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Hydrogeologic Setting and Potential for Denitrification in Ground Water, Coastal Plain of Southern Maryland

Water-Resources Investigations Report 00–4051

U.S. Department of the Interior
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by David E. Krantz and David S. Powars

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Conversion Factors and Vertical Datum

Multiply	By	To obtain
foot (ft)	0.3048	meter
mile (mi)	1.609	kilometer

Concentrations of chemical constituents dissolved in water are expressed in milligrams per liter (mg/L).

Vertical Datum: In this report, "sea level" refers to the National Geodetic Vertical Datum of 1929–A geodetic datum derived from a general adjustment of the first-order level nets of the United States and Canada, formerly called Sea Level Datum of 1929.

Water Year: A water year is the 12-month period from October 1 through September 30. The water year is designated by the calendar year in which it ends; for example, the year ending September 30, 1993, is called "Water Year 1993."

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Abstract

The types and distribution of Coastal Plain sediments in the Patuxent River Basin may contribute to relatively low concentrations of nitrate (typically less than 1 milligram per liter) in stream base flow because of the chemical reduction of dissolved nitrate (denitrification) in ground water. Water chemistry data from synoptic stream base-flow surveys in the Patuxent River Basin show higher dissolved nitrate concentrations in the Piedmont than in the Coastal Plain section of the watershed. Stream base flow reflects closely the chemistry of ground water discharging from the surficial (unconfined) aquifer to the stream. Because land use in the sampled subbasins is virtually the same in each section, differences in the physical and geochemical characteristics of the surficial aquifer may explain the observed differences in water chemistry. One possible cause of lower nitrate concentrations in the Coastal Plain is denitrification within marine sediments that contain chemically reduced compounds. During denitrification, the oxygen atoms on the nitrate (NO_3^-) molecule are transferred to a reduced compound and N_2 gas is produced. Organic carbon and ferrous iron (Fe^{2+}), derived from the dissolution of minerals such as pyrite (FeS_2) and glauconite (an iron alumino-silicate clay), can act as reducing substrates; these reduced chemical species are common in the marine and estuarine deposits in Southern Maryland. The spatial distribution of geologic units and their lithology (sediment type) has been used to create a map of the potential for denitrification of ground water in the surficial aquifer of the Coastal Plain in Southern Maryland.

Introduction

Nitrate in the ground water of shallow Coastal Plain aquifers poses a potential health risk to humans and an environmental risk to estuarine ecosystems. The surficial (or water-table) aquifer system acts as both a transport pathway and a reservoir for nitrate derived from nonpoint sources at or near the land surface. Much of the total nitrogen load to surface-water bodies comes from ground-water discharge as stream base flow. In the study area, the Coastal Plain of Southern Maryland, most of the drinking-water supply is pumped from wells in deeper confined aquifers rather than from the surficial aquifer, which is directly impacted by nitrate contamination from nonpoint sources. Consequently, for Southern Maryland, nitrate in ground water is not an issue of drinking-water quality, but is a critical component of the total nutrient load to the Patuxent River and Chesapeake Bay estuaries. In a joint project with the Maryland Department of the Environment (1985–1995), and later with the Maryland Department of Natural Resources (1995–present), the U.S. Geological Survey (USGS) has been monitoring nonpoint-source nutrient loading in the Patuxent River watershed since 1985 to estimate total annual loads of nitrogen and phosphorus delivered to the river and the estuary.

Nutrient-control policies are often applied uniformly to a state or management region without allowing for differences in the response of the hydrologic system. The physical and chemical properties of the surficial aquifer system vary considerably within a region, and areas with certain types of sediment may be less susceptible to nitrate contamination than other areas. This report summarizes the near-surface hydrogeology of the Coastal Plain in the Patuxent River Basin, and describes how the geochemical characteristics of marine and estuarine silts may reduce nitrate in ground water by denitrification. The distribution of sediments with low, intermediate, and high potential for denitrification is shown in a map of Southern Maryland. This information may be used by planning agencies for evaluating land-use policies related to nutrient management.

Monitoring Nutrient Loading in the Patuxent River Basin

For the project with the State of Maryland, the USGS measured nutrient loads from streams in the Patuxent watershed, related nutrient loads to land use, and developed a watershed model calibrated with hydrologic, water-quality, and land-use data. The results of the study will be used to evaluate management tools for meeting total maximum daily load (TMDL) targets and nitrogen- and phosphorus-reduction goals of the Patuxent Nutrient Control Strategy (Office of Environmental Programs, 1983). The State of Maryland has also set a goal of reducing controllable nitrogen and phosphorus loads to the Chesapeake Bay by 40 percent from 1985 levels by the year 2000 (Galloway, 1993); the data from the study are valuable for assessing any changes in nitrogen and phosphorus loads that have resulted from nutrient-control practices implemented to meet this goal.

To quantify nutrient loads, six fixed water-quality monitoring stations were installed in the watershed to supplement five existing gaging stations. This network has provided time-series data used to analyze the temporal variability of nutrient concentrations and to estimate total annual nutrient loads. Three synoptic sampling surveys of stream base flow were conducted in 1993, 1994, and 1995 at 74 sites distributed throughout the Piedmont and Coastal Plain sections of the Patuxent River Basin (fig. 1a); however, dissolved nitrate was analyzed for only 54 of these sites. The chemistry (or water quality) of stream water at base flow is very similar to that of the ground water discharging to the stream, with little influence from storm runoff.

Preston (1996) described the monitoring network and summarized the initial results of water-quality sampling from the fixed stations and the synoptic surveys. Preston and Summers (1997) calculated nutrient and suspended-sediment loads (mass per year) and yields (mass per unit area per year) for water years 1986–90 from the monitoring-station data. They also partitioned the loading contributed by direct runoff and base flow by applying a hydrograph-separation method to the records of streamflow and nutrient concentrations. Lizárraga (1999) extended the evaluation of the time-series data from the five monitored subwatersheds to include water years 1986–96, and compared concentrations, trends, and loads with the goals of the 40-percent nutrient-reduction strategy.

The greatest contrast in base-flow nutrient concentrations in the Patuxent River watershed is between the Piedmont and Coastal Plain sections of the basin. Mean nitrate concentrations in Piedmont streams range from 1.5 to 2.5 mg/L as N (milligrams per liter as nitrogen), with maximum values as high as 12.0 mg/L (Preston, 1996). Coastal Plain streams in the Patuxent watershed have consistently lower mean nitrate concentrations, with values typically below 0.5 mg/L and maximum values no greater than 4.0 mg/L.

Relation of Nitrate Concentrations to Land Use and Location within the Patuxent River Basin

The primary nonpoint sources of nitrate entering the ground water are from agricultural and residential applications of fertilizer, and effluent from septic tanks commonly used in rural areas. Consequently, sources of nitrate are typically linked to land use. Atmospheric deposition of nitrate is a significant nonpoint source, but it is distributed broadly throughout the Patuxent watershed and not directly associated with land use (Fisher and Oppenheimer, 1991). The distribution of land use for the sampled subbasins in the Piedmont section of the Patuxent River Basin is not significantly different from that of the Coastal Plain (table 1). However, because the synoptic surveys were designed to sample low-order streams (the small headwater streams of the drainage system), the distribution of land use in the sampled subbasins may not be representative of land use for the entire Piedmont section compared with the entire Coastal Plain section, as depicted in figure 1b.

For both the Piedmont and Coastal Plain sites, base-flow nitrate concentrations correlate with 1990 land-use data (Maryland Department of the Environment, 1991) (fig. 1b) as either percentage agriculture (fig. 2a), percentage forest (fig. 2b), or percentage urban plus residential (fig. 2c). These relations are shown as separate linear regression lines for the Coastal Plain and Piedmont trends in figure 2. The r^2 values for the Coastal Plain linear regressions are very low (0.01 to 0.15) because the slope of the line is near zero; however, the F statistics for nitrate versus percentage agriculture and nitrate versus percentage forest indicate that these regressions are statistically significant (at $p = 0.003$ and 0.14, respectively). The slope of the line relating nitrate to percentage agriculture is much lower for Coastal Plain sites than for Piedmont sites, implying consumption or dilution of ground-water nitrate in the surficial aquifer of the Coastal Plain. Nitrate concentrations from sites in three subbasins, Killpeck Creek and Lewis Creek in St. Marys County and Full Mill Branch in southeastern Prince Georges County (fig. 1a), deviate from the nitrate–land use trends for the Coastal Plain sites but fall within the trends for the Piedmont. Nitrate values from these three apparently anomalous subbasins (highlighted in red in figure 2) were not included in calculating the regression lines for the Coastal Plain.

