations of water leaving the herbaceous portion of Mill Swamp (Fig. 4). An oxygen monitor in that area recorded frequent overnight anoxia. Phosphorus fluxes probably coincide with those events.

Subsurface water - The nutrient composition of subsurface water, interstitial water near the wetland surface, appears to be primarily controlled by the annual pattern of flooding and drawdown. Brinson and his colleagues (Brinson et al., 1983 and 1984) have studied the interaction between surface and subsurface water in a North Carolina alluvial swamp forest. They found that

nitrate and ammonium interactions were closely coupled to denitrification, the ability of ammonium to be adsorbed on cation exchange sites during periods of flooding, and the conversion of ammonium to nitrate during periods of draw-down. During periods of drawdown, nitrate did not increase in subsurface water due to denitrification. Ammonium did not accumulate in subsurface water suggesting that microbial assimilation was not very important in the alluvial swamp system. Yarbrow et al. (1984) found different results in North Carolina swamps that had been drained. Nitrogen and phosphorus losses were greater in drained swamps with continuously lowered watertables. The results of those two North Carolina studies demonstrate the importance of fluctuating watertables. Annual flooding is necessary in swamp systems because flooding replenishes nutrient supplies and organic matter needed to drive denitrification (Peterjohn and Correll, 1986). Surface flooding is also important if swamp systems are to retain phosphorus (Brinson et al., 1984). Drawdown periods cause alternating periods of aerobic and anaerobic conditions that are important to both organic matter decomposition and nitrogen loss through nitrification and denitrification (Brinson et al., 1984; Reddy and Patrick, 1975).

CONCLUSIONS

This preliminary research into nutrient processing in Mill Swamp has shown that there are differences between habitats and also differences between surface and subsurface water. However, we still do not know much about mechanisms responsible for the patterns nor do we know the impact that each of the habitats has on overall nutrient flux and retention. We are now in the process of building additional monitoring stations in Mill Swamp to quantify hydrologic fluxes through each of the habitats. We will then be able to more clearly define the role that the three habitats play in nutrient processing within Mill Swamp.

Acknowledgements—This research was supported in part by grants DEB-79-11563, and DEB-82-07212, from the Ecosystems Section of the National Science Foundation. We appreciate the logistical support of personnel at SERC. In particular we would like to thank Nancy Goff for assistance with analysis of water samples. Bob Woodley and Don Weller assisted with data analysis. Tom Jordan and Don Weller reviewed the manuscript.

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DISCUSSION: Whigham Paper

Comment (Correll): I am struck by some similarities with some of the things that Gilliam was talking about in terms of the influence of regulating the water table height on the nutrient dynamics. I am wondering how similarly this system responds as compared with some of the North Carolina coastal plain areas that are being regulated artificially for crop production. Could we see similar patterns if we knew enough about this system?

Question (Gilliam): How wide is this swamp where the road goes across?

Answer: Well, I guess in the upper part it might be 600 - 700 m across. At the road probably 400 m.

Question (Gilliam): How big an area are you talking about?

Comment (Correll): The total area is about 60 hectares.

Comment (Gilliam): In our situation we would consider that mostly riparian vegetation on a creek. An area that size down where we are, I don't believe would be called a swamp. We are talking about swamps that are much bigger.

Answer: I think the reason we call it a swamp is that historically that is what it was called. If it wasn't for the road going across it, I think it would just be a riparian zone. It would be a continuation of the riparian zone found further up the gradient.

Comment (Gilliam): One of the things we have noticed is that road beds turned out to be very effective dams to hold the water and to channelize it and create swamps upstream which are quite effective filters. These roads have done quite a bit for water quality downstream.

SEASONAL GEOCHEMICAL RELATIONSHIPS FOR SELECTED CONSTITUENTS

IN PRECIPITATION AND STREAM WATER IN FORESTED WATERSHEDS,

CATOCTIN MOUNTAINS, MARYLAND

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Abstract - Input-output balances for major ions and dissolved silica were measured for two small forested watersheds in the Catoctin Mountains of central Maryland in 1982 and 1983. Both watersheds are underlain by metabasaltic rock consisting of the minerals: chlorite [$Mg_5Al_2(Si_3O_{10})(OH)_8$], albite [$NaAlSi_3O_8$], epidote [$Ca_2FeAl_2Si_3O_{12}(OH)_1$], and actinolite [$Ca_2(Mg_3Fe_2)Si_8O_{22}(OH)_2$], and minor amounts of calcite [$CaCO_3$] and quartz [SiO_2]. Precipitation recorded in 1983 was approximately 60 percent greater than in 1982; however, the ratio of stream discharge to precipitation for both watersheds remained relatively constant at 0.50. Hydrogen, sulfate, and nitrate were the major ions in precipitation, whereas calcium, magnesium, bicarbonate, and silica were the major dissolved species in stream water. Seasonally high concentrations were observed for sulfate and hydrogen ions in precipitation during the summer. Concentrations of bicarbonate in streams were elevated during the summer as a result of increased biological activity. Surface runoff containing high concentrations of deicing salts applied to roads during the winter caused elevated concentrations of sodium and chloride in streams during the spring.

Geochemical weathering processes account for most of the observed seasonal differences between the chemistry of input precipitation and output streamflow. Chlorite, actinolite, and albite react incongruently

with CO_2 -charged water to form kaolinite, releasing cations, silica, and bicarbonate to stream water. Actinolite also reacts with dissolved oxygen to form goethite (FeOOH). Analysis of the stream chemistry using the computer program BALANCE suggests that approximately 5 times more dissolved oxygen reacts with actinolite during the summer months than during the other seasons. The relative amounts of minerals that react throughout the year remain fairly constant. Dissolution of albite and calcite account for 80 to 100 percent of the neutralization of the total hydrogen-ion input from precipitation and from carbonic-acid weathering. Even though calcite is present in extremely small quantities in the bedrock, its dissolution significantly affects the water chemistry because of its relatively high reactivity and location in the hydrologic flow path.

INTRODUCTION

In small forested watersheds, the chemical composition of surface and ground water is generally a result of reactions that take place between atmospheric deposition and the minerals in bedrock and soils. Extensive areas of the Eastern United States are presently being exposed to large influxes of strong acids from anthropogenic, atmospheric sources, commonly referred to as acid rain (Likens et al, 1979). This input of acidity to watershed systems may affect the rates of geochemical processes such as mineral dissolution, alteration, and chemical weathering (Johnson et al, 1981). The chemical character of stream water is influenced by these mineral reaction rates, as well as by biological processes and evapotranspiration.

In order to be able to predict the effect of the additions of acidic rain on watershed systems, it is essential to understand the geochemical reactions occurring in the watershed. Currently, some of these reactions and processes are being investigated in a study area in the Catoctin Mountains located in central Maryland (fig. 1). This area, which consists of two small watersheds, is underlain by the Catoctin Formation. This rock type was selected for two reasons: (1) it is

widespread in the Eastern United States, and (2) water associated with this bedrock type is potentially sensitive to acidification from atmospheric deposition because of the general nonreactivity of major minerals in the bedrock.

The purpose and scope of this report are twofold: (1) to characterize selected geochemical reactions occurring in the two small forested watersheds that comprise the study area with respect to seasonally different quantities of hydrogen ion during 1982 and 1983, and (2) to describe selected watershed processes that influence the chemical character of the stream water.

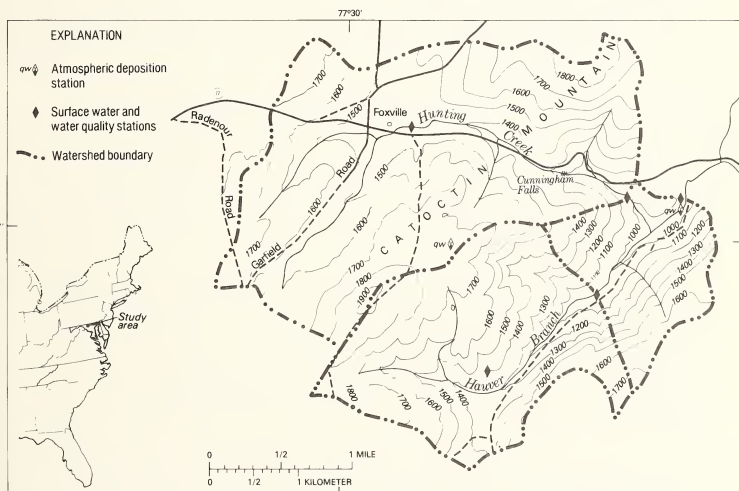


Figure 1.— Location of study watersheds and sampling sites for atmospheric deposition and stream water.

METHODS OF STUDY

During 1982-83, 90 precipitation samples were collected on a weekly basis using an Aerochem metrics Model 301^{*} atmospheric deposition collector. This is the same type of collector used at stations participating in the National Trends Network and the National Atmospheric Deposition Program (NADP). One collector is located in the center of the study area at an elevation of 530 m, and another collector is located on the eastern boundary of the study area at an elevation of 287 m (fig. 1). Two collectors were placed in the study area to investigate variability in the chemistry of precipitation with elevation difference. The volume of wet deposition is measured at each collection site using a weighing bucket rain gage. Chemical analyses for major ions along with volume measurement of the wet deposition are used to calculate the deposition input to the study area.

During 1982-83, 102 stream-water samples were collected at weekly intervals at a fixed point on each stream near the gaging station. The volume of surface-water outflow from the watersheds was measured by continuously gaging the two streams. Discharge data were generated from rating curves developed from periodic current meter measurements according to methods described in Buchanan and Somers (1969). The accuracy of the daily discharge values are reported to be within 10 percent (James et al, 1984).

Chemical analyses of major ions and dissolved silica along with volume measurement of the stream water provide the streamflow output from each watershed. Sampling according to a weekly time series has been shown to be an effective method for obtaining accurate annual budgets for major constituents in precipitation and stream water (Likens et al, 1977).

* Mention of trade names is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

Specific conductance, pH, alkalinity, and temperature were measured in the field. All stream samples and precipitation samples (provided there was sufficient volume) were filtered through 0.10 um membrane filters. These samples were stored in dark plastic bottles, chilled to 4°C, and were analyzed for sulfate, nitrate, and chloride by ion chromatographic techniques.

An aliquot from each sample was analyzed for alkalinity by an automatic incremental titration method and gran plot analysis (Stumm and Morgan, 1981). Samples to be analyzed for major cations, silica, and selected trace metals were preserved by depressing the pH to <2 with concentrated ultrapure nitric acid. Calcium, sodium, magnesium, and potassium were analyzed by atomic absorption spectrophotometric methods (Skougstad et al, 1979). Silica was determined colorimetrically according to the method of Skougstad et al (1979). In general, cation-anion balances for these analyses were within 15 percent of one another.

DESCRIPTION OF STUDY AREA

The Hunting Creek study area, 15.9 km² in size, is located in the Blue Ridge physiographic province in central Maryland (fig. 1). The study area consists of two smaller watersheds, both with a mature deciduous cover. The areas of Hauver Branch and Hunting Creek watersheds are 550 and 1,040 hectares, respectively.

Precipitation- The average annual rainfall, based on records from 1891 to 1944 was 112 cm. The lowest annual rainfall during this period was 65.8 cm and the highest, 166 cm (Bily, 1946). There was an average of 109 days with precipitation of 0.025 cm or more per year. The amount of precipitation was fairly well distributed during the year (Bily, 1946). Precipitation in the form of snow was highly variable and ranged from flurries to heavy depths (81 cm) in 1942. The average annual relative humidity was 68 percent during this period. The average annual temperature, based on the same period of record was 12°C, with a

minimum of -31°C in January and a maximum of 40°C in August.

More recent data (1931-80) from a National Weather Service station located about 32 km to the south confirm the even monthly distribution of precipitation amounts, with a mean annual precipitation amount of $112\text{ cm} \pm 18\text{ cm}$ during this period (National Oceanic and Atmospheric Administration, 1981). The mean annual temperature for this period of record is 12°C , identical with the data from the earlier period of record (1891 - 1944).

The velocity and direction of winds are highly variable from hour to hour. The average velocity is lowest in August and highest in March. The prevailing wind direction is from the northwest from October to April, and from the southwest during May through September.

Geology and Soils- The Catoctin Mountains in Maryland are underlain by a thick sequence of interbedded greenstone and meta-sedimentary rocks known as the Catoctin Formation of Precambrian age. This formation underlies the Lower Cambrian sedimentary rocks in the Blue Ridge province of northern Virginia, Maryland, and southern Pennsylvania, and unconformably overlies Precambrian granitic rocks. The original Catoctin lavas were basaltic and appear to have been normal plateau basalts (Reed, 1955). These lavas have subsequently been altered to greenstone by low-grade regional metamorphism. The major minerals in the greenstone are chlorite, epidote, albite, and actinolite, with small amounts of quartz and calcite. Accessory minerals are magnetite, ilmenite, hematite, and sphene (Stose and Stose, 1946; Reed, 1964). The greenstone commonly is amygdaloidal and the vesicles are filled with secondary minerals such as quartz, epidote and chlorite with lesser amounts of calcite, jasper, and orthoclase feldspar. Joint and fracture surfaces commonly are lined with the same secondary minerals found in the amygdules. The watersheds of Hauer Branch and Hunting Creek are developed on lava flows within the Catoctin Formation.

