

## EFFECTS OF LAND COVER AND GEOLOGY ON STREAM CHEMISTRY IN WATERSHEDS OF CHESAPEAKE BAY<sup>1</sup>

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**ABSTRACT:** We measured the base-flow stream chemistry in all the major physiographic provinces of the Chesapeake Bay drainage basin. The spatial variation of stream chemistry was closely related to differences in geology and land cover among the sampled watersheds. Some stream chemistry variables were strongly affected by geological settings in the watersheds while others were more influenced by land cover. The effects of land cover differed among chemical constituents and regions. Concentrations of Ca<sup>2+</sup>, Mg<sup>2+</sup>, pH, total alkalinity, and conductivity were mainly functions of carbonate bedrock, especially in the Great Valley. Nitrate-N and total dissolved N were closely related to cropland and increased as the percentage of cropland increased. The rate of increase varied from region to region with the highest in the Piedmont. Na<sup>+</sup> and Cl<sup>-</sup> were mainly affected by the percentage of developed area in a watershed, especially in the Coastal Plain and Piedmont. We observed no significant effects of region or land cover on species of phosphorus because samples were collected under base flow conditions and only dissolved forms were measured. Dissolved silicate (DSi) was not related to any other water chemistry variables. DSi increased as developed area decreased and cropland increased in the Coastal Plain, but these patterns were reversed in the Piedmont. There was no consistent pattern in the spatial variation of land cover effects on the reduced forms of N, dissolved organic P, dissolved organic matter, and K<sup>+</sup>.

(KEY TERMS: stream chemistry; land cover; geology; watershed studies; Chesapeake Bay.)

### INTRODUCTION

Water chemistry in natural systems is regulated by a complex suite of processes such as the geochemical weathering reactions of minerals derived from bedrock. However, human activities now play an increasingly important role in controlling water chemistry in streams, primarily in two ways. Human activities change watershed characteristics, such as land

cover, which in turn affect the biogeochemical processes that operate in the watershed. As a result, the influx of chemicals from the watershed to the stream can be enhanced or hindered. Stream chemistry can also be directly affected by the input of anthropogenic chemicals such as plant nutrients and toxic metals.

Human activities have greatly impacted the water resources of Chesapeake Bay, the largest estuary in the United States (Goldberg *et al.*, 1978). The deterioration of water quality in the Bay has mainly resulted from increased influx of anthropogenic chemicals to the Bay from streams in the drainage basin. Increases in watershed inputs of nutrients have led to eutrophic conditions in the system causing algal blooms, demise of submerged aquatic vegetation, low levels of dissolved oxygen, and declining stocks of living resources (Officer *et al.*, 1984; Correll, 1987; Haire *et al.*, 1992).

The water quality of streams in the Chesapeake drainage basin has come under increasing study, especially during the past decade (Puckett and Bricker, 1992; Correll *et al.*, 1994; Jordan *et al.*, 1997a, b, c; Miller *et al.*, 1997; Ator *et al.*, 1998; Lindsey *et al.*, 1998). The Chesapeake Bay basin has been included in a number of nation-wide water quality programs. Most of these studies have focused on assessing water-quality conditions in separate and often large river basins. For example, the U.S. Geological Survey's NAWQA (National Water-Quality Assessment) program assessed the water-quality conditions of the Potomac River basin and the lower Susquehanna River basin (Ator *et al.*, 1998; Lindsey *et al.*, 1998). These studies have been productive in assessing water quality conditions on a regional scale. However, when the effects of land cover on water

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chemistry of streams are studied, large watersheds pose some limitations because they are complex landscapes combining a variety of land cover types and geology. It is difficult to find large watersheds with contrasting land cover patterns, such as all forest or mostly agricultural. In addition, the in-stream processes may change nutrient concentrations in large streams and rivers, therefore confounding the effects of terrestrial processes.

In this paper, we describe a study of stream chemistry in small watersheds of Chesapeake Bay. This study is one part of long-term watershed research program in the Bay drainage by the Smithsonian Environmental Research Center (SERC), which began in the early 1970s. The purpose of this study is to investigate the effects of land cover on water chemistry of streams and the spatial variation of these effects among all the major physiographic provinces within the bay drainage. The specific objectives are: (1) to determine differences in stream chemistry among physiographic provinces with varied geology, (2) to determine the effects of land cover on different constituents in streams, and (3) to determine the spatial variation of land cover effects across the physiographic provinces. Unlike the previous studies by others, our study is focused on drainage watersheds of small, lower-order streams with a great diversity of land cover and geology. Focusing on small contrasting watersheds enables us to resolve effects of land cover and geology that would be confounded in large watersheds. This approach has already revealed previously unreported differences in land cover effects between the Coastal Plain and Piedmont physiographic provinces (Jordan *et al.*, 1997a, b, c). In this study, we further test those results and extend the approach to other chemical constituents and to other physiographic provinces of the Bay drainage basin.

## METHODS

### *Study Watersheds*

The watersheds studied are spatially distributed in 14 clusters throughout the Chesapeake drainage basin (Figure 1 and Table 1). Each cluster consists of a moderate-sized watershed or several contiguous watersheds. The sampling sites in each cluster are located at the outlet of the main watershed as well as on the tributaries of the stream draining the watershed. The contributing area of each sampling site is defined as its drainage watershed. The locations of the clusters were chosen to include the major geological-land cover types in each physiographic

province of the Chesapeake Bay drainage basin. Our primary goal was to observe the effects of land cover and differences in those effects among physiographic provinces rather than to exhaustively sample each province. Hence we did not choose watersheds in a random fashion as in the EPA's EMAP (the Environmental Monitoring and Assessment Program) program (Whittier and Paulsen, 1992). Instead, watersheds with strongly contrasting land covers were selected as sampling sites to maximize our chances to observe and quantify the effects of land cover and to detect differences in those effects among different geological settings. The sampling sites were first marked on 7.5' USGS quadrangle topographic maps, and their watershed boundaries were defined from contours on the same maps. Sampling sites and watersheds were digitized using the ARC/INFO geographic information system (GIS).

The sizes of the 424 study watersheds range from 5.5 to 48,010 ha. These watersheds have no sewage outfalls or other known point sources. The land cover in the watersheds ranges from 1.6-100 percent forest and 0-84 percent cropland, and the majority have low human populations and no large urban areas. Half of the watersheds have a developed area less than 1.3 percent of the total watershed area.

The 166,000 km<sup>2</sup> (64,000 mi<sup>2</sup>) drainage basin of Chesapeake Bay extends over four major physiographic provinces: Coastal Plain, Piedmont, Blue Ridge, and Appalachian. The Appalachian province has two subcategories: Appalachian Plateau and Ridge and Valley. The Ridge and Valley is further divided into Great Valley and Appalachian Mountain regions (Langland *et al.*, 1995). We overlaid the GIS coverages of study watershed boundaries and physiographic provinces (Langland *et al.*, 1995), and then classified study watersheds into physiographic groups based on the following: if 90 percent or more area of a watershed was within a physiographic region, then that watershed was classified in that physiographic group. Watersheds that did not meet this criterion were placed in a 'mixed' group. Of the 424 watersheds, 62 were in the Appalachian Plateau, 58 in the Appalachian Mountain, eight in the Blue Ridge, 25 in the Great Valley, 109 in the Piedmont, 127 in the Coastal Plain, and 35 in the mixed group. Watersheds in the mixed group were included in all the data analyses except for regional comparisons. Watersheds in the Blue Ridge group were also excluded from regional comparisons because the number of watersheds in that group was too small. As a result, five physiographic regions were used in inter-regional comparisons.

The Bay drainage basin is underlain by four major types of bedrock or substrate: carbonate rocks (limestone, dolomite, marble); crystalline rocks (schist,