The observed nitrate concentrations in the Coastal Plain of the Patuxent River Basin are low in comparison to ground-water and stream base-flow nitrate concentrations from the entire Maryland Coastal Plain. In a USGS National Water-Quality Assessment (NAWQA) survey on the Delmarva Peninsula, measured nitrate concentrations in ground water exceeded the U.S. Environmental Protection Agency drinking-water standard of 10 mg/L for one-third of the sites and were as high as 40–45 mg/L (Hamilton and others, 1993). Nitrate concentrations in stream base flow ranged from a natural background level of 0.1 mg/L to 11 mg/L (Shedlock and others, 1999). Base-flow nitrate concentrations for streams in the well-drained upland of the Delmarva Peninsula increase with percentage of agricultural land use in the watershed and show a trend similar to that in figure 2a for the Piedmont section of the Patuxent River Basin. In contrast, the poorly drained watersheds, particularly those with reducing conditions and evidence of denitrification in the surficial aquifer, have lower overall nitrate concentrations and the correlation of nitrate with

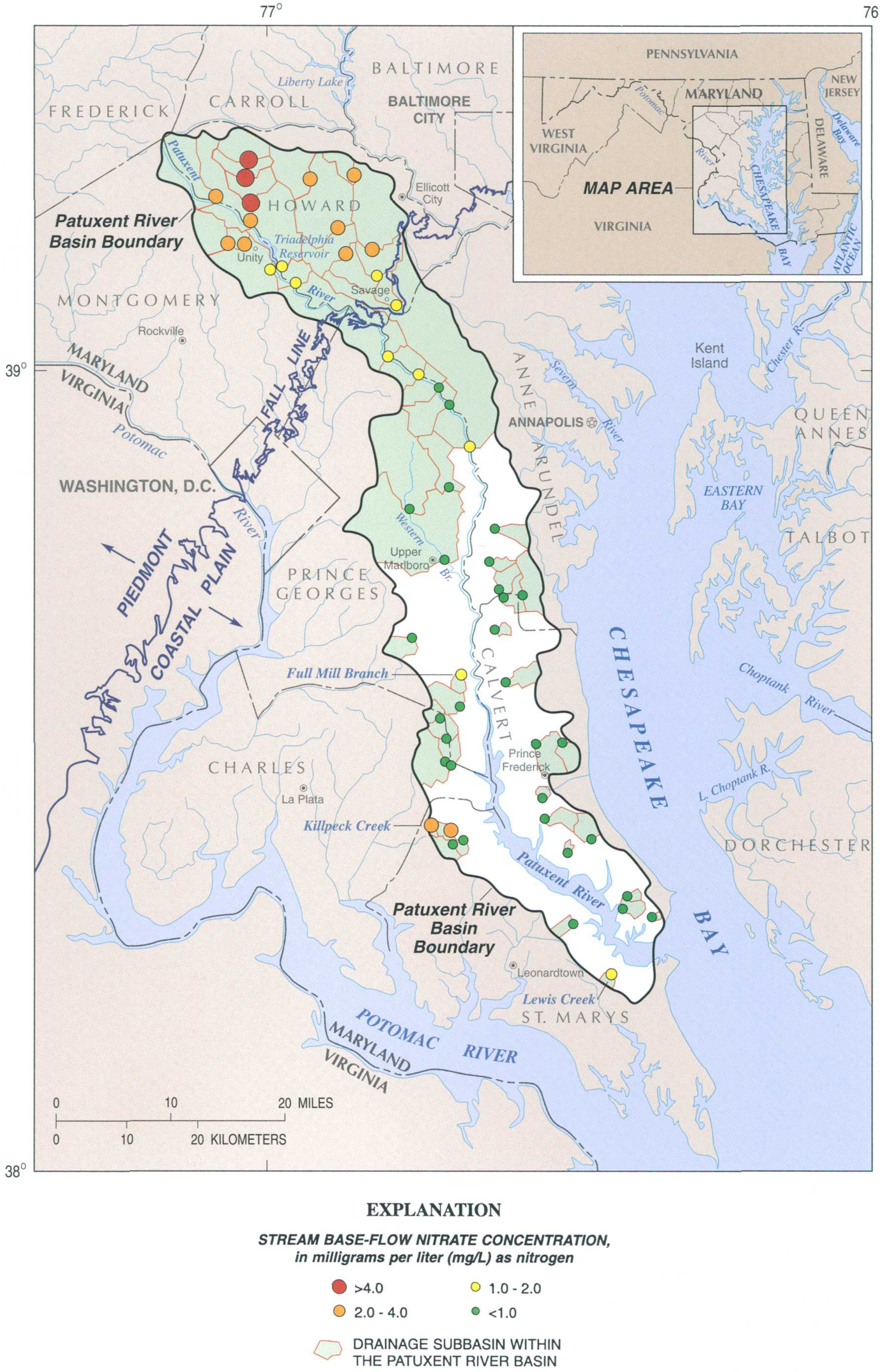


Figure 1a. Location of the Patuxent River Basin and stream base-flow sampling sites with nitrate concentrations combined from surveys in 1993, 1994, and 1995 in the Piedmont and Coastal Plain Provinces of the watershed for the nonpoint-source study.

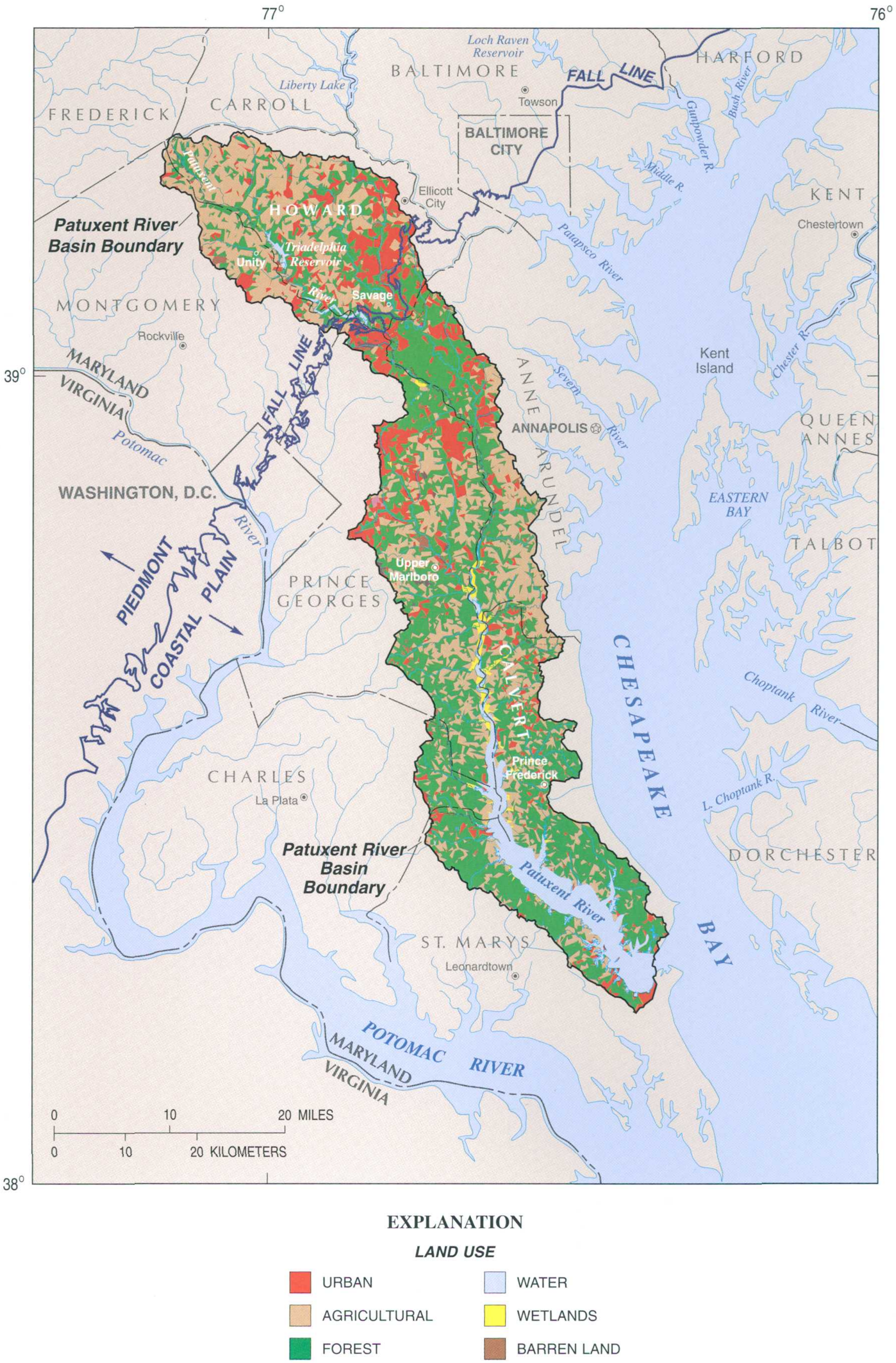


Figure 1b. Land use in the Patuxent River Basin, 1990 (from Maryland Department of the Environment, 1991).

Table 1. *Distribution of land use as percentage of basin area for subbasins in the Piedmont and Coastal Plain sections of the Patuxent River Basin, Maryland, that were sampled during base-flow synoptic surveys*

	Urban	Residential	Agricultural	Forest
Piedmont	11.2	19.0	29.6	37.6
Coastal Plain	10.3	19.5	29.7	38.1

Table 2. *Reactants and products of chemical reactions that reduce nitrate*

Nitrate (oxidant)	+	Reduced compound	=>	Reduced Nitrogen	+	Oxidized Products
NO_3^-		Organic Carbon		N_2 (gas)		$CO_2 + H_2O$ or $H^+ + HCO_3^-$
NO_3^-		Pyrite (FeS_2)		N_2 (gas)		Sulfate (SO_4^{2-}) + FeOOH
NO_3^-		Glauconite (Fe aluminosilicate)		N_2 (gas)		FeOOH + SiO_2

percentage of agricultural land use has a low slope, similar to the pattern observed for the Coastal Plain section of the Patuxent River Basin.

Geochemistry of Denitrification

Chemically reduced compounds in sediments may react with oxidizing agents carried by ground water; these reactions are commonly mediated by bacteria that derive energy from the process. The most abundant oxidant in the surficial aquifer is dissolved oxygen. Once oxygen has been depleted by chemical reduction, other oxidized compounds will be consumed in order of reactivity, starting with nitrate, followed by sulfate, and ending with methanogenesis. Denitrification is favored in oxygen-free reducing environments, such as those that may occur in the subsurface where sufficient organic material and reduced chemical species are present (Canter, 1997). In the process of denitrification, the nutrient nitrate (NO_3^-) is chemically reduced to relatively inert nitrogen gas (N_2).