The major soils derived from weathering of the Catoctin Formation in Frederick County, Md., belong to the Highfield Series — a group of medium textured, well developed, and generally well-drained soils (Matthews, 1956). In the study watersheds, these soils range in depth

from 0 to 150 cm, depending upon their location. Bedrock exposure is common on steep slopes. A large part of each of the watersheds is mapped as rough and stoney ground and the thickest soils occur in the valley bottoms. The A horizon of these soils is generally a porous loam and has soil slurry pH values (1:1 soil/water) ranging from 5.2 to 5.8. The subsoil (B horizon) ranges from 5.0 to 5.8 in slurry pH, contains large rock fragments, and commonly has a high content of iron oxyhydroxides. The substratum is saprolitic, being derived from and grading into the metabasalt. The thickness of the saprolite is highly variable depending upon location in the watershed. Saprolite thickness ranges from zero to about 1.5 m. Drainage of some of the flood plain and valley bottom soils is poor, creating saturated conditions in those areas during periods of heavy rainfall.

Hydrology— The average annual precipitation in the study area is 112 cm/yr. Long-term weather records show that precipitation is usually distributed relatively evenly throughout the year. The years 1982 and 1983 covered in this report, however, had very different precipitation distributions (fig. 2). Precipitation had large seasonal fluctuations

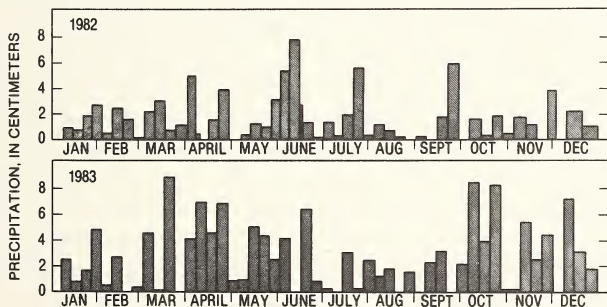


Figure 2.— Distribution of weekly precipitation amounts during 1982 and 1983.

in each of these years, and nearly 60 percent more fell in 1983 than in 1982. In 1982, which was a dry year, the watersheds received 95 cm of precipitation; about 70 percent fell in the first 6 months, which were followed by a dry summer and fall. In contrast, 1983 was an unusually wet year with 147 cm of precipitation. One third of this fell in the spring quarter, and an equal amount fell in the fall quarter following a dry summer.

Data from streams draining similar watersheds in this area indicate that about 55 percent of the incident precipitation leaves as stream discharge (James et al, 1984). In 1982, stream discharge of both Hauver Branch and Hunting Creek was 50 percent of precipitation input. In 1983, discharge of Hauver Branch was 48 percent and of Hunting Creek 54 percent of precipitation. It is surprising that the precipitation-discharge relationship remains nearly constant in view of the 60-percent difference in total precipitation between these 2 years.

Hauver Branch and Hunting Creek had large seasonal fluctuations in discharge in 1982 and 1983 (fig. 3a and b). The differences in flow are largely related to rainfall, temperature, antecedent soil-moisture conditions, and biological activity.

The seasonal effects of temperature and biological activity on water balance can be seen in table 1. During the first quarter of the year (January through March), most of the precipitation falling on the watersheds is discharged as streamflow. For example, in the first quarter of 1982 following a dry summer and fall, both basins discharged slightly more water as streamflow than entered as precipitation. This water must have been supplied from ground-water storage; however,

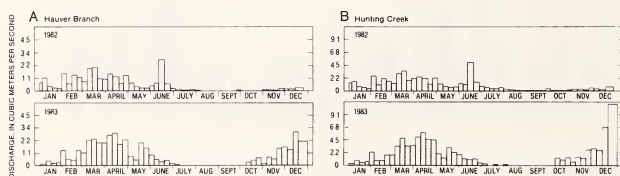


Figure 3.— Distribution of weekly discharge amounts during 1982 and 1983 for (A) Hauver Branch and (B) Hunting Creek.

Table 1. -- Seasonal water budgets for Hauver Branch and Hunting Creek watersheds during 1982 and 1983.
 [All values expressed in liters x 10⁸, and rounded to nearest tenth]

	Period	1982		1983	
		Precipitation	Stream	Precipitation	Stream
Hauver Branch Watershed	Jan - Mar	10.2	13.0	16.5	12.9
	Apr - June	19.5	10.1	26.8	15.1
	July - Sept	11.3	.7	10.5	.4
	Oct - Dec	8.6	1.1	27.6	11.0
		49.6	24.9	81.4	39.4
Hunting Creek Watershed	Jan - Mar	19.2	21.5	30.9	22.2
	Apr - June	36.5	19.1	50.2	30.2
	July - Sept	21.1	3.0	19.6	1.1
	Oct - Dec	16.0	2.8	51.8	28.6
		92.8	46.4	152.5	82.1

limited ground-water-level data are available for that period. Water-level data from an observational well in the study area show that the water table declined about 3 m during January through March, 1982. In the second quarter of the year, average daily temperature begins to rise and vegetation enters an active growth period. Only about 50 percent of the precipitation input leaves as stream discharge. In the third quarter of the year, temperature reaches its maximum, vegetation is fully developed, and only a small percentage of incident precipitation leaves as stream discharge. In the fourth quarter, temperature decreases, biological activity slows down and an increasing amount of precipitation input leaves the watershed as stream discharge.

Precipitation falling in the watersheds rapidly infiltrates into the soil during most of the year. Overland flow has occasionally been observed during the winter months when the top few inches of the soil are frozen and in areas that have steep slopes.

Residence time for water in the soil and saprolite is highly variable depending upon location in the study area and other factors such as antecedent moisture conditions. Ground water moves principally

through joints, along cleavage planes, or other irregular fracture zones (Fauth, 1977). Wells located in the Catoctin Formation have yields ranging from 0.3 L/s to about 0.63 L/s.

GEOCHEMICAL RELATIONSHIPS FOR SELECTED CONSTITUENTS

Seasonal Mean Concentrations of Dissolved Constituents in Precipitation and Stream Water- There are distinct differences between the chemical composition of the incoming precipitation and the stream water leaving each watershed. For precipitation collected in 1982 and 1983, sulfate and nitrate were the major anions and hydrogen the principal cation. For stream water, bicarbonate was the major anion and calcium and magnesium were the principal cations.

Precipitation Chemistry- A comparison of paired data collected at the two atmospheric deposition stations for 1982 and 1983 revealed that there is no significant difference in the concentrations of major dissolved ions in weekly samples of precipitation at the two different elevations (Katz et al, 1985). Based upon the agreement in chemistry of precipitation between the two stations, only data from the station located in the center of the study area are presented in this report (fig. 1).

Seasonal trends in concentrations of certain constituents in precipitation are apparent from the data of figure 4a and b. Based upon weekly composite samples of precipitation, it was found that the highest sulfate and hydrogen-ion concentrations in precipitation occur in the summer, whereas highest nitrate concentrations generally occur during the winter months. These data trends are consistent with other studies in the northeastern United States and have been described in detail by Bowersox and De Pena (1980) and Galloway and Likens (1981).

Chloride and sodium concentrations in precipitation also fluctuate seasonally. In 1982, the highest values for chloride and sodium were during the fall, whereas in 1983, chloride values were highest in the summer and sodium values were highest in the fall. The higher values may be related to a sea-salt origin for these two ions due to the regional atmospheric circulation pattern.

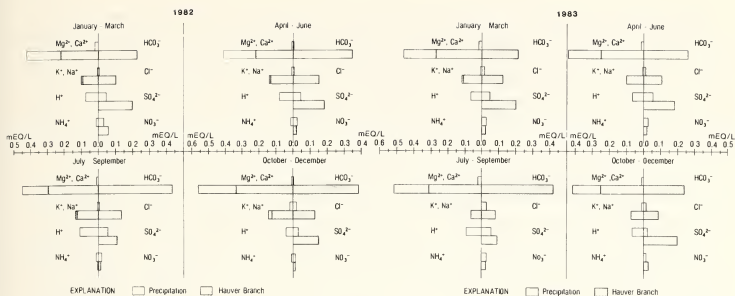


Figure 4.-- Seasonal volume-weighted concentrations of major ions in precipitation and Hauver Branch stream water for (A) 1982 and (B) 1983.

Some storms in the fall track from a northeasterly direction and sea-salt may be incorporated in these storm patterns. The overall Cl:Na ratio for 1982 was 1.1:1, which is less than the corresponding ratio of 1.8:1 for seawater. This may be indicative of additional sources for sodium in the study area precipitation. A similar observation was made during an earlier study located about 80 km east of the study area (Cleaves et al, 1974) and also was reported by the Hubbard Brook study in New Hampshire (Likens et al, 1977). In 1983, the overall chloride to sodium ratio was 2.1:1. The ratio, along with the higher chloride concentration during the summer were surprising considering that the majority of storms at this time of year originate from a westerly (inland) direction. Hydrochloric acid in the atmosphere is a frequent component of air pollution and may contribute to the elevated chloride levels (Gorham, 1961).

Stream-Water Chemistry- Streams draining both watersheds have similar chemical compositions that vary seasonally. The major dissolved ions in stream water are calcium, magnesium, and bicarbonate. These ions along with aqueous silica are the principal dissolved constituents derived from weathering reactions of minerals in the bedrock.

There are distinct differences between the composition of the incoming precipitation and the stream water leaving each watershed. The mean seasonal chemistry for Hauver Branch is nearly identical to that of Hunting Creek for 1982 and 1983. Differences between the season mean chemistry of precipitation and stream water during 1982 and 1983 are presented in Figure 4 for Hauver Branch. No bicarbonate (alkalinity) was found in precipitation, whereas seasonal volume-weighted mean concentrations of bicarbonate in stream water ranged from 210 to 440 umoles/L for Hauver Branch, and from 250 to 600 umoles/L for Hunting Creek for 1982 and 1983. Hydrogen and ammonium ions (1982 data) are depleted in stream water relative to precipitation indicating that these ions are consumed in biogeochemical reactions in the watersheds.

Stream discharge was sampled weekly for analysis of major dissolved constituents in 1982 and 1983. These data are summarized in Katz et al (1985). It was found that most of the dissolved load in both streams is carried during the first six months of the year (January through June). As flow decreases through the summer, concentrations of dissolved substances in the stream remain relatively constant, but the total load decreases proportional to flow.

Within a week after the first frozen precipitation event in 1982, it became apparent that deicing salt used on roads in the watersheds was entering the streams in runoff. The State of Maryland uses halite (sodium chloride) and sand mixed with small amounts of calcium chloride to control ice on State Route 77, the major road through the Hunting Creek watershed (figure 1). A mixture of sand, calcium chloride, and halite is used on roads in Cunningham Falls State Park. These soluble salts dissolve and are transported through the watersheds to the streams. Elevated concentrations of chloride, calcium, and sodium can be detected in the streams in a matter of days if temperature and other conditions are favorable for transport. In the Hauver Branch watershed, 17 and 13 percent of the total annual load of the stream was contributed by road salt and in the Hunting Creek watershed, 37 and 29 percent of the total annual load was due to road salt in 1982 and 1983, respectively (Katz et al, 1985).

Geochemical weathering has a large impact on the composition of the streamflow. The principal products of geochemical weathering, calcium,

silica, magnesium, and bicarbonate, make up the majority of the total dissolved solids in the stream water draining both watersheds. Bicarbonate values definitely increased from the beginning of May through the end of October coinciding with the growing season for vegetation.

Weathering Reactions and Seasonal Watershed Geochemistry-

Geochemical reactions occurring in a watershed can be quantified by integrating water chemistry data with mineralogical data. Weathering reactions along with atmospheric inputs and other watershed processes contribute dissolved materials to stream water. Direct anthropogenic additions to the watershed, such as road salt, also contribute to the dissolved load in stream water. The major minerals in the metabasalt include albite $[\text{NaAlSi}_3\text{O}_8]$, epidote $[\text{Ca}_2\text{FeAl}_2\text{Si}_3\text{O}_{12}(\text{OH})]$, chlorite $[\text{Mg}_5\text{Al}_2(\text{Si}_3\text{O}_{10})(\text{OH})_8]$, with smaller amounts of calcite $[\text{CaCO}_3]$ and actinolite $[\text{Ca}_2(\text{Mg}_3\text{Fe}_2)\text{Si}_8\text{O}_{22}(\text{OH})_2]$. The major clay mineral in the soil and saprolite is kaolinite $[\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4]$. Small amounts of smectite clay are observed in some of the poorly drained flood-plain soils, and hydrous iron oxides are common in the weathered material and soils. Seasonal stream-water compositions plotted on an activity diagram depicting equilibrium reactions in the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ suggest that kaolinite should be the stable clay phase in contact with this water (figure 5).

Net seasonal mass balances for mineral/water reactions and stream water chemistry were calculated using the computer program BALANCE (Parkhurst et al, 1982). These calculations define the amounts of minerals or phases entering or leaving the aqueous phase necessary to account for the observed changes in chemical composition between input to the watershed as precipitation and output from the watershed as stream water on a seasonal basis.

