GEOCHEMISTRY OF THE NORTHERN ATLANTIC COASTAL PLAIN AQUIFER SYSTEM

REGIONAL AQUIFER-SYSTEM ANALYSIS

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Geochemistry of the Northern Atlantic Coastal Plain Aquifer System

By LEROY L. KNOBEL, FRANCIS H. CHAPELLE, *and* HAROLD MEISLER

REGIONAL AQUIFER-SYSTEM ANALYSIS–
NORTHERN ATLANTIC COASTAL PLAIN

U.S. GEOLOGICAL SURVEY PROFESSIONAL PAPER 1404-L

U.S. DEPARTMENT OF THE INTERIOR
MARCH 3, 1849

1998

U.S. DEPARTMENT OF THE INTERIOR
BRUCE BABBITT, Secretary

U.S. GEOLOGICAL SURVEY
Thomas J. Casadevall, Acting Director

1998

Library of Congress Cataloging in Publications Data

Knobel, LeRoy L.
Geochemistry of the northern Atlantic Coastal Plain aquifer system / by LeRoy L. Knobel, Francis H. Chapelle, and Harold Meisler.
p. cm. — (Regional aquifer-system analysis—northern Atlantic Coastal Plain) (U.S. Geological Survey professional paper ; 1404-L)
Includes bibliographical references.
Supt. of Docs. no. : I19.16:1404-L
1. Water chemistry. 2. Aquifers—Atlantic Coast (U.S.). I. Chapelle, Frank. II. Meisler, Harold. III. Title. IV. Series. V. Series: U.S. Geological Survey professional paper ; 1404-L.
GB857.2.A85K56 1997
551.49'00974—dc20
94-28618
CIP
ISBN 0-607-88577-7

For sale by U.S. Geological Survey, Branch of Information Services
Box 25286, Federal Center
Denver, CO 80225

FOREWORD

THE REGIONAL AQUIFER-SYSTEM ANALYSIS PROGRAM

The RASA Program represents a systematic effort to study a number of the Nation's most important aquifer systems, which, in aggregate, underlie much of the country and which represent an important component of the Nation's total water supply. In general, the boundaries of these studies are identified by the hydrologic extent of each system and, accordingly, transcend the political subdivisions to which investigations have often arbitrarily been limited in the past. The broad objective for each study is to assemble geologic, hydrologic, and geochemical information, to analyze and develop an understanding of the system, and to develop predictive capabilities that will contribute to the effective management of the system. The use of computer simulation is an important element of the RASA studies to develop an understanding of the natural, undisturbed hydrologic system and the changes brought about in it by human activities and to provide a means of predicting the regional effects of future pumping or other stresses.

The final interpretive results of the RASA Program are presented in a series of U.S. Geological Survey Professional Papers that describe the geology, hydrology, and geochemistry of each regional aquifer system. Each study within the RASA Program is assigned a single Professional Paper number beginning with Professional Paper 1400.

Thomas J. Casadevall

Thomas J. Casadevall
Acting Director

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CONVERSION FACTORS AND VERTICAL DATUM

This report contains both metric and U.S. customary units as listed in the left column of the conversion table below.

Multiply	By	To obtain
	Length	
inch (in.)	25.4	millimeter (mm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
centimeter (cm)	0.3937	inch (in.)
	Area	
square mile (mi^2)	2.590	square kilometer (km^2)
	Volume	
gallon (gal)	3.785	liter (L)
milliliter (mL)	0.0338	fluid ounce (fl oz)
liter (L)	1.057	quart (qt)
	Mass	
ton (2,000 pounds)	0.9072	metric ton (1,000 kg)
milligram (mg)	0.000035	ounce avoirdupois (oz avdp)
gram (g)	0.03527	ounce avoirdupois (oz avdp)
	Mass per unit volume	
milliequivalents per liter (meq/L)	0.946	milliequivalents per quart (meq/qt)
millimoles per liter (mmol/L)	0.946	millimoles per quart (mmol/qt)
moles per liter (mol/L)	0.946	moles per quart (mol/qt)
milligrams per liter (mg/L)	0.05841	grains per gallon (gr/gal)
grams per milliliter (g/mL)	58410	grains per gallon (gr/gal)
	Pressure	
atmosphere, standard (atm)	101.3	kilopascal (kPa)
	Transmissivity	
square foot per day (ft^2/day)	0.0929	square meter per day (m^2/day)
	Specific conductance	
microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25°C)	1.0	micromho per centimeter at 25 degrees Celsius (µmho/cm at 25°C)

Temperature.—Both Fahrenheit degrees (°F) and Celsius degrees (°C) are used in this report for temperature. Conversions follow:

temp °F=(1.8 temp °C)+32
temp °C=(temp °F−32)/1.8

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

GEOCHEMISTRY OF THE NORTHERN ATLANTIC COASTAL PLAIN AQUIFER SYSTEM

By LeRoy L. Knobel, Francis H. Chapelle, and Harold Meisler

ABSTRACT

Sediments of the northern Atlantic Coastal Plain compose a complex multiaquifer flow system. On a large scale (greater than 500 square miles), ground water in this system evolves from predominantly calcium magnesium bicarbonate water with low dissolved-solids content and low pH, near outcrop-recharge areas, to predominantly sodium bicarbonate water with high dissolved-solids content and high pH, downgradient. This sodium bicarbonate water grades into a sodium chloride water. This large-scale, predictable progression of hydrochemical facies results from the summation of many smaller scale geochemical processes that depend chiefly on the sedimentary depositional environments of the aquifers. Nonmarine sediments contain predominantly quartz, feldspars, clay minerals, and grain-coating ferric oxyhydroxides deposited in freshwater, fluvial environments. The evolution of water chemistry in these sediments is characterized by dissolution of silicate minerals and by redistribution of iron by oxidation-reduction processes. Marine sediments contain carbonate shell material and authigenic clay minerals deposited in estuarine or marginal marine environments. The evolution of water chemistry in these sediments is dominated by carbonate dissolution-precipitation reactions and by cation exchange on the surfaces of marine clay. In both types of sediments, these reactions appear to be driven by local production of carbon dioxide. The metabolism of viable heterotrophic bacteria, which are present in numbers ranging up to 10^6 cells per gram, is a likely source of carbon dioxide production (10^{-6} to 10^{-3} millimoles per liter per year) in deep aquifers.

Remarkably similar patterns of hydrochemical facies are found in both nonmarine and marine deposits. This similarity implies that, although the chemical processes that take place in nonmarine aquifers (silicate hydrolysis) and marine aquifers (carbonate-mineral reactions) are dissimilar, when coupled with ion exchange, these processes can result in similar hydrochemical facies.

The surficial aquifer that mantles most of the study area is characterized by high rates of recharge and discharge and by relatively short flow paths. Many small-scale flow systems have developed in which water chemistry is controlled mainly by the marine or nonmarine nature of the sediments. Because of its proximity to land surface, water from the surficial aquifer locally has been affected by human activities. Nitrate contamination of this aquifer by animal wastes, effluent from septic systems, and land application of inorganic fertilizers is present in some areas.

A number of chemical processes occur in the saltwater-freshwater transition zone, including reverse ion exchange (sodium replacing calcium on exchange sites) and calcite precipitation. These processes progressively enrich ground water in calcium relative to seawater and deplete water in dissolved inorganic carbon.

INTRODUCTION

The northern Atlantic Coastal Plain aquifer system is a significant ground-water resource. In 1980, approximately 17.6 million people used about 1.4 billion gallons of ground water per day from this system for agricultural, industrial, and public supply purposes. As part of the U.S. Geological Survey's (USGS) Regional Aquifer-System Analysis Program (see Foreword), a comprehensive study of the geology, hydrology, and geochemistry of this aquifer system was initiated in 1979 (Meisler, 1980). The findings of this study are presented in USGS Professional Paper 1404, chapters A–M. This report (chapter L) describes the geochemistry of the northern Atlantic Coastal Plain aquifers. Other chapters in this professional paper series describe (1) the regional hydrogeologic framework of the aquifer system (Trapp, 1992); (2) the digital computer simulation of regional ground-water flow (Leahy and Martin, 1993); (3) finer scale digital computer simulations of ground-water flow and more detailed hydrogeologic frameworks for New Jersey, Delaware, Maryland, Virginia, and North Carolina (Meng and Harsh, 1988; Zapecza, 1989; Harsh and Laczniak, 1990; Vroblesky and Fleck, 1991; Fleck and Vroblesky, 1996; Winner and Coble, 1996; Giese and others, in press; Martin, in press); and (4) the occurrence and geochemistry of salty ground water (Meisler, 1989). Chapter A of Professional Paper 1404 by Trapp and Meisler (1992) summarizes the overall results and conclusions of the regional study.

The chemical quality of ground water is an important consideration in any assessment of an aquifer system. For an aquifer system to be a reliable economic resource, not only must predictable quantities of water be available, but the water must also be of predictable and suitable chemical composition. To predict the chemical quality of water in the aquifer system requires (1) sufficient water-chemistry data to be able to accurately delineate areal and vertical differences in water composition and (2) an understanding of the geochemical processes that control observed water composition.

PURPOSE AND SCOPE

The purpose of this report is to describe the geochemistry of the northern Atlantic Coastal Plain aquifer system. Specific goals are to define observed water composition in the major water-bearing units of this system and to describe the processes that led to that composition.

In order to accomplish these goals, this report has been organized into four main parts. The first part, a general definition and description of the hydrochemical facies, is designed to show large-scale areal differences of water chemistry in the major hydrologic units. The second part is an overview of the primary controls on the distribution of dissolved constituents in ground water. Scientific literature is identified that describes case studies illustrating some major chemical processes taking place in aquifers in the northern Atlantic Coastal Plain. The third part is an interpretation, again at a large scale, of how chemical processes in different sediment types have combined to produce observed patterns of hydrochemical facies. The fourth part (appendixes A–E) contains smaller scale case studies that illustrate selected chemical processes that modify ground-water composition.

DATA COMPILATION AND ANALYSIS

The first part of this report describes areal changes in ground-water chemistry at a large scale. The description is based on a large body of water-quality data that had been compiled for local studies and data programs that were completed in cooperation with agencies of the individual States. These data have generally been stored in the USGS National Water Data Storage and Retrieval System (WATSTORE). This system contains a computerized data base (Water-Quality File) for storing chemical data collected by Federal, State, and local organizations (Hutchison, 1975). The data base is maintained by the USGS at its National Center in Reston, Va., and is accessible to the general public (Kilpatrick, 1981).

Most of the entries are partial analyses, such as chloride determinations, and therefore cannot be used for areal interpretations of aquifer geochemistry. If an analysis is complete (all ionic species determined) and has no analytical error, then the sum of the meq/L (milliequivalents per liter) of cations should be equal to the sum of the meq/L of anions. In practice, it is not feasible to achieve this level of accuracy; however, the nearness to the standard is a good means of testing the acceptability of an analysis. Hem (1985, p. 164) suggested that the difference between the sum of the cations and the sum of the anions should not exceed 1 or 2 percent of the total of cations plus anions for waters where the total is greater than 5 meq/L. If the total is less than 5 meq/L, then the percentage level of acceptance should be increased. This standard is based on the assumption that all chemical species present in a sample have been accurately determined in the analysis. Because this is rarely the case, the level of acceptance for chemical analyses used in the present study was set at the 5- and 10-percent levels depending upon whether the total of cations plus anions was greater than or less than 5 meq/L. For the purposes of this report, this test is designated "the 5-percent test" for cation-anion balance. Unless otherwise indicated, all analyses used in this report have passed the 5-percent test for cation-anion balance. As part of this study, more than 15,000 chemical analyses were retrieved from WATSTORE. Of these, approximately 3,600 passed the 5-percent test for cation-anion balance and were tabulated by Knobel (1985). Additional data on water-quality, mineralogy, and microbial activity were collected during this study.

PREVIOUS STUDIES

The geochemistry of ground water in the study area has been under investigation for many years. Cederstrom (1943) delineated the areal distribution of Cl^- (chloride) in Virginia. He later expanded his work to include other ions and hypothesized a chemical framework to explain the occurrence of Na^+-HCO_3^- (sodium bicarbonate) water in Virginia (Cederstrom, 1945, 1946a,b). On the basis of a series of laboratory experiments, Foster (1950) proposed an alternative hypothesis to explain similar patterns in the deep aquifers of the Atlantic and Gulf Coastal Plains. Both investigators concluded that carbonate dissolution and ion exchange accounted for the occurrence of sodium bicarbonate water in the aquifers and that an aquifer-generated source of CO_2 (carbon dioxide) was required to account for the large concentrations of HCO_3^- (bicarbonate) observed in the deep aquifers. They disagreed, however, on the source of CO_2. Cederstrom (1945, 1946a,b) maintained that chemical or bacterially mediated sulfate reduction was the CO_2-generating process, whereas Foster (1950) concluded that it reflected progressive elimination of volatile components (carboxyl (COOH) and methyl (CH_3) groups for instance) present in lignitic organic material caused by slow "dynamochemical" changes (inorganic processes acting on lignitic material caused by increased temperature and pressure). Foster's hypothesis was accepted nearly universally, because SO_4^{-2} (sulfate) concentrations in ground water did not decrease as water moved through the aquifer system. Such a decrease would have been evidence of sulfate reduction.

Back (1961) classified hydrochemical facies and presented a method for mapping them based on work in the Atlantic Coastal Plain (Back, 1960). Seaber (1962, 1965) applied this method to the Englishtown Formation in New Jersey, and Back (1966) extended it to include the Coastal Plains of New Jersey, Delaware, Maryland, and Virginia.

Back and Barnes (1961) developed equipment and techniques to measure Eh (electrochemical potentials) in the field and later applied the techniques to the study of iron-rich ground water in southern Maryland (Barnes and Back, 1964). They also related iron content and Eh to ground-water-flow patterns (Back and Barnes, 1965).

Langmuir (1969c) reevaluated Gibbs free energy values for substances in the system Fe-O_2-H_2O-CO_2 and applied his results to the study of iron geochemistry in the Magothy and Raritan Formations in New Jersey (Langmuir, 1969a,b). Schluger and Roberson (1975) related iron content and Eh of ground water to the direction of flow and to the distribution of color variations in clay minerals in the Patapsco Formation, Maryland.

Cushing and others (1973) described and mapped zones of water quality for several aquifers on the Delmarva Peninsula of Delaware, Maryland, and Virginia. They also delineated freshwater and saline-water aquifers on geologic sections and discussed the chemical processes controlling the distribution of dissolved constituents in ground water.

Brown and Silvey (1973, 1977) conducted a study to determine the feasibility of underground storage and retrieval of freshwater in a brackish-water aquifer in Virginia. They concluded that decreases in hydraulic conductivity due to clay dispersion during injection could be minimized by chemical treatment with a solution of polymeric hydroxy aluminum.

Winograd and Farlekas (1974) investigated the problems associated with ^{14}C (carbon-14) dating of ground water from aquifers of deltaic origin in New Jersey. They concluded that CO_2 was being generated within the aquifer system and that apparent ages based on ^{14}C determinations were, therefore, not valid in that system.

Robertson (1979) noted a relation between NO_3^- (nitrate) concentrations and other factors, such as land use and depth to water table, during a reconnaissance study of ground-water quality in an unconfined aquifer in Sussex County, Del. Similar patterns were noted by Denver (1986) in a study of the unconfined aquifer in west-central and southwestern Delaware. She also described the overall water chemistry and discussed the geochemical processes that control it. Ritter and Chirnside (1984) studied NO_3^- concentrations in southern Delaware and related them to land use.

Baedecker and Back (1979a) noted that natural ground water in the vicinity of a landfill in Delaware was low in TDS (dissolved solids content). Leachate from the landfill contained higher TDS, and they attributed this to ion exchange of NH_4^+ (ammonium) ions in the leachate for metal ions on clay minerals. $\delta^{13}C$ (delta carbon-13) values of HCO_3^- in the leachate indicate fractionation during CH_4 (methane) formation. D or ^2H (deuterium) enrichment may be indicative of contamination processes. This work also revealed that chemical processes in landfills are analogous to those that occur in marine sediments (Baedecker and Back, 1979b). In particular, the lateral zonation of C (carbon), N (nitrogen), S (sulfur), O (oxygen), H (hydrogen), Fe (iron), and Mn (manganese) in landfills is similar to the vertical zonation of these species in marine sediments. They also discussed the chemical reactions that account for these sequences.

Spoljaric and Crawford (1979) conducted laboratory column experiments to determine the ability of glauconite to remove metal ions from solution by means of ion exchange reactions. They demonstrated that glauconite is effective at removing trace metals from solution. Wolff (1967), using X-ray and chemical techniques, studied the weathering of glauconite. He concluded that glauconite in outcrop areas of the Aquia Formation in Maryland weathers to form goethite, kaolinite, and dissolved constituents.

Russell and Krug (1980) discussed the controls on iron-ore deposits in the New Jersey Pine Barrens. They suggested that the type of ore deposited is related to soil maturity.

The value of ^3H or T (tritium) as a hydrologic tool for studying recharge to shallow aquifers was tested by Carlston and others (1960). They concluded that a water-table aquifer in New Jersey exhibited a layering of ground water of different ages and that tritium generated by thermonuclear explosions in the atmosphere could be found to a depth of approximately 50 ft, increasing upward from that depth to the water table.

Fusillo and others (1980) discussed the effects of ground-water chemistry as a control on acidity and pH (hydrogen ion activity) in Oyster Creek, N.J. They concluded that Fe^{+2} (ferrous iron) in ground water undergoes oxidation to Fe^{+3} (ferric iron) and hydrolysis to ferric hydroxide when the ground water discharges to the stream, thereby maintaining the pH of Oyster Creek at small values. Bachman (1984) described the distribution of chemical constituents in the Columbia aquifer in Maryland.

Chapelle (1983) described the ground-water geochemistry of the Aquia aquifer in southern Maryland, with emphasis on the carbonate dissolution reactions.

Chapelle and Drummond (1983) expanded this work to include the Piney Point–Nanjemoy aquifer, and Chapelle and Knobel (1983) described the geochemistry of the Aquia aquifer in relation to ion exchange processes.

Chapelle (1984a, 1985) described the distribution of ions and the chemical evolution of ground water in the Patuxent and Patapsco aquifers in the vicinity of Baltimore, Md., with emphasis on iron geochemistry and the effects of chemical microenvironments, mixing of freshwater and brackish water, ion exchange reactions, and silicate hydrolysis. The occurrence of O_2 (dissolved oxygen) and the origin of ferric hydroxide-cemented hardbeds in the Patuxent aquifer, Maryland, were discussed by Chapelle (1984b).

Knobel and Phillips (1988) noted that two types of recharge occur in the Magothy aquifer in Maryland and that differing hydrochemical facies are related to these types of recharge. They also described the geochemical processes that occur in the Magothy aquifer.

Chapelle and Knobel (1985) analyzed the occurrence of stable carbon isotopes in the Aquia aquifer, Maryland, and concluded that an aquifer-generated source of isotopically heavy CO_2 was necessary to account for the $\delta^{13}C$ values observed in Aquia aquifer water and suggested that bacterially mediated processes, such as methanogenesis, were a likely source of the heavy CO_2. Chapelle and others (1987) enumerated bacteria in cores of deep sediments from the Maryland Coastal Plain and demonstrated the potential for CO_2 production in the sediments by methanogenic and sulfate-reducing bacteria. The major geochemical processes occurring in the northern Atlantic Coastal Plain are summarized by Knobel and Chapelle (1986), Knobel and others (1987), and Meisler and others (1988).

The historical development of investigations dealing with salty ground water in the northern Atlantic Coastal Plain was described by Meisler (1989).

ACKNOWLEDGMENTS

The authors acknowledge Harry J. Hansen, David D. Drummond, and John W. Wilson of the Maryland Geological Survey for supplying and interpreting data. Roy C. Lindholm, Frederic R. Siegel, and Anthony G. Coates of The George Washington University helped to interpret data. D. Jay Grimes and Joseph L. Zelibor, Jr., of the University of Maryland characterized the microbial populations of sediment cores, and Gideon C. Okpokwasili, University of Port Harcourt, Nigeria, provided technical assistance with the microscopy. William D. Silvey, deceased, formerly with the USGS, influenced the organization of this study and conducted the early work on saltwater-freshwater relations. Diane M. Roberts, USGS, typed the manuscript and helped with the illustrations.

DESCRIPTION OF THE STUDY AREA

LOCATION AND EXTENT

The northern Atlantic Coastal Plain covers an area of about 50,000 mi^2, extending from the southern boundary of North Carolina northeastward to Long Island Sound, N.Y. It is bounded on the west by the Fall Line—generally defined as the contact between Coastal Plain sedimentary deposits and older predominantly crystalline rocks—and on the east by the Atlantic Ocean (fig. 1). The Coastal Plain is underlain by a wedge-shaped body of primarily unconsolidated sediments that dip gently seaward. The wedge thickens from a featheredge at the Fall Line to 8,000 ft along the Atlantic coast of Maryland near Ocean City and 10,000 ft at Cape Hatteras, N.C.

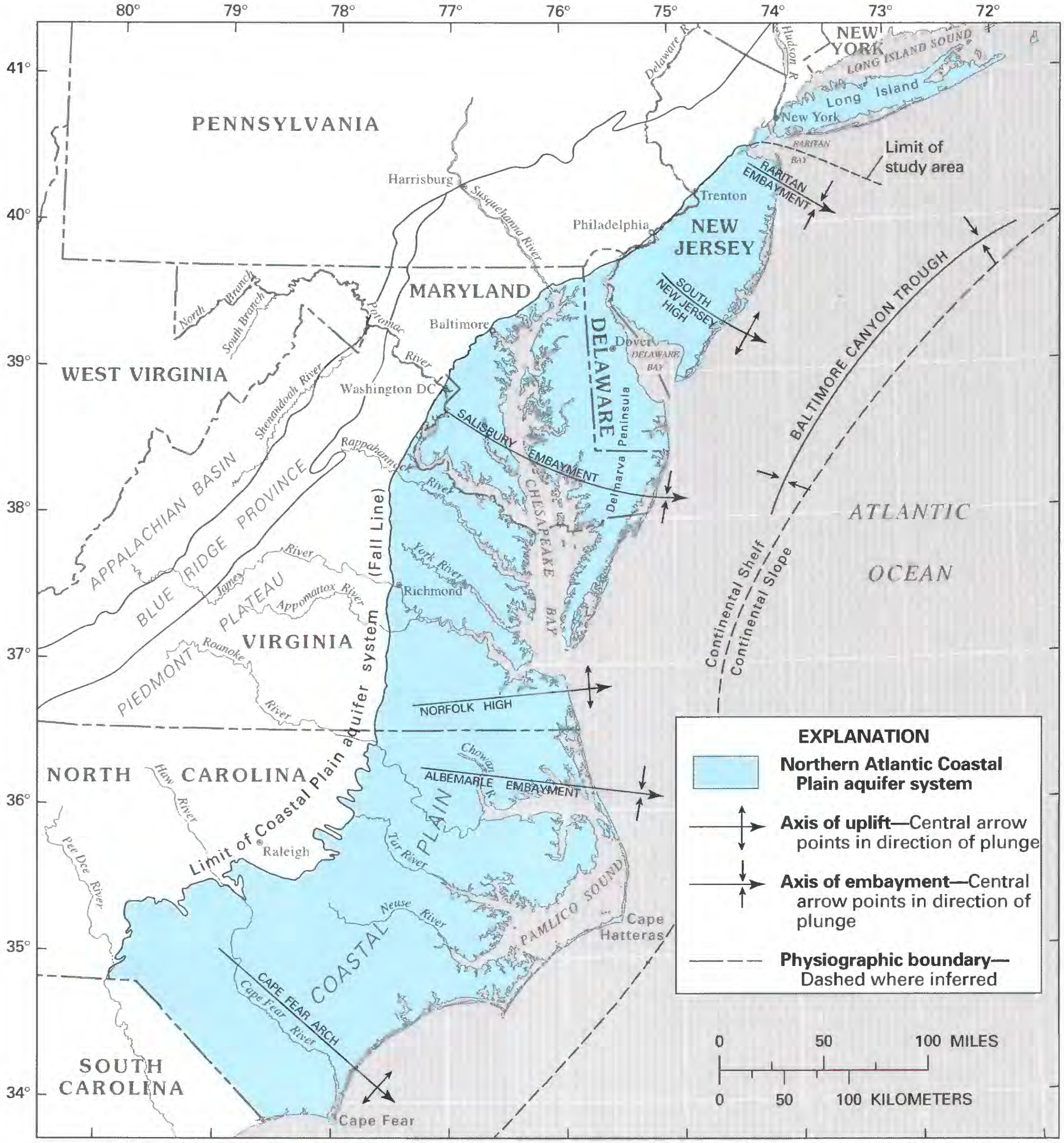
The sedimentary wedge extends offshore, underlying the continental shelf, to the continental slope. The geochemistry of the offshore area has been discussed in previous reports (Meisler and others, 1984; Meisler, 1989) and will not be considered in detail here. Similarly, the geochemistry of the Coastal Plain of Long Island, N.Y., has been extensively studied (Pearson and Friedman, 1970; Ragone and others, 1976; Ragone, 1977; Katz and others, 1978; Kreitler and others, 1978; Porter and others, 1978; Flipse and others, 1984) and is not included in this report. Thus, the study area considered in this report consists of the Coastal Plains of New Jersey, Delaware, Maryland, Virginia, and North Carolina (fig. 1).

PHYSIOGRAPHY

Brief descriptions of the physiography of the northern Atlantic Coastal Plain were given by Trapp and Meisler (1992, p. A5–A6) and Leahy and Martin (1993, p. K5–K6). Altitudes of land surface in the northern Atlantic Coastal Plain range from sea level to more than 700 ft in the study area. The topography varies from extensive, flat, coastal swamps and marshes to rolling uplands (Heath, 1984). The configuration of water levels in an unstressed ground-water flow system is related to physiography (Bredehoeft and others, 1982), which, in turn, is related to the lithology of the sediments and the structural processes that have occurred.

CLIMATE

The distribution of dissolved constituents in ground water is affected by climate (Drever, 1982, p. 197–198). Temperature of shallow ground water is relatively constant and slightly higher than local mean annual air temperature (Todd, 1980, p. 309). Ground-water temperature



Base modified from U.S. Geological Survey digital data, 1:2,000,000, 1972

Positions of structural features adapted from Uchupi (1968), Maher (1971), and Owens and Gohn (1985).

FIGURE 1.—Location of study area in the Atlantic Coastal Plain (modified from Trapp and Meisler, 1992, fig. 1).

is one factor that controls the rates of reaction of various minerals with water. The study area is generally humid with normal annual average air temperatures increasing southward from 53.7°F in New Jersey (U.S. Department of Commerce, 1973a) to 62.3°F in North Carolina (U.S. Department of Commerce, 1973b).

Ground water in the northern Atlantic Coastal Plain is derived largely from precipitation. The normal annual average precipitation ranges from 43.1 in. on the New Jersey Coastal Plain (U.S. Department of Commerce, 1973a) to 50.9 in. on the central Coastal Plain of North Carolina (U.S. Department of Commerce, 1973b).

HYDROGEOLOGY

Sediments underlying the northern Atlantic Coastal Plain form a multilayered aquifer system containing interbedded lenses of sand, silt, clay, gravel, and limestone. In places, the sediments are cemented by authigenic minerals.