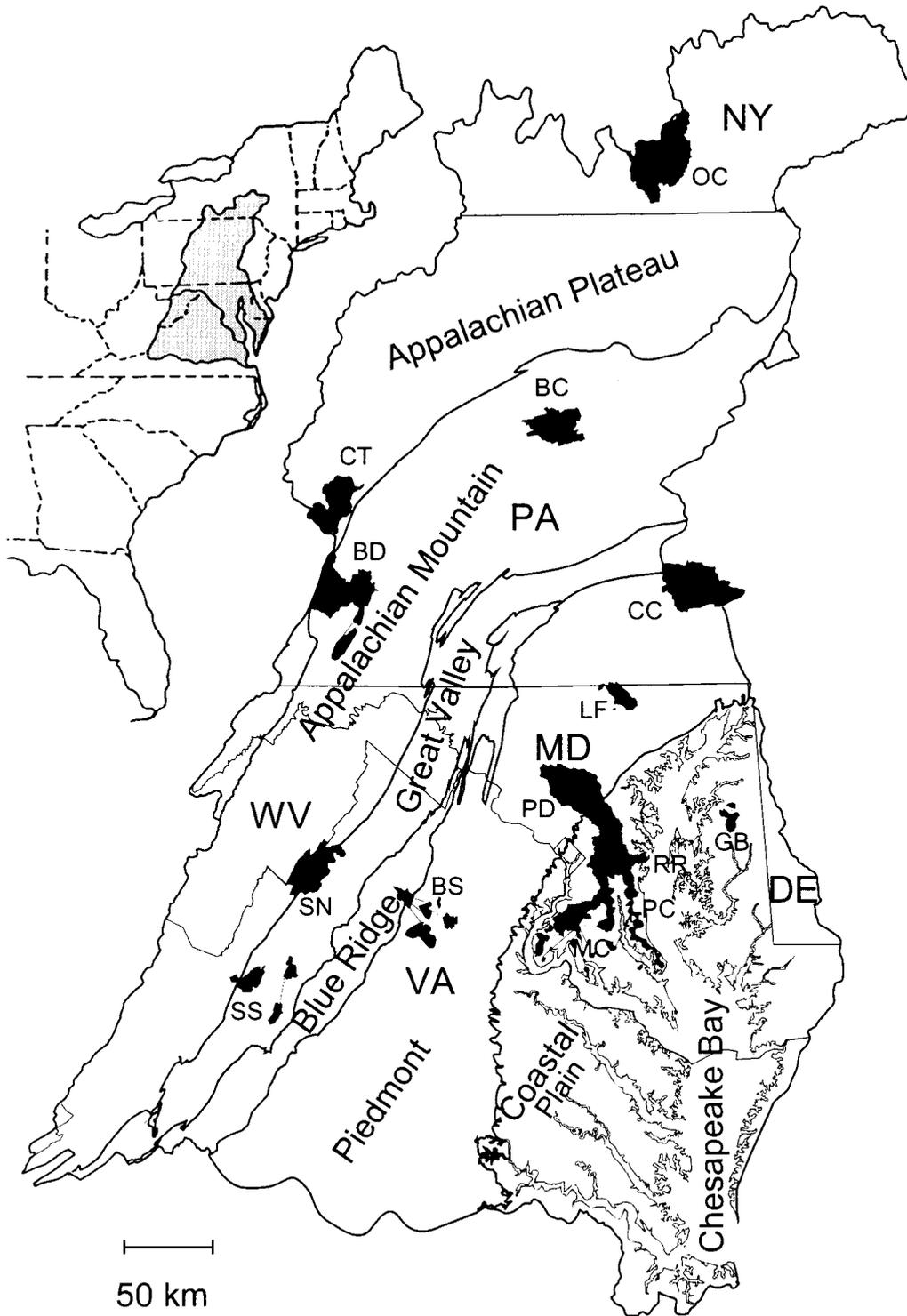


Figure 1. Locations of Study Watershed Clusters (black shading). Inset indicates the location of the Chesapeake drainage in the Eastern U.S. physiographic provinces (from Langland *et al.*, 1995).

granite, quartzite, gneiss); siliciclastic rocks (sandstone, siltstone, shale, conglomerates); and unconsolidated sediments (Langland *et al.*, 1995). The area of

a rock type in a watershed was obtained by overlaying the GIS coverage of watershed boundary with the coverage of bedrock (Langland *et al.*, 1995). Measured as

TABLE 1. Locations of Study Watershed Clusters.

Cluster*	State	Longitude	Latitude	Sampling Period
BD	Pennsylvania	78°24′	40°00′	July 1997-April 1998
BC	Pennsylvania	76°54′	40°54′	July 1992-June 1993; May 1996-March 1998
BS	Virginia	78°06′	38°42′	April 1995-November 1995
CC	Pennsylvania	76°18′	40°06′	July 1992-June 1993; April 1994-April 1997
CT	Pennsylvania	78°30′	40°42′	July 1997-April 1998
GB	Maryland	75°54′	39°00′	July 1992-June 1993
LF	Maryland and Pennsylvania	76°42′	39°24′	July 1992-June 1993
MC	Maryland	77°12′	38°24′	March 1997-March 1998
OC	New York	76°18′	42°06′	July 1992-June 1993; November 1997-February 1998
PC	Maryland	76°43′	38°29′	October 1995-January 1998
PD	Maryland	76°52′	39°07′	October 1995-January 1998
RR	Maryland	76°36′	38°54′	September 1992-June 1993
SN	Virginia	78°36′	38°48′	April 1995-November 1995
SS	Virginia	78°54′	38°12′	April 1995-November 1995

\*BD: Bedford; BC: Buffalo Creek; BS: Brandy Station; CC: Cocalico Creek; CT: Carroltown; GB: German Branch; LF: Little Falls; MC: Mattawoman Creek; OC: Owego Creek; PC: Patuxent River in the Coastal Plain; PD: Patuxent River in the Piedmont; RR: Rhode River; SN: North Shenandoah; SS: South Shenandoah.

TABLE 2. Regional Means of Percent Area of Substrate Types in Study Watersheds.

	Coastal Plain	Piedmont	Great Valley	Appalachian Mountain	Appalachian Plateau
Carbonate Bedrock	0.0	5.2	80.5	23.1	10.1
Crystalline Bedrock	0.0	70.1	0.0	0.0	0.0
Siliciclastic Bedrock	0.0	24.1	19.5	76.9	89.0
Unconsolidated Sediments	100.0	0.6	0.0	0.0	0.0

percent area of a watershed, the regional means of the four types of bedrock or substrate for the five physiographic regions are given in Table 2. The classification of physiographic provinces is closely related to geology. As shown in Table 2, the two Appalachian provinces are mainly underlain by siliciclastic rocks; the Coastal Plain completely by unconsolidated sediments; the Great Valley by carbonate rocks; and the Piedmont by crystalline rocks.

#### Land Cover Data

Land cover data for the study watersheds were obtained from the Environmental Monitoring and Assessment Program (EMAP) of the U.S. Environmental Protection Agency (USEPA, 1994). This database was developed for the Chesapeake Bay basin using remotely sensed land cover data from Landsat Thematic Mapper images. At the level of

individual pixels or landscape patches, such land cover data do not resolve cropland from grassland with high degree of classification accuracy. However, when land cover data are aggregated to larger spatial units, such as whole watersheds or counties, the proportion of cropland estimated from the EMAP land cover is strongly correlated with the true proportion of cropland from agricultural census or ground verified land use data (Weller *et al.*, 1996; Weller *et al.*, unpublished analysis). The proportion of each land cover category in a watershed was obtained by overlaying the EMAP cover with the GIS coverage of watershed boundaries. In this study, proportions of four major land cover categories were used: forest, cropland, grassland, and developed area. Measured as percent area of a watershed, the averages of the four land cover categories for the five physiographic regions are given in Table 3.

TABLE 3. Regional Means of Percent Area of Land Cover Types in Study Watersheds.

	Coastal Plain	Piedmont	Great Valley	Appalachian Mountain	Appalachian Plateau
Cropland	15.5	19.7	26.4	22.2	8.5
Forest	46.2	35.5	19.7	63.2	66.6
Grassland	22.6	37.8	50.2	11.9	19.2
Developed	15.5	6.2	3.6	0.5	1.5

### Sample Collection and Chemical Analyses

The stream sampling was designed to represent average annual concentrations of dissolved constituents in base flow. Four or more grab (synoptic) samples were collected from each of the 424 watersheds over a period of four seasons or longer. The sampling periods varied among the watershed clusters (Table 1). The watersheds in the three Virginia clusters (BS, SN, and SS) were not sampled in the 'true winter' months because of a scheduling problem. The last samples were collected in late November 1995 (Table 1) as a substitute for winter sampling. The total number of samples remained four or more for each watershed in the three clusters. Unless the water sample collected in the winter was substantially different from other three or more samples for the same watershed, lack of 'true winter' samples will not significantly affect the annual average and subsequent data analysis.

Sampling was not conducted during or immediately following rainfall events so that samples represented base-flow chemistry. In addition, automated samplers were used in some of the watersheds to continuously monitor stream flow and collect water samples during high flow as well as base flow. In this paper, we only describe the analysis of stream chemistry under base flow conditions. Samples were taken in polyethylene bottles that were cleaned with chromic acid cleaning solution, rinsed with distilled water, and then rinsed in the stream several times. Samples were immediately filtered through Millipore HA filters that had been prewashed with distilled water, then immediately placed on ice until analysis (Correll *et al.*, 1994).