Input to BALANCE includes: (1) natural mineral phases found in bedrock and soils such as albite, chlorite, actinolite, calcite, kaolinite and goethite (table 2); (2) the differences between the mean seasonal concentrations of major ions and silica in stream water (table 3a) and precipitation (table 3b); (3) dissolved carbon dioxide, a

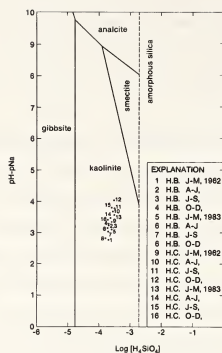


Figure 5.-- Activity diagram for the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ showing the seasonal composition of water from Haver Branch (HB) and Hunting Creek (HC) during 1982 and 1983 (modified from Drever, 1982).

Table 2.-- Reactants and products for reaction models obtained from BALANCE calculations for Haver Branch and Hunting Creek watersheds, 1982 and 1983.

Reactants	Products
SEASONAL PRECIPITATION CHEMISTRY	SEASONAL STREAM CHEMISTRY
ALBITE -- $\text{NaAlSi}_3\text{O}_8$	-- $\text{Na}^+, \text{Mg}^{2+}, \text{Ca}^{2+}, \text{K}^+$
CHLORITE -- $\text{Mg}_5\text{Al}_2(\text{Si}_3\text{O}_{10})(\text{OH})_8$	-- $\text{Cl}^-, \text{SO}_4^{2-}, \text{HCO}_3^-, \text{NO}_3^-$
CALCITE -- CaCO_3	-- H_4SiO_4
ACTINOLITE -- $\text{Ca}_2(\text{Mg}_3\text{Fe}_2)\text{Si}_8\text{O}_{22}(\text{OH})_2$	GOETHITE -- FeOOH
CARBONIC ACID -- CO_2	KAOLINITE -- $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$
DEICING SALTS -- $\text{NaCl}, \text{CaCl}_2$	
DISSOLVED OXYGEN -- O_2	

Table 3a.--Seasonal volume-weighted concentrations of major species in stream water for 1982 and 1983 used in BALANCE program calculations. (all values in micromoles per liter (um/L))

		HAUVER BRANCH										
		Ca	Mg	Na	Si	C _T ^{1/}	Cl	Fe	Al	RS ^{2/}	pH ^{3/}	
1982	JAN-MAR	111	104	92.1	201	340	103	0	0	1360	26.6	
	APR-JUN	110	96	133	215	411	152	0	0	1640	22.2	
	JUL-SEP	147	102	125	216	508	132	0	0	2030	39.0	
	OCT-DEC	168	114	125	219	452	123	0	0	1810	12.5	
1983	JAN-MAR	137	97	111	247	273	123	0	0	1090	32.5	
	APR-JUN	126	96	98.7	176	302	103	0	0	1210	29.1	
	JUL-SEP	158	101	112	197	520	130	0	0	2080	34.8	
	OCT-DEC	126	82	71.6	161	306	87.2	0	0	1220	28.6	

HUNTING CREEK

1982	JAN-MAR	144	109	264	249	365	344	0	0	1460	23.4
	APR-JUN	137	101	276	268	454	328	0	0	1820	19.8
	JUL-SEP	186	109	239	314	498	316	0	0	1990	33.1
	OCT-DEC	297	130	361	219	562	329	0	0	2250	10.5
1983	JAN-MAR	164	100	271	309	311	246	0	0	1240	31.1
	APR-JUN	151	94	180	222	360	219	0	0	1440	22.8
	JUL-SEP	230	130	196	253	641	272	0	0	2560	28.5
	OCT-DEC	158	80	179	189	335	250	0	0	1340	25.0

^{1/}Total Carbon (C_T) for stream water calculated from average temperature, pH, and alkalinity data using MATEQF (Plummer and others, 1976).

^{2/}RS denotes the redox state of the solution. RS was calculated from this relationship:
 $CT \times 4 + O_2 \times 4 = RS$

^{3/}Contribution of H ion from acid precipitation, as percent of total H ion.

Table 3b.--Seasonal volume-weighted concentrations of major species in precipitation for 1982 and 1983 used in BALANCE program calculations. (all values in micromoles per liter (um/L))

		Ca	Mg	Na	Si	C _T ^{1/}	Cl	Fe	Al	RS ^{2/}	H	ToC ₂ ^{3/}
1982	JAN-MAR	5.85	1.68	6.98	0	22.8	6.52	0	0	101	76.0	2.28
	APR-JUN	2.76	0.69	11.0	0	15.1	9.93	0	0	70.4	80.8	16.7
	JUL-SEP	5.05	1.08	6.40	0	12.2	5.60	0	0	101	160	22.2
	OCT-DEC	4.81	1.32	9.93	0	20.0	19.7	0	0	90	41.5	7.44
1983	JAN-MAR	6.35	0.61	7.61	0	22.8	15.0	0	0	101	65.6	2.28
	APR-JUN	5.65	1.96	5.96	0	15.1	11.0	0	0	70.4	64.6	16.7
	JUL-SEP	8.95	2.19	5.98	0	12.2	26.7	0	0	101	141	22.2
	OCT-DEC	3.89	1.61	9.40	0	20.0	16.3	0	0	90	64.3	7.44

^{1/}Total carbon (C_T) values for precipitation calculated from seasonal mean temperatures and P co₂ using this relationship:

$$H_2CO_3 = K_H \times P \text{ co}_2$$

^{2/}RS denotes the redox state of the solution. RS was calculated from

$$CT \times 4 + O_2 \times 4 = RS$$

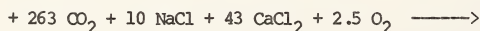
^{3/}Seasonal mean value of air temperature in degrees Celsius.

principle reagent in weathering reactions; (4) de-icing salts, halite and calcium chloride; and (5) dissolved oxygen, involved in the oxidation of ferrous iron (Fe^{2+}) in actinolite to ferric iron (Fe^{3+}) in iron oxyhydroxides and goethite (FeOOH). The mineral epidote is not included in the BALANCE calculations, because it is believed to play a relatively minor role in governing water chemistry. Epidote commonly stands out in relief with quartz on weathered surfaces suggesting that it is more resistant to weathering than other minerals in the bedrock.

Sulfate and nitrate also were not included in the mass balance calculations for three main reasons: (1) Sulfur or nitrogen species are not present in any of the mineral phases in the bedrock or soils, (2) it was beyond the scope of the study to attempt to quantify the amount of sulfate and nitrate that are taken up by vegetation during the growing season (May through October), and (3) the excess amount of sulfate leaving the watershed (Katz et al, 1985) is believed to be related to inputs from dry deposition. We are not able to quantify the amount or composition of sulfur species in dry deposition entering the watersheds. However, a recent study in western Maryland (Campbell et al, 1983) found that hydrogen ion and ammonium ion were also enriched by about 50 percent in bulk precipitation relative to wetfall only, corresponding to the similar enrichment of sulfate and nitrate.

A total of sixteen "reaction models" or balanced chemical equations were calculated using BALANCE for the four time periods during 1982 and 1983 for the Hauver Branch and Hunting Creek watersheds. An example of one of these reaction models is presented below for Hauver Branch watershed for the January through March period, 1982.

Precipitation + 75 Albite + 18 Chlorite + 54 Calcite + 4.2 Actinolite
chemistry



Stream + 8.4 Goethite + 55 Kaolinite
chemistry

The coefficients presented in the above equation are those which chemically balance the reaction between the measured seasonal precipitation chemistry and the bedrock and soil minerals which produce the measured seasonal stream chemistry. A total of 16 different sets of coefficients were obtained from each reaction model. The ranges of values for these coefficients are presented in Figures 6a and b.

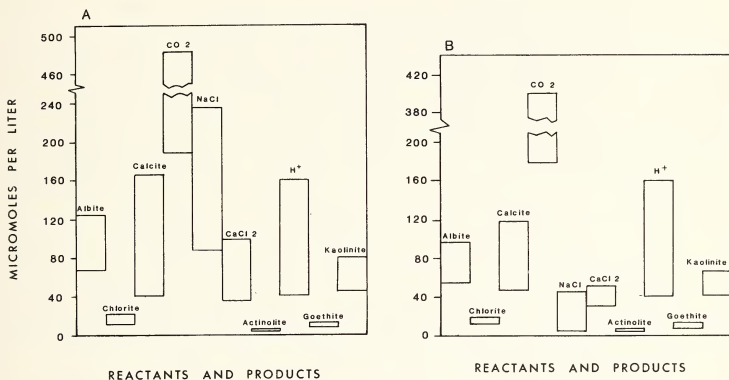
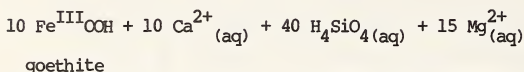
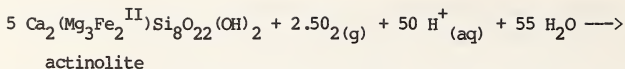


Figure 6.— Range of values for coefficients in seasonal reaction models for 1982 and 1983 calculated using BALANCE for (A) Haver Branch watershed and (B) Hunting Creek watershed.

We have assumed that even though the system is near saturation in terms of oxygen, only enough of this available oxygen reacts with actinolite to oxidize ferrous iron to ferric iron. A value of 2.50 $\mu\text{mole/L}$ (0.08mg/L) dissolved oxygen was used for calculations during the winter, spring, and fall seasons. Furthermore, we assume that the reaction of actinolite to form goethite is as follows (using data for Haver Branch, January–March, 1982, as an example):



During the summer months (July through September), we assume that more oxygen reacts with actinolite to produce more goethite. The increased input of oxygen may be driven by higher respiration rates of biota which introduce more oxygen or less saturated soil conditions allowing more oxygen to be present. Using an input value of 0.42 mg/L of dissolved oxygen, the relative amounts of minerals that react during the summer months are very similar to the amounts of reacting minerals during the rest of the year. This finding agrees with the fairly uniform stream chemistry (sampled during base flow) throughout the entire year. It is important to note that the coefficients for the mineral phases calculated by BALANCE are very sensitive to the input values of dissolved oxygen. It was found that after many input values were tried, the most reasonable results (Figure 6) were those obtained using the aforementioned dissolved oxygen values of 0.08 and 0.42 mg/L for the different seasons.

Several important observations can be made regarding the geochemical reactions occurring in these watersheds. First of all, calculations using the results obtained from BALANCE and seasonal volume-weighted concentrations of H in precipitation yield information on the relative importance of strong acids from atmospheric deposition as opposed to carbonic acid in weathering reactions. The water that reacts with the minerals in the soil and bedrock falls as precipitation charged with strong acids. In addition, biological processes in the soil contribute carbon dioxide to the soil atmosphere at concentrations well above those in the ambient atmosphere. The strong acids from precipitation together with carbonic acid from the soil attack minerals and release dissolved components to the water. For example, the most reactive mineral, calcite, contributes Ca^{2+} and HCO_3^- to the

water upon dissolution. If the aggressive agent is a strong acid, one mole of HCO_3^- will be released per mole of calcite dissolved. If carbonic acid is the weathering agent, then 2 moles of HCO_3^- will be released per 1 mole of calcite dissolved. Acid attack of silicate minerals such as albite contributes base cations and silica to the water. If the H ion comes from carbonic acid, HCO_3^- will be the anion balancing the base cations. Iron and aluminum contained in the silicate minerals precipitate as hydrous oxides and kaolinite. Furthermore, the amount of each of these minerals (calcite, albite, chlorite, and actinolite) that must react is constrained by the observed water chemistry. Strong mineral acids from precipitation contributed about 13 to 39 percent and 11 to 38 percent of the total H to mineral weathering at Hauver Branch and Hunting Creek watersheds, respectively (Table 3a). Even though the contribution of H from strong acids in precipitation is generally highest during the summer months (July through September) for both watersheds, the total amount of minerals weathering during this period is the lowest (table 4).

The second observation is that the seasonal stream chemistry can be explained by mineral reactions. Calculations using BALANCE indicate that the weathering of two minerals, calcite and albite, along with the anthropogenic addition of halite and calcium chloride, contributed the bulk of dissolved solids to the stream water during 1982 and 1983. Albite weathers predominantly to kaolinite and possibly to small amounts of other clay minerals. A detailed analysis of the clay mineralogy of the soils is in progress.

A third observation from the BALANCE calculations is that the amounts of neutralization of H^+ input from precipitation and from carbonic acid by major minerals on a seasonal basis remained fairly uniform for both watersheds during both years. The following percentage ranges were observed for the various major minerals in terms of neutralizing the total H^+ inputs in both watersheds: albite (34 to 61 percent), calcite (25 to 55 percent), chlorite (7 to 12 percent), and actinolite (2 to 4 percent).

The fourth observation is that the actual amounts of minerals that react, as calculated by BALANCE, are dependent upon the amount of water that is available for reaction during each season. To obtain these amounts, one would multiply the relative amounts of each mineral that reacts, as calculated by BALANCE, by the volume of water entering each watershed seasonally (table 4), corrected for evapotranspiration losses. If these calculations are done, it is evident that the most weathering occurs during the season with the most rainfall and the lowest evapotranspiration losses (table 1). Generally, the three month period with the highest rainfall and the lowest evapotranspiration rate is the April through June period (table 4). However, due to an unusually wet Fall in 1983, extremely high quantities of water were available for reaction with the minerals in the watersheds (table 4).