Three common groups of reduced compounds in Coastal Plain sediments react with nitrate: organic carbon compounds, sulfide minerals, and certain iron silicates and aluminosilicates (table 2). Organic carbon compounds are generally the most reactive reduced substrate, and are abundant in soils, marsh muds, and estuarine sediments. Sulfide compounds, such as the iron sulfide mineral pyrite (FeS_2), are also common in marsh and estuarine sediments. Pyrite will dissolve to release ferrous iron (Fe^{2+}) and sulfide (S^-) ions that react quickly to reduce nitrate and produce ferric oxyhydroxides (FeOOH) and sulfate (SO_4^{2-}). Iron silicate and aluminosilicate minerals, such as the clay mineral glauconite, generally react more slowly than organic carbon and sulfides but may be a major component of some marine sediments and a significant source of ferrous iron. Glauconite is produced on the outer continental shelf under low-oxygen conditions, and is abundant in the ancient marine sediments in the Patuxent River Basin.

Natural Attenuation of Nitrate in Ground Water

Processes associated with the hydrogeologic setting of the Patuxent River Basin may allow natural attenuation of anthropogenic nitrate. Natural attenuation is the decrease in concentration of dissolved nitrate in ground water by plant uptake, by dilution through dispersion and mixing with low-nitrate water, or by consumption in a chemical reaction such as denitrification.

The uplands in the Coastal Plain of the Patuxent River Basin are capped by coarse fluvial sands and gravels that are very permeable and extensively weathered. These sediments have little potential for denitrification. In contrast, marine sediments in the shallow subsurface contain reduced compounds and minerals that are chemically active in oxidation-reduction reactions (also referred to as "redox reactions").

Previous studies have shown that most of the fertilizer nitrate applied to fields is consumed in the soil zone. Approximately 15 to 25 percent of the nitrate, however, is carried with rain water through the unsaturated zone and into the saturated zone (the water table) (Hallberg and Keeney, 1993). This dissolved nitrate is transported by ground-water flow in the surficial aquifer to discharge into streams or estuaries.

A working hypothesis is that ground water flowing through surficial coarse sands and gravels will show little or

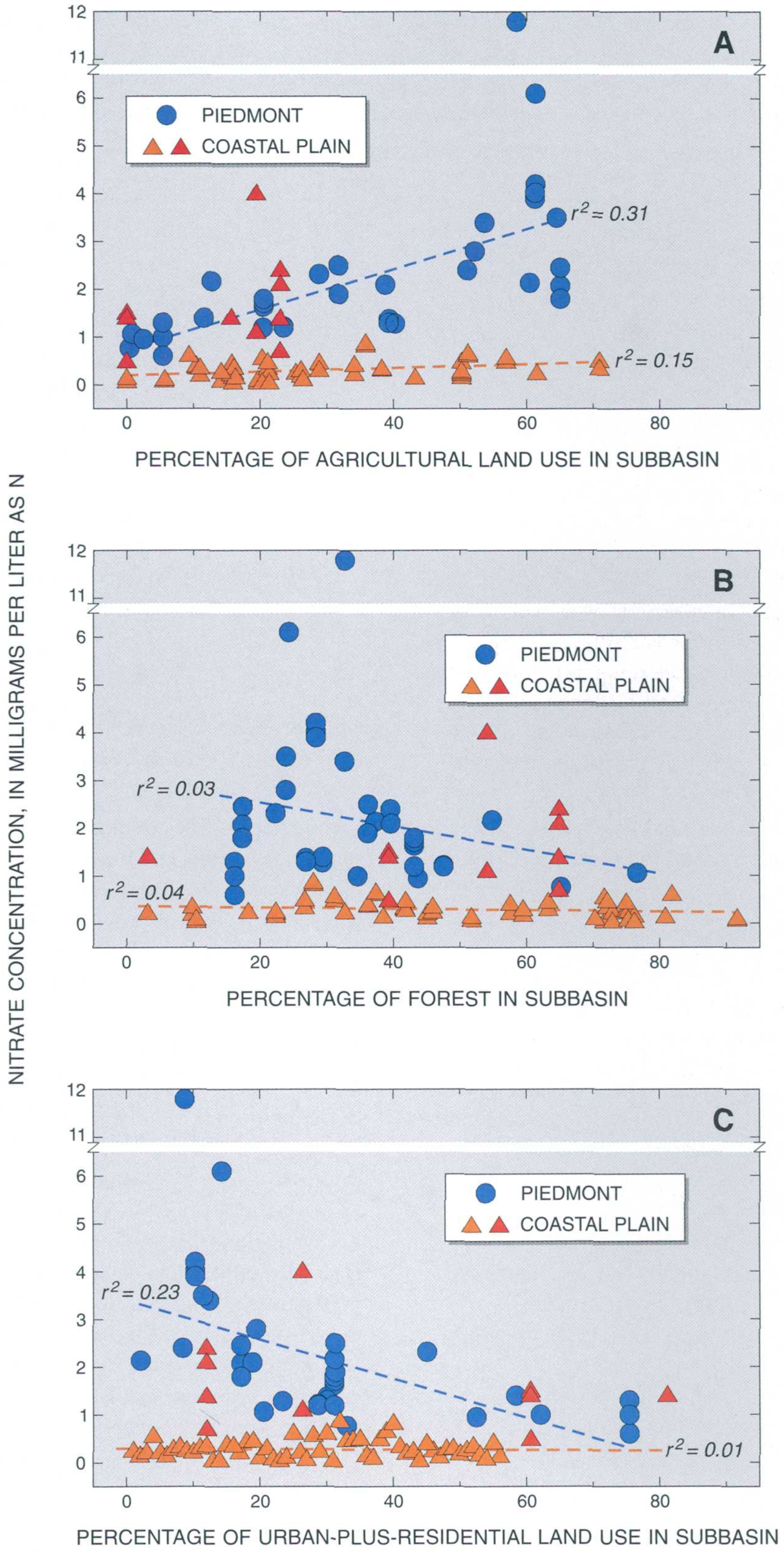


Figure 2. Relation of dissolved nitrate concentrations in stream base flow to percentage of (**A**) agricultural land, (**B**) forest, and (**C**) urban and residential land in each subbasin. *[Red triangles represent Coastal Plain sites at Full Mill Branch, Killpeck Creek, and Lewis Creek (locations shown in figure 1a); nitrate concentrations at these sites are higher than other Coastal Plain sites and lie on the trend for the Piedmont sites.]*

no decrease in nitrate concentration. Water that discharges from a sandy surficial aquifer as stream base flow or directly to tidal tributaries will have virtually the same nitrate concentration as it did when it recharged the saturated zone. In contrast, ground water that contacts or flows through marine silts that contain abundant reduced compounds or sediments that are rich in organic matter should show a significant decrease in nitrate because of denitrification.

Sufficiently detailed geologic and hydrologic data are not available to evaluate the hypothesized relationship between the lithology (sediment type) of the surficial aquifer and the chemistry of ground water and stream base flow in the Patuxent River Basin; therefore, this report describes the general characteristics of the hydrogeologic setting that lend themselves to denitrification. McCartan and others (1998) developed a similar approach for exploring the relation between rock type and streamwater quality regionally for the Maryland and Virginia sections of the Chesapeake Bay watershed. Their evaluation included the consolidated rocks of the Piedmont and Appalachian Provinces as well as the unconsolidated sediments of the Coastal Plain. Their classification organized mapped rock units into "lithogeochemical units" based on similar chemical characteristics; for example, the "resistate" group includes rocks composed primarily of quartz, feldspar, and light-colored clays (such as kaolinite) that have little chemical reactivity. They found that two critical processes associated with streamwater quality, acid neutralization and removal of dissolved nitrate, correlated strongly with rock type in the watersheds of selected stream reaches. On a regional scale, streams flowing through areas with rocks that have abundant organic carbon and/or sulfide ("carbonaceous–sulfidic" rocks) have low nitrate concentrations; McCartan and others (1998) inferred that the nitrate was removed by chemical reactivity (denitrification) with the reduced components of the rock.

The diagrams in figure 3 depict ground-water flow through a surficial aquifer of coarse sands and gravels overlying a marine silt. The valley cross sections represent a small, low-order stream high on the upland near the drainage divide (section X–X′); a middle reach of the stream (section Y–Y′); and a deeply incised lower reach that has cut into the silt layer (section Z–Z′). The subsurface silt layer is much less permeable than the overlying gravel and is more chemically reactive. The physical boundary between the silt and the gravel is both a hydrologic and a chemical (redox) boundary. Nitrate transported by ground water along flow paths that intersect the redox boundary will be chemically reduced to N_2 (gas).

The concentration of nitrate in ground water discharging to the stream is controlled by the source (or input) and any consumption or dilution along the way. In section X–X′, most of the flow paths through the surficial aquifer pass through only the gravels, without contacting the silt. Because few flow paths contact the marine silt, there is little denitrification, and nitrate concentrations reflect those of the sources.

In section Y–Y′, the deeper flow paths intersect the top of the silt. Because of the permeability contrast, ground water will tend to flow laterally across this boundary with some infiltration into the silt. In this setting, a small fraction of the total volume of water discharged to the stream will have undergone denitrification; however, the nitrate transported along the shallow flow paths will not be affected. The stream in section Y–Y′ will also receive a small volume of old water from long, deep flow paths through the marine silt; this water should have virtually no nitrate.

In section Z–Z′, the top of the silt is closer to the land surface and the stream valley has cut down into the silt layer. The deeper flow paths carry ground water into the silt, and many of the intermediate flow paths intersect the top of the silt. Only the shallow flow paths close to the stream flow exclusively through the gravel. In this setting, a significant percentage of the total volume of ground water discharging to the stream may undergo denitrification. In an extreme case, which is not depicted in figure 3, the marine silt would be exposed at the land surface.