Trapp (1992) divided the sedimentary sequence of the aquifer system into eleven regional aquifers separated by nine confining units. The relations among regional aquifers, local hydrogeologic units, and geologic formations are shown in plate 1. Also shown in plate 1 are aquifer numbers used in a three-dimensional model of ground-water flow (Leahy and Martin, 1993). The basis for definition of the aquifers is continuity of permeability. The geographical extent and vertical distribution of aquifers and confining units are depicted by a series of maps (pls. 2–6) and hydrogeologic sections (pls. 7–8), respectively. Also shown in these plates are the hydrochemical facies for each aquifer, which are discussed in this report. The locations of the hydrogeologic sections are shown in plate 7*A*. Trapp (1992) gave a complete description of the regional aquifers and confining units. The descriptions of the aquifers are briefly summarized here.

Surficial aquifer.—The uppermost aquifer throughout its extent in the study area (pl. 2*A*) is composed of mostly unconsolidated marine and nonmarine sand and gravel, which range in age from Miocene to Holocene. The surficial aquifer is unconfined, and its top is the water table, which varies with time. The top of the surficial aquifer, represented in plate 2*A*, is the approximate average altitude of the water table for the period 1980–84 (Trapp, 1992).

Upper Chesapeake aquifer.—The upper Chesapeake aquifer underlies the surficial aquifer and, in places, is hydraulically connected to it. The extent of the aquifer is shown in plate 2*B*; it is predominantly marine in origin. The aquifer consists largely of sand with associated gravel, clay, shells, and lignitic material, which range in age from Miocene to Pliocene (Trapp, 1992). The upper Chesapeake aquifer is commonly confined; however, in outcrop areas, it makes up part of the regional water table.

Lower Chesapeake aquifer.—The lower Chesapeake aquifer is a marine sand that includes diatomaceous material and shell debris in the northern part of the study area and phosphatic material, shells, and local limestone beds in North Carolina (Trapp and Meisler, 1992). In places, the sand layers are separated by silt and clay (Trapp, 1992). The extent of the lower Chesapeake aquifer is shown in plate 3*A*. The sediments are of Oligocene, Miocene, and Pliocene age (Trapp and Meisler, 1992, p. A9). Locally, the aquifer forms part of the regional water table.

Castle Hayne–Piney Point aquifer.—The Castle Hayne–Piney Point aquifer is marine in origin and underlies a large part of the study area (pl. 3*B*). It contains limestone of Oligocene and Eocene age in North Carolina. Throughout the rest of its extent, the Castle Hayne–Piney Point aquifer includes glauconitic sand and shell material with indurated shell beds of Eocene to early Miocene age.

Beaufort–Aquia aquifer.—The Beaufort–Aquia aquifer is a marine aquifer (pl. 4*A*) composed primarily of fossiliferous glauconitic quartz sand with indurated shell beds and sand layers. The aquifer is of Paleocene age.

Peedee–Severn aquifer.—The Peedee–Severn aquifer is the uppermost regional aquifer in the northern Atlantic Coastal Plain composed of Cretaceous sediments. The Peedee–Severn aquifer is absent from Virginia and southern Maryland (pl. 4*B*). The aquifer is marine in origin and is composed of sand with glauconite and shell material. In North Carolina, sand is interbedded with black marine clay and beds of impure limestone.

Black Creek–Matawan aquifer.—The Black Creek–Matawan aquifer is absent from Virginia (pl. 5*A*). In Maryland and Delaware, it is restricted to the northern Delmarva Peninsula and is marine in origin. In New Jersey, it contains marine and deltaic deposits, and, in North Carolina, fluvial and fluviomarine deposits. The marine sediments include glauconite and, in places, are fossiliferous. The aquifer sediments are of Late Cretaceous age.

Magothy aquifer.—The Magothy aquifer does not occur south of Maryland (pl. 5*B*). In Maryland, the sand aquifer is made up of fluvial and marginal-marine deposits of the Magothy Formation of Late Cretaceous age. Vroblesky and Fleck (1991) described the regional aquifer in Maryland and Delaware. In New Jersey, the regional aquifer consists of the upper aquifer of the Potomac–Raritan–Magothy aquifer system (Zapecza, 1989, p. B11–B12). The aquifer includes feldspars and micas (Trapp and others, 1984, tables 3, 13, and 14) and pieces of lignitized wood (Glaser, 1969, p. 35) that are common in fluvial and marginal-marine sediments.

Upper Potomac aquifer.—The upper Potomac aquifer is restricted in its extent to the southern part of the study area (pl. 5*B*). It is primarily marine to marginal marine in origin, and the sediments are of Late Cretaceous age. However, in southern Maryland, it includes nearshore marine sand that Hansen and Wilson (1984, p. 11) identified as Paleocene age. Meng and Harsh (1984, p. 31–33; 1988, p. C41–C42) named equivalent sand beds in northern Virginia the "Brightseat aquifer," and these are also included in the upper Potomac regional aquifer. The local Brightseat aquifer, which is part of the regional upper Potomac aquifer in northern Virginia and southern Maryland, was correlated in some chapters of Professional Paper 1404 with the Paleocene Brightseat Formation. However, later work by USGS paleontologists, as reported by Trapp (1992, p. G28), indicated that the sediments of the Brightseat aquifer were of late Early Cretaceous (Albian) age and therefore were not part of the Brightseat Formation.

In North Carolina, the aquifer is mostly nonfossiliferous. In Virginia, the deeper part of the aquifer is carbonaceous and micaceous. The shallower part, called the Brightseat aquifer in northern Virginia and southern Maryland, is micaceous and includes glauconite, lignite fragments, and sparse shells.

Middle Potomac aquifer.—In North Carolina, the middle Potomac aquifer was deposited under nearshore marine conditions and contains some feldspathic sand and silty clay of continental origin; from Virginia northward to Delaware Bay, it consists of fluvial sand interlensing with silt and clay; in New Jersey, it is fluvial in origin, except for marine beds along the coast (pl. 6*A*). The sediments are Early Cretaceous to Late Cretaceous in age.

Lower Potomac aquifer.—The lower Potomac aquifer is the lowermost aquifer containing freshwater. Its extent is shown in plate 6*B*. It consists mostly of deposits of Early Cretaceous age but may include some beds of Jurassic age. The sediments typically are fluvial and deltaic in origin; however, the lower Potomac includes some marine beds in North Carolina. The proportion of marine beds, including limestone, increases seaward (Winner and Coble, 1996). The sediments typically include feldspar, lignite, and mica.

Material underlying the lower Potomac aquifer.—The lower Potomac aquifer overlies a brine aquifer—the Waste Gate aquifer—on the Delmarva Peninsula (Hansen, 1982, 1984). Elsewhere, it overlies silt and clay, saprolite (weathered bedrock), or unweathered basement material; these materials may function as a confining unit underlying the Coastal Plain aquifer system (Trapp, 1992, p. G31).

PATTERNS OF GROUND-WATER FLOW

Ground-water flow influences the distribution of dissolved constituents in the northern Atlantic Coastal Plain. As water moves through the porous media, it reacts with minerals and transports dissolved chemical species away from the reaction site along aquifer flow paths. Leahy and Martin (1993) simulated ground-water flow in the northern Atlantic Coastal Plain using a three-dimensional ground-water-flow model that was modified to improve the simulation of confining-bed and aquifer pinchouts (Leahy, 1982). Leahy and Martin (1993) used Trapp's (1992) description of the hydrogeologic framework as the basis for simulating 10 aquifers and 9 confining beds.

The configuration of the water table in the study area (pl. 2*A*) generally reflects the topography. The water table is a subdued reflection of the topography—high where land-surface altitudes are high (such as hilltops and upland deposits) and low where land surfaces are low (such as stream valleys and coastal areas). Recharge to the unconfined aquifer takes place at topographic highs, and discharge takes place at topographic lows. Most of the recharge to the unconfined aquifer discharges locally to streams, estuaries, sounds, and other surface-water bodies, resulting in numerous, complex, local flow systems. Leahy and Martin (1986, p. 170) estimated that about 1 in./yr becomes recharge to the deeper, confined aquifers. Simulated prepumping potentiometric surfaces for nine confined aquifers in the study area have been discussed in detail by Leahy and Martin (1993). Figures 2 and 3 show the prepumping head distributions in the Castle Hayne–Piney Point aquifer and the middle Potomac aquifer, respectively. Head distributions in these aquifers are representative of two different types of flow patterns in the northern Atlantic Coastal Plain aquifer system.

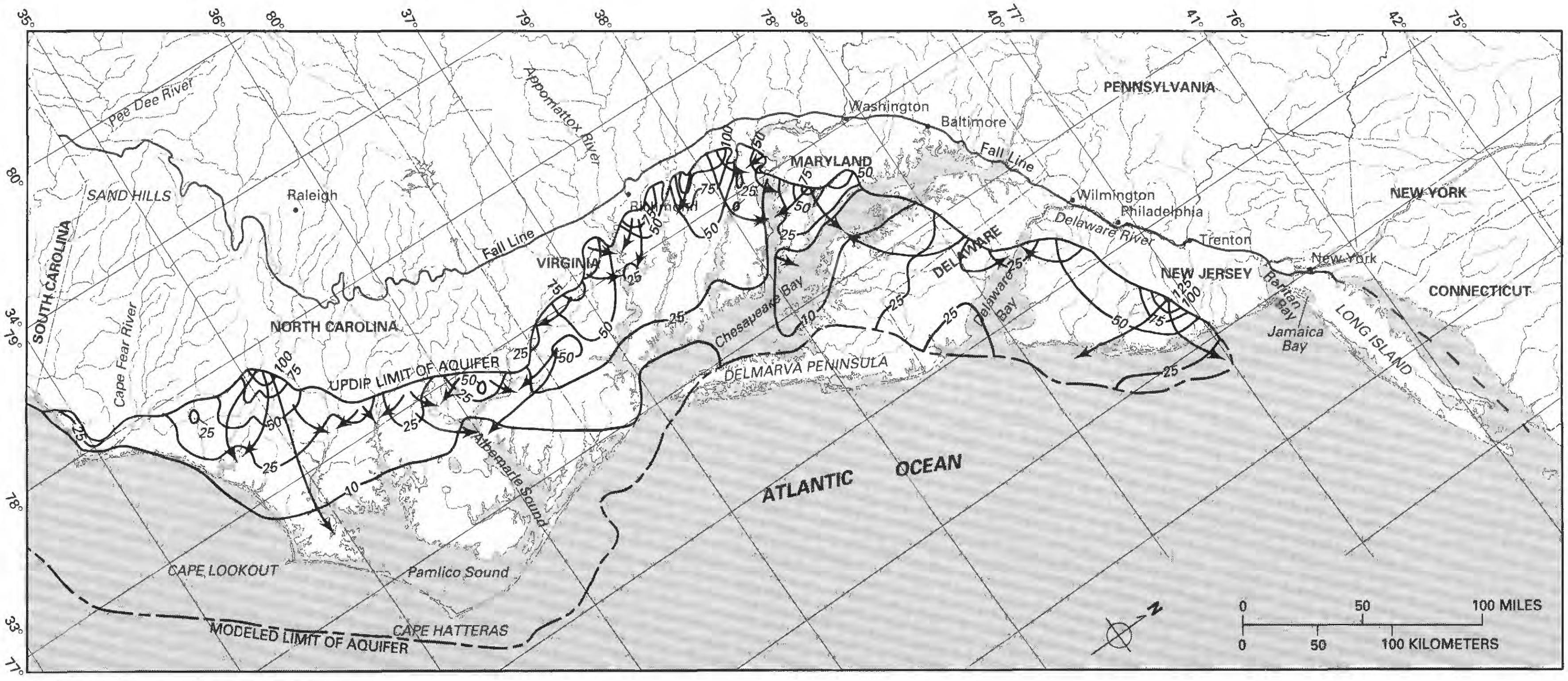
The Castle Hayne–Piney Point aquifer is typical of a shallow aquifer that discharges to major surface-water bodies (fig. 2). The effect is that small, isolated flow systems dominate the hydrology of this aquifer. In addition, head gradients are relatively steep and flow paths are short, resulting in shorter ground-water residence time compared with that for deep aquifers.

The middle Potomac aquifer is typical of a deep aquifer in the study area. Leahy and Martin (1986, p. 170) pointed out that the smooth water-level contours in this aquifer reflect a deeper regional ground-water flow that is not affected by overlying surface-water bodies (fig. 3) except in the updip part of the aquifer near the outcrop areas. The small hydraulic gradient and comparatively long flow paths suggest that the rate of ground-water flow is sluggish away from the outcrop, thereby increasing the residence time of ground water.

Recharge to the confined aquifers is generally downward in the updip parts of the aquifers, and discharge from the deep aquifers is by upward leakage through confining units into overlying aquifers and surface-water bodies. A detailed description of the hydrology of the northern Atlantic Coastal Plain was provided by Leahy and Martin (1993). Their work is partly based on, and is mathematically compatible with, subregional models described in other chapters in Professional Paper 1404:

Chapter	*Area covered*	*Author*
H	New Jersey	Martin (in press).
J	Maryland, Delaware, and the District of Columbia.	Fleck and Vroblesky (1996).
F	Virginia	Harsh and Laczniak (1990).
M	North Carolina	Giese, Eimers, and Coble (in press).

The grid orientation for the subregional models coincides with that for the regional model except for the New



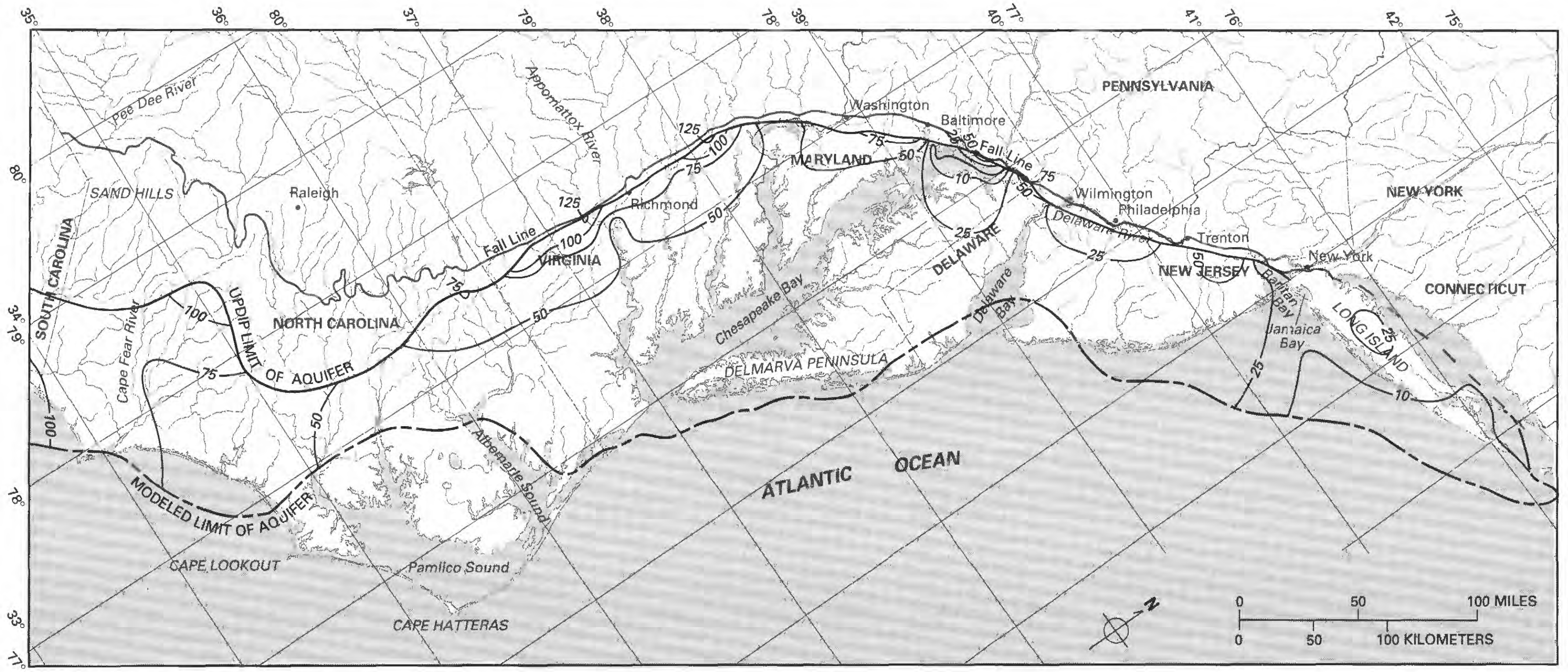
Base enlarged from U.S. Geological Survey National Atlas, 1970, 1:7,500,000

EXPLANATION

—25— **Potentiometric contour**—Shows altitude of simulated prepumping potentiometric surface. Contour interval, in feet, is variable. Datum is sea level

←—— **Generalized direction of ground-water flow**

FIGURE 2.—Simulated prepumping potentiometric surface for the Castle Hayne–Piney Point aquifer (from Trapp and Meisler, 1992, fig. 4).



Base enlarged from U.S. Geological Survey
National Atlas, 1970, 1:7,500,000

EXPLANATION

—50— **Potentiometric contour**—Shows altitude of simulated prepumping potentiometric surface. Contour interval, in feet, is variable. Datum is sea level

FIGURE 3.—Simulated prepumping potentiometric surface for the middle Potomac aquifer (from Leahy and Martin, 1993, pl. 12*B*).

Jersey grid, which is slightly rotated. The node size of the subregional models is about one-fourth that of the regional model. As a result, the subregional models provide more detailed model results than the regional model.

GEOGRAPHICAL DISTRIBUTION OF DISSOLVED CONSTITUENTS

SOURCES OF DISSOLVED CONSTITUENTS

The dissolved-solids load of ground water is a reflection of the net mass transfer among the gaseous, solid, and aqueous phases and represents the chemical history of the ground water. When water enriched in carbon dioxide and oxygen comes into contact with minerals, chemical reactions begin to occur. The reaction of ground water with minerals dissolves solid material, which is subsequently carried away in ground-water flow. This process continues as long as ground water has the capacity to dissolve the minerals with which it is in contact. Because of the variability in the types of minerals present in a ground-water system and their respective solubilities, the dissolved-solids load of ground water is variable and ranges from extremely dilute (infiltrating rainwater) to highly concentrated (as in a brine). The source of the solute content of ground water is the composite total of all the minerals and gases with which the water has come into contact. The most important mineral and gaseous sources for individual dissolved species in northern Atlantic Coastal Plain ground water are summarized in table 1.

HYDROCHEMICAL FACIES

Ground water in the Atlantic Coastal Plain from New Jersey to North Carolina has been classified into four hydrochemical facies—variable composition, calcium plus magnesium bicarbonate, sodium bicarbonate, and sodium chloride—and five ranges of dissolved-solids concentrations (0–250, 250–500, 500–1,000, 1,000–2,000, and greater than 2,000 mg/L). The hydrochemical facies are defined by the predominance (greater than 50 percent in units of milliequivalents per liter) of particular cations and anions. For example, the sodium bicarbonate hydrochemical facies is defined by water in which sodium makes up greater than 50 percent of total cations and bicarbonate makes up greater than 50 percent of total anions. This definition differs from the more detailed definition used by Back (1966, p. A13, table 2, and fig. 5). Distributions of both the hydrochemical facies and dissolved-solids concentrations are shown on maps for each of nine regional aquifers (pls. 2–6). Hydrochemical facies also are shown on several hydrogeologic sections (pls. 7–8); the hydrogeologic units on the sections were delineated by Trapp (1992). Hydrochemical facies and dissolved-solids concentrations in the surficial aquifer have not been depicted because of their variability. The distributions of hydrochemical facies and dissolved-solids concentrations depicted in plates 2–8 are generalized; individual analyses may differ from the predominant chemical character or dissolved-solids concentration.

The hydrochemical facies, as is evident from plates 2–6, follow a general coastward, or downdip, sequence from variable composition to calcium plus magnesium bicarbonate to sodium bicarbonate to sodium chloride—although one or both of the first two hydrochemical facies may be absent from parts of some aquifers. Also, dissolved-solids concentrations generally increase in the downdip direction. Examination of section *A–A'* (pl. 8*C*) indicates that the same sequence generally takes place with increasing depth at any given location. However, the sequence is reversed in some areas; two examples are shown in plates 7*B* and 8*B*.

DATA BASE

The delineation of hydrochemical facies and dissolved-solids concentrations is based on 2,320 chemical analyses of water samples from 2,230 wells that tap 10 aquifers of the northern Atlantic Coastal Plain. The analyses are distributed by State as follows: New Jersey, 580 analyses from 536 wells; Delaware, 72 analyses from 65 wells; Maryland, 538 analyses from 532 wells; Virginia, 477 analyses from 462 wells; and North Carolina, 653 analyses from 635 wells. Aquifer designation for each analysis was determined by comparing the altitude of the screen setting in each well to the altitude of each aquifer as mapped by Trapp (1992).

The wells, along with well location, date of collection, hydrochemical facies, and dissolved-solids range, are tabulated by Meisler and Knobel (1994). The 2,320 chemical analyses used for delineating hydrochemical facies and dissolved-solids range are a subset of the 3,600 analyses listed by Knobel (1985). Multiple samples from a single well listed by Knobel (1985) were used only if the multiple samples represent different hydrochemical facies or different categories of dissolved solids. All but 63 of the 2,320 analyses have been tested for cation-anion balance and meet “the 5-percent test” described by Knobel (1985, p. 5); see the section on “Data Compilation and Analysis” in this report. Untested analyses, noted by Meisler and Knobel (1994), are from Bain (1970) and from the files of the North Carolina Department of Natural Resources and Community Development.

TABLE 1.—*Sources of chemical species in ground water of the northern Atlantic Coastal Plain*

Chemical species	Sources	References
Calcium (Ca^{+2})	Dissolution of carbonate minerals (calcite, aragonite, and dolomite). Decomposition of sulfate, phosphate, and silicate minerals. Ion exchange reactions with minerals such as montmorillonite and glauconite, which act as sources and sinks.	Chapelle and Knobel, 1983; Knobel and Chapelle, 1986.
Carbon:		
Carbon dioxide (CO_2)	Contact with atmosphere, plant respiration, aerobic decomposition of organic detritus in the unsaturated zone, diagenesis of lignite, and action of anaerobic bacteria (both methanogenic and sulfate reducing).	Foster, 1950; Pearson and Friedman, 1970; Winograd and Farlekas, 1974.
Carbonic acid (H_2CO_3)	Reaction of CO_2 and H_2O.	Chapelle, 1983; Chapelle and Knobel, 1985; Knobel, 1985.
Bicarbonate (HCO_3^-)	Dissociation of H_2CO_3. Also from reaction of CO_2 with carbonate minerals.	Chapelle and others, 1987.
Carbonate (CO_3^{-2})	Dissociation of HCO_3^-.	
Chloride (Cl^-)	Not abundant in sedimentary rocks except in evaporites, which occur beneath the Atlantic Continental Shelf and Slope. Chloride is also deposited on the land with rainfall, and some of it reaches aquifers. Brines and ocean water contain large concentrations of chloride and may mix with ground water.	Arnow, 1961; Swenson, 1965, table 1; Mattick and Bayer, 1980, p. 8, fig. 5; Schaefer, 1983; Meisler and others, 1984; Meisler, 1989.
Iron (Fe^{+2}, Fe^{+3})	Iron is common in sediments, and iron minerals act as sources and sinks. Fe^{+2} (ferrous iron) is derived from the sulfide minerals, pyrite and marcasite, and the iron carbonate, siderite. Fe^{+3} (ferric iron) is derived from the oxide, hematite, and the amorphous oxide and oxyhydroxide compounds. Fe^{+2} and Fe^{+3} are derived from the mixed oxide, magnetite. Fe^{+2} and (or) Fe^{+3} are derived from the iron silicate minerals such as the pyroxenes, the amphiboles, biotite, and glauconite.	Barnes and Back, 1964; Back and Barnes, 1965; Langmuir, 1969a; Chapelle, 1984a; Knobel and Phillips, 1988.
Magnesium (Mg^{+2})	Dissolution of dolomite, magnesian calcite, and dark-colored minerals such as the pyroxenes, the amphiboles, and biotite. Seawater and brine, when mixed with ground waters, are also sources.	Meisler and others, 1984; Knobel and Phillips, 1988; Meisler, 1989.
Oxygen (O_2)	Contact with atmosphere and soil gas.	Chapelle, 1984b; Knobel and Phillips, 1988.
Potassium (K^+)	Dissolution of orthoclase, microcline, mica (especially biotite), and glauconite.	Chapelle and Knobel, 1983; Knobel and Phillips, 1988.
Silica (SiO_2)	The abundance of silicon in the Earth's crust is second only to that of oxygen. Silicon combines with oxygen and other elements to form a wide variety of silicate minerals. Crystalline quartz (SiO_2) is the most abundant silicon compound in sediments, but it is very stable under conditions prevailing in the Coastal Plain and, therefore, is not a major source of dissolved silica. Weathering of the complex silicate minerals (feldspars, micas, pyroxenes, amphiboles, and glauconite) and dissolution of diatomaceous shell material yield dissolved silica.	Mason, 1966, table 3.9; Faust and Aly, 1981, tables IX, X, and XI, p. 225–228; Knobel and Chapelle, 1986, p. 189; Knobel and Phillips, 1988.
Sodium (Na^+)	Intruding seawater or brine is a major source in saline ground water. In fresh ground water in nonmarine sediments, the dissolution of plagioclase is a major source of sodium. Also, ion exchange reactions with minerals such as glauconite remove dissolved Ca^{+2}, Mg^{+2}, and K^+ from water and replace them with Na^+.	Foster, 1950; Chapelle and Knobel, 1983; Meisler, 1989.
Sulfate (SO_4^{-2})	Deposited on land surface by rainfall, and some enters the ground water with recharge. Solution of SO_4^{-2} minerals, gypsum and anhydrite, and oxidation of metallic sulfides. Seawater and brine may contribute large amounts of sulfate where they mix with ground water.	Junge and Werby, 1958; Meisler and others, 1984; Hem, 1985.

DEFINITION OF HYDROCHEMICAL FACIES

Water of Variable Composition

Ground water in the areas depicted on the hydrochemical-facies maps as having variable composition either (1) has no predominant anion or cation or (2) has a predominant cation or anion that differs from sample to sample so that no specific facies could be mapped. Also, ground water in which sulfate is the predominant anion occurs within the area mapped as "variable composition" in several aquifers in New Jersey and Maryland (pls. 2*B*, 5*B*, and 6). Ground water of variable composition occurs along the updip limit of several aquifers in New Jersey, Maryland, and North Carolina. The most widespread occurrence of variable composition ground water is in the shallowest of the nine mapped aquifers—the upper Chesapeake aquifer (pl. 2*B*). The dissolved-solids concentrations of variable-composition ground water are generally less than 250 mg/L, although concentrations in the range of 250 to 500 mg/L occur in southwestern New Jersey.

Calcium Plus Magnesium Bicarbonate Water

In the calcium plus magnesium bicarbonate water, calcium plus magnesium makes up greater than 50 percent of the cations (calcium generally predominates over magnesium), and bicarbonate makes up greater than 50 percent of the anions. This water generally occurs along the updip limit of the aquifers or downdip from water of variable composition. The facies has been mapped in the nine aquifers; it is most extensive in the upper Chesapeake (pl. 2*B*) and Castle Hayne–Piney Point (pl. 3*B*) aquifers of North Carolina. The dissolved-solids concentrations in ground water of this facies are generally less than 250 mg/L. Larger concentrations (generally 250–500 mg/L) are most common in North Carolina (pls. 2*B*, 3, and 4*A*).

