

Prepared in cooperation with the New Jersey Department of Environmental Protection

# Pore-Water Quality in the Clay-Silt Confining Units of the Lower Miocene Kirkwood Formation and Hypothetical Effects on Water Quality in the Atlantic City 800-Foot Sand, Northeastern Cape May County, New Jersey, 2001

Scientific Investigations Report 2006-5134

U.S. Department of the Interior U.S. Geological Survey

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## **Conversion Factors, Datums, and Abbreviations**

#### Inch/Pound to SI

Multiply	Ву	To obtain
	Length	
inch (in.)	2.54	centimeter (cm)
foot (ft)	0.3048	meter (m)
	Flow rate	
million gallons per day (Mgal/d)	0.04381	cubic meter per second (m <sup>3</sup> /s)
	Pressure	
bar	100	kilopascal (kPa)
pound per square inch (lb/in <sup>2</sup> )	6.895	kilopascal (kPa)
	Density	
pound per cubic foot (lb/ft <sup>3</sup> )	16.02	kilogram per cubic meter (kg/m <sup>3</sup> )

#### SI to Inch/Pound

Multiply	Ву	To obtain
	Volume	
liter (L)	0.2642	gallon (gal)
	Mass	
gram (g)	0.03527	ounce, avoirdupois (oz)
	Density	
gram per cubic centimeter (g/cm <sup>3</sup> )	62.4220	pound per cubic foot (lb/ft <sup>3</sup> )

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

°F=(1.8×°C)+32

Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as follows:

°C=(°F-32)/1.8

Vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88).

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

Altitude, as used in this report, refers to distance above the vertical datum.

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius ( $\mu S/cm$  at 25 °C).

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter ( $\mu$ g/L).

Additional Water-Quality Abbreviations

μL, microliter mL, milliliter cc, cubic centimeter nm, nanometer mm, millimeter mg/L, milligrams per liter μg/L, micrograms per liter

## Pore-Water Quality in the Clay-Silt Confining Units of the Lower Miocene Kirkwood Formation and Hypothetical Effects on Water Quality in the Atlantic City 800-Foot Sand, Northeastern Cape May County, New Jersey, 2001

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## Abstract

Pore water was extracted from clay-silt core samples collected from a borehole at Ocean View, west of Sea Isle City, in northeastern Cape May County, New Jersey. The borehole intersects the lower Miocene Kirkwood Formation, which includes a thick sand and gravel unit between two clay-silt units. The sand and gravel unit forms a major confined aquifer in the region, known as the Atlantic City 800-foot sand, the major source of potable water along the Atlantic Coast of southern New Jersey. The pore water from the core is of interest because the borehole intersects the aquifer in an area where the ground water is sodium-rich and sulfidic. Locally in the aquifer in central and southern Cape May County, sodium concentrations are near the New Jersey secondary drinking-water standard of 50 mg/L (milligrams per liter), and typically are greater than 30 mg/L, but chloride and sulfate do not approach their respective secondary drinking-water standards except in southernmost Cape May County. Pore waters from the confining units are suspected to be a source of sodium, sulfur, and chloride to the aquifer. Constituent concentrations in filtered pore-water samples were determined using the inductively coupled plasma-mass spectrometry analytical technique to facilitate the determination of low-level concentrations of many trace constituents.

Calcium-sodium-sulfate-bicarbonate, calcium-chloridesulfate, calcium-sulfate, and sodium-sulfate-chloride-bicarbonate type waters characterize samples from the deepest part of the confining unit directly overlying the aquifer (termed the "lower" confining unit). A sodium-chloride-sulfate type water is dominant in the composite confining unit below the aquifer. Sodium, chloride, and sulfate became increasingly dominant with depth. Pore water from the deepest sample recovered (1,390 ft (feet) below land surface) was brackish, with concentrations of sodium, chloride, and sulfate of 5,930, 8,400, and 5,070 mg/L, respectively. Pore-water samples from 900 ft or less below land surface, although mineralized, were fresh, not brackish. Sodium concentrations ranged from

51.3 to 513 mg/L, with the maximum concentration found at 882 ft below land surface in the composite confining unit below the aquifer. Chloride concentrations ranged from 46.4 to 757 mg/L, with the maximum concentration found at 596 ft below land surface in the "lower" confining unit, and were higher than those in pore water from the same units at Atlantic City, N.J. Concentrations of chloride in the composite confining unit below the aquifer were consistently greater than 250 mg/L, indicating that the confining unit can be a source of chloride at depth. Of the major anions, sulfate was the constituent whose concentration varied most, ranging from 42 to 799 mg/L. The maximum concentration was found at 406 ft below land surface, in the upper part of the confining unit overlying the aquifer and the Rio Grande water-bearing zone (termed the "upper" confining unit). Sulfide was not detected in any pore-water sample despite the presence of abundant quantities of sulfate and sulfide in the aquifer. The absence of sulfide in the pore waters is consistent with the hypothesis that sulfate is reduced in the aquifer. The presence of arsenic, at concentrations ranging from 0.0062 to 0.0374 mg/L, is consistent with the absence of sulfide and the possible presence of iron in the pore water.

## Introduction

The confined Atlantic City 800-foot sand aquifer is the major source of potable water along the southern New Jersey coast. The aquifer and the overlying and underlying confining units are part of the lower Miocene Kirkwood Formation (table 1). The aquifer is composed of a thick body of sand and gravel interbedded between two brown to gray clay-silt confining units (fig. 1). Large withdrawals (20 Mgal/d) are made from the aquifer to supply the large summer population at resort centers in southeastern New Jersey (Nawyn, 1997). The potentiometric head in the aquifer is substantially below the National Geodetic Vertical Datum of 1929 (NGVD 29) (fig. 2), and continues to decline at a rate of about 1 ft/yr at

			Hydrogeologic unit		
Series	Geologic unit	Hydrologic characteristics	From Zapeca (1989), Miller and others (1994), Pucci and others (1997), and Sugarman (2001)	Model layer (From Martin, 1998) (see figure 1)	
	Cohansey Sand	A major aquifer system. Ground water occurs generally under wa- ter-table conditions.	Kirkwood-Cohansey aquifer system	A9	
		Thick, diatomaceous clay bed.	Upper confining unit <sup>1</sup>	C8	
Miocene		Confining unit is present along New Jersey coast and for a short	Rio Grande water-bearing zone		
	Kirkwood Formation	distance inland.	Lower confining unit <sup>1</sup>	A8	
		A major aquifer along the coast.	Atlantic City 800-foot sand		
Oligocene and Eocene deposits	See Miller and others (1994; 2001)	Poorly permeable silt and clay.	Composite confining unit	C7	

Table 1.	Lower Miocene,	Oligocene, and	d Eocene	geologic	and hydroge	eologic	units of the	New Jersey	Coastal Plain
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<sup>1</sup>Grouped by Sugarman (2001) as the Wildwood-Belleplain confining unit

the center of the cone of depression in southern Atlantic and northern Cape May Counties (Lacombe and Rosman, 1997). From 1997 to 2002, the potentiometric head in the aquifer declined 11 ft at Ocean City, N.J. (Lacombe and Rosman, 2001). As a result, many of the coastal areas of Cape May County are experiencing, or are at risk from, saltwater intrusion (fig. 3).

Sodium-dominated waters are common in coastal areas of the New Jersey Coastal Plain (Back, 1960). Results of a sampling program conducted from 1989 to 1992 (Lacombe and Carleton, 2001) indicate that concentrations of sodium in the confined Atlantic City 800-foot sand in most of southern Cape May County were greater than 50 mg/L, the New Jersey secondary drinking-water standard (N.J. Administrative Code, 2002) (fig. 4). The U.S. Environmental Protection Agency (USEPA) recommends 20 mg/L as a health and monitoring advisory level (U.S. Environmental Protection Agency, 1991). The sodium in the aquifer probably does not result from saltwater intrusion because it is not balanced by equal molar amounts of chloride throughout most of the extent of the aquifer in the county, possibly as a result of cation exchange that can increase the amount of sodium without a corresponding increase in the amount of chloride. Concentrations of sodium and sulfate in the aquifer increase greatly with depth and increase with distance to the south (Reilly, 2001; McAuley and others, 2001).

Leakage of inorganic constituents, including sodium, chloride, sulfate, and sulfide, from the overlying and underlying confining units to the Atlantic City 800-foot sand may increase with changes in hydrodynamic stress and change the composition of the water in the aquifer. Upconing in the brackish Piney Point aquifer below the confining unit underlying the Atlantic City 800-foot sand and a cone of depression in the infrequently used Rio Grande water-bearing zone above the confining unit overlying the Atlantic City 800-foot sand are clear indications that hydraulic stress is propagating throughout the geohydrologic section (table 1; fig. 2) in the area (Lacombe and Rosman, 2001; Lacombe and Carleton, 2001). Therefore, pore water from the confining unit either above or below the Atlantic City 800-foot sand (depending on local flow directions) could be leaking to the aquifer.

