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THE CHESAPEAKE BAY WATERSHED: EFFECTS OF LAND USE AND GEOLOGY ON DISSOLVED NITROGEN CONCENTRATIONS

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Abstract: We measured the concentrations of dissolved nitrogen fractions in the streams draining 153 subwatersheds of Chesapeake Bay. Six "clusters" of nested watersheds were sampled eight times during the period from the summer of 1992 to the summer of 1993. Clusters were located on the Coastal Plain (2) in Maryland, the Piedmont (1) in Maryland and Pennsylvania, and in the Appalachians (3) in Pennsylvania and New York. Clusters were selected to avoid urbanized areas, but included forest, cropland, pastureland, and residential areas. The sampling times included before, during, and after the record spring Susquehanna River freshet of 1993. Concentrations of nitrate and dissolved ammonium were measured in all samplings of all subwatersheds, while dissolved organic nitrogen was measured on a subset of sites.

Differences in concentrations of dissolved nitrogen fractions were related to the proportion of forest versus agriculture on the subwatersheds and to geological differences among clusters. Although little nitrate was discharged from any of the forested watersheds, high concentrations were discharged from agricultural watersheds. The concentrations of nitrate discharged from agricultural watersheds were highest in the Great Valley, followed by the Ridge and Valley, Piedmont, Coastal Plain, and Appalachian Plateau. Concentrations of dissolved ammonium were 20-fold lower than nitrate and there was less variation among sites, but the Conestoga River usually had the highest and Owego Creek the lowest concentrations. Concentrations of dissolved organic nitrogen were higher than ammonium concentrations but 10-fold lower than nitrate concentrations.

For primarily forested watersheds, nitrate concentrations were much lower. Coastal Plain forests had the lowest nitrate concentrations, but the highest ammonium concentrations. Dissolved organic nitrogen concentrations were much less variable among both forested and agricultural watersheds and thus constituted a larger proportion of total nitrogen in streams draining forested sites.

INTRODUCTON

The watershed of the Chesapeake Bay is approximately 178,000 km² and includes the District of Columbia and Maryland and parts of New York, Pennsylvania, West Virginia, Delaware, and Virginia (Correll 1987, Seitz 1971). About 67% of the watershed is in the Appalachians, 15% in the Piedmont, and 18% in the Atlantic coastal plain physiographic provinces. The Appalachian province is composed of three geological subcategories, the Appalachian Plateau, the Ridge and Valley region, and the Great Valley. Of these, the Ridge and Valley is the most extensive in area. The coastal plain province may also be divided into inner and outer coastal plain regions. The outer coastal plain is very sandy and is relatively level, while the inner coastal plain has nutrient rich, well-developed fine sandy loam soils and typically

has fairly steep slopes even though the overall relief is small. Major land uses include forest land (especially in the Appalachians), cropland, pastureland, and residential. The distribution or arrangement of land uses also differs characteristically among these physiographic provinces. For example, in the Ridge and Valley region, agriculture is localized in the valleys where the soils are productive and the ridges are usually forested. In the coastal plain, well-drained uplands are farmed, while the wetlands of the drainage divides and the riparian zones are usually forested (Hamilton et al. 1993).

Our goal is to assess the nutrient dynamics of this interesting but complex forested and agricultural landscape in order to better understand the current nonpoint sources of nutrients from the

various nonurbanized parts of the watershed and the primary factors that control these nutrient sources. We believe that these pieces of information are needed to underpin better management of the watershed to reduce diffuse nutrient inputs to Chesapeake Bay. Much of our watershed research has been a long-term study of the Rhode River watershed, a coastal plain tributary to Chesapeake Bay (e.g., Correll 1977, 1981, Correll and Dixon 1980, Correll and Ford 1982, Correll et al. 1984, Correll et al. 1992, Jordan et al. 1991a, 1991b). Five years ago, we began to expand this research to other parts of the coastal plain (Correll 1991) and subsequently to the Piedmont regions of the Bay's watershed. Here, we report some of the results of a one-year exploratory study in which 153 streams were sampled in six geologically different regions of the Chesapeake Bay watershed. Our goal in this paper is to describe the major patterns of concentrations of dissolved nitrogen fractions in land discharges from the Chesapeake Bay watershed, especially their relationship to rural land uses and spatially prevalent geological formations.

METHODS

Sampling Sites

For each geological region or subregion, we selected the drainage basin of a moderate-sized watershed or in some cases several contiguous watersheds. Sampling stations always included the mainstem stream or streams draining this basin area, as well as stations on the larger tributaries or upstream reaches of this mainstem stream, and some headwaters of low-order tributaries. The combination of all sampling sites within the larger drainage basin was called a watershed "cluster." As much as possible, we selected the smaller subwatersheds we sampled to be representative of various combinations of agricultural and forested land use.