Sodium Bicarbonate Water

In the sodium bicarbonate water, sodium makes up greater than 50 percent of the cations, and bicarbonate makes up greater than 50 percent of the anions. This water generally occurs downdip from the calcium plus magnesium bicarbonate water. It has been mapped in the nine aquifers and is most extensive in the middle Potomac (pl. 6*A*) and upper Potomac (pl. 5*B*) aquifers. Dissolved-solids concentrations in the sodium bicarbonate water generally range up to about 1,000 mg/L, except in New Jersey, where they are generally less than 500 mg/L.

Sodium Chloride Water

In the sodium chloride water, sodium makes up more than 50 percent of the cations, and chloride makes up more than 50 percent of the anions. This water generally occurs downdip from the sodium bicarbonate water. It is the dominant facies in the deepest, farthest downdip parts of the nine aquifers. Areas where sodium chloride water occurs at relatively shallow depths are the vicinity of Delaware Bay, the peninsula between the York and James Rivers in Virginia, north of Albemarle Sound in North Carolina, and near the Cape Fear River in North Carolina. These areas are most evident on section *A–A′* (pl. 8*C*) but also can be discerned on the hydrochemical facies maps as updip projections of the sodium chloride water. Dissolved-solids concentrations in sodium chloride ground water from North Carolina to Delaware generally are greater than 1,000 mg/L. Smaller concentrations occur locally, such as in the vicinity of the Cape Fear River (pls. 4*B* and 5*A*) and Albemarle Sound (pl. 2*B*) in North Carolina, on the York–James Peninsula (pls. 5*B* and 6*A*) in Virginia, and near the Delaware estuary (pls. 5*B* and 6) in Delaware. In New Jersey, dissolved-solids concentrations of sodium chloride water generally are greater than 500 mg/L, but smaller concentrations occur near the Delaware estuary (pl. 6) and in the upper Chesapeake aquifer (pl. 2*B*) along the coast.

A saltwater-freshwater transition zone, which lies entirely within the sodium chloride water, was studied by Meisler and others (1984) and Meisler (1989). The transition zone is characterized by increases in concentrations of chloride and dissolved solids with increasing depth. Also, concentrations of calcium, magnesium, sodium, potassium, and sulfate generally increase with increases in chloride concentration and depth. Bicarbonate concentration, on the other hand, tends to decrease as chloride concentration and depth increase. The relation of concentrations of these ions to concentrations of chloride indicates that the saltwater-freshwater transition zone in North Carolina is primarily a mixture of fresh sodium bicarbonate water and seawater. From Virginia to New Jersey, the transition zone appears to be largely a mixture of fresh sodium bicarbonate water and a sodium-calcium chloride brine that has chloride concentrations several times that of seawater. A similar brine occurs beneath the seawater-freshwater mixing zone in the vicinity of Pamlico and Albemarle Sounds in North Carolina. The origin of the brines is uncertain. The most likely source is the leaching of evaporite strata of probable Early Jurassic age beneath the continental shelf (Meisler, 1989). The broad saltwater-freshwater transition zone probably developed as a result of saltwater circulation caused by large-scale sea-level fluctuations during the late Tertiary and Quaternary; repeated advance and retreat of the salty ground water caused the freshwater and saltwater to mix.

PROGRESSION OF FACIES

The general coastward progression of the hydrochemical facies described above and the concomitant increase in dissolved-solids concentration depicted in plates *2B* and 3–6 are largely the result of natural (prepumping) freshwater flow patterns in the aquifer system. The processes of dissolution, precipitation, and ion exchange that take place as the freshwater moves through the sediments, and that account for most of the downgradient progression of freshwater facies, are described in the appendixes to this report and in cited references. Distribution of the sodium chloride water is also related to the freshwater flow system; this water occurs in the deepest, farthest downgradient parts of the aquifer system, where freshwater heads are generally lowest. Indeed, the shallow occurrences of the sodium chloride water described above coincide with major areas of ground-water discharge, where freshwater heads are lowest and saltwater can be expected to be shallowest.

Examples of the downgradient progression of hydrochemical facies can be seen in plates *2B* and 3–6 along the following flow paths: (1) from New Jersey, Maryland, and Delaware to the Delaware River and Bay (pls. *4B*, *5B*, and 6), (2) from the Washington–Baltimore area to upper Chesapeake Bay east of Baltimore (pl. *6A*), (3) from near the western limit of the Coastal Plain of Virginia to lower Chesapeake Bay and the York–James Peninsula (pls. *3B*, *4A*, *5B*, and *6A*), (4) from the Washington–Baltimore area to Delaware Bay (pl. *5B*), (5) from near the western limit of the Coastal Plain sediments in southern Virginia toward Albemarle Sound in North Carolina (pls. 3, *4A*, *5B*, and *6A*), (6) from the western limit of the Peedee–Severn aquifer of North Carolina to the Cape Fear River (pl. *4B*), and (7) from the upgradient parts of the aquifers eastward and northeastward toward Pamlico and Albemarle Sounds in North Carolina (pls. *2B*, 3–4, and *5A*).

The considerable depth of the saltwater-freshwater transition zone along the coast of New Jersey and the occurrence many miles offshore of ground water that is fresher than seawater do not appear to be related to current natural freshwater flow. Meisler and others (1984) developed a finite-difference cross-sectional model to test the hypothesis that the location of the saltwater-freshwater transition zone is related to long-term lower sea levels. Model simulations suggest that the occurrence and distribution of relatively fresh ground water (compared to seawater) in southern New Jersey reflect average sea levels, from the Miocene to the Holocene, that were 50 to 100 ft below present sea level. Farther south, particularly in southeastern Virginia and North Carolina, where saltwater is generally shallower than in New Jersey and where water that is fresher than seawater does not extend very far offshore, average long-term sea levels during Miocene-Holocene time were generally higher relative to land surface than sea levels in New Jersey.

CONTROLS ON THE DISTRIBUTION OF DISSOLVED CONSTITUENTS

MINERAL STABILITY

TEMPERATURE AND PRESSURE

The concentrations of inorganic constituents in ground water are controlled by the types, abundance, and reaction rates of minerals in the aquifer. Nearly all minerals react with ground water to some extent; however, minerals that react slowly have less effect on the chemical composition of ground water than do minerals that react rapidly (Chapelle, 1983, p. 546). Goldich (1938) studied the weathering of igneous and metamorphic rocks and proposed a silicate-mineral stability series associated with rock weathering. He attributed the differences in mineral stability to the changing equilibrium conditions during formation of the minerals (such as changing temperature and pressure in a magma), which have been described by Bowen (1922). Goldich (1938, p. 56) suggested that the equilibrium conditions at the time of silicate-mineral formation are significantly different from surface conditions and that this is the reason for mineral weathering and the variability in rates of mineral weathering. The effects of magma equilibrium conditions on rates of mineral weathering can be illustrated with the minerals plagioclase, potassium feldspar, and quartz. Of the three minerals, plagioclase is the first to crystallize from a magma when temperature and pressure in the magma are highest. As temperature and pressure in the magma decrease, potassium feldspar is the next mineral to crystallize. Similarly, quartz is the last mineral to crystallize, when magma temperature and pressure are lowest. If these minerals are subsequently exposed at the Earth's surface, the order of mineral weathering follows the order of crystallization. Plagioclase was the first to crystallize from the magma and consequently is the first to weather (least stable) at the Earth's surface because of the larger difference between temperature and pressure of mineral formation and temperature and pressure of mineral weathering. Potassium feldspar is intermediate in stability at the Earth's surface, and quartz is the most stable of the three minerals.

On the basis of normative mineral calculations, Garrels (1976, p. 76–78) inferred a "'rank list' of minerals and their relative rates of reaction." This list is in general agreement with Goldich's (1938, p. 56) stability series.

Other minerals, such as calcite and pyrite, that are formed at or near the Earth's surface, do not undergo large changes in temperature and pressure. The stability of these minerals is influenced more by changes in pH and concentrations of dissolved gases such as CO_2 and O_2. In general, however, calcite is more prone to weathering than feldspar minerals (Stumm and Morgan, 1981, p. 544–545).

DISSOLVED GASES

Recharge in the northern Atlantic Coastal Plain is derived mostly from atmospheric precipitation. It is generally saturated with respect to atmospheric CO_2 (partial pressure = $10^{-3.5}$ atmospheres) and O_2 (partial pressure = $10^{-0.68}$ atmospheres). As the infiltrating water passes through the soil zone, it accumulates additional CO_2 (Pearson and Friedman, 1970, p. 1780). The dissolved gases increase the capacity of the H_2O (water) to react with minerals.

Dissolved CO_2 causes ground water to provide H^+ (hydrogen ions):

$$H_2O + CO_2 \rightarrow H_2CO_3, \qquad (1)$$

$$H_2CO_3 \rightarrow H^+ + HCO_3^-, \qquad (2)$$

and

$$HCO_3^- \rightarrow H^+ + CO_3^{-2}. \qquad (3)$$

Oxidation of various species forms H^+, anions, or precipitates; it also releases e^- (electrons) for the simultaneous reduction of other species. For example, FeS_2 (pyrite) in the presence of dissolved oxygen is converted to ferrous, sulfate, and hydrogen ions:

$$FeS_2 + H_2O + 3.5O_2 \rightarrow Fe^{+2} + 2SO_4^{-2} + 2H^+. \qquad (4)$$

In this reaction, sulfur is oxidized and oxygen is reduced. Similarly, Fe^{+2} in an oxygenated ground water is oxidized to Fe^{+3}—which is incorporated into ferric hydroxide or a precursor solid phase such as FeOOH (ferric oxyhydroxide) and H^+:

$$Fe^{+2} + 2.5H_2O + 0.25O_2 \rightarrow Fe(OH)_3 + 2H^+. \qquad (5)$$

In this case, as in the previous example, oxygen is the reduced species.

HYDROGEN ION ACTIVITY (pH)

The effective concentration of hydrogen ion in ground water could be expressed in the same manner as the concentration of any other dissolved constituent. However, because hydrogen ion generally occurs at trace concentrations, it is more practical to express the effective concentration of hydrogen ion as a logarithmic function of its activity, pH. The term pH is defined as the negative base-ten logarithm of the hydrogen ion activity in moles per liter (Hem, 1985, p. 61). The range of the pH scale is normally from 0 to 14. A pH of 7.0 is considered neutral, less than 7.0 is considered acidic, and greater than 7.0 is considered alkaline. Because the pH scale is logarithmic, a ground water with a pH of 4.0 has 10 times as many hydrogen ions (0.0001 moles per liter) as one with a pH of 5.0 (0.00001 moles per liter). The activity of hydrogen ion in ground water is important because it is the primary aggressive agent in the chemical weathering of rocks and minerals. The normal range of pH in ground-water systems is reported to be from 6.0 to 9.0 by Freeze and Cherry (1979, p. 100), but the pH can be larger (alkaline springs) or smaller (acid mine drainage). The pH of rainwater is commonly less than 6.0 (Hem, 1985, p. 63).

The activity of hydrogen ion in ground water is controlled by various processes; three of the most important follow:

1. Buffering by dissolved carbon dioxide species—Ground water is considered to be buffered if the pH changes little with the addition of small amounts of acid or base. Solutions that contain weak bases or acids, such as carbonic acid, generally tend to have a narrow range of pH. In order for the pH to remain constant when a base is added to the solution, a continuous source of hydrogen ion is required (eqs. 1–3). The dissolved carbon dioxide species cause ground water to provide adequate hydrogen ions to buffer most ground-water systems. Matthess (1982, p. 60) pointed out that this mechanism is probably the cause for the narrow range of pH in most natural waters.
2. Oxidation-reduction reactions—Although carbon dioxide buffering tends to restrict the range of pH in many ground-water systems, other systems show marked variation in pH. For example, the oxidation of sulfur in pyrite (eq. 4) and the subsequent oxidation of the ferrous ion (eq. 5) can maintain the pH at values much lower than the buffering range of the carbon dioxide species. This can be an important process in outcrop areas rich in iron sulfide minerals such as pyrite and marcasite.
3. Consumption of hydrogen ion by chemical reactions—Many reactions involved in the chemical weathering of rocks and minerals consume hydrogen ion. Weathering of alkali feldspar minerals in an acid environment releases cations to ground water. This tends to stabilize excess silica in solution (Mason, 1966, p. 160–161) and forms bicarbonate ion. A typical reaction produces

clay, consumes hydrogen ion, and increases the pH (Powell and Larson, 1985, p. 6–7):

$$\underset{\text{oligoclase}}{Na_{0.7}Ca_{0.3}Al_{1.3}Si_{2.7}O_8} + 1.3CO_2 + 1.95H_2O \rightarrow \underset{\text{kaolinite}}{0.65Al_2Si_2O_5(OH)_4} + 0.7Na^+ + 0.3Ca^{+2} + 1.4SiO_2 + 1.3HCO_3^-. \qquad (6)$$

Likewise, dissolution of carbonate minerals (like calcite) consumes hydrogen ion, produces bicarbonate and calcium ions, and increases pH and alkalinity:

$$CaCO_3 + H_2O \rightarrow Ca^{+2} + HCO_3^- + OH^-. \qquad (7)$$

Other weathering reactions have a similar effect of increasing the pH of ground-water systems.

PATTERNS OF GROUND-WATER FLOW

Water is a dipolar molecule and rapidly hydrates the ions released as minerals dissolve. The hydrated ions are subsequently transported away from reaction sites by ground-water flow. Velocities of ground-water flow in the northern Atlantic Coastal Plain are typically small. William B. Fleck (USGS, written commun., 1986) estimated average velocities to be on the order of 3.65 to 36.5 ft/yr near Waldorf, Md., in aquifers equivalent to the Magothy and middle Potomac aquifers of this report. Hence, hydrated ions can be transported on the order of 3.65 to 36.5 ft away from the reaction site in 1 yr.

Two-dimensional ground-water flow in porous media can be represented by the following equation:

$$\frac{\partial}{\partial x}\left(T_x \frac{\partial h}{\partial x}\right) + \frac{\partial}{\partial y}\left(T_y \frac{\partial h}{\partial y}\right) + W_{(x,y,t)} = S\frac{\partial h}{\partial t}, \qquad (8)$$

where

T = transmissivity,
S = storage coefficient,
h = hydraulic head,
W = volume injection (+) or withdrawal (–) rate per unit area,
x, y = cartesian coordinates, and
t = time.

Solution of equation 8 by approximation or analog techniques yields a hydraulic head distribution for a given set of initial and boundary conditions. The head distribution can be depicted in map form, and equipotential lines can be drawn. From these maps, flow lines can be constructed perpendicular to the equipotential lines so as to pass through any point on the map, thereby allowing the distance along a flow path, from the recharge area to the point, to be measured. Changes in water chemistry along these flow paths can be analyzed in one dimension.

Solute transport in one dimension can be represented by the following equation:

$$\frac{\partial C}{\partial t} = -V\frac{\partial C}{\partial x} + D\frac{\partial^2 C}{\partial x^2} + r_l + r_s, \qquad (9)$$

where

$\frac{\partial C}{\partial t}$ = change in concentration with respect to time,
$-V\frac{\partial C}{\partial x}$ = change in concentration due to transport by the flow system (V=particle velocity),
$D\frac{\partial^2 C}{\partial x^2}$ = change in concentration due to the effects of dispersion,
r_l = change in concentration due to reactions in the liquid phase, and
r_s = change in concentration due to reactions with the solid phases.

By combining the reaction terms and assuming dispersion is negligible, equation 9 can be rewritten as:

$$\frac{\partial C}{\partial t} \approx -V\frac{\partial C}{\partial x} + (r_l + r_s). \qquad (10)$$

Equation 10 indicates that the change in concentration with respect to t (time) is proportional to the change in concentration with respect to x (distance), plus any changes due to reactions. The proportionality constant is the ground-water-flow velocity. Darcy's law,

$$Q = \bar{v}A\Theta = -KA\frac{dh}{dl}, \qquad (11)$$

can be used to solve for average velocities between hydraulic heads resulting from the solution of equation 8 where

$\bar{v}$ = average velocity,
Θ = effective porosity as a decimal fraction,
dh = change in head over distance dl,
dl = change in distance,
Q = discharge,
A = cross-sectional area normal to flow direction,
K = hydraulic conductivity, and

$$\bar{v} = -\frac{Kdh}{\Theta dl}. \qquad (12)$$

Coupling equation 10 with the assumption that head distributions have not changed significantly since water entered the aquifer suggests that changes in concentration with respect to time are approximately represented by changes in concentration with respect to distance plus any increases or decreases in concentration due to reactions. This is an important simplification because it allows substitution of distance for time when graphing changes in concentration along a reaction pathway and isolates the variable of interest, changes in concentration due to chemical, physical, and biological processes. This simplification assumes (1) that a flow line in a two-dimensional system can be represented by a one-dimensional expression of solute transport, (2) that the solution to equation 8 is an accurate representation of the flow system, (3) that concentration changes due to the effects of dispersion are negligible, (4) that the potential field (hydraulic head distribution) has not changed significantly with time, (5) that average velocities represented by equation 12 are relatively constant in time and space, and (6) that the hydrologic properties of the aquifer are distributed uniformly. Although none of these assumptions is entirely valid in natural aquifer systems, the results of studies using distance along a flow path as the reaction-path variable are often useful for identifying natural geochemical processes controlling ground-water chemistry on a regional scale. This technique has been used extensively in studying the geochemistry of the northern Atlantic Coastal Plain.

The use of principles contained in equations 8 through 12 was illustrated by Knobel and Phillips (1988). A steady-state solution to equation 8, using a finite-difference approximation, was given for the Magothy aquifer, Maryland. Representative flow lines were drawn on the map, and equation 10 was assumed to represent water chemistry changes along the flow lines. Distances along flow lines were measured for each sampling point, and the concentrations of selected constituents were plotted as functions of distance along a flow line in a series of illustrations that were used by Knobel and Phillips (1988) to interpret the geochemistry of the Magothy aquifer, Maryland.

CATION EXCHANGE REACTIONS

Cation exchange reactions are important geochemical processes that modify ground-water composition in deep confined aquifer systems. The Aquia aquifer in southern Maryland is an example of how these reactions affect water chemistry (Chapelle and Knobel, 1983). The Aquia aquifer contains between 30 and 60 percent glauconite, an iron-bearing silicate of the illite family that is an efficient cation exchange medium. Furthermore, because glauconite is an authigenic mineral that forms in marine environments, most of the available exchange sites are initially filled with sodium. In the outcrop area, dissolution of carbonate shell material produces calcium and magnesium ions that exchange with sodium on glauconite. The removal of these cations from solution and their replacement with sodium follows a predictable pattern. Calcium is the first dissolved ion to be removed from solution and is followed by magnesium and potassium. This observed succession agrees exactly with the theoretical stability of these cations on exchange sites and also with the observed composition of Aquia glauconite. Near the outcrop area, therefore, much of the total exchange capacity of the glauconite is filled with calcium. Downgradient, however, where less reaction has occurred, most of the exchange capacity is filled by sodium. The Aquia aquifer and most other Coastal Plain aquifers thus act as large cation-exchange columns that separate dissolved cations according to their stability on exchange sites. This process is a major factor in the development of the observed succession of hydrochemical facies (calcium-magnesium to sodium) in Coastal Plain aquifers.

ENVIRONMENTS OF SEDIMENT DEPOSITION

Sediments of the northern Atlantic Coastal Plain were deposited either in marine environments (that is, below high tide) or in nonmarine environments (above high tide). Although the large-scale hydrology of marine and nonmarine aquifers may be similar, their chemical behavior is quite different. This difference is due primarily to differences in lithology. Marine units are characterized by an abundance of carbonate minerals, a complex suite of clay minerals, and a large percentage of Na^+ (sodium) associated with clay-mineral exchange sites. Nonmarine units have little carbonate material, a simple clay-mineral suite dominated by kaolinite and illite, and a large percentage of Ca^{+2} (calcium) plus Mg^{+2} (magnesium) associated with clay-mineral exchange sites.

As meteoric water recharges marine and nonmarine aquifers, the occurrence of distinctly different types of reactions reflects the mineralogical differences in those aquifers. In marine aquifers, dissolution of carbonate material rapidly increases concentrations of Ca^{+2} and HCO_3^- (bicarbonate) until calcite saturation occurs. This leads to precipitation of calcite and the formation of calcite-cemented hardbeds (Chapelle and Drummond, 1983). As ground water continues to move downgradient, Ca^{+2} is exchanged for Na^+ to form a sodium bicarbonate water. A classic example of this type of process is given by the Beaufort–Aquia aquifer of southern Maryland and was described in detail by Chapelle (1983) and Chapelle and Knobel (1983, 1985).

As meteoric water recharges nonmarine aquifers, the absence of carbonate material is reflected by the lack of HCO_3^- accumulation in ground water. Major chemical processes are feldspar dissolution, pyrite dissolution, and precipitation-dissolution reactions involving ferric oxyhydroxides. These reactions lead to a Ca^{+2} + Mg^{+2}–HCO_3^- water—which contains the same constituents found in marine-aquifer ground water—but, in general, nonmarine-aquifer water is more dilute. Typical HCO_3^- concentrations in nonmarine aquifers near recharge areas are generally less than 100 mg/L (milligrams per liter). As water flows downgradient, Ca^{+2} and Mg^{+2} are replaced by Na^+, but this process typically requires longer flowpath segments than in marine units. This replacement leads to a Na^+–HCO_3^- water. This sequence of processes is illustrated by the Patuxent aquifer near Baltimore, Md. (Chapelle, 1985).

Perhaps the best example of how sediment depositional environments affect ground-water chemistry was described by Knobel and Phillips (1988) for the Magothy aquifer of southern Maryland. In the northern part of this aquifer, which is predominantly nonmarine in origin, recharge occurs directly in the outcrop area. In the southern part of the aquifer, however, the Magothy does not crop out at the surface and is recharged by leakage from overlying marine sediments. These two regions of the aquifer, which are otherwise identical in a lithologic and mineralogic sense, exhibit strikingly different water-chemistry trends—water in the marine-recharged part evolving to a high Na^+–HCO_3^- water (HCO_3^- concentrations greater than 100 mg/L) and water in the nonmarine-recharged area remaining a fairly dilute Ca^{+2} + Mg^{+2}–HCO_3^- water (HCO_3^- concentrations less than 100 mg/L).

PROXIMITY TO SOURCES OF RECHARGE: THE SURFICIAL AQUIFER

The surficial aquifer in the northern Atlantic Coastal Plain is composed of marine and nonmarine sediments of variable age (Trapp, 1992). It is an unconfined aquifer, and its top is the water table (pl. *2A)*, which fluctuates with time in response to changes in recharge. Because the water-table surface is near the land surface, the aquifer geochemistry is affected by land use. As a result, local geochemical systems have developed, and water quality varies geographically. It is not possible to completely describe all of these localized systems; however, Denver (1986) gave a detailed summary of the processes that occur in the largely nonmarine unconfined aquifer in west-central and southwestern Delaware. She identified incongruent dissolution of silicate minerals, oxidation-reduction processes, ion exchange processes, and land use as factors that control water chemistry in the unconfined aquifer of Delaware. Her work is the basis for the example in appendix C. Similar processes occur in the surficial aquifer throughout the study area.

MIXING OF WATERS HAVING DIFFERENT COMPOSITIONS

Ground water in the northern Atlantic Coastal Plain contains variable amounts of dissolved solids. The total dissolved-solids content of ground water ranges from a few milligrams per liter in concentrated rainwater (appendix C) to a few thousand milligrams per liter (pls. *2B* and 3–6). Many of the geochemical processes that control the distribution of dissolved ions in ground water are discussed in preceding sections or in appendixes A–C; however, little has been said about changes in the stability of dissolved ions and their concentrations when two or more ground waters having different chemical compositions mix. In addition, ground water that is in hydraulic connection with surface-water bodies—such as the ocean, bays, rivers, and lakes—may mix with those bodies under certain conditions.

The purpose of this section is to discuss how the mixing of waters having different compositions affects water chemistry. In general, two effects of mixing are possible. The stabilities of the phases can all remain the same after mixing, or the stability of one or more phases can change as a result of that mixing. The former condition is rare, but simple dilution of all constituents results:

$$C_f = \sum_{i=1}^{n} \alpha_i C_i, \qquad (13)$$

where

C_f = concentration of a constituent in the final solution,

C_i = concentration of a constituent in the *i*th initial solution, and

α_i = volumetric proportionality constant of the *i*th initial solution with the restriction that $\sum_{i=1}^{n} \alpha_i = 1$.

If the stability of one or more phases changes, the final water will either be undersaturated or oversaturated with respect to that phase, and the water will adjust to a new equilibrium condition by dissolution-precipitation reactions. When this condition occurs, not all ions are affected. For example, Cl^- is a very conservative ion (Quinby-Hunt and Turekian, 1983), and it can attain extremely large concentrations without entering into chemical reactions. Its concentration after mixing can normally be described by equation 13. Conversely, Ca^{+2} may enter into a variety of chemical reactions as a result of minor concentration changes. Such changes can result in diagenetic effects such as changes in porosity. Runnells (1969) described the controls on mixing and its effects on ground-water chemistry. The effects of mixing on water chemistry in the northern Atlantic Coastal Plain are illustrated by a series of examples.

MIXING FRESH GROUND WATER WITH SEAWATER

The Atlantic Ocean borders the study area to the east and provides a source of seawater to mix with ground water in the shallow aquifers of the Atlantic Coastal Plain. The mixing may occur naturally when freshwater heads are too low to offset the movement of saltwater in response to density differences between seawater and ground water, or it may be induced when freshwater heads are artificially lowered by pumping. Mixing of seawater with shallow ground water is common in the coastal areas of New Jersey (Schaefer, 1983), Maryland and Delaware (Slaughter, 1962), Virginia (Cederstrom, 1943), and North Carolina (LeGrand, 1956). A detailed example of saltwater intrusion along the coast of New Jersey is provided in appendix D, which is based on the work of Schaefer (1983).

MIXING FRESH GROUND WATER WITH BRACKISH WATER AND REVERSE ION EXCHANGE

The study area contains several brackish-water bodies. Examples are the Raritan, Delaware, and Chesapeake Bays; Pamlico Sound; and numerous estuaries. All of these brackish-water bodies mix to some degree with fresh ground water in adjacent shallow aquifers. When brackish water and freshwater mix, the more concentrated brackish water is diluted. In addition, the influx of Na^+ reverses the normal selectivity order of ions for exchange sites, and ion exchange reactions proceed in a direction opposite to that observed in freshwater aquifers. An example of brackish-water–freshwater mixing and reverse ion exchange in the lower Potomac aquifer of Maryland was given by Chapelle (1985).

CALCITE PRECIPITATION AS A RESULT OF MIXING

Cyclic movement of the offshore brine described by Meisler and others (1984) has caused an enrichment of Ca^{+2} in a broad zone of mixed waters in the northern Atlantic Coastal Plain. When fresh ground water containing large concentrations of HCO_3^- mixes with the brine containing large concentrations of Ca^{+2}, the probable result is water saturated with respect to calcite. Subsequent precipitation of calcite decreases alkalinity and pH. Concentrations of Ca^{+2} are also depleted, but the concentrations of HCO_3^- are small relative to the Ca^{+2} concentrations, and the decrease in Ca^{+2} is masked. A brief summary of the processes that occur during the mixing of freshwater and the calcium-enriched brine and that were described by Meisler and others (1984) is presented in appendix E.