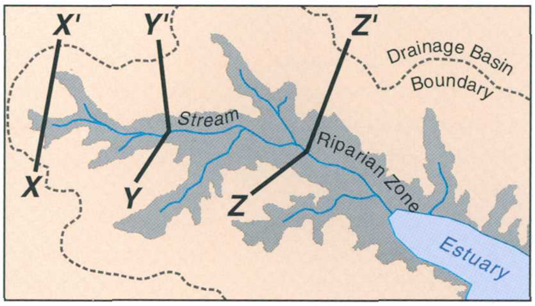
Hydrogeologic Setting of the Patuxent River Basin

The hydrogeologic framework of the Patuxent River Basin and the Coastal Plain in Southern Maryland is the physical system through which ground water flows to discharge into the streams and estuaries. The distribution of the types and chemical properties of the sediments, and the flow paths that the ground water takes through those sediments, are controlled by the regional stratigraphy. The geologic setting and history are described in this section and related to the hydrostratigraphy of the surficial aquifer and the regional confined aquifers with the purpose of explaining where in the system denitrification may occur.

Geologic Setting and History

The head of the Patuxent River drainage is in the central Maryland Piedmont west of the Fall Line. The river crosses the Inner and Middle Coastal Plain of Southern Maryland and intersects the Chesapeake Bay near Solomons Island. Along this course, the river valley cuts into the igneous and metamorphic crystalline rocks of the Piedmont and the unconsolidated sediments of the Coastal Plain.

The crystalline basement rocks dip steeply toward the southeast. These rocks are exposed at the land surface west of the Fall Line, and dip to 3,000 ft below land surface at the mouth of the Patuxent River. The overlying wedge of Coastal Plain sediments also thickens to the southeast because of the regional dip of the basement rocks, with progressively younger units exposed away from the Fall Line.



- **Section X-X'** cuts across a first-order stream high on the upland, with a thick sequence of sand and gravel overlying a marine silt. The top of the silt is a redox boundary, and ground water contacting the silt will undergo denitrification. In section X-X', a relatively small percentage of the total volume of ground water flowing through the surficial aquifer contacts the marine silt.
- **Section Y-Y'** crosses a middle reach of the stream where the valley has cut deeper into the upland gravel. The deep flow paths and some of the intermediate flow paths intersect the redox boundary at the top of the silt.
- **Section Z-Z'** is lower in the drainage basin with a broad and deeply incised valley that cuts into the marine silt. All but the shortest and shallowest flow paths contact the silt, and a large percentage of the ground water in the surficial aquifer may undergo denitrification before discharging to the stream.

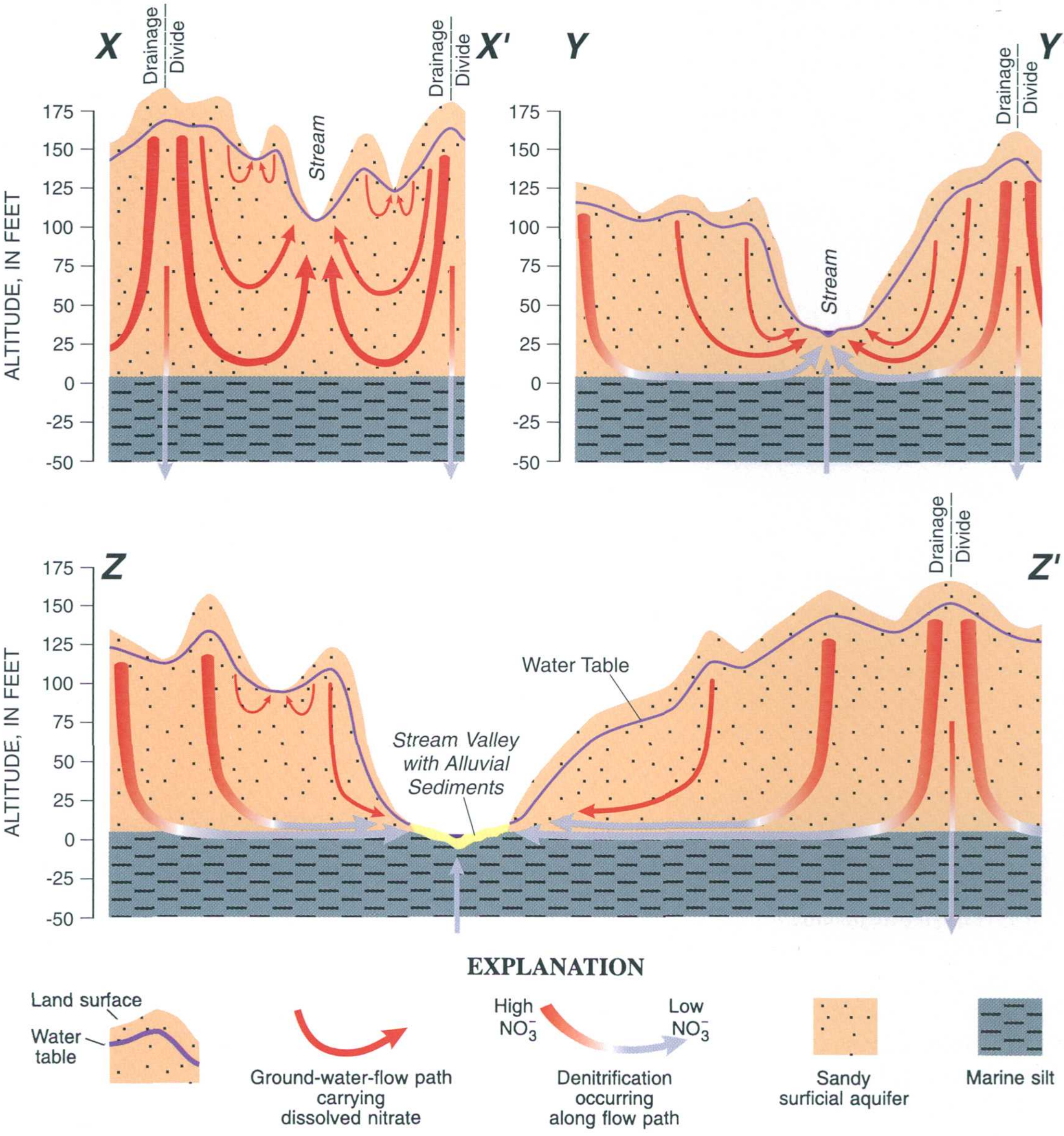


Figure 3. Ground-water flow transporting dissolved nitrate through the surficial aquifer, with denitrification at a redox-active boundary in the subsurface.

Table 3. *Geologic age and depositional environments of sedimentary units in the Coastal Plain of the Patuxent River Basin, Maryland*

[Years before present are rounded and do not imply deposition during entire period; ka = 1,000 years (kilo annum); Ma = 1 million years (mega annum)]

STRATIGRAPHIC UNIT (S)	GEOLOGIC AGE	YEARS BEFORE PRESENT	DEPOSITIONAL ENVIRONMENT/ DOMINANT SEDIMENT TYPE
Holocene and Modern estuarine sediments	Holocene	0-10 ka	Transition from fluvial sands to estuarine sandy silts and organic-rich muds with sea-level rise.
Lowland Deposits [A]	Pleistocene	100 ka to 1.5 Ma	Estuarine muddy sands and sandy silts deposited during interglacial high stands of sea level.
Upland Gravels	Late Miocene and Pliocene	1.5-10 Ma	Extensive deposition of fluvial coarse sands and gravels overlain by silts from the ancestral Potomac River.
Chesapeake Group—*Includes St. Marys, Choptank, and Calvert Formations*	Middle Miocene	11-17 Ma	Marine silts and marginal marine silty sands deposited on the inner continental shelf.
Pamunkey Group—*Includes Piney Point, Nanjemoy, Marlboro Clay, and Aquia Formations*	Early Tertiary Paleocene and Eocene	35-65 Ma	Glauconitic marine sands with beds of silt-clay deposited on the inner to middle continental shelf.
Magothy, Matawan, and Monmouth Formations	Late Cretaceous	65-85 Ma	Marine sands and silty sands deposited in near-shore and inner-shelf environments.
Potomac Group	"Middle" Cretaceous [B]	85-110 Ma	Complexly interbedded fluvial-deltaic channel sands and gravels with silt and clay overbank deposits.

[A] As used by Glaser (1971); see McCartàn (1989a, b) for descriptions of mapped Pleistocene units.

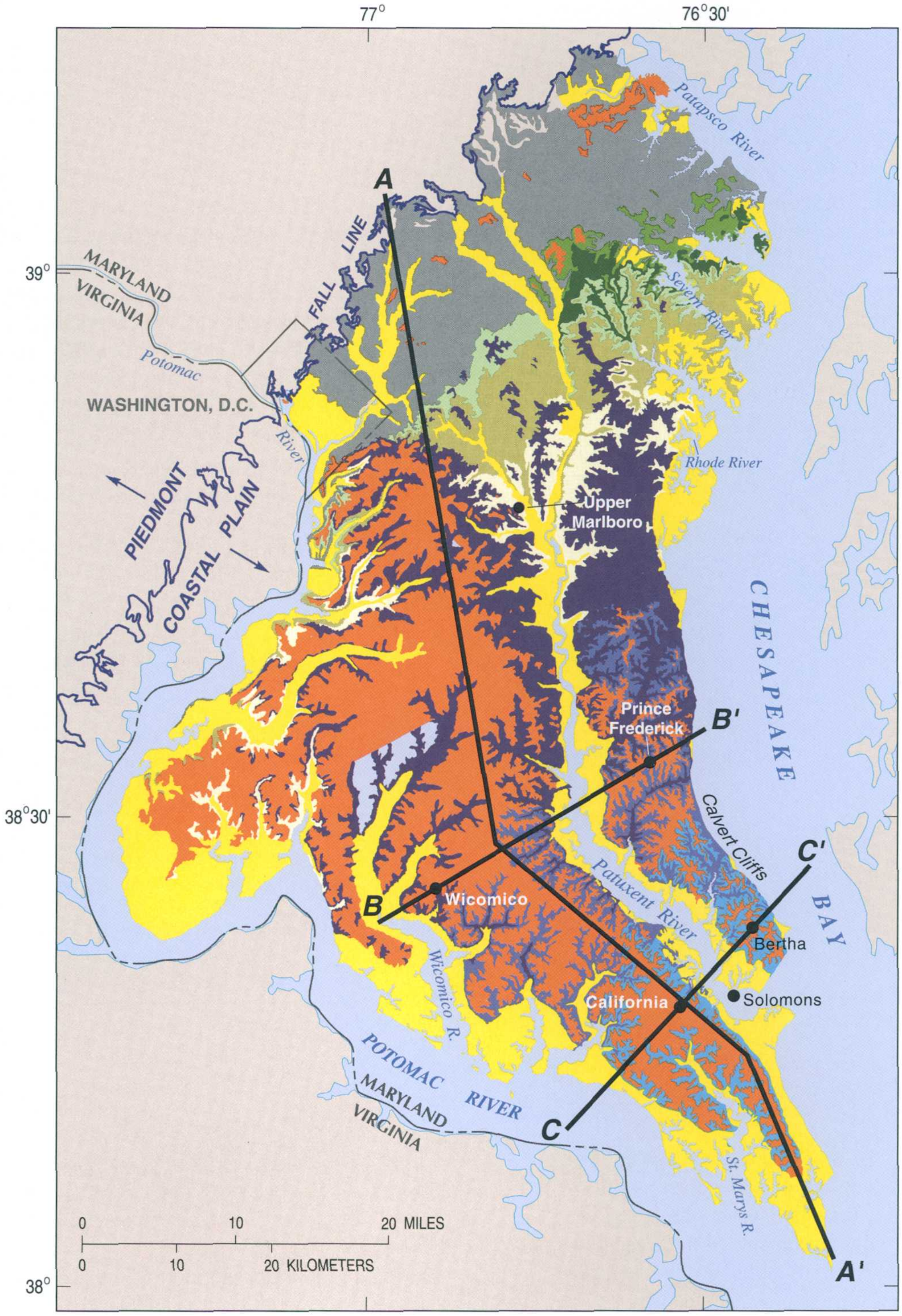
[B] "Middle" refers to the late part of the early Cretaceous and early part of the late Cretaceous.