The U.S. Geological Survey (USGS), in cooperation with the New Jersey Department of Environmental Protection (NJDEP), has conducted a series of investigations to determine the effects of the composition of pore water in the confining units on the quality of water in the adjacent confined aquifers in the New Jersey Coastal Plain. Because the concentrations of sodium in the confined Atlantic City 800foot sand in most of southern Cape May County are greater than 50 mg/L, and because the aquifer is the major source of potable water along much of the southern New Jersey coast, the investigations have focused primarily on this aquifer and the overlying and underlying confining units. The NJDEP needed to determine the concentrations of constituents in pore water in the confining units and their vertical and horizontal distributions to assess the possible effects of the pore water on the quality of water in the Atlantic City 800-foot sand.

In this study, which is one in a series of geochemical investigations, the USGS, in cooperation with the NJDEP, characterized the composition of pore water in the confining



- C1 Confining unit between the lower and middle Potomac-Raritan-Magothy aquifers
- K-T boundary Cretaceous-Tertiary boundary

**Figure 1.** Generalized representation of simulated prepumping flow in a hydrogeologic section through the southern Coastal Plain of New Jersey (Modified from Martin, 1998) and location of boreholes.





Figure 2. Potentiometric surface of the Atlantic City 800-foot sand, Cape May County, New Jersey, September 5-9, 1989. (Modified from Lacombe and Rosman, 2001)



**Figure 3.** Areas experiencing or threatened by saltwater intrusion in Cape May County, New Jersey. (Modified from Lacombe and Carleton, 2001)

units overlying and underlying the Atlantic City 800-foot sand at Ocean View, northeastern Cape May County, N.J., southwest of Ocean City and west of Sea Isle City, N.J. (figs. 3-5). Pore-water samples were obtained from clay-silt core samples of the confining units from the 1,500-ft borehole (U.S. Geological Survey station number 391044074433201) completed at Ocean View, N.J. This borehole intercepts the aquifer and the enclosing confining units near the most sodium-rich and sulfidic part of the aquifer in central Cape May County, as determined by chemical analyses of ground water (Reilly, 2001; unpublished data on file at the U.S. Geological Survey New Jersey Water Science Center in West Trenton, N. J.). Pore water obtained from this borehole was sampled because (1) the borehole is farther downdip in the lower part of the Kirkwood Formation than other boreholes sampled to date (2004), (2) the aquifer water from the confined Atlantic City 800foot sand in most of east-central and southeastern Cape May County is sulfidic (Reilly, 2001; unpublished data on file at the U.S. Geological Survey New Jersey Water Science Center in West Trenton, N.J.), and (3) sodium (Na) concentrations in water are near the NJDEP 50-mg/L secondary drinking-water standard (Reilly, 2001; Lacombe and Carleton, 2001).

#### **Purpose and Scope**

This report describes the composition of pore water in the confining units of the Kirkwood Formation in Cape May County, N.J. Thirteen 1-ft-long subsamples were removed from the continuous core through the Kirkwood Formation at Ocean View, N.J. The subsamples are from the section of core that includes the clay-silt confining units immediately above and below the Atlantic City 800-foot sand. Pore water collected from the subsamples was analyzed for concentrations of sodium, chloride, sulfate, sulfide, additional selected major ions, and selected trace elements. This report documents the concentrations and the vertical and horizontal distributions of these constituents on the basis of the samples collected. The water types obtained from the core are characterized. Sediment in the core is described in general for the sampled sections and in detail for the individual samples. The quality of pore water from the core at Ocean View is compared to that of water from the other cores collected in the series of studies completed in the region to date (2004). The possible effects of the quality of pore water from the confining units on the quality of water in the aquifer are discussed.

#### **Previous Work**

The distribution of strontium (Sr) and Sr isotopes in pore water from the same confining units investigated here was studied by Szabo and others (1997) to evaluate potential sources of solutes. The Sr in sea water in many different time periods has had unique isotopic signatures that changed linearly through time, allowing for a precise form of "age-dating" of marine-shell-bearing sedimentary deposits (Faure, 1982). The technique can be used to interpret the age of stratigraphic sequences in the New Jersey Coastal Plain (Sugarman and others, 1993) because the shells from the strata of different geologic time periods have preserved the unique isotopic signatures. Sr-isotopic signatures of pore water in a sediment core collected from the lower Miocene Kirkwood Formation at Atlantic City were much less radiogenic (smaller relative concentrations of Sr-87) than those of pore water in the adjoining shell-material-rich sediment and matched those in shell-material-rich sediment from deep stratigraphic intervals with less radiogenic signatures. The Sr-isotopic composition of the pore water may indicate that the water has been in contact with different (Oligocene and Eocene) confining-unit sedimentary-shell components. The disequilibrium in the Sr-isotopic ratios of water to adjoining shell material in the confining units could be indicative of inputs of Sr from variously aged geologic material in the confining units below. The isotopic composition of Sr in water also changes gradually from the northern to the southern extent of the Atlantic City 800-foot sand (Reilly, 2001), becoming less radiogenic toward the south, as the aquifer becomes deeper. The change in the isotopic ratios in the aquifer could be indicative of inputs from the confining units of less radiogenic Sr (and perhaps other solutes) that thus increase in concentration toward the south, where the aquifer is deepest and ground-water flow has the least velocity. This interpretation is consistent with the groundwater flow paths proposed by Martin (1998). The Sr-isotope data indicate that confining-unit pore water could be leaking to the aquifer.

An additional investigation of the Atlantic City 800foot sand and the enclosing confining units indicates that the composition of the pore water is highly variable and characterized by high concentrations of dissolved sodium (maximum value, 280 mg/L) and sulfate (maximum value, 894 mg/L) (Pucci and others, 1997). The vertical distribution of solutes in the pore water was aligned along a concentration gradient of the confining units to the aquifer, indicating that the confining units were potential sources of solutes to the aquifer. Depending on local concentration gradients and directions of advective flow, the confining unit either above or below may be a source of sodium, chloride, and sulfate to the aquifer, as is the case for Sr. The Sr-isotope data indicate that at Atlantic City, N.J., just north of Cape May County, the confining unit below the aquifer may be the most important source of Sr (Szabo and others, 1997).

The release of sulfate from the confining units is believed to provide an electron acceptor for bacteria that metabolize or ferment organic matter, resulting in the production of organic acids (Chapelle and McMahon, 1991). The process of sulfate reduction to sulfide and the presence of organic acids leads to dissolution of shell materials. The divalent calcium and magnesium released from shell dissolution can be exchanged for monovalent sodium through cation exchange on clayey substrates. The presence of sulfide in water from the aquifer has long been suspected because of the strong odor of the water, especially in Cape May County. Recent work indicates



**Figure 4.** Sodium concentrations in water samples from the Atlantic City 800-foot sand, Cape May County, New Jersey, 1989-92. (Modified from Lacombe and Rosman, 2001)

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**Figure 5.** Lithology, pore-water sample locations, core recovery, and hydrogeologic units, lower Miocene Kirkwood Formation, Leg 174AX Ocean View borehole, Cape May County, New Jersey. (Modified from Miller and others, 2001)



**Figure 5.** Lithology, pore-water sample locations, core recovery, and hydrogeologic units, lower Miocene Kirkwood Formation, Leg 174AX Ocean View borehole, Cape May County, New Jersey.—Continued



**Figure 5.** Lithology, pore-water sample locations, core recovery, and hydrogeologic units, lower Miocene Kirkwood Formation, Leg 174AX Ocean View borehole, Cape May County, New Jersey.—Continued

that sulfide concentrations in the aquifer increase with depth, especially in Cape May County (Reilly, 2001; unpublished data on file at the U.S. Geological Survey New Jersey Water Science Center in West Trenton, N.J.). The substantial increase in the concentration of sodium from north to south in confined aquifers, including the Atlantic City 800-foot sand (about 30 mg/L in the northern part of Cape May County, typically slightly more than 50 mg/L in the central part, and as high as 390 mg/L in the southern part) likely results from, or is affected by, the sequence of chemical reactions hypothesized by Chapelle and McMahon (1991).

## Hydrogeologic Setting

Regional hydrogeologic units of the New Jersey Coastal Plain were delineated principally by Zapecza (1989) (table 1). Martin (1998) modeled the hydrogeologic formations of the New Jersey Coastal Plain to simulate ground-water flow in the regional system. Those model layers that relate to the borehole intervals discussed in this report are identified in figure 1. A list of studies of confining-unit pore waters conducted from 1997 to the present (2004) also is provided in figure 1.