BACTERIAL PROCESSES IN GROUND-WATER CHEMISTRY

It is customary in chemistry to distinguish between biologically mediated chemical reactions (biochemistry) and chemical reactions that occur without biological mediation (inorganic chemistry). In studying ground-water chemistry, however, it is not always possible to make this distinction. Some important processes, cation exchange reactions, for example, are obviously inorganic. In the case of other processes, however, the biologic or nonbiologic nature is less clear, as, for example, when organic carbon oxidizes to carbon dioxide:

$$CH_2O + O_2 \rightarrow CO_2 + H_2O. \tag{14}$$

At high temperatures, this process proceeds spontaneously as fire. At low temperatures, however, this process is known to occur only with the mediation of micro-organisms. This implies that the consumption of dissolved oxygen along aquifer flow paths that occurs in most Coastal Plain aquifers also requires micro-organisms. It follows that micro-organisms, particularly heterotrophic bacteria, must be present in deep aquifers and that they probably affect ground-water chemistry.

Such interpretations, however, require direct evidence of bacterial populations. Chapelle and others (1987) gave a detailed example of enumerating viable bacteria in deep (40–550 ft) aquifers of Maryland. Sulfate reduction and methanogenesis were identified as metabolic strategies for some of these bacteria, which were found in numbers between 10^3 and 10^6 cells per gram of sediment. These numbers are much smaller than those found in typical soils and aquatic sediments (approximately 10^7 to 10^{10} cells per gram). Thus, although bacteria are demonstrably present, it is clear that the environment of deep aquifers is different from that of surface sediments. This difference also is evident from rates of CO_2 production in deep aquifers. Estimated rates of CO_2 production from the middle Potomac aquifer of Maryland (Chapelle and others, 1987) range from 10^{-6} to 10^{-3} (mmol/L)/yr (millimoles per liter per year). In contrast, abyssal marine sediments exhibit bacterial CO_2 production rates of between 10^{-2} and 10^4 (mmol/L)/yr. Thus, although bacterial processes occur in deep aquifers, it is evident that the rates of these processes are slow compared to the rates in surface environments.

It is generally accepted that certain processes important in Coastal Plain aquifers, such as sulfate reduction, are bacterially mediated (Back, 1966). The importance of bacterial mediation is less clear with respect to other oxidation-reduction reactions. For example, dissolution of ferric oxyhydroxides affects the geochemistry of dissolved iron in many aquifer systems (Chapelle, 1985; this report, appendix C). In many studies of ground-water chemistry, dissolution of ferric oxyhydroxides is considered to occur without bacterial mediation (Back and Barnes, 1965). In studies of aquatic surface sediments, however, the opposite view is taken, and this process is generally regarded as being bacterially mediated (Lovely and Phillips, 1988).

Although not conclusive, available ground-water chemistry data indicate that ferric iron reduction is bacterially mediated. Concentrations of iron in anoxic aquifers commonly are observed to be directly proportional to concentrations of dissolved inorganic carbon (Chapelle, 1985; this report, appendix C). This observation suggests that organic carbon is the primary reducing agent for ferric iron reduction:

$$Fe(OH)_3 + 0.25CH_2O + 1.75H^+ \rightarrow Fe^{+2} + 0.25HCO_3^- + 2.5H_2O, \qquad (15)$$

and that, because this process occurs at low temperature, bacteria facilitate the electron transfer.

It is likely that bacteria have many direct and indirect effects on the geochemistry of ground water in the northern Atlantic Coastal Plain. Sorting out the different kinds of bacterial processes that do and do not occur will be an important research topic in the future.

INTERPRETATION OF HYDROCHEMICAL FACIES, BY AQUIFER

Back (1966) studied hydrochemical facies in the northern Atlantic Coastal Plain. His study area included the Coastal Plain in New Jersey, Delaware, Maryland, and Virginia. This study encompasses the area studied by Back and includes the Coastal Plain of North Carolina. The definition of hydrochemical facies described earlier in this report also varies from the more detailed definition used by Back (1966, p. A13, table 2, and fig. 5).

The vertical distribution of hydrochemical facies is shown on a series of hydrogeologic sections; four sections (pls. 7*B*, 7*C*, 8*A*, and 8*B*) are aligned approximately parallel to the regional dip of the sediments, and one (pl. 8*C*) is aligned approximately parallel to the regional strike. These sections can be readily compared with the fence diagrams used by Back (1966). In this report, the hydrochemical facies of the northern Atlantic Coastal Plain are defined for each of the aquifers described by Trapp (1992), and chemical processes that most likely control the distribution of the hydrochemical facies are identified for each aquifer.

SURFICIAL AQUIFER

Hydrochemical facies in the surficial aquifer are too variable to map at the scale of this study. The reasons for the variability are largely related to land use and are discussed in detail in appendix C of this report.

UPPER CHESAPEAKE AQUIFER

NORTH CAROLINA AND VIRGINIA

In the westernmost part of the upper Chesapeake aquifer (pl. 2*B*) in North Carolina and Virginia, the hydrochemical facies is designated as variable composition(?). The chemical data in this area are too sparse to identify the type of facies present. Seaward of this area, the dissolved-solids concentration (TDS) increases to a maximum of more than 2,000 mg/L near Albemarle Sound. The changes in hydrochemical facies, in the direction of increasing TDS, from calcium plus magnesium bicarbonate to sodium bicarbonate to sodium chloride are typical of shell-material dissolution followed first by ion exchange and then by mixing with brackish water, seawater, or both. Secondary-calcite cementation of shell material may take place, as indicated by the presence of indurated shell limestones in the Greenville area of North Carolina (Brown, 1959, p. 26). These processes are consistent with the prepumping head distribution of the aquifer in this area (Leahy and Martin, 1993, pl. 10*A*) and with the aquifer lithology (Trapp, 1992). In North Carolina and Virginia, the aquifer contains shell beds, which act as a source of Ca^{+2} and Mg^{+2}, and clayey material, which acts as an exchange substrate. The aquifer is sufficiently shallow so that mixing with brackish water from Pamlico and Albemarle Sounds and seawater from the Atlantic Ocean has occurred.

MARYLAND, DELAWARE, AND NEW JERSEY

In Maryland and Delaware, the upper Chesapeake aquifer is confined to the Delmarva Peninsula. It is entirely covered by the surficial aquifer; however, there is significant hydraulic connection between the two units (Cushing and others, 1973, p. 45–46). In New Jersey, the surficial aquifer is missing, except on the tip of the Cape May Peninsula, and the upper Chesapeake is an unconfined aquifer. Hence, like the surficial aquifer, the upper Chesapeake aquifer contains hydrochemical facies that are highly variable over short distances, and the facies are mapped as variable composition in most of the area. Dissolved solids generally are less than 250 mg/L throughout the area, and, locally, the sulfate facies predominates. The sodium chloride hydrochemical facies dominates a narrow band along the New Jersey coast because of mixing with seawater, and some mixing with seawater undoubtedly occurs along the Atlantic coast of the Delmarva Peninsula, but the variable composition hydrochemical facies masks it. The Virginia part of the

Delmarva Peninsula has either the calcium plus magnesium bicarbonate or the sodium bicarbonate hydrochemical facies, probably because of increased amounts of carbonate dissolution and ion exchange.

In areas where the upper Chesapeake aquifer is unconfined and contains ground water of variable composition (pl. 2*B*), the geochemical processes controlling the water chemistry are similar to the processes described for the surficial aquifer. These processes are summarized in appendix C. The presence of the sulfate facies indicates that sulfate is probably generated by oxidation of sulfide minerals such as pyrite (eq. 4).

LOWER CHESAPEAKE AQUIFER

NORTH CAROLINA

In the lower Chesapeake aquifer in North Carolina, the progression of hydrochemical facies from calcium plus magnesium bicarbonate to sodium bicarbonate to sodium chloride and the general increase in TDS (pl. 3*A*) toward the coast follow the predevelopment ground-water-flow patterns (Leahy and Martin, 1993, pl. 10*B*). Brown (1959, p. 14) pointed out that the area contains shells and thin beds of shelly limestone. The presence of these carbonate materials suggests that dissolution-precipitation reactions involving carbonate minerals are the cause of the calcium plus magnesium bicarbonate hydrochemical facies. The sodium bicarbonate hydrochemical facies indicates that ion exchange is an active process. The downgradient presence of the sodium chloride hydrochemical facies results from mixing with either seawater or brackish water.

Brown (1959, p. 14) also noted that collophane (a phosphate mineral) is the most abundant mineral in the aquifer. Mass transfer of phosphatic material is discussed in appendix A of this report, and the collophane in the lower Chesapeake aquifer is the most likely source for HPO_4^{-2} (aqueous phosphate) in this area, which indicates that dissolution of the phosphate mineral is an active process in this area.

DELMARVA PENINSULA: DELAWARE, MARYLAND, AND VIRGINIA

The general increase of TDS from the limit of the lower Chesapeake aquifer in the Delmarva Peninsula toward the Atlantic Ocean is in agreement with the prepumping potentiometric surface for this aquifer (Leahy and Martin, 1993, pl. 10*B*). Once again, the progression of hydrochemical facies from calcium plus magnesium bicarbonate to sodium bicarbonate to sodium chloride is in the direction of regional ground-water flow. The lower Chesapeake aquifer contains abundant carbonate shell material, some secondary calcite mineralization, and diatomaceous shell material (Cushing and others, 1973, p. 6–9). The diatom shells are particularly common in the basal part of the aquifer.

The chemical processes controlling the distribution of hydrochemical facies in the lower Chesapeake aquifer appear to be dissolution-precipitation reactions involving carbonate minerals, ion exchange reactions involving clays and amorphous material, mixing of sodium bicarbonate water with seawater or brackish water, and dissolution of amorphous silica that composes the diatom shells. These processes are discussed as follows: carbonate dissolution and precipitation reactions (Chapelle, 1983; Chapelle and Drummond, 1983; Chapelle and Knobel, 1985), ion exchange reactions (Chapelle and Knobel, 1983), chemical processes in the saltwater-freshwater transition zone (Chapelle, 1985; this report, appendixes D and E), and dissolution of amorphous silica (appendix B).

NEW JERSEY

The part of the lower Chesapeake aquifer in New Jersey that is mapped as the variable composition hydrochemical facies roughly coincides with the part of the aquifer that Trapp (1992) noted as being in hydraulic connection with the overlying upper Chesapeake aquifer. Because the upper Chesapeake is unconfined and because the upper and lower aquifers are hydraulically connected, the geochemical processes controlling the water chemistry are similar to those in the surficial aquifer, which are discussed in appendix C of this report. The low TDS content in the New Jersey part of the lower Chesapeake aquifer is typical of surficial aquifer water chemistry. The other hydrochemical facies in New Jersey occur in areas having overlying confining beds and are caused by processes similar to those occurring on the Delmarva Peninsula.

CASTLE HAYNE–PINEY POINT AQUIFER

NORTH CAROLINA

Most of the Castle Hayne–Piney Point aquifer in North Carolina has a TDS content less than 1,000 mg/L and has the calcium plus magnesium bicarbonate hydrochemical facies (pl. 3*B*). This aquifer is composed of limestone with secondary recrystallization, and the calcium plus magnesium bicarbonate hydrochemical facies results from dissolution-precipitation reactions involving the limestone. These reactions are discussed in detail in the section of this report on limestone terranes—appendix A. The Castle Hayne–Piney Point aquifer in North Carolina is the aquifer affected by the mass transfer of phosphatic material (appendix A).

The narrow strip of the sodium bicarbonate hydrochemical facies and the broader strip of the sodium chloride hydrochemical facies downgradient (pl. 3*B* and fig. 2) from the calcium plus magnesium bicarbonate hydrochemical facies result from ion exchange reactions and mixing with seawater.

VIRGINIA, MARYLAND, DELAWARE, AND NEW JERSEY

The downgradient (pl. 3*B* and fig. 2) progression of hydrochemical facies from calcium plus magnesium bicarbonate to sodium bicarbonate to sodium chloride and the generally increasing TDS content in the same direction in the Castle Hayne–Piney Point aquifer in Virginia, Maryland, Delaware, and New Jersey are the results of dissolution of carbonate shell material, ion exchange (with glauconite serving as the exchange substrate), and mixing of a sodium bicarbonate water with brackish water, seawater, or a highly concentrated brine.

BEAUFORT-AQUIA AQUIFER

NORTH CAROLINA, VIRGINIA, AND MARYLAND

The North Carolina, Virginia, and Maryland parts of the Beaufort–Aquia aquifer are lithologically similar and consist predominantly of glauconitic quartz sand with thin shell beds and, in North Carolina, thin limestone beds. Some shell beds and sandy layers are cemented by calcite.

In Maryland, a small area near the western boundary of the aquifer (pl. 4*A*) contains ground water with the variable composition hydrochemical facies. This area is situated along the outcrop of the Aquia Formation where hydraulic gradients are steep and flow direction is toward the Chesapeake Bay (Leahy and Martin, 1993, pl. 11*A*). As a result, no distinct pattern of hydrochemical facies has developed. Apart from this small area, the progression of hydrochemical facies is from calcium plus magnesium bicarbonate to sodium bicarbonate to sodium chloride along the general direction of flow (Leahy and Martin, 1993, pl. 11*A*). There is also a general increase in TDS in the direction of ground-water flow. The sodium chloride hydrochemical facies does not occur in Maryland and is areally restricted in Virginia because of a lithologic facies change in the sediments. East of the aquifer limit (pl. 4*A*), the Aquia Formation is not considered an aquifer (Trapp, 1992). The large area in North Carolina with the sodium chloride hydrochemical facies is the result of mixing, probably with seawater.

The distribution of the calcium plus magnesium bicarbonate and sodium bicarbonate hydrochemical facies is typical of dissolution of carbonate shell material, precipitation of secondary calcite cement, and cation exchange of ions in solution for ions on glauconite exchange sites. These processes were described in detail for the Maryland part of the aquifer by Chapelle (1983), Chapelle and Drummond (1983), and Chapelle and Knobel (1983, 1985). The same processes appear to be active in Virginia and North Carolina.

NEW JERSEY

The Beaufort–Aquia aquifer is equivalent to part of the Vincentown Formation in New Jersey. The aquifer is restricted to a narrow band, limited by a clay facies at the southeastern boundary (Zapecza, 1989, p. B15–B16, pl. 19). The aquifer consists of sparsely glauconitic quartz sand and fossiliferous, calcareous quartz sand (Trapp, 1992). The ground water in New Jersey is dilute (TDS less than 250 mg/L except for a small area adjacent to Delaware Bay) and has the calcium plus magnesium bicarbonate hydrochemical facies. Small areas of variable composition and sodium bicarbonate hydrochemical facies are also located near Delaware Bay (pl. 4*A*). The dominant geochemical processes in the New Jersey part of this aquifer are most likely dissolution-precipitation of shell material with some ion exchange.

PEEDEE-SEVERN AQUIFER

NORTH CAROLINA

In North Carolina, the Peedee–Severn aquifer is approximately equivalent to the Peedee Formation. It consists of fine sand layers interbedded with gray to black marine clay and contains indurated layers of shells and shell fragments (Brown, 1959, p. 25). The area with hydrochemical facies of variable composition (pl. 4*B*) has TDS contents usually less than 250 mg/L and is situated along the southwestern boundary of the aquifer. Geochemical processes apparently have not progressed sufficiently to establish a definite pattern of hydrochemical facies in this area; however, the predominant processes are probably the same as those in the area with the calcium plus magnesium bicarbonate hydrochemical facies just to the north, which result from dissolution-precipitation reactions involving shell material.

As ground water moves downgradient (Leahy and Martin, 1993, pl. 11*B*), ion exchange modifies the chemical composition to a sodium bicarbonate water. The sodium bicarbonate water mixes with salty ground water to form the sodium chloride hydrochemical facies. TDS content increases in the direction of ground-water flow.

MARYLAND, DELAWARE, AND NEW JERSEY

The Peedee–Severn aquifer includes sediments that were locally referred to as the Monmouth Formation or the Monmouth Group in Maryland, Delaware, and New Jersey (Jordan, 1967, p. 6–8). *Exogyra cancellata*, a well-known Late Cretaceous fossil, is present in these sediments, as noted by Jordan (1967, p. 7), and a similar fossil, *Exogyra costata*, was noted by Glaser (1968, p. 15) in Maryland. Glauconite is common in the Peedee–Severn aquifer in this area (Trapp, 1992).

The prepumping potentiometric map for this aquifer (Leahy and Martin, 1993, pl. 11*B*) indicates that flow directions were generally in the direction of increasing TDS. The progression of hydrochemical facies from calcium plus magnesium bicarbonate to sodium bicarbonate to sodium chloride is in the same direction. These lateral changes in water chemistry are similar to changes in the Beaufort–Aquia aquifer, Maryland. The reaction models developed for the Beaufort–Aquia aquifer included dissolution-precipitation reactions involving carbonate minerals (Chapelle, 1983; Chapelle and Drummond, 1983; Chapelle and Knobel, 1985) followed by ion exchange (Chapelle and Knobel, 1983). The same processes, or similar ones, are most likely contributing to the water chemistry of this aquifer. The sodium chloride hydrochemical facies results from mixing with a brine or seawater, as suggested by Meisler and others (1984). Three small areas contain the variable composition hydrochemical facies. These areas are either at local recharge or discharge areas or between them (Leahy and Martin, 1993, pl. 11*B*). The lack of distinct hydrochemical facies in these areas reflects either insufficient time for their development or mixing with brackish water or seawater.

BLACK CREEK–MATAWAN AQUIFER

NORTH CAROLINA

North Carolina has a complex pattern of hydrochemical facies in the Black Creek–Matawan aquifer (pl. 5*A*). The complexity results primarily from differences in aquifer lithology, mineralogy, and flow patterns. The aquifer is roughly separated into two flow cells by a major discharge feature along the Cape Fear River (compare Leahy and Martin, 1986, fig. 111, and Leahy and Martin, 1993, pl. 11*C*). In the area south of the Cape Fear River, flow is from the recharge area along the western limit of the aquifer and is either (1) approximately parallel to the South Carolina border toward the Atlantic Ocean or (2) toward the Cape Fear River (see Leahy and Martin, 1993, pl. 11*C*). North of the Cape Fear River and south to southeast of Raleigh, the prepumping potentiometric surface (Leahy and Martin, 1993, pl. 11*C*) exhibits a potentiometric high, indicating a recharge area. This area is situated at the junction of the calcium plus magnesium bicarbonate, sodium bicarbonate, and variable composition hydrochemical facies shown in plate 5*A*. Flow is away from the recharge area in one of three general directions: (1) toward the Cape Fear River, (2) east to northeast toward Cape Lookout, Cape Hatteras, or Pamlico Sound, or (3) generally northeast, approximately parallel to the western limit of the aquifer, toward Albemarle Sound.

In North Carolina, the Black Creek–Matawan aquifer consists of the Black Creek and Middendorf Formations (Trapp, 1992). The Middendorf Formation is fluviomarine in origin, and its outcrop roughly coincides with the Sand Hills area (fig. 1) in North Carolina (Swift and Heron, 1969, p. 213). The Middendorf Formation is known for its fossil leaves and other plant fossils (Swift and Heron, 1969, p. 215). It is fine to medium, crossbedded sand and contains clay fragments and clay layers (Trapp, 1992). Swift and Heron (1969, p. 214–215) also noted the presence of mud layers and associated oxidized layers, rich in Fe_2O_3, which they interpreted as being partly post-depositional. Fluvial sediments commonly contain trace amounts of silicate minerals such as feldspars and micas.

The area of variable composition hydrochemical facies roughly corresponds to the outcrop area of the Middendorf Formation and extends downdip in the direction of ground-water flow. The variable chemical composition of the ground water probably results from dissolution of silicate minerals and oxidation-reduction reactions involving fossilized plant debris and iron minerals. Similar processes have been discussed for part (Region I) of the Magothy aquifer in Maryland (Knobel and Phillips, 1988).

The Black Creek Formation is also fluviomarine in origin. It is a lignitic, glauconitic, fossiliferous sand that contains gray clay layers. The outcrop is a broad band east of the Middendorf Formation outcrop (Swift and Heron, 1969, fig. 2). As ground water moves from the area with variable hydrochemical facies (pl. 5*A*) into the glauconitic sediments of the Black Creek Formation, it is modified to a sodium bicarbonate hydrochemical facies by ion exchange processes. The part of the area with the sodium bicarbonate hydrochemical facies that has TDS contents of less than 250 mg/L and that is in contact with and lies to the east of the area of variable composition hydrochemical facies is the area where ion exchange processes are going on.

The area mapped as the calcium plus magnesium bicarbonate hydrochemical facies is roughly contained within the outcrop of the Black Creek Formation. The predominant chemical process in this area is dissolution of carbonate shell material. As water moves from this area along aquifer flow paths, shell material continues to dissolve, and dissolved Ca^{+2} and Mg^{+2} exchange for Na^{+} on glauconite exchange sites. The ground water takes on a sodium bicarbonate character, and the TDS content increases. The sodium bicarbonate ground water mixes with seawater (or possibly a brine), resulting in the sodium chloride hydrochemical facies in the part of the aquifer farthest from the recharge areas.

MARYLAND AND DELAWARE

The Black Creek–Matawan aquifer in Maryland and Delaware consists of the Matawan Formation and the Matawan Group, respectively. It is a marine sand that is dark gray, fine grained, glauconitic, and silty to clayey. The prepumping potentiometric surface of this aquifer is very flat (Leahy and Martin, 1993, pl. 11*C*), implying sluggish ground-water flow. The mature hydrochemical facies in this area (sodium bicarbonate and sodium chloride) are probably the result of ion exchange and mixing.

NEW JERSEY

The Black Creek–Matawan aquifer in New Jersey consists of the permeable part of the Englishtown Formation (Trapp, 1992). The hydrochemical facies of this aquifer in New Jersey have been described in detail by Seaber (1965). The results of this study are in general agreement with those of Seaber (1965) except that the sodium bicarbonate hydrochemical facies as mapped in plate 5*A* covers a slightly larger area than mapped by Seaber. An additional difference is that Seaber (1965, fig. 7) showed a narrow band of $Ca^{+2} + Mg^{+2}\text{–}SO_4^{-2} + Cl^-$ water along the western edge of the aquifer. This type of hydrochemical facies would be equivalent to our variable composition hydrochemical facies, possibly with SO_4^{-2} as the dominant anion. The differences between our results and those of Seaber (1965) are largely due to differences in the scale of the two studies and related differences in the areal definition of the aquifer (ours extends farther south than his).

The aquifer is a nonfossiliferous, lignitic, fine to medium quartzose sand with some iron-cemented layers (Seaber, 1965, p. B11). Recharge takes place at a potentiometric high (Leahy and Martin, 1993, pl. 11*C*) just downdip from the outcrop, and some ground water flows toward and discharges in the outcrop. Oxidation-reduction reactions involving iron minerals take place in this area, which corresponds to Seaber's (1965, fig. 7) band of $Ca^{+2} + Mg^{+2}\text{–}SO_4^{-2} + Cl^-$ hydrochemical facies. The recharge from the overlying Peedee–Severn aquifer (pl. 4*B*) is a calcium plus magnesium bicarbonate water. The water moves along aquifer flow paths in the direction of increasing TDS. It is converted to a sodium bicarbonate water by ion exchange processes. The processes in this aquifer are similar to the ones taking place in part (Region II) of the Magothy aquifer, Maryland, that were discussed in detail by Knobel and Phillips (1988).

MAGOTHY AQUIFER IN MARYLAND, DELAWARE, AND NEW JERSEY

In Maryland and Delaware, the Magothy aquifer is equivalent to the Magothy Formation; in New Jersey, it is equivalent to the Magothy Formation where it is recognized, or to the upper part of the undifferentiated Potomac Group and Raritan and Magothy Formations. The Late Cretaceous fluvial to marginal-marine deposits of the Magothy aquifer consist of well-stratified to crossbedded, very fine to medium quartz sand with abundant, discontinuous layers of carbonaceous material, clayey silts (Trapp, 1992), and iron-cemented sand (Glaser, 1969, p. 60–61; Knobel and Phillips, 1988). Knobel and Phillips (1988) also noted the presence of plagioclase and potassium feldspar, muscovite, biotite, lignite, pyrite, montmorillonite (which is an efficient exchange substrate), and many other trace minerals.

The hydrochemical facies in this area are related to the types of chemical processes that take place, and these are influenced by the type of recharge to the Magothy aquifer. Recharge occurs in two ways: (1) through the outcrop area, which roughly parallels the western limit of the aquifer (pl. 5*B*), and (2) by downward leakage from overlying aquifers. In Maryland, the Aquia aquifer east of Washington, D.C., is the source of the leakage (Leahy and Martin, 1993, compare their pls. 11*A* and 12*A*). The direction of ground-water flow is predominantly east or southeast, toward Chesapeake Bay and the Delmarva Peninsula. In New Jersey, the Black Creek–Matawan aquifer northeast of Trenton is the source of the leakage (Leahy and Martin, 1993, compare their pls. 11*C* and 12*A*). The direction of ground-water flow is predominantly south or southwest, toward Delaware Bay and the Delaware River. Some localized flow occurs in both areas, toward nearby outcrop areas or surface-water drainage systems.

In Maryland, the recharge is calcium plus magnesium bicarbonate in character and changes to sodium bicarbonate along aquifer flow paths. This change is due primarily to ion exchange. In the eastern part of the area containing the sodium bicarbonate hydrochemical facies, the increase in TDS reflects an increase in bicarbonate concentrations that probably results from addition of CO_2 to the ground water by microbial processes and from subsequent reaction of the CO_2 with minerals in the aquifer. It also is possible that the added CO_2 reacts with water to form H^+ and HCO_3^-, with the H^+ exchanging for Na^+ on cation exchange sites. These processes have been described in detail by Knobel and Phillips (1988) and Chapelle and others (1987). In New Jersey, the same patterns can be observed in the direction of increasing TDS. On the basis of work conducted by Winograd and Farlekas (1974), we think that the same type of chemical processes are occurring in New Jersey.

The narrow band of variable composition hydrochemical facies along the western boundary of this aquifer (pl. 5*B*) approximately corresponds to the outcrop area of the aquifer. The sulfate facies is locally important. In this area, dissolved oxygen (O_2) from the atmosphere reacts with pyrite and lignite. Sulfate, from the oxidation of pyrite, can remain in solution or be reduced, depending on local oxidation-reduction conditions. In oxidizing environments, Fe^{+2} is unstable, and solid ferric hydroxide forms. These processes account for the sporadic distribution of the sulfate facies as well as the presence of iron cement (Knobel and Phillips, 1988). Langmuir (1969a) and Winograd and Farlekas (1974) suggested that similar processes take place in New Jersey. The sodium chloride hydrochemical facies results from mixing with surface water from Delaware Bay or the Atlantic Ocean, or from mixing with the deep brine identified by Meisler and others (1984).

UPPER POTOMAC AQUIFER IN NORTH CAROLINA, VIRGINIA, AND MARYLAND

The upper Potomac aquifer consists of Upper Cretaceous marine and marginal-marine sands, except in northern Virginia and southern Maryland, where it consists of nearshore marine sand of late Early Cretaceous age (Meng and Harsh, 1988, p. C42; Trapp, 1992, p. G28). The marginal-marine sediments are fine to medium quartz sands with mica and carbonaceous material. They are interbedded with silty, micaceous, carbonaceous clay layers. In North Carolina, the aquifer is the nonfossiliferous upper part of the Cape Fear Formation of Late Cretaceous age. In Virginia, the marginal-marine sediments are the upper part of the Potomac Formation and form the deeper part of the upper Potomac aquifer. The nearshore marine sediments in southern Maryland (Hansen and Wilson, 1984, p. 11) and the equivalent sediments in northern Virginia (Meng and Harsh, 1984, p. 31–33; 1988, p. C41–C42), which make up the shallower part of the upper Potomac aquifer, are micaceous and include glauconite, lignite fragments, and sparse shells (Trapp, 1992, p. G28).