The Coastal Plain sediments range in age from the late part of the early Cretaceous (approximately 110 million years ago) to Holocene (the past 10,000 years), and were deposited in a variety of environments from fluvial (riverine) to marine (table 3). Each stratigraphic group represents several formations that were deposited in similar environments during a particular time interval.

The oldest sediments in the Coastal Plain are the fluvial sands and deltaic and flood-plain silts of the Cretaceous Potomac Group (Glaser, 1971). This thick sequence directly overlies the basement rocks and is exposed at the land surface in a wide band along the innermost Coastal Plain (fig. 4). Over time, the continental margin subsided and marine flooding extended farther inland. The marine sands and silty sands of the upper Cretaceous Magothy, Matawan, and Monmouth Formations and the lower Tertiary Pamunkey Group were deposited in a continental shelf setting; many of these units contain abundant glauconite. A prominent cycle of sea-level highstands during the middle Miocene deposited the marine silts and sandy silts of the Chesapeake Group in a basin that covers much of Southern Maryland. These fossil-rich sediments are exposed in the Calvert Cliffs.

During the late Miocene and early Pliocene, the ancestral Potomac River migrated across the Southern Maryland Coastal Plain and spread a thick (10–50 ft) sheet of coarse channel sands and gravels overlain by 10–15 ft of flood-plain silts (Hack, 1955; Schlee, 1957). These Upland Gravels cap much of the higher ground in the Coastal Plain of the Patuxent River Basin; in many places, however, the upper silty unit has been removed by erosion.

From the late Pliocene through the Pleistocene, large-amplitude sea-level cycles driven by the growth and decay of continental ice sheets caused the rivers to cut deep, V-shaped valleys during sea-level lowstands that were flooded during highstands to form tidal estuaries. During the sea-level rise of each cycle, coarse sediments were deposited to partially fill the valley. At the peak of each highstand, organic-rich



EXPLANATION

COASTAL PLAIN STRATIGRAPHIC UNITS

- 🟨 Pleistocene Lowland Deposits
- 🟧 Upper Miocene and Pliocene Upland Gravels
- 🟦 Middle Miocene St. Marys Formation
- 🟪 Middle Miocene Choptank Formation
- ⬛ Middle Miocene Calvert Formation
- ⬜ Eocene Nanjemoy Formation
- 🟫 Paleocene Aquia Formation
- 🟩 Upper Cretaceous Monmouth Formation
- 🟩 Upper Cretaceous Matawan Formation
- 🟩 Upper Cretaceous Magothy Formation
- ▩ Lower Cretaceous Potomac Group (Fluvial)

Figure 4. Surficial geology of Southern Maryland [modified from the Geologic Map of Maryland (Cleaves and others, 1968)]. *(Transects of cross sections are shown in figures 5 and 6.)*

silts, sandy silts, and silt-clays were deposited throughout the estuary. This cycle of downcutting, flooding, and infilling of the estuary occurred repeatedly during the Pleistocene to create a series of stair-step terraces and scarps (the eroded banks and shorelines) along the margins of the Patuxent River valley. The associated estuarine sedimentary units are the "Lowland Deposits," as used by Glaser (1971).

Surficial Geology

The Upland Gravels cap most of the peninsula between the Patuxent and Potomac Rivers (fig. 4), but are thinner and less extensive east of the Patuxent River in Calvert County. Older marine sediments underlying the Upland Gravels are exposed in the bluffs along the Patuxent River and stream banks. Where the Upland Gravels were originally thin and/or have been subsequently removed by erosion, the marine units are exposed over broad areas of the land surface, such as the extensive outcrop of the Calvert Formation in northern Calvert and southern Anne Arundel Counties.

As shown on the geologic map (fig. 4) and the stratigraphic dip section (fig. 5), progressively older Tertiary marine sediments are exposed or lie directly beneath the Upland Gravels moving from the Chesapeake Bay toward the Fall Line. From southeast to northwest along transect A–A′ (fig. 4), these outcropping or subcropping units are as follows: (1) the St. Marys, Choptank, and Calvert Formations of the Chesapeake Group; (2) the Nanjemoy, Marlboro Clay, and Aquia Formations of the Pamunkey Group; (3) a narrow band of Cretaceous marine sediments of the Monmouth, Matawan, and Magothy Formations; and (4) a wider band of the fluvial Cretaceous Potomac Group.

The Pleistocene Lowland Deposits form a rim around the modern estuaries and tidal tributaries from sea level to altitudes as high as 80 ft. Where these estuarine sediments fill old channels, they are typically 50 to 80 ft thick, but can be 200 ft thick (Otton, 1955; Glaser, 1971); elsewhere, the Lowland Deposits form a thin veneer 5 to 20 ft thick over eroded Tertiary units.

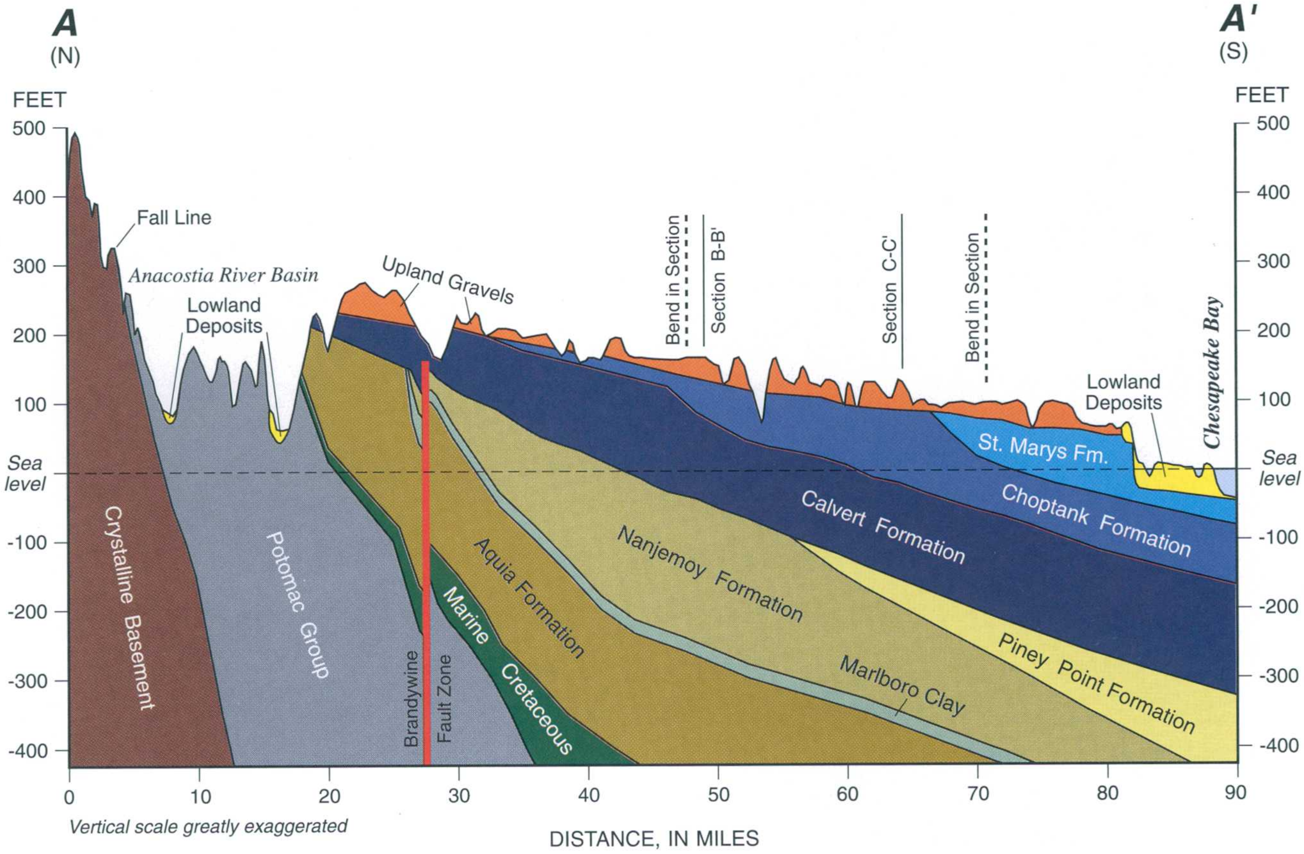


Figure 5. Generalized geologic section from the Fall Line to the Chesapeake Bay approximately along the regional dip. *(Transect line A-A′ shown in figure 4.)*

Hydrostratigraphic Units

Hansen (1996) redefined the hydrogeologic units in Southern Maryland to clarify the relation between the hydrostratigraphic and lithostratigraphic units. Fundamentally, hydrostratigraphic units (aquifers and confining beds) are defined by their water-bearing properties, whereas lithostratigraphic units (groups and formations) are defined by sediment characteristics and bounding surfaces (such as erosional unconformities). Hansen's revision subdivides the lithostratigraphic groups and formations, and places these into specific regional aquifers or confining layers based on hydrologic properties (table 4). In many cases, the boundaries of the aquifers differ from those of the formations. For example, the Piney Point–Nanjemoy aquifer includes not only the sands in the Piney Point and upper Nanjemoy Formations, but also the sands at the base of the overlying Calvert Formation; however, it excludes the fine-grained sediments at the base of the Nanjemoy Formation, which are placed in the Middle Confining Bed.