Water samples were analyzed for pH, conductivity, total alkalinity, dissolved organic matter,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ , sulfate ( $\text{SO}_4^{2-}$ ), silicic acid ( $\text{H}_4\text{SiO}_4$ ), and various species of N and P. The holding time before analysis varied among the chemistry variables. Conductivity and pH were measured within 24 hours of arrival in the lab. Sulfate,  $\text{Cl}^-$ , and nitrate were analyzed within three days. Dissolved inorganic C and organic C, phosphate, ammonium, total Kjeldahl N, and total P were analyzed within two days. Samples

for the major cations,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , were acidified with nitric acid within four days of arrival in the lab, and stored at 4°C until analysis. Samples for dissolved silicic acid were stored at 4°C in plastic bottles until analysis. The major cations and dissolved silicic acid were very stable in the described conditions. Their holding time ranged from days to two months. Measurements of pH were made on air-equilibrated samples with an expanded range pH meter and a Ross electrode. Conductivity was measured with a YSI model 32 meter. When inorganic carbon in the water sample was high, total alkalinity was measured by potentiometric titration to end points of pH 4.5 and 4.2 with 0.02 N  $\text{H}_2\text{SO}_4$  using a Schot Gerate TR 156 automatic titrator (APHA, 1989). For samples with low inorganic C, either titration or a carbon analyzer (Shimadzu, TOC5050) was used. The measurement of dissolved inorganic carbon (DIC) by the carbon analyzer was converted to total alkalinity using the empirical equation, Total Alkalinity =  $-0.30 + 0.92 \cdot \text{DIC}$  ( $r^2 = 0.99$ ). We derived the equation by measuring 39 samples from different provinces with both titration and the carbon analyzer and then regressing total alkalinity against DIC. Dissolved organic matter (DOM), or dissolved organic carbon (DOC), was analyzed as chemical oxygen demand (COD) when inorganic carbon in the sample was high (Jordan *et al.*, 1997a, b). DOC was also analyzed using the carbon analyzer for samples with low inorganic carbon. The measurement of COD was divided by an empirically determined factor of 9.724 to convert from gcal COD/L to mg C/L.  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , were determined by atomic-absorption spectroscopy with a Perkin/Elmer model 5000. In some cases, these ions were determined by Inductively Coupled Plasma (ICP) emission spectroscopy with a Perkin/Elmer model 2000.  $\text{Cl}^-$  and sulfate ( $\text{SO}_4^{2-}$ ) were analyzed with a Dionex model 4000 ion chromatograph. Dissolved silicic acid (commonly referred to as dissolved silicate or DSi) was analyzed with a Technicon Auto-Analyzer II by Technicon method 696-82W.

Details of chemical analyses of N and P species are given by Jordan *et al.* (1997a, b). Briefly, phosphate ( $\text{PO}_4^{2-}$ ) was analyzed by reaction with stannous chloride and ammonium molybdate (APHA, 1989). Total

dissolved P (TDP) was measured using a perchloric acid digestion (King, 1932). Ammonium ( $\text{NH}_4^+$ ) was measured by oxidation to nitrite (Strickland and Parsons, 1972). Total dissolved Kjeldahl N (TDKN) was determined using the Kjeldahl digestion (Martin, 1972; APHA, 1989). The sum of nitrite and nitrate ( $\text{NO}_3^-$ ) was analyzed by cadmium reduction (APHA, 1989). Dissolved organic P (DOP) was calculated by subtracting  $\text{PO}_4^{2-}$  from TDP. Dissolved organic N (DON) was calculated by subtracting  $\text{NH}_4^+$  from TDKN. Total dissolved nitrogen (TDN) was the sum of TDKN and nitrate.

### *Statistical Analyses*

The measurements of chemistry variables from different sampling dates were averaged for individual watersheds, and the watershed averages were used for data analysis. Factor analysis was applied to identify groups of related variables of stream chemistry. Regression analysis was then used to investigate the effects of land cover on factor scores and the spatial variation of these effects among physiographic regions. All the statistical analyses were performed using the Statistical Analysis System (SAS, 1989).

### *Factor Analysis*

Factor analysis was used in this study to identify the related chemistry variables so that their relationships with land cover and physiography could be analyzed on a group basis. Factor analysis methods are commonly used statistical procedures in hydrogeochemistry. Factors can be related to actual processes that influence the behavior of stream chemistry variables. A number of studies have employed factor analysis, or the closely related principal component analysis (PCA), to investigate processes controlling the chemical composition of groundwater and streams (Dawdy and Feth, 1967; Reid *et al.*, 1981; Christophersen and Hooper, 1992; Puckett and Bricker, 1992; Evans *et al.*, 1996; Miller *et al.*, 1997). Factor analysis can also simplify the interpretation of large multivariate data sets by identifying groups of variables that behave similarly. An analysis of a group of variables can be conducted together, rather than a separate (redundant) analysis for each individual variable. The estimated values of common factors, called factor scores, may also be used as inputs to subsequent statistical analyses.

In factor analysis, we first determined the factor structure. The factor structure is usually described with the number of factors retained, the loadings and

communalities of variables, and the proportions of the total sample variance explained by factors (Johnson and Wichern, 1982). After the factor structure was determined, the values of the factors for individual watersheds (factor scores) were estimated and used as inputs to the subsequent regression analysis. The estimation involves linear transformation of the original observations using the covariance structure of original variables and the factor structure from the factor analysis. Score values are expressed in standard deviations with mean zero and variance one (Johnson and Wichern, 1982). Factor scores of individual watersheds represent the relative strength of the relation of a watershed to a factor and, in turn, to the group of chemistry variables the factor represents (Puckett and Bricker, 1992).

### *Regression Analysis*

We used regression analysis to test for the spatial effects of land cover and physiography on water chemistry. The dependent variables in the regression models were factor scores for the groups of water chemistry variables identified by factor analysis. The independent variables were physiographic province (a categorical variable with five provinces) and percentage of land cover in a watershed (a continuous variable). The relationship between a factor and the two independent variables can be considered as the effects of land cover and physiography on the group of water chemistry variables represented by the factor. The resulting regression models can include one or both independent variables. Models with two independent variables can include or exclude the interaction between land cover and physiographic province. By comparing results from these possible regression models, one can test several hypotheses about the effects of land cover and physiographic province. The four possible outcomes include: (1) no significant effects of either land cover or physiographic province (no spatial effects); (2) significant differences among provinces but no land cover effects; (3) a significant effect of land cover that applies consistently to all provinces; and (4) significant land cover effects that differ among physiographic provinces. Only the first and last of these outcomes occurred in this study (see the next section). The last outcome results when the interaction effect of land cover and physiographic province is significant in the model. In this case, the regression lines of water chemistry versus land cover for different physiographic provinces can be statistically compared to identify which provinces have significantly different water chemistry-land cover relationships.

For each water chemistry factor, we examined the effects of four land cover types (forest, cropland, grassland, and developed land) in four separate regression models. Percentages of different land cover types are likely to be highly correlated because land cover percentages must sum to 100. As shown in Table 3, the four categories of land cover considered in this study comprised on average at least 95 percent of the total area of a watershed in each of the five physiographic provinces. Including these land cover variables in the same regression model can cause the problem of multicollinearity (Draper and Smith, 1981), which could cause the effect of one land cover to be confounded by another. By considering models for one land cover at a time, we avoided the confounding effects.

Mathematically, the effects of land cover and physiographic province on any factor of water chemistry (or the group of chemistry variables represented by the factor) can be described as follows,

$$F_{ijk} = \mu + \alpha_i + B_j + \alpha B_{ij} + e_{ijk} \quad (1)$$

where  $F_{ijk}$  is scores of a factor;  $\mu$  is the mean;  $\alpha_i$  is the effect of physiography,  $i = 1, \dots, 5$ ;  $B_j$  is the effect of land cover,  $j = 1, 2, 3, 4$ ;  $\alpha B_{ij}$  is the interaction effect of land cover and physiography;  $e_{ijk}$  is the error term; and  $k$  is the number of watersheds in a combination of province and land cover.

Land cover is measured by the percentage of a land cover category in a watershed. This percentage varies from category to category, and also from watershed to watershed. Therefore, the effect of land cover in the model is a random variable, and is denoted with a capital letter (B). On the other hand, the effect of physiography is fixed (nominal), and is denoted with a Greek letter ( $\alpha$ ).

## RESULTS

### *Inter-Annual Variability of Stream Chemistry*

Watersheds in some clusters were sampled in different years. Some were sampled in more than one year (Table 1). We used those watersheds with multiple years of sampling to analyze the inter-annual variability of stream chemistry. We compared and statistically tested for differences in stream chemistry variables among physiographic provinces in different years. We analyzed the effects of land cover and geology on stream chemistry and the inter-province variation of these effects in different years. Some

watersheds showed significant inter-annual changes in some chemistry variables. However, the same spatial patterns of stream chemistry and the effects of land cover and physiography were observed for different years. In short, the inter-annual variability of stream chemistry did not significantly affect the overall results and interpretation of the effects of land cover and geology, and the spatial variation of these effects across the major physiographic regions.

### *Spatial Variation of Stream Chemistry*

Nearly all the stream chemistry variables differed significantly among the physiographic regions (Table 4). The highest mean concentrations or values of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ , pH, DON, TDKN, conductivity, and total alkalinity were found in the Great Valley. The Piedmont had the highest concentrations of nitrate and TDN. The highest concentrations of  $\text{Na}^+$  and  $\text{Cl}^-$  were found in the Coastal Plain and Piedmont. The concentrations of DSI were the highest in the Coastal Plain, lower in the Piedmont, and the lowest in other physiographic regions. The concentrations of  $\text{SO}_4^{2-}$  were the highest in the Appalachian Plateau, but not significantly different among other regions.  $\text{PO}_4^{2-}$  and TDP were the lowest in the Appalachian Plateau, but not significantly different among other regions. DOP, DOM, and  $\text{NH}_4^+$  were higher in the Coastal Plain, Great Valley, and Piedmont than in the Appalachian Mountain and Plateau.

