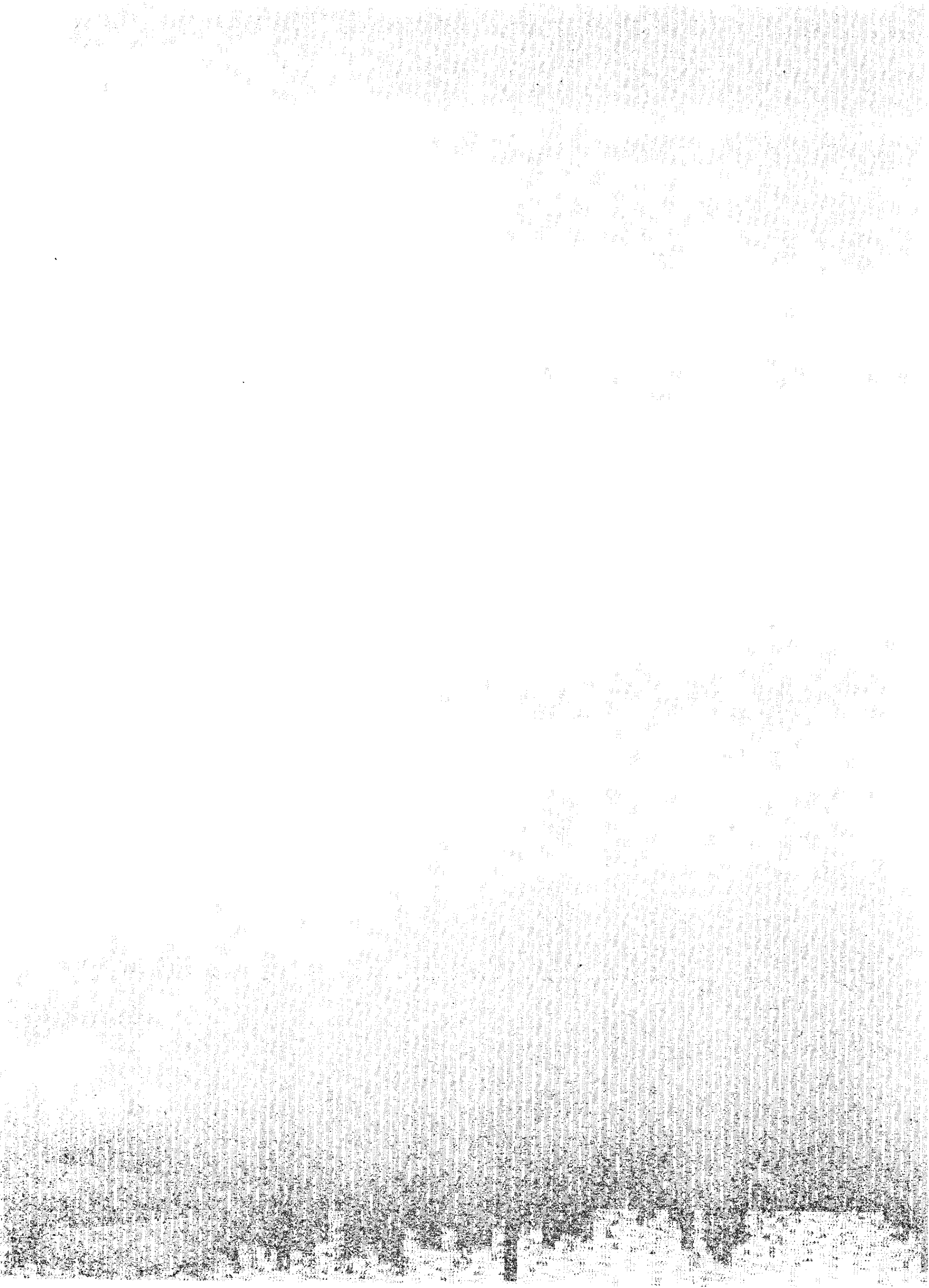
The Geochemical Evolution of Aqueous Sodium in the Black Creek Aquifer, Horry and Georgetown Counties, South Carolina



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Myrtle Beach, and
The City of North
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U.S. DEPARTMENT OF THE INTERIOR
March 3, 1849

The Geochemical Evolution of Aqueous Sodium in the Black Creek Aquifer, Horry and Georgetown Counties, South Carolina

By ALLEN ZACK and IVAN ROBERTS

Prepared in cooperation with the Georgetown County Water and Sewer District, Grand Strand Water and Sewer Authority, South Carolina Water Resources Commission, The City of Myrtle Beach, and The City of North Myrtle Beach

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CONTENTS

FIGURES

TABLE

The Geochemical Evolution of Aqueous Sodium in the Black Creek Aquifer, Horry and Georgetown Counties, South Carolina

By Allen Zack *and* Ivan Roberts

Abstract

The Black Creek aquifer contains dilute seawater near the North Carolina State line, probably the result of incomplete flushing of ancient seawater. Data do not indicate that the dilute seawater has migrated toward areas of fresh ground-water withdrawals. The concentration of chloride in ground-water samples ranges from 5 to 720 milligrams per liter and that of sodium from 160 to 690 milligrams per liter.

Ion-exchange reactions (sodium for calcium and fluoride for hydroxyl) occur with the calcium carbonate dissolution reaction which produces calcium, bicarbonate, and hydroxyl ions. The reaction sequence and stoichiometry result in an aqueous solution in which the sum of bicarbonate and chloride equivalents per liter is equal to the equivalents per liter of sodium.