Hydrostratigraphic Sections

Representative cross sections that show the hydrostratigraphic units in the Patuxent River study area are presented in figures 6a and 6b. These two sections are approximately along strike, that is, perpendicular to the regional dip of the Coastal Plain strata. The Benedict Bridge section (fig. 6a) is farther updip (closer to the Fall Line), than the Solomons Island section (fig. 6b).

The general stratigraphic sequence can be explained using borehole 2 (StM–Bb4) in figure 6a as a reference. The glauconitic sands of the upper part of the Aquia Formation, which comprise the Aquia aquifer, appear at the base of the section, deeper than 150 ft below sea level. These sands are overlain by the Marlboro Clay and the clayey silts of the lower Nanjemoy Formation that form the Middle Confining Bed described by Hansen (1996). The Piney Point–Nanjemoy aquifer is represented only by the glauconitic sands of the upper Nanjemoy Formation from 95 to 40 ft below sea level; this site is updip of the subsurface pinch-out

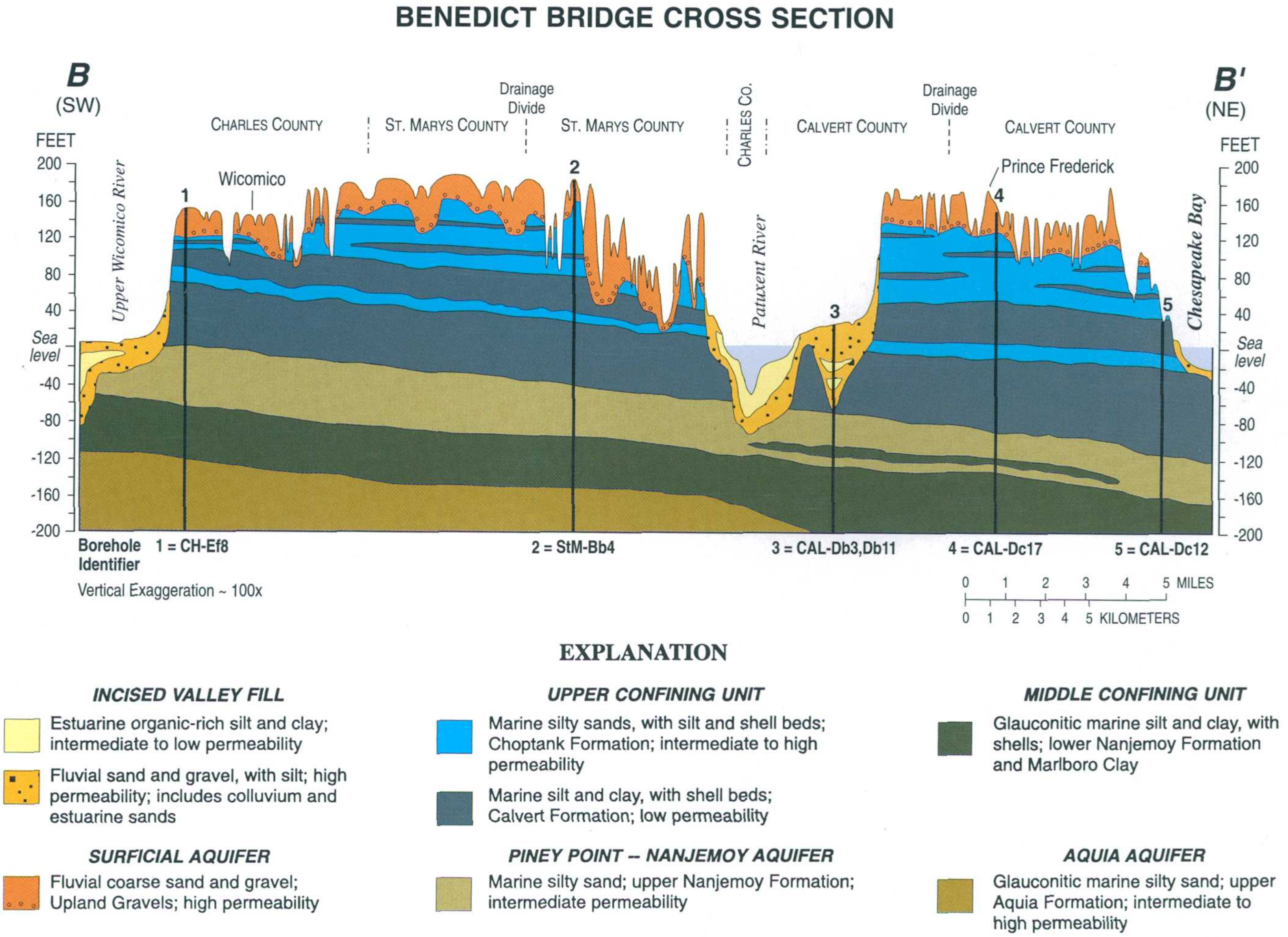


Figure 6a. Hydrostratigraphic section (Benedict Bridge section B-B') through the Middle Coastal Plain of the Patuxent River Basin approximately along the regional strike. *(Transect line B-B' shown in figure 4.)*

of the Piney Point Formation. The silts of the Calvert Formation (40 ft below to 80 ft above sea level) and the sandy, shelly silts of the Choptank Formation (80 to 185 ft above sea level) make up the Upper Confining Bed. Approximately 20 ft of Upland Gravels cap the sequence and form the surficial aquifer along with the more permeable beds in the upper Choptank Formation. The Lowland Deposits fill the valleys cut by the Patuxent River and the larger tributaries, and form a rim around the valley margins. Typically, the valley fill will have a lower section of coarse fluvial sands and gravels covered by finer-grained estuarine deposits.

The Solomons Island section (fig. 6b) differs from the Benedict Bridge section because of the regional dip. The lower Tertiary units (the Aquia and Nanjemoy Formations and the Marlboro Clay) are much deeper. The uppermost part of the Piney Point–Nanjemoy aquifer, which is comprised of the Piney Point Formation and sands of the lower Calvert Formation, appears in the section deeper than 150 ft below sea level. The Upper Confining Bed is represented here by a thicker sequence of the Calvert and Choptank Formations, with the addition of the St. Marys Formation. Sandy beds in the upper part of the St. Marys Formation and the Eastover Formation combine with the Upland Gravels to form the surficial aquifer, which is commonly 70 to 90 ft thick.

Toward the Fall Line from the Benedict Bridge section, the wedge of Chesapeake Group sediments thins and becomes sandier, which lessens its effectiveness as a confining unit. The Aquia and Piney Point–Nanjemoy aquifers, which are confined downdip, rise in altitude to crop out or subcrop shallowly in the vicinity of Upper Marlboro and Bowie, Maryland.