The distribution of prepumping head in the western part of this aquifer is similar to that in the overlying aquifers: the Black Creek–Matawan aquifer in North Carolina, and the Beaufort–Aquia aquifer in Virginia and Maryland (Leahy and Martin, 1993, compare their pls. 11*A*, 11*C*, and 12*A*). It is likely, however, that the upper Potomac aquifer receives some recharge from the overlying aquifers. The similarities in the distribution of the calcium plus magnesium bicarbonate, sodium bicarbonate, and variable composition hydrochemical facies in the upper Potomac aquifer to the distribution of the same hydrochemical facies in the overlying parts of the Black Creek–Matawan aquifer in North Carolina (pl. 5*A*) and the Beaufort–Aquia aquifer in Virginia and Maryland (pl. 4*A*) are consistent with recharge by downward leakage in these areas. The shapes of the hydrochemical facies patterns are smoother in the upper Potomac aquifer, and the calcium plus magnesium bicarbonate and variable composition hydrochemical facies occupy less area in the upper Potomac aquifer than the corresponding hydrochemical facies in the overlying aquifers. Conversely, the sodium bicarbonate hydrochemical facies occupies a larger proportion of the aquifer area in the upper Potomac aquifer.

The low TDS contents imply that the predominant process taking place in the part of the aquifer with TDS contents below about 500 mg/L is ion exchange. The increase in TDS content toward the east suggests that CO_2 is generated in the aquifer, possibly by microbial activity, and subsequently reacts with aquifer minerals such as the feldspar and mica minerals. Ca^{+2} and Mg^{+2} released during these reactions exchange for Na^+ on clay-mineral surfaces. These processes were discussed by Chapelle and others (1987). Another possibility is the reaction of CO_2 and H_2O (eq. 1), dissociation of H_2CO_3 (eq. 2), and subsequent exchange of H^+ for Na^+ on clay-mineral surfaces. The sodium chloride hydrochemical facies along the Atlantic Ocean (pl. 5*B*) is the result of mixing.

MIDDLE POTOMAC AQUIFER

NORTH CAROLINA AND VIRGINIA

In North Carolina, the middle Potomac aquifer is made up of the lower part of the Cape Fear Formation of Late Cretaceous age; in Virginia, it is the middle part (Early Cretaceous) of the Potomac Formation (Trapp, 1992). In North Carolina, the aquifer is fine to medium sand of nearshore marine origin and feldspathic sand and silty clay of continental origin. In Virginia, it is fine to coarse sand of fluvial origin, interlensing with silt and clay (Trapp, 1992).

Comparison of prepumping potentiometric surfaces for the overlying upper Potomac aquifer (Leahy and Martin, 1993, pl. 12*A*) and the middle Potomac aquifer (this report, fig. 3) indicates that downward flow occurs throughout most of the area. There is, however, some lateral flow crossing the North Carolina–South Carolina border—from equivalent aquifers in South Carolina—that moves toward Pamlico Sound (fig. 3). In Virginia, lateral flow is from potentiometric highs along the aquifer's western boundary toward the Chesapeake Bay or Pamlico Sound. The distribution of the calcium plus magnesium bicarbonate and the sodium bicarbonate hydrochemical facies in the Virginia and North Carolina parts of this aquifer (pl. 6*A*) results primarily from the combined effects of silicate hydrolysis reactions followed by ion exchange or by downward leakage of water with similar hydrochemical facies from the overlying upper Potomac aquifer. The latter process is dominant in North Carolina. The sodium chloride hydrochemical facies results from mixing of the sodium bicarbonate water with seawater or with the brine described by Meisler and others (1984).

MARYLAND, DELAWARE, AND NEW JERSEY

In Maryland, the middle Potomac aquifer contains most of the Patapsco Formation (Early and Late Cretaceous) and its approximate equivalents in the undifferentiated Potomac Group. In Delaware, the aquifer is the upper part of the Potomac Formation, and, in New Jersey, it is the water-bearing section of the Raritan Formation of Late Cretaceous age and middle part of the Potomac Group and Raritan and Magothy Formations, undifferentiated. In the Raritan Bay area, it is the Farrington Sand Member of the Raritan Formation (Trapp, 1992).

In Maryland, Delaware, and New Jersey, the aquifer is fluvial in origin, except along the coast of New Jersey where marine beds are present. In Maryland and Delaware, it is composed of fine to coarse sand, interlensing with silt and clay. In New Jersey, the aquifer is composed of lenticular sand bodies interbedded with clay and silt. In the Raritan Bay area, the aquifer is sand with lignite and pyrite (Trapp, 1992).

The prepumping potentiometric surface of the Maryland, Delaware, and New Jersey parts of the middle Potomac aquifer (fig. 3) is similar to that of the Magothy aquifer (Leahy and Martin, 1993, pl. 12*A*). The general distributions of the hydrochemical facies and TDS of the middle Potomac aquifer (pl. 6*A*) are also similar to those distributions in the Magothy aquifer (pl. 5*B*) except for two small areas of the sodium chloride hydrochemical facies and a more restricted distribution of the variable composition hydrochemical facies (pl. 6*A*). The small areas containing the sodium chloride hydrochemical facies are located where hydraulic heads are either low relative to surrounding areas—near Wilmington, Del.—or low relative to the underlying lower Potomac aquifer—the circular area—(Leahy and Martin, 1993, compare their pls. 12*B* and12*C*). The area near Wilmington results from mixing with brackish water from the Delaware River, probably induced by pumping. The circular area results from mixing with water moving upward from the lower aquifer. The chemical processes occurring in the rest of the area are the same as those described for the overlying Magothy aquifer.

LOWER POTOMAC AQUIFER

The lower Potomac aquifer is predominantly Lower Cretaceous sediments of fluvial and deltaic origin. It may contain some Jurassic sediments along the coast (Trapp, 1992).

NORTH CAROLINA AND VIRGINIA

In North Carolina, the lower Potomac aquifer contains salty water everywhere, except for a small area with the sodium bicarbonate hydrochemical facies in the northwestern part of the aquifer. The aquifer has not been extensively defined in North Carolina because of the lack of freshwater. In Virginia, the aquifer is the lower to middle Lower Cretaceous part of the Potomac Formation. The hydrochemical facies and TDS (compare pls. 5*B* and 6), flow patterns (Leahy and Martin, 1993, pl. 12), and lithology (Trapp, 1992) are similar to those in the upper Potomac and middle Potomac aquifers. The chemical processes described for those aquifers also occur in the lower Potomac aquifer.

MARYLAND, DELAWARE, AND NEW JERSEY

In Maryland, along the aquifer outcrop, the lower Potomac aquifer is approximately equivalent to the Patuxent Formation. Downdip, it is the lower, dominantly sandy zone of the Potomac Group, undifferentiated. In Delaware, the aquifer generally corresponds to the lower hydrologic zone of the Potomac Formation, and, in New Jersey, to the lower part of the Potomac Group and Raritan and Magothy Formations, undifferentiated.

The aquifer lithology is similar to that of the middle Potomac aquifer and the Magothy aquifer. The hydrochemical facies patterns and TDS trends (pls. 5*B* and 6) and the flow directions (Leahy and Martin, 1993, pl. 12) are also similar to trends in those aquifers. The chemical processes taking place in this area of the lower Potomac aquifer are typical of nonmarine to marginal marine sediments and were described in the parts of this report on the upper Potomac aquifer, the Magothy aquifer, and the middle Potomac aquifer.

OBSERVATIONS

The patterns of hydrochemical facies in the aquifers considered in this report (pls. 2*B* and 3–6) are variable in their geographic distribution; however, the trends of TDS and the progression of hydrochemical facies along aquifer flow paths are remarkably similar. There is a general increase of TDS in the direction of ground-water flow and a change in hydrochemical facies from variable composition to calcium plus magnesium bicarbonate to sodium bicarbonate to sodium chloride, although the former two are not always present. These trends have been recognized by many investigators in the Atlantic Coastal Plain (Cederstrom, 1946b; Foster, 1950; Seaber, 1962; Back, 1966) and have been attributed to the dissolution of carbonate minerals followed by ion exchange and mixing with salty water. This report further substantiates those processes.

It is notable, however, that these patterns are found in the nonmarine as well as the marine deposits. This implies that dissimilar chemical processes that take place in nonmarine aquifers (silicate hydrolysis) and marine aquifers (carbonate-mineral reactions), when coupled with ion exchange, can result in similar hydrochemical facies.

SUMMARY AND CONCLUSIONS

The chemical composition of ground water in the northern Atlantic Coastal Plain aquifer system reflects physical, chemical, and biologic processes. Physical processes, such as hydrodynamic dispersion, affect concentration gradients between fresh and salty ground-water bodies. Chemical processes, which include mineral dissolution and precipitation, ion exchange reactions, and oxidation-reduction reactions, change the composition of ground water along aquifer flow paths. Biologic processes, such as the metabolism of heterotrophic bacteria, produce carbon dioxide in deeply buried sediments. These three classes of processes act in concert to modify ground-water composition according to predictable patterns.

On a large scale, there is a predictable progression of hydrochemical facies in the northern Atlantic Coastal Plain aquifers. In updip areas characterized by rapid recharge rates, water is variable in composition and is not dominated by any single cation or anion. Downgradient from this, water tends to be characterized by a calcium plus magnesium bicarbonate composition that subsequently grades to sodium bicarbonate. In the most downgradient parts of the Coastal Plain aquifers, water characterized by large sodium chloride concentrations may occur.

On a smaller scale, the types of operative chemical processes that affect ground-water composition depend on the depositional environment of the water-bearing sediments. Sediments deposited in nonmarine, fluvial environments tend to lack reactive carbonate shell material or sodium-rich clay minerals. In consequence, ground water associated with these sediments is often observed to be low in dissolved solids. Dissolution of silicate minerals, such as feldspars, and oxidation-reduction reactions involving ferric oxyhydroxides are important chemical processes. In contrast, sediments deposited in marine sedimentary environments generally contain reactive minerals, and ground water associated with these sediments tends to be mineralized. Dissolution of carbonate shell material, combined with cation exchange reactions, tends to produce water containing large concentrations of sodium and bicarbonate.

The surficial aquifer, which overlies much of the study area, is a mosaic of geochemical systems, and there is much variability in water chemistry. Much of this variability reflects differences in aquifer lithology. In areas overlain by organic-matter-rich silts and clays, ground water tends to be anoxic and contains relatively large concentrations of dissolved iron. In areas characterized by sandy materials, ground water is generally under oxidizing conditions, lacks dissolved iron, and may contain measurable nitrate concentrations. Evaporation-induced concentration of rainwater appears to significantly affect water chemistry in some environments. Dissolution of silicate minerals and cation exchange reactions are also important processes in some environments. Because the surficial aquifer occurs near land surface and is unconfined, aquifer geochemistry is sensitive to land use. In agricultural areas, application of fertilizers containing nitrogen, potassium, and phosphorus compounds may significantly affect water chemistry. In addition, septic tank effluent or landfill leachates may affect local water quality.

Cation exchange reactions are important geochemical processes that modify ground-water composition in deep confined aquifer systems. The removal of cations from solution and their replacement with sodium follows a predictable pattern. Calcium is the first dissolved ion to be removed from solution and is followed by magnesium and potassium. This observed succession agrees exactly with the theoretical stability of these cations on exchange sites. Near the outcrop area, much of the total exchange capacity is filled with calcium. Downgradient, where less reaction has occurred, most of the exchange capacity is filled by sodium. Most Coastal Plain confined aquifers thus act as large cation-exchange columns that separate dissolved cations according to their stability on exchange sites. This process is a major factor in the development of the observed succession of hydrochemical facies (calcium-magnesium to sodium) in Coastal Plain aquifers.

The commonly observed reaction of calcium replacing sodium on exchange sites in freshwater aquifers may be reversed by brackish-water intrusion. Because brackish water contains relatively high concentrations of sodium and magnesium in solution, calcium (rather than sodium) is replaced on exchange sites. Where the composition of endmember waters can be accurately assessed, this "reverse exchange" can be verified by mass-balance calculations. In the saltwater-freshwater transition zone, where endmember waters are not well defined, reverse exchange may be important.

The metabolism of bacteria in deeply buried sediments is an important geochemical process in Coastal Plain aquifers. Cored sediments from the deep (40 to 550 ft) subsurface of Maryland showed the presence of a significant viable bacterial population (10^3 to 10^6 bacteria per gram sediment [dry weight]). Sulfate reduction and methanogenesis were identified as metabolic strategies for some of the bacteria. It is probable, however, that other metabolic strategies are utilized by a significant portion of the bacteria. The presence of viable bacteria suggests that bacterial metabolism progressively adds carbon dioxide to ground water flowing through the sediments. Subsequent reaction of carbon dioxide with carbonate or silicate minerals results in increasing bicarbonate concentrations along aquifer flow paths. Bacterial metabolism is the principal geochemical process that drives the development of high-bicarbonate facies in Coastal Plain aquifers.

Remarkably similar patterns of hydrochemical facies are found in both nonmarine and marine deposits. This similarity shows that dissimilar chemical processes that take place in nonmarine aquifers (silicate hydrolysis) and marine aquifers (carbonate-mineral reactions), when coupled with ion exchange, can result in similar hydrochemical facies.

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APPENDIXES A–E

APPENDIX A: LIMESTONE TERRANES, PHOSPHATE DIAGENESIS, AND SIDERITE CEMENTATION–NORTH CAROLINA AND NEW JERSEY

LIMESTONE TERRANES–NORTH CAROLINA

The North Carolina Coastal Plain contains an extensive reef complex that is composed of molluscan limestone with substantial amounts of secondary recrystallization. This deposit grades laterally into a bryozoan limestone and downward into a calcareous sand (Brown and others, 1972). Typical subsurface sections in Beaufort and Martin Counties are commonly dolomitic, gray to white, shell-limestones (Brown, 1959, p. 13–14). In North Carolina, this deposit is equivalent to the regional Castle Hayne–Piney Point aquifer described by Trapp (1992) or to the North Carolina Castle Hayne aquifer described by Winner and Coble (1996).

The equation

$$(Ca_{1-X}\,Mg_X)CO_3 + CO_2 + H_2O \leftrightarrow (1-X)Ca^{+2} + XMg^{+2} + 2HCO_3^- \quad (A1)$$

describes water chemistry resulting from dissolution-precipitation reactions involving calcite, aragonite, and magnesium calcite and applies to the Castle Hayne–Piney Point aquifer in North Carolina. Because dolomitic limestones are common in the Castle Hayne–Piney Point aquifer, dissolution of dolomite also applies:

$$0.5CaMg(CO_3)_2 + CO_2 + H_2O \rightarrow 0.5Ca^{+2} + 0.5Mg^{+2} + 2HCO_3^-. \quad (A2)$$

Equations A1 and A2 both predict that two moles of HCO_3^- will be produced for each mole of Ca^{+2} + Mg^{+2}. If HCO_3^- concentration is plotted as a function of Ca^{+2} + Mg^{+2} concentration, then a straight line with a slope of two should result. HCO_3^- concentration is plotted as a function of Ca^{+2} + Mg^{+2} concentration in figure A1 for all available analyses of ground water from the Castle Hayne–Piney Point aquifer in North Carolina (Knobel, 1985, table 9). A straight line with a slope of two is drawn through the data for comparative purposes. The preponderance of observed data closely matches model-predicted values, which suggests that either of the carbonate dissolution equations (eq. A1 or A2) is a good representation of the chemical system in this area.

MASS TRANSFER OF PHOSPHATIC MATERIAL–NORTH CAROLINA

In Beaufort County, N.C., the Castle Hayne Limestone—equivalent to the Castle Hayne–Piney Point aquifer—is unconformably overlain by sediments of questionable middle Miocene age (Brown, 1959, p. 14). The latter sediments are commonly referred to as the Pungo River Formation (Heath, 1975) and are equivalent to the lower Chesapeake aquifer. They consist of quartz sand and collophane (a mineral containing phosphate). The collophane is in the form of brown spherules showing oolitic or banded structure (Brown, 1959, p. 14).

Hard, dark phosphate locally caps the Castle Hayne aquifer in areas where it is overlain by Pungo River sediments. The cap extends several inches into the limestone. Miller (1982, p. 11) attributed the phosphate layer to solution of francolite (which is similar to collophane) by downward percolating ground water in the Pungo River Formation and redeposition of phosphate in the permeable limestone of the Castle Hayne aquifer. This hypothesis is consistent with Berner's (1980, p. 171) observation that aqueous phosphate may rapidly precipitate to form apatite in the presence of fine-grained particles of $CaCO_3$. The surfaces of $CaCO_3$ particles act as nucleation sites for apatite crystallization. The exact chemical compositions of the dissolving and precipitating minerals are unknown, but the aqueous phosphate probably reprecipitates somewhat like the following equation (Stumm and Morgan, 1981, p. 284):

$$CaCO_3 + 0.2H^+ + 0.6HPO_4^{-2} + 0.2H_2O \rightarrow 0.1Ca_{10}(PO_4)_6(OH)_2 + HCO_3^-, \quad (A3)$$

where fluorine may substitute for the hydroxyl ion (Deer and others, 1966, p. 505). McArthur (1985, p. 34) indicated that diagenetic weathering of phosphate minerals and recrystallization favor the formation of fluorapatite. Carroll (1959, p. 768) pointed out that phosphates of the alkaline earths form at high pH values, which is consistent with the range of pH (7.1 to 8.4) reported by Knobel (1985, p. 69) for the Castle Hayne–Piney Point aquifer in Beaufort County. Although it cannot be definitely concluded that the above mechanism is occurring in Beaufort County, it is likely that this process—or a similar one—accounts for the phosphate cap on the Castle Hayne–Piney Point aquifer in North Carolina.

SIDERITE CEMENTATION–NEW JERSEY

In the New Jersey Coastal Plain, $FeCO_3$ (siderite) is a common mineral. For example, it has been observed as concretions in the gradational contact between the Woodbury Clay and the Englishtown Formation (Seaber, 1965, p. B11) and as a finely crystalline cement in the Tinton Formation (Owens and others, 1977, p. 51; Wolfe, 1977, p. 278). Seaber (1965, p. B23) pointed out that iron concentration in water from the Englishtown Formation decreased away from the outcrop and suggested that the decrease may have resulted from precipitation of iron minerals such as $FeCO_3$:

$$Fe^{+2} + HCO_3^- \rightarrow FeCO_3 + H^+. \qquad (A4)$$

Precipitation of $FeCO_3$ generally occurs under reducing conditions when sulfur concentrations are low (Hem, 1985, p. 77). With currently available data, it is not possible to evaluate the extent of $FeCO_3$ precipitation in the New Jersey Coastal Plain.

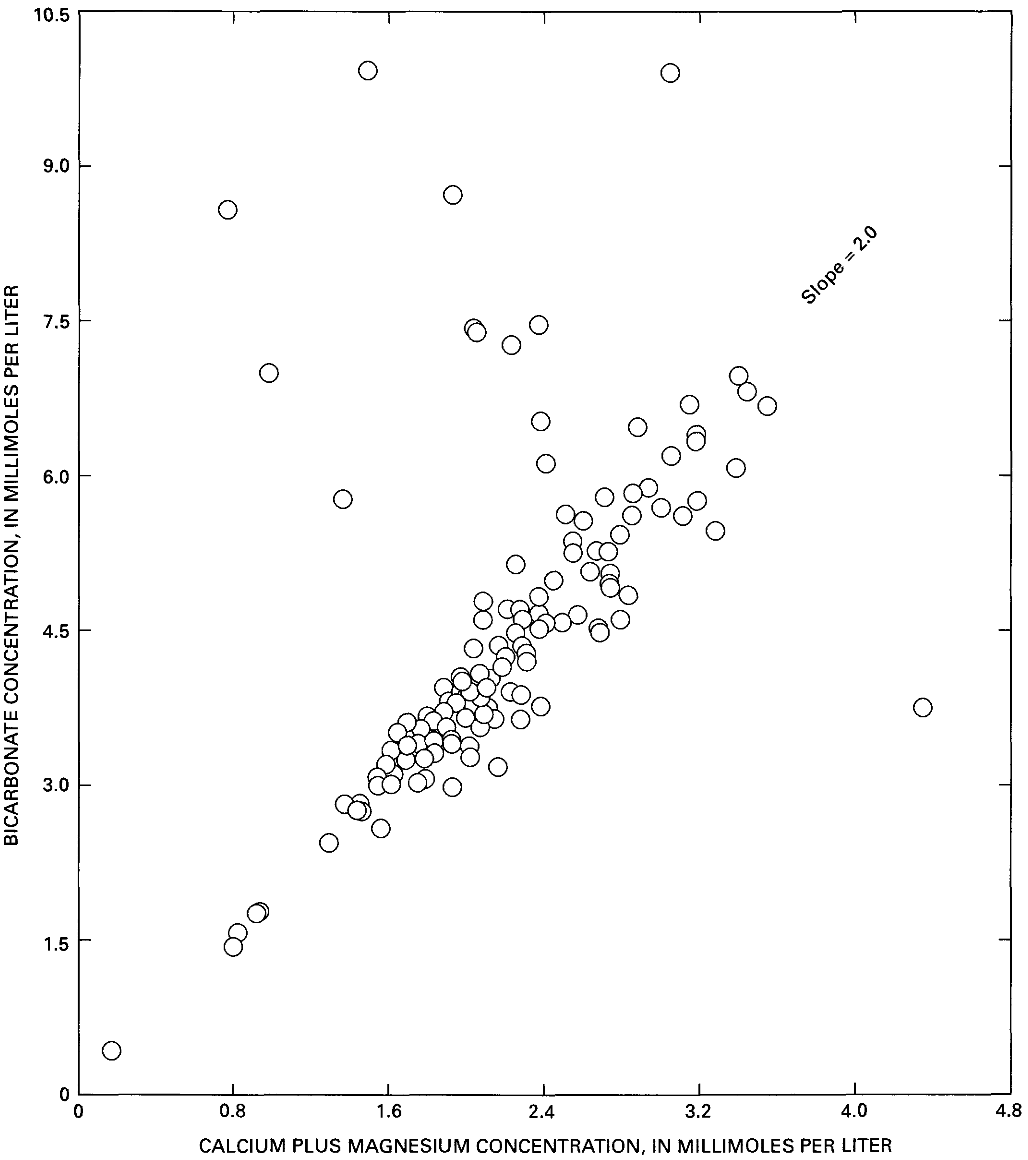


FIGURE A1.—Bicarbonate (HCO_3^-) concentration as a function of calcium plus magnesium (Ca^{+2} + Mg^{+2}) concentration for analyses of water taken from the Castle Hayne–Piney Point aquifer in North Carolina (from Knobel and Chapelle, 1986, fig. 121).

APPENDIX B: DISSOLUTION OF AMORPHOUS SILICA–MARYLAND AND DELAWARE

The theoretical controls on the concentration of dissolved silica (SiO_2) in ground water are the solubilities of quartz (lower limit) and amorphous silica (upper limit). The equilibrium constants at 25°C are 0.0001 for quartz and 0.002 for amorphous silica (Drever, 1982, p. 90). These values correspond to concentrations of 6 and 120 mg/L, respectively. The actual concentrations of silica in ground water, however, commonly fall between these values. For example, the basal parts of the Miocene sediments on the Delmarva Peninsula are highly diatomaceous. They are characterized by abundant shell material and the lack of glauconitic material (Cushing and others, 1973, p. 6). Cushing and others (1973, p. 43) referred to these sediments as the Cheswold aquifer. Gibson (1971, p. 10–12) described similar sediments in Maryland, which are known as the Calvert and Choptank Formations. Knobel (1985) listed water-quality data for these sediments (Delaware, 122CSLD; Maryland, 122CLVR, 122CPNK, and 122CSLD), which are equivalent to the lower Chesapeake aquifer described by Trapp (1992). Because diatom shells are composed of amorphous silica, they are less stable in ground water than crystalline quartz. As a result, concentrations of dissolved silica are elevated in these sediments relative to concentrations in the study area as a whole. The mean and median silica concentrations for 44 samples from diatom-rich sediments both are approximately 51 mg/L, whereas the mean and median concentrations of 3,469 samples for the entire northern Atlantic Coastal Plain are approximately 20 and 15 mg/L, respectively.

Chapelle and Drummond (1983, p. 93–95) studied silica concentrations in the Piney Point–Nanjemoy aquifer, which is equivalent to the Maryland part of the Castle Hayne–Piney Point aquifer that underlies the diatom-rich sediments of the lower Chesapeake aquifer in Maryland. Mack and others (1971, p. 55) observed that silica concentrations in water from these sediments in the northern part of Talbot County averaged 50 mg/L. Chapelle and Drummond (1983, p. 95) hypothesized that vertical leakage from the overlying lower Chesapeake aquifer into the Castle Hayne–Piney Point aquifer caused the large silica concentrations. One problem with this hypothesis is that water in equilibrium with amorphous silica should have much larger silica concentrations (about 120 mg/L) (Drever, 1982, p. 90) than those observed in the lower Chesapeake and Castle Hayne–Piney Point aquifers. If the source of silica is dissolution of diatoms, then an additional mechanism must be limiting silica concentrations to the observed values.

Reaction of dissolved silica with the silica minerals in the aquifer is likely to be the limiting factor. To test this hypothesis, a phase diagram calculated by Garrels (1976) is used. Garrels (1976, p. 75) plotted the compositions of waters from various rock types as a function of Na^+, H^+, and dissolved silica in the system $Na_2O–Al_2O_3–SiO_2–H_2O$. He concluded that waters evolve to the kaolinite-montmorillonite boundary and subsequently evolve along it. This evolution effectively limits dissolved silica concentrations to less than 70 mg/L.

If a similar mechanism occurs in the Castle Hayne–Piney Point aquifer, then a similar pattern should develop. Figure B1 shows available water analyses of Castle Hayne–Piney Point water plotted according to the method of Garrels (1976). The figure demonstrates that the composition of the water evolves along the kaolinite-montmorillonite boundary. This trend is consistent with increasing sodium concentrations and decreasing hydrogen ion concentrations along aquifer flow paths. This diagram implies that silica concentrations adjust to the changing $\log_{10} [Na^+]/[H^+]$ ratio so that the water composition remains in the kaolinite stability field. This adjustment strongly suggests that the stability relation of kaolinite and montmorillonite is the controlling mechanism that limits the concentration of dissolved silica in water from the Castle Hayne–Piney Point aquifer in Maryland.

Although diatomaceous sediments also exist in New Jersey and Virginia, they tend to be associated with the finer grained silts and clays for which water analyses are not available. These sediments probably contain elevated silica concentrations also.

In addition to causing large silica concentrations, diatoms may provide an exchange medium. Dissolution of carbonate shell material (eq. A1) generates a calcium bicarbonate water that is subsequently modified by ion exchange to form a sodium bicarbonate water:

$$X^{+2}_{aq} + 2Y \cdot Ex_{ad} \leftrightarrow 2Y^{+}_{aq} + X \cdot Ex_{ad}, \qquad \text{(B1)}$$

where X^{+2} is a divalent cation, Y^+ is a monovalent cation, Ex is an exchanging substrate, aq indicates aqueous, and ad indicates adsorbed. The exchanging medium may be montmorillonite or the amorphous diatom material itself. Carroll (1959, p. 773) pointed out that amorphous gel material in the Skye diatomite, Scotland, has a cation exchange capacity of about 75 to 100 meq/100 g and that amorphous material probably adds cation exchange capacity to the host sediments.