### *Factor Analysis*

Factor analysis identified five groups (factors), each representing a set of related water chemistry variables. Principal factor analysis and maximum likelihood factor analysis were both applied to the data in this study, and then the results were compared to see if the two methods substantially confirm the same factor structure. These two methods revealed a similar factor structure with five factors retained. Therefore, only results from the principal factor analysis are reported unless otherwise indicated (Table 5). We determined the number of factors based on a combination of (1) the results of the scree test and eigenvalue rule, (2) the proportions of sample variance explained, and (3) subject matter knowledge (Zwick and Velicer, 1986). After the number of factors was determined, the retained factors were rotated using the varimax method. The purpose of rotation is to achieve a simple structure in which each variable loads highly on a single factor and has small-to-

TABLE 4. Comparison of Regional Means of Stream Chemistry Variables. (Tukey's studentized range test with an experimentwise significance level of 0.05. Different letters indicate significant differences for the same parameter horizontally among physiographic regions.)

	Measurement Units	Coastal Plain	Piedmont	Great Valley	Appalachian Mountain	Appalachian Plateau
Ca <sup>2+</sup>	mg/L	14.6 <sup>c</sup>	20.0 <sup>bc</sup>	62.7 <sup>a</sup>	26.6 <sup>b</sup>	21.8 <sup>b</sup>
Cl <sup>-</sup>	mg/L	23.7 <sup>a</sup>	21.9 <sup>a</sup>	12.1 <sup>b</sup>	6.7 <sup>b</sup>	11.8 <sup>b</sup>
Conductivity	µMhos/cm	182.4 <sup>b</sup>	213.5 <sup>b</sup>	447.5 <sup>a</sup>	213.9 <sup>b</sup>	194.2 <sup>b</sup>
DOM	mg C/L	4.6 <sup>a</sup>	3.6 <sup>b</sup>	4.1 <sup>ab</sup>	2.4 <sup>c</sup>	2.3 <sup>c</sup>
DON	mg N/L	0.30 <sup>b</sup>	0.30 <sup>b</sup>	0.43 <sup>a</sup>	0.18 <sup>c</sup>	0.22 <sup>c</sup>
DOP	µg P/L	12.0 <sup>a</sup>	12.3 <sup>a</sup>	14.0 <sup>a</sup>	7.6 <sup>b</sup>	7.3 <sup>b</sup>
DSi	mg Si/L	6.9 <sup>a</sup>	4.8 <sup>b</sup>	2.8 <sup>c</sup>	2.6 <sup>c</sup>	2.6 <sup>c</sup>
K <sup>+</sup>	mg/L	2.4 <sup>b</sup>	2.4 <sup>b</sup>	3.7 <sup>a</sup>	1.5 <sup>c</sup>	1.3 <sup>c</sup>
Mg <sup>2+</sup>	mg/L	3.6 <sup>d</sup>	6.3 <sup>c</sup>	19.3 <sup>a</sup>	8.8 <sup>b</sup>	6.0 <sup>c</sup>
Na <sup>+</sup>	mg/L	13.3 <sup>a</sup>	10.6 <sup>ab</sup>	4.9 <sup>c</sup>	3.5 <sup>c</sup>	7.3 <sup>bc</sup>
NH <sub>4</sub> <sup>+</sup>	mg N/L	0.08 <sup>ab</sup>	0.09 <sup>a</sup>	0.11 <sup>a</sup>	0.05 <sup>bc</sup>	0.03 <sup>c</sup>
NO <sub>3</sub> <sup>-</sup>	mg N/L	1.0 <sup>c</sup>	3.4 <sup>a</sup>	1.7 <sup>bc</sup>	2.1 <sup>b</sup>	0.8 <sup>c</sup>
pH	pH Value	7.2 <sup>d</sup>	7.6 <sup>bc</sup>	8.2 <sup>a</sup>	7.7 <sup>b</sup>	7.4 <sup>cd</sup>
PO <sub>4</sub> <sup>2-</sup>	µg P/L	25.0 <sup>ab</sup>	35.4 <sup>a</sup>	21.0 <sup>ab</sup>	13.0 <sup>ab</sup>	4.5 <sup>b</sup>
SO <sub>4</sub> <sup>2-</sup>	mg S/L	6.2 <sup>b</sup>	4.1 <sup>b</sup>	6.0 <sup>b</sup>	5.4 <sup>b</sup>	13.2 <sup>a</sup>
Total Alkalinity	mg C/L	5.7 <sup>d</sup>	10.1 <sup>c</sup>	46.4 <sup>a</sup>	17.8 <sup>b</sup>	8.7 <sup>cd</sup>
TDKN	mg N/L	0.38 <sup>b</sup>	0.41 <sup>b</sup>	0.54 <sup>a</sup>	0.22 <sup>c</sup>	0.25 <sup>c</sup>
TDN	mg N/L	1.0 <sup>b</sup>	3.4 <sup>a</sup>	2.2 <sup>b</sup>	2.3 <sup>ab</sup>	1.0 <sup>b</sup>
TDP	µg P/L	32.8 <sup>ab</sup>	46.5 <sup>a</sup>	35.0 <sup>ab</sup>	20.6 <sup>ab</sup>	14.2 <sup>b</sup>

TABLE 5. Varimax Rotated Factor Loadings From Principal Factor Analysis.

	Factor 1 (carbonate)	Factor 2 (organic)	Factor 3 (P)	Factor 4 (NaCl)	Factor 5 (nitrate)	Communality
Ca <sup>2+</sup>	<b>0.96*</b>					0.97
Mg <sup>2+</sup>	<b>0.94</b>					0.90
Conductivity	<b>0.90</b>					0.99
Total Alkalinity	<b>0.89</b>					0.89
pH	0.47					0.39
TDKN		<b>0.97</b>				0.96
DON		<b>0.94</b>				0.92
NH <sub>4</sub> <sup>+</sup>		<b>0.77</b>				0.69
DOM		0.71				0.57
K <sup>+</sup>		0.62				0.62
DOP		0.50	0.70			0.75
TDP			<b>0.98</b>			0.99
PO <sub>4</sub> <sup>2-</sup>			<b>0.97</b>			0.97
Cl <sup>-</sup>				<b>0.95</b>		0.94
Na <sup>+</sup>				<b>0.93</b>		0.90
NO <sub>3</sub> <sup>-</sup>					<b>0.86</b>	0.89
TDN					<b>0.86</b>	0.89
SO <sub>4</sub> <sup>2-</sup>					-0.49	0.51
DSi						0.09
Variance Explained (percent)	22	20	13	12	11	

\*Loadings greater than 0.75 are in bold. Loadings less than 0.45 are not reported.

moderate loadings on the remaining factors. This facilitates the interpretation of the factors (Johnson and Wichern, 1982).

For the purpose of interpretation, factor loadings were classified into three categories: high loadings ( $> 0.75$ ), moderate loadings ( $0.45$ - $0.75$ ), and low loadings ( $< 0.45$ ) (Puckett and Bricker, 1992; Evans *et al.*, 1996; Miller *et al.*, 1997). For the sake of clarity, low loadings are not reported in Table 5.

Five retained common factors explained 78 percent of the total sample variance. For 12 of the 19 measured chemistry variables, the variance explained by these five factors (communality) is 89 percent or higher. For the other seven variables, the communality for  $K^+$ ,  $NH_4^+$ , DOM, DOP, pH, and  $SO_4^{2-}$  ranges from 39 to 75 percent. DSi did not have significant loadings on any of the factors. Only 9 percent of its sample variance was explained (Table 5).

The first factor had high positive loadings for  $Ca^{2+}$ ,  $Mg^{2+}$ , conductivity, and total alkalinity, and a moderate loading for pH. Scores of this factor were strongly related to the proportion of carbonate rock area in a watershed (Figure 2a). The chemistry variables represented by this factor, such as  $Ca^{2+}$ , had similar relationships with carbonate rock (Figure 2b). The Great Valley is mainly underlain by carbonate rock (on average, 80 percent of the total area of a watershed), while the Coastal Plain has no carbonate rock. The Great Valley had the highest and the Coastal Plain the lowest mean scores of this factor (Figure 3). This pattern is consistent with the high values of  $Ca^{2+}$ ,  $Mg^{2+}$ , pH, conductivity, and total alkalinity in the Great Valley and with the low values of the same chemistry variables in the Coastal Plain (Table 4). This factor is hereafter referred to as the carbonate factor.

The second factor had high positive loadings for  $NH_4^+$ , DON, and DTKN, and moderate loadings for  $K^+$ , DOM, and DOP. This factor is closely related to the reduced forms of nitrogen and organic forms of other nutrients. As such, it could be called the organic factor. The highest mean scores of this factor were found in the Great Valley and the lowest in the two Appalachian regions (Figure 3). The spatial variation of this factor across the physiographic regions was consistent with that of the group of chemistry variables represented by the factor, especially  $NH_4^+$ , DON, and DTKN (Table 4). Geology did not seem to have any significant effects on this factor. Only non-significant or marginal correlations were found between scores of this factor and any rock types.

The third factor could be called the P factor because of high loadings of  $PO_4^{2-}$  and TDP and moderate loading of DOP on this factor. Scores of this factor showed no significant spatial variation among physiographic regions (Figure 3). This is consistent

with the spatial pattern of P species, especially  $PO_4^{2-}$  and TDP (Table 4). No significant correlations were found between the factor scores and any rock types.