Calcium ions are exchanged for sodium ions derived from sodium-rich clays upgradient of the dilute seawater. The cation-exchange reaction equilibrates at a sodium concentration of 280 milligrams per liter. Amounts of sodium greater than 280 milligrams per liter are contributed from dilute seawater. The cation-exchange reaction approaches an equilibrium which represents a mass-action limit in terms of the ratio of sodium to calcium in solution versus the ratio of exchangeable sodium to calcium on clay surfaces. Where the limit of calcium carbonate solubility is approached and dissolution ceases, some precipitation of calcite probably takes place. The dissolution of calcite exposes fossil shark teeth which release fluoride ions to the ground water through anion exchange with aqueous hydroxyl ions.

INTRODUCTION

Dilute seawater within the Black Creek aquifer of Horry and Georgetown Counties, S.C. (fig. 1), limits the usefulness of ground water as a reliable water supply. A high concentration of chloride or sodium in a water supply renders the water impotable but is not considered to be dangerous to health, according to the U.S. EPA (Environmental Protection Agency) and the South Carolina Department of Health and Environmental Control. EPA has imposed a secondary drinking-water limit of 250 mg/L for chloride (U.S. Environmental Protection Agency, 1977). In the Black Creek aquifer of Horry and Georgetown Counties, this limit corresponds to total dissolved solids of approximately 625 mg/L and a sodium concentration of 420 mg/L. Although the EPA has not established a limit for sodium concentration, the literature of modern medicine and science indicates that a high sodium concentration in drinking water might be considered harmful to heart-disease patients on a sodium-free diet.

Analyses of water samples collected from wells screened in the Black Creek aquifer, the major water supply for residents of the two-county area, indicate that seawater-free ground water of meteoric origin generally contains less than 280 mg/L sodium and less than 40 mg/L chloride. In water samples containing sodium and chloride concentrations greater than 280 mg/L and 40 mg/L, respectively, the ratio of the increase in sodium to the increase in chloride is approximately equal to the Na/Cl ratio of seawater (fig. 2), suggesting that the ground water is a mixture of water of meteoric origin and seawater. Seawater contains about 11,000 mg/L sodium and 19,800 mg/L chloride (Plummer and others, 1976, p. 16–26). Whereas the occurrence of dissolved chloride in the Black Creek aquifer can be attributed to both recharge input and residual seawater, the occurrence of dissolved sodium cannot be attributed solely to these sources and must necessarily result from other geochemical processes within the aquifer.

In 1980, the U.S. Geological Survey began an investigation to describe the geochemical evolution of aqueous sodium in the Black Creek aquifer in terms of dissolution and ion-exchange reactions. The study was conducted in cooperation with the following agencies in Horry and Georgetown Counties: Georgetown County Water and Sewer District, Grand Strand Water and Sewer Authority, South Carolina Water Resources Commission, The City of Myrtle Beach, and The City of North Myrtle Beach.