It is important to note that the balanced equations or reaction models obtained from BALANCE are defined by the phases and the amounts of each phase necessary to account for the resultant stream-water chemistry. However, these reaction models are not necessarily unique solutions which define the reactions between precipitation and the minerals in bedrock and soils. The models are extremely useful in studying the weathering reactions occurring during baseflow in the watershed, and they do account for the chemistry of the stream water on a seasonal basis.

Table 4.-- Approximate total amount of minerals reacting during each season, as calculated from BALANCE results, precipitation, and evapotranspiration.
(All values in kilograms)

	Hauver Branch Watershed		Hunting Creek Watershed	
	1982	1983	1982	1983
Jan - Mar	208	317	785	957
Apr - Jun	241	336	780	998
Jul - Sep	18.3	11.1	125	50
Oct - Dec	32.7	213	158	946

SUMMARY AND CONCLUSIONS

During 1982 and 1983, precipitation and stream water were sampled weekly for quantity and chemical composition in two small forested watersheds located in the Blue Ridge physiographic province of central Maryland. Both watersheds are completely underlain by the Catoctin Formation, a bedrock type composed of the minerals chlorite, albite, epidote, and actinolite, with minor amounts of calcite and quartz.

There are distinct differences between the chemical composition of the incoming precipitation and the stream water leaving each watershed. For precipitation collected during 1982 and 1983, sulfate and nitrate were the major anions, and hydrogen the principal cation. For stream water and ground-water samples, bicarbonate was the major anion, and calcium and magnesium were the principal cations.

Seasonal trends in the concentrations of certain constituents were clearly apparent in precipitation and in the stream water draining both watersheds. Highest concentrations of hydrogen ion and sulfate in precipitation were observed during the summer months (July through September). Conversely, highest nitrate concentrations in precipitation were observed during the winter months (January through March) In stream water, bicarbonate concentrations were highest during the summer. Concentrations of sodium and chloride were elevated well above their annual average during the spring months, following winter application of deicing salt and sand to main roads in each watershed. The concentrations of the principal dissolved constituents resulting from weathering reactions of minerals comprise the majority of the total dissolved solids in the stream water draining both watersheds. There is no discernible correlation between weekly concentrations of calcium, magnesium, and silica in stream water draining the watersheds with the wide fluctuations in discharge observed throughout 1982 and 1983.

Geochemical weathering processes account for most of the observed seasonal differences between the chemistry of input precipitation and output streamflow. The aluminosilicate minerals (chlorite, actinolite, albite, and epidote) react incongruently with CO_2 - charged water to form kaolinite, releasing cations, silica, and bicarbonate to stream

water. Actinolite also reacts with dissolved oxygen to form goethite (FeOOH). Analysis of the seasonal chemistry of stream water and precipitation using the computer program BALANCE suggests that approximately 5 times more dissolved oxygen reacts with actinolite during the summer months than during other seasons; as a result, more goethite is formed during the summer months. The relative amounts of minerals that react throughout the year remain fairly constant. For 1982 and 1983, in terms of total quantities of reacting minerals, the greatest amount of weathering occurred during April through June, the interval with the highest rainfall and one of the lowest evapotranspiration rates. The dissolution of calcite and albite account for at least 80 percent and as much as 100 percent of the neutralization of the total H^+ input from precipitation and from carbonic acid weathering. Even though calcite is present in the bedrock in extremely small amounts, it plays a major role in governing water chemistry because of its high reactivity and its location in the hydrologic flow paths in the watersheds.

Acknowledgements

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DISCUSSION: Katz Paper

Question (Alaback): I had a question as to what those coefficients for the various mineral constituents you are talking about meant? Were they something you derived based on the relative abundance of that mineral in the bedrock or was that simply the result of a regression?

Answer: Those are essentially numbers which are required to balance the chemical reactions.

Question (Alaback): So the underlying assumption you made was that the spring water chemistry was totally predicated on the geochemical weathering plus the external inputs of precipitation and road salt? Is that correct?

Answer: Well, we measured the stream water chemistry, so that is a known. We entered the precipitation chemistry and that was a known. By difference we were able to calculate the net change in chemistry. Now in order to explain that net change in chemistry, we had to have reactions with certain minerals in the system and derive those coefficients which make a balanced reaction.

Question (Alaback): But, it was possible so you didn't get into anything dealing with the soil or vegetative components?

Answer: Right, biomass was neglected.

Question (Pionke): You had pointed out that at certain seasons you were likely to have a greater reaction occurring and this accounted for these higher concentrations you observed. Since you measured a lot of these with samples taken at the weir, there would be travel time when you got the samples relative to wherever the reaction was occurring to enrich it. May, March, and June is when most of the mineralogical reactions were occurring. Is the travel time quick enough that you can make those statements, or is it possible that you have a substantial delay due to travel time such that you might be talking about something happening in midwinter or fall in the watershed. Is it just the effect of travel time you are observing?

Answer: That is a good question. I think that travel time changes throughout the year depending upon the amount of precipitation. During the spring season where there is very little vegetation, and we get a large amount of precipitation, I think we see fairly short travel times. Whereas in the summer, fall when there is a lot of vegetation trapping the incoming precipitation, I think the travel time may be on the order of 3 to 6 months. That is why we see lag in the nitrogen coming out. I think it is about a 3 month lag from when the leaves actually fall and decay until where we actually see the nitrogen coming out in the outflow.

Question (Meisinger): Could some of your excess salt be coming in as road salt?

Answer: We thought about that, but as of this time haven't been able to answer the question.

Question (Pionke): With respect to road salt, it looked like the loss of sodium was about uniform throughout all the seasons. In other words, it really didn't change. I realize your road salt is only about 20% sodium chloride, but would you expect over a 2-year period, especially if your dealing with roads with fractures and cracks, that you should have started picking up a correspondingly high sodium concentration and an unnaturally high chloride concentration in the spring when road salt was the primary source of chloride.

Answer: Yes, I really expected that. I am really not sure why the sodium doesn't correlate well with chloride. There may be some other reactions occurring with sodium and it may be exchanging in the soil with other constituents.

Question (Weller): I was wondering how your model accounts for potential biological reactions like denitrification. Is that included in your balance equation?

Answer: Well, nitrogen and sulphur were not included in the balance reaction. What we are trying to balance here are the major ions that are produced from minimal weather reactions and from our initial work it appears that we can account for the concentrations of the major cations produced from weathering reactions fairly well.

Question (Weller): Our data show that a large portion of the nitrate is retained out of the precipitation and that is a major factor in the hydrogen cycling of the system so that if it were included in a modeling application a different solution would be obtained which would indicate a different balance of minerals.

Answer: That is a good point. We essentially neglected the influence of biomass in the model, and we really had no way of quantifying the denitrification reactions and some of the other reactions that are occurring in the biomass. We essentially treated the biota as a steady state system.

Question (Correll): I wonder if you have any data on bulk precipitation to compare with the wetfall data on inputs and how things would differ if you

were using bulk precipitation?

Answer: Unfortunately, we don't. We are collecting bulk precipitation now, and we also have put out some glass slides treated with a special epoxy which we hope will collect dryfall.

Comment (Blood): We are looking at chemistry of throughfall, and we found out that this water coming through the canopy oftentimes is 2 to 5 times higher in the concentrations of sulfate. A lot of this has to do with the particulate dryfall collecting on the canopy which is washed off by the rain.

Question (Katz): Do you see a corresponding increase in the calcium or other cations in the throughfall?

Answer (Blood): Yes, there is an elevation in cations in the throughfall.

Comment (Correll): If you are going to deal with the nitrate issue Weller brought up, it doesn't really matter as far as the hydrogen budget goes whether it is denitrified or is assimilated by the biota. It will have the same impact so that you might still deal with that just by looking at how much disappears in the system and assuming it goes one of those two routes. It has the same effect on the geochemistry either way. You could try to factor that in without knowing which way it goes.

NITROGEN INPUT/OUTPUT RELATIONSHIPS FOR THREE FORESTED
WATERSHEDS IN EASTERN TENNESSEE

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Abstract--Atmospheric inputs of N were evaluated at three forest sites in eastern Tennessee from February 1982 through May of 1984. Estimated atmospheric N inputs ranged from 8.0 to 13.2 kg ha⁻¹ yr⁻¹ depending on the method of estimation and study site location. Streamflow N outputs ranged from 2.4 to 4.4 kg ha⁻¹ yr⁻¹ during the same period. System retention of atmospheric input, dependent on method of input calculation, ranged from 52 to 79 percent. Based on the results of this study, our best estimate of N input derived from the sum of wetfall, dryfall, gaseous NO and NO₂, and estimated HNO₃ vapor is 11.6, 11.3, and 13.2 kg ha⁻¹ yr⁻¹ at Cross Creek, Camp Branch, and Walker Branch, respectively. Retention percentages based on these estimates of input were 66, 79, and 67 percent. The data collected suggest that the importance of gaseous NO and NO₂ input can vary considerably with location and that HNO₃ acid vapor may be an even more important form of N input.

Key words--atmospheric deposition, water quality, wetfall, dryfall, precipitation chemistry

INTRODUCTION

Because atmospheric deposition of N compounds represents a potentially important source of N to the forest system, numerous studies have been undertaken to quantify inputs via precipitation. However, as noted by Soderlund (1977), estimates of the amount of N input via dry deposition vary widely. Consequently, it is important that the magnitude of total atmospheric N deposition (wet + dry) be quantified to the highest degree possible since these inputs may have both positive and negative impacts on forest growth, water quality, and water quantity.

Atmospheric monitoring studies have established that NO and NO₂ are the most important forms of nitrogen air pollutants, and these same studies have also established that NO and NO₂ can occur in elevated concentrations at points considered to be remote from a pollution source (Lodge and Pate,

1966; Ripperton et al., 1979). Atmospheric residence times of these compounds have been calculated to range from 4 to 72 hours (Robinson and Robbins, 1970; Chang et al., 1979; Spicer, 1982) allowing sufficient time for transport and subsequent deposition outside of the source area.

With this background information in mind, a study was formulated and conducted in order to (1) quantify and compare N inputs via wet and dry deposition to three forested watersheds with potentially different atmospheric loading rates, (2) compare atmospheric N inputs and streamflow N losses, and (3) compare N input/output data with standing N pool data for the same three sites.

STUDY SITES

The three study sites utilized in this study were: Camp Branch ($35^{\circ} 38'N$ $85^{\circ} 18'W$), Cross Creek ($35^{\circ} 41'N$ $85^{\circ} 51'W$), and Walker Branch ($35^{\circ} 58'N$ $84^{\circ} 17'W$) all located in the eastern portion of the Tennessee Valley Region. These sites are located varying distances from major source areas such as urban centers and coal-fired power plants (Fig. 1).

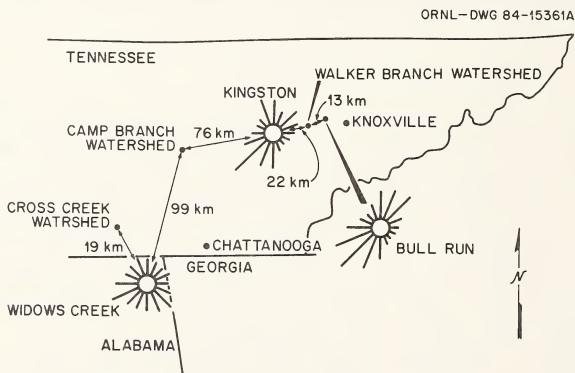


Fig. 1. Locations for the Camp Branch, Cross Creek, and Walker Branch study sites relative to major urban centers and coal-fired power plants. Wind rose data from the power plants are used to reflect transport winds in the area.

The Cross Creek and Camp Branch sites are located in the Cumberland Plateau physiographic region while Walker Branch is located in the Ridge and Valley province (Fenneman, 1938). The vegetation complex on the Plateau is dominated by the drier phase oaks with limited areas of more mesic species, while the Walker Branch site grades from mesophytic oak dominated stands to mixed mesophytic stands. Soils express an even greater degree of contrast. Plateau soils are thin (<1.5 m), infertile, poorly buffered, and derived from a sandstone base, whereas Walker Branch soils -- derived from dolomitic limestone -- are thick (>30 m), well buffered, and moderately fertile. Hydrologically, periods of intermittent flow are common on the Plateau during the late summer and fall while Walker Branch flow is generally continuous. Climate in the region is temperate and continental; winters are moderate with short cold periods, and the summers are mild to hot. The precipitation pattern during the year is characterized by wet winters, comparatively dry springs followed by relatively wet summers and dry falls. Average annual precipitation is on the order of 150 cm.

Examination of the Widows Creek wind rose data (Fig. 1) indicate a fairly even distribution of wind directions with some bias toward the south and west. Cross Creek receives wind directly from the 22.5° wide sector containing the Widows Creek Steam Plant approximately seven percent of the time. Historically, during periods when dispersion conditions were poor and the Widows Creek plant was operating with short stacks, significant amounts of plume transport occurred into side valleys adjacent to the main valley in which the plant is located. Cross Creek is located at the end of a side valley northwest of the plant site. With the installation of a tall stack in the late 1970s, this phenomenon no longer occurs with any regularity. However, this historical influence may have impacted existing standing pool levels.

Prevailing wind directions at the Camp Branch site, as inferred from the Kingston and Bull Run data, appear to be concentrated in the southwest with significant contributions from the northeastern quadrant also. Based on 100 m wind patterns, neither Kingston nor Widows Creek would be expected to contribute substantially to loadings at Camp Branch. The closest major urban area in the dominant downwind direction would be Huntsville, Alabama, located ~160 km from the site.