Six clusters of sites were selected (figure 1). Two were in the inner coastal plain. One consisted of 13 sites on the Rhode River watershed south of Annapolis, Maryland and the other included 23 sites on the German Branch of the Choptank River near Centreville, Maryland. One cluster was in the Piedmont and consisted of 21 sites on the Little Falls tributary of the Gunpowder River in Baltimore County, Maryland and York County, Pennsylvania. Another cluster was in the Great Valley region of the Appalachians and included 36 sites on the Conestoga River near Lancaster, Pennsylvania. One cluster was in the Ridge and Valley region of the Appalachians and consisted of

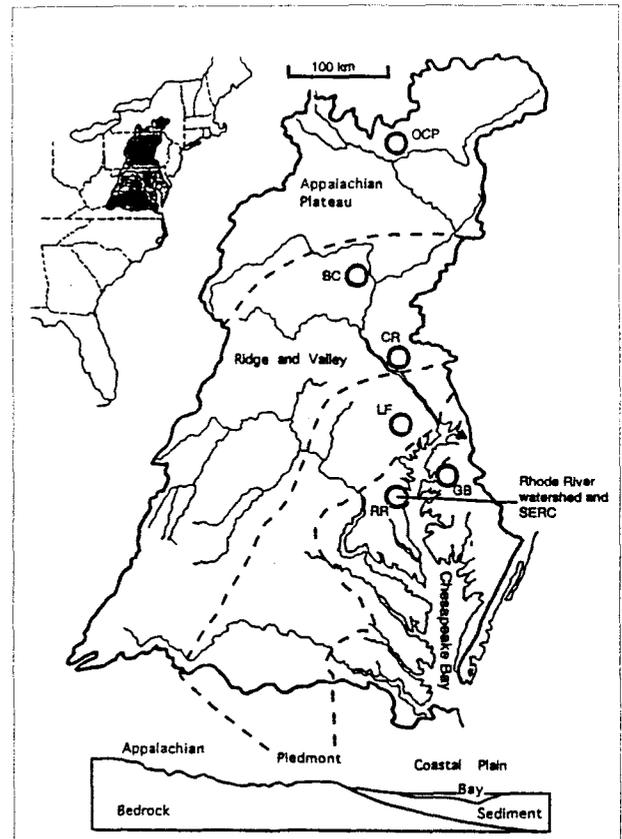


Figure 1. The Chesapeake Bay watershed in relation to the eastern United States. Circles mark the sites of our six watershed cluster sampling areas. The cluster sites are labeled RR for Rhode River, GB for German Branch, LF for Little Falls, CR for Conestoga River, BC for Buffalo and White Deer Creeks, and OCP for Owego, Catatank, and Pipe Creeks. The bottom figure shows a cross section through the physiographic provinces.

24 sites on the Buffalo Creek White Deer Creek basins in northern Pennsylvania near Lewisburg. The sixth cluster was in the Appalachian Plateau region of the Appalachians near Owego, New York. It consisted of 36 sites on Owego, Catatank, and Pipe Creeks.

Percentages of the various watershed basins that were forested were estimated from the amount of green area on U.S. Geographical Survey (USGS) topographic quadrangle maps. In our initial field surveys, we found these maps to quite accurately delineate forested areas. For our cluster sites, we purposely avoided basins that contained large towns or cities and associated point sources of nutrients. We also avoided areas impacted by coal mining. For this analysis we assumed, as a first approximation, that areas not forested were

agricultural. The proportion of each sampling site's drainage basin in forest and agriculture was classified within 20% ranges (0-20%, 20-40%, 40-60%, 60-80%, and 80-100%).

Collection and Analysis of Samples

Each of the 153 stream stations were sampled eight times over a one year period. Samplings were taken (1) 15-18 July 1992, (2) 30 August - 2 September 1992, (3) 12-15 October 1992, (4) 30 November - 2 December 1992, (5) 1-4 March 1993, (6) 5-7 April 1993, (7) 3-6 May 1993, (8) 8-10 June 1993. Samples were taken in polyethylene bottles that were prerinsed in the stream several times. Samples were immediately filtered through Millipore HA filters (nominal 0.4 μm pore size) that had been prewashed with distilled water, then immediately placed on ice until analysis, which was within two weeks.

Nitrate was analyzed by ion chromatography except when concentrations were below $1 \mu\text{mole l}^{-1}$, when it was analyzed by nonautomated colorimetry after copper amalgam reduction to nitrite (American Public Health Administration 1976). Ammonium was analyzed by the hypochlorite oxidation technique (American Public Health Administration 1976). Total Kjeldahl nitrogen (TKN) was digested according to Martin (1972), and the resultant ammonium was steam distilled and analyzed by Nesslerization (American Public Health Administration 1976). Organic nitrogen was calculated as TKN minus ammonium and total nitrogen was calculated as the sum of TKN and nitrate. Triplicate analyses were routinely performed on about 10% of the samples to assess analytical precision.

