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24. VARIATIONS IN PORE-WATER QUALITY, MINERALOGY, AND SEDIMENTARY TEXTURE OF CLAY-SILTS IN THE LOWER MIOCENE KIRKWOOD FORMATION, ATLANTIC CITY, NEW JERSEY[1]

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ABSTRACT

Properties of and pore-water solute chemistry in confining units in the New Jersey Coastal Plain were studied to determine whether leakage of solute-enriched pore water from confining units affects regional aquifer-water chemistry, which ultimately may result in aquifer waters with high sodium and bicarbonate concentrations. Pore-water samples collected from a continuously cored borehole in the lower Miocene Kirkwood Formation at Atlantic City, NJ, were analyzed: 15 samples were obtained from clay-silt confining-unit sediments, and four samples were from silt interbeds in the sand of the major confined aquifer in the region, the Atlantic City 800-ft sand. The samples were analyzed to assess interrelations among mineralogy, texture, fluid-retention properties, sediment chemistry, and pore-water chemistry, and to document the scale of variation in these properties.

Linear regressions were developed to describe the relations of constituents dissolved in 14 pore-water samples collected from the lower confining unit overlying the Atlantic City 800-ft sand and from the silt interbeds in the upper sand unit of the Atlantic City 800-ft sand. The regressions were for concentrations of magnesium and calcium ($m = 0.27$, $R^2 = 0.99$); concentrations of sodium and the sum of calcium and magnesium ($m = 0.17$, $R^2 = 0.92$); concentrations of sulfate and the sum of calcium and magnesium ($m = 1.14$, $R^2 = 0.99$); and concentrations of sodium and sulfate ($m = 0.14$, $R^2 = 0.89$). The percentage of fine sand was greatest in the shallowest sampled interval, where pore-water concentrations of calcium, magnesium, and sulfate were greatest.

The pore-water samples were of three distinct water-quality types (hydrogeochemical facies): a calcium-sulfate type, a mixed calcium-sodium-sulfate-chloride-bicarbonate type, and a sodium-sulfate-bicarbonate-chloride type. The first two types were found only in the lower confining unit; the third type was found only in the composite confining unit underlying the Atlantic City 800-ft sand. Each of these hydrogeochemical facies generally is found within distinct intervals over a range of tens of feet in the core.

Krige estimates of pore-water–constituent variations with depth were made by using only the analytical results for the 14 samples from the lower confining unit overlying the Atlantic City 800-ft sand and the silt interbeds in the upper sand unit of the Atlantic City 800-ft sand. Geostatistical analysis of the pore-water–quality data generally resulted in two types of semivariograms. One semivariogram type best fits concentration trends with depth for calcium, magnesium, strontium, sodium, sulfate, and specific conductance; lithium and chloride may also fit this semivariogram type. The other semivariogram type best fits concentration trends with depth for silica, cation exchange capacity, and dissolved inorganic carbon. The scale of variation of the concentrations and properties is indicated by the maximum lag autocorrelation distance of the theoretical semivariograms (the range) and ranged from 44 to 110 ft (13.4–33.5 m). The scale of variation of pore-water major-ion concentrations of sulfate, chloride, calcium, and magnesium alone is on the order of 65–70 ft (19.8–21.3 m). The semivariograms for all pore-water constituents except silica have significant variance at the smallest lag distance, indicating that the constituent concentration varied over a larger scale than the sampling interval.

The dominant exchangeable cation in the sediment is calcium. Cation exchange reactions do not appear to be the dominant process in the sediments of the lower confining unit above the Atlantic City 800-ft sand, because a linear correlation exists between the concentration of sodium and the sum of calcium and magnesium concentrations in the pore water; concentrations of all these constituents increase in the upward flow direction, and the ratio of sodium to chloride in the pore water is about 1.0.

Two significant principal components explained 82.5% of the total variation in pore-water solute chemistry. Principal component 1 represents about 53% of the variation in pore-water quality and includes calcium, magnesium, sulfate, strontium, and lithium. Coupled chemical processes in the confining units, such as incongruent dissolution of carbonate and other mineral phases or redox transformations of sulfur, likely explain the covariance of these constituents. Principal component 2 represents about 30% of the variation and includes sodium, dissolved inorganic carbon, and chloride. Covariance of sodium and chloride probably is caused by the presence of residual seawater.

INTRODUCTION

Pore water from sediments collected from marine-deposited confining units in the northern coastal plain of New Jersey (Fig. 1) contained elevated concentrations of sulfate (2200 mg/L, or greater than 45 milliequivalents per liter [meq/L]; Pucci and Owens, 1989). Elevated concentrations of sulfate also have been reported in marine-deposited confining units in the Atlantic Coastal Plain in Maryland (Chapelle and Lovely, 1990) and South Carolina (Chapelle and McMahon, 1991) and in the southern New Jersey Coastal Plain (Pucci et al., 1992). Concentrations of calcium, magnesium, and sodium are greater in the confining units than in the adjacent aquifers. The flow of sulfate-rich, mineral-laden water through confining units to aquifers is believed to affect water-quality trends in Atlantic Coastal Plain aquifers through chemical processes (Chapelle and Knobel, 1983; Back, 1985; Pucci and Owens, 1989; Chapelle and McMahon, 1991; Pucci et al, 1992; Pucci and Owens, 1994). Release of sulfate from

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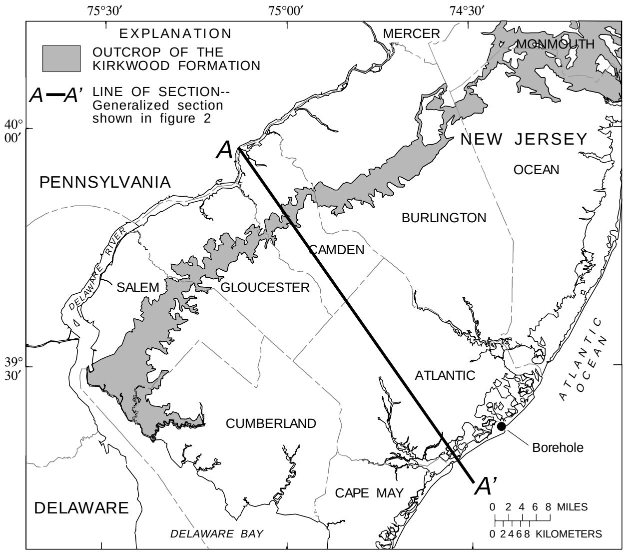
Previous Chapter Table of Contents Next Chapter



Base modified from U.S. Geological Survey digital data, 1:100,000, 1983, Universal Transverse Mercator projection, Zone 18

Figure 1. Location of borehole, line of section, and outcrop of the Kirkwood Formation, New Jersey Coastal Plain.

confining units can provide an electron acceptor for bacteria that metabolize or ferment organic matter, resulting in the production of CO_2 or organic acids (Chapelle and McMahon, 1991; Pucci et al., 1992) and leading to the dissolution of carbonate minerals. The exchange of divalent calcium and magnesium cations released during this process for monovalent sodium through cation exchange mechanisms in clayey substrates increases the concentration of sodium in ground water and results in the evolution of sodium bicarbonate-type water in the deep parts of the aquifers from the calcium bicarbonate-type water typical in the shallow parts of the aquifers (Chapelle and Knobel, 1983; Chapelle, 1983).

The source of the sulfate in the pore water is unknown. Sediments in the New Jersey Coastal Plain do not contain primary deposits of evaporitic minerals, such as gypsum (Owens and Sohl, 1969), and these minerals were not present as primary minerals in cores collected in 1985, 1989, and 1993 (Pucci et al., 1992; Miller et al., 1994). Results of previous studies of pore-water chemistry in aquifers and confining units in the coastal plain of New Jersey (Pucci and Owens, 1989; Pucci et al., 1992) show that the presence of sulfate ions is not the result of dilution of seawater. Factors that affect sulfate hydrogeochemistry in confining units include geochemistry, biogeochemistry, transport processes, and lithologic and mineralogic variations. Pucci and Owens (1989) and McMahon and Chapelle (1991) suggest that isolated microbiological environments are present in confining units and that the bacteria within them use sulfate through microbially mediated dissimilatory sulfate reduction. Postdepositional pyritic concretions, which probably represent the mineralogic sinks of sulfate-reduction reactions, are present at or near the contact between the aquifer and confining unit (Pucci and Owens, 1989; Chapelle and McMahon, 1991; Pucci et al., 1992). The assumption that cross-formational fluxes are diffusion driven (Pucci and Owens, 1989; Chapelle and McMahon, 1991) rather than advection-driven leads to estimates for sulfate transport and minimum rates at which sulfate reduction and other coupled chemical reactions occur. Determining the source of dissolved sulfate, its rate of transport, and the coupled chemical processes by which it affects water quality in confined aquifers are large-scale objectives of the ongoing study of confining-unit chemistry of which this study is a part.

The number of sampling intervals in any single hydrogeologic unit was limited in the previous pore-water studies, because they focused on chemical variations among several sedimentary layers or in the entire sequence. Therefore, the variations in pore-water quality through a vertical section of an individual hydrogeologic unit were not well characterized. Defining the scale of variation of physical and chemical features of aquifer and confining-unit sediments is critical to understanding the nature of coupled chemical reactions in these sediments. The primary objectives of this investigation, therefore, were to (1) evaluate pore-water chemistry in a single confining unit of the New Jersey Coastal Plain, (2) explore correlations between pore-water chemistry and the mineralogic and textural properties of core sediment, and (3) determine whether continuous chemical gradients exist, especially for the sulfate ion that would support the hypothesis that solutes migrate diffusively toward adjacent aquifers. Core samples used for pore squeezing in this investigation were collected from a continuous cored borehole (Ocean Drilling Program Leg 150X) during June 22 through 27, 1993, at the U.S. Coast Guard Station at Atlantic City (Fig. 1) by Lafayette College and the U.S. Geological Survey in collaboration with Rutgers University, Lamont-Doherty Earth Observatory, and the New Jersey Geological Survey.

This report describes the variations in lithology, sedimentary texture, mineralogy, cation exchange capacity (CEC), and concentrations of major ions and selected trace elements in pore water from 19 core samples collected at regular intervals from the clay-silt confining units above and below, and from clay-silt layers within, the confined water-bearing zone of the Atlantic City 800-ft sand, which is a major water-bearing unit in the region. The samples were collected from 551 to 842 ft (168.9–256.6 m) below land surface. The water-chemistry data are analyzed statistically, correlations among water-quality constituents are reported, and the relation of variations in water quality to the regional flow system is discussed. The continuous distribution of pore-water constituents is interpolated to clearly define chemical gradients, and possible chemical processes that may affect these gradients are identified.

Hydrogeology

Hydrogeologic Units

Regional hydrogeologic units of the New Jersey Coastal Plain were delineated principally by Zapecza (1989). Martin (in press) 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 cored interval discussed in this report are identified in Figure 2. Hydrogeologic formations described by Zapecza (1989) and Miller et al. (1994) and Martin's model layers that correspond to the study area are listed in Table 1.

Confining Unit Overlying the Atlantic City 800-ft Sand

Zapecza (1989) identifies a thick, extensive confining unit within the lower to middle Miocene Kirkwood Formation (Sugarman et al., 1993). It is rich in diatoms; Zapecza (1989) refers to it as the "great diatom bed." Miller et al. (1994) divide this confining unit at Atlantic City into the "upper" confining unit, 408–512 ft (124.4–156.1 m) below land surface, and the "lower" confining unit, 548–665 ft (167.0–202.7 m) below land surface. Martin (in press) calculates the vertical hydraulic conductivity of the upper confining unit (Layer C8; Table 1) to be 2.96×10^{-5} ft/d (9.0×10^{-6} m/d).

Rio Grande water-bearing zone. This minor aquifer lies within the "great diatom bed" of Zapecza (1989) atop the lower confining unit (Table 1). The Rio Grande water-bearing zone is sandy and is generally less than 40 ft (12.1 m) thick in the coastal area in Atlantic County. All samples were collected below the Rio Grande water-bearing zone (Fig. 3).

Lower Confining Unit

This unit is between the overlying Rio Grande aquifer and the underlying Atlantic City 800-ft sand. It is the unit most sampled in this

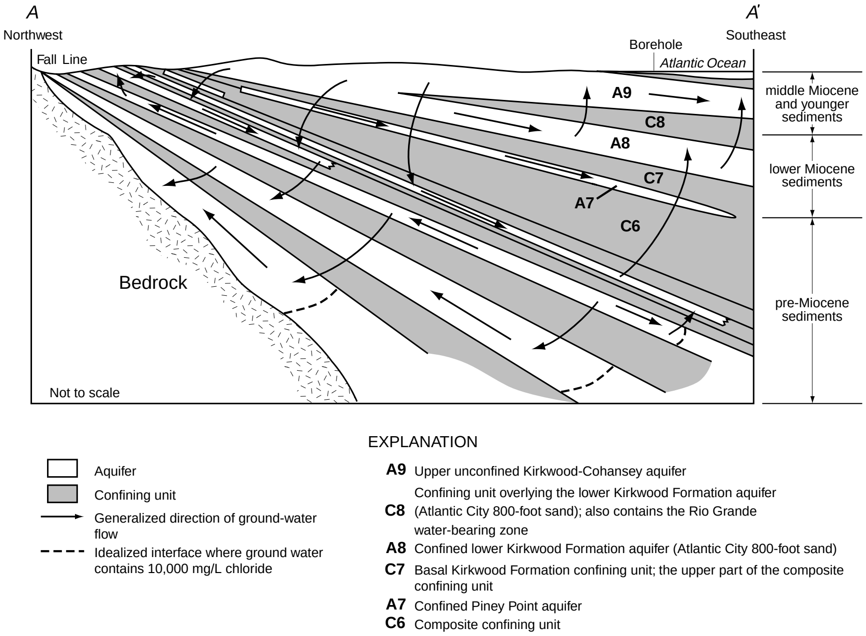


Figure 2. Simulated prepumping flow in a generalized section of the New Jersey Coastal Plain (modified from Martin, in press, fig. 74; line of section shown in Fig. 1).

Table 1. Tertiary–lower Miocene geologic and hydrogeologic units of the New Jersey Coastal Plain and stratigraphic position of the sampled section.

System	Series	Geologic	Lithology	Hydrologic characteristics	Hydrogeologic unit: Zapecza (1989) and Miller (1994)	Hydrogeologic unit: Martin (in press)*
Tertiary	Miocene	Pennsauken Formation	Sand, quartz, light colored, heterogeneous clayey, pebbly	A major aquifer system. Ground water occurs generally under water-table conditions.	Kirkwood-Cohansey aquifer system	A9
		Bridgeton Formation				
		Beacon Hill Gravel	Gravel, quartz, light colored, sandy			
		Cohansey Sand	Sand, quartz, light-colored, medium-to-coarse-grained, pebbly			
		Kirkwood Formation	Sand, quartz, gray and tan, very fine-to-medium-grained, micaceous; and dark-colored diatomaceous clay	Thick, diatomaceous clay bed, also known as the "great diatom" confining unit, is present along New Jersey coast and for a short distance inland.	"Upper" confining unit	C8
					Rio Grande aquifer	
					"Lower" confining unit	A8
				A thick water-bearing sand. A major aquifer along the coast.	Atlantic City 800-ft sand	
				Poorly permeable silt and clay sediments.	Alloway Clay or equivalent member of "composite" confining unit	C7
	pre-Miocene and Eocene deposits					

Notes: * = Martin's (in press) designations were applied for regional flow modeling simplification (see Fig. 2). Modified from Zapecza (1989) and Miller (1994).

study. The confining-unit thickness increases in the downdip direction from less than 100 ft (30.5 m) in Atlantic County (Fig. 1) to more than 300 ft (91.4 m) south of the Atlantic City area (Zapecza, 1989; Mullikin, 1990).

Atlantic City 800-ft Sand

This lower Miocene unit lies within the lower part of the Kirkwood Formation (Table 1). The Atlantic City 800-ft sand is generally more than 150 ft (45.7 m) thick near the core site (Zapecza, 1989) and thickens to the southeast (downdip). Martin (in press) modeled the Rio Grande water-bearing zone, the lower confining unit, and the Atlantic City 800-ft sand as one aquifer layer (Unit A8; Fig. 2). The calibrated transmissivity of the combined unit at the borehole site is ~6000 ft^2/d (557.4 m^2/d). This is the most productive aquifer along the barrier beaches from Cape May County north to Ocean County, and provides most of the water supply to Atlantic City.

The updip extent of the Atlantic City 800-ft sand is based on the updip limit of the overlying lower confining unit. Northwest of this demarcation, the Kirkwood Formation is hydraulically connected to the overlying Cohansey Sand, forming a thick, unconfined aquifer.