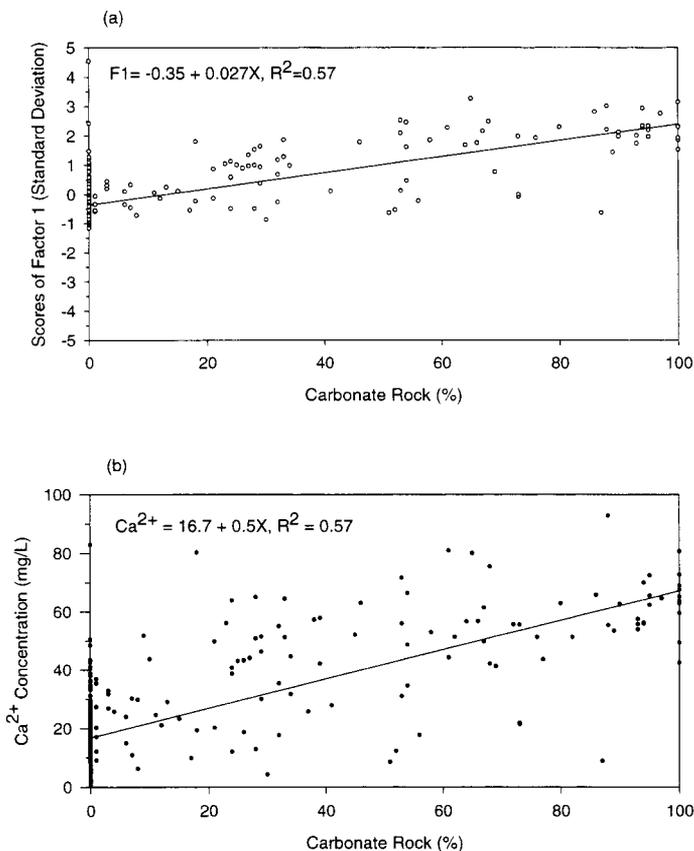


Figure 2. Relationships of Proportion of Carbonate Bedrock in Study Watersheds: (a) With Factor 1 (the carbonate factor), and (b) With  $Ca^{2+}$  Concentration.

The fourth factor had high positive loadings for  $Na^+$  and  $Cl^-$ , suggesting processes related to dissolution of sodium chloride ( $NaCl$ ). The highest mean scores occurred in the Coastal Plain and Piedmont (Figure 3). The spatial pattern of this factor among the physiographic regions was consistent with those of  $Na^+$  and  $Cl^-$  (Table 4). The factor scores had a significant positive correlation with percent area of unconsolidated sediments in a watershed ( $r = 0.37$ ). However, the correlation with unconsolidated sediments probably reflects the influence of land cover on this factor in the Coastal Plain (discussed later), which was the only region underlain by unconsolidated sediments.

The fifth factor was mainly associated with high positive loadings for nitrate and TDN. Sulfate ( $SO_4^{2-}$ )

had a moderate negative loading on this factor according to principal factor analysis. However, the results from the maximum likelihood factor analysis were somewhat different. The loading of sulfate on this factor from the maximum factor analysis was much lower (-0.16). Also, the loadings of nitrate and total N were 0.94 and 0.93 as compared to 0.86 and 0.86 from principal factor analysis (Table 5). These are the only major differences in the factor structure between the two methods. Since nitrate is the dominant species in TDN, this factor could be called the nitrate factor. The Piedmont had significantly higher mean scores than any other physiographic regions (Figure 3). This is consistent with the spatial variation of nitrate and TDN (Table 4). Only marginal correlations ( $|r| < 0.3$ ) were found between scores of this factor and any rock types.

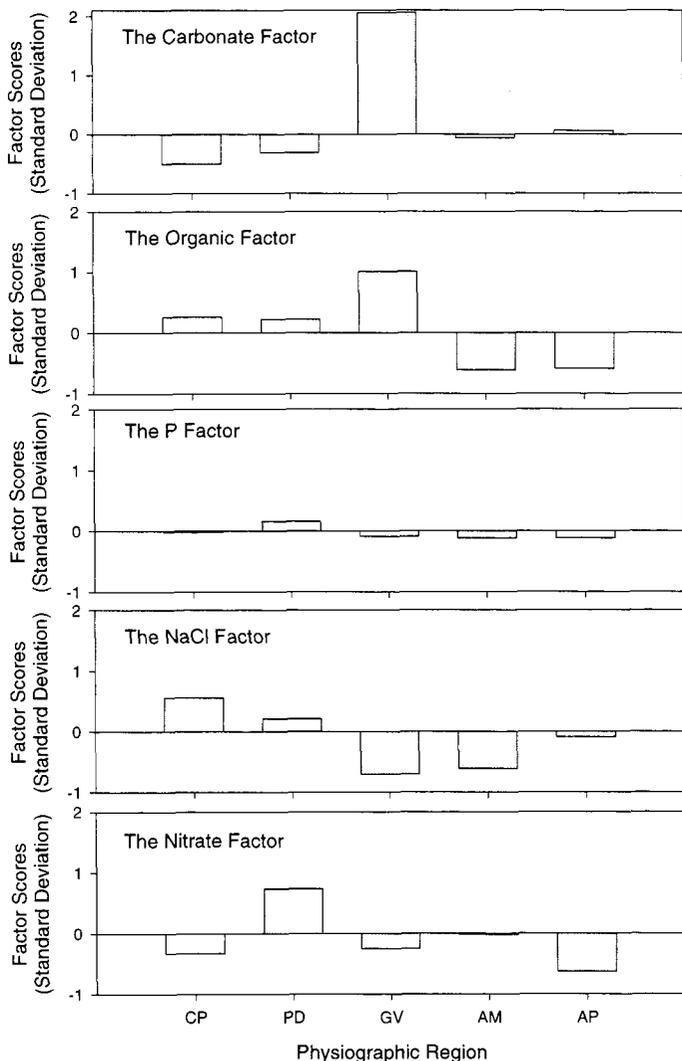


Figure 3. Regional Means of Factor Scores for the Coastal Plain (CP), Piedmont (PD), Great Valley (GV), Appalachian Mountain (AM), and Appalachian Plateau (AP).

DSi did not have significant loadings on any of the five factors, so it was apparently not related to any other water chemistry variables. The concentration of DSi was correlated positively with unconsolidated sediments ( $r = 0.53$ ), negatively with siliciclastic rocks ( $r = -0.48$ ), and marginally with other rock types ( $|r| < 0.3$ ). The correlations with rock types reflect the spatial patterns of DSi among physiographic regions (Table 4). The highest DSi was found in the Coastal Plain, which was underlain completely by unconsolidated sediments. The lowest DSi was found in the two Appalachian regions mainly underlain by siliciclastic rocks (Table 2).

### Regression Analysis

Regression analyses revealed significant effects of both land cover and physiographic province for four of the five water chemistry factors. For the P factor, none of the regression analyses for the four land covers was statistically significant, suggesting no significant influence of land cover on P and lack of statistically significant variation in P among the physiographic provinces. For the other four water chemistry factors, there were four regression analyses relating the four factors to four land covers measured as percentages of the total area of a watershed. In all 16 cases, the interaction between land cover and physiographic province was statistically significant, indicating that land cover significantly affects water chemistry in at least one province (but not necessarily in all provinces) and that the chemistry to land cover relationships differ significantly among the provinces. In this case, it is not statistically valid to test for the effect of one independent variable (either land cover or province alone) without considering the effect of the other. Therefore, we report results only from regression models including both land cover and physiographic province and their interaction.

To determine how each chemistry factor-land cover relationship differed among provinces, we first identified provinces where the slope of regression line relating the factor scores to the land cover were not significantly different from zero. Then for the remaining provinces with non-zero slopes, we performed all possible pairwise comparisons between their regression lines. To relate four water chemistry factors to four land cover categories in five physiographic provinces, we essentially fitted 80 regression lines (Figures 4-7). Our objective was to test for land cover effects on water chemistry in different geological settings rather than to report predictive models for particular chemicals. Therefore, Figures 4-7 present the patterns of significant effects of land cover and geological setting rather than an exhaustive table of

coefficients and statistics for 80 regression relationships. In the following discussion, a relationship is described as significant if the p-value is less than 0.05, marginally significant if the p-value is between 0.05 and 0.1, or nonsignificant if the p-value is greater than 0.1.

The four regression models for the carbonate factor explained 54 percent to 62 percent of its variance. As shown in Figure 4, forest did not have significant effect on this factor in the Great Valley, but showed significant influence in other regions. Forest showed positive effects in the Appalachian Plateau, and negative effects in the rest regions. The slope of regression lines was greater for the Appalachian Mountain than for the Coastal Plain and Piedmont. Cropland showed positive relationships with this factor in the Appalachian Mountain and Piedmont, but nonsignificant relationships in other regions. The slope of regression lines was greater for the Appalachian Mountain than the Piedmont. Grassland did not have significant effects on this factor in the Great Valley, but showed significant influences in all other regions: positive for the Appalachian Mountain and Coastal Plain, and negative for the Appalachian Plateau and Piedmont. The slope of regression lines was greater for the Appalachian Mountain than the Coastal Plain. Significant positive relationships between the proportion of developed area and this factor were found only for the Appalachian Mountain and Piedmont with a greater slope of regression line for the Appalachian Mountain (Figure 4a).