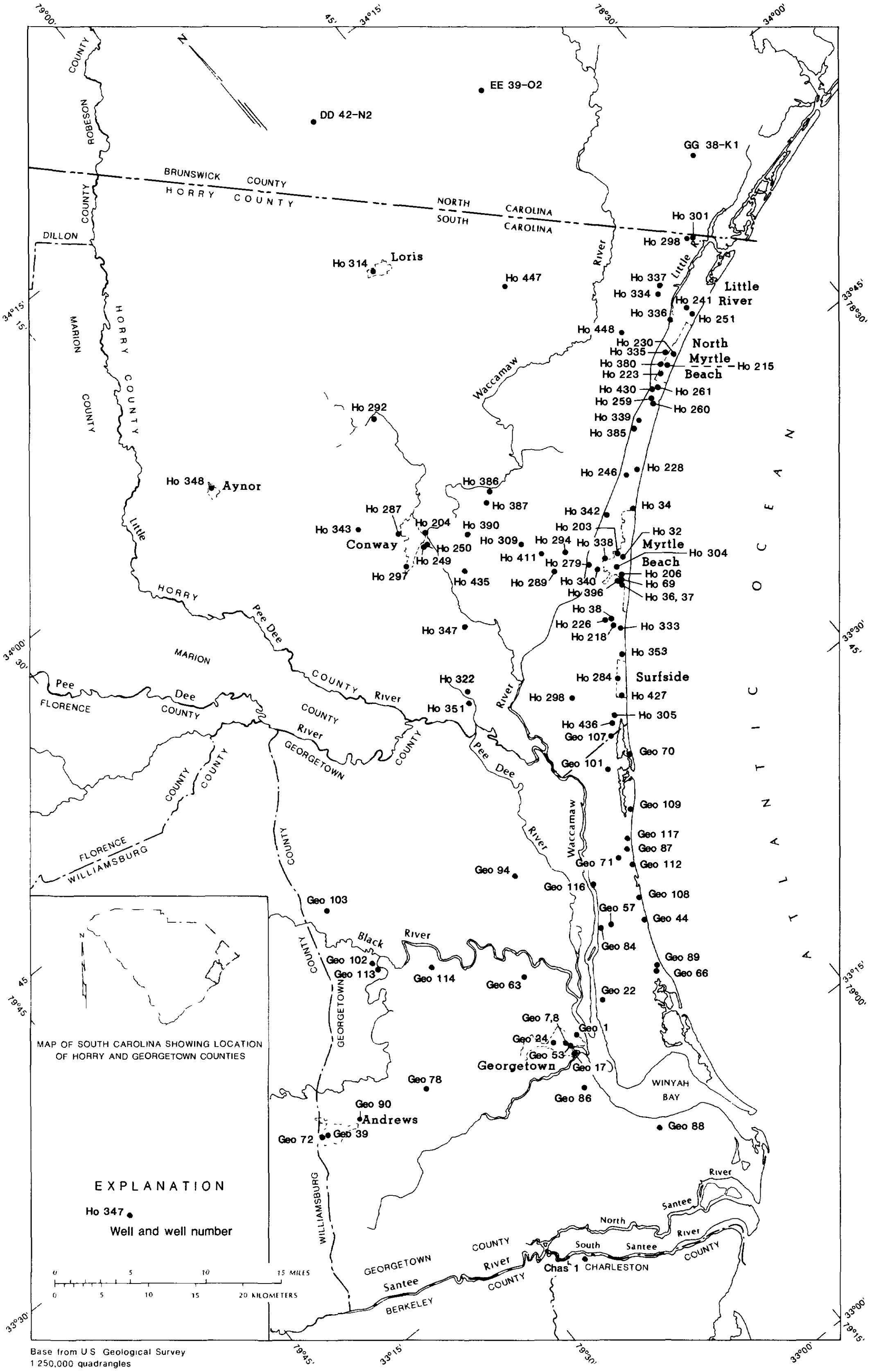

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Figure 1. Location of Horry and Georgetown Counties, South Carolina, and vicinity, principal geographic features, and well sites.

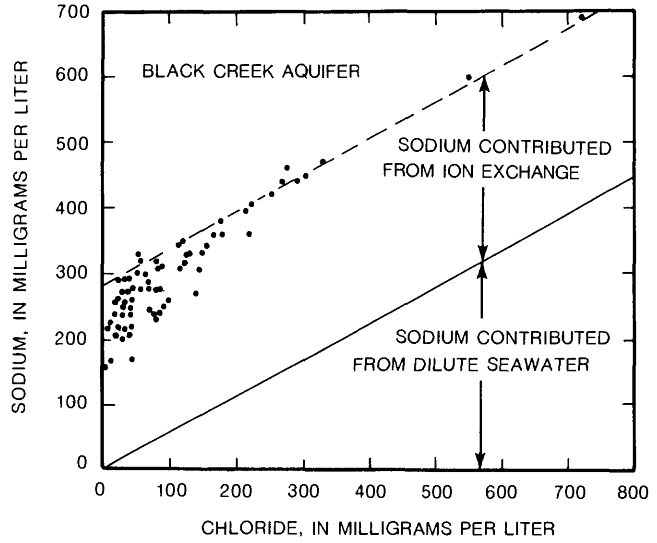


Figure 2. Relation of sodium to chloride in water from the Black Creek aquifer and in dilute seawater.

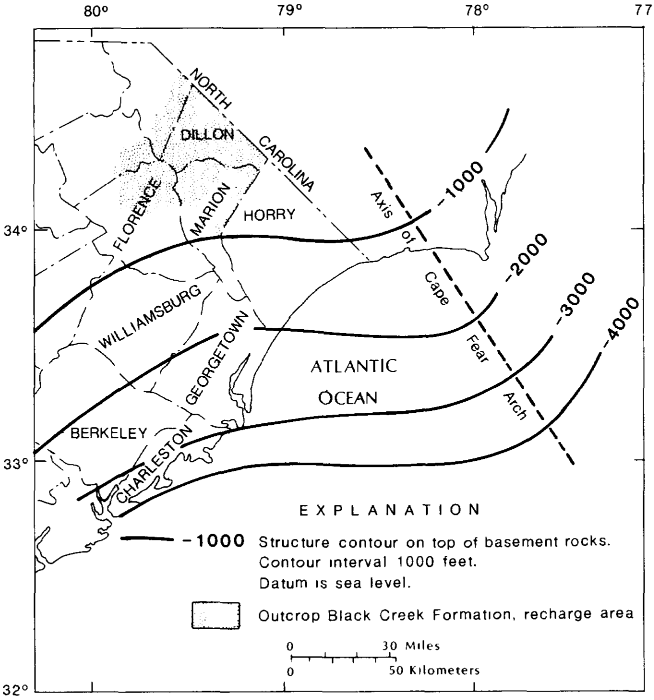
GEOLOGY

Numerous investigators have described the stratigraphy, structure, and mineralogy of Cretaceous and Tertiary sediments of the South Carolina Coastal Plain. Swift and Heron (1969) list some of the investigators.

The Upper Cretaceous formations in Horry and Georgetown Counties consist of the Middendorf Formation, which rests unconformably on the basement rock, and, in ascending order, the Black Creek Formation and the Peedee Formation. These formations consist of time-transgressing facies which were deposited in marine and marginal-marine environments of the transgressive Late Cretaceous sea. The contact of the Middendorf with the Black Creek appears to be interfingering and "the Black Creek-Peedee contact is a ravinement or disconformity cut by the transgressing Peedee sea" (Swift and Heron, 1969, p. 201).

The Black Creek Formation consists of laminated, dark-gray clay interbedded with gray to white, fine to very fine glauconitic, phosphatic, and micaceous quartz sand. Nodules of pyrite and marcasite as well as lignite fragments and other carbonaceous materials are common. Thin, relatively continuous layers of hard, impervious, calcite-cemented quartz sand containing fossil shark teeth are abundant in the upper third of the formation.

The strike of Coastal Plain sediments in the two-county area is generally northeast. The dip which is southeast (Zack, 1977, p. 22) has resulted from an accretion of sediments from the landward source in the coastal area and by downward flexure of the Coastal Plain. The downwarping is regional and accounts for the numerous facies changes found throughout the geologic formations. Erosion exposed the updip limits of the sediments. The area of the outcrop of the Black Creek Formation is shown in figure 3.