A continuous, relatively thin semiconfining unit, which ranges in thickness from 10 to 30 ft (3.0–9.1 m), lies within the Atlantic City 800-ft sand (Zapecza, 1989) and divides it into "upper" and "lower" parts (Fig. 3). This thin confining unit is located ~735–740 ft (224.0–225.5 m) below land surface at the borehole site. Most production wells in this area are screened in the lower part of the Atlantic City

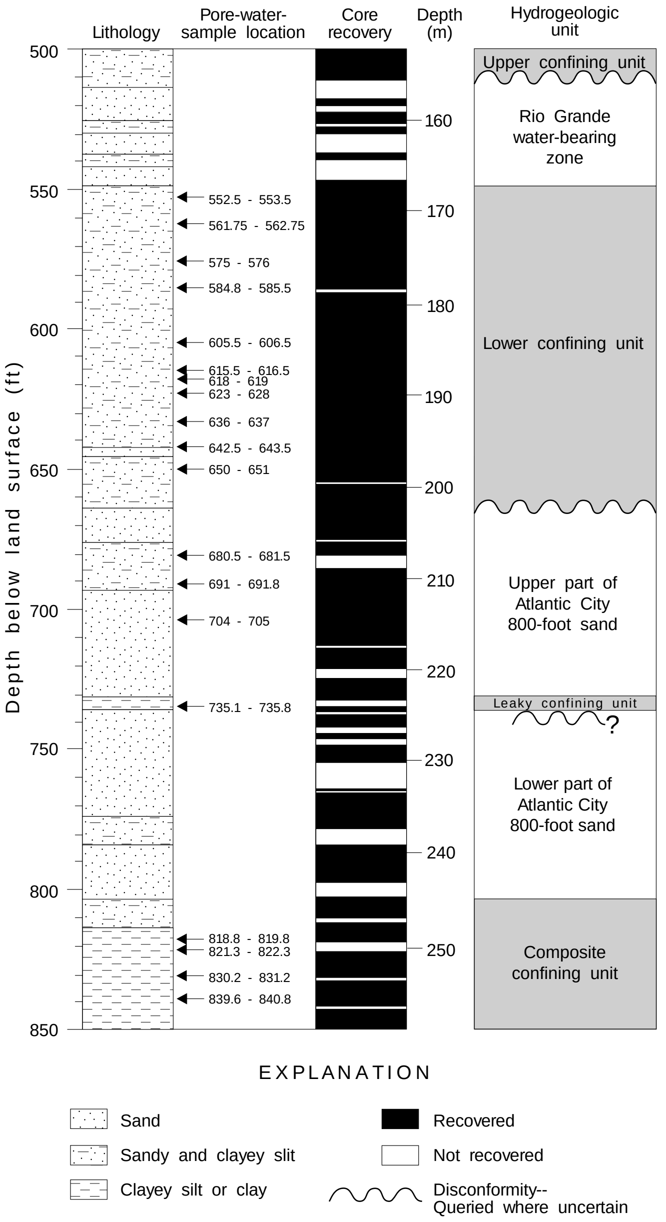


Figure 3. Stratigraphic column and samples of core collected for analysis, lower Miocene Kirkwood Formation, 500–850 ft, Atlantic City, New Jersey Coastal Plain.

800-ft sand (Mullikin, 1990). Unpublished results of an aquifer test at Atlantic City indicate that significant amounts of water can leak through this thin silt seam, which acts as a leaky confining unit within the aquifer (Tilley and Straus, New Jersey Geological Survey, pers. comm., 1978).

Composite Confining Unit

The uppermost section of the "composite" confining unit underlies the Atlantic City 800-ft sand, at the base of the Kirkwood Formation (Zapecza, 1989; Fig. 3). The thickness of the composite confining bed increases greatly downdip, from less than 50 ft (15.2 m) at the outcrop in Ocean County to more than 1190 ft (362.7 m) in Cape May County. In Martin's (in press) model, this unit is the "basal Kirkwood confining unit" (model Layer C7), and the calibrated vertical hydraulic conductivity is 2.5×10^{-5} ft/d (7.6×10^{-6} m/d; Fig. 2).

Prepumping Ground-Water–Flow System

The chemical characteristics of the pore water analyzed in this study evolved before pumping began. Regional recharge occurred by infiltration in topographically high outcrop areas and by leakage through overlying strata. Lateral regional ground-water flow was generally downdip toward the low-lying areas where water discharged upward through sediments to the Atlantic Ocean in the east and southeast (Fig. 2). Martin (in press) determined that the prepumping flow was predominantly upward at the borehole site and increased in velocity with shallower depths. Upward flow into the upper confining unit in the great diatom bed that overlies the Rio Grande water-bearing zone is about 0.1 in/yr (0.25 cm/yr). Water flows upward from the Atlantic City 800-ft sand into the lower confining unit. Upward flow through the composite confining unit from deeper strata is virtually zero. The traveltime of water from the recharge area through this deep unit is estimated to be millennia.

Hydrogeochemistry

Barton et al. (1993) compiled data that indicate an evolution in aquifer-water quality for the Atlantic City 800-ft sand from calcium-bicarbonate facies to sodium-bicarbonate facies southward along the shore in the vicinity of Atlantic City. Harriman and Sargent (1985) and Knobel (1985) indicate the same trend in water quality in the Piney Point aquifer along the south-central coast of New Jersey. Chapelle and Knobel (1983), who studied similar trends in the chemical facies of the Aquia aquifer of Maryland, suggest that chemical pathways for this facies change depend on the electron donor-electron acceptor couple that dominates redox reactions. Chapelle and McMahon (1991) report that the sulfate-sulfide redox couple may be the redox couple that strongly affects water quality in the coastal aquifer, resulting in the formation of sodium bicarbonate–type water.

Pore-water cation exchange reactions with the exchangeable clays in the confining units in the coastal plain probably affect water quality during cross-formational flow. Illite/smectite (I/S) and glauconite clays have the highest capacity for cation exchange in these sediments; the other clays, in decreasing order of reactivity, are illite and kaolinite. The presence of areas in which water quality has been significantly affected by ion-exchange reactions would cause the composition of clay minerals in the solids to vary.

METHODS AND QUALITY ASSURANCE

Core Sampling

Core samples were obtained at regular intervals from the entire thickness of sediments that confine the main water-bearing zone of the Atlantic City 800-ft sand. In the 150-ft (45.7-m) section overlying this zone, 14 samples were collected at ~10-ft intervals. Eleven of the 14 samples were collected from the lower confining unit at depths of 551–661 ft (167.9–201.5 m), and three samples were collected from interbedded silt and sand from the upper part of the Atlantic City 800-ft sand at depths of 681–705 ft (207.6–214.9 m). For purposes of contrast, four samples were collected from the upper 40 ft (12.2 m) of the composite confining unit underlying the Atlantic City 800-ft sand at depths of 818–840 ft (249.3–266.0 m), and one sample was from the thin silt confining layer located approximately in the middle of the aquifer at 736 ft (224.3 m). Subsamples from the core interval 618–628 ft (188.4–191.4 m) were mishandled during retrieval and, therefore, were labelled "618–623" and "623–628" because their associated depths could not be identified with certainty. Subsamples were collected only from portions of the confining units with no obvious fracturing or interbedded sand stringers.

A 6-mL volume of 2.5% suspension of fluorescent 0.5-µm diameter microspheres (Polysciences, Inc.) was added to 1 L of deionized water to form a tracer, which was added to the drilling mud to test for contamination of the core or penetration of the core by drilling fluids. Injection of the tracer at about the 550-ft depth (167.6 m) was not possible because the first batch of the tracer was mishandled. The tracer was injected when drilling reached 660 ft (201.2 m) below land surface. The final concentration of microspheres in the drilling mud was estimated to be 6×10^6 spheres/mL of drilling mud, one order of magnitude higher than that used by Chapelle and McMahon (1991). The total drilling-mud volume circulating in the drilling annulus and mud pit was estimated to be 1000 L.

Samples for core squeezing were selected from the freshly drilled core onsite. The core was collected by using a 10-ft-long (3.0 m), 1 7⁄8-in (4.76 cm) inner-diameter core barrel with a continuous mechanical rotary drilling rig. The recovered core was extruded onto 5-ft lengths (1.5 m) of semicylindrical polyvinyl chloride (PVC) screen. The extruded core was removed to an examining area, washed to remove the exterior coating of drilling mud, and photographed. Then a description of the core was logged.

Subsections of the core 1 ft (0.3 m) in length were removed from the 10-ft sections (3.0 m) of core by cutting with a steel knife sterilized with isopropyl alcohol before each use. The 1-ft (0.3 m) cylindrical core subsamples were lined with aluminum foil sterilized by cauterizing heat, placed into a fabricated core holder, and cut lengthwise with the sterilized knife. The persons handling the core wore latex gloves to prevent contamination of the samples. This initial cutting method was unacceptable because core subsamples tended to break into chunks. Thereafter, the core was placed onto a 1-ft-long (0.3 m), semicylindrical section of 2-in (5.1 cm) inside-diameter PVC lined with sterile aluminum foil. This section was placed on top of matching semicylindrical section of PVC casing secured to a plywood base (also lined with sterile aluminum foil), creating a unit with horizontal slit opening between the two PVC semicylinders. The end of the unit was placed against a wooden block and held manually to brace the core sample. The core sample was cut lengthwise with the serrated knife. This method minimized breakage of the core.

The semicylindrical core subsample retained for pore-water extraction was wrapped in layers of aluminum foil, labeled, and placed in clear lucite-plastic anaerobe jars that were 12 in (0.3 m) high and 8 in (0.2 m) in diameter. Samples that initially did not fit into these jars were bent or cut until they fit. An antioxidant reagent packet and a paper towel moistened with deionized water were placed in the bottom of the jar to minimize core oxidation and desiccation. The anaerobe jar was sealed, evacuated to less than 0.01 atm, and filled with dry-nitrogen gas. This evacuation and filling process was repeated twice. Four or five core subsamples were placed together in each of six anaerobe jars. Core subsamples were stored in an ice cooler in the field or in a laboratory refrigerator at 4°C for 1 day to several weeks before the pore water was mechanically extracted.

Selection of Subsamples

To determine whether the core subsamples could acquire moisture from condensation, presumably from the moistened towels, a core subsample was cut into four pieces, each of which weighed about 40 g. Each of the four core subsample splits was wrapped separately with sterile aluminum foil and placed in a small beaker, which then was weighed. Each beaker was returned to an anaerobe jar, under nitrogen with a wet towel, and refrigerated. After 6 days, there was no significant weight change (less than 0.01 g) in any of the core subsample splits, which indicated that condensation in the samples was minimal.

The core subsamples were assessed for damage by inspection of each core in a glove box. Each anaerobe jar was introduced to a collapsible glove box that was flushed with 10 volumes of dry nitrogen gas, then kept in a steady stream of 1–2 L/min of dry nitrogen gas. Each core subsample was partially unwrapped, described, recorded, and rewrapped. Less than 25% of the core subsamples appeared fractured or desiccated; these were rejected for core-squeezing experiments.

Determination of Microsphere Concentration

Inspection for microsphere contamination as an indication of contamination with drilling fluids generally followed the procedure described by Chapelle and McMahon (1991). Only unfractured core-subsample segments were examined. A 0.5-cm inside-diameter stainless-steel cork borer was pressed through the aluminum foil into the sediment. A small sediment sample was transferred to the bores, which was then removed. The sediment was extruded onto a cutting-glass surface by applying pressure through the borer annulus with a Teflon tube. As many as three borings penetrating to different depths in the core subsample were made with the cork borer (Table 2).

Forty-nine slides were prepared from these core segments for examination with a Zeiss epi-fluorescent microscope to determine whether the core subsamples were contaminated by the fluorescent microspheres added to the drilling mud. Microspheres were readily visible with “type A” low-fluorescence oil on a standard microsphere slide when viewed at 400× magnification (field-of-view diameter = 285 mm). Initially, slides were viewed by examining 40 fields of view, but subsequently only 20 fields were examined. No microspheres were observed in any of the 49 slides.

A sample of the drilling-mud suspension was allowed to settle for nearly 2 months before a 10-mL subsample was eluted and placed on a microscope slide. In this sample, two microspheres were observed in 30 fields of view (Table 2). The detection of microspheres within the drilling fluid, but not in core material (Table 2), indicates that the samples from unfractured core, which were chosen for pore-water extraction, were not contaminated by the drilling fluid. The composition of the drilling fluid (Sample D-9, Table 4) is dominated by sodium and chloride (360 and 460 mg/L, respectively); pore-water samples are calcium or sodium, and sulfate dominated.

Determination of Sediment Texture and Clay Mineralogy

The presence of sulfide minerals and carbonate shells or minerals was noted after subsamples of core material were examined by hand lens and binocular microscope. Sediment-size fractions were defined by sieve analysis and hydrometry.

Bulk sediment and oriented (<2 mm) sediment samples were examined by X-ray diffraction to determine clay mineralogy. Standard extraction, sample-preparation, glycolation, and X-ray diffraction techniques were used (Carroll, 1970).

Table 2. Summary of microsphere quality-assurance counts, Atlantic City, NJ, borehole.

Depth of cored sediment (ft below land surface)	Number of borings from core subsample	Number of segments viewed	Microsphere count
680	1	3	0
691	3	11	0
704	2	6	0
735	2	5	0
818	1	5	0
821	1	6	0
830	2	9	0
839	1	4	0
Drilling mud (after 2-month settling period)	NA	NA	2

Note: NA = not applicable.

Determination of Chemical Composition and Cation Exchange Capacity

The amount of labile iron in sediment was determined on an acidic aliquot by standard inductively coupled plasma-atomic emission spectroscopy (ICP-AES) after hydrochloric acid (HCl) digestion of the sediment. Twelve samples of sediment and six replicates were selected for analysis of labile iron forms. Two 1-g splits of sediment material were prepared for each of the 18 analyses and placed in acid-rinsed amber vials. A separate (third) split of each sample was used to determine weight loss and dry weight at 110°C for each sample.

For labile iron (II) assay, 5 mL of 0.5-M HCl (Lovley and Phillips, 1987) was added to one of the sample splits in a canula with a flowing oxygen-free, dry nitrogen atmosphere at 25°C. Extraction vials were also flushed with oxygen-free dry nitrogen. After 1 hr, the slurry was vortexed, and two aliquots of ~100 mL each of the supernatant were withdrawn and analyzed for iron. Ferrous ammonium sulfate was the iron (II) standard material and was standardized against National Institute of Science and Technology primary standard grade $K_2Cr_2O_7$.

Concentrations of total iron were determined by the following procedure. First, 5 mL of 0.25-M hydroxylamine HCl in 0.25-M HCl (Lovely and Phillips, 1987) was added to the remaining split sample. After 1 hr, two aliquots of the supernatant were withdrawn, as discussed previously, and the aliquots were analyzed for iron. The concentration of labile iron (III) was determined by difference: labile iron (III) equals labile iron (total) minus labile iron (II).

Reproducibility of the analysis for forms of labile iron was reasonable for most samples. Reproducibility for the remaining duplicates was poor. Except for one sample (from 626 ft [190.8 m]), the reproducibility of the weight loss on drying for duplicate samples also was poor. The weight-loss discrepancies are not large enough, however, to compensate for the differences in labile-iron concentrations between duplicates. Reproducibility of iron concentrations also was poor when analyses were conducted by colorimetry, indicating that poor reproducibility could result from the extreme variability of extraction efficiencies, the range of concentrations of labile iron in the sediment on a very small scale, or both.

Splits of sediment samples were analyzed for total sulfur and the operationally defined forms of sulfur: acid-soluble sulfate, organic sulfur, and sulfide. All sulfur concentrations were determined on evolved sulfur dioxide (SO_2) gas, after combustion of the sample in an oxygen atmosphere at 1370°C, by using infrared-absorption spectrophotometry (IR; Curry, 1990). An initial split sample was thus analyzed for total sulfur content. Two additional splits for each sample were taken. The first split was weighed and leached using 0.1-N (normal) HCl. Again, the leached residue was analyzed by IR for sulfur content. The acid-soluble sulfate content was determined as the difference between the concentration of total sulfur and the concentration of sulfur in the HCl-leached residue. The second split was weighed and sequentially leached with 0.1-N HCl and 0.1-M sodium pyrophosphate to remove both sulfate and organic sulfur, leaving only sulfide in the residue. The sulfide content was determined as the difference between the concentration of total sulfur and the concentration of sulfur in the sequentially leached residue. The organic sulfur content was computed as the difference between the total sulfur content and the sum of the acid-soluble sulfate content and sulfide content.

Elemental sulfur and highly insoluble sulfates, such as those in barite, are included in the sulfide content because they are not leached by either extractant (Papp et al., 1991). The precision of analyses of reference samples is estimated to be 2% for total sulfur, ~9% for acid-soluble sulfate, ~11% for organic sulfur, and ~2% for sulfide sulfur.

The total CEC of the clay and clay-silt samples was determined by A&L Analytic Laboratory, Memphis, Tenn. Exchangeable calcium, magnesium, sodium, and potassium were extracted from sediment samples by using 1-M ammonium acetate buffered at pH 7. Concentrations of the cations were determined by atomic adsorption spectroscopy (Thomas, 1982). The leached concentrations were reported as parts per million exchangeable by ammonium acetate, then normalized to the mass of the sediment in milliequivalents of cation per 100 grams of sediment (meq/100g).

Pore-Water Extraction

Enough core material was gouged from the inner section of core to fill about 110 cm^3 of a titanium mechanical squeezing device (Manheim, 1966). Pressure was applied by using a manual hydraulic jack. The extracted pore water was retrieved by using a 10-mL syringe with a 45-µm cellulose filter. The extracted pore-water sample was placed in screw-cap plastic test tubes under nitrogen gas; the test tubes were placed in anaerobe jars, also under nitrogen, and refrigerated. Extraction pressures, when most fluid was recovered, ranged from ~1000 to 7000 psi, and was allowed to reach a maximum of 9000 psi. Extraction time usually was between 0.5 and 1.0 hr, but occasionally was about 1.5 hr. Extraction procedures ceased when no flow into the tip of the syringe was observed for a period of several minutes. In selected cases, multiple aliquots were collected.

Characterization of Water Chemistry

Pore-water samples for inorganic analysis were diluted at a ratio of 1:1 (5-mL sample of the original aliquot +5-mL Nanopure deionized water) to yield 10 mL of solution, the volume required to complete microanalytic procedures. One milliliter of the solution was used to semiquantitatively measure major-cation concentrations by ICP-AES to estimate the specific conductance of each sample before further analysis. This scanning avoided excessive dilution of the samples before quantitative ICP-AES and ion-chromatography (IC) analysis. The dilution factors for individual analyses are listed in Table 3.

The ICP-AES quantitative analyses were performed by using direct-injection techniques simultaneously for samples and standards to minimize the amount of sample required for analysis (Fishman and Friedman, 1989). Standard Reference Water Samples were analyzed concurrently with the pore-water samples as the internal standards. No additional dilution was required because the calculated conductivity did not exceed 2000 µS/cm. All analytical results were well within acceptable limits outlined by Fishman and Friedman (1989).

IC analyses were conducted first and focused on determining the concentrations of sulfate, bromide, and nitrate. Gravimetrically calibrated pipettes were used for additional dilutions for the IC analysis. An optimum dilution of 200:1 for IC analysis was indicated by the peak heights on chromatograms from a test-run 1000-fold dilution and from two additional test runs with less-diluted samples. The volume of pore water necessary for analysis was less than 2 mL. This sample size nevertheless allowed for normal data-acquisition time by the instrument. Chloride concentrations were measured by using colorimetry with 1 mL of the initial 1:1 dilution sample (Fishman and Friedman, 1989).