Walker Branch, on the other hand, is downwind of the Kingston plant approximately 16 percent of the time and downwind of the Bull Run plant approximately seven percent of the time. Both Camp Branch and Cross Creek are located in undeveloped areas, thus ruling out other significant local sources of anthropogenic emissions. Walker Branch, however, is located near urban areas with considerable vehicular traffic and other sources of N emissions. Additional descriptive and quantitative information on the three study sites can be found in Ramseur and Kelly (1981), Kelly (1984), Henderson and Harris (1979), Johnson et al. (1980), and Kelly and Meagher (1985).

METHODS

Gaseous concentrations

Atmospheric concentrations of NO and NO_x were measured continuously at all three sites using a Monitor Labs Model 8440E Nitrogen Oxides Analyzer during the period February 1982 through May 1984. Heated teflon sample line (Unitherm No. 2256-35A00 FEP) was used for the continuous transport of ambient air from the sampling points located above and within the forest canopy (25, 7, and 1-m AGL at Cross Creek and Camp Branch; 40, 16, and 1-m at Walker Branch) to the NO-NO_x analyzer. Air flow rates were adjusted to compensate for differences in sample line lengths at the various sites such that a sample residence time of 30-seconds was used at all sites. An automated data logger system was used to store the data on site and to execute daily system checks using zero and span gases. Initial data editing was performed by the on-site software which calculated an average NO, NO₂, and NO_x concentration for the preceeding hour. The hourly average data were subjected to additional software reviews on the mainframe computer. The results of this software analysis were reviewed and any corrections or deletions were made before these data were entered into the data base (Kelly and Meagher, 1985).

For calculation of gaseous input estimates, hourly above canopy concentration means were combined with appropriate deposition velocities in the equation of Chamberlin (1953). Deposition velocities for NO and NO₂ were selected based on the recommendation of Nitz and Endlich (1983).

These authors suggest values of 0.2 cm s^{-1} and 0.07 cm s^{-1} for day and night, respectively, for both species. The works of McMahon and Dennison (1979) and Sehmel (1980) were used by Nitz and Endlich (1983) in developing the recommended deposition velocities. These day/night values were used to calculate NO and NO_2 nitrogen deposition during the growing season. During the non-growing season the 0.07 cm s^{-1} value was used for both day and night because of the lower available surface area and reduced atmospheric transport. The growing season was defined as April 16 through October 15 and the growing season photoperiod defined as 0600 through 1800 hours. A leaf area index of 5.0 was used with the Walker Branch data (Luxmoore et al., 1978). A value of 4.0 was used for Camp Branch and Cross Creek due to the reduced stature of the trees at these two sites.

Wetfall/dryfall

Wet only samples were collected on a weekly basis using two co-located discrete wet/dry type collectors. Sample buckets were returned to the laboratory and the sample volume determined. Following filtration through a Whatman No. 42 filter, the samples were stored in a refrigerator at 4°C until the end of the month at which time a volume proportional composite sample was made up for each collector. Wet samples were analyzed for total-N, $\text{NO}_3\text{-N}$, and $\text{NH}_4\text{-N}$ according to Standard Methods (1980). Appropriate blanks and blind standards were inserted into each sample set. Any obviously contaminated samples were discarded prior to compositing.

Since bulk precipitation (sample vessel continuously exposed to the atmosphere) samples are frequently used as a measure of total atmospheric input, comparison of values obtained by this method to those produced by other approaches was deemed appropriate. Two funnel-bottle type collectors were placed in a clearing in the forest at each study site. Samples were collected on a weekly basis, returned to the laboratory, and processed for chemical analysis in the same manner as the wet only samples.

Dry buckets from the previously mentioned wet/dry collectors were returned to the laboratory at bimonthly intervals. The dry bucket was rinsed with 500 ml of doubly distilled water and concentration values for water soluble $\text{NO}_3\text{-N}$, $\text{NH}_4\text{-N}$, and total-N determined (Standard Methods, 1980). The dry bucket was made of polyethylene and was 19.1 cm in diameter

and 21.0 cm tall for a total exposed surface area of 687.5 cm². Unexposed buckets were washed in the same manner as exposed buckets so that concentration values could be corrected for contamination due to the washing procedure.

Wetfall, dryfall, and bulk precipitation N concentration values were converted to input estimates through combination with the volume of water collected/added and multiplication by appropriate area factors for each type of collector. Leaf area index considerations were not introduced into the dry bucket input calculations.

Throughfall/stemflow

As an additional source of comparative data, throughfall and stemflow samples were collected on a weekly basis using the approach described in Kelly (1984). Throughfall samples were returned to the laboratory and processed for chemical analysis in the same manner as a wet only sample. Stemflow sample volumes were determined in the field and a volume proportional composite sample taken from each plot on a weekly basis. These samples were returned to the laboratory and processed for chemical analysis in the same manner as the wetfall samples. Throughfall concentration values were converted to input estimates through combination with the volume of water collected and multiplication by the appropriate area factor for the collector. Stemflow inputs were calculated based on the total area of the plot, the volume of stemflow collected, and the concentration values determined analytically (Kelly, 1984).

Output measurements

The primary form of N export from the system was assumed to be via streamflow. A typical flow measuring set-up of calibrated weir, stilling basin, and stage height recorder were used to obtain the flow measurements. Flow proportional sampling was used to collect stream water samples for chemical analysis. A refrigerated automatic sampler was used for sample collection and storage in the field. Samples were collected weekly and analyzed for total-N, NO₃-N, and NH₄-N according to Standard Methods

(1980). If no significant hydrologic events occurred during the course of the week, all the samples collected were composited to form one sample.

Standing pools

Nitrogen pool estimates were derived by standard techniques. Above- and belowground biomass pools were determined by the use of whole-tree harvest, root cores, regression techniques, and stand description data as described in Ramseur and Kelly (1981) and Henderson and Harris (1979). Biomass estimates were combined with total-N concentration values (Kelly, 1979; Henderson and Harris, 1979) to provide estimates of N for each biomass component.

Soil nitrogen pools were determined by establishing the extent of each soil mapping unit. Samples were collected from each mapping unit and a soil total-N determination made. The mass of N in the soil pool at each study site was estimated from concentration, bulk density, areal extent, and defined soil depth interval (60 cm) for each soil mapping unit (Kelly, 1979; Henderson and Harris, 1979).

Statistical analysis

All statistical analyses were conducted within the framework provided by the Statistical Analysis System (SAS Institute, 1982) and undertaken with the aid and direction of a statistical consultant. The GLM approach to analysis of variance was used to evaluate differences among sites for input data. Duncan's new multiple range test (Steele and Torrie, 1960) was used for mean separation analysis where indicated. The 0.05 level of probability was used as the criteria for accepting or rejecting null hypotheses pertaining to all data sets.

RESULTS

NO and NO₂ concentrations

As previously mentioned, direct deposition of NO and NO₂ can be a potentially important source of nitrogen input to forest ecosystems. Based on the data collected, NO₂ accounted for 64 to 88 percent of the measured NO_x at each site. The NO-NO₂ distribution was similar at Cross Creek

(12-88) and Camp Branch (14-86) with higher percentages of NO at Walker Branch (36-44). Since NO₂ is formed by NO oxidation in the atmosphere, the lower NO₂/NO ratio at Walker Branch is probably indicative of the influence of a local NO source or sources.

There were no statistically significant differences among the gaseous concentrations measured at the three different elevations at each site. Since the lower two elevations were within and below the forest canopy, respectively, it does not appear that the forest canopy is a significant sink for NO and NO₂. This is not surprising since both NO and NO₂ are only slightly soluble in water and are not readily removed by surfaces. Ambient NO₂ concentration levels at Walker Branch and to a lesser degree at Cross Creek (Fig. 2) appear to vary in an annual cycle with maximum levels in winter (December and January) and the lowest concentrations recorded in the summer (June-August). This trend was less evident in the Camp Branch data.

A cumulative frequency distribution for the NO_x data collected above the canopy at each of the three study sites is shown in Fig. 3. In each case, the data are log-normally distributed. However, the NO_x levels recorded at Walker Branch were substantially higher than those at the other two sites. The median NO_x concentrations at Camp Branch and Cross Creek were 1.5 and 1.8 ppb, respectively, while the median for Walker Branch was 7.2 ppb. It is also evident from these distributions that, although the median and average concentrations recorded at Camp Branch and Cross Creek were similar, the Cross Creek site experienced more high concentration episodes.

Estimates of gaseous NO and NO₂-N input

Comparison of monthly NO-N deposition estimates (Fig. 4) suggests a similar pattern of input at Cross Creek and Camp Branch with peak inputs occurring during the growing season. Walker Branch monthly input values do not seem to exhibit as distinct a seasonal pattern and, in fact, seem to be generally increasing during the last nine months of the study.

NO₂-N values exhibit considerably more month to month variation in concentration (Fig. 2) and therefore input (Fig. 5). In 1982 peak inputs occurred in the fall and early winter months while the next peak occurs

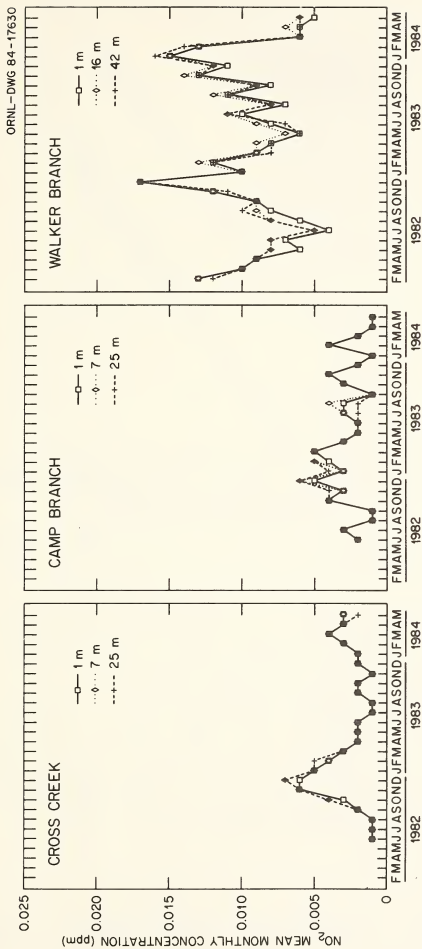


Fig. 2. Mean monthly NO₂ concentrations at the three study sites as a function of elevation above ground level.

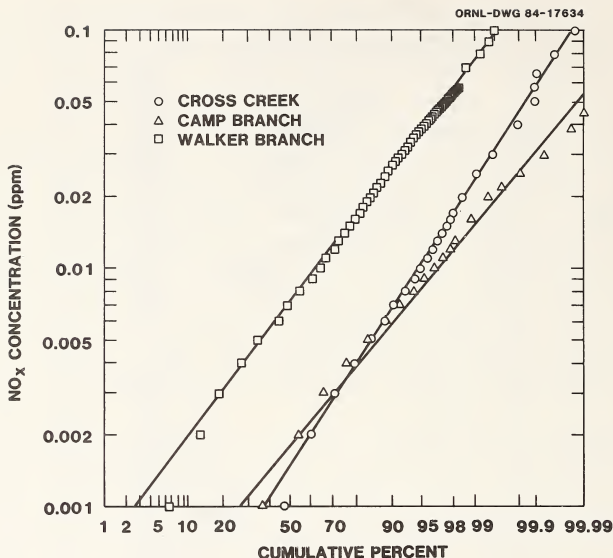


Fig. 3. Cumulative frequency distribution for NO_x concentration above the canopy at the three study sites.

during the spring months of 1984. At Camp Branch inputs fluctuate monthly with a general trend toward decreasing input at Camp Branch. Walker Branch inputs appear to peak during the late summer and early fall.

Mean annual inputs of N as estimated from the sum of NO and NO_2 -N were less than $1 \text{ kg ha}^{-1} \text{ yr}^{-1}$ at Camp Branch and Cross Creek and slightly more than two at Walker Branch (Table 1). The higher estimated deposition at Walker Branch reflects the much higher atmospheric N levels at that site relative to Cross Creek and Camp Branch.

Wetfall

Central to any discussion of wetfall inputs is the amount of precipitation occurring since both the concentration and amount of

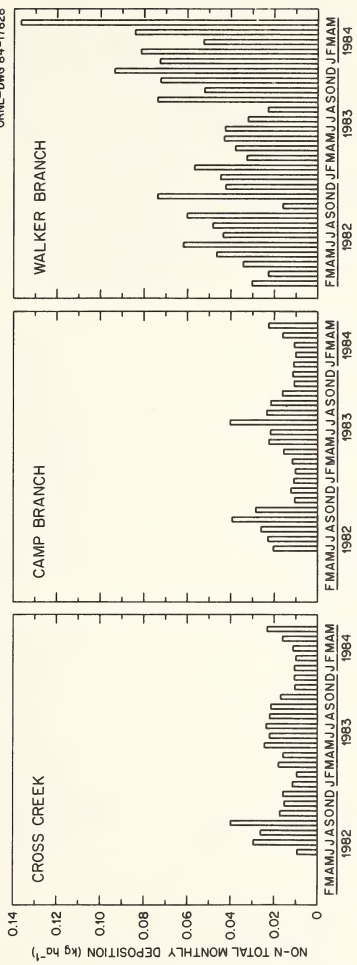


Fig. 4. Monthly NO-N input levels at the three study sites.