The combined effects of physiography and land cover on the organic factor were relatively weak compared to their effects on the carbonate factor, and explained only 24 percent to 35 percent of the variance. As shown in Figure 4b, forest had significant negative effects on this factor in all but one region, the Coastal Plain. The greatest regression line slope was found for the Great Valley. Cropland had marginally significant positive influence on this factor for the two Appalachian regions (p-values are 0.056 for Plateau and 0.096 for Mountain), but was not significant for other regions. Grassland was positively related to this factor in the Great Valley, Piedmont, and Appalachian Mountain with a greater slope of regression line for the Great Valley. The influence of developed area was positive for the Coastal Plain, but not significant for other regions (Figure 4b).

The NaCl factor was negatively influenced by the proportion of forest in a watershed in the Coastal Plain and Piedmont with a greater slope of regression line for the Coastal Plain. Cropland had marginally negative effects on this factor only in the Coastal Plain, but no significant effects in other regions. Grassland had a positive relationship with this factor

also in the Coastal Plain, but no significant relationships in other regions (Figure 4c). The strongest influences on this factor were those of developed area. Among the four models for this factor, the one with developed area as an independent variable had the highest percentage of variance explained (41 percent). Figure 5 shows the relationships of the proportion of developed area in the study watersheds with scores of the NaCl factor and with Na<sup>+</sup> concentrations. However, this relationship was found significant only in the Coastal Plain and Piedmont. In addition, a marginally significant positive relationship was found for the Appalachian Plateau (Figure 4c).

The nitrate factor was strongly affected by the proportion of cropland in a watershed. Among the four models for this factor, the one with cropland as an independent variable had the highest percentage of variance explained (60 percent). Cropland had significant positive relationships with this factor for almost all the physiographic regions except for a marginally significant relationship for the Great Valley (Figure 4d). Scores of this factor increased as the percentage of cropland increased, but the rate of increase varied from region to region (Figure 6a). The Piedmont had the greatest rate of increase, significantly higher than the average rate of all other regions. The chemistry variables represented by this factor, primarily nitrate, had a similar spatial pattern of the relationships with cropland (Figure 6b). Other land cover types except for forest did not have strong impact on this factor in most regions. Forest had significant negative effects in the Appalachian Mountain, Appalachian Plateau, and Piedmont, but no significant influence in the other regions. Grassland was not significantly related to this factor except for a positive relationship for the Appalachian Plateau. Developed area was not significantly related to this factor except for a negative relationship for the Piedmont (Figure 4d).

Since DSi was not related to any of the five factors, the same regression models were fitted to the original data of DSi. All four models were significant with the explained variance ranging from 39 percent to 55 percent. However, these were mainly explained by the differences in DSi among the physiographic regions. None of the land cover types had strong correlations with concentration of DSi in streams ( $|r| < 0.11$ ). The proportion of forest in a watershed had no significant effects on DSi in the model. For other land cover types, significant relationships with DSi were found only in the Coastal Plain and Piedmont. Cropland had a positive relationship with DSi in the Coastal Plain, a negative relationship in the Piedmont, and nonsignificant relationships in other regions. Grassland showed positive effects on DSi in the Coastal Plain, but was non-significant in other regions. Developed

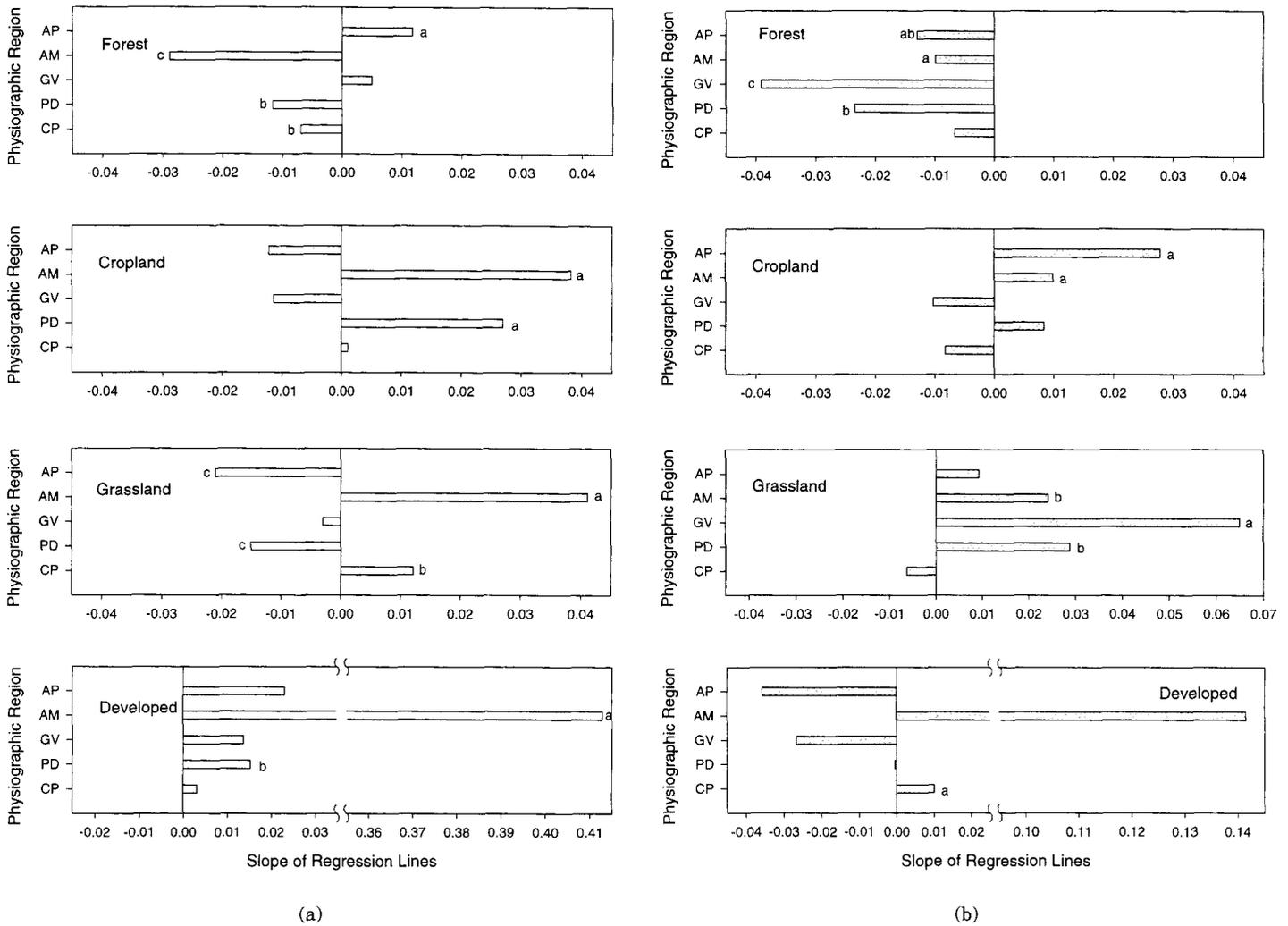


Figure 4. Inter-Regional Comparison of Regression Lines of Factor 1 (the carbonate factor, Figure 4a), Factor 2 (the organic factor, Figure 4b), Factor 4 (the NaCl factor, Figure 4c), or Factor 5 (the nitrate factor, Figure 4d) Against Proportion of a Land Cover Type in a Watershed. The abbreviations for the physiographic regions are the same as in Figure 3. A letter indicates that the slope of regression line is significantly different from zero for that region ( $p$ -value  $< 0.10$ ). Different letters indicate significant differences among the regions in slope of regression lines ( $p$ -value  $< 0.05$ ).

area had a negative relationship with DSi in the Coastal Plain, a positive relationship in the Piedmont, and non-significant relationships in other regions. In short, in the Coastal Plain, DSi increased as the proportion of cropland and grassland increased and developed area decreased. In the Piedmont, the relationships were reversed: DSi increased as cropland decreased and developed area increased (Figure 7).