Modified from Maher, 1971, Plate 4

Figure 3. Structure contours of the basement rocks, Cape Fear Arch, and area of outcrop of the Black Creek Formation.

The Cape Fear Arch is a southeastward-plunging basement nose which has influenced the migration of ground water. Its axis intersects the North Carolina coastline near the South Carolina State line (Maher, 1971, p. 22). The axial plunge increases sharply near the shoreline and gradually diminishes updip toward the Fall Line.

The area and depth distribution of dilute seawater in the Black Creek aquifer is determined by geologic events during and since the time the sediments were deposited. Clays, which were deposited in marine sediments, were sodium-rich as a result of seawater-clay interactions. Lowering of sea level and erosion have exposed the updip reaches of the sediments northwest of the project area (fig. 3) to recharge from rainfall. The freshwater has percolated downgradient and flushed the seawater southeastward. The extensive Black Creek aquifer consists of former seawater-bearing sands, now mostly occupied by freshwater (fig. 4). In the vicinity of Myrtle Beach, the lower sand of the Black Creek aquifer has been flushed of dilute seawater only as far southeastward as the Waccamaw River (fig. 1). In the Myrtle Beach area, this sand contains water that has as much as 900 mg/L chloride concentration but freshens abruptly updip beyond the zone of dispersion and diffusion. The remainder of the sands within the Black Creek Formation contains freshwater throughout the two-county area, except in the North Myrtle Beach-Little River area.

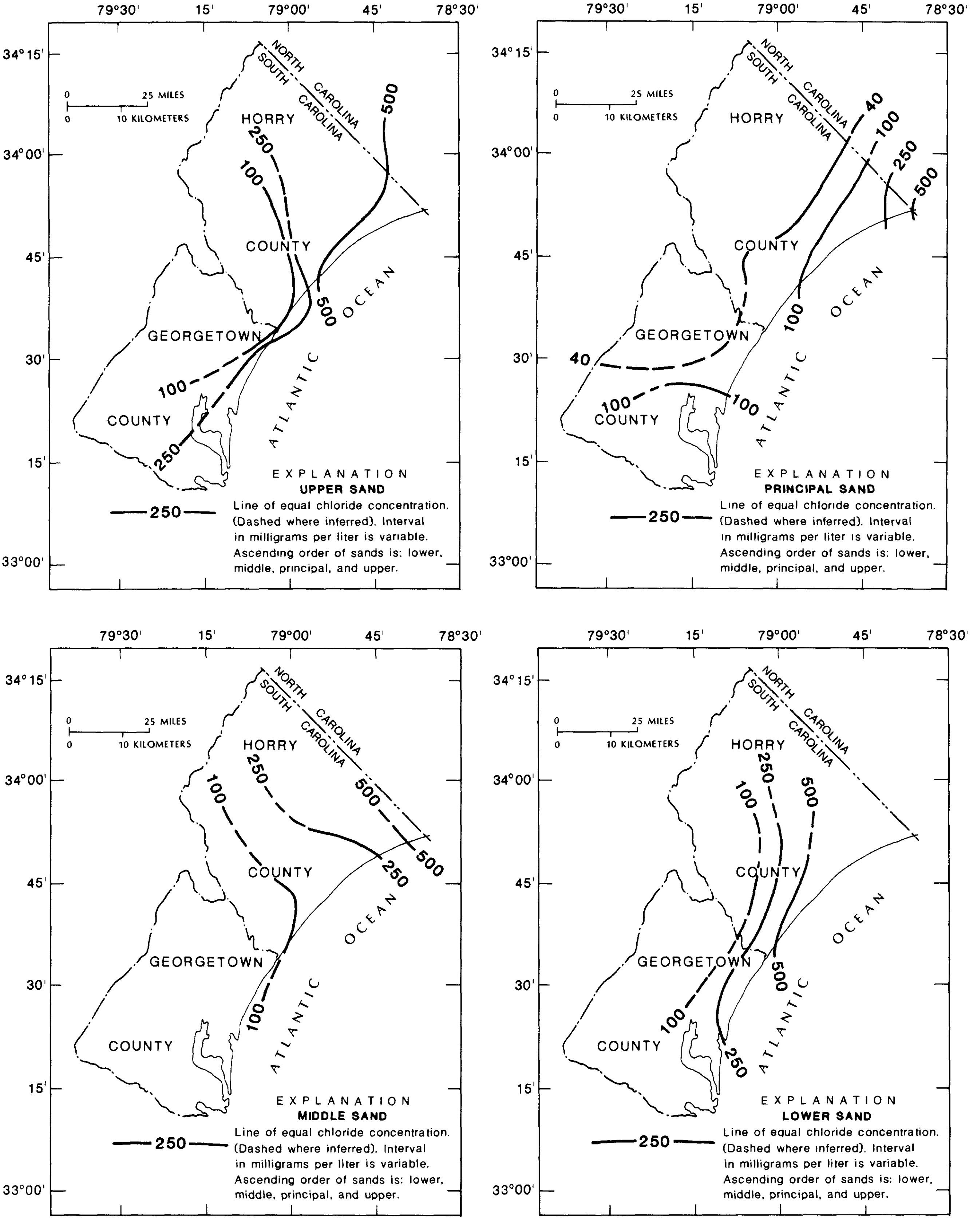


Figure 4. Approximate location of dilute seawater in sand units, Black Creek aquifer, in terms of equal chloride concentration exceeding the highest concentration of chloride derived strictly from meteoric sources, 40 mg/L.