RESULTS

Comparisons among Mainstem Streams

Nitrate concentrations were always highest in the Conestoga River, followed by German Branch, Little Falls, Buffalo Creek, Owego Creek (below the confluence of the East and West Branches), and Muddy Creek (the main tributary of the Rhode River), respectively (figure 2a). There was little variation in nitrate concentration seasonally except that the Conestoga River had lower concentrations in the summer and early fall of 1992 than later, and both Little Falls and Owego Creek had somewhat higher nitrate concentrations in early March. Concentrations of dissolved ammonium were much lower (20-fold) than those for

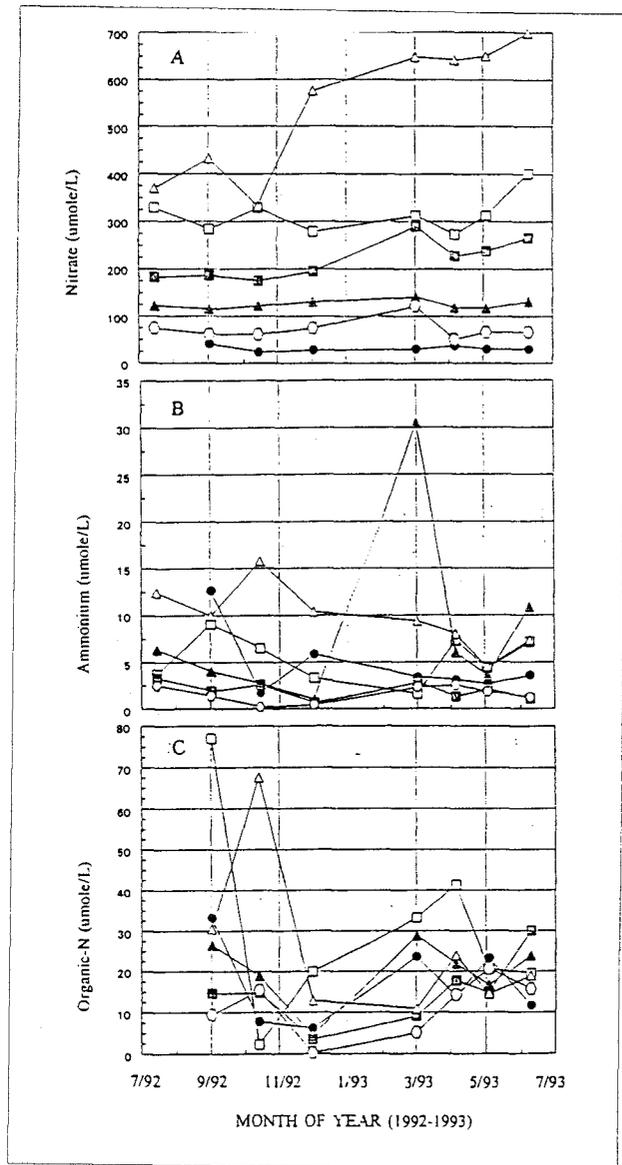


Figure 2. Comparison of time series of nitrogen fraction concentrations among mainstem stream stations for six watershed clusters. Panel A is nitrate, Panel B is dissolved ammonium, and panel C is dissolved organic nitrogen. Solid round data points are for Rhode River, open squares are for German Branch, shaded squares are for Little Falls, open triangles are for Conestoga River, shaded triangles are for Buffalo Creek, and open hexagons are for Owego Creek.

nitrate in all cases (figure 2b) and there was less variation among sites, but the Conestoga River usually had the highest concentrations and Owego Creek had the lowest concentrations most of the time. Concentrations of dissolved organic nitrogen (figure 2c) were higher than ammonium concentrations but much lower (10-fold) than nitrate concentrations. Owego

Table 1. Comparison of annual mean concentrations of nitrogen fractions in principal tributaries and mainstreams of watershed clusters. All concentrations are given in $\mu\text{moles l}^{-1}$