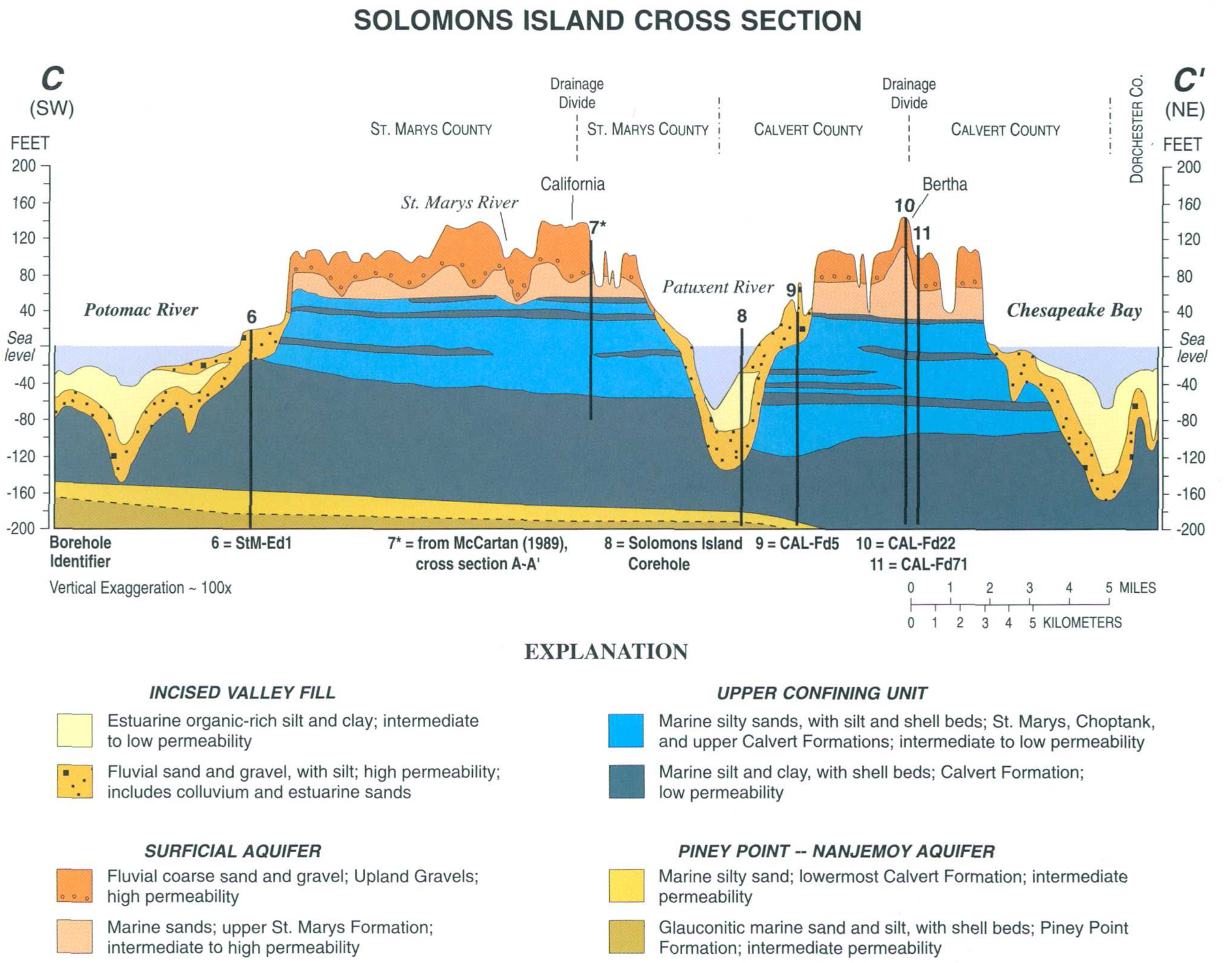


Figure 6b. Hydrostratigraphic section (Solomons Island section C-C') through the Middle Coastal Plain of the Patuxent River Basin approximately along the regional strike. *(Transect line C-C' shown in figure 4.)*

Table 4. *Hydrostratigraphic units in Southern Maryland in vertical position from shallowest (surficial aquifer) to deepest (Cretaceous units)*

[The Cretaceous Potomac Group overlies crystalline basement throughout the study area. Stratigraphy modified from Hansen (1996).]

HYDROSTRATIGRAPHIC UNIT	LITHOSTRATIGRAPHIC UNIT (S)	GEOLOGIC AGE
Surficial Aquifer	Lowland Deposits	Pleistocene to Holocene
	Upland Gravels	Late Miocene to Pliocene
	Sands in the upper Chesapeake Group [A]	Middle Miocene
Upper Confining Bed	Marine silts of the Chesapeake Group—St. Marys, Choptank, and Calvert Formations	
	Sands in lower Calvert Formation	
Piney Point–Nanjemoy Aquifer	Glauconitic sands of the Piney Point and upper Nanjemoy Formations	Eocene
Middle Confining Bed	Silts and clays in lower Nanjemoy Formation	
	Marlboro Clay	Latest Paleocene
Aquia Aquifer	Glauconitic sands of the Aquia Formation	Late Paleocene
Lower Confining Bed	Silty fine sands in lower Aquia Formation	
	Brightseat Formation and underlying fine-grained Cretaceous units	Early Paleocene
Cretaceous Units	Not specifically addressed by Hansen (1996). Includes the marine Magothy, Matawan, and Monmouth Formations and the fluvial Potomac Group.	Early to Late Cretaceous

[A] For example, the North Keys sand reported by Hack (1955); also, the upper beds of the St. Marys and Choptank Formations are commonly sandy and shelly.

Potential for Denitrification in Ground Water

Sediments with abundant reduced compounds—such as organic carbon, pyrite, or glauconite—act as an effective substrate for bacterially mediated chemical reduction and denitrification of nitrate dissolved in ground water. Sediments composed primarily of minerals that are resistant to dissolution and chemical reactivity—such as quartz grains in beach sands, and extensively weathered sediments—have little redox potential. In the case of weathering, reduced compounds and unstable minerals are chemically altered to hydrated and oxidized forms that are generally unreactive, such as the clay mineral kaolinite.

Evidence of Denitrification from Previous Studies

The process of denitrification of ground-water nitrate by interaction with fine-grained glauconitic marine sediments has been demonstrated at two Coastal Plain sites in Maryland. Böhlke and Denver (1995) compared the chemistry of ground water discharging to two first-order streams in Kent County, Maryland. They inferred from analyses of dissolved gases and nitrogen isotopes that the observed decrease in nitrate concentrations of ground water discharging to Morgan Creek was caused by denitrification where flow paths intersected the shallow subcrop of a clay-rich glauconitic fine sand at the base of the Aquia Formation. Subsequent observations of cores recovered from this area show an abrupt redox transition within the uppermost 1–2 ft of the clay-rich bed; it is likely that denitrification occurs in this narrow interval.

O'Connell and others (1997) had similar results from the drainage basin of a first-order tributary of the Rhode River in Anne Arundel County, Maryland; their site is close to the drainage divide with the Patuxent River watershed. Analyses of closely spaced vertical samples of ground water showed that oxygen reduction and denitrification occurred in a mottled transition zone at the top of a fine-grained glauconitic bed in the Nanjemoy Formation. Nitrate concentrations also decreased significantly in ground water flowing through Pleistocene estuarine sediments that are equivalent to the Lowland Deposits in the Patuxent River Basin.

Potential for Denitrification in the Coastal Plain of Southern Maryland

The characteristics of the Coastal Plain sediments in the Patuxent River Basin allow a qualitative assessment of their potential for chemical reduction and denitrification of ground water (table 5). The map of denitrification potential shown in figure 7 is based on the distribution and composition of sedimentary units mapped in Southern Maryland. It should be noted that this interpretation could not be verified because of a general lack of geochemical data from shallow wells in the Patuxent River Basin.

The Upland Gravels are composed primarily of chemically resistant minerals (such as quartz and chert) and are deeply weathered and highly permeable. These sediments should have little capacity for denitrification. The marine sands of the regional aquifers may have a slight potential for denitrification; those units with abundant glauconite have a significant ion-exchange capacity (Otton, 1955; Chapelle and Drummond, 1983), but it is not clear whether the rate of dissolution of glauconite in these sands is rapid enough to release sufficient ferrous iron to consume nitrate.

Table 5. *Geologic units in the Coastal Plain of Southern Maryland, their characteristics, and potential for denitrification of ground-water nitrate*

[Derived from Coastal Plain geologic units mapped and described by Cleaves and others (1968); Hansen (1968); Glaser (1971); McCartan (1989a, 1989b); McCartan and others (1995), and Hansen (1996)]

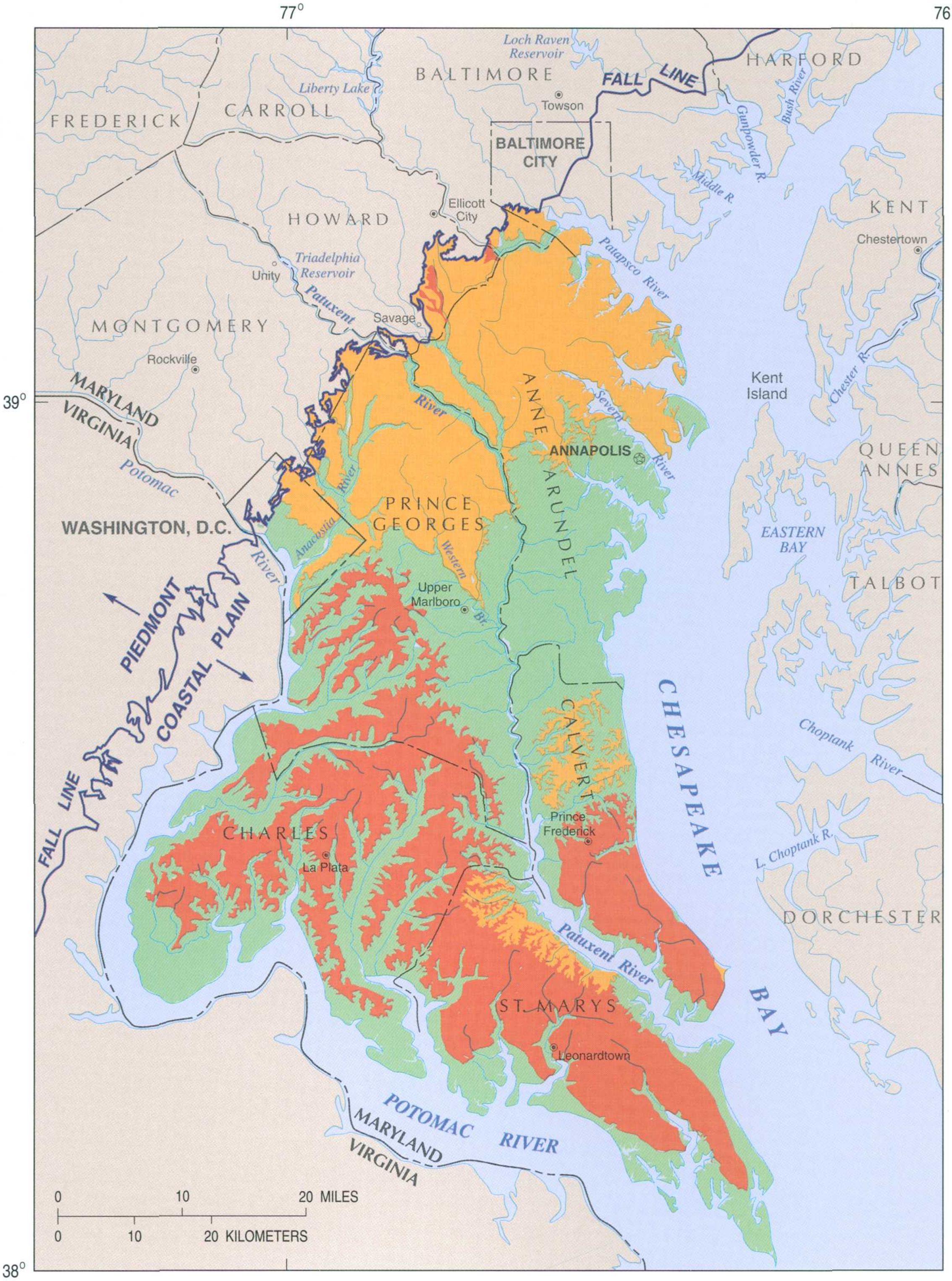
EXPLANATION FOR CATEGORIES OF DENITRIFICATION POTENTIAL

HIGH–sediments in the surficial aquifer have abundant reduced compounds that may react chemically to decrease ground-water nitrate concentrations.