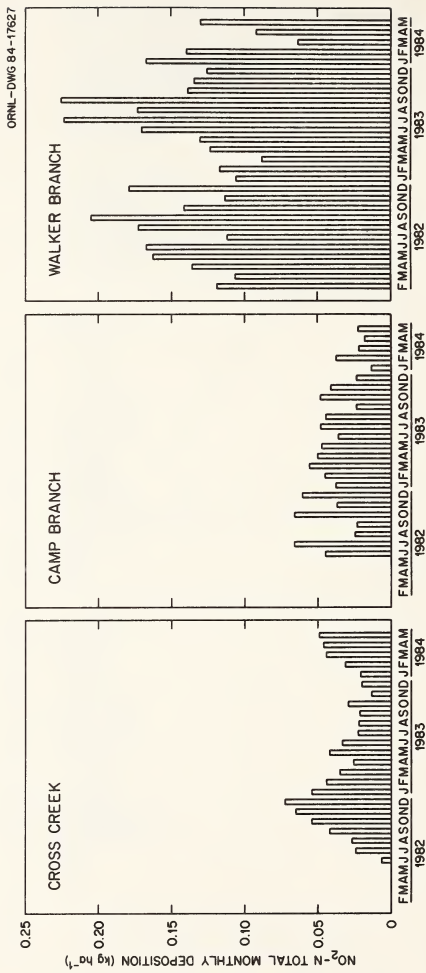


Fig. 5. Monthly NO₂-N input levels at the three study sites.

Table 1. Mean annual inputs of nitrogen via gaseous deposition at the three study sites

Location	kg ha ⁻¹ yr ⁻¹		
	NO-N	NO ₂ -N	NO + NO ₂ -N
Cross Creek	0.21	0.42	0.63
Camp Branch	0.22	0.47	0.69
Walker Branch	0.65	1.70	2.35

scavenging or washout will be largely a function of rainfall amount. Cross Creek received the greatest amount of precipitation with a total of 348.9 cm over the 28-month study period while Walker Branch and Camp Branch values were 305.5 and 294.0, respectively. Although all three sites are located in the same general area, monthly precipitation amounts do vary somewhat with location (Fig. 6).

Total-N concentration values in wetfall exhibit different patterns through time for each site (Fig. 7). A significant negative correlation was found for total-N concentration and wetfall volume. Values of R ranged from -0.20 at Camp Branch to -0.31 at Cross Creek. Statistical comparison of wetfall total-N input values (Table 2) indicated no significant differences

Table 2. Mean annual inputs of nitrogen via wetfall at the three study sites

Location	kg ha ⁻¹ yr ⁻¹		
	Total-N	NO ₃ -N	NH ₄ -N
Cross Creek	3.2	1.1	0.9
Camp Branch	2.9	1.0	0.9
Walker Branch	2.9	1.1	0.8

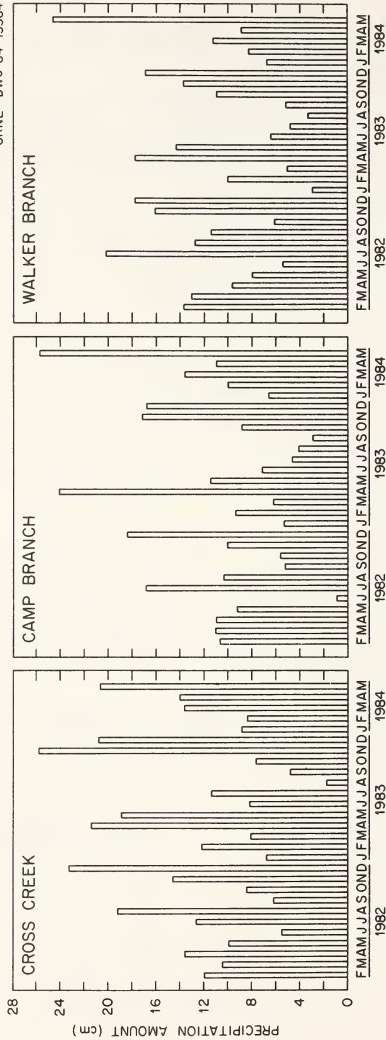


Fig. 6. Monthly precipitation values for each site during the study period February 1982 through May 1984 as determined by standard recording rain gauge measurements.

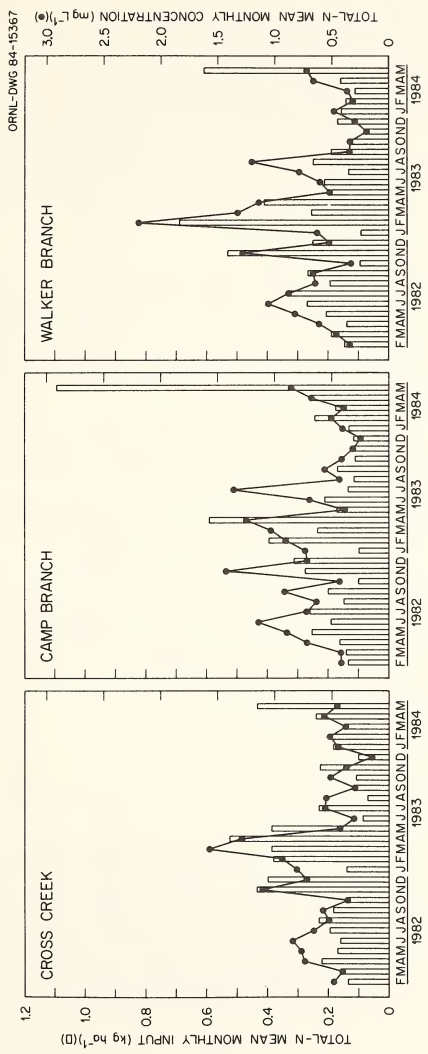


Fig. 7. Mean monthly wetfall total-N concentration (line) and input (bar) values for the three study sites.

among sites. Concentration patterns for wetfall $\text{NO}_3\text{-N}$ were quite similar for the Camp Branch and Walker Branch sites but differed from the trends observed at Cross Creek (Fig. 8). There was also a significant $\text{NO}_3\text{-N}$ and volume correlation ($R = -0.28$ to -0.39) observed at all sites but there was no correlation with $\text{NH}_4\text{-N}$. Annual inputs of wetfall $\text{NO}_3\text{-N}$ did not differ significantly among sites. Wetfall $\text{NH}_4\text{-N}$ inputs exhibited similar patterns of both concentration and input through time at all sites (Fig. 9).

Dryfall

There is a general concensus that the use of the dry bucket method to collect samples for dryfall determination is at best a questionable approach due to possible inconsistencies in sampling. Recognizing these limitations, the values obtained may be useful to provide at last a first approximation of dryfall input among similar study sites.

Statistical comparison of the mean annual input data (Table 3) indicated a significantly lower level of $\text{NO}_3\text{-N}$ input at Walker Branch.

Table 3. Mean annual inputs of nitrogen via dryfall at the three study sites

Location	kg ha ⁻¹ yr ⁻¹		
	Total-N	$\text{NO}_3\text{-N}$	$\text{NH}_4\text{-N}$
Cross Creek	4.4	1.4	1.3
Camp Branch	4.4	1.5	1.1
Walker Branch	4.1	1.0	1.0

Other forms of N input did not differ significantly among sites. Although the differences in input for these other N forms were not statistically significant, Walker Branch consistently had the lowest levels of dryfall input for all N species evaluated. Comparison of the individual sampling dates indicates the highest levels of dryfall input generally occur during

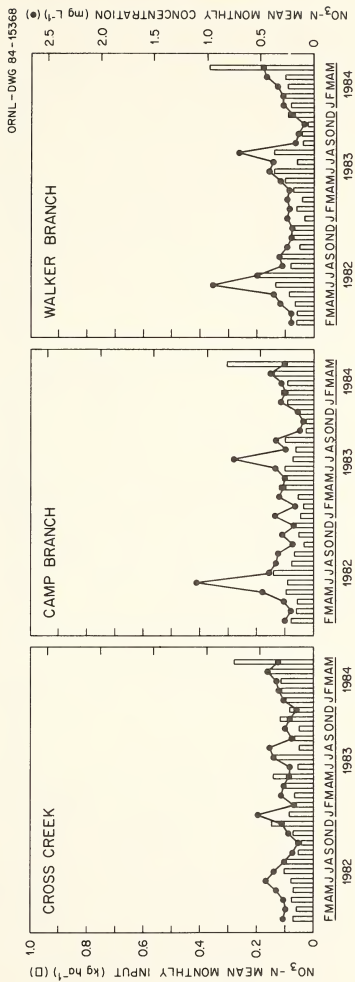


Fig. 8. Mean monthly wetfall $\text{NO}_3\text{-N}$ concentration (line) and input (bar) values for the three study sites.

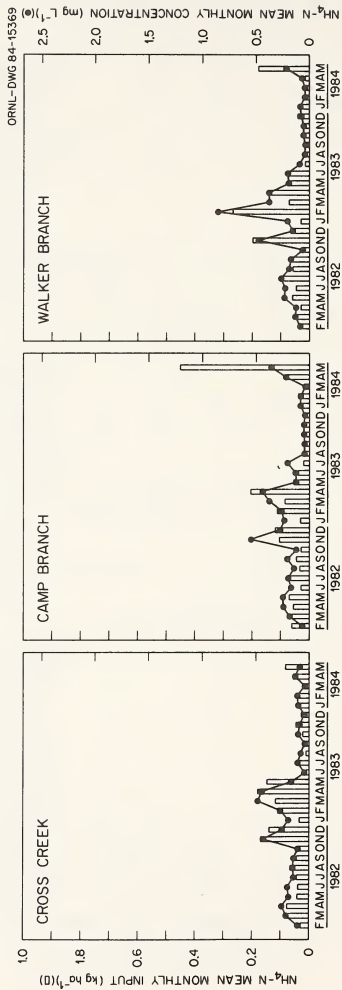


Fig. 9. Mean monthly wetfall $\text{NH}_4\text{-N}$ concentration (line) and input (bar) values for the three study sites.

the winter months. Furthermore, as might be expected, dryfall inputs appear to vary inversely with rainfall amount.

Lovett and Lindberg (1985) estimated dry deposition inputs of HNO_3 vapor and particulate $\text{NO}_3\text{-N}$ for Walker Branch of 3.6 and $1.2 \text{ kg ha}^{-1} \text{ yr}^{-1}$, respectively. Total $\text{NO}_3\text{-N}$ dry deposition from these two species ($4.8 \text{ kg ha}^{-1} \text{ yr}^{-1}$) exceeds the dryfall total-N value at Walker Branch (Table 3) and is almost five times the measured dryfall $\text{NO}_3\text{-N}$. There is no reason to believe that $\text{NO}_3\text{-N}$ deposition would fluctuate enough between the two measurement periods to account for this difference. Thus, we are forced to conclude that the dry collector greatly underestimates inputs from these N species. This conclusion is supported by the observation of Huebert (1985) that micrometeorological measures of HNO_3 vapor deposition exceeded those measured by surrogate surfaces by a factor of three. Thus, in order to properly account for this phase of dry N deposition, we will use the Lovett and Lindberg (1985) $\text{NO}_3\text{-N}$ dry deposition estimate in future calculations of total input at Walker Branch.

No independent measure of $\text{NO}_3\text{-N}$ dry deposition is available for the other two sites. However, an estimate of the relative HNO_3 vapor levels at the three sites can be made by comparing the wetfall $\text{NO}_3\text{-N}$ values. HNO_3 vapor is readily absorbed into cloud droplets and rain drops (Durham et al., 1981) and thus precipitation nitrate is a good measure of atmospheric HNO_3 vapor. Since wetfall $\text{NO}_3\text{-N}$ measurements suggest similar HNO_3 vapor and presumably nitrate particulate loadings at the three sites, the dryfall $\text{NO}_3\text{-N}$ deposition estimate of Lovett and Lindberg (1985) will be substituted at these two sites as well.

Streamflow outputs

The flashy nature of streams at Cross Creek and Camp Branch are evident when the monthly values from these two sites are compared to the Walker Branch flow values (Fig. 10). Comparison of the flow data in Fig. 10 with the precipitation amount data in Fig. 6 reinforces the observation that the Cross Creek and Camp Branch sites are more directly responsive to precipitation inputs. Comparison of precipitation amounts with streamflow outputs indicates a loss of approximately 70 percent of precipitation input as streamflow during the 28-month study period.

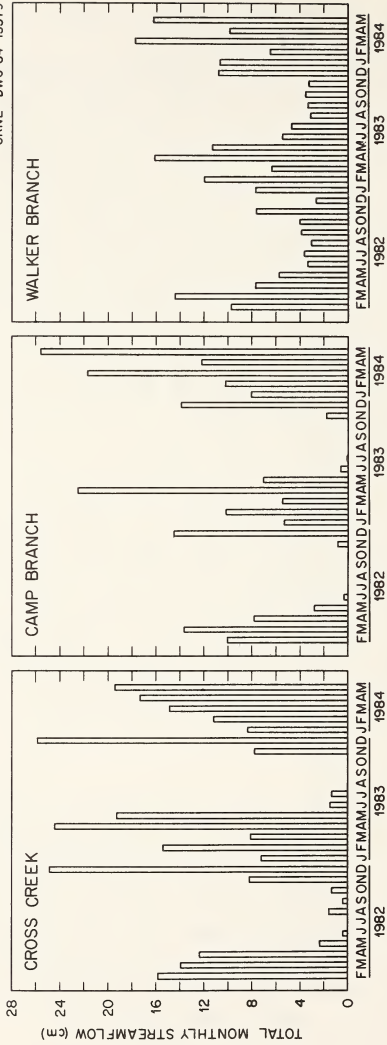


Fig. 10. Total monthly streamflow volume for the three study sites.