	Area(%)	Nitrate	Ammonium	Organic-N	Total-N
Rhode River Cluster					
N. Br. Muddy Creek	10.2	3.93	7.41		
Blue Jay Branch	8.7	30.8	4.36		
Williamson Br.	11.4	34.9	4.59		
<u>Main Br. Muddy Cr.</u>	<u>48.2</u>	<u>31.0</u>	<u>5.26</u>	<u>17.1</u>	<u>52.8</u>
Sum of Areas/Mean Conc.	78.5	25.1	5.26		
German Branch Cluster					
Headwaters Ger. Br.	12.7	133	6.12		
West Tributary	9.6	98.1	18.6		
East Tributary	9.6	109	6.16		
Wildcat Run	19.2	362	9.58		
<u>Mason Branch</u>	<u>8.7</u>	<u>235</u>	<u>9.43</u>		
Sum of Areas/Mean Conc.	59.8	187	9.43		
German Branch Mainstem	100	315	5.37	30.5	349
Little Falls Cluster					
First Mine Branch	7.9	261	1.83		
Second Mine Branch	10.5	289	2.25		
Third Mine Branch	7.9	219	1.39		
Owl Branch	6.3	164	0.973		
Bee Tree Run	15.3	236	0.955		
<u>North Branch</u>	<u>5.3</u>	<u>505</u>	<u>2.31</u>		
Sum of Areas/Mean Conc.	53.2	279	1.62		
Little Falls Mainstem	100	288	2.00	14.9	242
Conestoga River Cluster					
Muddy Creek	16.2	289	5.77	26.5	339
Cocalico Creek	41.2	494	14.8	24.6	561
Indian Run	3.5	784	7.34		
Middle Creek	7.8	580	5.95	20.7	633
<u>Hammer Creek</u>	<u>11.2</u>	<u>437</u>	<u>8.45</u>	<u>20.0</u>	<u>493</u>
Sum of Areas/Mean Conc.	79.9	535	8.46	23.0	506
Conestoga River Mainstem	100	544	9.71	25.6	603
Buffalo Creek Cluster					
Muddy Run	10.8	172	4.29		
Little Buffalo Creek	21.5	83.6	2.04		
North Fork Little Buf.Cr.	9.2	195	2.88		
Beaver Run	8.5	524	16.5		
<u>Sweitzer's Run</u>	<u>14.6</u>	<u>257</u>	<u>8.38</u>		
Sum of Areas/Mean Conc.	64.6	257	6.81		
Buffalo Creek Mainstem	100	125	8.12	20.1	154
Owego/Catatonk/Pipe Creeks Cluster					
Catatonk Creek Tributaries					
Michigan Creek	11.4	20.3	3.11		
Hoyt Creek	4.9	23.9	1.26		
Willseyville Creek	13.8	41.9	3.53		
East Br. Willsey. Cr.	8.9	17.5	0.768		
Sulphur Springs Creek	5.9	9.36	1.06		
South Branch	11.6	76.4	2.29		
Dean Creek	7.0	28.9	3.68		
<u>Miller Creek</u>	<u>7.3</u>	<u>24.9</u>	<u>1.48</u>		
Sum of Areas/Mean Conc.	70.8	30.4	2.15		
Catatonk Creek Mainstem	46.2	70.9	2.12	31.8	86.4
E. Br. Owego Cr. Mainstem	23.8	93.8	1.24	11.6	106
W.Br. Owego Cr. Mainstem	17.5	53.9	1.93	17.8	72.6
<u>Pipe Creek Mainstem</u>	<u>12.5</u>	<u>34.5</u>	<u>1.86</u>	<u>16.7</u>	<u>51.2</u>
Sum of Areas/Mean Conc.	100	63.3	1.79	19.5	78.9

Creek dissolved organic nitrogen concentrations were usually the lowest.

Mean annual concentrations of dissolved nitrogen fractions are summarized by watershed cluster, for the larger tributary subwatersheds in table 1. None of the listed subwatersheds is a subwatershed of any of the others in the list, and for each cluster these tributaries comprise over half of the mainstem stream's watershed. There was marked variability in annual mean nitrogen concentrations among these tributaries and sometimes the mean of the listed principal tributaries was quite different from the cluster's mainstem concentrations. For example, nitrate concentrations in German Branch tributaries ranged from 98 to 362 $\mu\text{mole l}^{-1}$ with a mean among tributaries of 187 $\mu\text{mole l}^{-1}$. German Branch itself had a mean concentration of 315 $\mu\text{mole l}^{-1}$. Ammonium concentrations in German Branch tributaries ranged from 6.1 to 18.6 $\mu\text{mole l}^{-1}$ and the mean among major tributaries was 9.4 $\mu\text{mole l}^{-1}$. German Branch itself had a mean concentration of ammonium of 5.4 $\mu\text{mole l}^{-1}$. In contrast, the Conestoga River means were similar to the means for its principal tributaries, even though both nitrate and ammonium varied widely among the tributaries (table 1). Of the total dissolved nitrogen for these cluster mainstem streams, organic nitrogen averaged 32, 9.0, 6.2, 4.2, 13, and 25%, respectively, for the Rhode River, German Branch, Little Falls, Buffalo Creek, Owego Creek, and Rhode River (table 1). Nitrate concentrations averaged 22 times those for the Rhode River. Annual mean dissolved ammonium concentrations were highest for the Conestoga River, followed by Buffalo Creek, German Branch, Rhode River, Little Falls, and Owego Creek (table 1). Dissolved ammonium concentrations for the Conestoga River averaged 5.4 times those for Owego Creek.

Comparisons among Forested Watersheds

We compared time series of dissolved nitrogen concentrations for watersheds that were mostly forested (80-100%) and that we felt were the best example for a given watershed cluster (figure 3). There were no highly forested tributaries in the

German Branch cluster region. Nitrate concentrations did not vary consistently with season and were usually about 10-fold lower for these forested subwatersheds than for cluster mainstem streams (figure 3a). Nitrate concentrations were always