In northern Horry County, the location of dilute seawater appears to be influenced by the Cape Fear Arch. Freshwater has not completely flushed the dilute seawater from the Black Creek aquifer on the flanks and summit of the Cape Fear Arch where concentrations of sodium and chloride are greater than 690 mg/L and 720 mg/L, respectively. Freshwater occurs in only localized areas on the flanks of the Cape Fear Arch (northern Horry County).

The transition from freshwater to salty water within individual sands of the Black Creek aquifer is represented by a wide zone of dispersion and diffusion. The location and geometry of each zone of dispersion and diffusion cannot adequately be determined because of the limited number and distribution of data points. The few existing wells are usually open to more than one water-producing zone, and a water sample usually represents a composite sample of unknown proportions of the water from the various producing zones. By using the best data available, a section location map (fig. 5) and geohydrologic cross sections showing the known and inferred locations of the zone of dispersion and diffusion were prepared (figs. 6 through 13). The zones are defined by chloride concentrations (generally used as an indicator of seawater) of 40, 100, 250, and 500 mg/L. A chloride concentration of 40 mg/L represents the highest concentration of chloride found in ground-water samples solely of meteoric origin in this area. Zones having higher concentrations indicate greater quantities of seawater in the aquifer with 250 mg/L being the secondary drinking water regulation for chloride (U.S. Environmental Protection Agency, 1977). For convenience, the aquifer has been divided into four sand units, each of which comprise several individual sands separated by clay or rock (calcite-cemented quartz sand). Within each of the four sand units, hydraulic continuity is believed to exist across the unit; the intervening clays and rocks provide hydraulic independence from unit to unit. For a more complete discussion of hydraulic continuity within the Black Creek aquifer see Zack (1977, p. 44).

Dilute seawater is present within geologic formations above and below the Black Creek Formation. The older Middendorf Formation contains dilute seawater throughout the two counties and is unacceptable as a water supply without extensive treatment. The Peedee Formation and younger Tertiary sediments contain salty water only where they are adjacent to the ocean and other salty surface-water bodies but are usually poor aquifers in terms of transmissivity. Locally, the shallow formations may contain freshwater very near the ocean.

The water of the Black Creek aquifer is generally the most suitable water supply in the two-county area: it is relatively low in calcium and magnesium, is iron- and sulfate-free, and is usually low in chloride. However, fluoride concentrations are as high as 5.5 mg/L in some locations (Zack, 1980, p. 4).

DISTRIBUTION OF DILUTE SEAWATER

The available data do not indicate that chloride concentration within the Black Creek aquifer has increased because of ground-water withdrawals (Zack, 1977, p. 61). Many wells continue to produce relatively freshwater in the vicinity of the dilute seawater. It is very difficult, however, to measure slow rates of saltwater movement even in ideally placed wells. In addition, the location of the zone of dispersion and diffusion under the Atlantic Ocean, southeast of the Myrtle Beach and Georgetown cones of depression (Zack, 1977, p. 43 and 45), is not known, and its rate of movement has not been measured. It is likely that some dilute seawater has moved inland in response to withdrawals even though movement has not been observed.

Occasionally, water withdrawn from a pumped well will increase in sodium and chloride; however, the geochemical makeup of the salty water in terms of Na^+, HCO_3^-, Ca^{++}, and pH indicates that it has been introduced to the well from either shallow overlying Tertiary aquifers, or from the underlying Middendorf Formation, and not from saltwater movement in the Black Creek aquifer itself.