### Hydrogeology

The lower Miocene Kirkwood Formation includes a thick sand and gravel unit between two clay-silt units that forms the major confined aquifer in the region, the Atlantic City 800-foot sand (Woolman, 1898; Zapecza, 1989). The aquifer generally is more than 150 ft thick near Atlantic City, N.J. (Zapecza, 1989), and at the borehole site (Miller and others, 2001), and thickens to the southeast (downdip). The updip extent of the Atlantic City 800-foot sand is delineated by the updip limit of the overlying confining unit. The potentiometric head in the Atlantic City 800-foot sand is substantially below the National Geodetic Vertical Datum of 1929 (NGVD 29) in southern Atlantic and northern Cape May Counties (Lacombe and Rosman, 1997; Lacombe and Rosman, 2001).

The confining units that overlie and underlie the Atlantic City 800-ft sand aquifer were termed the "upper" and "lower" confining units and the "composite" confining unit, respectively (Miller and others, 1994). The sediments comprising the confining units are within the lower Miocene Kirkwood Formation, with the exception of the basal part of the composite confining unit, which includes sediments that are late Cretaceous to Oligocene in age. The upper and lower confining units are separated in places by a thin sand lens known as the Rio Grande water-bearing zone (Miller and others, 1994). The upper and lower confining units were grouped as the Wildwood-Belleplain confining unit by Sugarman (2001), but because the Rio Grande water-bearing zone is thick in central Cape May County, the subdivisions of Miller and others (1994) of the upper and lower confining unit are used in this report for the sake of stratigraphic clarity. The uppermost

section of the composite confining unit forms the base of the Kirkwood Formation. Most of the composite confining unit consists of multiple fine-grained formations that range from Paleocene to Miocene in age. Its thickness increases greatly downdip (fig. 1); in fact, the composite confining unit is one of the thickest confining units in the New Jersey Coastal Plain (Zapecza, 1989) and is the one most often sampled for confining-unit studies in the State (Pucci and others, 1997). Zapecza (1989) summarizes the general geologic characteristics of these thick, extensive clay-silt confining units in the New Jersey Coastal Plain.

### Geology of the Eocene to Miocene Strata at Ocean View, New Jersey

Late Eocene and early Oligocene sediments in southeastern New Jersey have rarely been sampled because of the great depth at which they occur and because the strata thin or pinch out toward the west. Initial descriptions of these formations in southeastern New Jersey are provided by Owens and others (1988); additional descriptions are provided by Miller and others (1994). The borehole at Ocean View was installed to supplement available geologic information concerning these formations; the geology is described in detail by Miller and others (2001). The upper Eocene section at Ocean View (1,171.5-1,434.4 ft) is the thickest part to be cored in New Jersey (Miller and others, 2001) and is important because it is quite fossiliferous and exhibits minimal diagenetic alterations. The thick Oligocene section (895.5-1,171.5 ft) at Ocean View consists of six to eight sequences. The many shell beds in the Oligocene section are thick (commonly more than 1 ft thick) and are preserved with minimal alteration. They were used to obtain detailed Sr-isotopic age estimates for sedimentary sequences (Miller and others, 2001). The Kirkwood Formation (depth from land surface to top, 220.55 ft) at Ocean View is composed of three middle Miocene and four lower Miocene sequences (fig. 5). The Kirkwood sequences contain more shell beds at this location than at the Atlantic City or Bass River drilling locations farther north (Miller and others, 2001; Reilly, 2001). Shells from these shell beds were used to obtain Sr-isotopic age estimates that have been critical in dating sequences and sequence boundaries and in refining the geologic framework and sequence stratigraphy of the Miocene units established by Sugarman and others (1993).

The stratigraphic-sequence-based terminology for the lower Miocene sedimentary units that form the hydrogeologic units discussed in this report was defined by Sugarman and others (1993), Miller and others (1994), and Sugarman and Miller (1997). It was used by Miller and others (2001) to classify sedimentary sequences and correlate them with hydrogeologic units in the 1,500-ft-deep borehole at Ocean View, New Jersey, in north-central Cape May County, and is also used in this report (table 1). The absolute age of the Miocene stratigraphic sequences in the New Jersey Coastal Plain initially was determined by Sugarman and others (1993) and was

subsequently defined by Miller and others (1994) at Atlantic City, New Jersey. Sequences in the Tertiary sediments of New Jersey were explicitly correlated with aquifers by Sugarman and Miller (1997).

Silt and clay and occasional sand of Eocene and Oligocene age are found below a depth of 895 ft below land surface at Ocean View and form the lower part of the composite confining unit. Sand of lower Miocene age at a depth of about 800 ft forms the Atlantic City 800-foot sand aquifer. Silt of lower Miocene age forms the upper and lower confining units overlying the aquifer. Silt and sand of middle Miocene age forms the shallowest portions of the cored interval of the borehole and forms the upper confining unit as well as the overlying sand deposits. Despite the occasional sandy interbeds in some of the fine-grained units, all sampled intervals consist of silt, clay-silt, or clay (table 2a).

**Table 2a.**Lithologic description of core subsamples collected from the lower part of the Kirkwood Formation at Ocean View, CapeMay County, N.J.

[U.S. Geological Survey station number: 391044074433201]

Sub- sample number	Interval (feet below land surface)	Color	Lithologic description	
	Upper confining unit of Miller and others (1994)			
OC-1	387 - 388	5 GY 4/1, dark greenish gray	Silty clay, burrowed, minor opaque minerals, shell debris	
OC-2	393 - 394	5 G 4/1, dark greenish gray	Silty clay, laminated, occasional burrows	
OC-3	403 - 404	5 GY 4/1, dark greenish gray	Silty clay, generally laminated, occasional shells, opaque minerals, and quartz pebbles	
OC-4	437 - 438	5 Y 3/2, dark olive gray	Silty clay, small shell fragments, massive and slightly laminated, opaques	
		Lower confining	unit of Miller and others (1994)	
OC-5	547 - 548	5 Y 3/2, dark olive gray	Clay, blocky, with laminated clayey silt, shell beds	
OC-6	572 - 573	5 Y 3/2, dark olive gray	Clay, with minor silty laminates, blocky, shell fragments throughout	
OC-7	587 - 588	5 Y 3/2, dark olive gray	Clay, silty, laminated to finely bedded silty clay, occasional shells and shell beds	
OC-8	596 - 597	5 Y 3/2, dark olive gray	Clay, blocky, slightly silty, micaceous, possible burrows, rare shell fragments	
OC-9	608 - 609	5 Y 3/2, dark olive gray	Clay, blocky, slightly silty, massive, micaceous, rare shell fragments	
OC-10	620- 621	5 Y 3/2, dark olive gray	Clay, blocky, slightly silty, laminated, micaceous, abundant opaques, trace shell fragments	
Atlantic City 800-foot sand of Woolman (1898)—no samples collected				
Composite confining unit of Zapecza (1989)				
OC-11	880.5 - 881.2	7.5 YR 3/1, very dark gray	Silt, blocky, massive, slightly plastic, minor mica, occasional shells	
OC-12	887.2 - 888.0	7.5 YR 3/1, very dark gray	Silt, blocky, massive silt/clay, thin interbeds and laminae, minor mica, minor shells	
OC-13	1390.6 - 1391.25	2.5 Y 4/2, black	Clay, slightly silty, with thin plastic clay lenses, laminae bevelled by bioturbation, glauconitic	

#### Clay-Silts of the Upper Eocene Strata

From 1,379.6 to 1,402.9 ft below land surface, slightly glauconitic olive gray, slightly shelly silty clay overlies heavily burrowed very light green clay to silty clay. This previously unnamed sequence is termed "Sequence E10a" by Miller and others (2001), who tentatively correlate this sequence with sediments from 770.7 to 840.1 ft at Bass River and from approximately 1,330 to 1,352 ft at Atlantic City. The section contains variable facies that have aspects both of the silty clays of the overlying Absecon Inlet Formation (initially named at Atlantic City by Miller and others (1994) and first described in detail by Browning and others (1997)) and of the glauconitic clays and yellow clays of the underlying Shark River Formation. At 1,376.85 ft, the upper surface of the sequence is identified. The basal surface of the overlying sequence is erosional with clay rip-up clasts from the section below. Above 1,376.85 ft, the sediment changes texture and fines upward from clayey glauconite sand at the sequence boundary to slightly glauconitic silty clay.