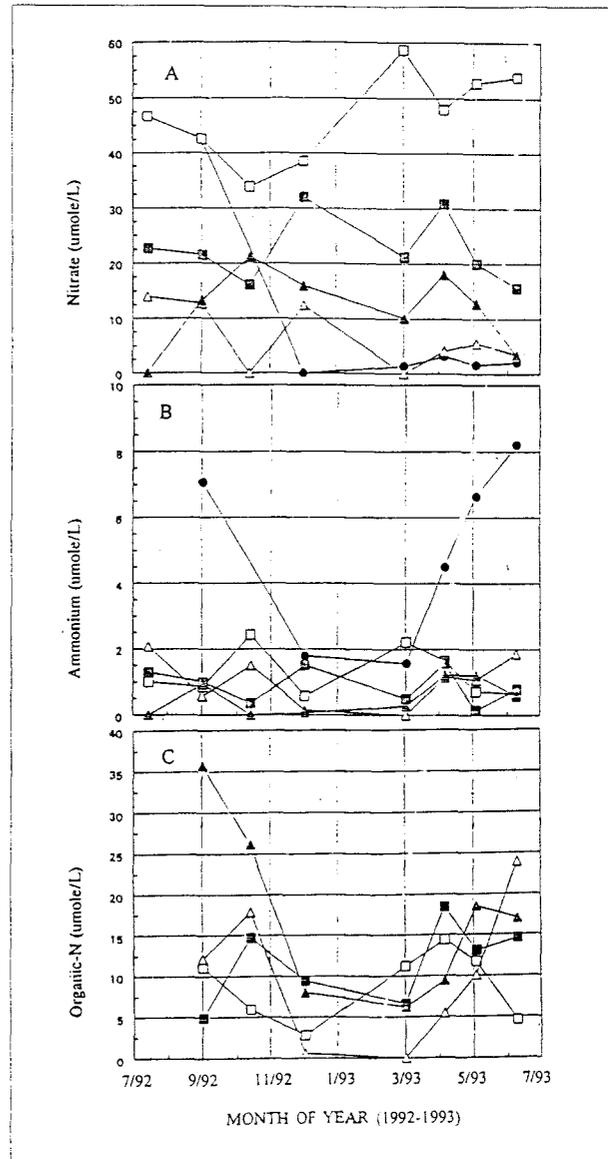


Figure 3. Comparison of time series of nitrogen fraction concentrations among selected primarily forested watershed streams for five watershed clusters. Panel A is nitrate, panel B is dissolved ammonium, and panel C is dissolved organic nitrogen. Solid round data points are for Rhode River mature forest control, open squares are for Little Falls, shaded squares are for Kettle Run in the Conestoga River basin, open triangles are for upper Deer Creek, and shaded triangles are for the northern tributary of the east branch of Willseyville Creek in the Catatunk Creek basin.

highest for the forested tributary of Little Falls. Dissolved ammonium concentrations were much lower than nitrate concentrations. Ammonium concentrations were generally lower in December and March and were usually the highest for Rhode River (figure 3b). Concentrations of dissolved organic nitrogen were also lower in December and March and were intermediate between those for nitrate and ammonium (figure 3c).

Annual mean concentrations for 18 primarily forested tributaries (table 2) demonstrate the variability among these sites, and the strong contrasts with the results from cluster mainstem streams (table 1). Nitrate concentrations were highest for the Conestoga River, followed by the Little Falls, Buffalo/White Deer Creek, Catatank Creek, and Rhode River tributaries (table 2). Dissolved ammonium concentrations were highest for the Rhode River forested tributaries, followed by the Conestoga River, Buffalo/White Deer Creek, Little Falls, and Catatank Creek tributaries. Dissolved organic

nitrogen was a higher proportion of total nitrogen in these forested subwatersheds than found in the cluster mainstem streams, averaging 15, 11, 53, and 57%, respectively, for the Little Falls, Conestoga River, Buffalo/White Deer Creek, and Catatank Creek forested tributaries (table 2).

Comparisons among Highly Agricultural Watersheds

Time series of nitrate and dissolved ammonium concentrations were compared among subwatersheds of each cluster dominated by agriculture. For example, five highly agricultural Conestoga River subwatersheds (figure 4a) had nitrate concentrations that varied from about 300 to about 1300 $\mu\text{mole l}^{-1}$. One that averaged about 800 to 900 $\mu\text{mole l}^{-1}$ was selected for comparison purposes. Nitrate concentrations were highest for the Conestoga River agricultural tributaries, followed by Buffalo Creek, German Branch, Little

Table 2. Comparisons of annual mean concentrations of nitrogen fractions among watersheds that were primarily forested. All concentrations are given in $\mu\text{moles l}^{-1}$