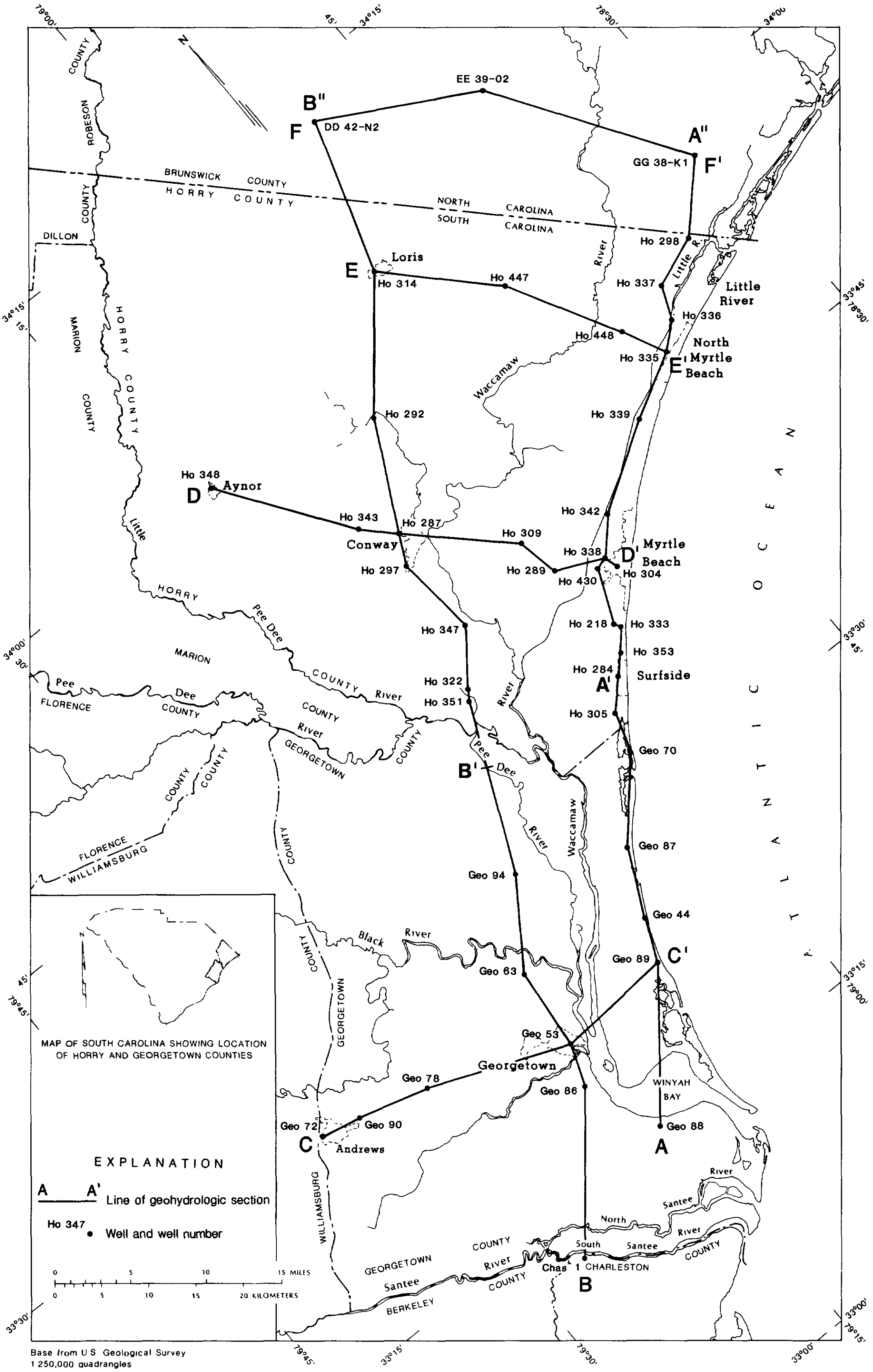
GEOCHEMISTRY

The geochemistry of seawater as it affects carbonate equilibria has been discussed in detail by Krauskopf (1979, p. 58–66), Garrels and Christ (1965, p. 100–107), and Stumm and Morgan (1981, p. 118–148). In addition, the geochemistry of calcite dissolution and ion-exchange reactions in the Black Creek aquifer has been studied by Zack (1980). Throughout the two-county area, the equivalents per liter of bicarbonate plus chloride approximately equal the equivalents per liter of sodium in water from the Black Creek aquifer (fig. 14). The relation holds for freshwater in the recharge areas as well as for dilute seawater in the vicinity of the Cape Fear Arch. This phenomenon and the general increase in the amount of calcium ions found in salty ground water (fig. 15) can be explained in terms of calcium carbonate solubility and cation exchange.

Within the Black Creek aquifer, two moles of bicarbonate are produced for every mole of calcium ions produced when the calcite cement in the sands dissolves in weak carbonic acid:

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca^{++} + 2HCO_3^- \quad (1)$$

The carbon dioxide, which forms the weak acid in water, is released from carbonaceous material in the Black Creek Formation (Foster, 1950, p. 33).



Base from U S Geological Survey
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Figure 5. Locations of geohydrologic cross sections in Horry and Georgetown Counties, South Carolina, and vicinity.