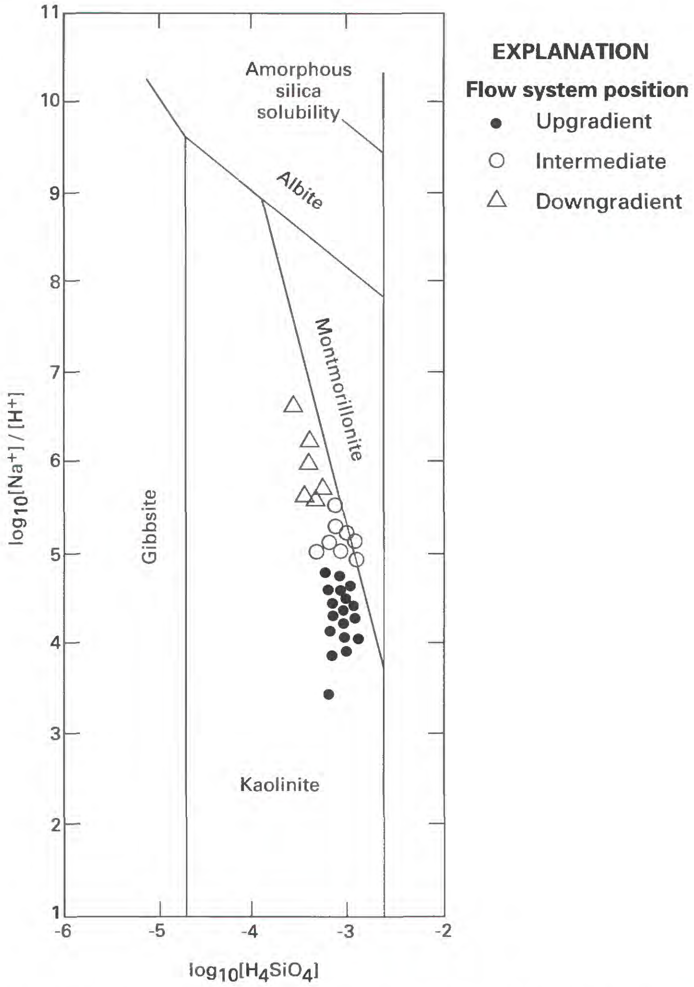


FIGURE B1.—Stability relations in the system Na_2O–Al_2O_3–SiO_2–H_2O with compositions of waters from the Castle Hayne–Piney Point aquifer, Maryland, superposed (modified from Chapelle and Drummond, 1983, fig. 56).

APPENDIX C: CHEMICAL PROCESSES COMMON IN THE UNCONFINED AQUIFER–DELAWARE

Water in the unconfined aquifer of Delaware (fig. C1) can be categorized into two broad types: (1) water occurring under natural or nearly natural conditions and (2) water affected by anthropogenic activities. This appendix discusses chemical reactions in both types of water and is based on work by Denver (1986).

NATURAL GROUND WATER

The geochemical processes controlling water quality in areas dominated by naturally occurring water are similar to those described by Chapelle (1985) for nonmarine sediments. Observed water chemistry results from concentration of atmospheric precipitation and its subsequent reaction with minerals in the aquifer.

RAINWATER CONCENTRATION AND OXIDATION-REDUCTION PROCESSES

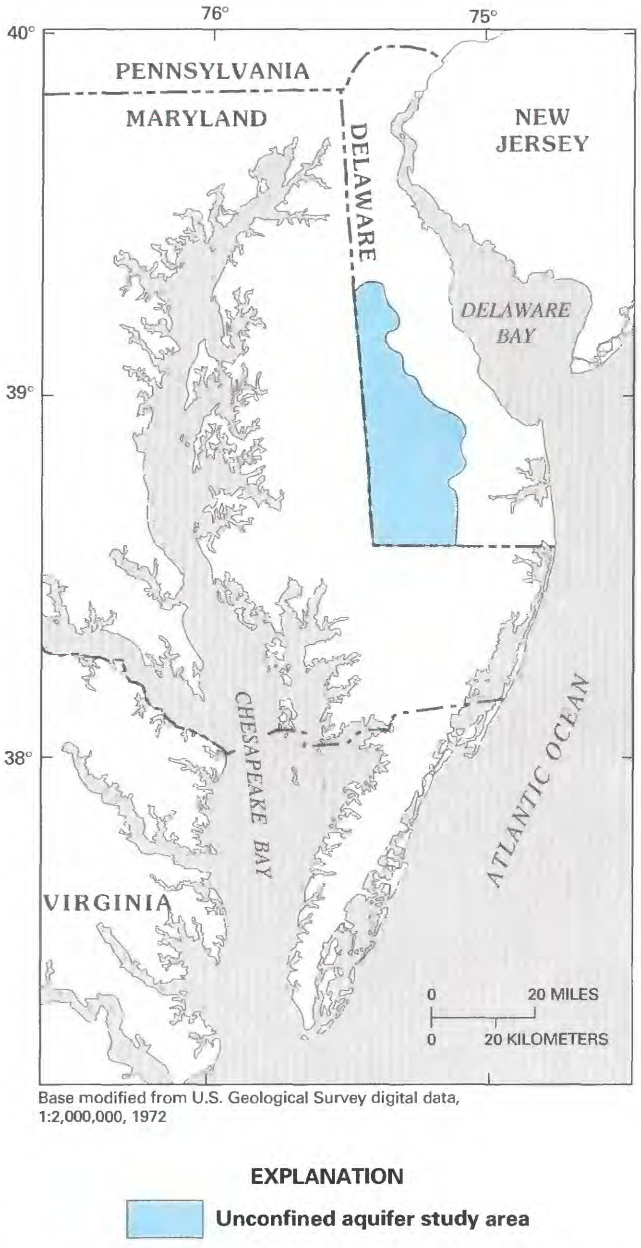
Table C1 shows the average composition of rainwater at Lewes, Del., for the period August 1978 to January 1983 and the calculated composition that would result from concentration by evaporation to about one-third of its original volume. Denver (1986, p. 18) pointed out that ground water in the unconfined aquifer tends to change from oxidizing (oxic) to reducing (anoxic) conditions as it moves away from the water table, where it is exposed to atmospheric gases, and as dissolved oxygen is depleted by chemical reactions involving oxidation-reduction (redox) processes.

Figure C2 shows the pE (pE=16.9 Eh) for selected redox couples. The pE—oxidation potential—of a system is large if O_2 is present in the water. For example, the pE is maintained at about 13.8 by the O_2/H_2O couple as long as the water contains free oxygen. After the O_2 is completely removed, the pE is reduced and maintained at successively smaller values by denitrification, reduction of manganese and iron species, sulfate reduction, and fermentation. Oxidation of organic material commonly accompanies reducing reactions in the unconfined aquifer. The ferrous ion (Fe^{+2}) is stable in reducing environments, and its reduction from ferric ion (Fe^{+3}) can be represented by:

$$Fe(OH)_3+0.25CH_2O+1.75H^+ \rightarrow Fe^{+2}+0.25HCO_3^-+2.5H_2O, \qquad (C1)$$

where the production of HCO_3^- adds alkalinity to the water.

If the ferrous ion subsequently comes in contact with O_2, oxidation to ferric ion takes place according to the following equation:



Base modified from U.S. Geological Survey digital data, 1:2,000,000, 1972

FIGURE C1.—Location of the unconfined aquifer in west-central and southwestern Delaware (modified from Denver, 1986, fig. 1).

TABLE C1.—*Average concentrations of dissolved ions in precipitation at a station in Lewes, Del., August 1978 to January 1983, and calculated concentrations after evaporation*

[Definitions: mg/L, milligrams per liter; mmol/L, millimoles per liter. From Denver (1986, table 2)]

Dissolved ion	Average concentration		Calculated concentration after evaporation to one-third of original volume[1]	
	mg/L	mmol/L	mg/L	mmol/L
Hydrogen, H^+..........	0.05	0.046	0.14	0.138
Sodium, Na^+.............	1.22	.053	3.66	.159
Ammonium, NH_4^+...	.23	.013	.69	.039
Potassium, K^+..........	.09	.002	.28	.007
Calcium, Ca^{+2}...........	.13	.003	.38	.009
Magnesium, Mg^{+2}.....	.13	.005	.38	.016
Chloride, Cl^-............	1.93	.054	5.79	.162
Sulfate, SO_4^{-2}...........	2.10	.022	6.30	.066
Nitrate, NO_3^-...........	1.23	.020	3.69	.060

[1] Typical concentration factor for Delmarva Peninsula (Cushing and others, 1973, p. 7).

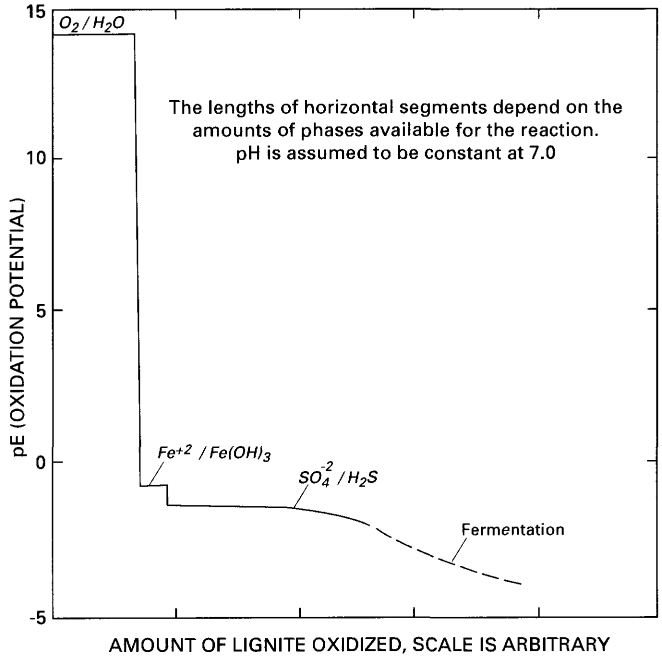


FIGURE C2.—Change in pE (oxidation potential) of water in contact with sediment as a function of the amount of lignite oxidized (from Chapelle, 1985, fig. 28).

$$Fe^{+2} + 0.25O_2 + 2.5H_2O \rightarrow Fe(OH)_3 + 2H^+. \quad (C2)$$

Ferric hydroxide coatings on sand grains in the oxic part of the unconfined aquifer probably result from processes similar to equation C2. In addition, iron-cemented sand layers that are common at the boundaries between layers of contrasting permeabilities in the unconfined aquifer probably result from mixing of oxic and anoxic water. The existence of different water types in the layers of different permeability most likely results from more rapid transport of O_2 in the coarse-grained sediments.

INCONGRUENT DISSOLUTION OF SILICATE MINERALS

Owens and others (1983, p. F18–F25) studied weathering profiles in sediments equivalent to the unconfined aquifer east of the study area. They defined two weathering cycles that produced an initial predominantly kaolinite-gibbsite-goethite assemblage indicative of intense leaching followed by a vermiculite-illite-amorphous iron oxide(?) assemblage that formed in the upper part of the sediments. These minerals are the result of postdepositional chemical weathering processes involving silicate minerals and oxidation-reduction reactions. Several reactions are tabulated in table C2 for the unconfined aquifer. Graphs similar to figure B1 were prepared for the unconfined aquifer in Delaware by Denver (1986, fig. 22, p. 65). Stability relations also were considered for the systems including K_2O and CaO. All analyses plotted in the kaolinite stability field, which indicates that kaolinite is the stable weathering product of complex aluminosilicate minerals in this aquifer. At low silica concentrations, gibbsite can form; however, as silica concentrations increase, gibbsite reacts with the silica to form kaolinite (eq. 4 in table C2).

ION EXCHANGE REACTIONS

A wide variety of clay minerals are present in the surficial sediments of the Delmarva Peninsula (Owens and Denny, 1979; Owens and others, 1983; Mixon, 1985). However, the clays most common in the soil zone of southwestern Delaware are kaolinite, illite, and vermiculite (Pickett, 1970). Clays in the deeper sediments of the unconfined aquifer are kaolinite, illite, and montmorillonite in varying proportions (Hess, 1977). All clay minerals exchange ions adsorbed on their surfaces for ions in solution to some extent (Garrels and Christ, 1965, table 8.2, p. 271). The exchange process occurs according to equations 5 and 6 in table C2 and was described by Chapelle and Knobel (1983). When the pH is smaller than

TABLE C2.—*Reactions used in calculating chemical mass balances of water from the unconfined aquifer in west-central and southwestern Delaware*

[Modified from Denver (1986, table 6)]

Incongruent dissolution reactions:

$$\overset{\text{plagioclase}}{4\mathrm{Na_{0.5}Ca_{0.5}Al_{1.5}Si_{2.5}O_8}} + 6\mathrm{H_2CO_3} + 11\mathrm{H_2O} \rightarrow 2\mathrm{Na^+} + 2\mathrm{Ca^{+2}} + 4\mathrm{H_4SiO_4} + 6\mathrm{HCO_3^-} + \overset{\text{kaolinite}}{3\mathrm{Al_2Si_2O_5(OH)_4}} \tag{1}$$

$$\overset{\text{biotite}}{\mathrm{KMg_3AlSi_3O_{10}(OH)_2}} + 7\mathrm{H_2CO_3} + 0.5\mathrm{H_2O} \rightarrow \mathrm{K^+} + 3\mathrm{Mg^{+2}} + 7\mathrm{HCO_3^-} + 2\mathrm{H_4SiO_4} + \overset{\text{kaolinite}}{0.5\mathrm{Al_2Si_2O_5(OH)_4}} \tag{2}$$

$$\overset{\text{orthoclase}}{\mathrm{KA1Si_3O_8}} + \mathrm{H_2CO_3} + 4.5\mathrm{H_2O} \rightarrow \mathrm{K^+} + \mathrm{HCO_3^-} + 2\mathrm{H_4SiO_4} + \overset{\text{kaolinite}}{0.5\mathrm{Al_2Si_2O_5(OH)_4}} \tag{3}$$

$$\overset{\text{gibbsite}}{\mathrm{A1_2O_3{\cdot}3H_2O}} + 2\mathrm{H_4SiO_4} \rightarrow 5\mathrm{H_2O} + \overset{\text{kaolinite}}{\mathrm{Al_2Si_2O_5(OH)_4}} \tag{4}$$

Ion exchange:

$$\mathrm{X^+_{aq}} + \mathrm{Y \cdot Ex_{ad}} \leftrightarrow \mathrm{Y^+_{aq}} + \mathrm{X \cdot Ex_{ad}} \tag{5}$$

$$\mathrm{X^{+2}_{aq}} + 2\mathrm{Y \cdot Ex_{ad}} \leftrightarrow 2\mathrm{Y^+_{aq}} + \mathrm{X \cdot Ex_{ad}} \tag{6}$$

Redox reactions:

Nitrification: $$\mathrm{O_2} + 0.5\mathrm{NH_4^+} \rightarrow 0.5\mathrm{NO_3^-} + \mathrm{H^+} + 0.5\mathrm{H_2O} \tag{7}$$

Iron reduction: $$\mathrm{Fe(OH)_3} + 1.75\mathrm{H^+} + 0.25\mathrm{CH_2O} \rightarrow \mathrm{Fe^{+2}} + 2.5\mathrm{H_2O} + 0.25\mathrm{HCO_3^-} \tag{8}$$

Sulfate reduction: $$0.5\mathrm{SO_4^{-2}} + \mathrm{CH_2O} \rightarrow 0.5\mathrm{H_2S} + \mathrm{HCO_3^-} \tag{9}$$

Bicarbonate depletion:

$$\mathrm{HCO_3^-} + \mathrm{H^+} \leftrightarrow \mathrm{H_2CO_3} \tag{10}$$

($\mathrm{H^+}$ from nitrification, reaction 7)

six, which is commonly the case in the unconfined aquifer (table C3), $\mathrm{H^+}$ displaces $\mathrm{Ca^{+2}}$, $\mathrm{Mg^{+2}}$, $\mathrm{K^+}$, and $\mathrm{Na^+}$ on exchange sites. At larger pH's, $\mathrm{H^+}$ is not strongly held on exchange sites, and $\mathrm{Ca^{+2}}$ and $\mathrm{Mg^{+2}}$ predominate.

MASS-BALANCE CALCULATIONS

Denver (1986, table 7) gave results of mass-balance calculations between water analyses for several samples of natural or virtually natural ground water and precipitation. The chemical processes used to achieve mass balance are summarized in table C2. The reactions shown in table C2 are a simplified representation of the natural geochemical system and are not the only reactions that could be used to achieve mass balance; however, given the uncertain knowledge of aquifer mineralogy and chemical composition of the recharge water, they are the most probable ones. On the basis of the mass-balance calculations, it appears that dissolution of silicate minerals and redox processes control water chemistry where the unconfined aquifer is not influenced by human activities.

ANTHROPOGENIC INFLUENCES ON GROUND-WATER CHEMISTRY

Anthropogenic influences on ground-water quality differ with the type of human activity. Some of the effects of industrial activities on water-quality in the Baltimore, Md., area were discussed by Chapelle (1985). Additional studies in New Jersey have focused on the effect of industrial and residential activities on ground-water quality in the area adjacent to the Delaware River downstream from Trenton, N.J. (Fusillo and others, 1984), and on the geochemical processes controlling ground-water chemistry in the same approximate area (Langmuir, 1969a,b,c). An example of the site-specific effects of waste-disposal activities on ground-water quality is given by a study of chemical processes affecting the generation and migration of leachate at the Army Creek landfill near Wilmington, Del. (Baedecker and Back, 1979a,b). Even though these types of activities account for a significant amount of land use in the northern Atlantic Coastal Plain, the predominant type of land use is agriculture. This section describes the effect of agricultural land use on water quality in the unconfined aquifer in Delaware (fig. C1). Crop and livestock production are the primary agricultural land uses in the study area (Denver, 1986).

CROP PRODUCTION

Plant growth is enhanced by the application of inorganic fertilizer, manure, and lime (hydrated calcium oxide). Inorganic fertilizer contains nitrogen, potassium, phosphorus, and several minor plant nutrients (Donahue, 1961, p. 170–172). Minor nutrients are present in fertilizer in such small quantities that they do not significantly affect water quality. Lime, including crushed limestone and dolomite, is used to buffer soil pH. In Delaware, crushed dolomite is the most commonly used form of buffering material. Poultry manure, a byproduct of egg and broiler production, is readily available in Delaware and is widely used as a fertilizer. Nitrogen is the primary constituent of poultry manure (Overcash and others, 1983), but it also contains other plant nutrients (table C4).

Nitrogen added to the soil for crop production is in the form of organic and ammonium compounds. Ammonium ($\mathrm{NH_4^+}$) is usually converted to nitrate ($\mathrm{NO_3^-}$), the stable oxidized form of dissolved nitrogen, in the soil zone by a two-step process known as nitrification. Ammonium ion is oxidized by nitrifying bacteria to nitrite ($\mathrm{NO_2^-}$):

$$\mathrm{NH_4^+} + 1.5\mathrm{O_2} \rightarrow \mathrm{NO_2^-} + \mathrm{H_2O} + 2\mathrm{H^+}. \tag{C3}$$

TABLE C3.—*Chemical constituents in water samples from wells in the unconfined aquifer in west-central and southwestern Delaware with natural or nearly natural water chemistry*

[Bicarbonate concentration was calculated from field alkalinity. Results shown in milligrams per liter except for pH or as noted; less-than sign (<) indicates that concentration was below specified detection limit. Data from Denver (1986, table 4)]

Constituent or physical characteristic	Well number									
	Jb31-1	Mc31-3	Md55-2	Nd25-3	Nd25-4	Nd25-5	Nd25-6	Ne54-3	Of41-1	Qc52-6
Date sampled (month-day-year)	6-9-83	9-11-83	9-9-83	10-18-83	10-14-83	10-18-83	10-18-83	3-14-83	2-9-83	9-8-83
Screened interval below land surface, in feet	22-27	41-61	?-50	117-122	85-90	49-54	39-44	72-82	97-117	60-120
Specific conductance, in µS/cm at 25°C[1]	90	132	40	72	47	56	49	39	59	43
pH[2]	5.6	6.3	5.8	6.4	6.4	5.9	5.8	5.6	6.0	5.4
Dissolved oxygen	2.2	0.0	3.4	0.4	0.1	3.6	2.3	2.6	8.5	3.1
Silica, SiO_2	20	23	30	34	35	23	23	14	28	16
Total recoverable iron, Fe_{Total}	0.76	5.6	0.04	2.6	4.3	0.02	0.01	0.3	0.7	<0.003
Calcium, Ca^{+2}	9.5	12.0	2.0	2.6	0.59	2.5	2.3	1.2	2.8	2.6
Magnesium, Mg^{+2}	1.6	2.1	0.22	0.64	0.17	0.45	0.36	0.35	0.59	0.9
Sodium, Na^+	5.1	6.2	5.4	10.0	7.1	7.2	6.7	4.4	6.7	4.8
Potassium, K^+	1.2	1.2	0.4	1.0	0.5	0.9	0.8	1.2	1.3	1.6
Nitrate plus nitrite as nitrogen, $NO_3^- + NO_2^-$ as N	0.61	0.19	0.23	<0.10	<0.10	2.3	0.03	<0.10	1.8	2.4
Ammonia as nitrogen, NH_3 as N	<0.01	0.13	<0.01	0.18	0.03	<0.01	0.03	<0.01	<0.01	0.02
Chloride, Cl^-	4.0	5.8	4.2	4.5	5.9	4.7	4.4	5.0	5.8	6.0
Bicarbonate, HCO_3^-	25.6	52.4	15.6	39.0	21.9	12.2	15.9	12.0	18.0	5.8
Sulfate, SO_4^{-2}	19.0	15.0	0.6	1.3	1.8	0.4	0.4	0.9	<5.0	2.0

[1] Microsiemens per centimeter at 25° Celsius.

[2] Negative base-10 logarithm of hydrogen ion activity in moles per liter.

TABLE C4.—*Major chemical components in poultry manure and sewage effluent*

[Concentrations in millimoles per liter. Table from Denver (1986, table 3). Data on poultry manure from Overcash, Humenik, and Miner (1983, p. 147–180); data on sewage effluent from LeBlanc (1982, p. 7)]

Component	Poultry manure	Sewage effluent
Calcium	773	0.30
Magnesium	176	.18
Sodium	132	2.26
Potassium	306	.30
Chloride	170	.93
Nitrogen, total	2,499	1.36
Sulfur	140	.39
Phosphorus, total	387	.06

Nitrite is oxidized to nitrate:

$$NO_2^- + 0.5O_2 \rightarrow NO_3^-. \qquad (C4)$$

Nitrifying bacteria are sensitive to a number of environmental influences such as variations in aeration, temperature, moisture, availability of exchangeable ions, fertilizers, and the ratio of carbon to nitrogen (Denver, 1986, p. 27). These environmental factors are related, therefore, to the rate and degree of nitrification in the soil zone. In anoxic environments, nitrate can be converted to nitrogen by a nitrate reduction process (Baedecker and Back, 1979b, p. 398):

$$6NO_3^- + 5CH_3OH \rightarrow 5CO_2 + 7H_2O + 6OH^- + 3N_2. \qquad (C5)$$

The dissolution of crushed dolomite adds Ca^{+2}, Mg^{+2}, and HCO_3^- to ground water according to equation C6:

$$0.5CaMg(CO_3)_2+CO_2+H_2O \rightarrow 0.5Ca^{+2}+0.5Mg^{+2}+2HCO_3^-. \qquad (C6)$$

In 1957, more than 65,000 tons of lime were used in Delaware (Donahue, 1961, p. 140). In addition to the ions produced by dissolution of dolomite and nitrification, dissolution of fertilizers also increases the concentration of K^+, Cl^-, Na^+, SO_4^{-2}, and total phosphorus (Donahue, 1961, p. 159–170, table 13) in ground water. Areas used for crop production generally have higher concentrations of these species than natural ground water.

LIVESTOCK PRODUCTION AND SEPTIC SYSTEMS

Manure stockpiles and accumulated animal wastes from livestock production on feedlots generate a leachate similar to that resulting from spreading poultry manure on croplands (table C4). Feedlots affect only a small percentage of west-central and southwestern Delaware, but those effects may be significant locally.

A similar leachate is generated by domestic septic systems. The effluent is discharged through tile drains or seepage beds. The dissolved species in septic-system effluent are the same as those in poultry manure; however, the concentrations are smaller (table C4). Comparable differences in water chemistry between the two effluents result. The effect that septic systems have on water chemistry is limited to the area just downgradient from the disposal field because of the effects of dilution and retardation of ions by adsorption. In residential areas with densely spaced septic systems, significant local effects on water chemistry can be observed.

RELATION OF NITRATE TO OTHER DISSOLVED SPECIES

Nitrate does not have a natural mineral source in the study area. Nitrate observed in the ground water results from inorganic and organic fertilizers and animal and human wastes. Large nitrate concentrations are associated with large concentrations of other soluble constituents of fertilizer. For example, Denver (1986, figs. 9 and 11) showed NO_3^- plotted as a function of Cl^- and K^+, respectively. Concentrations of Cl^- and K^+, which are constituents of organic fertilizer, increase with NO_3^- concentrations. A similar pattern occurs when NO_3^- concentration is plotted as a function of Ca^{+2} + Mg^{+2} concentrations (Denver, 1986, fig. 10). Ca^{+2} and Mg^{+2} come from the dissolution of crushed dolomite (eq. C6) applied to neutralize H^+ produced by nitrification (eqs. C3 and C4). The concentrations of such ions in ground water associated with crop production are considerably larger than those in ground water associated with other types of land use (Denver, 1986, figs. 9–11).

The concentrations of nitrate as functions of bicarbonate and iron concentrations are shown in figures C3 and C4, respectively. Bicarbonate (HCO_3^-) concentration is plotted as a function of iron concentration in figure C5 for analyses of anoxic water from the unconfined aquifer.

Figure C3 shows an inverse relation between nitrate and bicarbonate concentrations. Bicarbonate concentrations are less than 0.2 mmol/L (except for one sample) when nitrate concentrations exceed 0.2 mmol/L. Nitrate is produced in an oxygenated environment by nitrification (eqs. C3 and C4).

Apparently the H^+ produced by equation C3 reacts with HCO_3^-:

$$H^+ + HCO_3^- \rightarrow H_2CO_3, \qquad (C7)$$

and maintains HCO_3^- at small concentrations. The buffering effect of the reaction in equation C7 prevents the lowering of pH as sometimes happens when nitrification occurs. Ground water with large nitrate concentrations comes from agricultural wells, and ground water with large bicarbonate concentrations comes from wells in undeveloped areas (fig. C3).

Dissolved iron is common in reducing environments and is unstable in oxidizing environments. The converse is true for dissolved nitrate. As a result, there is an inverse correlation between the two in the unconfined aquifer (fig. C4). Water in some wells contains both nitrate and iron, an indication of redox disequilibrium or possibly of analytical error.

The similarity between figures C3 and C4 suggests that bicarbonate concentration may be related to iron concentration. Figure C5 shows that iron concentrations generally increase as bicarbonate concentrations increase in anoxic water. This trend probably results from processes similar to equation C1.

RELATION OF WATER CHEMISTRY TO DEPTH FOR NATURAL AND ALTERED WATER

Multiple test wells of different depths were installed at three sites to evaluate the vertical variability of water chemistry and the effects of land use (Denver, 1986, p. 54–60). Sites were selected to avoid the effects of pumping from other wells and to be representative of conditions typical of large parts of the unconfined aquifer.