Mean annual estimates of nitrogen export via streamflow (Table 4) differ somewhat with location and nitrogen form. Total export estimates are

Table 4. Mean annual nitrogen export via streamflow at the three study sites

Location	kg ha ⁻¹ yr ⁻¹		
	Total-N	NO ₃ -N	NH ₄ -N
Cross Creek	3.9	1.4	0.3
Camp Branch	2.4	1.1	0.2
Walker Branch	4.4	1.6	0.7

consistent with those reported by Likens et al. (1977) for Hubbard Brook and by Henderson and Harris (1979) for an earlier study at Walker Branch. Comparison of monthly total-N export values (Fig. 11) with monthly streamflow amounts (Fig. 10) does not indicate a consistent relationship between the amount of water and total-N leaving the system. All three sites exhibit an increase in total-N concentration and loss during the fall and winter period of 1982-83. However, a similar pattern is not present in the data from the same period in 1983-84 even though there was a similar increase in streamflow discharge.

One hypothesis for this inconsistent behavior could be that reduced plant uptake and/or increased root and microbial mortality during the hot dry summer of 1982 resulted in a sizable pool of N available for leaching during the non-growing season. The process does not recur in the second year due to either a depleted pool of leachable material and/or a recovery of the system with an increase in biological demand. Alternatively, it is interesting to note that wet inputs of total-N (Fig. 7) were higher during the 1982-83 period than in the 1983-84 period. Circumstantially, it would appear that the differences are more a function of wet deposition of total-N than any other factor.

Mean monthly streamwater total-N concentration for the 28-month study period was highest at Walker Branch (0.41 mg L⁻¹) with mean concentration

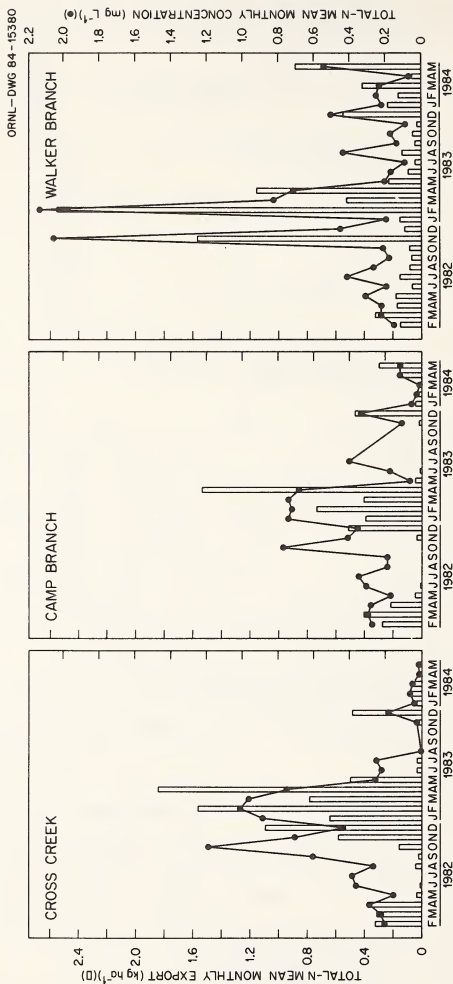


Fig. 11. Mean monthly streamflow total-N concentration (line) and export (bar) values for the three study sites.

values for Cross Creek and Camp Branch of 0.36 and 0.31 mg L⁻¹. Mean monthly NO₃-N concentrations at Camp Branch and Cross Creek were 0.02 mg L⁻¹ compared to 0.06 mg L⁻¹ at Walker Branch. The higher concentration values at Walker Branch are reflected in the monthly NO₃-N export values (Fig. 12) and in the mean annual export estimate (Table 4). Even though Cross Creek had a higher water flux, it lost less NO₃-N than Walker Branch. Comparison of NO₃-N export patterns (Fig. 12) with the inputs observed in wet deposition (Fig. 8) at Walker Branch indicated a significant positive relationship (R = 0.62) between observed wetfall, NO₃-N inputs, and streamflow NO₃-N outputs. This relationship did not hold for the Camp Branch and Cross Creek sites.

Trends in the concentration and export of NH₄-N (Fig. 13) are very similar to those observed for total-N (Fig. 11). Mean monthly concentration values for NH₄-N are 0.11, 0.12, and 0.15 mg L⁻¹ for Camp Branch, Cross Creek, and Walker Branch, respectively. Again, the slightly higher concentration values at Walker Branch result in a greater mean annual loss of NH₄-N (Table 4) than at the other two sites even though streamflow volume was less. NH₄-N, like total-N, exhibits an increase in output during the 1982-83 dormant season apparently in response to an increase in wetfall NH₄-N input. Correlation analysis indicated a significant positive relationship between wetfall NH₄-N input and streamflow output at Camp Branch (R = 0.84) and Cross Creek (R = 0.53) but not at Walker Branch. This trend is just the opposite of the relationship observed for NO₃-N.

SYNTHESIS

A basic consideration in any budgetary approach to impact evaluation is a comparison of inputs and outputs in order to determine a retention factor, as well as a comparison to the standing pools in the ecosystem. If inputs or outputs are small relative to the total pool, then impact would not be as great as it might be if inputs or outputs were large relative to the standing pool. However, a major consideration in any comparison to a total standing pool is the relative availability of the nutrient capital in that pool. If the pool is large but essentially unavailable or only slowly available, then a relatively small change in input or output may have a much

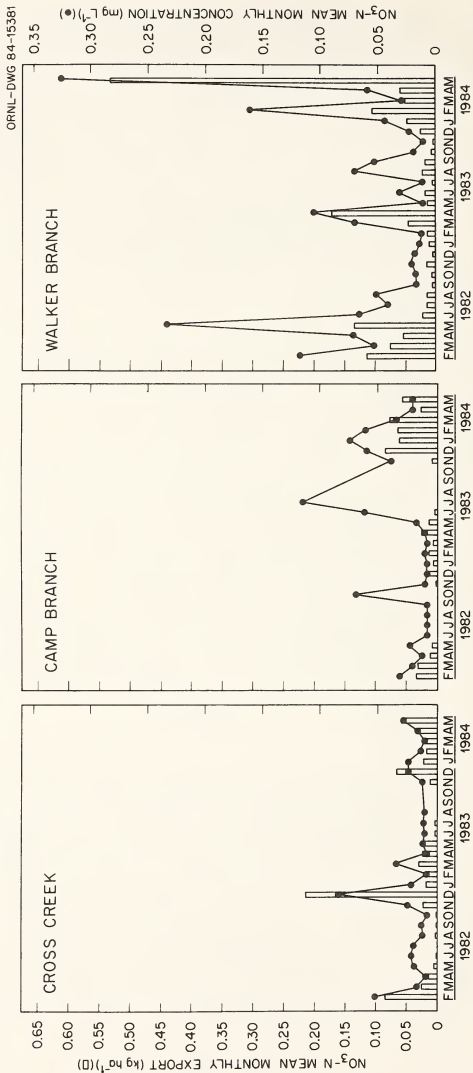


Fig. 12. Mean monthly streamflow NO₃-N concentration (line) and export (bar) values for the three study sites.

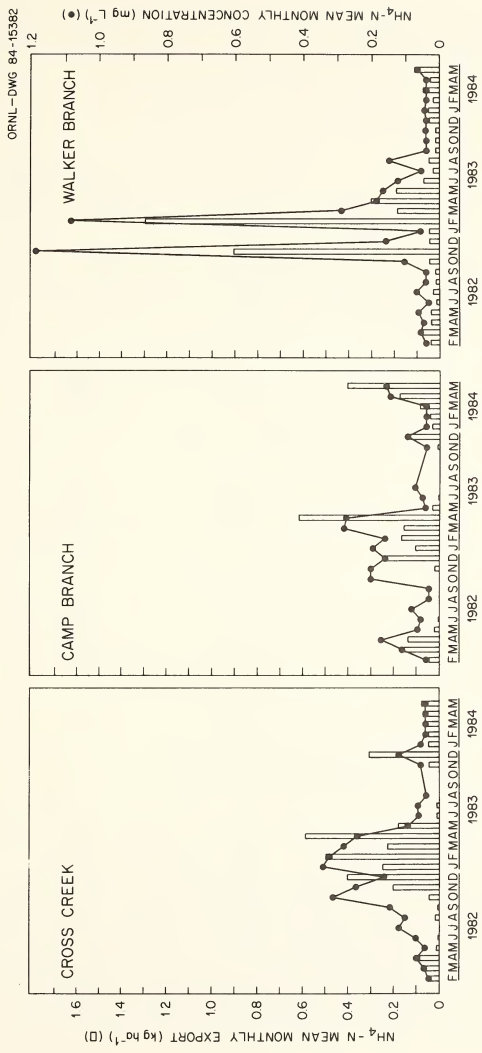


Fig. 13. Mean monthly streamflow $\text{NH}_4\text{-N}$ concentration (line) and export (bar) values for the three study sites.

greater impact. Conversely, if a relatively small pool is present in a largely available form, then what appears to be a sizable input may not have a major impact.

Standing nitrogen pools

The mineral soil is by far the largest reservoir of N at all sites (Table 5). However, it should be recognized that a great percentage of this

Table 5. Total standing pools of nitrogen in various ecosystem components at the three study sites

Component	kg ha ⁻¹		
	Cross Creek	Camp Branch	Walker Branch*
Vegetation			
Leaves	43	37	73
Boles/Branch	321	356	284
Roots	70	56	135
Soil			
01 Litter	61	47	166
02 Litter	72	101	98
Woody litter	80	43	68
Mineral soil (60 cm)	4,376	5,026	5,158
TOTAL POOL	5,023	5,666	5,982

*Taken from the work of Henderson and Harris (1979).

as well as the total pool is not available on an annual basis. Henderson and Harris (1979) estimate that approximately two percent of the total standing pool at Walker Branch ($129 \text{ kg ha}^{-1} \text{ yr}^{-1}$) is present in an available form. If the same percentage is applied to the Camp Branch and Cross Creek sites, approximately 113 and $100 \text{ kg ha}^{-1} \text{ yr}^{-1}$ of available N would be present. Although the mineral soil is the principal N reservoir, based on the calculations of Henderson and Harris (1979) it supplies, on an

annual basis, only four percent of the available pool. Decomposition/mineralization processes in the litter layers and root mortality appear to be the principal sources of available N from within the system (Henderson and Harris, 1979).

Input/output relationships

While there is a degree of commonality in the magnitude of the various estimates presented in Table 6, there also appear to be differences in

Table 6. Summary of nitrogen inputs as estimated by various methods and outputs as estimated by streamflow

	kg ha ⁻¹ yr ⁻¹		
	Cross Creek	Camp Branch	Walker Branch
INPUTS			
Throughfall + stemflow	13.4 (71)*	11.6 (79)	10.6 (58)
Bulk precipitation	12.4 (69)	10.9 (78)	12.4 (65)
Wetfall + dryfall + gaseous	8.2 (52)	8.0 (70)	9.4 (53)
Wetfall + dryfall + gaseous + estimated HNO ₃ vapor	11.6 (66)	11.3 (79)	13.2 (67)
OUTPUTS			
Streamflow	3.9	2.4	4.4

*Values in parenthesis represent percent of estimated input retained in the system.

either the form or efficiency of N measurement among methods. Based on the data in hand, the sum of wetfall, dryfall, gaseous deposition, and estimated HNO₃ vapor is judged to provide the best estimate of atmospheric N input. The different approaches summarized here also allow two different entry points into the system to be evaluated. For example, the sum of throughfall and stemflow provides an estimate of the amount of nitrogen delivered to the

forest floor. If one is interested in inputs from a water quality perspective, this sum provides a reasonable estimate of the N input which will ultimately interact with the soil and soil water system and end up as streamflow. Net retention estimates based this method of input calculation would provide values on the order of 6.2 to 9.5 kg ha⁻¹ yr⁻¹ or retention percentages ranging from 58 to 79 percent. Using this approach, Walker Branch with the highest total and available pools has the lowest retention value.

Whereas the sum of throughfall and stemflow represent atmospheric inputs which have been modified by interaction with the forest system, both bulk precipitation and the sum of wetfall, dryfall, and gaseous deposition represent atmospheric inputs delivered to the forest canopy. The latter two methods for estimating input to the forest canopy provide generally lower values (Table 6) than do the throughfall and stemflow sum. This difference is thought to be due to the failure of the summation method to account for the contribution of HNO₃ vapor, while the bulk precipitation value is generally lower due to the absence of leaching contributions. If bulk precipitation were used as the input estimate, the retention values would be similar to those observed for the sum of throughfall and stemflow with the exception-that the Walker Branch retention value would increase from 58 to approximately 65 percent (Table 6). However, if the sum of wetfall, dryfall, and gaseous deposition were used as the input estimate, then a very different picture would evolve with substantially lower retention values of 52, 70, and 53 percent for Cross Creek, Camp Branch, and Walker Branch, respectively. If the estimated contribution of nitric acid vapor is added to the wetfall, dryfall, and gaseous estimate, then retention values range from 66 to 79 percent (Table 6). Thus, depending on location and method of input calculation, nitrogen input retention values can range from 52 to 79 percent. Such a range in values has obvious implications if used in impact evaluation.