Concentrations of sulfate were qualitatively rescreened for gross errors by using a 1:20 dilution and turbidimetric analytical techniques. All values but two obtained by using turbidimetry were within about 25% of the IC-determined values; for those two samples, the IC-determined value appeared to be reasonable.

Table 3. Sample-dilution factors for types of chemical analyses, pore-fluid microsamples.

ICP-AES (for major cations and trace metals)	Carbon analyzer (dissolved inorganic carbon)	Colorimetry (for chloride)	Ion chromatography (for anions except chloride)
2	2	2	200

Note: ICP-AES = inductively coupled plasma-atomic emission spectroscopy.

Sulfur-isotopic ratios were determined by mass spectrometry after dissolved sulfate was coprecipitated as barite ($BaSO_4$) and converted to SO_2 by thermal decomposition (Tuttle et al., 1986). One sample was analyzed in triplicate to assess precision.

Because of the small sample volume required (200 μL) for the determination of dissolved inorganic carbon (DIC), no additional sample preparation was required. Analysis for DIC was completed by direct injection of the small volume of solution into a carbon analyzer.

Quality Assurance for Chemical Analyses

Laboratory quality-assurance procedures for chemical analyses of microvolume samples were intended to evaluate (1) the accuracy of analyses for sulfate and sodium, (2) the amount of sample contamination from the collection process, (3) the variation in pore-water chemistry between adjoining samples of core, and (4) the possibility of gross contamination of pore water with drilling fluid.

Quality assurance for chemical analyses focused on the accuracy of concentrations of sulfate and sodium and was intended to ensure that these constituents were not introduced during the sample-collection process. Sulfate and sodium were especially targeted for quality assurance because results of a study by Pucci et al. (1992) indicated that these two constituents would be the dominant components of pore water. A 100-mg/L sodium sulfate standard (Sample D-6, Table 4) was used to simulate the assumed composition of the dilute pore fluids to examine the accuracy of the analytical techniques used to determine concentrations of these constituents in these microsamples. A 100-mg/L sodium sulfate solution (Sample D-7, Table 4) and deionized water (Sample D-8, Table 4) were flushed through the core-squeezing equipment as process blanks.

Analysis for the sulfate in the sodium sulfate standard (Sample D-6) indicated a positive bias of about 20%, whereas the sulfate concentration in the equipment sulfate wash (Sample D-7) indicated a positive bias of only 2%. The sulfate concentration in the deionized-water equipment wash (Sample D-8) was 7.5 mg/L. The sodium concentration in the sodium sulfate standard (Sample D-6) indicated a positive bias of less than 10%, whereas the sodium concentration in the equipment wash (Sample D-7) was 4% higher than that in the standard solution. The analysis for sodium in the deionized-water equipment wash (Sample D-8) did not yield detectable concentrations of sodium (<0.4 mg/L). These differences indicate that results of analyses for sulfate were positively biased by ~10%–20%, with a minimum of 7.5 mg/L "excess" sulfate. Any sulfate contamination originating from the equipment was smaller in scale than the laboratory bias.

All quality-assurance and pore-water samples were reanalyzed for chloride by using colorimetry because initial IC results for quality-assurance samples indicated the possibility of a far greater positive bias for chloride than for sulfate, especially in the blanks. Colorimetry results indicated that chloride (0.60 mg/L) was the only other major constituent besides sulfate present in the deionized-water equipment blank in concentrations greater than 0.5 mg/L. The chloride concentration in the sodium sulfate–standard solution (Sample D-6; 0.23 mg/L) was lower than that measured in the sulfate standard–solution wash (Sample D-7; 0.92 mg/L) and the deionized-water wash (Sample D-8). These results indicated that the colorimetry technique resulted in a minor positive bias for chloride, and that minor contamination of the samples with chloride could have occurred. If contamination did occur, it added less than 1 mg/L of chloride to the samples.

For silica, DIC, and the remaining major cations except sodium, neither positive bias nor significant contamination (greater than 0.5 mg/L) of the samples by the equipment was noted. For the minor anions bromide, fluoride, nitrate, and phosphate, concentrations greater than the minimum reporting level (MRL) of 2 mg/L were not detected in either equipment-wash sample (although the presence of concentrations less than 2 mg/L cannot be ruled out). For the minor anion boron, contamination by equipment was negligible.

Minor contamination with most metals occurred as samples passed through the core-squeezing equipment. Gross contamination with zinc (>50 μg/L) of both the deionized-water and the sulfate standard occurred as the samples passed through the equipment. Gross contamination of the deionized-water equipment blank with barium (234 μg/L) and molybdenum (51 μg/L) was noted. Minor contamination of the deionized-water equipment blank with lead, iron, strontium, cadmium, and silver and of the sodium sulfate–standard equipment blank with boron and strontium was noted. Some of these contaminant "hits" could be caused by difficulty in separating concentration peaks from background noise during analysis for these metals in the microvolume samples.

The MRLs for aluminum, copper, chromium, nickel, and vanadium ranged from 10 to 20 μg/L. These metals were not present in concentrations greater than the MRLs in either equipment blank; however, these relatively high MRLs indicate that minor contamination may be present but not detectable. The MRLs for cobalt, lithium, and manganese ranged from 2 to 8 μg/L. Concentrations greater than these were not detected in the equipment blanks (Samples D-6 and D-7). Analyses of the equipment blank and the sodium sulfate wash identified the following conditions: lithium, vanadium, and manganese were not detected in equipment blanks, and minor amounts of iron, strontium, and aluminum were present in blanks as random contamination.

The variation in pore-water chemistry between two adjoining core samples was compared to the variation in pore-water chemistry within one of the samples (the core sample from a depth of about 626 ft

Table 4. Results of quality-assurance analyses of equipment blanks, standards, and drilling mud.

Sample number	Specific conductance (μS/cm)	Calcium (mg/L)	Magnesium (mg/L)	Sodium (mg/L)	Silica, as SiO_2 (mg/L)	Sulfate (mg/L)	Chloride (mg/L)	Bromide (mg/L)	Fluoride (mg/L)	Dissolved inorganic carbon (mg/L)	Nitrate + nitrite, as nitrogen (mg/L)	Orthophosphate as phosphorus (mg/L)	Boron (μg/L)	Barium (μg/L)	Iron (μg/L)
D-6*	229	0.18	0.02	49	0.02	119	0.23	<2	<2	0.31	<2	<2	38	18	<6
D-7**	234	0.52	0.17	51	0.20	121	0.92	<2	<2	0.44	<2	<2	39	18	<6
D-8†	2.4	0.18	<0.02	<0.4	0.12	7.5	0.60	<2	<2	0.30	<2	<2	<4	234	6
D-9‡	2000	40	14	360	6.8	210	460	<2	3.3	23	<2	<2	382	30	<6

Sample number	Manganese (μg/L)	Molybdenum (μg/L)	Aluminum (μg/L)	Strontium (μg/L)	Vanadium (μg/L)	Zinc (μg/L)	Lithium (μg/L)	Cadmium (μg/L)	Lead (μg/L)	Copper (μg/L)	Cobalt (μg/L)	Chromium (μg/L)	Nickel (μg/L)	Silver (μg/L)	Beryllium (μg/L)
D-6*	<2	<20	<10	1.8	<12	70	<8	<2	<20	<20	<6	<10	<20	<2	1
D-7**	<2	<20	<10	4.4	<12	125	<8	<2	<20	<20	<6	<10	<20	<2	<1
D-8†	<2	51	<10	5.4	<12	66	<8	2.6	27	<20	<6	<10	<20	2	<1
D-9‡	7	157	<10	769	<12	15	65	<2	29	<20	<6	<10	<20	<2	<1

Notes: μS/cm = microsiemens per centimeter. * = sodium sulfate standard solution with known composition of 100 mg/L SO_4. ** = mechanical core-squeezing equipment wash with sodium sulfate standard solution (100 mg/L SO_4). † = mechanical core-squeezing equipment wash with deionized water. ‡ = drilling fluid from a depth of 950 ft (289.6 m).

[190.8 m]). The analysis results for the two separate pore-water extracts from the single core sample were averaged, and the difference between the individual and average concentration was determined and was divided by the average concentration multiplied by 100, resulting in a percentage difference between an individual concentration and the average value. This value is termed the relative percent difference (RPD). The RPDs for the concentrations of most constituents present in the split samples were about 15% or less; however, the RPD for sulfate concentration was 34%. The RPD for sulfate concentration in the split sample was larger than that previously reported for pore-water split samples from New Jersey Coastal Plain cores (Pucci and Owens, 1989). The large RPD for sulfate concentration could result from natural variability, poor precision of the laboratory analysis, or both.

The RPD for most constituents in pore water from adjacent core samples generally was greater than 15%. This result indicates that concentrations of most pore-water constituents varied more between adjacent core samples than within individual core samples. Only concentrations of silica, aluminum, manganese, and lithium did not differ between adjacent samples than within individual samples.

Although the results of the analysis for sulfate appear to have a strong positive bias compared to the known value of sulfate in the sodium sulfate standard, analytical precision is considered sufficient to determine large differences in concentrations of sulfate in the samples. Because minor random strontium contamination in the deionized-water blank (5.4 µg/L) and the sodium sulfate equipment wash was greater than the concentration of strontium in the standard solution, the precision of the analyses for strontium concentrations could not be determined. However, the results of analyses for strontium were considered acceptable when the strontium concentration determined was much greater than the level of contamination.

Statistical Techniques

Geospatial Statistics

Geostatistical analysis and kriging of the pore-water constituent-concentration data were done to interpolate between measured concentrations of constituents to obtain a continuous concentration distribution with depth by using the computer program GEO-EAS, which was developed by the U.S. Environmental Protection Agency (Englund and Sparks, 1992). The program was used to interpolate the variations in pore-water composition and physical properties of sediment and pore water over the range from 552 to 705 ft (168.2–214.9 m) by using a weighted moving-average method of data contouring. This program was also used to compute the uncertainty of the interpolated values (Clark, 1979) at each depth, which is the kriged standard deviation (KSD).

Krige estimates were computed by using empirical semivariograms, which are plots of spatial covariance among sample measurements as a function of lag distance, or the interval between samples, along the borehole. Semivariograms are a means to describe the spatial covariance (distribution structure) of the data. The "range," or scale of autocorrelation (the point where variance no longer increases with increasing lag distance) represents the scale of variation. The nugget is the degree of variation caused by random noise and is determined at the minimum lag distances. The kriging process requires estimating theoretical semivariograms by trial-and-error fitting of the theoretical semivariogram models to empirical data to produce the most reliable matches between the semivariograms; therefore, the choice of the theoretical semivariogram model is critical. The spatial covariance is represented by the theoretical semivariogram for each constituent and physical property and is used in the numerical interpolation algorithm that relates the theoretical semivariogram to the kriged (interpolated) value. A detailed description of the procedure is beyond the scope of this report (see Journel and Huijbreghts, 1978; Clark, 1979). The GEO-EAS program was used to:

1. transform the data set to a distribution approximating a normal distribution;
2. select optimal lag distances for empirical semivariograms; and
3. iteratively evaluate and optimize the fit of the assigned theoretical semivariogram models, which were different for each pore-water–constituent concentration and sediment physical property.

The fit of the theoretical semivariograms was satisfactory over the small lag distances examined in the empirical semivariograms (lags generally less than 50 ft [15.2 m]). Therefore, the effects of large-scale trends on the kriged values could be, and were, neglected (Clark, 1979).

These statistical analyses were not conducted on pore-water quality data for the composite confining unit, because those samples were separated from samples collected from the lower confining unit by a hydrogeologic discontinuity and a large distance. Because samples from the composite confining unit do not represent variations in a continuously deposited unit of fine-grained sedimentary material (as do samples collected above the thin seam of silt within the Atlantic City 800-ft sand), the data could not be properly interpolated by kriging. Furthermore, geostatistical analysis of textural and mineralogic properties could not be completed because of insufficient data or extremely high variances in the data.

Principal Component Analysis

Principal component analysis was used as a data reduction technique to limit the number of variables that define most of the variation in the pore-water composition and, thus, group the data. All 19 samples were included in the analysis. Logarithmic transformations of all constituent concentrations, except those of silica and chloride, were needed to produce a normal population distribution. The principal-component algorithm included a correlation matrix and standardized variables for the computations. Only principal components that account for significant common variance (eigenvalues greater than 1) are discussed. Furthermore, for simplicity, only those component loadings that have an absolute value greater than 0.3 are reported. Positive components are an indication that the pore-water constituent varies in conjunction with other factors of that component; negative loadings are an indication of an inverse variation of a pore-water constituent with a component loading.

RESULTS

Extracted Pore-Water Volumes

The sediments from the shallow part of the lower confining unit yielded larger volumes of pore water at lower applied pressures than did the sediments from the deep part of the lower confining unit, the interbedded silts in the upper part of the Atlantic City 800-ft sand, the silt seam near the midpoint of the Atlantic City 800-ft sand, or the composite confining unit. The volume of pore water extracted from sediments ranged from 3.0 to 16.7 mL/100 cm^3 of sediment; water yield ranged from 0.04 to 0.44 cm^3/g of sediment (Table 5). Plots of cumulative volume extracted in relation to applied pressure are shown in Figure 4 for the subsamples with the longest extraction times. The subsamples are from selected core samples from 13 depths. Small variations in yield were observed for subsamples from the same depth—for example, Sample 11, depth 681 ft (207.6 m; Table 5). Yields from sediment samples from the composite confining unit ranged from 0.05 to 0.10 cm^3/g; in general, the sediment samples generally yielded less than 0.10 cm^3/g, whereas, the water yield from the silt stringers in the upper part of the Atlantic City 800-ft sand were about 0.10 cm^3/g (Fig. 4; Table 5).

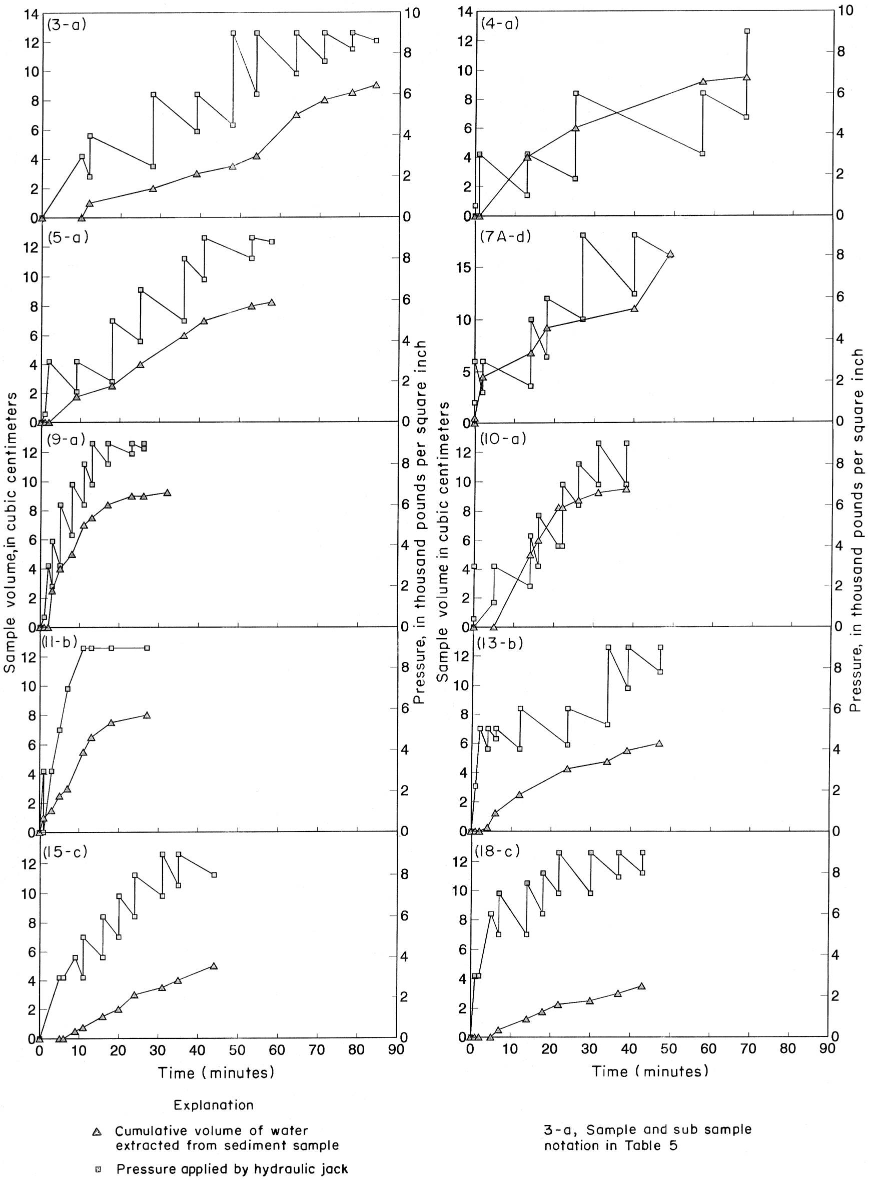


Figure 4. Cumulative volume of extracted pore water from sediments as a function of applied extraction-device pressure and time of extraction, lower Miocene Kirkwood Formation, Atlantic City, NJ.

Sediment Texture and Clay Mineralogy

Sediment Texture

The sediment is primarily silt-sized material (63.4%–77.5%) (Fig. 5A). Clay-sized particles account for 7.4%–17.0% of the sediment, and sand-sized particles account for 9.9%–21.9% (Tables 6, 7; Fig. 5A). The distribution of sand-sized particles varies most between adjoining samples from the shallow part of the lower confining unit (Fig. 5B).