#### Clay-Silts of the Lower Miocene Strata

The basal (Kw0 and Kw1) sequences of the Kirkwood Formation are typically clayey (fig. 5). Deep-water (shelf) deposits dominate at the base and include micaceous shelly silty clay (880-889.6 ft) and shelly silty clay (872.1-879.1 ft) deposits. Uniform silty clay from 862 to 863.8 ft caps the basal clayey part of the Kw1 sequence.

Laminated micaceous silt and silty fine sands, and thin sand laminae with silt interbeds characterize the sediments from 810 to 863 ft. The section coarsens upwards and grades into medium- to coarse-grained sand (the aquifer). The silts and clays recovered from the borehole from the interval from 810 to 863 ft contain more sand than is typical of the Kw1 sequence elsewhere in New Jersey. Miller and others (2001) ultimately concluded that the sediments in the section typically were sufficiently sandy that they likely were hydraulically connected to the aquifer.

The thick coarse-grained sand from 640 to 810 ft is classified as the aquifer. The environment of deposition of the sand changes from a deep-shelf-type deposit to a nearshoretype deposit at a sequence boundary at about 775.9 ft. The coarse shelly sands from 640 to 775.9 ft represent the upper half of the Kw1a sequence deposited predominantly in nearshore environments.

Above the coarse sand, the upper part of the Kirkwood Formation is present as a mostly fine-grained unit and is classified into three additional sequences (Kw2, Kw3, and CH1). Alternating beds of silt, sandy silt, and massive clayey silts are present from 580 to 640 ft, the basal part of the Kw2 sequence. Sediments from 538 to 580 ft contain sandy laminae in places but laminated slightly micaceous clayey silts are predominant. Laminated micaceous sandy silt forms a sequence boundary at 531.6 ft (Kw2a1), indicating a change in the environment of deposition. The upper part of the Kw2 sequence is more variegated than the lower part. Variegated clay, silt, sand, and shell beds are admixed from 450 to 531.6 ft. Slightly shelly, clayey silts are present from 433.25 to 441.5 ft. An irregular, heavily burrowed contact at 433.25 ft is interpreted as a maximum flooding surface (maximum transgression) and forms the boundary among sediments deposited in different environments. Laminated beds of shelly silty sands immediately overlie this boundary. Poorly sorted, clayey, medium-coarse sand dominates the section from 410.05 to 433.25 ft. A noticeable contact forms the basal sequence boundary of the Kw3 sequence at 410.05 ft.

A thick section of silt and clay is present from 360 to 410 ft. This thick fine-grained section is capped by a unit of homogeneous laminated gray clay (352.5-360 ft). An irregular surface (at 352.2 ft) marks the top of this unit, the shallowest thick and nearly homogeneous fine-grained unit intercepted by the borehole. Shell beds and shelly silts dominate from 327.1 to 352.2 ft. These shell beds form the uppermost part of the Kw3 sequence. Variegated clay, silt, sand, and shell beds are admixed from 244 to 327.1 ft. This variable mix of sediments forms the basal part of the CH1 sequence. Sand predominates in the borehole above a depth of 244 ft. The contact between the Kirkwood Formation and the Cohansey Sand above is likely a "sand-on-sand" contact, and its exact depth is uncertain.

## **Methods of Study**

Sediment samples were collected from the 1,500-ft-deep borehole drilled cooperatively at Ocean View west of Sea Isle City, New Jersey (fig. 2), by USGS, NJDEP, and Rutgers University. Pore water was collected from subsamples of confining-unit materials, especially those immediately above and below the Atlantic City 800-foot sand (fig. 5). Concentrations of many dissolved and isotopic constituents in the confining-unit pore water were determined. Constituents of greatest interest are sulfate (SO<sub>4</sub>), sulfide, sodium (Na), chloride (Cl), and strontium (Sr).

Samples were collected using techniques described in detail by Pucci and others (1997) and Reilly (2001). Concentrations of Sr and major and minor cations were determined by inductively coupled plasma-mass spectrometry (ICP-MS) on about 5 mL of undiluted pore-water sample, as opposed to the method used by Pucci and others (1997) and Reilly (2001), inductively coupled plasma-atomic emission spectroscopy (ICP-AES) on about 5 mL of sample diluted 1:1 with deionized water. In addition, a previously developed technique for determining sulfide concentrations (Cline, 1969) was modified slightly (unpublished data on file at the U.S. Geological Survey Water Science Center in West Trenton, N.J.) and was used to analyze the pore water for sulfide.

#### **Initial Collection of Sediment**

The Kirkwood Formation at Ocean View extends from 220 to 1,002 ft below land surface (Miller and others, 2001). Within this interval, the fine-grained materials of the upper, lower, and composite confining units adjoining the Atlantic City 800-foot sand were sampled (fig. 5). Sediment materials from the fresh core were logged and described in detail at the site before subsampling, removal, and storage. Every 10 to 15 ft, a 9-in. piece of corehole that was competent, unfractured, and without sandy interbeds was selected for further analysis. Sandy interbeds are common at 220 to 290 ft and the interval was not sampled. The sandy interval from 627 to 880 ft that composes the aquifer also was not sampled. Intervals with shell material were noted for later removal of the shells. Sample selection for pore-water extraction from these shelly intervals was difficult because the shell beds generally were friable and also could not be sampled. Closely spaced shell beds are common at 290 to 360 ft and 433 to 531 ft; therefore, these intervals were not sampled. The slow drilling process precluded timely sampling at the interval from 888 to 1,002 ft; therefore, only a few samples were collected despite the generally fine-grained nature of the sediment. Only one sample was collected below the Oligocene Period boundary at 890 ft; this sample was collected at 1,391 ft, near the base of the upper Eccene sediments just above the middle Eccene Shark River Formation (table 2a).

The core subsample was removed with a sharp knife precleaned with deionized water followed by isopropyl alcohol and then flamed. The core subsample was wrapped in autoclaved Al-foil to prevent dessication, was immediately transferred to anaerobe jars containing nitrogen ( $N_2$ ) atmosphere, and was placed on ice in darkness. The subsamples in the anaerobe jars were stored in the laboratory refrigerator at 4 °C to prevent oxidation of the borehole material and bacterial growth. Thirteen subsamples of 9-in. lengths of core were collected for analysis of pore water (table 2a).

# Extraction of Confining-Unit Pore-Water Samples

Pore water was extracted using standard pore-squeezing methods (Manheim, 1966). A newly constructed titanium mechanical squeezing device was used to apply pressures of as much as 10,000 bars. The pressure was gradually increased to 10,000 bars over 1 hour; the volume of the extracted pore water was measured every 15 minutes at 2,500-bar increments. Pore water was collected with a 10-mL precleaned (with deionized water (DIW)) plastic syringe through an in-line 45micron syringe Millipore cellulose filter. The extracted volume at each pressure interval, the final volume and weight of the fluid extracted, and the weight of the sediment before and after extraction were recorded. All handling of borehole material, except the actual pore-water extraction, was completed in an N<sub>2</sub>-filled glove bag. Extracted pore water for analysis was placed in precleaned screw-cap Teflon test tubes. Pore-water samples collected for analysis for sulfide were stored in anaerobe jars in an  $N_2$ -gas atmosphere and refrigerated until analysis no more than 7 days after extraction. Extracted volumes are given in table 2b.

#### Quality Assurance

Quality assurance included collection of four sample splits for analysis for anions. Analysis of an equipment blank, an equipment wash with a known standard, and a known standard submitted blind had been completed in previous studies (Pucci and others, 1997; Reilly, 2001). Results of those studies show that sample handling did not cause appreciable contamination, and equipment-cleaning procedures were adequate.

Minor contamination with trace elements occurred as samples passed through the core-squeezing equipment. Gross contamination with zinc (>50  $\mu$ g/L) and molybdenum (51  $\mu$ g/L) was noted by Pucci and others (1997). In the current study, therefore, neither zinc nor molybdenum was analyzed for. Analysis of the equipment blanks and the sodium sulfate wash showed that lithium, vanadium, and manganese were not detected in the equipment blank, and minor amounts of iron, strontium, and aluminum were present in blanks as random contamination (Pucci and others, 1997).

#### Analysis of Pore Water

ICP-MS was used to determine concentrations of major and minor cations on about 5 mL of pore-water sample with no dilution. The absence of dilution allows for lower detection capability than is achievable with ICP-AES analysis on samples diluted with DIW. ICP-MS allows for determination of sub-microgram-per-liter concentrations of many trace elements that cannot be determined by ICP-AES (Faires, 1993; Garbarino, 1999).

Concentrations of major anions (Cl and  $SO_4$ ) and nutrients (orthophosphate and nitrate) were determined by ion chromatography on 5 mL of undiluted sample. Concentrations of minor anions bromide (Br) and iodine (I) were determined by colorimetry.