Site 1.—Poorly drained soils predominate around site 1. Two wells were installed with screens at 20 to 25 ft (Lc42–2) and 50 to 55 ft (Lc42–1) below the land surface, which is 58 ft above sea level (table C5). The wells tap zones that appear to be hydraulically connected, and the deeper well is screened near the bottom of the unconfined aquifer. The wells at this site are representative of wells in an area of natural ground-water chemistry slightly influenced by human activities.

The two wells have similar water quality; however, the slightly larger Na^+ and Cl^- concentrations in the shallower well may indicate contamination from a septic system located just upgradient from the site. Dissolved oxygen concentrations are zero, dissolved iron concentrations are large, and nitrate concentrations are less than the detection limit in both wells, which indicates reducing conditions. Hydrogen sulfide gas (H_2S) has a distinctive odor and was noticed during sample collection. The presence of H_2S and dissolved iron indicate that sulfate reduction (eq. 9 in table C2) and ferric iron reduction (eq. 8 in table C2) are taking place at this site.

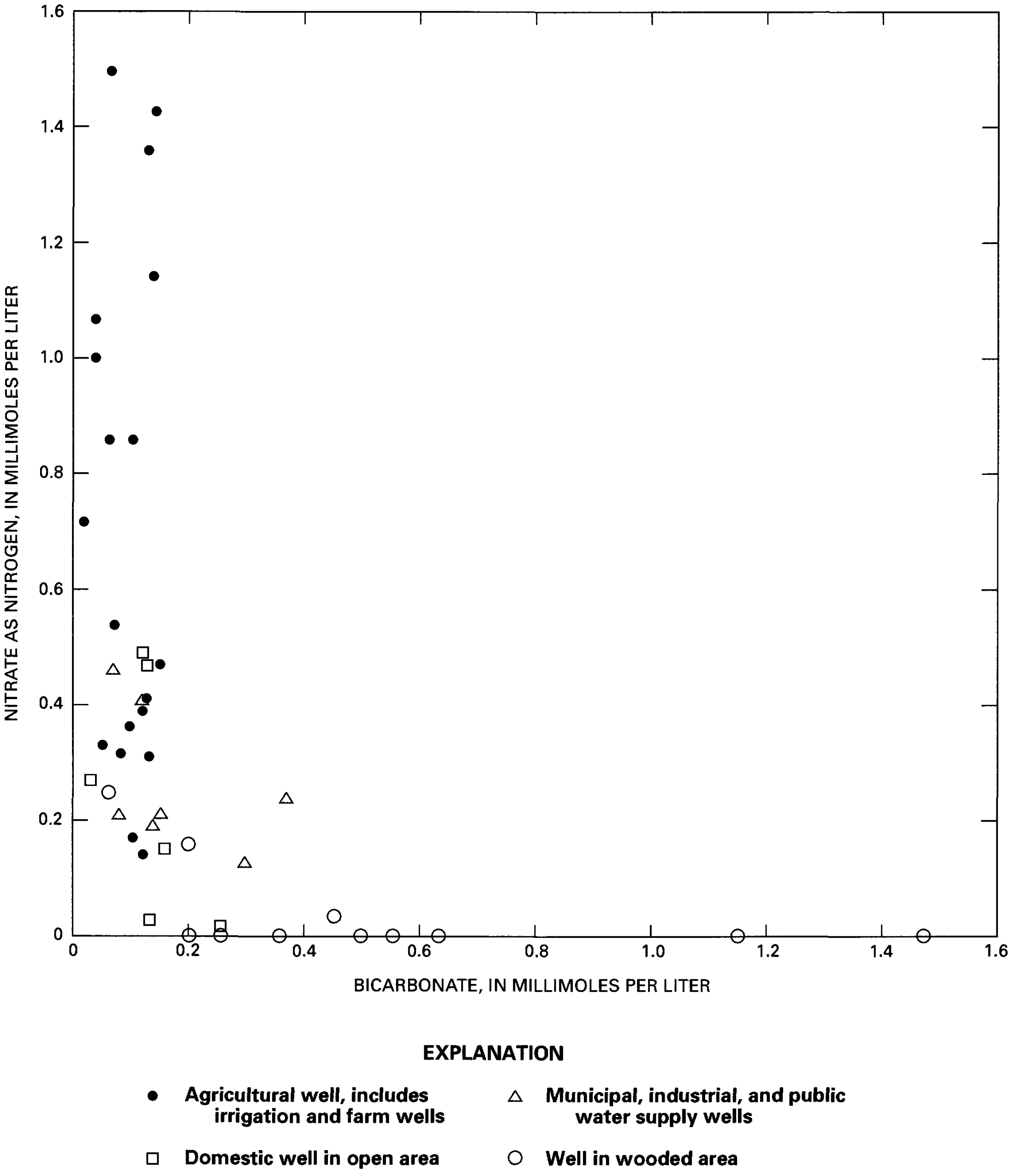


FIGURE C3.—Nitrate concentration as a function of bicarbonate concentration for water in the unconfined aquifer, Delaware (from Denver, 1986, fig. 13).

Homeowners' reports indicate that there is considerable local variation in dissolved-iron concentration near site 1. This suggests that redox conditions also vary. A soil boring at a wooded site near the wells passed through 4 ft of sand and ended at a hard cemented layer that could not be penetrated. This layer probably formed from iron precipitation (eq. C2) at a sediment boundary where water under reducing conditions mixed with water containing dissolved oxygen.

Site 2.—Site 2 is in a predominantly wooded area of poorly drained to moderately well drained soils. Four wells were installed with screens at 39 to 44 ft (Nd25–6), 49 to 54 ft (Nd25–5), 85 to 90 ft (Nd25–4), and 112 to 117 ft (Nd25–3) below the land surface, which is 50 ft above sea

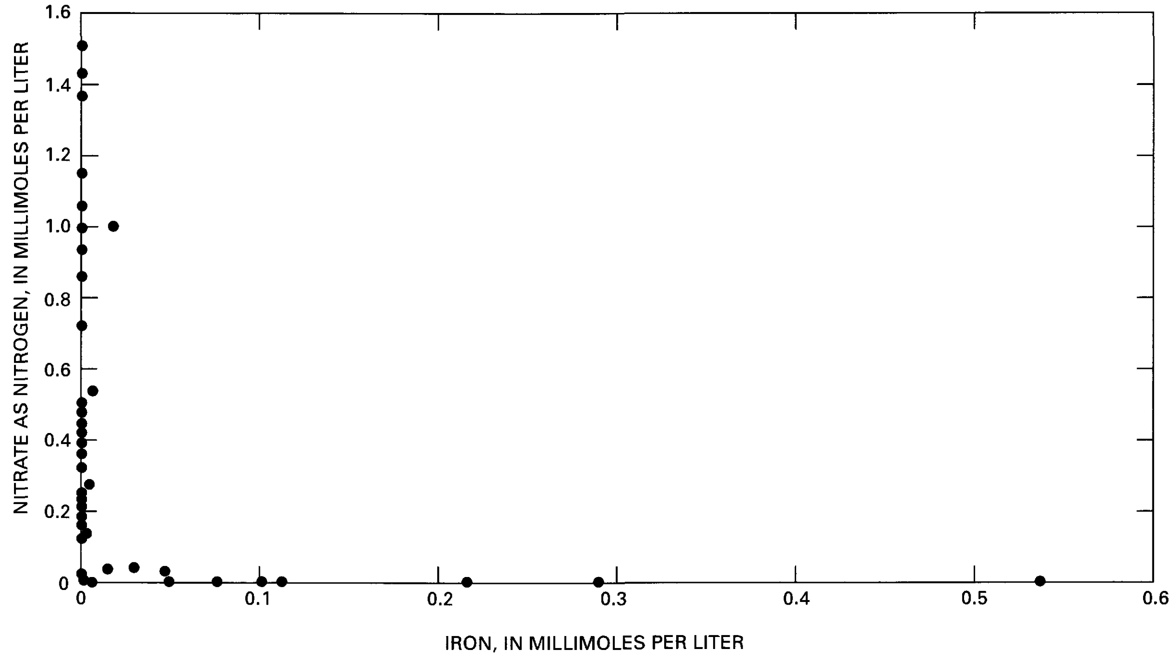
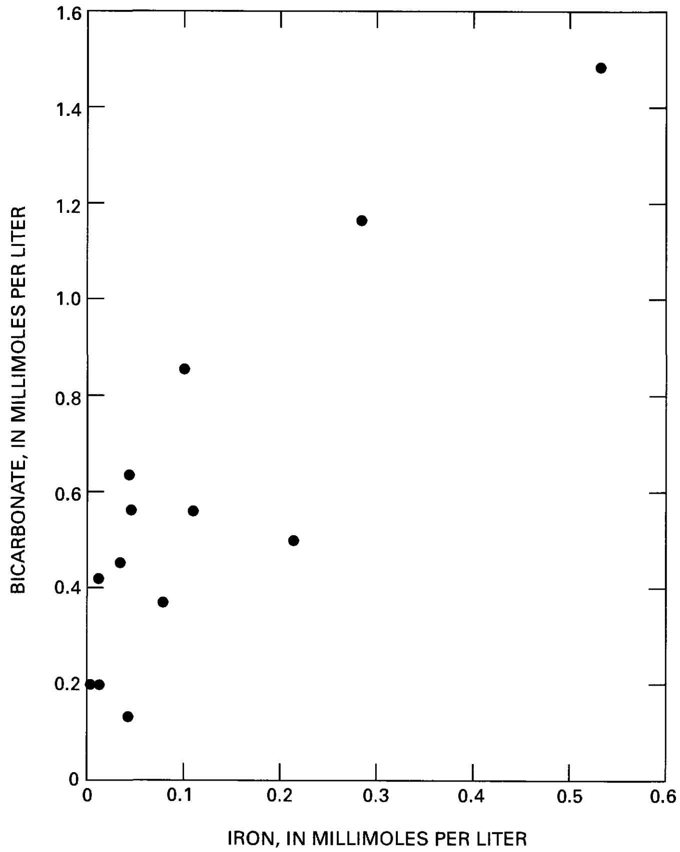


FIGURE C4.—Nitrate concentration as a function of iron concentration for water in the unconfined aquifer, Delaware (from Denver, 1986, fig. 17).

level. Uniform fluctuation of water levels in the four wells indicates that they tap zones that are hydraulically connected (Denver, 1986, p. 58). The wells at this site are representative of wells in an area with natural water chemistry.

The two shallower wells contain nitrate but no dissolved iron, which indicates oxidizing conditions. Conversely, the two deeper wells contain iron but no dissolved nitrate, which indicates a reducing environment. These conditions reflect depletion of free oxygen by processes like equations 5, 14, C3, and C4, followed by reduction processes like equations C1 and C5 and equation 9 in table C2. The deeper wells also have larger silica concentrations, which probably indicate that more incongruent dissolution of aluminosilicate minerals has taken place than in the shallower wells. Finally, the small concentrations of Ca^{+2} and Mg^{+2} and the slightly larger concentrations of Na^{+} in all four wells indicate that some ion exchange has occurred.

Site 3.—Site 3 is in an agricultural area of predominantly well drained and excessively well drained soils.



← FIGURE C5.—Bicarbonate concentration as a function of iron concentration for anoxic water in the unconfined aquifer, Delaware (from Denver, 1986, fig. 16).

TABLE C5.—*Chemical constituents in water samples from wells in the unconfined aquifer in west-central and southwestern Delaware*

[Site 1 (well-number prefix Lc) is slightly affected by human activity; site 2 (prefix Nd) has natural water chemistry; site 3 (prefix Pd) is influenced by crop-production practices. See text for explanation. Results shown in milligrams per liter except for pH or as noted; less-than sign (<) indicates that concentration was below specified detection limit. Condensed from Denver (1986, table 11)]

Constituent or physical characteristic	Well number							
	Lc42–1	Lc42–2	Nd25–3	Nd25–4	Nd25–5	Nd25–6	Pd33–3	Pd33–4
Date sampled (month-day-year)	2–28–83	2–28–83	12–28–82	12–28–82	1–4–83	1–7–83	2–18–83	2–22–83
Elevation of land surface (NGVD of 1929), in feet	58	58	50	50	50	50	35	35
Screened interval below land surface, in feet	50–55	20–25	112–117	85–90	49–54	39–44	42–47	89–94
Specific conductance, in µS/cm at 25°C[1]	77	79	76	34	49	47	204	79
Dissolved solids (residue at 180°C)	94	99	87	63	56	60	135	74
pH[2]	6.2	5.9	6.3	6.1	5.9	5.8	5.5	5.6
Silica, SiO_2	35	35	33	35	22	24	17	21
Alkalinity as $CaCO_3$	34	29	32	10	12	14	7.0	5.0
Sulfate, SO_4^{-2}	29	5.2	<5.0	<5.0	2.0	<1.0	<5.0	<5.0
Chloride, Cl^-	5.9	15	4.9	5.3	4.5	4.1	15	7.2
Nitrate plus nitrite as nitrogen, $NO_3^- + NO_2^-$ as N	<0.10	<0.10	0.13	<0.10	2.10	1.20	16	5.7
Calcium, Ca^{+2}	6.3	6.4	2.3	0.52	2.3	2.2	10	3.9
Magnesium, Mg^{+2}	1.5	1.7	0.55	0.13	0.44	0.34	3.2	0.95
Sodium, Na^+	7.2	12	15	5.7	6.8	6.8	16	9.1
Potassium, K^+	1.0	1.1	1.1	0.4	0.90	0.80	4.0	2.2
Total recoverable iron, Fe_{Total}	13	27	1.4	3.7	0.018	<0.003	0.017	0.013

[1] Microsiemens per centimeter at 25° Celsius.

[2] Negative base-10 logarithm of hydrogen ion activity in moles per liter.

Two wells were installed with screens at 42 to 47 ft (Pd33–3) and 89 to 94 ft (Pd33–4) below the land surface, which is 35 ft above sea level. Similar water-level fluctuations indicate a probable hydraulic connection between the zones tapped by the wells. The wells at this site are representative of wells in an area with water chemistry influenced by crop-production practices.

The large nitrate and small iron concentrations in both wells indicate that oxidizing conditions extend deeper at site 3 (94 ft) than at the other two sites (less than 85 ft at site 2 and 20 ft at site 1). This condition can be accounted for by increased speed of dissolved oxygen transport in the predominantly well drained and excessively well drained soils.

The specific conductance and concentrations of Ca^{+2}, Mg^{+2}, Na^+, K^+, NO_3^-, and dissolved solids are larger in water from the shallow well at site 3 (Pd33–3) than in any of the wells in table C5. The concentration of Cl^- is larger than that in all wells except for well Lc42–2, which is probably contaminated by septic-system effluent. Silica concentration, alkalinity, and pH are smaller than for wells at other sites. These data are consistent with dissolution of fertilizer and lime (eq. C6) and ammonium oxidation (eqs. C3 and C4). Concentrations of ions in water from the deeper well at site 3 (Pd33–4) are similar to those of the shallow well but are smaller (table C5). This is most likely because of the effects of dilution by mixing with unaffected water from deeper in the aquifer.

Denver (1986, fig. 20) noted the temporal variation of pH and alkalinity at well Pd33–3. She concluded that larger values in the winter resulted from decreased activity of nitrifying bacteria in the soil zone, and that, as temperatures increased, H^+ produced by increased nitrification processes decreased pH and provided a source of H^+ to remove HCO_3^- from solution (eq. 10 in table C2).

GENERALIZATIONS

The water chemistry in the nonmarine, unconfined aquifer in Delaware is controlled by incongruent dissolution of silicate minerals, redox conditions, ion exchange processes, and land use. The water can be broadly categorized into natural ground water and water influenced by human activities. The water quality differs somewhat with depth and time, particularly in areas where fertilizer is used.

Many of Denver's (1986) findings are supported by other studies in the area. Demicco (1982) documented the inverse relation between iron and nitrate in western Kent County, Del., and related it to soil type, land use, and geomorphology. Iron concentrations were generally large in water from wells screened in poorly drained wooded areas and small in water from wells screened under agricultural fields. Demicco (1982) also noted that nitrate concentrations varied directly with concentrations of many other ions.

Harrington (1981) noted that poorly drained areas were characterized by reducing environments and that well-drained areas were characterized by oxidizing environments. She also noted significant statistical correlations between (1) large NO_3^- concentrations and high pH or large Cl^- concentrations, and (2) large iron and small H^+ concentrations. Both NO_3^- and Cl^- concentrations increased as a function of specific conductance. Ritter and Chirnside (1982, 1984) found (1) that large NO_3^- concentrations were associated with agricultural areas, (2) that poultry manure and fertilizer were the main sources of NO_3^-, (3) that leachate from septic systems contributed some NO_3^- to ground water in residential areas, (4) that ground water in forested areas had small NO_3^- concentrations, and (5) that large iron and small NO_3^- concentrations were associated with poorly drained soils. Robertson (1979) found a range of NO_3^- concentrations of 0–224 mg/L in more than 800 water samples from southeastern Delaware and concluded that NO_3^- concentrations were (1) large in well-drained agricultural areas and decreased with depth, (2) small in poorly drained areas, and (3) locally associated with point sources such as livestock production areas and improperly constructed septic systems.

The findings of Denver (1986) and other investigators regarding the unconfined aquifer in Delaware are based on work conducted on nonmarine sediments. The surficial aquifer of the northern Atlantic Coastal Plain also contains marine and marginal marine sediments. These sediments commonly contain carbonate minerals, pyrite, and glauconite, which are not present in the unconfined aquifer of Delaware. Even though the mineralogy differs in other parts of the surficial aquifer, the chemical processes are probably analogous. For example, where carbonate shell material is present, liming is not required for balancing soil pH. However, dissolution of the shell material would buffer the H^+ released by nitrification:

$$\begin{aligned}&(Ca_{1-X}Mg_X)CO_3+H_2O\\ &\quad\leftrightarrow (1-X)Ca^{+2}+XMg^{+2}+HCO_3^-+OH^-. \qquad (C8)\end{aligned}$$

This reaction is analogous to dissolution of crushed dolomite (eq. C6); however, the proportion of Ca^{+2} to Mg^{+2} released into solution is different. Another example is soils containing glauconite—these soils would tend to be more effective cation exchange mediums than other soils, and exchange activity would influence the amount of Na^+, K^+, Ca^{+2}, and Mg^{+2} in the ground water. Also, incongruent dissolution of glauconite—which is sometimes used as a natural fertilizer—releases K^+ to solution (Chapelle and Knobel, 1983, eq. 10). Because K^+ is one of the essential elements for plant growth, practices of applying inorganic fertilizer may vary from place to place. Finally, the presence of pyrite—or other iron sulfide minerals—in oxidizing environments would allow pyrite oxidation (eq. 4) to take place, providing a source for iron and sulfate. Even though differences in the processes affecting water quality occur in other parts of the Coastal Plain, the same general water-quality patterns can be expected to occur.

APPENDIX D: SALTWATER INTRUSION OF THE UPPER CHESAPEAKE AQUIFER–NEW JERSEY

Schaefer (1983) delineated areas in the New Jersey Coastal Plain with significant saltwater intrusion problems. The areas he identified (fig. D1) are adjacent to the Atlantic Ocean, Raritan Bay, and the tidal part of the Delaware River. The area of saltwater intrusion in southern Cape May County (fig. D2) is discussed in detail because it provides a well-documented case of changes in the position of the saltwater transition zone with time. The Cohansey Sand, which is equivalent to the upper Chesapeake aquifer in southern Cape May County, is the only source of freshwater south of the Cape May Canal (Schaefer, 1983, p. 37), and chloride (Cl^-) concentrations have been closely monitored since 1958. Water-quality data are listed in table D1, and well locations are shown in figure D2.

Cl^- concentrations as a function of time, for the period 1964 to 1981, are shown for four wells in figure D3. The two wells closest to the coast, Harbeson-Walker Refractories Company well 2 and Cape May City Water Department (WD) well 1, have shown a relatively steady increase in Cl^- concentration since about 1965. Cape May City WD well 2 started to show increasing Cl^- concentrations about 1973, and Cl^- concentrations in Cape May City WD well 3 were relatively constant throughout the period of record (1967 to 1981). Intermittent measurements were made for Cl^- concentrations at two other wells located near the coast (fig. D2)—West Cape May Observation well 1 (map no. 150) and Cape May City WD Columbia Avenue well 1 (map no. 11). The concentration at the former increased from 220 mg/L in 1965 to 490 mg/L in 1977, and the concentration at the latter increased from 690 mg/L in 1964 to 850 mg/L in 1977. The trends in Cl^- concentration with time in these wells and the location of wells relative to the coastline suggest that seawater is moving laterally from the ocean toward the wells.

Figure D4 shows lines of equal Cl^- concentration for 1977 that are superposed on a map prepared by Gill (1962) that shows lines of equal Cl^- concentration for 1958. Inspection of the 50- and 500-mg/L lines for the two years indicates that salty water is moving inland toward Cape May City WD wells 2 and 3. Schaefer (1983, p. 34) estimated the lateral distance of movement during the period to be about 2,500 ft and attributed the slight changes in the shape of the lines to changes in the distribution of ground-water withdrawals. Similar movements of salty water and its mixture with ground water in shallow aquifers can be expected in other coastal areas of the northern Atlantic Coastal Plain, especially if the aquifers are hydraulically connected to the ocean and are being pumped for local water-supply purposes.

Base modified from
U.S. Geological Survey
digital data, 1:2,000,000, 1972

EXPLANATION

▨ **Area of significant saltwater intrusion**

┬┬┬ **Line of 250-milligram-per-liter chloride concentration in the Magothy aquifer and older sediments**—Chloride concentrations increase south and east of line (from Luzier, 1980, p. 6)

FIGURE D1.—Location of areas with significant saltwater intrusion problems in the New Jersey Coastal Plain (modified from Schaefer, 1983, fig. 1).

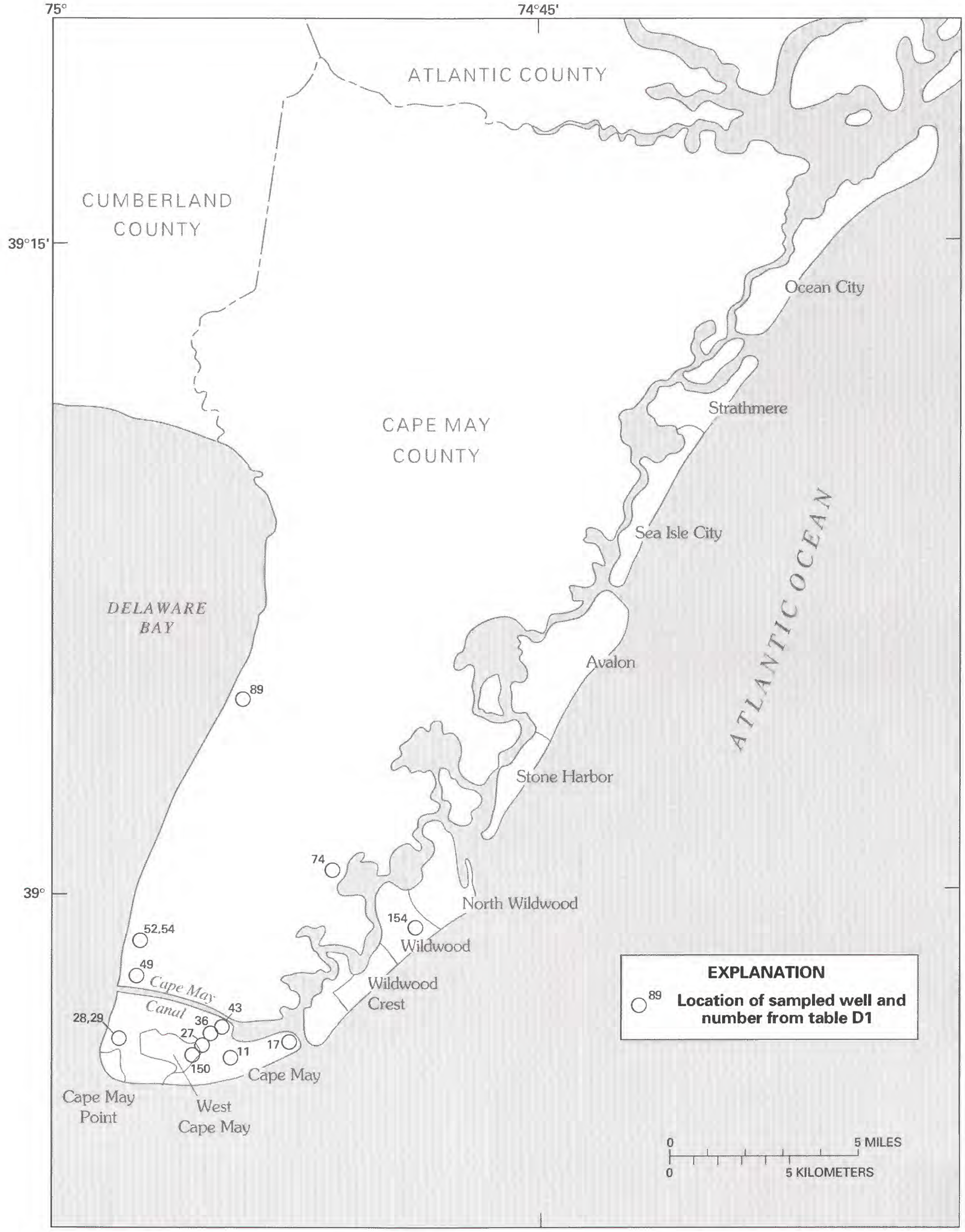


FIGURE D2.—Location of water-quality sampling sites in Cape May County, N.J. (from Schaefer, 1983, fig. 11). Well information is in table D1.