	Nitrate	Ammonium	Organic-N	Total-N
Rhode River Cluster				
N. Br. Sellman Cr.	7.52	3.27		
Mature Forest Control	7.28	4.26		
<u>S. Br. Muddy Creek</u>	<u>11.5</u>	<u>2.11</u>		
Mean Concentration	8.75	3.21		
Little Falls Cluster				
Small Eastern Trib.	46.8	1.26	8.81	57.0
Conestoga River Cluster				
Hdwtrs. Cocalico Cr.	80.1	5.91		
Seglock Run	114	1.00		
Furnace Run	89.6	1.09	11.7	105
<u>Kettle Run</u>	<u>22.5</u>	<u>0.893</u>		
Mean Concentration	76.6	2.22		
Buffalo/White Deer Creeks Cluster				
Hdwtrs. Main Br. Buf. Cr.	2.41	0.821	8.39	12.1
Hdwtrs. N. Br. Buff. Cr.	38.0	1.83		
Little Buff. Cr.	83.6	2.05		
Sand Spring Run	13.5	1.21	8.79	23.3
<u>White Deer Creek</u>	<u>6.55</u>	<u>1.04</u>	<u>11.7</u>	<u>19.1</u>
Mean Concentration	28.8	1.39	9.62	18.2
Catatank Creek Cluster				
Hdwtrs. Michigan Cr.	4.36	2.64	17.3	24.5
E. Br. Willseyville Cr.	17.5	0.768		
W. Trib. E. Br. Wil. Cr.	7.60	0.482		
N. Trib. E. Br. Wil. Cr.	11.8	0.536	20.1	41.3
<u>Miller Creek</u>	<u>24.9</u>	<u>1.48</u>		
Mean Concentration	13.2	1.18	18.7	32.9

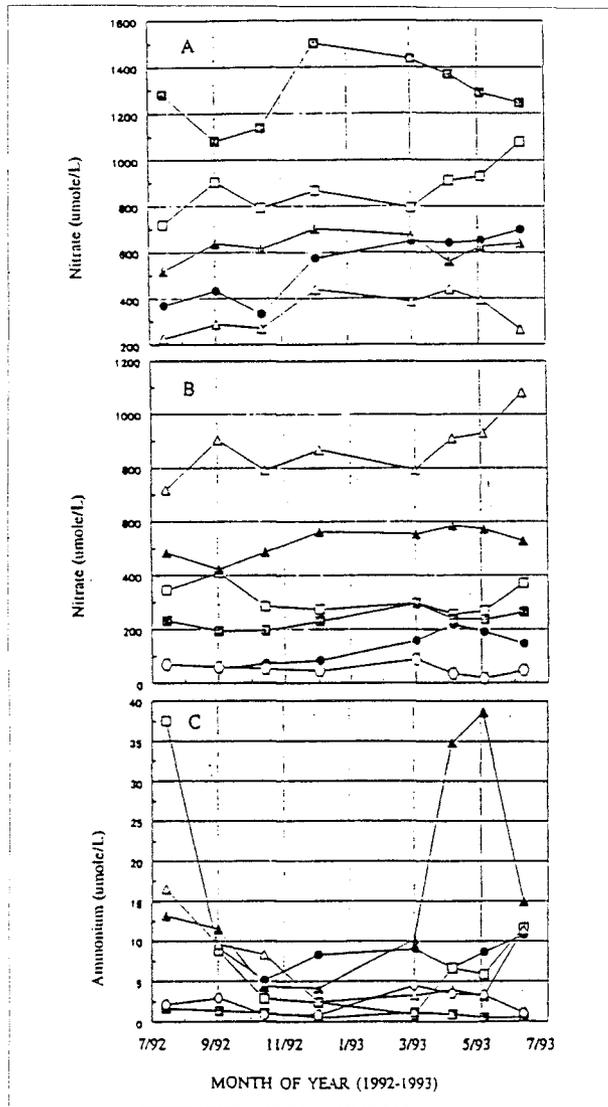


Figure 4. Comparison of time series of nitrogen fraction concentrations among selected highly agricultural subwatersheds for six watershed clusters. Panel A shows nitrate concentrations for five sites in the Conestoga River basin. Solid round data points are for the Conestoga River mainstem above Lancaster, Pennsylvania; open squares are for Indian Run, shaded squares are for a small northeastern branch of Middle Creek, and shaded triangles are for upper Hammer Creek. Panel B (nitrate) and panel C (ammonium) are comparisons among representative agricultural subwatersheds of the six clusters. Solid round data points are for the Rhode River watershed, open squares are for Wildcat Branch of the German branch, shaded squares are for Bee Tree Run in the Little Falls basin, open triangles are for Indian Run in the Conestoga River basin, shaded triangles are for Beaver Run in the Buffalo Creek basin, and open hexagons are for a western tributary of the east branch of Owego Creek.

Falls, Rhode River, and Owego Creek (figure 4b). Dissolved ammonium concentrations were much lower than nitrate concentrations (figure 4c) and tended to be highest for the Buffalo Creek tributaries, especially in the spring and summer.

Nitrogen concentration data for all stations within each cluster were grouped by the proportion of each drainage basin that was forested (table 3 and figure 5). Quite different patterns were found for nitrate (figure 5a) and dissolved ammonium concentrations (figure 5b). For all watershed clusters except the Rhode River and Owego Creek clusters, nitrate concentrations were strongly inversely related to the percentage of forest on the tributary watersheds. For the Rhode River, there was a clear inverse relationship, but the slope was much lower. The Conestoga River, Buffalo Creek, and Little Falls clusters had the steepest slopes (figure 5a). Ammonium concentrations had relatively little relationship to the proportion of forest on the tributary subwatershed (figure 5b), although both German Branch and Rhode River concentrations increased with increasing proportions of forest. Likewise, there was no clear pattern for dissolved organic nitrogen (table 3), although there were fewer data.