Concentrations of dissolved sulfide were determined by colorimetry with methylene blue after co-precipitation with zinc acetate in a pH-10 sodium hydroxide (NaOH) solution (Cline, 1969). The reporting level for NaOH is 0.01 mg/L. In a 10-mm path length glass rectangular cuvette, 1 mL of Reagent A (a mixture of sulfuric acid, zinc acetate, NN-dimethyl-pphenylene-diamine sulfate, and deionized water), 1 mL of the sample, and 0.02 mL of Reagent B (ferric chloride and DIW) were combined, in that order. A Perkin Elmer Lambda 4A spectrophotometer, zeroed with deionized water at 660 nm (nanometers), was used to determine the solution absorbance at this wavelength. The peak absorbancy, which occurs after 2 minutes of reaction, was documented. Working standards were made from a 10-mg/L stock standard solution prepared by

[U.S. Geold	ogical Survey sta	ution number:	201044014C								
Sub- sample number	Collection depth (feet below land surface)	Sub- sample identifier	Extraction date (mo/dy/yr)	Pre- extraction weight (g)	Post- extraction weight (g)	Difference in weight (g)	Extracted volume total (cc)	Extracted volume, 15 min at 2,500 psi (cc)	Extracted volume, 30 min at 5,000 psi (cc)	Extracted volume, 45 min at 7,500 psi (cc)	Extracted volume, 60 min at 10,000 psi (cc)
					Upper c	onfining unit (	of Miller and	others (1994)			
0C-1	388.6	А	12/05/01	49.62	39.27	10.35	8.9	5.0	7.0	8.1	8.9
0C-1	388.6	В	12/11/01	46.92	39.96	6.96	4.5	3.4	4.0	4.2	4.5
0C-1	388.6	С	12/13/01	49.26	42.20	7.06	6.0	4.5	5.2	5.8	6.0
0C-2	393.9	А	12/13/01	51.56	43.03	8.53	7.4	5.0	6.2	7.0	7.4
0C-2	393.9	В	12/21/01	49.52	40.87	8.65	7.2	5.0	6.6	7.0	7.2
0C-3	404.8	А	12/09/02	48.99	39.96	9.03	7.2	6.3	7.0	7.1	7.2
0C-3	404.8	В	12/09/02	49.32	39.88	9.44	8.0	6.7	7.6	7.8	8.0
0C-4	438.0	А	01/11/02	49.98	42.92	7.06	6.2	6.0	6.1	6.2	6.2
0C-4	438.0	В	01/16/02	48.21	40.91	7.30	9.9	5.6	6.1	6.5	6.6
0C-4	438.0	С	01/23/02	49.53	42.07	7.46	6.2	6.0	6.2	6.2	6.2
					Lower c	onfining unit	of Miller and	others (1994)			
0C-5	547.0	А	01/23/02	49.02	39.18	9.84	8.2	5.7	7.3	7.8	8.2
0C-5	547.0	В	01/25/02	49.93	39.48	10.45	9.1	6.0	8.1	0.0	9.1
0C-6	572.1	А	01/24/02	48.80	41.41	7.39	5.9	4.4	5.3	5.6	5.9
0C-6	572.1	В	01/25/02	49.97	42.35	7.62	6.1	4.7	5.6	5.8	6.1
0C-7	587.3	А	01/30/02	49.34	40.93	8.41	7.6	6.0	6.9	7.5	7.6
0C-7	587.3	В	01/30/02	49.82	42.28	7.54	6.4	5.1	5.9	6.4	6.4
0C-7	587.3	С	01/31/02	49.63	41.45	8.18	7.1	5.6	6.3	7.0	7.1
0C-8	596.5	А	02/01/02	49.26	37.12	12.14	5.8	3.2	4.6	5.2	5.8
0C-8	596.5	В	02/01/02	49.84	42.44	7.40	6.4	5.6	6.0	6.3	6.4
0C-8	596.5	С	02/08/02	49.84	41.84	8.00	6.7	5.0	5.4	6.3	6.7
0C-9	608.8	А	02/08/02	49.36	42.97	6.39	5.5	3.4	4.2	4.8	5.5
0C-9	608.8	В	02/04/02	49.98	42.47	7.51	6.8	4.9	6.0	6.4	6.8
0C-9	608.8	C	02/13/02	49.60	42.14	7.46	6.0	4.2	5.2	5.8	6.0
OC-10	620.3	А	02/15/02	49.39	42.61	6.78	5.4	5.1	5.2	5.3	5.4
OC-10	620.3	В	02/20/02	49.59	42.11	7.48	6.0	5.3	5.3	5.9	6.0
OC-10	620.3	С	02/20/02	49.48	40.23	9.25	6.9	4.9	5.8	6.8	6.9

Table 2b. Weight before and after squeezing, volume of pore water extracted, and water yield at various extraction pressures for core subsamples collected from the lower next of the Kirkwood Formation at Ocean View County N.J.

Methods of Study

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Weight before and after squeezing, volume of pore water extracted, and water yield at various extraction pressures for core subsamples collected from the lower part of the Kirkwood Formation at Ocean View, Cape May County, N.J.—Continued Table 2b.

**Extracted volume** 60 min at 10,000 psi (cc) 2.5 2.5 9. 1.9 2.1 1.2 6.1 1.3 1.8 1.3 ∟. 2.2 1.1 1.1 4.4 2.1 2.1 2 Extracted volume, 45 min at 7,500 psi 2 drops 2 drops 2 drops 2 drops (00) Ś Ś 1.2 1.08.1 -Ś 0 [.] Ś ŝ 9 4 0 0 0 [U.S. Geological Survey station number: 39104407443201; subsample identification: A, B, C; g, grams; cc, cubic centimeters; min, minutes; psi, pounds per square inch] 30 min at 5,000 psi Extracted volume, 2 drops 1 drop 1 drop (00) ci ci C C 0 0 0 C  $\overline{}$ 0 0 0 0 0 0 0 0 Atlantic City 800-foot sand of Woolman (1898) -- no samples collected Extracted volume, 15 min at 2,500 psi (CC) Composite confining unit of Zapecza (1989) 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 С 0 0 0 Extracted volume total (cc) 2.5 2.5 2.0 6.1 1.01.01.91.21.3 1.8 1.3 L. C. 4.4 2.2 2.1 1.1 1.1 2.1 2.1 Difference in weight 3.49 3.90 3.15 3.10 2.39 2.99 2.17 .76 3.13 3.46 3.25 2.37 2.39 2.03 2.81 2.52 3.20 3.07 .28 .55 (g) extraction weight (g) 46.46 46.39 46.16 46.55 47.18 46.43 46.82 47.57 47.56 46.80 47.92 48.14 48.28 45.57 45.34 46.80 46.91 46.91 46.67 45.71 Postextraction weight (g) 49.30 49.66 49.20 49.32 49.36 49.62 49.20 49.35 49.06 49.24 49.58 49.93 49.17 49.92 49.94 49.95 48.94 49.90 49.83 49.71 Pre-Extraction (mo/dy/yr) 02/27/02 02/27/02 03/11/02 03/14/02 02/26/02 03/01/02 03/04/02 03/05/02 03/08/02 03/11/02 03/11/02 03/12/02 03/13/02 03/20/02 03/28/02 04/01/02 04/01/02 02/22/02 02/28/02 03/01/02 date identifier sample Sub-Ω Щ [L Ċ Щ  $\triangleleft$ В ∢ В  $\mathbf{C}$  $\checkmark$ Ξ C [T\_ G Η  $\cup$ below land Collection depth (feet surface) 881.7 881.7 881.7 881.7 881.7 881.7 888.0 888.0 888.0 888.0 888.0 888.0 888.0 888.0 888.0 391.2 391.2 391.2 391.2 881.7 sample number 0C-12 OC-12 0C-12 0C-12 0C-12 0C-12 0C-12 0C-12 0C-12 0C-13 0C-13 Sub-0C-11 0C-11 0C-11 0C-11 0C-13 0C-13 OC-11 OC-11 OC-11

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OC-13

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adding 0.0765 g of crystalline sodium sulfide to 1 L deoxygenated DIW. The DIW was stripped of oxygen by bubbling with oxygen-free high-purity helium gas in an  $N_2$ -filled glove bag for 1 hour.

The use of a small volume of sample limited the detection capability of the method for sulfide concentration. A 50-mm path length glass rectangular cuvette was tried, but the small sample volume had to be diluted with oxygen-free DIW to provide enough volume to fill the cuvette to the required height. This latter technique resulted in less repeatability of measurements than use of the standards prepared by the same method, and ultimately was discontinued.