### DISCUSSION

The stream chemistry in watersheds of the Chesapeake Bay drainage basin varied among physiographic regions. The spatial variation of stream chemistry

was closely related to differences in geology and land cover among the watersheds. Some stream chemistry variables were more strongly affected than others by geological settings in the watersheds. The concentrations of  $Ca^{2+}$ ,  $Mg^{2+}$ , pH, conductivity, and total alkalinity in streams were primarily related to prevalence of carbonate rock in the watershed, especially in the Great Valley. DSi was closely related to unconsolidated sediments in the Coastal Plain. For these variables, geology was a more dominant influence than land cover/land use. The effects of land cover on these stream chemistry variables were often contingent on the strength of geological influence. The variation of land cover in watersheds of the Great Valley did not seem to alter the hydrogeological processes enough to significantly influence the variables related to the

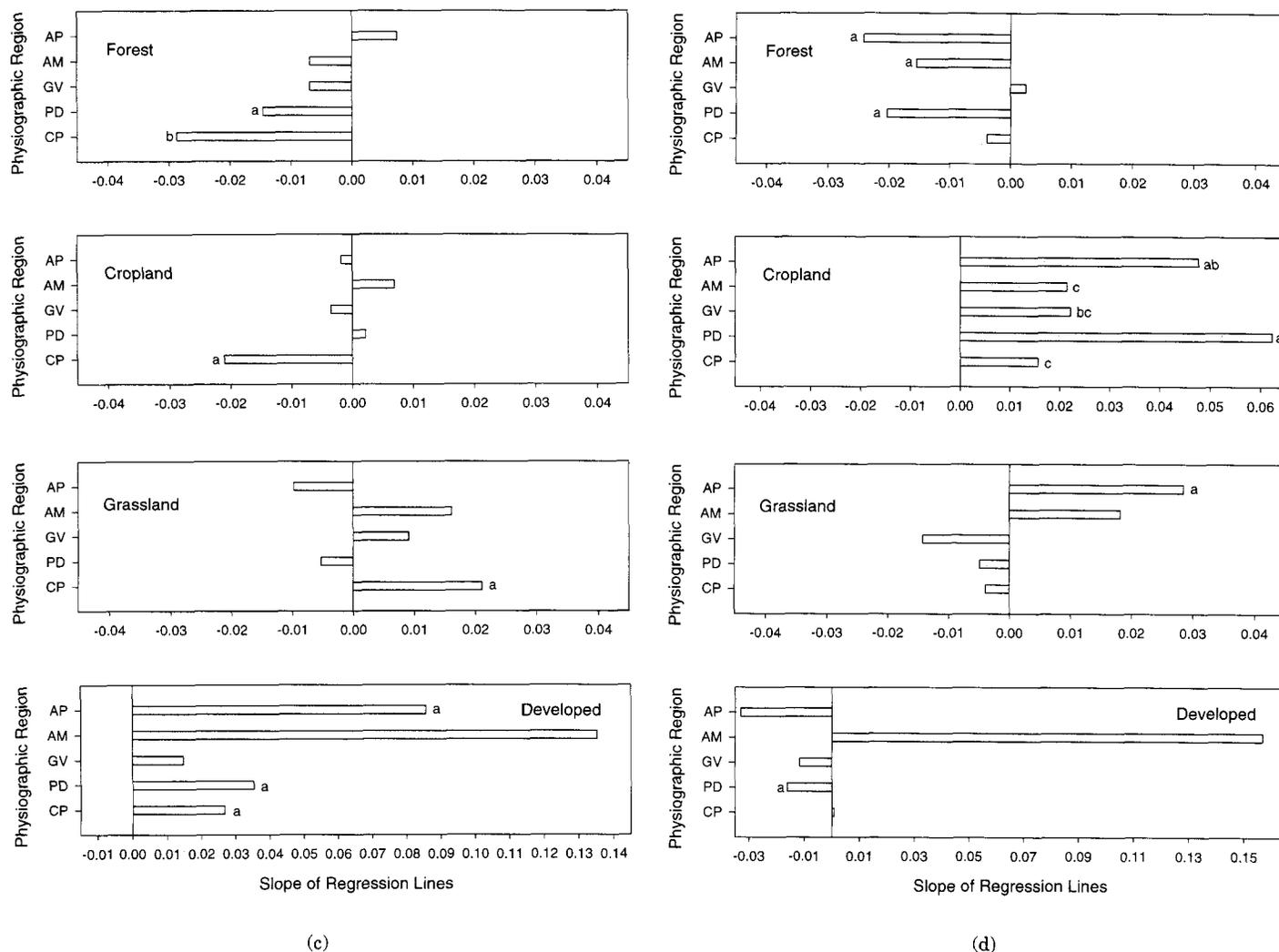


Figure 4. Inter-Regional Comparison of Regression Lines of Factor 1 (the carbonate factor, Figure 4a), Factor 2 (the organic factor, Figure 4b), Factor 4 (the NaCl factor, Figure 4c), or Factor 5 (the nitrate factor, Figure 4d) Against Proportion of a Land Cover Type in a Watershed. The abbreviations for the physiographic regions are the same as in Figure 3. A letter indicates that the slope of regression line is significantly different from zero for that region (p-value < 0.10). Different letters indicate significant differences among the regions in slope of regression lines (p-value < 0.05) (cont'd.)

carbonate factor. In other regions, carbonate rock was a minor component of bedrock, and its effect was not as dominant as in the Great Valley. Land cover in these regions showed some significant effects on the chemistry variables of the carbonate group.

On the other hand, some other stream chemistry variables were more strongly affected by land cover than geology, mainly nitrate, Na<sup>+</sup>, and Cl<sup>-</sup>. Nitrate was closely related to the proportion of cropland in a watershed. The concentration of nitrate in a stream increased as the percentage of cropland in a watershed increased. This is consistent with the literature on the relationships between nitrate in water resources and cropland/or agricultural activities (Beaulac and Reckhow, 1982; Osborne and Wiley, 1988; Power and Schepers, 1989; Smith *et al.*, 1987,

1993; National Research Council, 1989, 1993; Hunsaker and Levine, 1995; Jordan and Weller, 1996; Liu *et al.*, 1997; Jordan *et al.*, 1997a, b, c; Ator *et al.*, 1998; Lindsey *et al.*, 1998). The concentrations of Na<sup>+</sup> and Cl<sup>-</sup> in the studied streams were primarily related to developed area in a watershed. The highest average concentrations of Na<sup>+</sup> and Cl<sup>-</sup> were found in the Coastal Plain, which had the highest average developed area among all physiographic regions. Also the effects of developed area on these two variables were significantly only for the Coastal Plain and Piedmont, the two regions with the highest proportions of developed area in a watershed. The major source of Na<sup>+</sup> and Cl<sup>-</sup> was anthropogenic input, especially from developed areas. A number of human activities contribute to salt contamination in streams, such as

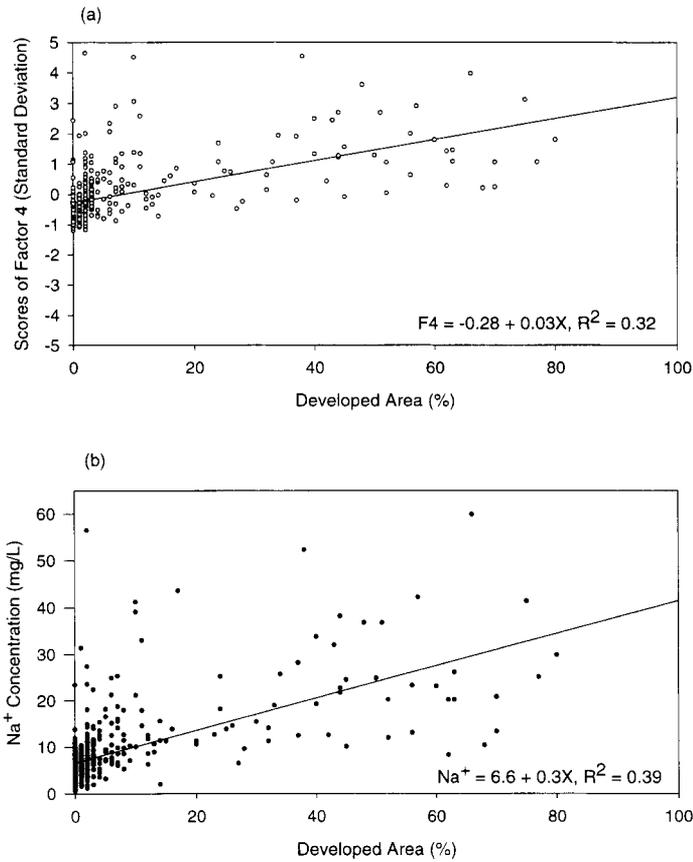


Figure 5. Relationships of Percent Developed Area in Study Watersheds: (a) With Factor 4 (the NaCl factor), and (b) With Na<sup>+</sup> Concentration.

application of salt on roads in the winter to melt snow and ice. Septic tanks in some suburban areas are another important non-point source of salt contamination of streams. In addition to daily domestic consumption of salt, use of salt to regenerate water softeners for drinking water can make a significant contribution to salt release from septic tanks (Sherwood, 1989; Puckett and Bricker, 1992). The wet deposition of sea salt might also be a cause for higher Na<sup>+</sup> and Cl<sup>-</sup> concentrations in the Coastal Plain and Piedmont streams because of their nearness to the Bay and the ocean.