The percentage of silt-sized material varies greatly in a 60-ft section (18.3 m) of the lower confining unit that directly underlies the Rio Grande water-bearing zone. Sample 4, from 585 ft (178.3 m), is 63.4% silt-sized material, whereas Sample 5, from a depth of 606 ft (184.7 m), is 77.2% silt-sized material (Fig. 5A). Such sharp textural differences are present primarily above the depth of 616 ft (187.8 m), in the upper half of the lower confining unit. The abundance of silt-sized material varies little below 616 ft (187.8 m); however, the samples from 651 and 681 ft (198.4 and 207.6 m) are 77.5% and 70.4% silt-sized material, respectively. In the sediment of the composite confining unit and in the thin silt seam within the Atlantic City 800-ft sand, the percentage of silt-sized material ranges from 67.3% to 70.1%.

Results of particle-size analysis also showed that the percentage of sand-sized grains in the 60-ft (18.3-m) section of the lower confining unit that directly underlies the Rio Grande water-bearing zone ranged from 9.7% to 21.9% (Fig. 5B). The amount of sand-sized grains varied inversely with the amount of silt-sized material above the depth of 616 ft (187.0 m; Fig. 5A). The amount of sand-sized material is more uniform: in the lower half of the lower confining unit, it ranges from 12.2% to 15.9%; within the silt seams in the Atlantic City 800-ft sand, it ranges from 14.7% to 16.1%; and in the composite confining unit, it ranges from 14.2% to 15.7%.

Results of particle-size analysis indicated that the sand-sized particles in all the samples consisted mostly of very fine sand (sieve size 0.05–0.1 mm) and comprised from 5.8% to 13.3% of the sediment samples by weight (Table 7). Very coarse, coarse, medium, and fine sand (sieve sizes 1–2 mm, 0.5–1.0 mm, 0.25–0.5 mm, and 0.1–0.25 mm, respectively) account for more than 25% of sand-sized grains in several samples from the depth interval 553–585 ft (168.6–178.3 m); these samples contain the largest percentage of sand-sized material (Fig. 5A).

Below a depth of 585 ft (178.3 m) in the lower confining unit, coarse, medium, and fine sand comprise less than 1% of bulk sediment and generally less than 10% of the total amount of sand-sized

Table 5. Sediment description, weight of squeezed sediment after transport to lab in anaerobic containers, volume of pore-water extraction, and water yield from core samples.

Hydrogeologic unit	Sample number	Subsample designation	Sample depth (ft)	Description of sediment and/or core condition	Extraction time (min)	Weight of sediment subsample (g)	Volume of water extract (cm^3)	Water yield (cm^3/g)
Lower confining unit	1	a	553	Brownish black material; crumbly	42	NA	13.2	NA
	1	b	553		65	NA	15.0	NA
	2	a	562	Dark-brown material; large chunks	34	NA	9.5	NA
	2	b	562		40	NA	14.1	NA
	2	c	562		34	NA	9.5	NA
	3	a	575	Dark-brown silt-like material; crumbly	83	38.9	8.5	0.22
	3	b	575		46	54.0	8.5	0.16
	3	c	575		48	48.2	9.0	0.19
	4	a	585	Dark green-brown silty sediment; large chunks	67	NA	9.5	NA
	4	b	585		40	NA	14.7	NA
	4	c	585		49	51.3	16.2	0.32
	5	a	606	Moist silty green-brown material	58	36.0	8.3	0.23
	5	b	606		40	NA	8.0	NA
	6	a	616	Crumbly dark-brown clayey silt; few fractures	29	NA	8.3	NA
	6	b	616			NA	6.5	NA
	7A	a	619	Dark-brown silty material; slightly moist; intact	56	NA	13.8	NA
	7A	b	619		83	NA	12.5	NA
	7A	c	619		38	40.3	11.0	0.27
	7A	d	619		49	44.7	16.2	0.36
	7A	e	619		21	41.3	13.4	0.32
	7B	a	626	Dark-brown silty material; slightly moist; intact	40	NA	11.7	NA
	7B	b	626		47	NA	9.5	NA
	7B	c	626		76	NA	11.7	NA
	7B	d	626		62	49.8	16.0	0.32
	7B	e	626		53	47.9	11.5	0.24
	7B	f	626		88	38.0	16.7	0.44
	7B	g	626		62	33.7	10.3	0.30
	8	a	637	Dark-brown silt material; fractured	39	NA	14.2	NA
	9	a	643	Dark-brown materials with many broken shells; crumbly	32	48	9.0	0.19
	10	a	651	Brownish green, silty material; stiff, brittle	39	51.1	9.5	0.19
	11	a	681	Brownish black and micaceous silt; consists of many pieces of sediment collected together	36	72.9	3.0	0.04
	11	b	681		27	70.1	8.0	0.11
Upper sand of Atlantic City 800-ft sand	12	a	691	Dark-brown micaceous clay-silt material; competent	56	NA	5.5	NA
	12	b	691		30	NA	6.0	NA
	13	a	705	Brownish silt material; crumbly	36	53.5	6.8	0.13
	13	b	705		48	58.7	6.0	0.10
Thin silt seam in Atlantic City 800-ft sand	14	a	736	Dark-brown clayey silt; competent, few fractures	74	NA	3.6	NA
	14	b	736		60	NA	3.2	NA
	14	c	736		56	NA	3.6	NA
Composite confining unit	15	a	819	Competent, dark-brown material, plastic	40	49.4	5.0	0.10
	15	b	819		26	60.2	3.0	0.05
	15	c	819		43	62.0	5.0	0.08
	16	a	822	Competent, dark-brown clay-like material	59	NA	7.0	NA
	16	b	822		35	NA	3.2	NA
	16	c	822		9	39.7	3.1	0.08
	17	a	831	Dark-brown, silty clay, micaceous; competent	44	NA	9.5	NA
	18	a	840	Dark greenish brown clayey silt; few fractures, competent	30	42.6	3.8	0.09
	18	b	840		46	69.1	3.5	0.05
	18	c	840		43	54.9	3.5	0.06

Notes: ft = feet below surface. NA = not available.

material, and very coarse sand does not exceed 2.5% of the bulk sediment (Table 7). Grain sizes in the sand-sized fraction below 606 ft (178.3 m) in the lower confining unit are nearly uniform and are dominated by very fine sand (9.3%–13.2%) with minor amounts of very coarse sand (1.5%–1.8%; Fig. 5B). The range in the percentage of sand-sized material in the composite confining unit is small compared to that in the lower confining unit above 619 ft (188.7 m).

The range of percentages of clay-sized material present throughout the lower confining unit, from a depth of 553–637 ft (168.6–194.2 m), is minor but notable. Adjoining samples from the base of the lower confining unit (Samples 9 and 10, from 643 and 651 ft [196.0 and 198.4 m], respectively) differ significantly in their percentages of clay-sized material. A hiatus (unconformity) at 666 ft reflects a slight change in the relative position of the shoreline with respect to the Atlantic City area at the time of sediment deposition, resulting in a slightly different sediment texture below this depth. The silt in the upper part of the Atlantic City 800-ft sand is slightly sandier but otherwise texturally more homogeneous than that at the base of the overlying lower confining unit. The percentage of clay-sized material in the composite confining unit is also relatively constant, ranging from 15.6% to 17.0%; this percentage, however, is higher than that for the lower confining unit (Fig. 5A).

Clay Mineralogy

The exchangeable clays (I/S) are typically the most abundant clay minerals in the lower confining unit, in many samples comprising 50% or more of the clay fraction (Fig. 6; Table 7). Their abundance

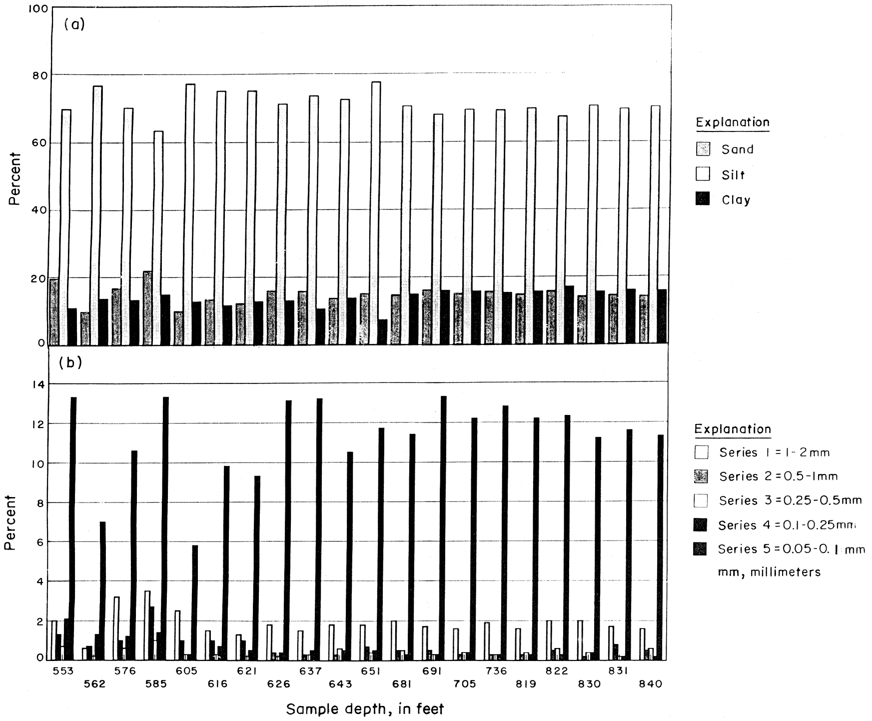


Figure 5. Variation of (**A**) sediment texture and (**B**) sand-size particle distribution with depth in sediment samples from the lower Miocene Kirkwood Formation, Atlantic City, NJ.

Table 6. Descriptive statistics for selected pore-water constituents, sediment chemistry constituents, clay mineralogy and sediment texture, and water yield, lower Miocene Kirkwood Formation, Atlantic City, NJ.

Constituents	Number of samples	Minimum	25th percentile	Median	75th percentile	Maximum	Mean	SD
Selected pore-water constituents								
Calcium (mg/L)	19	5.8	31.6	37.8	149.8	256.8	43.1	73.3
Magnesium (mg/L)	19	1.2	6.22	8.5	25.8	43.8	28.7	12.3
Sodium (mg/L)	19	30.3	41.8	56.7	95.6	279.6	55.0	62.6
Sulfate (mg/L)	19	56.7	83.6	161.4	480.4	894.3	286.8	246.4
Chlorine (mg/L)	19	20.2	47.4	66.8	73.1	99.7	59.5	20.1
Dissolved inorganic carbon (mg/L)	19	4.2	8.6	13.0	18.0	27.0	11.0	6.7
Nitrate (mg/L)	19	<2.0	<2.0	<2.0	2.7	3.4	—	—
Phosphate (mg/L)	19	<2.0	<2.0	<2.0	<2.0	<2.0	—	—
Fluorine (mg/L)	19	<2.0	<2.0	<2.0	<2.0	3.3	—	—
Bromine (mg/L)	19	<2.0	<2.0	<2.0	<2.0	<2.0	—	—
Boron (μg/L)	19	162.0	310.0	459.0	1436.0	2320.0	467.0	681.0
Strontium (μg/L)	19	46.0	281.0	430.0	1407	2466.0	759.0	691.0
Lithium (μg/L)	19	15.8	22.2	31.6	42.8	80.3	34.1	15.2
Iron (μg/L)	19	<6.0	<6.0	<6.0	6.2	19.6	—	—
Manganese (μg/L)	19	<2.0	2.4	3.8	15.9	67.4	8.8	—
Aluminum (μg/L)	19	<10.0	<10.0	<10.0	19.5	27.6	—	—
Vanadium (μg/L)	19	<12.0	<12.0	<12.0	23.5	143.8	—	—
Silica (mg/L)	19	9.7	24.3	50.5	67.5	79.3	57.3	24.0
Sediment chemistry								
Cation exchange capacity (meq/100g)	19	10.6	13.7	17.1	22.8	25.0	18.7	5.1
Exchangeable Calcium (ppM)	19	2220	2890	4630	5370	5980	4410	126
Exchangeable Magnesium (ppM)	19	246.0	350.0	443.0	502.0	718.0	471	113.4
Exchangeable Potassium (ppM)	19	146.0	193.0	300.0	344.0	382.0	286	77.4
Exchangeable sodium (ppM)	19	74.0	120.0	154.0	233.0	479.0	216	110.3
Iron, total extractable (μm/g)	12	9.9	18.5	19.7	25.2	36.3	21.9	6.7
Iron (+2) extractable (μm/g)	12	8.7	12.4	14.5	16.0	19.2	14.3	3.0
Iron (+3) extractable (μm/g)	12	1.2	3.7	6.0	11.1	18.0	7.6	5.1
Total sulfur (mg/100g)	12	9.3	20.3	23.1	25.6	34.5	22.5	6.1
Sulfate (mg/100g)	12	1.0	2.8	3.4	4.4	6.0	3.5	1.4
Sulfide (mg/100g)	12	6.5	10.9	14.7	16.1	23.2	14.1	4.3
Organic sulfur (mg/100g)	12	1.8	3.4	4.9	6.4	8.2	5.0	2.0
Clay mineralogy and sediment properties								
Percent clay in sediment	19	7.4	12.80	13.80	15.60	17.00	13.7	2.36
Illite/smectite in clay (%)	19	29.40	39.80	51.00	39.80	85.30	53.3	14.32
Illite in clay (%)	19	10.50	18.70	22.70	31.40	43.20	25.6	8.38
Potassium in clay (%)	19	4.20	17.00	19.60	33.90	40.50	22.5	10.27
Water yield (cm^3/g)	12	.07	.08	.19	.24	.33	.16	.09

Notes: SD = standard deviation. mg/L = milligrams per liter; μg/L = micrograms per liter; mg/100 g = milligrams of dissolved constituent per 100 g of sediment; mg/g = milligrams per grams of sample; μg/g = micrograms per gram; meq/100g = milliequivalents per 100 g of sediment. Sediment chemistry constituents = total labile iron, labile Fe (II), labile Fe (III), exchangeable calcium, magnesium, sodium, and potassium, total cation exchange capacity, and for total sulfur, sulfate, sulfide, and organic sulfur.

Table 7. Texture of sediment and mineralogical composition of clays, lower Miocene Kirkwood Formation, Atlantic City borehole, Atlantic City, NJ.

		Grain size (%)			Sand grain-size distribution (%)					Clay mineralogy (%)		
Sample number	Sample depth (ft below land surface)	Clay	Silt	Sand, total	Very coarse sand	Coarse sand	Medium sand	Fine sand	Very fine sand	Illite/smectite	Illite	Kaolinite
Lower confining unit												
1	553	10.8	69.7	19.5	2.0	1.3	0.7	2.1	13.3	73	15	12
2	562	13.6	76.7	9.7	0.6	0.7	0.2	1.3	7.0	49	31	20
3	575	13.2	70.2	16.6	3.2	1.0	0.6	1.2	10.6	60	23	17
4	585	14.8	63.4	21.9	3.5	2.7	1.0	1.4	13.3	56	21	22
5	606	12.8	77.2	9.9	2.5	1.0	0.3	0.3	5.8	58	22	20
6	616	11.7	75.0	13.3	1.5	1.0	0.3	0.7	9.8	40	43	17
7-A	619	12.8	75.0	12.2	1.3	1.0	0.2	0.5	9.3	51	33	16
7-B	626	13.0	71.1	15.9	1.8	0.4	0.2	0.4	13.1	49	30	20
8	637	10.6	73.5	15.8	1.5	0.3	0.3	0.5	13.2	39	22	39
9	643	13.8	72.4	13.7	1.8	0.3	0.6	0.5	10.5	46	40	14
10	651	7.4	77.5	15.1	1.8	0.7	0.4	0.5	11.7	85	10	4
Silt stringers, upper part of the Atlantic City 800-ft sand												
11	681	14.9	70.4	14.7	2.0	0.5	0.5	0.3	11.4	64	18	18
12	691	16.0	67.9	16.1	1.7	0.5	0.3	0.3	13.3	60	23	17
13	705	15.7	69.3	15.0	1.6	0.3	0.4	0.4	12.2	64	18	19
14	736	15.3	69.1	15.6	1.9	0.3	0.3	0.3	12.8	57	19	24
Composite confining unit												
15	819	15.6	69.7	14.8	1.6	0.3	0.4	0.3	12.2	29	32	39
16	822	17.0	67.3	15.7	2.0	0.5	0.6	0.3	12.3	44	22	34
17	831	16.0	69.5	14.5	1.7	0.8	0.2	0.2	11.6	35	29	36
18	840	15.7	70.1	14.2	1.6	0.5	0.6	0.2	11.3	32	27	40

Note: Percentages do not always sum to 100% as a result of rounding.

varies inversely with the amount of kaolinite or illite (Fig. 6A). Illite generally is present in moderate amounts (10%–43%), whereas kaolinite is present in low to moderate amounts (4%–39%). Illite in general comprises less than 40% of the clay throughout all the sampled units, with the highest percentages in the lower confining unit. This distribution of clay minerals is typical of the "southern facies" of clay-mineral distribution on the continental margin of the eastern United States described by Hathaway (1972). Kaolinite is present in the largest percentages in the samples from the composite confining unit, where it comprises from 34% to 40% of the clay-mineral fraction. In the composite confining unit, the amounts of kaolinite, illite, and I/S mixed-layer clays are nearly equal, and the overall clay-mineral composition varies only slightly (Table 7).

The percentage of clay minerals, especially of the I/S mixed-layer clays, varies most in the lower confining unit, where the abundance of I/S ranges from 39% to 85% of the clay-mineral fraction. Clay-mineral composition in the lower confining unit, especially the percentage of I/S, can vary significantly in a short vertical distance, as in Samples 1 and 2 (from 553 and 562 ft [168.6 and 171.3 m], respectively) and Samples 9 and 10 (from 643 and 651 ft [196 and 198.4 m], respectively). In the composite confining unit, variation is less but can still occur, as in Samples 15 and 16 (from 819 and 822 ft [249.6 and 250.5 m], respectively; Table 7).

Water yield from the lower confining unit is greater than that from the composite confining unit, whereas the percentage of clay-sized particles in the lower confining unit is smaller than that in the composite confining unit. Water yield from the lower confining unit does not correlate with the percentage of individual clay minerals.