TABLE D1.—*Well information and chloride concentrations from selected saltwater-monitoring wells in Cape May County, N.J., 1977 water year*

[Date sampled: Month, day, and year of sample collection. Definitions: mg/L, milligrams per liter; Col, Columbia Avenue; Obs, observation; Ref Co, Refractories Company; TWP MUA, Township Mutual Utilities Authority; WATSTORE, a U.S. Geological Survey data base; WD, Water Department. From Schaefer (1983, table 6)]

Map no. (fig. D2)	Local well identifier used in WATSTORE	Elevation of land surface above sea level (feet)	Screened interval below land surface (feet)	Date sampled	Chloride (mg/L)
150	West Cape May 1 Obs.	7	283–293	9–15–77	490
11	Cape May City WD Col 1.	11	281–321	9–15–77	850
27	Cape May City WD 1.	12	277–306	8–31–77	140
28	Harbeson-Walker Ref Co 2.	10	235–265	8–31–77	196
29	Harbeson-Walker Ref Co 1.	10	296–321	8–31–77	270
17	US Coast Guard 1	11	292–322	8–31–77	45
36	Cape May City WD 2.	12	174–282	8–31–77	40
43	Cape May City WD 3.	15	174–276	8–31–77	22
49	Higbee Beach 3 Obs.	6	240–250	9–16–77	16
52	Lower TWP MUA 1.	18	241–262	8–31–77	14
54	Lower TWP MUA 2.	12	212–247	8–31–77	13
154	Wildwood WD Pine 2.	10	304–354	9– 1–77	120
74	Wildwood WD Rio Grande 29.	8	191–231	8–31–77	12
89	Oyster Lab 4 Obs	7	195–210	9–16–77	10

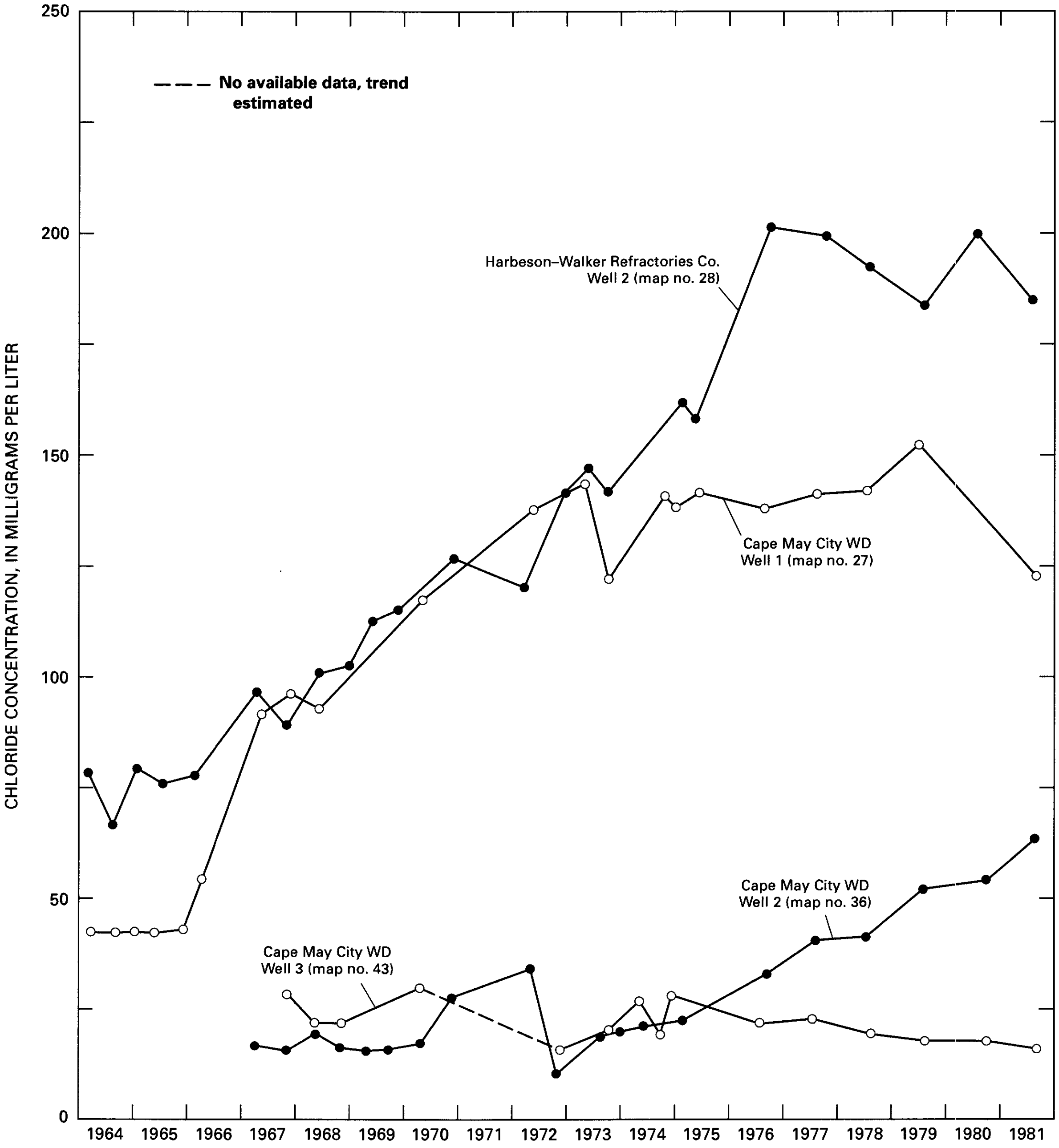
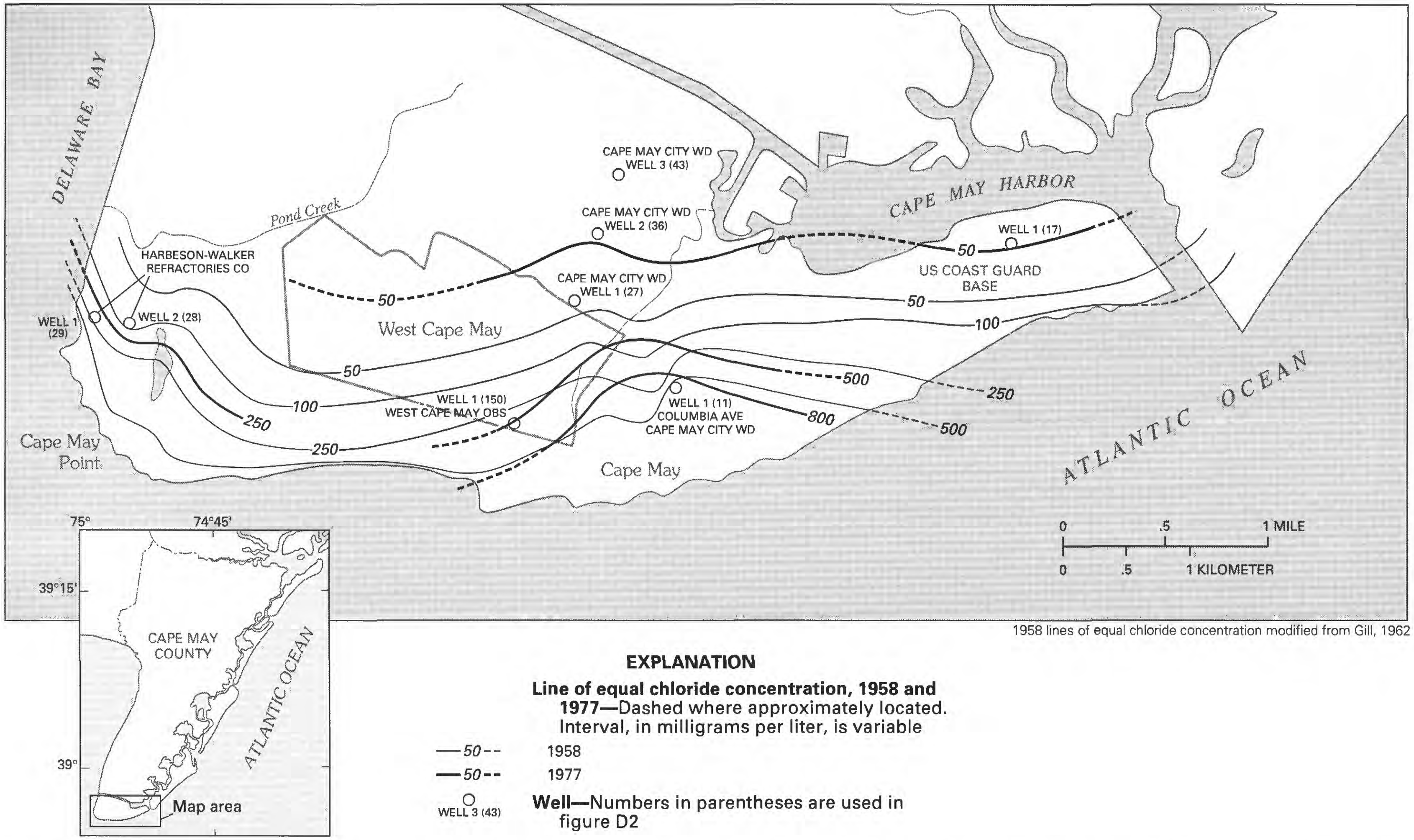


FIGURE D3.—Chloride concentrations of water from selected wells tapping the Cohansey Sand in southern Cape May County, N.J. (from Schaefer, 1983, fig. 12). Well locations are shown in figures D2 and D4. WD, Water Department.



1958 lines of equal chloride concentration modified from Gill, 1962

FIGURE D4.—Lines of equal chloride concentration for the Cohansey Sand in southern Cape May County, N.J., 1958 and 1977 (from Schaefer, 1983, fig. 13).

APPENDIX E: CALCITE PRECIPITATION AS A RESULT OF MIXING

The presence of a broad saltwater-freshwater transition zone in the northern Atlantic Coastal Plain was interpreted by Meisler and others (1984, p. 16) as the result of saltwater circulation responding to historic eustatic sea-level fluctuations. As sea level rises, saltwater invades the sediments and mixes with fresher water. As sea level declines, the fresher water advances seaward, and the process of mixing continues. Repeated advance and retreat of the saltwater have thus produced a broad zone of mixed waters in which saltwater predominates in deeper and seaward parts, and freshwater predominates in the shallower and landward parts. The water from the deeper part of the aquifer system is a brine with Cl^- concentrations greater than those in seawater. For example, well DO–CE 88 at Cambridge, Md., the Crisfield Airport well at Crisfield, Md., and the Esso Hatteras well at Cape Hatteras, N.C., have Cl^- concentrations of about 1.4, 2.2, and 4.0 times the Cl^- concentration in seawater, respectively (Meisler and others, 1984, table 2; this report, table E1). Meisler and others (1984, figs. 10–17 and table 2) used conservative mixing theory to demonstrate that reverse ion exchange processes occur in the part of the Coastal Plain sediments occupied by salty ground water.

The concentration of Ca^{+2} as a function of Cl^- concentration is shown in figure E1. The lines in figure E1 represent conservative mixing lines for freshwater and seawater, or freshwater and water from either the Esso Hatteras well or the Crisfield Airport well. Figure E1 shows that the observed concentrations of Ca^{+2} are larger than the Ca^{+2} concentrations that would be expected from the mixing of freshwater and seawater. This trend is consistent with reverse cation exchange where Na^+ replaces Ca^{+2} on solid-phase exchanging material:

$$2\mathrm{Na}^+ + \mathrm{Ca{\cdot}Ex} \rightarrow \mathrm{Ca}^{+2} + \mathrm{Na_2{\cdot}Ex}. \qquad \text{(E1)}$$

Another method of evaluating cation exchange processes is to examine the relative concentrations of dissolved Ca^{+2} and Na^+. If reverse ion exchange is taking place, the relative concentration of Ca^{+2} and Na^+ should increase and decrease, respectively, as Cl^- concentration increases. Dissolved Na^+ as an equivalent fraction of the total cation composition is shown in figure E2*A* as a function of Cl^- concentration. Dissolved Ca^{+2} is shown in figure E2*B*. Trapp and others (1984, table 20) noted that two sediment samples taken from cores recovered from

TABLE E1.—*Chemical constituents in salty-ground-water samples from selected wells, northern Atlantic Coastal Plain*

[Definitions: Do., ditto; dash (—), data not available. Adapted from Meisler and others (1984, table 2)]

Well name	Concentrations, in millimoles per kilogram water								pH[1]	Calcite saturation index (SI)[2]
	Calcium	Magnesium	Sodium	Potassium	Chloride	Sulfate	Bicarbonate	Silica		
Anchor Ragovin well, New Jersey	55.56	19.15	528.3	3.11	628.1	0.22	2.54	0.18	[3]6.6	+0.20
DO–CE 88 (Cambridge, Md., test well)	73.46	20.46	618.2	1.25	796.1	7.03	.97	.24	[3]7.60	+.74
SO–DD 47 (Crisfield Airport well, Crisfield, Md.)	184.82	20.75	887.3	3.30	1241.6	11.18	.62	.27	[3]6.7	–.02
Do.	190.80	22.59	983.8	1.65	1276.0	9.19	.88	.30	[3]6.3	–.12
Do.	192.89	21.64	840.7	1.70	1272.0	9.72	.88	.29	[3]6.7	+.20
Moores Bridge well, Norfolk, Va	67.69	35.83	559.0	3.23	748.0	10.83	.84	.92	[3]7.13	+.02
Do.	74.93	35.54	568.7	3.21	775.0	11.16	2.23	.20	[3]6.4	+.12
Esso Hatteras well, Cape Hatteras, N.C.	202.84	60.64	1777.9	—	2278.3	9.90	1.84	—	—	—
Seawater[4]	10.66	55.07	485.4	10.58	565.8	29.26	2.41	.07	8.22	+.74

[1] Negative base-10 logarithm of hydrogen ion activity in moles per liter.

[2] Calculated by the computer program WATEQF (Plummer and others, 1976).

[3] Field measurement.

[4] Seawater concentrations from Plummer and others (1976).

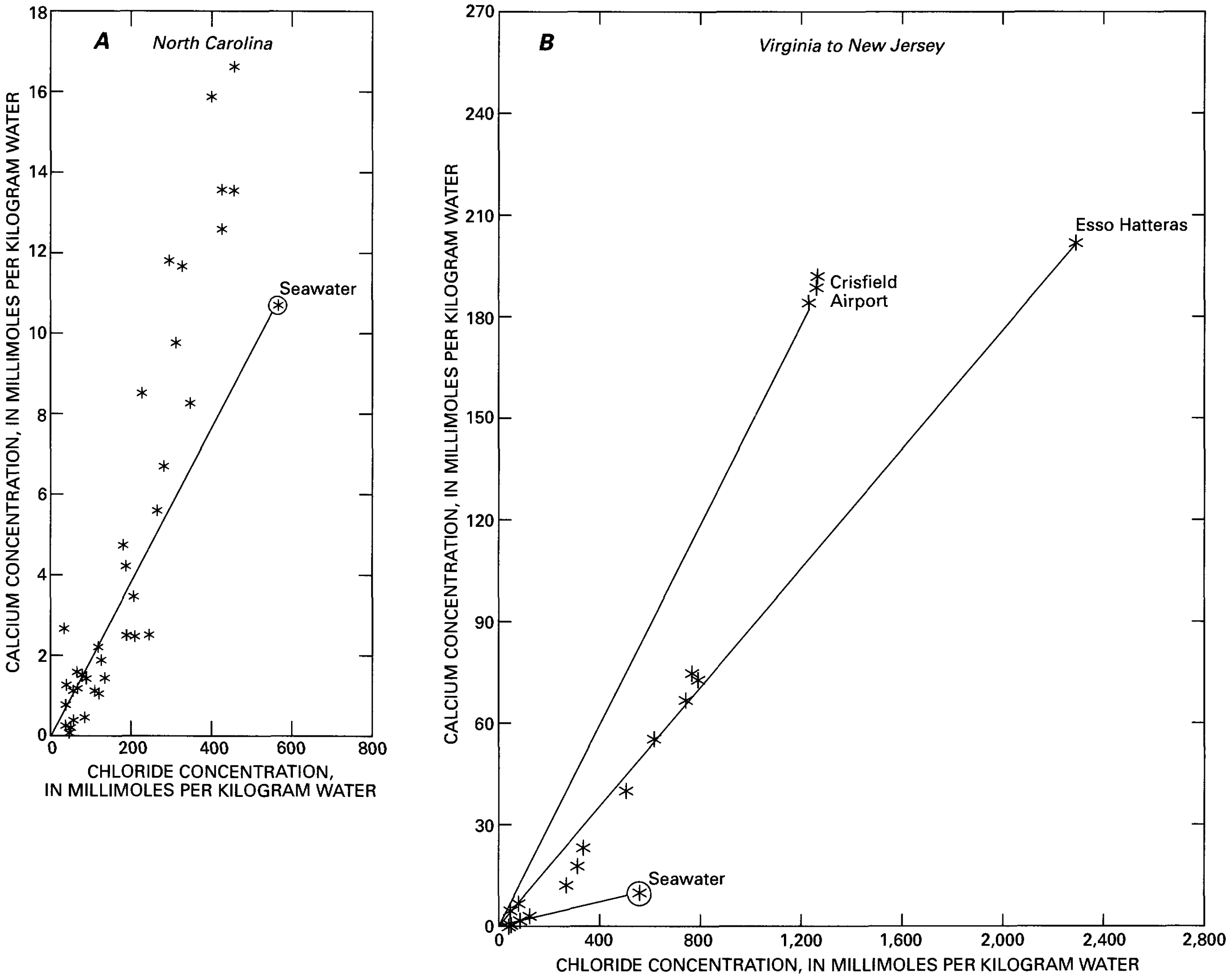


FIGURE E1.—Relation of calcium concentration to chloride concentration in wells in the saltwater-freshwater transition zone of the Coastal Plain in (*A*) North Carolina and (*B*) Virginia to New Jersey (from Meisler and others, 1984, fig. 10). Data are plotted in two graphs because the chemistry of the transition zone differs substantially in the two areas; however, data for the Esso Hatteras well, North Carolina, more closely resemble data from Virginia to New Jersey and have been plotted with them in this figure and figures E2 and E3. Lines denote conservative mixing curves.

the transition zone at the Cambridge, Md., test well contained larger concentrations of exchangeable Na^+ than Ca^{+2}. The observed trends of relative Ca^{+2} and Na^+ concentrations in salty ground water and the larger concentration of absorbed Na^+ on exchanging material in the transition zone are consistent with reverse ion exchange as an operative process.

The combined effects of mixing and reverse ion exchange increase the Ca^{+2} concentration in the zone of mixing defined by Meisler and others (1984). The absolute concentrations of Ca^{+2} range from about 7 to 19 times the Ca^{+2} concentration of seawater for the three wells mentioned above (table E1). These high concentrations suggest that chemical reactions involving Ca^{+2} may take place as a result of the enrichment of Ca^{+2} ions in the aqueous phase.

In addition to Ca^{+2} enrichment in the brine, pH values are slightly smaller than seawater pH. The wells in the Atlantic Coastal Plain with Cl^- concentrations greater than the Cl^- concentration in seawater have pH values ranging from 6.3 to 7.6 (table E1). For comparison, seawater has a pH of about 8.2. No pH is available for the Esso Hatteras well, which has the largest known Cl^- concentration in the study area. The pH of the deepest sample from the Cambridge well is also slightly smaller than the pH values of five samples taken from shallower

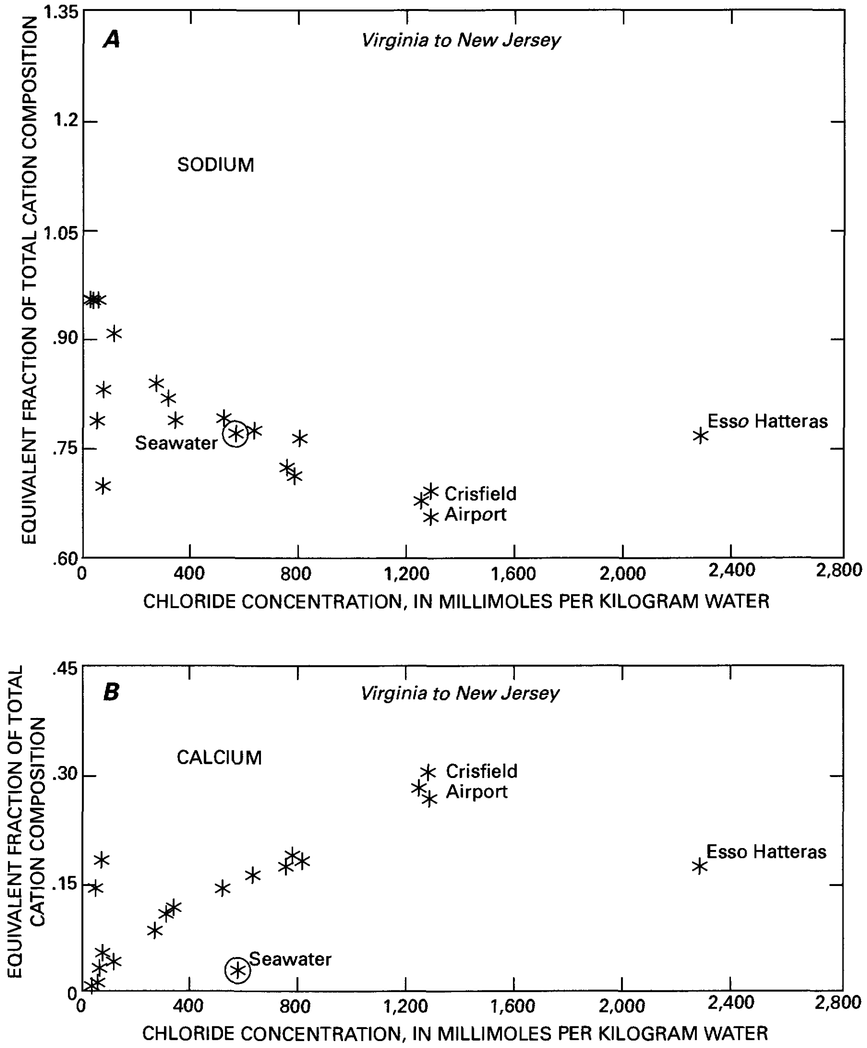


FIGURE E2.—Relation of (*A*) sodium and (*B*) calcium concentrations (expressed as an equivalent fraction of total cations) to chloride concentration in wells in the saltwater-freshwater transition zone of the Coastal Plain in Virginia to New Jersey (from Meisler and others, 1984, fig. 17).

depths at the same location. Four water samples from shallower depths (1,418–2,644 ft below the land surface, which is 4.42 ft above sea level) with densities representative of freshwater have pH's ranging from 8.4 to 8.7. The next depth sampled (3,829 ft) had a density of 1.003 g/mL (grams per milliliter) and a pH of 7.8, whereas the most concentrated sample (3,183 ft) had a density of 1.032 g/mL and a pH of 7.6 (Trapp and others, 1984, table 18). These limited observations suggest that some geochemical process may be lowering the pH of the more concentrated water in the study area.

Alkalinity (as bicarbonate) in the salty ground water is plotted as a function of Cl^- concentration in figure E3. Bicarbonate concentrations generally decrease as Cl^- concentrations increase.

Runnells (1969) pointed out that mixing two waters of differing chemical composition can cause the resulting water to be in a state of disequilibrium, which causes dissolution-precipitation reactions to occur. If water with large Ca^{+2} concentrations (brine) comes in contact with water containing large bicarbonate concentrations (fresh ground water), supersaturation with respect to calcite is likely to occur, resulting in precipitation of calcite:

$$Ca^{+2} + HCO_3^- + OH^- \leftrightarrow CaCO_3 + H_2O. \qquad \text{(E2)}$$

This reaction is consistent with large Ca^{+2} and decreasing HCO_3^- concentrations and a lowering of pH. If precipitation of $CaCO_3$ is taking place, then the water should have calcite SI's (saturation indices) that are posi-

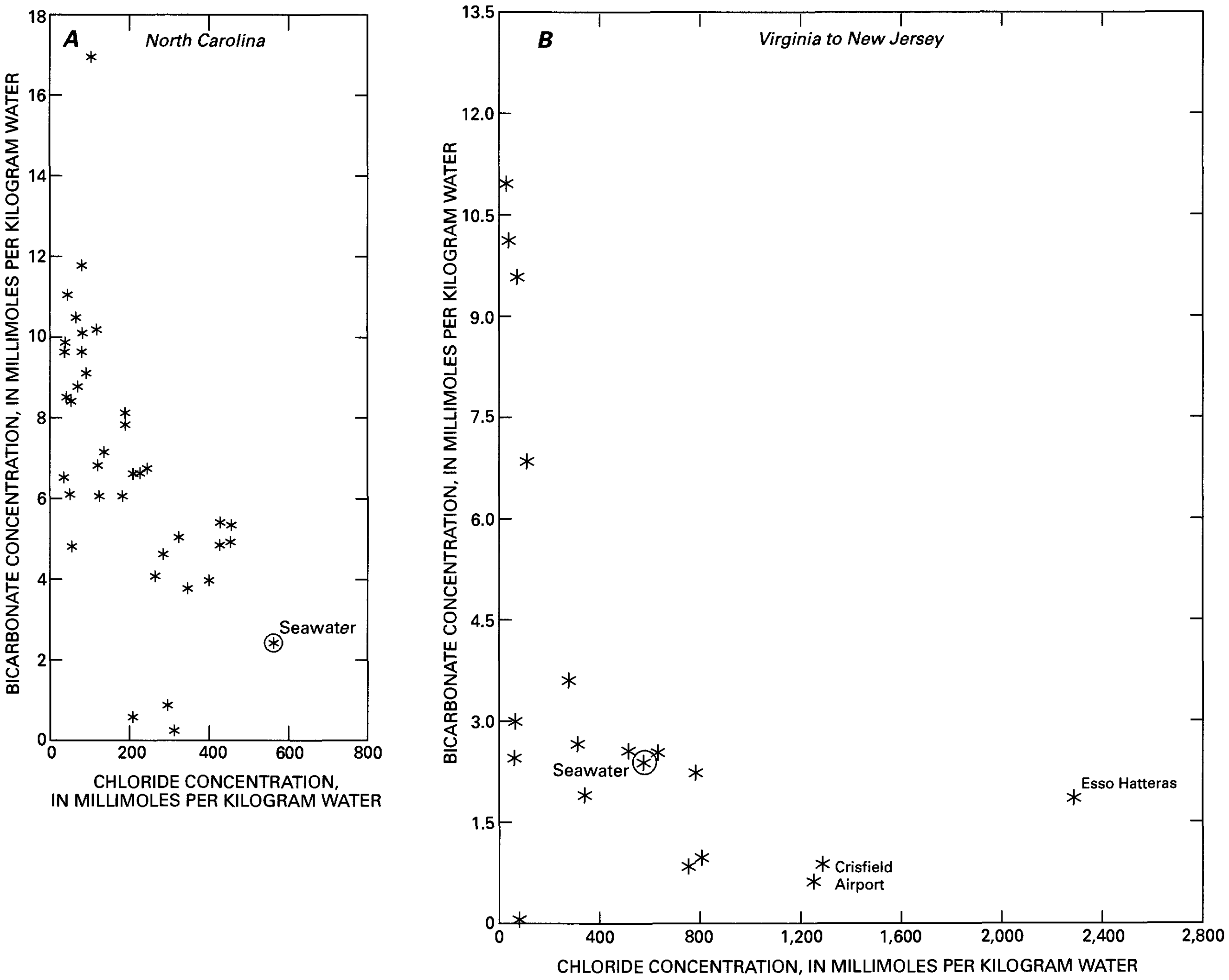


FIGURE E3.—Relation of bicarbonate concentration to chloride concentration in wells in the saltwater-freshwater transition zone of the Coastal Plain in (*A*) North Carolina and (*B*) Virginia to New Jersey (from Meisler and others, 1984, fig. 15).

tive. SI's with respect to calcite, as calculated by WATEQF (Plummer and others, 1976), for water samples more concentrated than seawater are listed in table E1. The SI's generally indicate that the water is either supersaturated, or nearly so, with respect to calcite. Langmuir (1971) suggested that SI's within 0.1 of zero should be considered to indicate saturation.

The evidence presented here for calcite precipitation in the transition zone of the Atlantic Coastal Plain is indirect evidence and is highly tenuous; however, Trapp and others (1984, p. 35) noted that observable quantities of calcareous material are present in the sediments associated with the salty ground water at Cambridge, Md. It cannot be definitely concluded from available data that calcite precipitation is occurring in the transition zone of the study area, but some geochemical process must be depleting alkalinity in this zone. Another possible mechanism for depleting alkalinity and lowering pH is precipitation of siderite:

$$Fe^{+2} + HCO_3^{-} \rightarrow FeCO_3 + H^{+}. \qquad (E3)$$

Dissolved iron is present in the deepest water sampled at the Cambridge test well, as indicated by precipitation of ferric hydroxide in the sample bottle of a filtered and untreated sample. It should be noted, however, that Hem (1985, p. 77) suggested that, in the presence of sulfur, Fe^{+2} commonly forms ferrous polysulfides and that the Cambridge sample contained 665 mg/L SO_4^{+2}. The limited data available indicate that precipitation of calcite (eq. E2) is more probable than precipitation of siderite (eq. E3), especially at Cambridge, Md.

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ISBN 0-607-88577-7

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