Land cover not only had different effects on different water chemistry variables, but also showed spatially different effects on the same variables. The effects of the same land cover were significant in some physiographic regions, but not in others (Figures 4-7). The relationships between the same land cover and the same variables changed from region to region, from positive to negative, or vice versa (e.g., Figures 4 and 7). The magnitude of the land cover effects

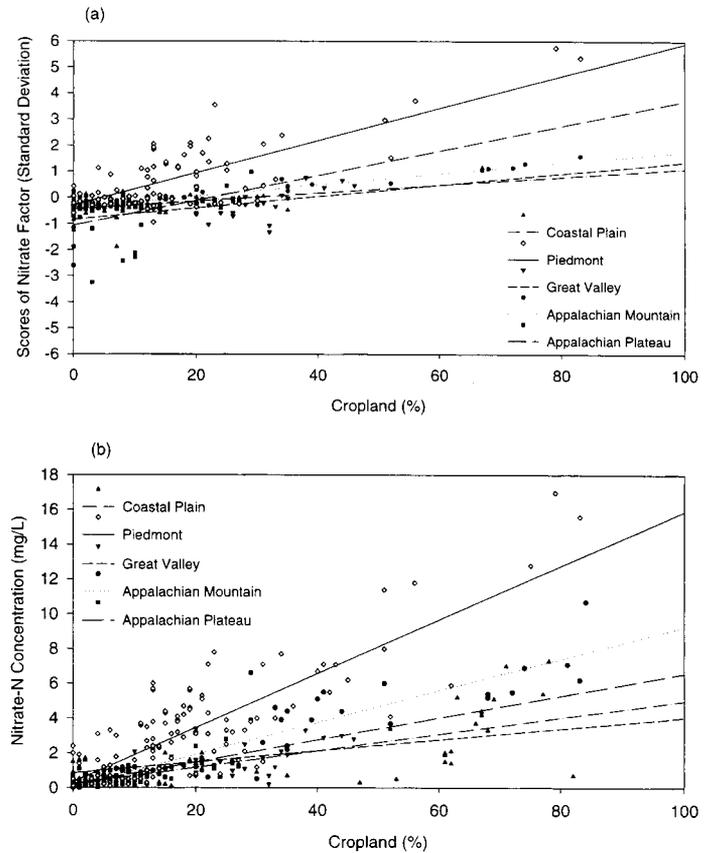


Figure 6. Inter-Regional Comparison of the Relationships of Proportion of Cropland in Study Watersheds: (a) With Factor 5 (the nitrate factor), and (b) With Nitrate Concentration.

changed from region to region even if the relationships with the chemistry variables remained the same among the regions (e.g., Figure 6).

Regional differences in geology contributed to the spatial variation of land cover effects. For example, none of the land cover types had significant effects on the variables of carbonate group in the Great Valley although the same land cover showed significant effects on the same variables in other regions (Figure 4a). Nitrate concentration in a stream increased as the percentage of cropland in a watershed increased. The same qualitative relationship was true for every physiographic region, only the rate of increase varied from region to region with the Piedmont having the greatest rate of increase (Figure 6). As reported by Jordan *et al.* (1997a, b, c), differences in hydrogeology could be the main cause for the differences in the relationships between nitrate concentrations and proportions of cropland in the Piedmont and Coastal Plain. The results from the present study extend the regional differences in the relationships to other physiographic provinces in the Chesapeake drainage. The

concentration of DSi in streams of the Piedmont watersheds increased as developed area increased and cropland decreased. These relationships were reversed in the Coastal Plain (Figure 7). Land use often depends on soils and topography, especially agricultural land use. The observed effects of land cover on DSi may reflect the relationships between DSi and soils. Further study of the abundance of readily mobilized silica in soils would help clarify the relationships between land use and DSi concentrations in streams.

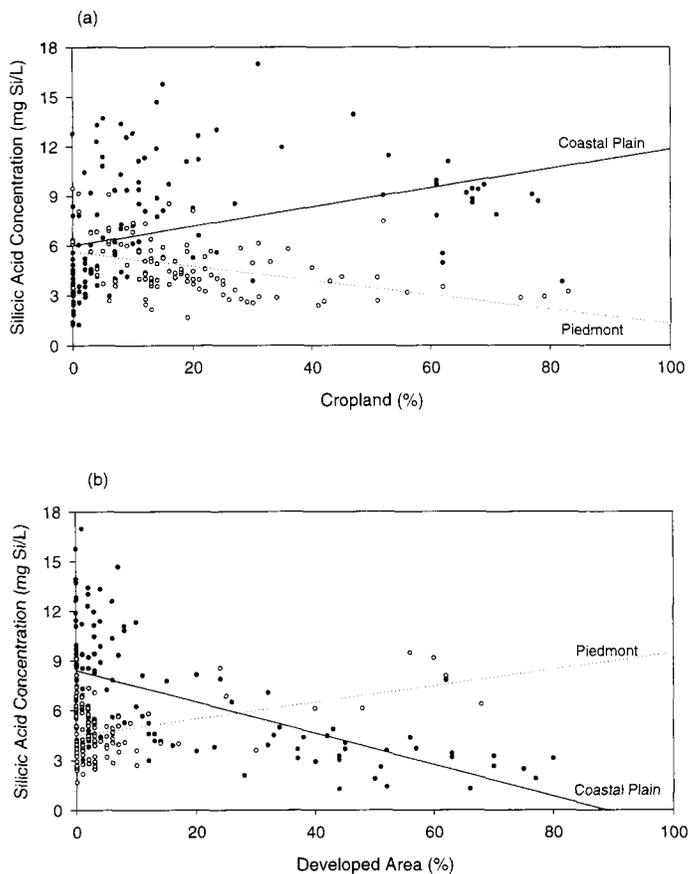


Figure 7. Relationships of Silicic Acid Concentration in Study Watersheds: (a) With Proportion of Cropland and (b) With Percent Developed Area.

The lack of variation of phosphorus among different physiographic regions in this study was most likely due to the fact that water samples were collected under base flow conditions, and only dissolved forms of P were measured. Most forms of phosphorus are not very mobile because they are adsorbed onto soil particles. A large fraction of P fluxes in streams is associated with suspended solids, which are transported mainly during episodic high flows (Johnson *et al.*, 1976; Jordan *et al.*, 1997a). The concentrations of particulate forms of P could increase several orders of

magnitude during storm events (Correll *et al.*, 1999b). As such, the bulk of P fluxes in streams occur during periods of high flows (Johnson *et al.*, 1976). Some studies show that higher concentrations of dissolved P also occur during the period of high stream flows (Hill, 1981). Therefore, accurate estimates of total P fluxes in streams cannot be obtained from measurements of dissolved P during base flow. In this case, much of P transport in the streams may have been missed in the measurement. For the same reason, the effects of land cover on P fluxes in the streams may not appear in the water samples. Some studies have reported similar levels of P in watersheds with different land uses, or lack of significant land use effects on P concentrations in streams (Jordan *et al.*, 1997a, b; Miller *et al.*, 1997). However, many studies in the literature have shown that when its major components are accounted for, P flux is strongly influenced by land use, especially intensive agriculture (Hill, 1981; Correll *et al.*, 1999a, b). Since nonpoint source anthropogenic inputs of P from cropland are closely related to processes of runoff and soil erosion, soil erodibility may have a significant impact on the ratio of dissolved/particulate forms of P as well as the total P fluxes in streams.

There was no consistent pattern in the spatial variation of land cover effects on the reduced forms of N, dissolved organic P, dissolved organic matter, and  $K^+$ . Except for forest, which had negative effects on these variables in all regions but the Coastal Plain (Figure 4b), different land cover types seemed to dominate in different regions. In the Coastal Plain, only developed area had significant effects on these variables; in the Great Valley and Piedmont, only the effects of grassland were significant; and in the two Appalachian regions, the effects of cropland were dominant. Organic forms of nutrients are strongly associated with suspended solids in streams. As with phosphorus, much of these organic nutrients would be missed in measurement of dissolved forms under base flow conditions.

Synoptic sampling under base flow conditions is more appropriate for some stream chemistry variables than others. For those constituents in streams that are strongly associated with suspended solids during periods of high flow, much of their transport in streams is missed in the measurement. To obtain an accurate estimate of those constituents, storm runoff periods must be sampled. A more appropriate approach is to use automated samplers that continuously monitor stream flow and collect water samples at a variable time interval according to flow rate (Jordan *et al.*, 1997a, b; Correll *et al.*, 1999a). Both particulate and dissolved forms of chemical constituents should be measured for a full account of their fluxes. On the other hand, some other constituents, such as

nitrate, move primarily as dissolved forms. Although their fluxes could increase dramatically during high flow, studies have shown that the concentrations of nitrate and other dissolved inorganic forms of nutrients often remain low and do not change very much during storm events (Burt and Arkell, 1987; McDuffett *et al.*, 1989; Correll *et al.*, 1999b). Synoptic sampling of these constituents under base flow conditions is a very efficient and cost-effective method for quantifying their concentrations in streams and testing relationships with geographic controls.

In summary, this study examined stream chemistry in an unusually large number of small watersheds with strongly contrasting land cover patterns and geological characteristics. With the unique data set and combined application of factor analysis and regression, we were able to resolve the different effects of land cover and geology on many aspects of stream chemistry among several major physiographic provinces in the Chesapeake Bay drainage basin. Our previous work has shown the differences in the effects of cropland on nitrate between the Coastal Plain and Piedmont (Jordan *et al.*, 1997a, b, c). The present study confirmed our earlier work and, in addition, showed the regional differences in the effects of other land covers on other water chemistry variables among other provinces. These findings will help improve our understanding of the spatial effects of land cover/land use on stream chemistry in general and the spatial variation of human impacts on watershed discharges throughout the Chesapeake Bay drainage basin in particular.

#### ACKNOWLEDGMENTS

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