Sediment Composition and Cation Exchange Capacity

Sediment Composition

Percentage of Organic Carbon

The sediment in the core is brown (Table 5) as a result of the high organic-carbon content, which ranges from 1.29% to 2.89% of the sediment by weight (Table 8). The organic-carbon content in adjacent samples varies greatly (Table 8); no consistent trend with depth was apparent. Sediments adjacent to sandy units are less carbonaceous than sediments farthest from sandy units. Sediments farthest from the sands generally contain about 1.6% organic carbon. The most carbonaceous sediments are in the depth interval from 575 to 616 ft (175.3–187.8 m), near the top of the lower confining unit but somewhat below the Rio Grande water-bearing zone. Organic-carbon content exceeds 1.6% in three of four samples at this depth. In contrast, organic-carbon content is 1.48% and 1.38% in samples collected immediately below the Rio Grande water-bearing zone at 553 ft (168.6 m) and 562 ft (171.3 m), respectively. Organic-carbon content is 1.29% in the Atlantic City 800-ft sand at 705 ft and 1.33% in samples from the top of the composite confining unit immediately below the Atlantic City 800-ft sand at 819 and 822 ft (249.6 and 250.5 m). Leythaeuser et al. (1988) documented the presence of many organic compounds in deep interbedded clay/sand units. They found that the presence of organic-carbon compounds increased with distance from contacts between coarse- and fine-grained sediments.

The organic-carbon content generally is highest in sediments with the greatest percentage of silt-sized material. For example, the sample from a depth of 606 ft (184.7 m), which contains 2.89% organic carbon, consists of 77% silt-sized grains. Because of their high organic content, the confining-unit sediments are expected to be sulfur-rich.

Forms of Sulfur

Sulfur is abundant in the sediment samples. The total-sulfur content in the lower confining unit ranges from 0.93% to 2.53% of the sediment by weight (Table 8). Differences in sulfur content between adjacent samples range from small (especially at depths from 606 to 619 ft [184.7–188.7 m], about 0.1% or less) to large (especially at the depths 651–681 ft (198.4–207.6 m), about 1.6%; Fig. 7A). Total-sulfur content was greatest (3.45%) in the silt seam near the middle of the Atlantic City 800-ft sand. With the exception of Sample 10 from the base of the lower confining unit, total sulfur in sediment was lowest in the shallowest samples, which contained the highest concentrations of dissolved sulfate.

The dominant form of sulfur in the core is sulfide (Fig. 7G; Table 8). The sulfide content of sediment samples from the composite confining unit is greater than that of samples from the lower confining unit; the percentage of sulfide by weight is greater in two of the three samples from the composite confining unit (Samples 15 and 16, maximum = 1.76%) than in any of the samples from the lower confining

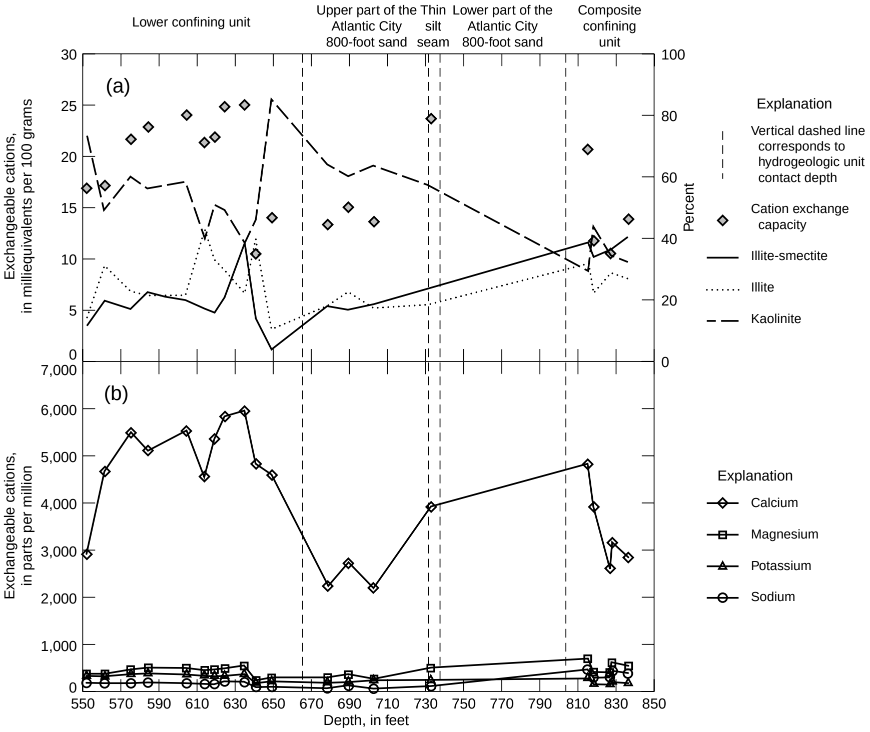


Figure 6. Relation of (**A**) cation exchange capacity and clay-mineral abundance, and (**B**) exchangeable calcium, magnesium, sodium, and potassium to depth in sediment samples from the lower Miocene Kirkwood Formation, Atlantic City, NJ.

Table 8. Concentrations of forms of sulfur and labile iron and organic carbon in sediment form lower Miocene Kirkwood Formation, Leg 150X Atlantic City borehole, Atlantic City, NJ.

Sample number	Sample depth (ft below land surface)	Form of sulfur (%)				Form of labile iron (μmol/g)			Organic carbon(%)
		Sulfur, total	Sulfate, acid soluble	Sulfide	Organic sulfur	Labile iron, total	Labile iron (II)	Labile iron (III)	
Lower confining unit									
1	553	1.99	0.46	1.06	0.47	21.5	10.3	11.2	1.48
2	562	1.63	0.33	1.08	0.22	18.4 (14.9)	12.2 (12.0)	6.2 (2.9)	1.38
3	575	—	—	—	—	—	—	—	1.81
4	585	—	—	—	—	—	—	—	1.33
5	606	2.27	0.19	1.59	0.49	20.0 (19.4)	15.0 (15.7)	4.4 (4.3)	2.89
6	616	2.16	0.60	1.13	0.43	29.4	16.1	13.3	1.61
7-A	619	2.17	0.36	1.50	0.31	—	—	—	1.44
7-B	626	—	—	—	—	24.4 (26.0)	13.7 (14.3)	10.7 (11.7)	1.53
8	637	2.57	0.34	1.57	0.66	25.5	19.2	6.3	1.62
9	643	—	—	—	—	—	—	—	1.38
10	651	0.93	0.10	0.65	0.18	9.9	8.7	1.2	1.58
Silt stringers, upper part of the Atlantic City 800-ft sand									
11	681	2.53	0.54	1.21	0.78	36.3	18.3	18.0	1.53
12	691	—	—	—	—	—	—	—	1.48
13	705	—	—	—	—	—	—	—	1.29
14	736	3.45	0.31	2.32	0.82	18.6 (19.5)	12.8 (13)	5.8 (6.5)	1.64
Composite confining unit									
15	819	2.61	0.36	1.76	0.49	19.3 (13.0)	14.1 (10.8)	5.2 (2.2)	1.33
16	822	2.40	0.27	1.61	0.52	18.8 (18.2)	15.3 (15)	3.5 (3.2)	1.33
17	831	—	—	—	—	—	—	—	1.62
18	840	2.35	0.32	1.44	0.59	16.3 (21.4)	14.9 (18.0)	1.4 (3.4)	1.58

Note: Values in parentheses are results of duplicate analysis.

unit (maximum = 1.59%; Fig. 7A; Table 8). Sulfide content is greatest (2.32%) in the silt bed near the middle of the Atlantic City 800-ft sand. Sulfide content was not related to sediment texture.

Acid-soluble sulfate and organic sulfur account for less than one-third of the total sulfur in all the samples (Fig. 7A). Sulfate is more abundant in the lower confining unit than in the composite confining unit and is most abundant in the upper half of the lower confining unit from 552 to 619 ft (168.2–188.7 m). No sample collected below 619 ft (188.7 m) contained more sulfate than organic sulfur.

Organic sulfur was more abundant than acid-soluble sulfate in nine of the 12 sediment samples analyzed (Table 8). The amount of organic sulfur was greatest in the thin silt seam near the midpoint of the Atlantic City 800-ft sand (0.82%; Table 8; Sample 14). Organic-sulfur content was relatively uniform with depth in the composite confining unit but varied greatly with depth in the lower confining unit.

Forms of Labile Iron

Iron (II) was more prevalent than iron (III). Iron (II) was the predominant form of labile iron in 11 of the 12 sediment samples; the exception was the sample from a depth of 551 ft (167.9 m; Fig. 7B). In samples from the lower confining unit, concentrations of total labile iron ranged from 9.9 to 36.3 μmol/g; the smallest and largest concentrations were present in adjacent Samples 10 and 11 from depths of 651 and 681 ft (198.4 and 207.6 m), respectively, at the base of the unit. Minimal differences in total labile iron content were noted among samples from the middle part of the lower confining unit, and among samples from the composite confining unit.

The ranges in total labile iron content and labile iron (II) content, in general, are greater in the lower confining unit than in the composite confining unit, but the ranges overlap. Sediment samples from the lower confining unit, with the highest content of total labile iron, also contained significant amounts of labile iron (III; Fig. 7B). Concentrations of labile iron (III) were lower in the composite confining unit (range = 1.4–5.2 µmol/g) than in the lower confining unit (range = 1.2–13.3 µmol/g, with all but two values greater than 5 µmol/g). In both confining units, concentrations of labile iron (II) were greater than concentrations of labile iron (III); the concentration ranges overlap in the lower confining unit, but not in the composite confining unit.

The distributions of reduced sulfur (sulfide), oxidized sulfur (sulfate), and total sulfur were similar to the distributions of labile iron (II), iron (III), and total extractable iron, respectively (Fig. 7). In general, for both sulfur and labile iron, reduced forms were more dominant in the composite confining unit than in the lower confining unit, and concentrations of the reduced forms increased with depth in the lower confining unit.

Cation Exchange Capacity

The CEC in the samples ranges from 10.6 to 25.0 meq/100 g of sediment (Fig. 6A; Table 9). Samples from the upper three-fourths of the lower confining unit (553–637 ft [168.6–194.2 m]) tend to have higher CEC values than samples from the deepest part of the lower confining unit, the composite confining unit, or the thin silt seams within the Atlantic City 800-ft sand. The samples with the highest percentage of I/S have the lowest CECs (Fig. 6A).

Concentrations of exchangeable calcium, magnesium, sodium, and potassium as a function of depth are plotted in Figure 6B, and concentrations are reported in Table 9. These show that divalent calcium and, to a much smaller extent, magnesium are the predominant exchangeable cations, followed by monovalent potassium and sodium. More sodium, magnesium, and, to a lesser extent, potassium, in

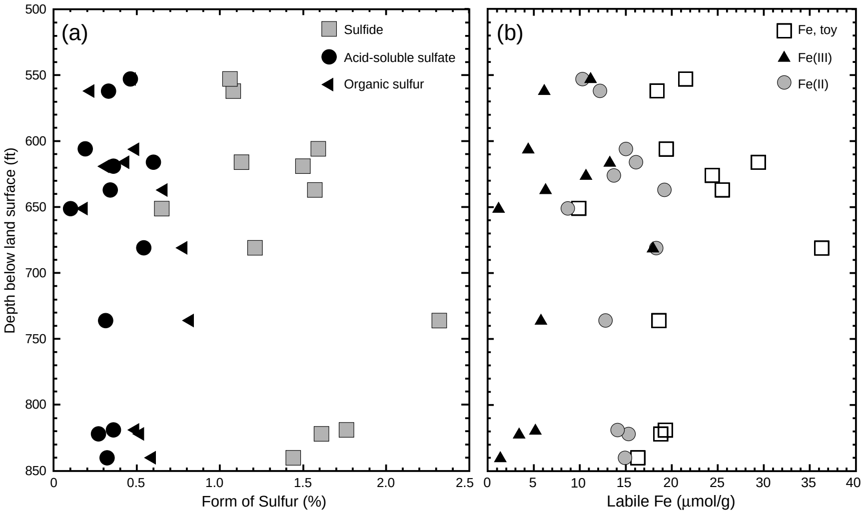


Figure 7. Variations in concentrations with depth of (**A**) forms of sulfur and (**B**) forms of labile iron, lower Miocene Kirkwood Formation, Atlantic City, NJ.

Table 9. Cation-exchange capacity and exchangeable-cation concentration in sediment from the lower Miocene Kirkwood Formation, Atlantic City borehole, Atlantic City, NJ.

Sample number	Sample depth (ft below land surface)	Cation exchange capacity (meq/100 g)	Exchangeable cations (ppm)			
			Calcium	Magnesium	Potassium	Sodium
Lower confining unit						
1	553	16.9	2920	363	310	154
2	562	17.1	4660	350	300	148
3	575	21.6	5510	452	349	146
4	585	22.8	5120	495	380	171
5	606	24.0	5550	502	365	171
6	616	21.3	4560	443	323	150
7A	619	21.8	5370	466	328	161
7B	626	24.8	5860	491	344	233
8	637	25.0	5980	550	382	185
9	643	10.6	4850	246	169	96
10	651	14.1	4630	309	231	108
Silt stringers, upper part of the Atlantic City 800-ft sand						
11	681	13.4	2270	311	179	74
12	691	15.1	2770	385	209	146
13	705	13.7	2220	295	249	74
14	736	23.7	3960	526	280	120
Composite confining unit						
15	819	20.7	4850	718	302	479
16	822	11.8	3960	430	182	306
17	831	16.7	3190	637	209	455
18	840	13.9	2890	561	193	407

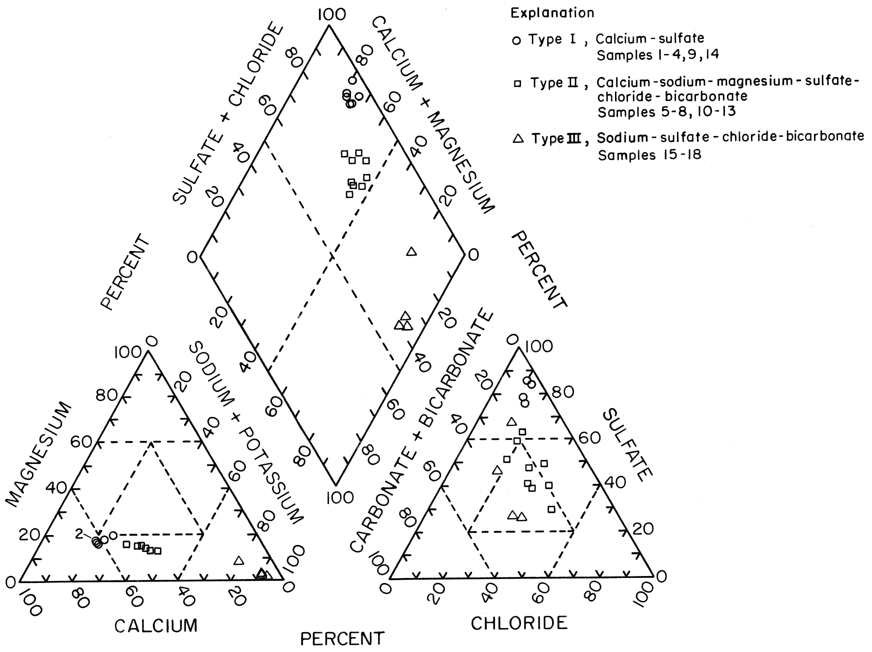


Figure 8. Trilinear plot of pore-water chemistry, lower Miocene Kirkwood Formation, Atlantic City, NJ.

both relative and absolute concentration terms, are available for exchange in the composite confining unit than in the lower confining unit.

Pore-Water Chemistry

The 19 pore-water samples represented three distinct water-quality types, as determined from trilinear diagrams (Fig. 8). Two dominant water types are present in the lower confining unit and the upper part of the Atlantic City 800-ft sand area. The four samples from the shallowest part of the lower confining unit (553–585 ft [168.6–178.3 m]) are a calcium-sulfate–type water (Type I, Fig. 8). This type of water also is found in a deeper sample from the same unit (651 ft [198.4 m]) and in the sample from the thin silt seam near the midpoint of the Atlantic City 800-ft sand (Sample 14, 736 ft [224 m]). The basal part of the lower confining unit and the silt interbeds in the upper part of the Atlantic City 800-ft sand (605–705 ft [184.4–214.9 m]) contain a mixed calcium-sodium-magnesium-sulfate-chloride-bicarbonate–type water (Type II, Fig. 8). A sodium-sulfate-chloride-bicarbonate–type water (Type III, Fig. 8) is dominant in the composite confining unit. No correlation between lithology and water type was discernible.

Calcium is the dominant cation, and sulfate is the dominant anion in all four samples from the shallowest part of the lower confining unit, in the outlier sample from 651 ft (198.4 m), and in the sample from the thin silt seam near the midpoint of the Atlantic City 800-ft sand at 736 ft (224 m). Either calcium or sodium was the dominant cation in the remaining samples from the lower confining unit and the upper part of the Atlantic City 800-ft sand; the anions were of a mixed type. Sodium is the dominant cation in all pore-water samples from the composite confining unit. Chloride is the dominant anion in the two pore-water samples from the deep part of the composite confining unit (831 and 840 ft [253.3 and 256.0 m]). Carbonate is the dominant anion in one sample from this unit (819 ft [248.6 m]); the sample from 822 ft (250.5 m) is a mixed-anion type.

Because the three water-quality types generally are found at distinct depth intervals, they are an indication of the scale of variation of hydrogeochemical facies within the confining units (tens of feet). Smaller scale variations in chemical facies are present, however. For example, the samples from 651 and 736 ft (198.4 and 224 m) collected from the lower confining unit and from silt within the Atlantic City 800-ft sand, respectively (Fig. 8; Table 10), are both Type I facies, whereas water in adjoining samples was Type II. In the composite confining unit, the distribution of the chemical facies, as indicated by the dominant anion, varies greatly on a scale of 10 ft or less.

Distributions of Cations and Silica with Depth

Concentrations of the major cations in all the pore-water samples range as follows: calcium = 5.8–257 mg/L; magnesium = 1.2–44 mg/L; and sodium = 30–280 mg/L (Table 10). The generalized trends in concentrations with depth of all the major cations are similar, especially in samples from 553 to 705 ft (167.9–214.9 m; Fig. 9).