LOW–sediments in the surficial aquifer are unreactive and will not affect ground-water nitrate concentrations.

INTERMEDIATE–applied to geologic units with mixed and variable sediment type; individual beds may have a high denitrification potential, but the unit may be composed mostly of sediments with a low denitrification potential.

GEOLOGIC UNIT (S)	DEPOSITIONAL ENVIRONMENT	SEDIMENT TYPE	DENITRIFICATION POTENTIAL
Holocene estuarine sediments	Fluvial to estuarine	Sandy silts to organic-rich muds with pyrite; moderate to low permeability.	**HIGH**
Lowland Deposits	Estuarine	Muddy sands to sandy silts with organic matter and pyrite; moderate to low permeability.	**HIGH**
Upland Gravels	Fluvial	Coarse sands and gravels, primarily quartz and chert; weathered and oxidized; very high permeability.	**LOW**
Chesapeake Group—*Includes St. Marys, Choptank, and Calvert Formations*	Marine (inner shelf)	Silt to silty sand, variable amounts of glauconite and pyrite; may have sandy, shelly beds; generally low permeability.	**HIGH**; except **LOW** for sandy beds in the upper Choptank and upper St. Marys Formations.
Pamunkey Group—*Includes Piney Point, Nanjemoy, Marlboro Clay, and Aquia Formations*	Marine (inner to middle shelf)	Glauconitic sands with interbedded silts; pyrite common in silts; lower Nanjemoy and lower Aquia primarily silts.	**INTERMEDIATE** (mixed)
Magothy, Monmouth, and Matawan Formations	Marine (nearshore to inner shelf)	Sand and silty sand, variable amounts of glauconite and pyrite; moderate to high permeability.	**INTERMEDIATE**
Potomac Group	Fluvial-deltaic	Sand and gravel interbedded with silt and clay; some pyrite and organic matter; highly variable permeability.	**INTERMEDIATE** (mixed)



EXPLANATION

POTENTIAL FOR DENITRIFICATION IN THE SURFICIAL AQUIFER

🟩 HIGH 🟧 INTERMEDIATE 🟥 LOW

Figure 7. Potential for denitrification of ground water in the surficial aquifer, Coastal Plain of Southern Maryland. *(Areas with low potential for denitrification are most susceptible to nitrate contamination of ground water.)*

In contrast, the regional confining beds typically have abundant reduced compounds and, by definition, low permeability, which impedes ground-water flow and increases reaction time between the ground water and sediments. The Holocene sediments in the modern estuary also have very high redox potential because of high concentrations of organic carbon, pyrite, and other reduced iron compounds; however, the effectiveness of these sediments in natural attenuation of ground-water nitrate depends largely on the specific flow paths of discharge to the estuary. Many of the Lowland Deposits have beds of fine-grained sediments with abundant reduced compounds, and probably have an intermediate to high potential for denitrification. But sandy units within the Lowland Deposits that have high permeability, relatively rapid ground-water flow rates, and low concentrations of reduced compounds may be well oxygenated (Hayes and Bachman, 1996) and would have a low potential for denitrification.

A low potential for denitrification indicates a high susceptibility to nitrate contamination, and vice versa. Accordingly, the color scheme in figure 7 shows areas with low potential for denitrification (high susceptibility) as red, and areas with high potential for denitrification (low susceptibility) as green.

Areas with Low Potential for Denitrification Low-order streams that drain the broad upland between the Patuxent and Potomac Rivers are the most susceptible to contamination from ground-water nitrate discharged from the surficial aquifer. The thick cap of the Upland Gravels has virtually no potential for denitrification after dissolved nitrate has passed through the soil zone.

In southeastern St. Marys County and the southern tip of Calvert County, the Upland Gravels overlie marine sands of the Choptank and St. Marys Formations (fig. 6b); however, the lower sections of both formations have laterally extensive beds of silt that act as confining beds and redox boundaries. Consequently, some denitrification may occur at the base of the surficial aquifer, but the water chemistry of streams in these areas will depend on ground-water flow paths and the geometry and total thickness of the combined stack of gravels overlying the marine sands. These areas are categorized as having a low or intermediate potential for denitrification.

Areas with High Potential for Denitrification Two geologic units that cover a large area in Southern Maryland have a high potential for denitrification. These are the Lowland Deposits and the Calvert Formation (fig. 4). The Lowland Deposits are Pleistocene estuarine sediments that originally contained abundant organic matter and reduced mineral phases. The organic matter may still be preserved in fine-grained sediments, but has mostly been removed from sandier beds by oxidation and ground-water flow (McCartan, 1989a, b). Most of these sediments have abundant reduced iron and sulfide compounds that are redox active.

The Lowland Deposits range in age from approximately 100,000 to 1.5 million years old. The older units of the Lowland Deposits occur at higher elevations (as high as 80 ft), are more deeply weathered, and are more deeply incised by streams than the younger units. Deep weathering removes or chemically alters the reduced compounds that are effective substrates for denitrification. The lower-elevation, younger terraces of the Lowland Deposits have very low relief, with low hydraulic gradients, and are generally poorly drained. Ground water moves slowly through these units, which increases chemical reaction time. These younger deposits generally are not deeply weathered. Because of these differences in age, degree of weathering, and degree of stream incision within the Lowland Deposits, there is probably a gradient of potential for denitrification from high for the younger units to intermediate for the older units.

The marine silts of the Calvert Formation crop out at or near the land surface over a broad area of southern Anne Arundel and northern Calvert Counties. Elsewhere, in Charles and northwestern St. Marys Counties, the Calvert Formation lies directly under the Upland Gravels. Although the Calvert Formation is predominantly a silt, it has some beds of silty fine sand and some with abundant shells. The Calvert Formation becomes sandier updip, toward the northwest, reflecting a shallower shelf environment.

Areas with Intermediate Potential for Denitrification Many of the geologic units in Southern Maryland are classified between the two extremes of high and low denitrification potential. In some cases, individual beds or sections of a formation may have sediments with high redox reactivity, but the formation as a whole may have a mixed sediment type and is therefore categorized as having an intermediate potential for denitrification. For example, the lower section of the Nanjemoy Formation (the Potapaco Member), which is part of the Middle Confining Bed (Hansen, 1996), is a silt deposited in a pro-delta environment and should be redox active. In contrast, the upper section of the Nanjemoy Formation (the Woodstock Member) is a glauconitic shelf sand that is part of the Piney Point–Nanjemoy aquifer, and should have a relatively lower potential for denitrification. Generally, the individual beds within Coastal Plain formations have not been mapped in sufficient detail to accurately represent their distribution in figure 7.

Other geologic units, such as the Potomac Group, have complex bedding with a wide range of lithologies. These units can only be described as mixed sediment type and assigned an intermediate denitrification potential.

Summary

The chemistry of stream base flow corresponds closely to the chemistry of ground water in a surficial aquifer that discharges to the stream. In the Patuxent River Basin in Maryland, the most significant factors related to dissolved nitrate concentrations in stream base flow are physiographic province (Piedmont versus Coastal Plain) and land use. The highest nitrate concentrations are found consistently in Piedmont watersheds and in areas of agricultural land.

The type and distribution of sediments in the Coastal Plain may affect the natural attenuation of ground-water nitrate. A hypothesis is presented that in areas with marine silts exposed at the land surface or present in the shallow subsurface, base-flow nitrate concentrations will be low because of denitrification. Conversely, in areas where the surficial aquifer is a thick sequence of sand and gravel, the potential for denitrification of ground water will be low and base-flow nitrate concentrations will be higher.

Fine-grained marine and estuarine sediments commonly have abundant organic carbon and chemically reduced iron and sulfur compounds. The reduced compounds are an effective substrate for denitrification by the chemical reduction of nitrate (NO_3^-) to nitrogen gas (N_2). Nitrate may also react with some iron aluminosilicates, such as the clay mineral glauconite, which is abundant in many of the upper Cretaceous and lower Tertiary marine sediments in Southern Maryland. Sands and gravels composed of chemically resistant minerals such as quartz and chert have no reactivity in oxidation-reduction reactions.

Areas of high, intermediate, and low potential for denitrification of ground-water nitrate were identified for the Coastal Plain of Southern Maryland, including the Patuxent River Basin. An interpretive map was derived from the bulk sediment characteristics and distribution of the stratigraphic units in the Geologic Map of Maryland.

Areas capped by the Upland Gravels, a sequence of fluvial sands and gravels up to 50 ft thick, are classified as having a low potential for denitrification. A large area underlain by the estuarine sediments of the Lowland Deposits and the marine silts of the Calvert Formation are categorized as having a high potential for denitrification. The chemical characteristics of water in formations with mixed sediment types lie between the two extremes and these formations are assigned an intermediate potential for denitrification.

These interpretations have not been verified by geochemical and hydrologic investigations, and should be used with caution. Further field study would help to quantify stream base-flow chemistry, the characteristics of the surficial aquifer, and the geochemistry, flow paths and residence times of ground water in order to test the hypothesis of denitrification by Coastal Plain sediments with chemically reduced compounds.

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