## **Composition of Pore Water**

Results of pore-water sample analyses are provided in table 3. Median values for each constituent are provided in table 4. The composition of the pore-water samples is represented by the trilinear diagram in figure 6. Analytical results for sulfate, chloride, and the other halides in three of four sequential duplicate samples are almost identical (within about + 1 percent) (table 3). The relatively high aluminum concentration in sample OC-3 (200287) was considered suspect because the composition of the pore water was dissimilar to that of the surrounding samples (table 3). Minor amounts of iron, strontium, and aluminum were present in blanks collected with the same extraction equipment by Pucci and others (1997); therefore, the high concentration of aluminum in sample OC-3 was considered to be a result of random contamination. Major findings concerning sulfate, sulfide, chloride, and trace-element distribution are discussed below.

The composition of pore-water samples from the core from Ocean View is more diverse than that of the samples from Atlantic City (Pucci, 1997; Reilly, 2001). All three types of water present at Atlantic City—calcium-sulfate (type I), calcium-sodium-magnesium-sulfate-chloride-bicarbonate (type II), and sodium-sulfate-chloride-bicarbonate (type III) are also present at Ocean View. Six samples are classified as one of these three types (fig. 6). Three additional types of water are present at Ocean View, although one is a subtype. Three samples are classified as subtype IIc, calcium-sodiumbicarbonate-chloride water. Two samples each are classified as water type IV, sodium-chloride-sulfate water, and water type V, calcium-chloride-sulfate water.

Various water-quality types generally are found at distinct depth intervals. There are two types of water in the upper confining unit. The shallowest part of the upper confining unit is dominated by calcium-magnesium-sodium-sulfate-chloridebicarbonate water. The middle of the unit contains calcium sulfate-type water (fig. 6). The base contains a subtype, calcium-sodium-bicarbonate-chloride-sulfate water.

Three dominant water types are present in the lower confining unit. Calcium-sodium-bicarbonate-chloride-sulfate water characterizes samples from the shallowest part of the lower confining unit, whereas calcium-chloride-sulfate water characterizes samples from the middle part of the lower confining unit and calcium-sulfate water characterizes water from the deepest part. Sodium-sulfate-chloride-bicarbonate and sodium-chloride-sulfate type waters are dominant in the composite confining unit below the aquifer. These facies generally are consistent, though not exactly, with types I to III observed in the same units at nearly the same depths at Atlantic City, N.J., by Pucci and others (1997). The exception is the sodiumchloride-sulfate type (type IV) water, present at a depth of 1,390 ft, which was not observed by Pucci and others (1997).

The vertical distribution of the chemical facies is an indication of the scale of hydrogeochemical facies within the confining units (tens of feet) and may be indicative of patterns of flushing (volumes of water exchanged). The presence of more chloride indicates less flushing and an increase in the chloride to sodium ratio. The highest chloride concentration, 8,400 mg/L, was found at the greatest depth, 1,390 ft below land surface. Chloride concentrations are higher at Ocean View (46.4-757 mg/L) than at Atlantic City (20-100 mg/L) (Szabo and others, 1997; Pucci and others, 1997), excluding the concentration in core sample OC-13, which is Oligocene. Somewhat similar patterns of chemical composition are noted for the same units at Bass River and Atlantic City, N.J., although the concentrations differ in magnitude. Sulfate-rich water types are found primarily above the aquifer, and sodium-, chloride- and sulfate-dominated water types are found primarily below the aquifer. It is possible that the chemical composition of the confining units evolves in a somewhat predictable manner, and that patterns of chemical evolution are related to depth and distance from the outcrop, the orientation of flow paths (Martin, 1998), and flushing.

Concentrations of the major cations for all the pore-water samples, except the one from 1,390 ft, which is brackish, differ across a wide range (tables 3 and 4). Concentrations of calcium range from 18.9 to 225 mg/L; magnesium, from 10.9 to 59.2 mg/L: and sodium, from 51.3 to 513 mg/L. Concentrations of sodium increased consistently with depth in the lower confining unit from 548 to 610 ft, an indication that ion exchange increased with depth. Sodium concentrations were highest below the Atlantic City 800-foot sand. Concentrations of strontium range from 0.539 to 2.33 mg/L and vary directly with concentrations of chemically similar calcium (both are divalent cations). Lithium concentrations in pore-water samples ranged from 0.0263 to 0.744 mg/L (median, 0.039 mg/L, table 3). Lithium concentrations were highest in the pore water from the composite confining unit (fig. 7).

Chloride concentrations ranged from 46.4 to 757 mg/L; typically, concentrations in the composite confining unit below the Atlantic City 800-foot sand were higher than those in the lower confining unit above the sand. The exception is the middle part of the lower confining unit, where concentrations of chloride are elevated (fig. 7). Chloride concentrations ranged from greater than 100 mg/L to 757 mg/L in the middle part of the confining unit and were higher there than in the same units at Atlantic City, where chloride concentrations rarely Pore-water concentrations of selected constituents in samples collected from the lower part of the Kirkwood Formation at Ocean View, Cape May County, N.J., **Table 3.** 2001.

n number: 391044074433201; number in parentheses is parameter	
feet; BLS, below land surface; mg/L, milligrams per liter; <, less than; E, estimated value;, no data; U.S. Geological Survey stati	te used to identify the constituent, property, or characteristic in the U.S. Geological Survey water-quality database (NWIS)]

code used	n to recurring un	e consument, pr	operty, or cital			igical out vey we	aici-quattiy uai	(CT M LT) SEPOR						
			Depth, bottom of interval	pH (Units)	Calcium, filtered (ma/L)	Magnesium, filtered (mq/L)	Potassium, filtered (mq/L)	Sodium, filtered (ma/L)	Bromide, filtered (ma/L)	Chloride, filtered (ma/L)	Fluoride, filtered (ma/L)	lodide, filtered (ma/L)	Sulfate, filtered (mg/L, as	Silica, filtered (ma/L, as
Sub- samule	Sub- samnle	Extraction	(ft BLS)										sulfate)	silica)
number	identifier	date	(72016)	(00400)	(00915)	(00925)	(00935)	(00630)	(71870)	(00640)	(00620)	(71865)	(00945)	(00955)
					Up	per confining u	unit of Miller a	nd others (19	994)					
0C-1	200285	12/5/2001	389	1	70.8	21.2	17.8	105	<1.2	159	E0.8	0.08	155	48.7
0C-2	200286	12/13/2001	395	8.3	80.8	24.2	18	97.5	<1.2	101	×.	×. 8	218	49.6
0C-3	200287	1/9/2002	406	8.1	225	59.2	28	116	<1.5	85.9	×. 8	×.1	799	36.3
0C-4	200288	1/11/2002	439	8.6	64.5	16.7	13.6	73.2	<1.5	78.8	E4	<.1 .1	74.8	55.9
					Lov	ver confining u	unit of Miller a	ind others (19	<b>394)</b>					
0C-5	200289	1/23/2002	548	1	54.5	10.9	13.8	48.5	<1.5	52.2	E4	<.1 .1	42	59.4
0C-5	201012	1/24/2002	548	-	1	1	ł	ł	<5.8	72.6	ł	4.>	52.8	1
0C-6	200291	1/24/2002	573	8.2	57.6	11.7	13.8	51.3	<1.5	54.2	4>	<.1 .1	79.9	58.2
0C-7	200299	1/30/2002	588	8.3	77.3	15.6	16.6	53.7	<1.5	329	E4	<.1 .1	303	50.3
0C-7	201011	1/31/2002	588	1	ł	1	1	1	1	336.5	4>	<.1 .1	316	1
0C-8	200290	2/1/2002	596	8.2	105	21.3	18.4	61	<1.5	757	E4	<.1 .1	388	53.6
0C-9	200292	2/8/2002	610	8.3	113	23.5	18.8	51.8	<1.5	46.4	4>	<.1 .1	268	53.7
0C-9	201014	2/9/2002	610	!	1	1	1	!	<1.5	47.3	E4	<.1 .1	267	
OC-10	200295	2/15/2002	621	8.2	144	28.9	16.2	50.9	<1.5	49.3	4	<.1	420	51.3
				A	tlantic City 8(	00-foot sand of	Woolman (18	98) no san	nples collect	ted				
					0	omposite cont	fining unit of <b>z</b>	apecza (198;	(6					
0C-11	200296	2/22/2002	882	8.3	44.5	26.9	18	513	<1.5	281	4>	<.1 .1	560	22.9
0C-12	200298	3/4/2002	889	8.5	18.9	14.4	16	487	<1.5	376	4>	ł	452	20.8
0C-12	201013	3/5/2002	889	1	ł	ł	ł	ł	<1.5	381	E4	<.1	447	ł
0C-13	200297	3/22/2002	1,390	8.2	348	356	147	5,930	29.9	8,400	4>	<.1	5070	32.9