Concentrations of dissolved iron were less than the MRL of 6 µg/L in eight of 12 pore-water samples from the lower confining unit and in two of four pore-water samples from the composite confining unit. The maximum concentration of dissolved iron was 20 µg/L, in the sample from 651 ft (198.4 m). The sediment from which this pore-water sample was collected contained the lowest concentration of labile iron. The ratios of labile iron (III) to labile iron (II) and acid-soluble sedimentary sulfate to sedimentary sulfide were low in this sample, indicating a strongly reducing environment in which iron could be soluble. Concentrations of manganese ranged as follows: <2–39 µg/L for samples from the lower confining unit, 4–67 µg/L for samples from the silt seams in the upper part of the Atlantic City 800-ft sand, and <2–8 µg/L for samples from the composite confining unit. The concentration of manganese was highest in the sample from 736 ft (224.3 m), in the thin silt seam within the Atlantic City 800-ft sand. On the basis of the low ratio of labile iron (III) to labile iron (II) in the sediment, this sample also appears to be from a reducing environment. Other samples that could be from reducing environments did not contain high concentrations of manganese, however.

Concentrations of manganese in pore water were consistently highest (16–39 µg/L) in the sulfate-rich, pore-water samples from 553 to 585 ft (168.2–178.3 m) in the lower confining unit. Although some of the other pore-water samples—for example, those from 616 and 643 ft (187.8 and 196.0 m)—also contained high concentrations of sulfate, they generally contained minimal concentrations of manganese.

No strong trend in concentrations of dissolved iron and manganese with depth or relative to the concentration of other dissolved constituents was noted (Fig. 9). Concentrations of dissolved manga-

Table 10. Chemical compositions of pore water from clay-silt, lower Miocene Formation, Atlantic City borehole, Atlantic City, NJ.

Sample number	Sample depth (ft below land surface)	pH	Specific conductance (µS/cm)	Calcium (mg/L)	Magnesium (mg/L)	Sodium (mg/L)	Silica, as SiO_2 (mg/L)	Sulfate (mg/L)	Chloride (mg/L)	Dissolved inorganic carbon (mg/L)	Sample number	Boron (µg/L)	Strontium (µg/L)
Lower confining unit													
1	553	7.8	2210	257	44	96	49	894	100	7.8	1	592	2470
2	562	8.0	1710	200	33	77	60	636	72	14	2	459	1870
3	575	8.3	1340	160	26	64	56	480	56	11	3	594	1410
4	585	8.3	1400	150	28	72	51	484	69	13	4	522	1530
5	606	8.0	470	37	7.1	48	69	96	74	9.9	5	421	360
6	616	7.7	770	78	15	57	68	175	81	18	6	599	740
7-A1	619	8.2	440	32	6.4	42	79	57	68	9.4	7-A1	330	310
7-B1	626	8.2	550	44	8.5	50	78	92	62	13	7-B1	377	430
7-B2	626	8.2	—	55	10	51	71	155	62	11	7-B2	470	530
8	637	8.2	430	35	6.7	37	79	72	43	10	8	359	320
9	643	8.6	1500	163	30	80	55	555	67	13	9	1440	1580
10	651	8.6	620	57	11	51	62	195	47	14	10	310	540
Silt stringers, the upper part of the Atlantic City 800-ft sand													
11	681	7.7	380	33	6.8	31	33	115	26	6.7	11	165	320
12	691	8.1	410	32	6.2	36	30	93	48	6.1	12	162	280
13	705	8.2	320	26	4.9	30	34	72	20	8.6	13	205	240
14	736	7.7	1000	99	22	55	24	395	34	4.2	14	309	940
Composite confining unit													
15	819	8.7	860	11	3.1	175	15	161	48	25	15	1610	120
16	822	8.6	1630	38	16	280	13	470	69	27	16	1950	640
17	831	8.8	720	8.6	3.0	147	9.7	84	78	25	17	1790	120
18	840	8.5	660	5.8	1.2	134	13	69	73	20	18	2320	46

Notes: µS/cm = microsiemens per centimeter. Values in parentheses are results of duplicate analyses.

nese were somewhat higher and had a wider range than concentrations of dissolved iron. This difference indicates that the pore-water concentrations of these redox-sensitive elements may be controlled by different geochemical reactions: the range of the oxidation-reduction potential of the confining units is such that manganese reduction (solubilization) can occur rapidly or completely or both, but iron reduction is slow. Alternatively, if the environment is strongly reducing, dissolved iron could be removed from solution by sulfide, forming iron-sulfide mineral phases.

Concentrations of strontium ranged from 46 to 2470 µg/L, and correlated directly with concentrations of chemically similar calcium (Fig. 9). In the pore-water sample from 822 ft (250.5 m) in the composite confining unit, the strontium concentration (640 µg/L) was substantially greater than the concentration that was expected from the interpreted corresponding calcium concentration (38 mg/L), if linear covariation of the concentrations (not shown) is assumed. Lithium concentrations in pore-water samples ranged from 16 to 80 µg/L (Table 10; median for 19 samples = 31.7 µg/L), with a relatively smooth decrease in concentration with depth similar to that observed for the major cations. Pore-water samples from 606, 643, and 822 ft (184.7, 196.0, and 250.5 m), however, contained higher concentrations of lithium than the adjacent samples (Fig. 9). The samples from 643 and 822 ft (196.0 and 250.5 m) also contained higher sodium concentrations than the adjacent pore-water samples.

Concentrations of silica increased in pore water from the lower confining unit from 49 mg/L at 553 ft (168.2 m) to a maximum value of about 79 mg/L at 637 ft (194.2 m). Concentrations of silica in the lower confining unit were greatest in the samples from 606 to 637 ft (184.7–194.2 m), where dissolved-sulfate concentrations tended to be relatively low (Fig. 9). The concentration of silica in the lower confining unit was lowest in pore-water samples from areas adjacent to the Rio Grande water-bearing zone and the Atlantic City 800-ft sand. Silica concentrations in the composite confining unit were low (9.7–15 mg/L; Table 10). The maximum silica concentration in the lower confining unit was about 5.5 times the maximum silica concentration in the composite confining unit (Table 10).

Distributions of Anions with Depth

Concentrations of sulfate in pore-water samples from the lower confining unit, like concentrations of sodium, calcium, and magnesium, decreased smoothly with depth. Of the major anions, sulfate concentrations varied most, from 57 to 894 mg/L—nearly a 16-fold difference between the highest and lowest concentrations. Concentrations of sulfate in the four shallowest pore-water samples from the lower confining unit, from 553 to 585 ft (168.6–178.3 m), were consistently greater than 450 mg/L. In contrast, sulfate concentrations in samples from the middle and lower parts of the lower confining unit were significantly lower than 200 mg/L, except those in two samples from depths of 643 ft (196.0 m; 555 mg/L) and 651 ft (198.4 m; 195 mg/L). Sulfate concentrations decreased consistently with depth in samples from 651 to 705 ft (198.4–214.9 m) in the upper sand unit of the Atlantic City 800-ft sand; the trend of decreasing sulfate concentrations with depth was smoothest in this section of core. The sulfate concentration was substantially greater than the expected concentration at 643 ft (196.0 m). Concentrations of sulfate in pore-water samples from 736 and 822 ft (224.0 and 250.5 m) also were much greater than those in pore water from adjoining samples.

Chloride concentrations also decreased with depth, but both the relative and absolute magnitude of the decrease was much smaller for chloride than for sulfate (Fig. 9). Chloride concentrations decreased steadily with depth for the samples from 553 to 705 ft (167.9–214.9 m) in the lower confining unit and the Atlantic City 800-ft sand, with the exception of samples from 616 and 643 ft (187.8 and 196.0 m). Chloride concentrations were somewhat greater in the composite confining unit below the Atlantic City 800-ft sand (48–78 mg/L) than in the silt stringers in the upper part of the Atlantic City 800-ft sand and the basal portion of the lower confining unit (20–67 mg/L). Chloride concentrations increased with depth below the contact of the composite confining unit with the Atlantic City 800-ft sand.

In the lower confining unit, concentrations of DIC varied even less than did concentrations of chloride (Fig. 9; Table 10). Concentrations of DIC generally were nearly uniform from 562 to 585 ft (171.3–178.3 m) and from 626 to 651 ft (190.8–198.4 m). They were greatest near the center of the lower confining unit [18 mg/L at 616 ft (187.8 m)], were low in adjoining samples [less than 10 mg/L at 606 and 626 ft (184.7 and 190.8 m)], and decreased sharply at the upper margin of the unit. Pore-water samples from various depths that contained sulfate in concentrations greater than 450 mg/L also contained DIC in concentrations greater than 10 mg/L, except the sample from 553 ft (168.2 m) at the upper margin of the lower confining unit (7.8 mg/L). DIC concentrations were greater in the composite confining

Table 10 (continued).

Iron (µg/L)	Aluminum (µg/L)	Manganese (µg/L)	Vanadium (µg/L)	Lithium (µg/L)	δ^{34}S, sulfate (‰)
Lower confining unit					
<6	<10	39	<12	45	-5.7 (-5.6)
<6	<10	20	<12	43	3.8 (2.9)
7	<10	16	<12	28	3.7 (3.0)
<6	<10	17	<12	43	—
14	16	6	14	80	—
<6	<10	<2	<12	32	—
<6	16	3	<12	22	6.9 (6.7)
<6	<10	5	13	22	4.2 (3.6)
<6	19	3	17	30	—
6	<10	3	<12	25	—
<6	<10	<2	<12	43	1.2 (1.1)
20	<10	7	<12	35	—
Silt stringers, the upper part of the Atlantic City 800-ft sand					
<6	20	2	22	22	—
<6	<10	4	15	16	—
<6	<10	4	27	22	—
<6	<10	67	<12	33	—
Composite confining unit					
6	33	3	55	36	—
<6	16	8	23	52	—
10	61	2	125	20	—
<6	47	<2	144	21	—

unit (20–27 mg/L) than in the lower confining unit (Table 10). In relation to sulfate concentrations, DIC concentrations were proportionately lower in pore-water samples from the lower confining unit than in samples from the composite confining unit. DIC concentrations were lowest (4.2–8.6 mg/L) in silt stringers in the upper part of the Atlantic City 800-ft sand.

Geostatistical Models of Distributions of Pore-Water Composition with Depth

Variations in pore-water composition with depth were evaluated statistically by examining the most continuously sampled interval, 553–705 ft (168.6–214.9 m), which includes the lower confining unit and the upper part of the Atlantic City 800-ft sand. Plots of measured concentration values for selected pore-water constituents, kriged estimates of the data distribution, and kriged standard deviations, all as a function of depth, are shown in Figure 9. The general variability of concentrations of major pore-water constituents and values of CEC and pH were defined statistically in terms of the semivariogram (Table 11).

Kriged values of concentrations of the major reactive constituents (calcium, magnesium, sodium, sulfate, and chloride) in pore water generally tended to be greatest in the shallowest samples. This trend indicates that the concentrations of these constituents increase as ground water moves along the prepumping flow path in the lower confining unit toward the overlying Rio Grande water-bearing zone. Major-ion concentrations were significantly higher in the pore-water samples from the lower confining unit and the composite confining unit than in those from the silt seams in the Atlantic City 800-ft sand, or in water from the aquifer itself, as indicated by water-quality data for nearby wells screened in the Atlantic City 800-ft sand (Barton et al., 1993). Generally, the interpolated curves indicate that chemical gradients exist for most of the pore-water constituents, from zones in the central or upper part of the lower confining unit toward the underlying aquifer. These gradients are smooth and fairly continuous (Fig. 9).

In the numerical algorithm used to estimate the variation in the concentration of each pore-water constituent and the value of each sediment property by the krige method, the values associated with the four nearest samples were used for interpolation. Generally, all four values used for the interpolation were associated with samples from locations less than 50 ft (15.2 m) from the depth for which the value was interpolated. This distance is within the semivariogram range, or scale of autocorrelation (Clark, 1979; Table 11).

Interpretation of the semivariograms was confounded by the poor fit between the empirical and theoretical semivariograms at large lag distances. Autocorrelation between sample values would be expected to diminish as the distance between the samples in the borehole increases. The semivariogram curves therefore would be expected to approach a constant variance as the distance between autocorrelated samples (the lag distance) increases. The lag distance at which constant variance is reached is the "sill" (Table 11). No constant variance as a function of lag distance was noted for the quality of pore water from the Atlantic City borehole (Fig. 10), which explains in part the poor fit between the empirical and theoretical semivariograms. Furthermore, the curves in the empirical semivariograms are not smooth and continuous as a function of lag distance (Fig. 10). This characteristic indicates that the empirical semivariograms are composed of two or more large-scale spatial-distribution trends in the measured values for the plotted depth interval. These large-scale trends could have been analyzed if more samples had been collected.

The smallest variances occurred over lag distances of less than about 50 ft (15.2 m). The minimum variance at small lag distances, known as the "nugget" (Table 11), is caused by randomness in sample values (true random variation). If sampling intervals were more closely spaced than 10 ft (3.0 m), which was the average interval between samples (the smallest lag distance), the nugget might be reduced. This, in turn, could also improve the fit between the empirical and theoretical semivariograms.

Two dominant types of empirical semivariograms resulted from plotting the pore-water–quality data. The two semivariogram types can be distinguished on the basis of the following characteristics: the lag distance at which the sill is reached; the shape of the semivariogram as defined by the lag distances at which the minimum and maximum variances are found; and the nugget as a percentage of the sill, which is an indication of the degree to which the variance is the result of randomness at small lag distances. The first semivariogram type (Type I) is characteristic of calcium, magnesium, strontium, sodium, sulfate, chloride, and specific conductance (Fig. 10). All Type I empirical semivariograms show maximum variances (sills) at lag distances of 50–55 ft (15.2–16.8 m). Minimum variances are at lag distances of ~75–85 ft (22.9–25.9 m), and moderate variances are at lag distances larger than 85 ft (25.9 m). Lithium- and chloride-concentration data also may fit Type I empirical semivariograms. Chloride concentrations show less variance at small lag distances than other Type I variables (Table 11; Fig. 10), a result consistent with the minor steady decrease in chloride concentration with depth in the lower confining unit and in the upper part of the Atlantic City 800-ft sand (Fig. 9). Maximum concentrations of the constituents represented by Type I empirical semivariograms were present at or near 570 ft (173.7 m). Low concentrations were present at or near depths of 620 and 695 ft (189.0 and 211.8 m). The empirical semivariogram emphasizes that the compositions of pore-water samples from depths of 620 and 695 ft, 75 ft apart (189.0 and 211.8 m, 22.8 m apart) are more similar than those of the pore-water samples from depths of 570 and 620 ft, 50 ft apart (173.7 and 189.0 m, 15.3 m apart). At lag distances greater than 100 ft, the variances increase rapidly to values greater than the sill. The increase in variances at lag distances greater than 85 ft may be related to a large-scale trend, which may indicate the change in sediment texture from silt to interbedded sand and silt, or may result from the decrease in sample density with depth.

The nugget as a percentage of the sill in Type I semivariograms is relatively small for concentrations of calcium, magnesium, strontium, sodium, and sulfate, and for specific conductance; it ranges from 19% to 37%. The nugget as a percentage of the sill for concentrations of chloride and lithium was larger (77% and 63%, respectively) than for concentrations of the other constituents (Table 11).