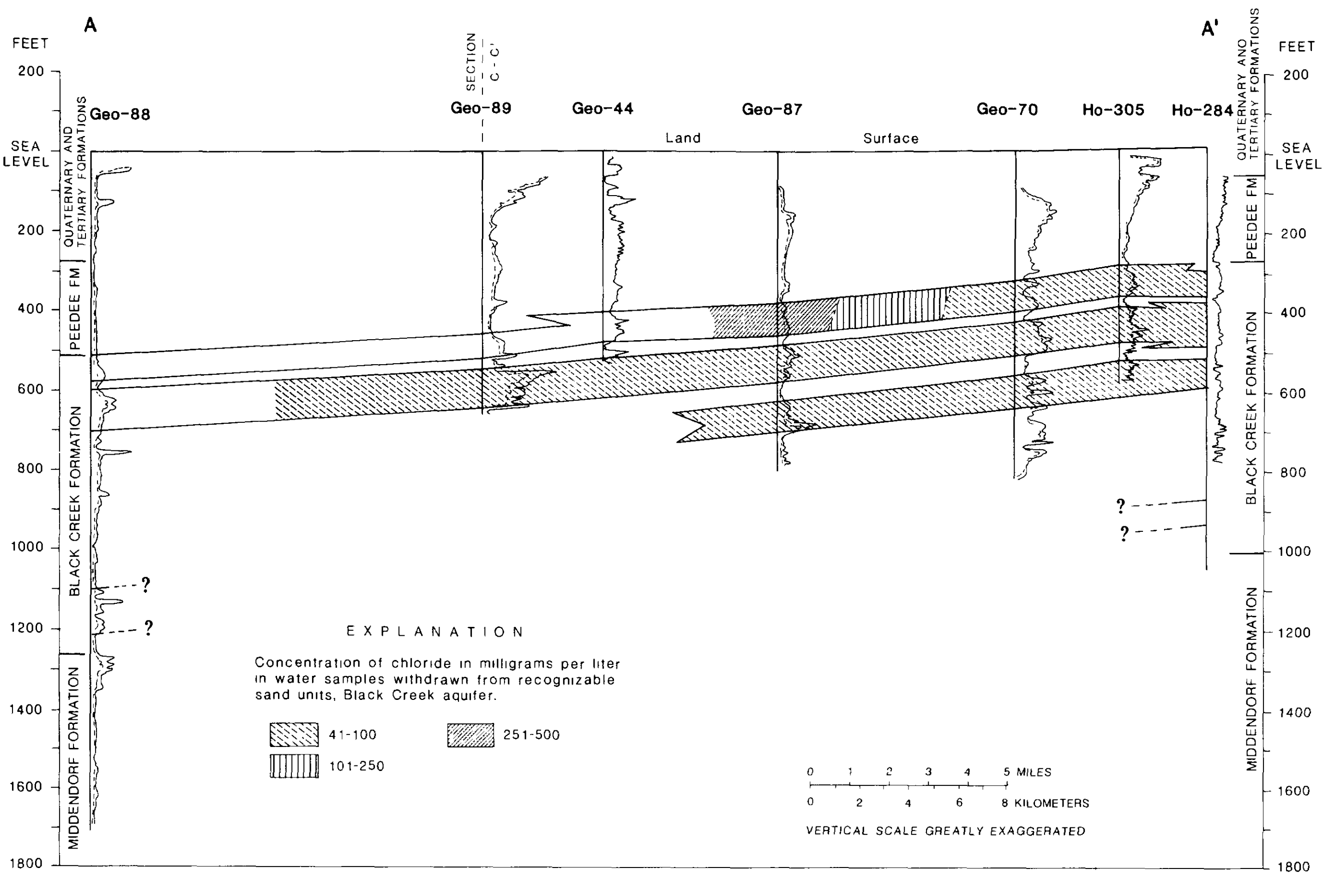

Figure 6. Geohydrologic cross section A-A′ showing the known and inferred locations of the zone of dispersion and diffusion in the Black Creek aquifer of Horry and Georgetown Counties, South Carolina, and vicinity.

Deffeyes in Stumm and Morgan (1981, p. 185–191) shows that the addition of CO_2 in the system increases the total concentration of dissolved carbonic species without changing alkalinity,[1] but with a decline in pH. However, in the Black Creek aquifer, pH is consistently high (about 8.3 units) and is probably buffered from a combination of ion-exchange reactions (discussed later) and equilibrium with carbonate minerals (Thorstenson and others, 1979, p. 1496).

As the water moves downgradient through carbonaceous materials, pH is nearly constant. Calcite and carbon dioxide are readily available within the system, and bicarbonate (or, strictly speaking, alkalinity) increases. The dissolution reaction progresses near the calcite solubility phase boundary. This boundary describes calcite saturation in terms of concentrations of calcium and bicarbonate at a particular pH.

Selected ionic concentrations and the saturation index of calcite for seven typical water-quality analyses are given in table 1. Saturation index is defined as the log of the ratio of ionic-activity product divided by the solubility product for a particular mineral. It represents the degree of saturation of a mineral in an aqueous solution. Positive values of saturation index imply supersaturation, negative values indicate undersaturation, and values near zero indicate saturation or nearly so. The analyses are representative of WATEQ (Truesdell and Jones, 1974) calculations for water-quality analyses of water withdrawn from wells distributed throughout Horry and Georgetown Counties. WATEQ is a computer program that takes, as input, individual chemical analyses, including field pH, temperature, and redox potential, and computes the equilibrium distribution of preselected inorganic aqueous species. The saturation indices in table 1 imply that all water samples are undersaturated with respect to calcite except for Little River which is at saturation.

As water moves downgradient, the concentration of bicarbonate ions is relatively unaffected by clays and other noncarbonate minerals in the aquifer. The concentration of sodium increases, however, because sodium-rich

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[1] The alkalinity and the concentration of bicarbonate in milliequivalents per liter are nearly equal in most ground water having a pH of less than 9.0.