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[ft, feet: BLS, below land surface; mg/L, milligrams per liter; <, less than; E, estimated value, .-., no data; U.S. Geological Survey station number: 391044074433201; number in parentheses is parameter code used to identify the constituent, property, or characteristic in the U.S. Geological Survey water-quality database (NWIS)]

	و	1.	1 0/		2	•	۲ ر	,						
Sub- camila	Sub- samula	Extraction	Phosphorus, ortho, filtered (mg/L, as phospho-	Aluminum, filtered (mg/L)	Arsenic, filtered (mg/L)	Barium, filtered (mg/L)	Boron, filtered (mg/L, as Boron)	lron, filtered (mg/L)	Lithium, filtered (mg/L)	Manganese, filtered (mg/L)	Nickel, filtered (mg/L)	Strontium, filtered (mg/L)	Sulfide, filtered (mg/L)	Vanadium, filtered (mg/L)
number	identifier	date	(00671)	(01106)	(01000)	(01005)	(01020)	(01046)	(01130)	(01056)	(01065)	(01080)	(00746)	(01085)
					Upper c	sonfining uni	t of Miller an	nd others (	1994)					
0C-1	200285	12/5/2001	<0.28	0.02	0.0134	0.0202	0.464	<0.2	0.038	0.0394	0.010	0.776	<0.015	0.0125
0C-2	200286	12/13/2001	<.28	.058	.0233	<.02	.494	E.16	.0459	.0294	.00498	.888	<.015	.0135
0C-3	200287	1/9/2002	<.35	.742	.018	.0483	69.	<.2	.0692	.0823	.00872	2.33	<.015	.0157
0C-4	200288	1/11/2002	<.35	.02	.0353	<.02	.299	<.2	.0342	.0084	.00554	.702	<.015	.0104
					Lower c	confining uni	t of Miller a	nd others (	1994)					
0C-5	200289	1/23/2002	<.35	.036	.0338	<.02	.504	<.2	.0263	.0047	.00692	.539	<.015	6600.
0C-5	201012	1/24/2002	4.>	1	1	1	1	1	1	1	1	1	1	1
0C-6	200291	1/24/2002	<.35	.02	.0267	<.02	.458	<.2	.0284	.0048	.00604	.566	<.015	.0105
0C-7	200299	1/30/2002	<.35	.022	.0169	<.02	.64	<.2	.0305	.006	.00542	.758	<.015	7600.
0C-7	201011	1/31/2002	<.35	1	1	1	1	ł	1	1	1	1	1	1
0C-8	200290	2/1/2002	<.35	.037	.031	<.02	.579	<.2	.0399	.0089	.00948	1.02	<.015	.01
0C-9	200292	2/8/2002	<.35	.023	.013	<.02	.737	<.2	.0428	.0101	.00836	1.09	<.015	.0121
0C-9	201014	2/9/2002	<.35			1	1	1	1	1	1	ł	1	1
OC-10	200295	2/15/2002	<.35	.034	.0374	<.02	609.	<.2	.0352	600.	.00756	1.34	<.015	.0106
				Atlanti	c City 800-fo	ot sand of M	Voolman (18:	98)—no sa	mples colle	cted				
					Comp	osite confin	ing unit of Z	apecza (19	(68					
0C-11	200296	2/22/2002	<.35	.02	.0066	<.02	2.61	<.2	.0743	.0099	.011	1.14	<.015	.0206
0C-12	200298	3/4/2002	<.35	.056	.0062	<.02	3.28	<.2	.0744	.0076	.0125	0.554	<.015	.0267
0C-12	201013	3/5/2002	<.35	ł	ł	ł	ł	ł	ł	1	ł	ł	!	ł
0C-13	200297	3/22/2002	<.35	.064	.0116	.0542	4.19	E.17	.62	.0566	.255	17.4	<.015	.0058

 Table 4.
 Summary statistics for selected constituents in pore-water samples collected from the borehole in the lower Miocene

 Kirkwood Formation at Ocean View, Cape May County, N.J., 2001.

<b>[U.S. Geological Surve</b> ]	v station number:	391044074433201;	Concentrations an	e in milligrams	per liter: <	less than
		,		0		/

Constituent	Total number of samples	Minimum	1st quartile	Median	3rd quartile	Maximum
pH (standard units)	10	8.1	8.2	8.3	8.3	8.6
Calcium	12	18.9	21.225	70.8	109.00	225
Magnesium	12	10.9	15.55	21.3	25.55	59.2
Potassium	12	13.6	14.9	17.8	18.20	28
Sodium	12	48.5	51.55	73.2	110.50	513
Bromide	12	<1.2	<1.5	<1.5	<1.5	5.8
Chloride	12	46.4	63.4	85.9	220	757
Silica	12	20.8	42.5	51.3	54.8	59.4
Sulfate	12	52.9	117.45	268	436	799
Phosphorus, ortho	12	<0.28	<0.35	<0.35	<0.35	1.4
Aluminum	12	0.02	0.02	0.034	0.047	0.742
Arsenic	12	0.006	0.013	0.023	0.032	0.037
Barium	12	< 0.02	<0.02	<0.02	<0.02	0.048
Boron	12	0.299	0.479	0.579	0.714	3.28
Iron	12	0.16	<0.2	<0.2	<0.2	<0.2
Lithium	12	0.026	0.035	0.040	0.058	0.074
Manganese	12	0.005	0.008	0.009	0.020	0.082
Nickel	12	0.005	0.006	0.008	0.010	0.013
Strontium	12	0.539	0.634	0.888	1.115	2.33
Vanadium	12	0.010	0.010	0.012	0.015	0.027

exceeded 100 mg/L. Of the major anions, sulfate was the constituent with the most variation; concentrations ranged from 42 to 799 mg/L, about a 19-fold difference between highest and lowest concentrations. The concentration of sulfate in the pore-water sample from 405 ft was much greater than that in pore water from adjoining core samples. In samples from most of the upper parts of the lower confining unit (548-573 ft), sulfate concentrations were the lowest determined. The sediment matrix there is somewhat siltier and sandier (coarser grained) than at 405 ft, which is near the base of a silty-clay zone. Sulfate concentrations increased substantially from 573 to 588 ft and were greater than 250 mg/L in all samples below this depth; this increase appears to correspond to a substantial increase in clay content (fig. 2) (Miller and others, 2001). Concentrations of dissolved inorganic carbon (DIC) were not determined analytically; they were computed by difference. The concentrations of DIC were small relative to the concentrations of chloride and sulfate; the negative charge of chloride and sulfate typically nearly balances the positive charge from the measured cations (DIC). Sulfide was not detected in the pore water despite its reported presence in the aquifer (unpublished data on file at the U.S. Geological Survey New Jersey Water Science Center in West Trenton, N.J.).

Concentrations of dissolved iron were less than the laboratory reporting limit (LRL) of 0.2 mg/L. Arsenic was detected consistently at concentrations ranging from 0.0062 mg/L to 0.0374 mg/L (table 3).



OC-1 Core subsample number

**Figure 6.** Trilinear diagram showing the distribution of major ions in pore-water samples from a core collected at Ocean View, Cape May County, N.J., 2001.



**Figure 7.** Scatter plot showing concentrations of sodium, chloride, sulfate, and lithium in pore-water samples obtained from a core collected at Ocean View, N.J., 2001, in relation to depth.

## Hypothetical Movement of Constituents in Pore Water from Confining Units to the Atlantic City 800-Foot Sand

The pore water in the samples from the lower Kirkwood Formation collected from the Ocean View, New Jersey, borehole contained substantial amounts of sodium, chloride, sulfate, strontium, and arsenic (table 3). Constituents present in high concentrations in pore waters in the confining units have the potential to leak to the aquifer (Pucci and others, 1997). Physical, biological, and geochemical processes all have been hypothesized to likely affect the movement of these constituents.

#### **Sodium and Chloride**

The pore water could contribute considerable sodium and chloride to the Atlantic City 800-foot sand. Detection of concentrations of chloride elevated above background concentrations, more than 281 mg/L, in the uppermost part of the composite confining unit immediately below the aquifer (table 3) is an indication that the confining units (especially the composite) could be a source of chloride at depth. The chloride concentration at 1,390 ft (8,400 mg/L) indicates chloride concentrations increase with depth below the uppermost part of the composite confining unit. An isolated interval in the lower confining unit from 588 to 596 ft also contained elevated concentrations of chloride (329-757 mg/L). The relation between chloride concentrations at this isolated interval and those at depth is not known. The sodium concentration at 1,390 ft (5,930 mg/L) indicates that sodium concentrations also increase with depth below the uppermost part of the composite confining unit, where the concentration of sodium was 513 mg/L. Concentrations of sodium typically were about 50 mg/L in the lower confining unit and about 100 mg/L in intervals in the upper confining unit. Concentrations of sodium greater than 50 mg/L throughout all the confining units, and concentrations in some intervals (typically in the composite confining unit) of 500 mg/L or greater, are consistent with the evolution of sodium-rich waters (Na concentrations at or near 50 mg/L) within the aquifer, with pore waters as a source of sodium, even in the absence of chloride facies.