DISCUSSION

Among our study watersheds, those with the highest nitrate concentrations were in the Appalachian province, which accounts for two-thirds of the entire Chesapeake Bay watershed. Susquehanna River discharge, which accounts for about 50% of the total watershed flow and originates almost entirely in the Appalachians, had a mean of 89 umolar nitrate in the spring from 1984 to 1988 (Jordan et al. 1991a).

In this study we measured the concentrations of nitrate discharged from three geologically and culturally different subregions of the Appalachians (table 1). In our Great Valley study cluster, we found quite high, 544 umolar, mean nitrate concentrations in the Conestoga River just above Lancaster, Pennsylvania. However, these concentrations were similar to those reported for 1985-1988 and 1988-1989 of 557 and 595 umolar, respectively, for the river downstream from Lancaster during base-flow. The high nitrate concentrations probably reflect the fact that the Conestoga River basin is highly agricultural with 52% cropland and 11% pasture in 1989. Much of the basin is within Lancaster County, which has some of the highest livestock densities in the United States. The

Table 3. Annual mean concentrations of nitrogen fractions on streams draining watersheds with differing proportions of forest. All concentrations are given in umoles^{l-1}.

A. Coastal Plain Province				
Forest (%)	Nitrate	Ammonium	Organic-N	Total-N
Rhode River Cluster				
20-40	77.3	5.64		
40-60	40.6	4.76		
60-80	32.9	4.64	17.3	54.9
80-100	33.8	25.1		
German Branch Cluster				
0-20	297	8.67		
20-40	209	5.61	24.7	239
40-60	14.1	13.2		
60-80	17.1	21.0		
B. Piedmont Province				
Little Falls Cluster				
Forest (%)	Nitrate	Ammonium	Organic-N	Total-N
0-20	355	1.91	12.8	375
20-40	245	1.59	15.1	267
40-60	209	1.08		
80-100	46.8	1.26	8.81	57.0
C. Appalachian Province				
1. Great Valley				
Conestoga River Cluster				
Forest (%)	Nitrate	Ammonium	Organic-N	Total-N
0-20	626	8.88	17.3	672
20-40	366	7.06	23.5	414
40-60	127	6.17		
80-100	76.6	2.22	11.7	92.0
2. Ridge and Valley				
Buffalo/White Deer Creeks Cluster				
0-20	379	8.83	17.5	408
20-40	308	8.38		
40-60	194	5.53	22.5	224
60-80	125	2.10		
80-100	27.7	1.36	7.56	34.4
3. Appalachian Plateau				
Owego/Catatonk/Pipe Creeks Cluster				
20-40	32.6	2.90	16.5	51.8
40-60	43.8	1.77	15.5	60.4
60-80	49.5	2.94		
80-100	13.6	1.43	17.4	32.2

livestock of Lancaster County produced about 4,500 metric tons of manure in 1982, and this production had been increasing rapidly since 1969 (Edwards and Seay 1987). Discharges from the Pequea Creek basin, which lies just south of the Conestoga River basin, averaged 300 umolar nitrate from 1977 to 1979 (Ward 1987). The Pequea Creek basin was also highly agricultural, with 54% rowcrops and 12% pasture.

Our Ridge and Valley study cluster (Buffalo Creek) had fairly intensive agriculture, but this was confined to a smaller proportion of the total basin than in the Conestoga River basin. Forested ridges comprise about half of the total Buffalo

Creek basin. This land cover difference is reflected in the somewhat lower (257 umolar) nitrate concentrations we found in Buffalo Creek compared to the Conestoga River. In contrast, our Appalachian Plateau study site, the Owego/Catatonk/Pipe Creeks region, has substantial agricultural lands, but most of this land is used for low-density livestock grazing on the plateau. Relatively little land is in row crops, primarily in the narrow valleys. This difference in the intensity of agricultural land use may be the reason why nitrate concentrations averaged only 63 umolar in these drainage basins.