The second semivariogram type (Type II) is characteristic of the distributions of the concentrations of DIC and silica, and the CEC. All Type II semivariograms show maximum variances (sills) at larger lag distances than Type I semivariograms (Fig. 10). Variance for the DIC concentration semivariogram is greatest at a lag distance of 110

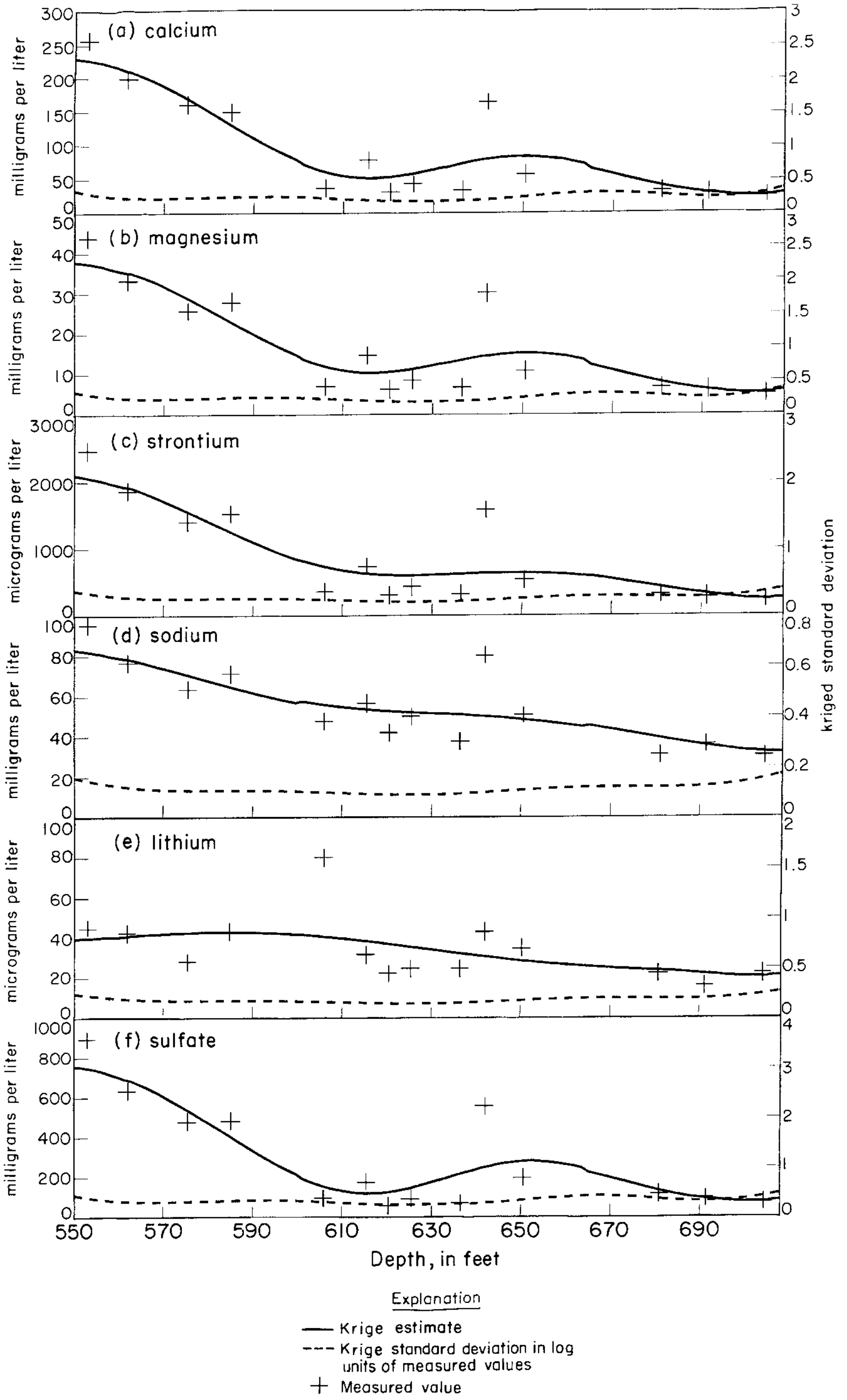


Figure 9. Variations in pore-water composition with depth, krige estimates of pore-water composition with depth, and estimated krige standard deviation from the 553- to 705-ft depth interval in the lower Miocene Kirkwood Formation in the Atlantic City, NJ, borehole for concentrations of (**A**) calcium, (**B**) magnesium, (**C**) strontium, (**D**) sodium, (**E**) lithium, (**F**) sulfate, (**G**) dissolved inorganic carbon, (**H**) chloride, and (**I**) silica; (**J**) specific conductance; (**K**) total cation exchange capacity of the sediment; and (**L**) pH.

ft (33.5 m); the variance for the concentration of silica and for the CEC is greatest at a lag distance of about 70 ft (21.3 m). Type II semivariograms have decreasing variances at larger lag distances. Maximum concentrations of these constituents are centered at about 625 ft (190.5 m); low concentrations are centered at about 555 ft (169.2 m) and 690 ft (210.3 m; Fig. 9). The empirical semivariogram emphasizes these data groupings: differences in the concentrations of these constituents between the pore-water samples centered at 555 and 690 ft, 135 ft apart (169.2 and 210 m, 41.1 m apart) are smaller than those between the pore-water samples centered at 625 and 555 ft, 80 ft apart (190.5 and 169.2 m, 24.4 m apart) or 625 and 690 ft, 65 ft apart (190.5 and 210.7 m, 19.8 m apart).

The nugget as a percentage of the sill for concentrations of the measured constituents was smallest, about 4%, for silica (Table 11). The small nugget and the nugget-to-sill ratio indicate that randomness is a relatively small component of the semivariogram, allowing for a good fit between the empirical and theoretical plots. This result is consistent with the observation that the pore-water concentration of silica changed smoothly with depth (Fig. 9). The sampling interval of about 10 ft (3 m) was most appropriate for accurately interpolating the variation with depth for those constituents and properties that have the lowest nugget-to-sill ratio (Table 11). For the CEC and DIC concentration, the nugget as a percentage of the sill accounted for a significant portion of the variance (about 35% and 53%, respective-

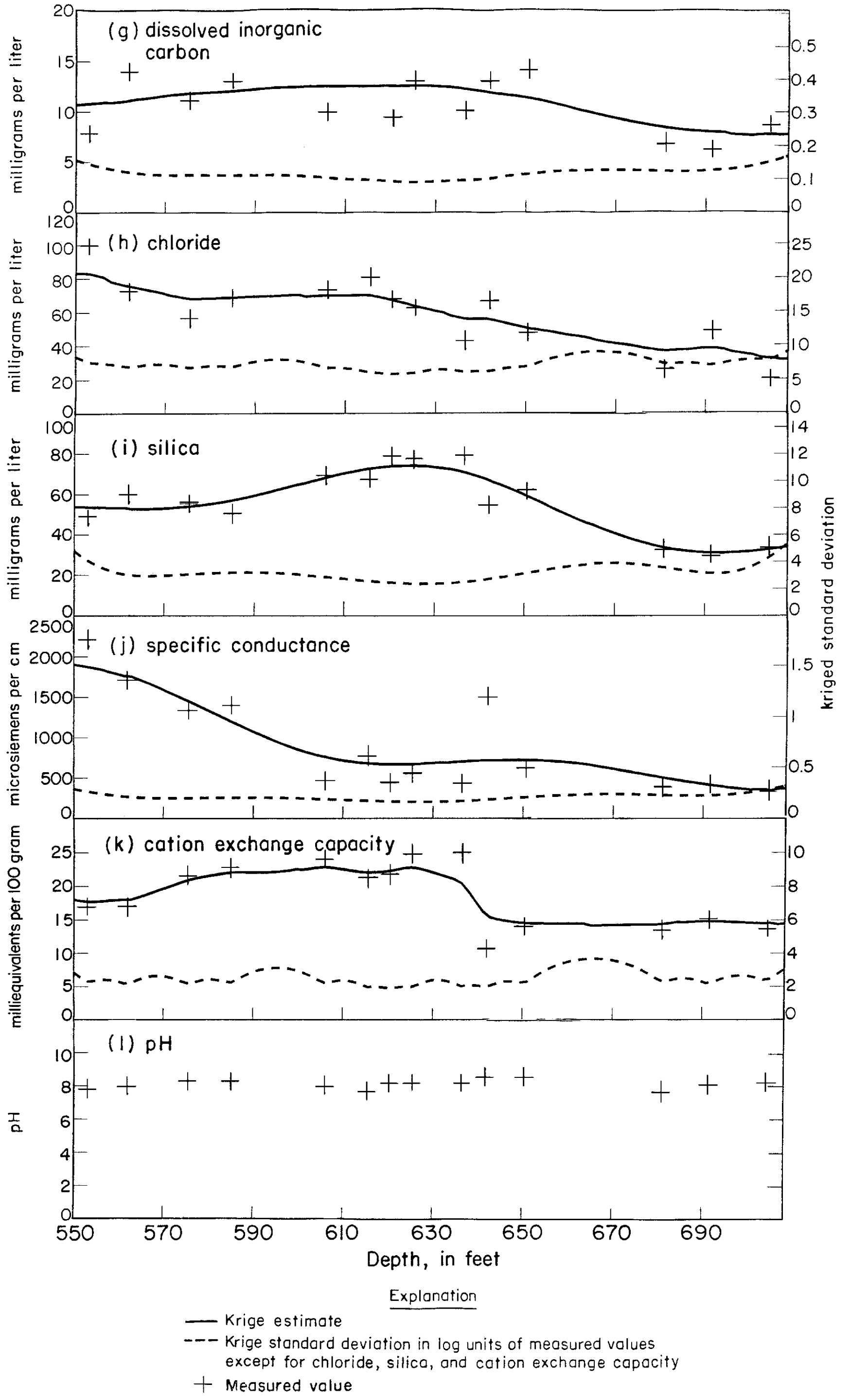


Figure 9 (continued).

ly). The scale of variation for calcium, magnesium, strontium, sulfate, and specific conductance (all of the Type I semivariograms except for sodium) is assumed to be indicated by the semivariogram range (Table 11). The ranges for constituents and properties vary from 65 to 95 ft, and average 66 ft (19.8–29.0 m, average = 20.1 m). The scale of variation for silica and DIC concentrations and for the CEC is indicated by the ranges of the Type II semivariograms, which vary from 44 to 95 ft and average 74 ft (13.4–27.4 m, average = 22.6 m). The scales of variation defined by the semivariogram ranges (Table 11) for most constituents are consistent with the approximate scales of variation of the hydrogeochemical facies as interpreted from trilinear diagrams (Fig. 8).

Regressions Between Concentrations of Pore-Water Constituents

The similarity in concentration trends with depth among the major cations in the pore-water samples from depths of 553–705 ft (168.6–214.9 m) is indicated by high correlation coefficients (greater than +0.86). Results of linear regression indicate that the correlations between the concentrations in milliequivalents per liter of magnesium and calcium (slope m = 0.27, R^2 = 0.99; Fig. 11A) and between the concentrations of sodium and the sum of the concentrations of calcium and magnesium (m = 0.17, R^2 = 0.92; Fig. 11B) are linear. The linear correlations and the similarity in the slopes of the regressions indicate that concentrations of calcium, magnesium, and sodium in

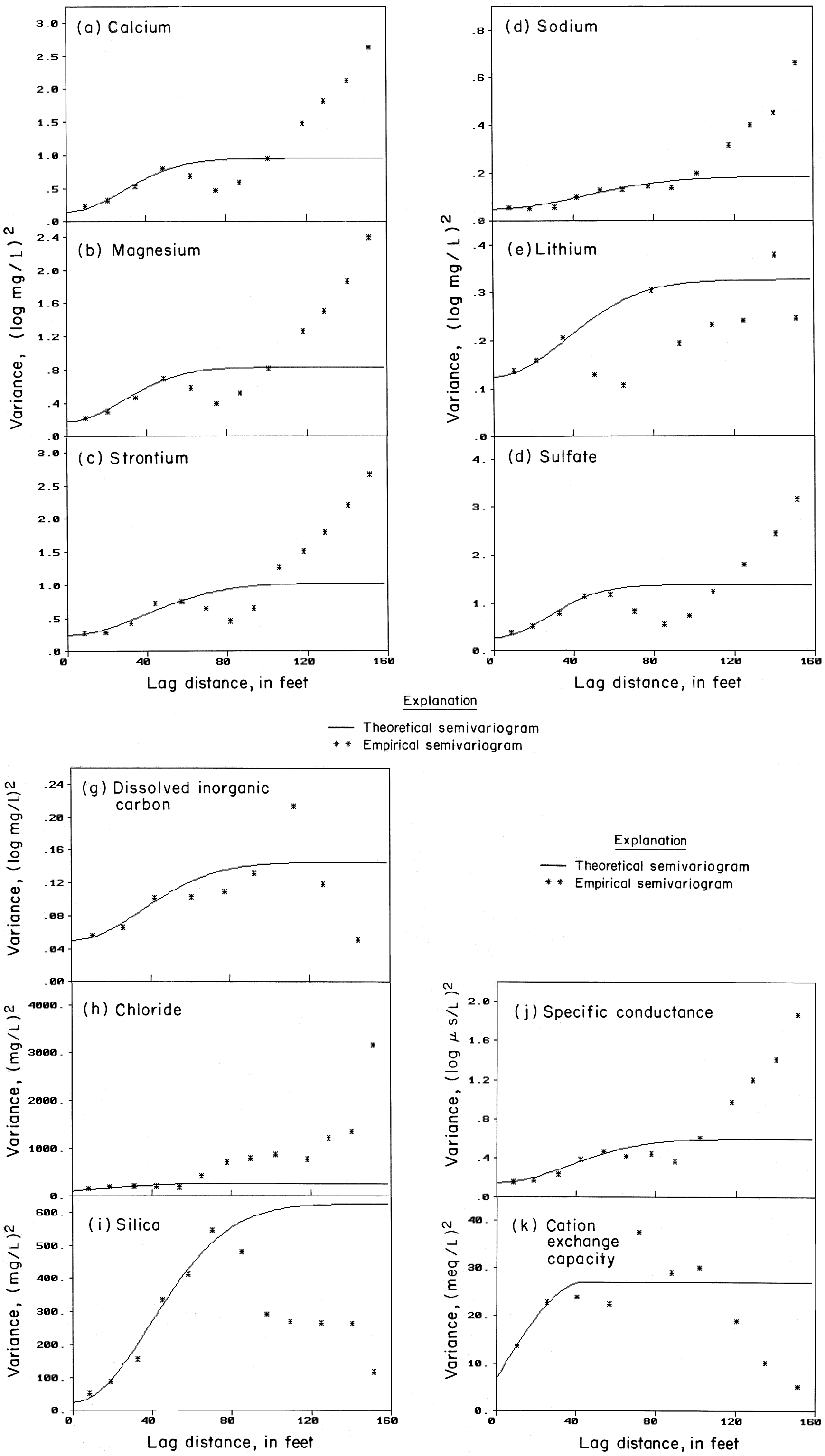


Figure 10. Semivariograms representing pore-water composition from 553 to 705 ft in the lower Miocene Kirkwood Formation, Atlantic City, NJ, for concentrations of (**A**) calcium, (**B**) magnesium, (**C**) strontium, (**D**) sodium, (**E**) lithium, (**F**) sulfate, (**G**) dissolved inorganic carbon, (**H**) chloride, and (**I**) silica; (**J**) specific conductance; and (**K**) total cation exchange capacity of the sediment.

pore-water samples all decrease nearly proportionately with depth over the 553- to 705-ft (168.6–214.9 m) depth interval. Concentrations of all three cations also correlate strongly with concentrations of sulfate in this depth interval. Results of linear regression indicate that the relations between the sum of the concentrations of calcium and magnesium and the concentration of sulfate ($m = 1.14$, $R^2 = 0.99$; Fig.11C) and between the concentrations of sodium and sulfate ($m = 0.14$, $R^2 = 0.89$; Fig. 11D) also are linear. Sodium concentrations were linearly proportional to sulfate concentrations in pore-water samples from the composite confining unit. The concentration of sodium did not correlate with the sum of the concentrations of calcium and magnesium in the composite confining unit, although this relation was found to be nearly linear for the samples from the lower confining unit (Fig. 11B).

The ratio of sodium concentration to chloride concentration in the lower confining unit and the upper part of the Atlantic City 800-ft

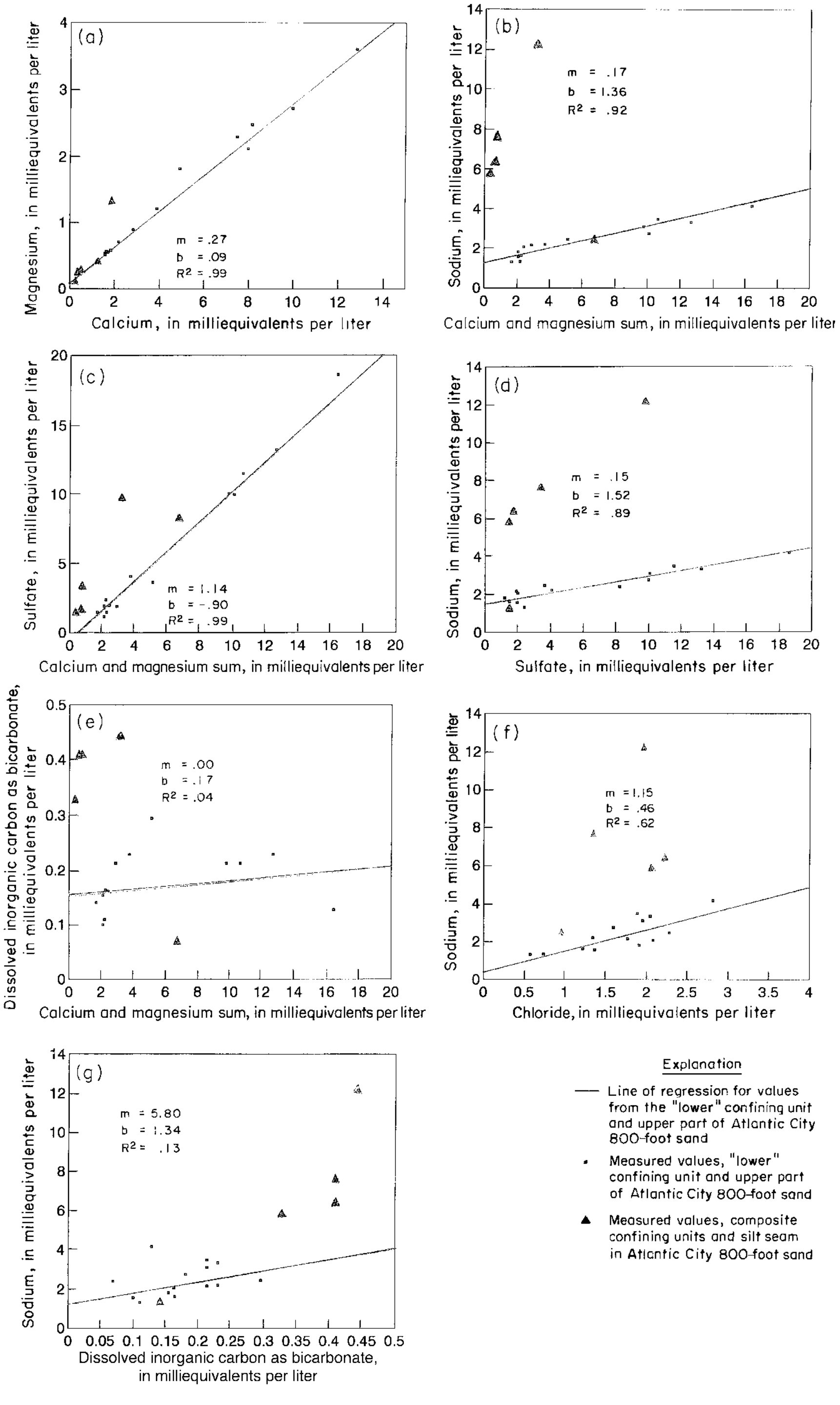


Figure 11. Linear regressions illustrating relations between (**A**) magnesium and calcium, (**B**) sodium and the sum of calcium and magnesium, (**C**) sulfate and the sum of calcium and magnesium, (**D**) sodium and sulfate, (**E**) dissolved inorganic carbon and the sum of calcium and magnesium, (**F**) sodium and chloride, and (**G**) sodium and dissolved inorganic carbon in pore water, all from the lower Miocene Kirkwood Formation, Atlantic City, NJ.

sand ranges from ~1.2 to nearly 2 and varies colinearly (m = 1.14, R^2 = 0.62; Fig. 11F). Sodium-to-chloride equivalence ratios were largest for the samples in which sulfate concentrations were highest, but did not exceed a value of 3. The sodium-to-chloride equivalence ratio decreased from about 6 to slightly less than 3 with increasing depth below the upper margin of the composite confining unit. The relation of sodium concentration to DIC concentration for pore-water samples from the lower confining unit and the upper part of the Atlantic City 800-ft sand could not be described as linear (m = 5.8, R^2 = 0.129; Fig. 11g).