Comparing any of the input estimates (Table 6) to the total pool values (Table 5) indicates that most inputs represent less than 0.3 percent of the total pool. Comparison with the available pools provides values ranging from 7.0 to 13.4 percent. Using the sum of wetfall, dryfall, gaseous, and estimated HNO₃ vapor as the best estimate, then atmospheric input at the

three sites would be equivalent to approximately 10 percent of the estimated available pool. If annual input was assumed to be constant at a rate equal to 10 percent of the available pool, and if it was further assumed that all of this input remained in the available pool, then the size of the available pool would double in approximately seven years. Such an increase would obviously have the potential to produce an impact. However, this is certainly not likely to be the case since a major portion of the nitrogen input would not remain in the available pool. Assuming that the distribution of available nitrogen (~2 percent) to the total nitrogen pool held constant, then it would require approximately 350 years of input at current levels to double the size of the available pool.

It is particularly important to acknowledge that all values reported here, both measured and estimated, have errors associated with them. Throughfall, stemflow, bulk precipitation, and wetfall can be used with considerable confidence because their estimation errors are small and generally known. Dryfall, gaseous, and HNO_3 vapor estimates, on the other hand, generate a lower level of confidence because of potential errors in establishing the concentration data base for dryfall. Secondly, since input calculations of dryfall, gases, and HNO_3 vapor are based largely on deposition velocities which are at best chosen semi-subjectively, the potential exists for other errors of unknown magnitude. Finally, since N fixation and denitrification were not addressed in this study, the difference between atmospheric deposition and stream export may not represent completely system storage or retention. In no case should any of these values be considered as absolute, but viewed as first approximation indicators.

SUMMARY AND CONCLUSIONS

Atmospheric inputs of N were evaluated at three forest sites in eastern Tennessee from February 1982 through May of 1984. Based on data collected during this period, estimated atmospheric N inputs for the three sites ranged from 8.0 to 13.2 $\text{kg ha}^{-1} \text{yr}^{-1}$ depending on the method of estimation and study site location. Nitrogen outputs via streamflow ranged from 2.4 to 4.4 $\text{kg ha}^{-1} \text{yr}^{-1}$. System retention of atmospheric input, dependent on method of input calculation, ranged from 52 to 79 percent.

Based on the results of this study, our best estimate of N input derived from the sum of wetfall, dryfall, gaseous NO and NO₂, and estimated HNO₃ vapor is 11.6, 11.3, and 13.2 kg ha⁻¹ yr⁻¹ at Cross Creek, Camp Branch, and Walker Branch, respectively. These observations are in keeping with the generalization that most forest systems tend to accumulate N. The data collected further suggest that the importance of gaseous NO and NO₂ input can vary with location and that HNO₃ vapor may be an even more important input form. The best estimate input values presented here are thought to be conservative values but, even at that, dry inputs exceed wetfall by a factor of three. Finally, annual inputs equal approximately 10 percent of the available N pool and are retained within the system at a rate equivalent to approximately 70 percent of input.

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DISCUSSION: Kelly Paper

Comment (Peterjohn): Could you clarify how you determined what was available in your nitrogen pool?

Answer: We didn't do that in this study. That was summarized in a paper by Henderson and Harris within the same sites. They did incubation studies to determine nitrogen availability.

Question (Correll): Do you know of anybody who is routinely measuring N_2O_5 or nitric acid by trying to trap it in an airstream through a chemical trap.

Answer: There are filter pack techniques to do what we have done here. There are problems with those also. They are not as straight forward as you would think they might be. They work really well for SO_2 . But they don't work as well for nitrogen. I don't know of anybody at this point who is routinely doing it. A filter pack or that type of approach is proposed in the high elevation study EPA is planning to fund.

Question (Kuenzler): In your final inputs and outputs did you include organic nitrogen?

Answer: Yes.

Question (Correll): I want to follow up on that point. Did it include just dissolved inputs and outputs or particulate as well?

Answer: Just dissolved.

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

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

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

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

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

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

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

INTRODUCTION

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

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

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

METHODS

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

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

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

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

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

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

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

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

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

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

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

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

Table 2. pH of bulk precipitation and stream water

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

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

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

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

Ion	Annual flux (eq ha ⁻¹ yr ⁻¹)					Average seasonal flux (eq ha ⁻¹ season ⁻¹)			
	1981	1982	1983	1984	Mean	Mar.- May	June- Aug.	Sep.- Nov.	Dec.- Feb.
	Bulk precipitation								
Hydronium	1004	581	1077	741	851	253	266	169	163
Ammonium	221	194	223	326	241	97	72	34	38
Sodium	132	178	311	232	213	71	38	43	61
Calcium	114	181	145	161	150	60	31	26	34
Magnesium	91	141	111	90	108	38	15	21	33
Potassium	45	69	42	81	59	18	13	10	18
Sulfate	908	799	1030	1050	947	288	278	182	199
Nitrate	374	372	538	360	411	132	103	79	97
Chloride	410	258	378	273	330	112	61	66	90
Biphosphate	5	6	8	17	9	4	3	1	1
Stream water									
Hydronium	2	4	26	15	12	7	<1	<1	4
Ammonium	3	4	15	9	8	4	2	<1	2
Sodium	77	147	479	334	259	144	39	7	69
Calcium	63	132	418	333	237	126	31	5	75
Magnesium	95	201	616	383	324	182	40	7	94
Potassium	33	72	233	97	109	69	15	4	21
Sulfate	271	414	1375	899	740	412	82	21	226
Nitrate	5	8	32	13	14	10	1	<1	3
Chloride	81	106	380	233	200	106	25	6	62
Biphosphate	1	4	9	6	5	3	1	<1	<1

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

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

RESULTS

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

Table 4. Additional constituents of stream water[†]

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

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

^{**}Number of concentration measurements made.

^{*}Assuming annual stream discharge of 17.3 cm (Table 1).

[†]Assuming ionic forms of Al³⁺, Fe²⁺, and Mn²⁺.

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

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

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

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

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

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

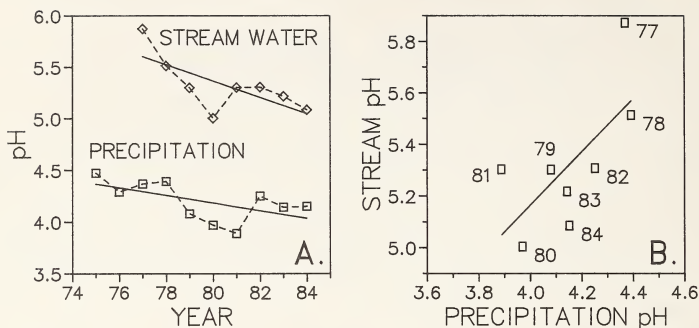


Fig. 1. Trends in average annual pH. Average pH was calculated as in Table 2 over water years extending from December thorough November. (A) shows time plots of pH and linear regressions of pH against time. The regression for precipitation was $Y = -0.0372 X + 4.37$ ($r^2 = 0.36$, $F_{1,8} = 4.41$, $P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

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

Table 5. Charge balances for precipitation and stream water (eq ha⁻¹ yr⁻¹)

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

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

[†] Σcations - Σanions.

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

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

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

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

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

* Assumes that the unmeasured precipitation input is zero.

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

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

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

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

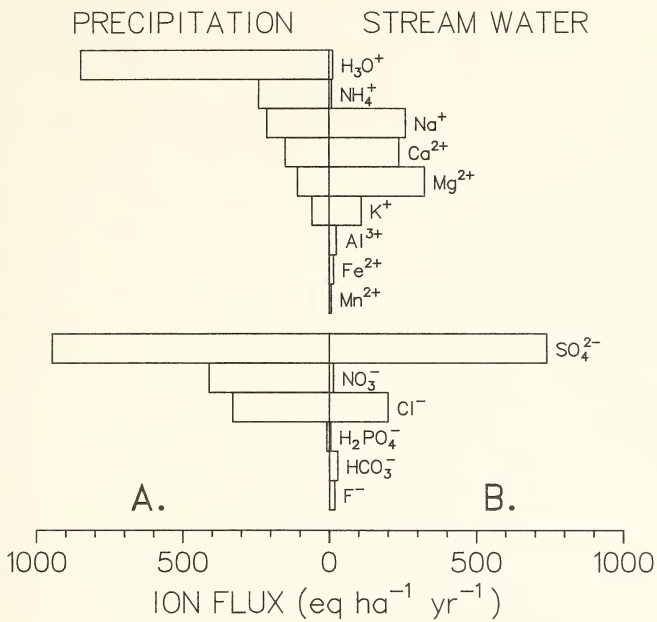


Fig. 2. Average annual ion fluxes in precipitation (A) and stream water (B).

for each ionic equivalent of metal lost.

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

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

4. Immobilization of ions in the soil can give apparent neutralization of hydronium ions. For example, if ammonium ion is adsorbed to the soil particles, then the hydronium ion associated with the ammonia molecule is also immobilized. Similarly, sulfate ions may be adsorbed in soils high in sesquioxides, such as gibbsite ($\text{Al}[\text{OH}]_3$), hematite (Fe_2O_3), or limonite ($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$). Although this adsorption is not a true neutralization, it also immobilizes the associated hydronium ions (or other cations) that were paired with the sulfate in precipitation so that those cations do not appear in the ecosystem output (Johnson *et al.*, 1982; OTA, 1985).

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

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

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

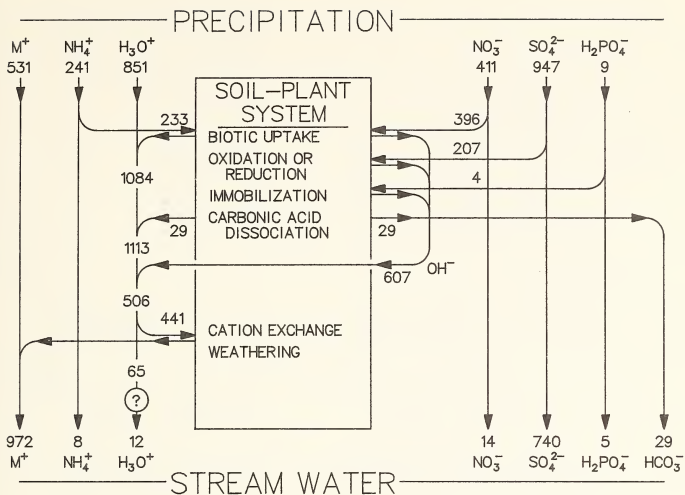


Fig. 3. Schematic acid budget. Numbers are average annual ion or acid fluxes in eq/ha from Tables 3, 4, and 6. The question mark represents the 5% of the total acid input of $1113 \text{ eq ha}^{-1} \text{ yr}^{-1}$ that is not accounted for by the above acid sinks, yet does not appear in the stream water.

DISCUSSION

Acid budget - The low pH and high concentrations of sulfate and nitrate in bulk precipitation confirm that the Rhode River site is receiving significant acid deposition. The average annual pH of 4.14 puts the site in the zone of most acidic rainfall ($\text{pH} \leq 4.2$) within the acid rain belt of the eastern U.S. (OTA, 1985). The forested watershed studied here presently neutralizes over 98% of the total acidity in bulk precipitation, but the unneutralized portion does have an effect on stream pH, as demonstrated by the parallel declines in the pH of precipitation and stream water and by the correlation of stream pH

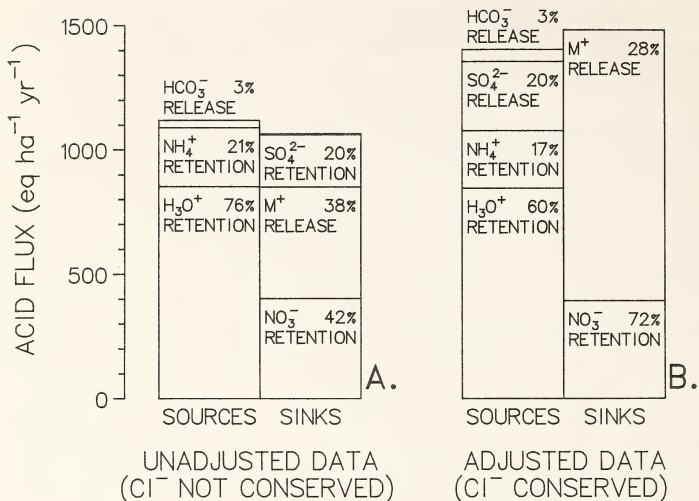


Fig. 4. Net production and net neutralization of acidity. (A) is the unadjusted acid budget while (B) includes an adjustment that balances the chloride budget (see discussion).

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

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

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

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

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

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

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

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

Table 7. Cation loss rates

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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DISCUSSION: Weller Paper

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

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

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

Answer: The average is about 5.2.

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

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

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

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

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