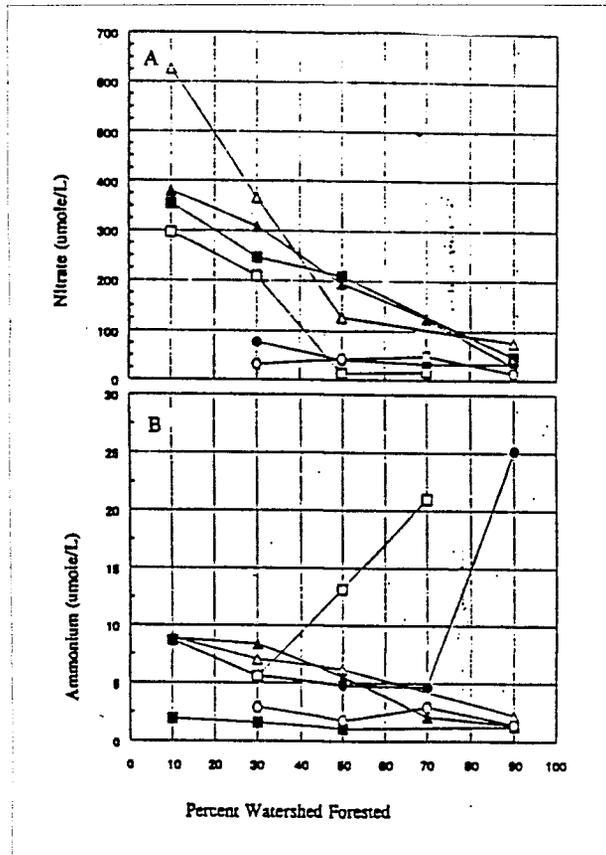


Figure 5. Comparison of mean annual nitrate (panel A) and dissolved ammonium (panel B) for the subwatershed sites of each watershed cluster, grouped by percent of forest on the subwatershed. Symbols for the cluster data points are the same as for figure 2.

In the coastal plain (table 1), mean nitrate concentrations in German Branch discharges were 315 $\mu\text{mole/L}$, while in Rhode River discharges nitrate only averaged 25 $\mu\text{mole/L}$. We think that this is the result of two factors. First, the German Branch watershed is much more agricultural, with most of the area in row crop fields that are usually double cropped. The Rhode River watershed is only about 30% agricultural, with little or no double cropping. Second, Rhode River watershed streams are almost continuously lined with wide bands of riparian forest, while many sections of German Branch streams have thinner strips of forest or almost no riparian forest. These coastal plain riparian forests often are very effective at removing nitrate from both surface overland flows during storms (Peterjohn and Correll 1984), and from shallow groundwater moving from upland fields to stream channels (Correll 1991, Correll and Weller 1989, Jordan et al. 1993, Peterjohn and Correll 1986).

In our Piedmont cluster site on Little Falls, nitrate concentrations were also high. The annual mean for one tributary approached the levels found in the Conestoga River (table 1). The majority of the land on the watershed of Little Falls is in row crops and most of the stream discharge is groundwater. The high nitrate concentrations we measured in these streams may reflect high leaching from cropland fields and relatively inefficient removal of nitrate in the riparian zones.

Our measurements of nitrate concentrations in streams draining primarily forested basins in the Appalachians (table 2) can be compared to an 8-year mean of 1.1 $\mu\text{mole/L}$ reported by Lynch and Corbett (1990) for forested basins in the Ridge and Valley region of central Pennsylvania. Our average nitrate concentrations were higher for primarily forested sites in all clusters, and were much higher on average for primarily forested sites on the Conestoga River basin (table 2). Many of our watersheds contained some houses or other disturbance. This is reflected in the variations among sites (table 2). For example, Kettle Run is the watershed with the least human disturbance in the Conestoga River cluster, and it had an annual mean nitrate concentration of only 22.5 $\mu\text{mole/L}$. Similarly, the headwaters of the main branch of Buffalo Creek and White Deer Creek had the least disturbance in our Buffalo Creek cluster, and they had annual mean nitrate concentrations of 2.4 and 6.6 $\mu\text{mole/L}$, respectively (table 2). The mature forest control watershed in the Rhode River cluster, which truly has no disturbance except atmospheric deposition, had an annual mean of 7.3 $\mu\text{mole/L}$ nitrate in its discharges. This may be an indication that mature forests are less efficient at utilizing atmospheric inputs (Aber et al. 1989). Because few if any of our watersheds were truly entirely undisturbed forest, we summarized annual nutrient concentrations for all watersheds within 20% ranges of forest cover within each cluster (table 3 and figure 5). We plan to further refine the land use analyses, but it is already clear that forested watersheds discharged very low nitrate concentrations compared with highly agricultural watersheds, with the possible exception of the Appalachian Plateau cluster.

ACKNOWLEDGEMENTS

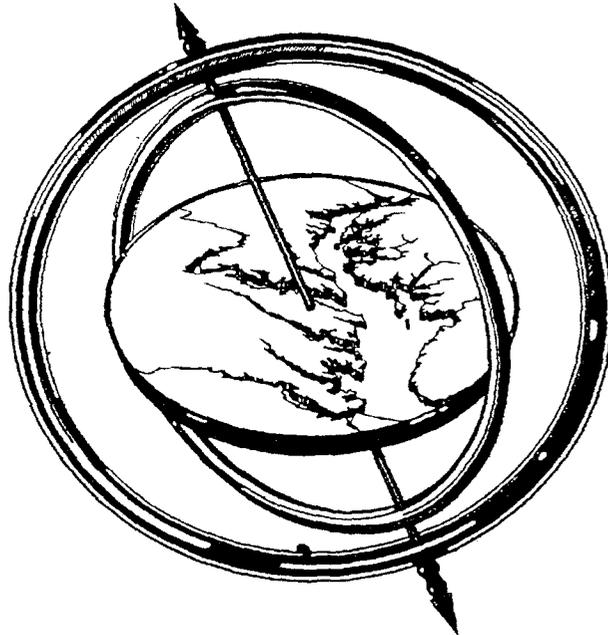
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