The pore-water concentrations of the major-cation constituents (calcium, magnesium, and sodium) are not linearly related to the concentrations of the same cations in the exchangeable form ($R^2 < 0.05$).

Constituent Groups Responsible for Variations in Pore-Water Composition

Results of principal-component analysis of nine pore-water constituents for all 19 samples are shown in Table 12. Two principal components explained 82.5% of the total variation in constituent con-

Table 11. Summary of semivariogram characteristics and kriged statistics for selected pore-water constituents for the lower Miocene Kirkwood Formation, Atlantic City, NJ, borehole, 551–705 ft.

Constituent	Log option	Sill	Range	Nugget	Model	Optimal lag space	KSD of mean
Calcium (mg/L)	on	0.80	70	0.15	G	13.5	0.50
Magnesium (mg/L)	on	0.65	70	0.18	G	13.5	0.53
Strontium (µg/L)	on	0.78	95	0.25	G	12.5	0.59
Sodium (µg/L)	on	0.14	110	0.05	G	14.5	0.41
Lithium (µg/L)	on	0.20	90	0.13	G	14.5	0.41
Sulfate (mg/L)	on	1.10	65	0.28	G	13.0	0.68
DIC (mg/L)	on	0.10	88	0.05	G	17.0	0.26
Chloride (mg/L)	off	150.0	70	115.0	S	12.0	13.8
Silica (mg/L)	off	600.0	95	25.0	G	13.0	6.6
SC (µS/L)	on	0.45	90	0.15	G	12.0	0.46
CEC (meq/g)	off	20.0	44	7.0	S	16.0	4.2

Notes: mg/L = milligrams per liter; µg/L = micrograms per liter; µS = microsiemens; meq/L = milliequivalents per liter; DIC = dissolved inorganic carbon; SC = specific conductance; and CEC = total cation exchange capacity. Log option indicates whether constituent data was log normalized for kriging as follows: on = log normalized; off = not log normalized. Sill and nugget units are in variance units, which are $(\log mg/L)^2$ units for all constituents except silica and chloride, which are in $(mg/L)^2$ units and CEC, which is in $(meq/g)^2$. Range and optimal lag spacing are in units of feet. Theoretical semivariogram model types are G = gaussian; S = spherical. KSD = krige standard deviation; KSD of mean is in square root units of the variance of the constituent.

centrations in the pore-water sample population. Principal component one (PC1) accounts for 52.5% of the total variation and has dominant loadings of calcium, magnesium, sulfate, strontium, silica, and lithium; all loadings are positive. Principal component two (PC2) accounts for 30% of the total variation and has dominant loadings (all positive) of sodium, DIC, and chloride, and a negative loading of silica. The negative loading of silica is an indication of an inverse relation to those constituent concentrations accounted for in the significant variation (by convention, those components with eigenvalues greater than 1).

DISCUSSION

Chemical Processes

PC1 has major positive loadings of calcium, magnesium, sulfate, strontium, lithium, chloride and silica (Table 12) for the 19 pore-water samples. Coupled chemical processes (dissolution of shells, salts, and minerals; clay-mineral transformations; and redox reactions and microbial processes) result in correlations between these constituents; because they likely are controlled by these same processes, they group together in PC1. Sodium, chloride, and DIC together are the major positive factors, and silica is the major negative loading factor for PC2. This indicates that a second type of major chemical process occurs in the pore water. These processes may include mixing reactions, exchange reactions, and clay-mineral transformations.

Dissolution Reactions

The molar ratio of magnesium to calcium was ~0.268–0.339 (Fig. 11A) in pore water from the lower confining unit and the silt seams in the upper part of the Atlantic City 800-ft sand. This result indicates that these cations are derived principally from dissolution of shell material (Wollast et al., 1971). Carbonate shells are present throughout the Kirkwood Formation (Sugarman et al., 1993); their dissolution produces calcium and magnesium cations in solution. A similar conclusion was reached regarding the source of highly correlated concentrations of dissolved calcium and magnesium (Fig. 11A) in the fine-grained marine sediments from the confining units in the three other New Jersey boreholes previously investigated: two in Freehold and Howell Townships in the northern New Jersey Coastal Plain, and one in Clayton Township in the southern New Jersey Coastal Plain (Pucci et al., 1992). Evaporitic-mineral (gypsum) sources of these dissolved-cation constituents, or of correlative sulfate (Fig. 11C), are considered unlikely because evaporitic minerals have not been found in any of these boreholes (Pucci et al., 1992).

Oxidation-Reduction Reactions

The source of the high concentrations of sulfate in the pore water is not known, but the presence of abundant sulfate is likely coupled to shell-dissolution reactions and oxidation-reduction reactions that transform organic matter in the sediment. Sulfate in high concentrations in pore water can serve as an electron acceptor (electron sink) for bacteria metabolizing or fermenting organic matter (which is abundant in the sediment), leading to the production of CO_2 (Chapelle and Lovley, 1991; Pucci et al., 1992) or dissolved organic acids. The presence of sulfate-reducing microbes in these sediments has been verified in laboratory experiments (Szabo et al., 1996). Microbially mediated redox reactions in the confining units, which involve sulfur, carbon, and oxygen, may be a source of dissolved sulfate, because they can generate sulfate by anaerobic oxidation of pyrite. Microbially mediated transformations also control release of organically bound sulfur, which is found in relative abundance in the sediment and may be a source of the sulfate.

Microbially mediated activity can involve suitable electron acceptors other than sulfate, such as iron (III), if it is available and energy sources (such as organic carbon) are nonlimiting. Concentrations of labile iron (III) in lower Miocene Kirkwood Formation sediment samples collected from the Atlantic City borehole (1.2–18.0 mM/g in the lower confining unit and silt from the upper part of the Atlantic City 800-ft sand, and 1.4–5.2 mM/g in the composite confining unit) were slightly higher than those reported by Chapelle and McMahon (1991) for confining-unit sediments retrieved from the South Carolina Coastal Plain (0.5–10 mM/g). Chapelle and McMahon (1991) concluded that this range of concentrations of labile iron (III) was just high enough for the iron to be significant as an electron acceptor for microbial reactions. Lovley and Phillips (1987) and Chapelle and Lovley (1991) report that shallow sediments characterized by active labile iron (III) reduction contained 100–200 mM/g labile iron (III). The presence of high concentrations of dissolved sulfate and various forms of sulfur in the sediment from the Kirkwood Formation indicates that sulfur, not iron, is likely the dominant electron sink for bacterial metabolic activity.

Pucci and Owens (1989) hypothesize that much of the variation in concentrations of pore-water constituents in the confining-unit sediments from the Freehold, NJ, borehole could be explained by the occurrence of coupled microbially mediated reactions using glauconite and carbonate-mineral substrates. However, glauconite deposits are

Table 12. Principal component–analysis correlation coefficients for all samples for major pore-water chemical constituents from the lower Miocene Kirkwood Formation, Atlantic City, NJ, borehole, 551–840 ft.

Constituent	Components 1	Components 2	Communalities
Strontium	0.989	—	1.00
Magnesium	0.986	—	1.00
Calcium	0.978	—	1.00
Sulfate	0.865	0.361	1.00
Lithium	0.578	0.366	0.65
chloride	0.339	0.584	0.84
Silica	0.420	-0.489	0.94
Sodium	—	0.986	0.98
Dissolved inorganic carbon	—	0.785	0.85
Principal component eigenvalue	4.34	2.48	
Variance explained by each component			
Proportion	0.525	0.300	

Notes: — = correlations with absolute values less than 0.30 have been eliminated for clarity. Only principal components with eigenvalues greater than 1 are considered significant. N = 19.

absent from the depth interval investigated at Atlantic City, again indicating that transformations of sulfur and organic compounds are likely the dominant forms of oxidation-reduction reactions in sediments there.

Mixing Reactions

Correlated linear increases in both sodium and chloride concentrations in the pore water may be caused by intermixing of freshwater and unflushed saline connate water or seawater that remains in the sediment pores from the last eustatic high when the New Jersey Coastal Plain was submerged (Meisler et al., 1985). Sodium concentrations are substantially lower, however, in the lower confining unit (maximum = 96 mg/L) than in the composite confining unit (maximum = 280 mg/L), whereas chloride concentrations are about the same in both units, indicating that the chemical behavior of sodium in the pore water is different from that of chloride. Concentrations of sodium in the lower confining unit and the upper part of the Atlantic City 800-ft sand are linearly related to concentrations of chloride, and variations in the sodium-to-chloride ratio are substantially smaller than variations in this ratio in the composite confining unit. As reported by Martin (in press), the vertical flow rate through the composite confining unit is minimal compared to that through the lower confining unit. Therefore, smaller amounts of sodium and chloride may have been removed from the former than from the latter by advective flushing because the last eustatic high trapped seawater in the Tertiary sediments of the Atlantic Coastal Plain.

Positive loadings for silica in PC1 and negative loadings in PC2 indicate that high concentrations of dissolved silica are more likely a result of, or are coincident with, the various coupled chemical processes represented by PC1 (mineral dissolution) and are subdued by the processes represented by PC2 (mixing of saline and freshwater, and ion exchange).

Ion Exchange

The dominant exchangeable cation in the sediments from both confining units is calcium. The concentration of exchangeable calcium generally increases with total CEC. The order of cation selectivity for exchange is calcium>magnesium>potassium>sodium (Freeze and Cherry, 1979). The relative proportions of the exchangeable cations on the exchange substrate in the sediment (assumed to be clays) follow this sequence in the lower confining unit, whereas in the composite unit, more sodium than potassium is present in the exchangeable phase. This difference may result from differences in clay mineralogy between the two confining units (the combined percentage of kaolinite and illite is greater in the composite confining unit than in the lower confining unit). The flow history and cation concentrations of water previously in contact with the exchanging media may also have been different in the two confining units.

Pore-water concentrations of calcium, magnesium, strontium, and sodium in the lower confining unit correlate and increase in the direction of upward flow (Figs. 9A–D), but an inverse correlation of the sum of calcium and magnesium concentrations to sodium concentrations is noted in the composite confining unit (Fig. 11B). If cation exchange is an important reaction along the flow path currently in the lower confining unit, then the sum of calcium and magnesium concentrations should decrease and sodium concentrations should increase along the upward flow path. Cation exchange, therefore, appears unlikely to be an important reaction in the lower confining unit. This inverse relation of calcium and magnesium to sodium is noted, however, in the composite confining unit (Table 10). A similar relation among these cations has been reported previously for pore-water samples from several confining units in the coastal plain where cation exchange appeared important (Meisler et al., 1985; Pucci and Owens, 1989); this indicates that ion exchange likely is of major importance there.

The rate of flushing of seawater from the sediment also may control differences in exchangeable-cation content in the two confining units investigated. The sediments of the composite confining unit may have been flushed with a smaller volume of freshwater than the sediments of the lower confining unit. This hypothesis is consistent with flow simulations of Martin (in press).

Clay-Mineral Transformations

Silica concentrations in pore water were high but were not linearly related to the concentrations of other dissolved constituents or the abundance of any specific clay mineral in the sediment. Concentrations of lithium in the pore water from the lower Kirkwood Formation at Atlantic City, NJ, were much higher than those recorded at previously drilled updip boreholes in the New Jersey Coastal Plain. Because lithium and silica are important components of clay minerals, these data indicate that reactions involving clay-mineral transformations may be important in determining water chemistry. The effects of clay-mineral transformations on water chemistry, however, are not readily evident and require further investigation.

Concentration Gradients

Significant constituent-concentration gradients exist within the confining units, especially for calcium, magnesium, strontium, sodium, and sulfate. Large concentration gradients potentially can drive large net amounts of diffusive transport of species outward from these confining units. Concentration gradients in the lower confining unit and the upper part of the Atlantic City 800-ft sand indicate that diffusive fluxes of most constituents could be downward through these silty sediments. Pore-water constituent–concentration gradients at the contact between the Atlantic City 800-ft sand and the overlying sediments of the lower confining unit are large; however, characterization of the concentration gradient was hindered by the fact that sample density near the contact of the aquifer with the confining unit was low. Interbedded fine sand and silty sand present at and near the contact could not be sampled properly because of contamination with drilling fluids. The concentration gradients determined from the available data nevertheless indicate that diffusion may be a mechanism of constituent movement from the confining units. This tendency of downward movement (diffusion) along the concentration gradient for the lower confining unit, however, is opposite the tendency for solutes to move in the upward direction of advective flow.

SUMMARY AND CONCLUSIONS

Solute chemistry and properties of confining units in the New Jersey Coastal Plain were studied to determine their effects on regional aquifer-water quality. It is hypothesized that leakage of solute-enriched water from confining units affects regional water chemistry. The distributions of, scale of variations of, and interrelations among fluid-retention properties, mineralogy, texture, and pore-water chemistry were determined for 19 core samples from confining-unit sediments from the lower Miocene part of the Kirkwood Formation at Atlantic City, NJ.

Water yield from sediments ranged from 0.04 to 0.44 cm^3/g. Water yields from the upper part of the lower confining unit were higher than those from the upper part of the Atlantic City 800-ft sand and the composite confining unit. An inverse correlation between sediment kaolinite content and water yield was noted.

Trends in and ranges in concentrations of the major cations calcium, magnesium, and sodium were similar in the lower confining unit and the upper part of the Atlantic City 800-ft sand. Concentration ranges were as follows: calcium = 5.8–257 mg/L; magnesium = 1.2–44 mg/L; and sodium = 30–280 mg/L. Correlations are significant and linear between concentrations of magnesium and calcium ($m = 0.27$, $R^2 = 0.99$), sodium and the sum of calcium and magnesium ($m = 0.17$, and $R^2 = 0.92$), sulfate and the sum of calcium and magnesium ($m = 1.14$, and $R^2 = 0.99$), and sodium and sulfate ($m = 0.14$, $R^2 = 0.89$). In the composite confining unit, sodium concentrations are directly correlated to sulfate concentrations, but inversely correlated to those of calcium and magnesium.

Sulfate concentrations ranged from 57 to 894 mg/L. Variations in sulfate concentrations with depth emulated those in calcium, magnesium, and sodium concentrations in the lower confining unit and the upper part of the Atlantic City 800-ft sand, and those in sodium concentrations in the composite confining unit. Concentrations of chloride (20–100 mg/L) and DIC (4.2–27 mg/L) varied less than sulfate concentrations and were less closely correlated with the major-cation concentrations.

Dissolved-iron concentrations were less than the minimum reporting limit of 6 μg/L in eight of 12 samples from the lower confining unit and two of four samples from the composite confining unit. Manganese concentrations ranged from <2 to 67 mg/L and were somewhat higher and more variable than iron concentrations. Strontium concentrations ranged from 46 to 2470 μg/L and linearly covaried with concentrations of calcium and magnesium.

CEC generally was greatest in the upper part of the lower confining unit (553–638 ft [168.6–194.5 m]) and did not correlate with the percentage of I/S. Exchangeable calcium was present in greater concentrations than any of the other exchangeable cations in all the sediments. Exchangeable sodium was relatively more important in the composite confining unit than in the lower confining unit or the upper part of the Atlantic City 800-ft sand.

Iron (II) is more prevalent than iron (III) as the predominant labile iron form in sediment samples. The dominant sulfur form is sulfide, which accounts for more than half the sulfur in all the samples. Sulfide content varies strongly and is apparently neither depth dependent nor related to texture. Reduced forms of both iron and sulfur, in general, are proportionately more prevalent with depth.

Three distinct hydrogeochemical facies are represented in the pore water: a calcium-sulfate type (Type I), which is principally found in the upper part of the lower confining unit; a mixed-cation and mixed-anion type (Type II), which is principally found in lower part of the lower confining unit and the upper part of the Atlantic City 800-ft sand; and a sodium-sulfate-chloride-bicarbonate–type (Type III), which dominates the water in the composite confining unit. Trilinear plots show that the hydrogeochemical facies vary on a scale of about 50 ft (15.2 m).

Two general forms of semivariograms fit the spatial distribution of most of the major pore-water constituents, specific conductance, and CEC. One form of semivariogram (Type I) was characteristic of calcium, magnesium, strontium, sodium, sulfate, specific conductance, and possibly lithium and chloride. Another form (Type II) was characteristic of silica, DIC, and CEC. The scale of variation (defined here as the semivariogram range) was 65–95 ft (19.8–29.0 m) for Type I semivariograms and 44–95 ft (13.4–27.4 m) for Type II semivariograms. This analysis is limited, however, by the sample size and the fact that the theoretical semivariograms did not match the empirical semivariograms over large lag distances.

Statistical analysis of the principal components was performed on the concentrations of major pore-water constituents from all 19 samples and demonstrated significant overall multivariate correlations and the presence of related constituents that could be classified into groups. Two principal components account for 82.5% of the variation in the samples. About 53% of the variation is explained by PC1 loadings (including calcium, magnesium, strontium, sulfate, and lithium) and is interpreted to represent coupled chemical reactions (carbonate-mineral and shell dissolution, redox transformations of sulfur and iron, microbial utilization and degradation of organic matter, and possible clay-mineral transformations). About 30% of the variation is explained by PC2 loadings (including sodium, DIC, and chloride) and is interpreted as the effects of mixing of residual seawater with freshwater recharge, but may also indicate cation exchange.

The semivariogram range for the pore-water constituents was used as an estimator of the spatial scale of correlation for each major pore-water constituent; the scale of variation in major ions in pore water is on the order of 44–90 ft (13.4–27.4 m). Concentration gradients, especially those of sulfate, calcium, magnesium, strontium, and sodium, were large and indicated that potential diffusive transport of these constituents from the lower confining unit to the aquifer is downward into the Atlantic City 800-ft sand, and opposes the upward direction of advective flow.

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Previous Chapter

Table of Contents

Next Chapter