Chloride concentrations in the aquifer increase to the south, although more slowly than the sodium concentrations (Lacombe and Carleton, 2001). The substantial increase in the concentration of sodium in the confined Atlantic City 800-foot sand, especially in the central part of Cape May County, without the corresponding increase in chloride concentrations therefore likely results from, or is affected by, the sequence of ongoing chemical reactions within and at the margins of the confining units, as hypothesized by Chapelle and McMahon (1991) and McMahon and others (1992).

Sodium-chloride type water was not found by Pucci and others (1997) in the composite confining unit at Atlantic City, but was found in the composite confining unit at Ocean View in this study. The presence of greater concentrations of chloride in all the confining units at Ocean View than at Atlantic City (Pucci and others, 1997) is consistent with the hypothesis that less freshwater flushing occurs in the downgradient part of the aquifer, to the south of Atlantic City, where the flow model of Martin (1998) indicates flow is likely to be upward through the composite confining unit to the aquifer.

The extraction volume at each pressure interval decreased substantially with depth at Ocean View (table 2b), a physical property that also is consistent with the concept of minimal circulation at depth within the clay confining units. The clay component is more notable in samples OC5 to OC13, where total extraction volumes and initial 15-minute volumes were smaller than those in samples collected at shallower intervals. The relative effects of depth and geology (clay content) cannot be resolved for these samples, however.

#### Sulfate, Sulfide, Iron, Arsenic, and Strontium

Because constituents other than sodium and chloride (such as sulfide, iron, and arsenic) can degrade water quality, a greater understanding of the concentrations of these constituents and the magnitude of movement of the constituents to the aquifer is needed. The use of improved analytical techniques for the determination of trace-element and sulfide concentrations has provided new geochemical data on pore-water composition. Despite the fact that the Atlantic City 800-foot sand in central Cape May County is sulfidic (Reilly, 2001) and abundant quantities of sulfate are present in the pore water, sulfide was not detected in the pore water, although the analytical method used by Cline (1969) was modified to improve detection capability. Sulfate-rich water is present in all confining units at both Atlantic City and Ocean View. The distribution of the sulfur-bearing constituents is consistent with the hypothesis of Chappelle and McMahon (1991) and McMahon and others (1992) that sulfate-rich pore water leaks to the aquifer where sulfide may be formed by sulfate reduction.

A study of the relation of sulfate-reducing bacteria to pore-water sulfate concentration in confining units, as discussed by Szabo and others (1996), could provide additional scientific information regarding the nature of the chemical reactions occurring at the confining-unit/aquifer interface, where sulfate reduction may be greatest (McMahon and Chappelle, 1991). Bottrell and others (2000) hypothesize that sulfate-reducing bacteria are sufficiently large to prevent them from living in the small pores likely to be encountered in fine-grained material of the confining unit. The population distribution of other types of bacteria that play a role in electron transfer (oxidation/reduction) reactions might need to be determined as well. For example, results of experiments by Chapelle and Lovely (1992) indicate that sulfate reduction might be inhibited in the presence of iron-reducing bacteria. Iron-reducing bacteria from these sediments have not been characterized, but Pucci and others (1997) documented the

abundant presence of (oxidized) iron(III) in the sediments of the lower Kirkwood Formation, which might serve as the energy source for populations of iron-reducing bacteria.

Measured concentrations of dissolved (filtered) iron in the pore water in this study typically were less than 0.2 mg/L, the laboratory reporting limit (LRL); concentrations in some samples were estimated at 0.16 to 0.17 mg/L. The estimated pore-water iron concentrations are greater than those of sulfide, although current laboratory techniques do not allow verification of the estimated iron concentrations. In the absence of sulfide, however, iron species might dominate electron-transfer reactions in the confining units.

The use of the ICP-MS analytical technique to determine constituent concentrations in pore-water samples was an important part of this study because it facilitated the determination of relatively low-level concentrations of many trace constituents, with the exception of iron. Of most significance is the presence of elevated concentrations of dissolved arsenic. The presence of arsenic is consistent with the absence of sulfide in the pore water because arsenic generally is insoluble in the presence of sulfide (Nordstrom and Archer, 2003; Moore and others, 1988). Furthermore, the presence of arsenic is consistent with the possible presence of iron in the pore water.

Additional sampling of water from the confined aquifer and of the sediment material would be needed to determine the specie of the arsenic in the water and the source of the arsenic in the sediment. It is not known, for example, whether minerals such as glauconite in the Kirkwood Formation are arsenic bearing, although they do contain arsenic when found in other Coastal Plain sediments in New Jersey (Dooley, 1998). A mineral such as glauconite, which is present in moderate amounts, could be responsible for most of the ion exchange (Chappelle and Knobel, 1983) and could be the source of arsenic and iron as well. Because arsenic is monoisotopic (Garbarino, 1999), isotopic techniques such as those pioneered by Szabo and others (1997) to trace constituent movement from confining units could not be applied.

### **Summary and Conclusions**

The U.S. Geological Survey, in cooperation with the New Jersey Department of Environmental Protection, conducted a study to determine the composition of pore water in the confining units overlying and underlying the Atlantic City 800-foot sand in southern New Jersey. Pore-water quality was determined from core samples of the confining units ("upper," "lower," and "composite") in the lower Miocene Kirkwood Formation collected from a borehole at Ocean View, N.J., southwest of Ocean City and west of Sea Isle City, N.J. The quality of the pore water from this core is of considerable interest because the borehole intersects the aquifer in its most sodium-rich and sulfidic part in central Cape May County, N. J. Sodium concentrations in this area increase rapidly to the south. Pore water obtained from this core is important because (1) the borehole is located farther south (downdip) than other boreholes sampled to date (2004), (2) adjoining aquifer water is sulfidic, and (3) sodium concentrations in the adjoining aquifer are near the 50-mg/L New Jersey drinking-water standard.

The composition of pore water from the confining units at the site was highly variable. Calcium-sodium-sulfate-bicarbonate, calcium-chloride-sulfate, calcium-sulfate, and sodiumsulfate-chloride-bicarbonate type waters characterize the samples collected from the deepest part of the confining unit directly overlying the aquifer (lower confining unit). Sodiumchloride-sulfate is the dominant water type in the confining unit underlying the aquifer (composite confining unit). Sodium and chloride become dominant with depth. At a depth of 1,390 ft, the chloride concentration was 8,400 mg/L and the sodium concentration was 5,930 mg/L. Concentrations of chloride greater than 250 mg/L in the composite confining unit indicate that the confining units can be a source of chloride at depth. At Ocean View, chloride concentrations greater than 250 mg/L also were found occasionally in the confining unit directly above the aquifer (the lower confining unit).

Sulfide was not detected in the pore water despite the presence of abundant quantities of sulfate (42–799 mg/L), excluding the water from core sample OC-13, which is Eocene (older) and despite the reported presence of sulfide in the aquifer. This finding is consistent with the hypothesis that sulfate is reduced in the aquifer. The presence of elevated concentrations of arsenic (0.0062-0.0374 mg/L) in the filtered pore water is consistent with the absence of sulfide. Concentrations of iron were estimated to be about 0.16 to 0.17 mg/L, indicating that iron species might be the dominant redox couple in the pore waters.

The substantial increase in the concentration of sodium and sulfide to the south in the confined Atlantic City 800foot sand, especially in the central part of Cape May County, without a corresponding increase in chloride concentrations, therefore, likely results from, or is affected by, the sequence of ongoing chemical reactions within and at the margins of the confining units. The presence of sulfate-rich pore water is consistent with the previously proposed hypothesis that sulfaterich pore water leads to an increase in ion exchange and the evolution of sulfide- and sodium-rich water in the confining unit and the aquifer. The potential movement of arsenic along with the sodium, chloride, and sulfate to the confined aquifer from the confining units could degrade the quality of water in the aquifer. Physical, biological, and geochemical processes all have been hypothesized to affect the movement of each of these constituents. Improved analytical determinations of concentrations of iron, sulfide, arsenic species, and other chemical or biological indicators of oxidation-reduction processes might allow the relative importance of the various geochemical processes to be determined.

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