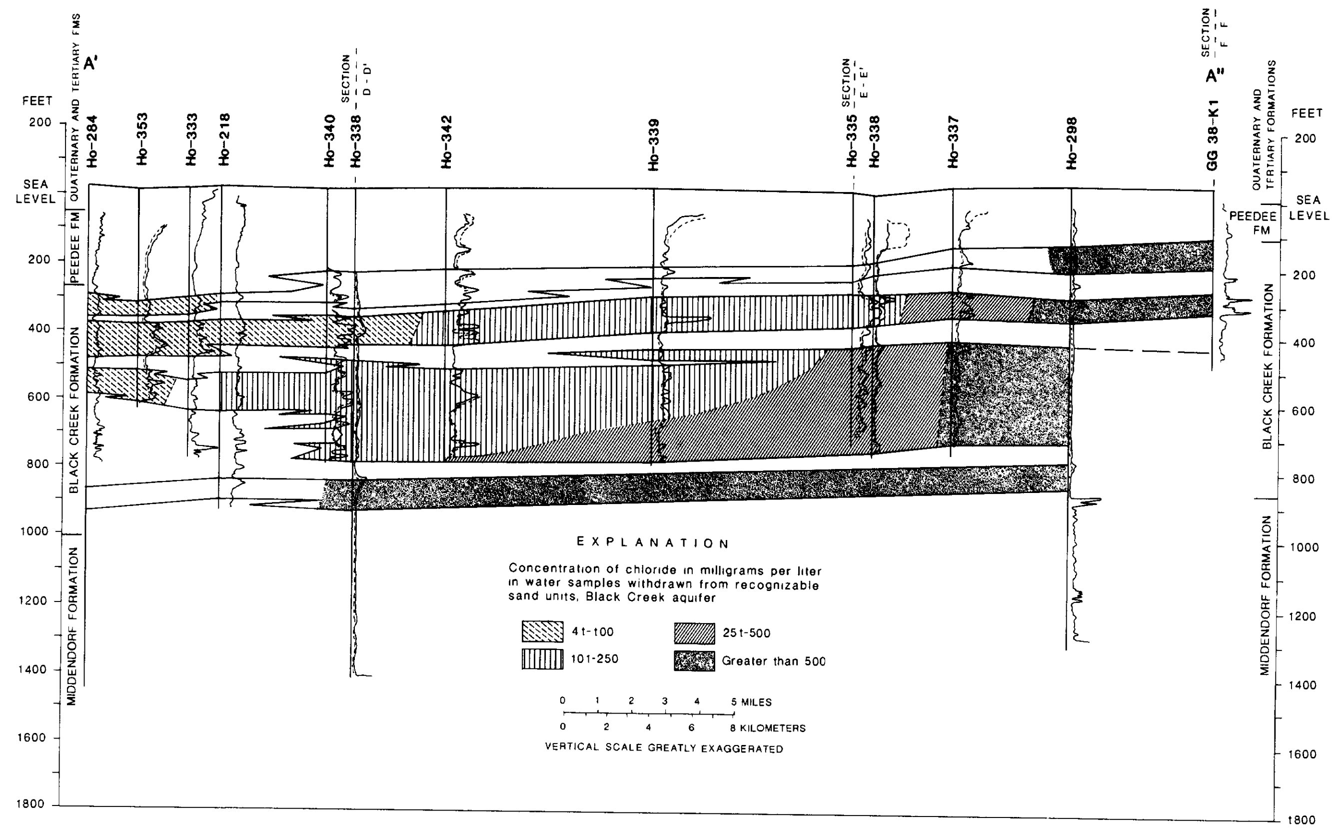

Figure 7. Geohydrologic cross section A'-A'' showing the known and inferred locations of the zone of dispersion and diffusion in the Black Creek aquifer of Horry and Georgetown Counties, South Carolina, and vicinity.

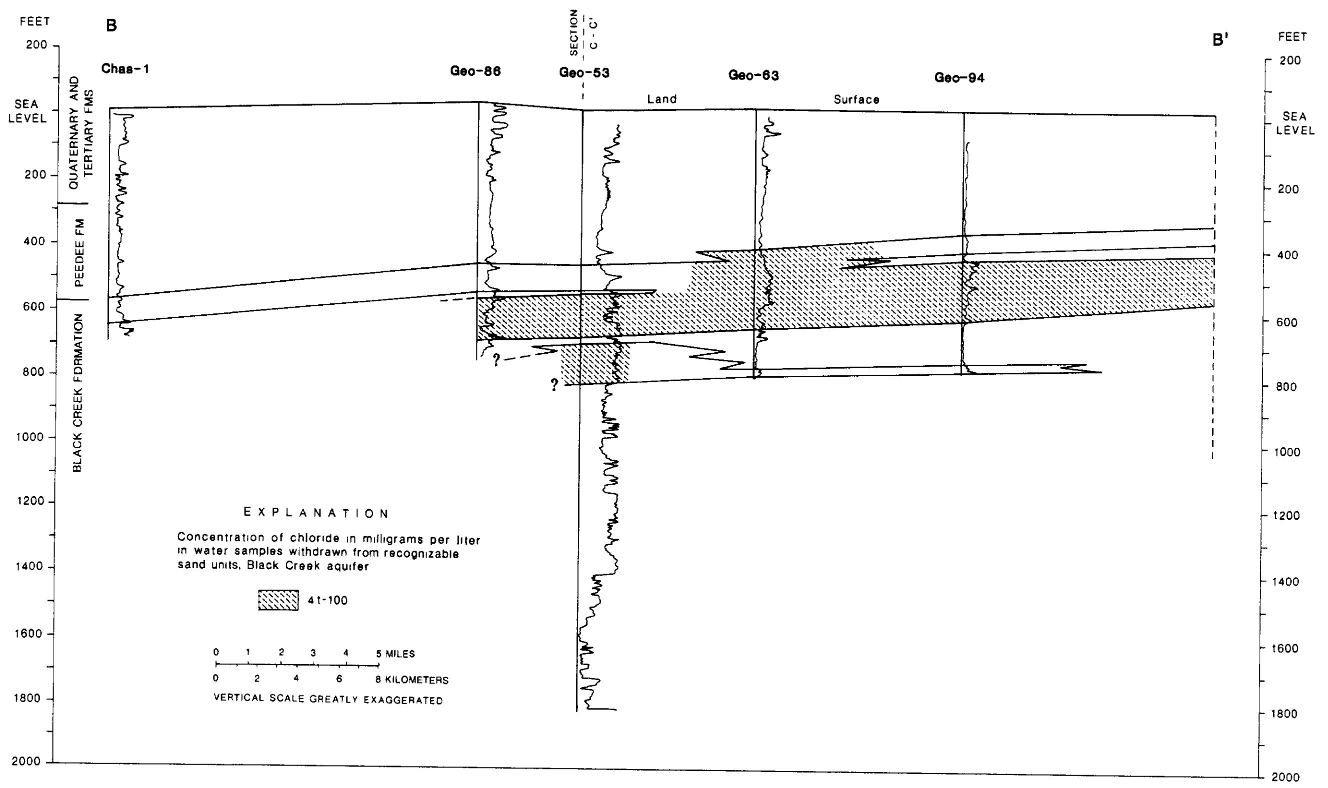

Figure 8. Geohydrologic cross section B–B' showing the known and inferred locations of the zone of dispersion and diffusion in the Black Creek aquifer of Horry and Georgetown Counties, South Carolina, and vicinity.

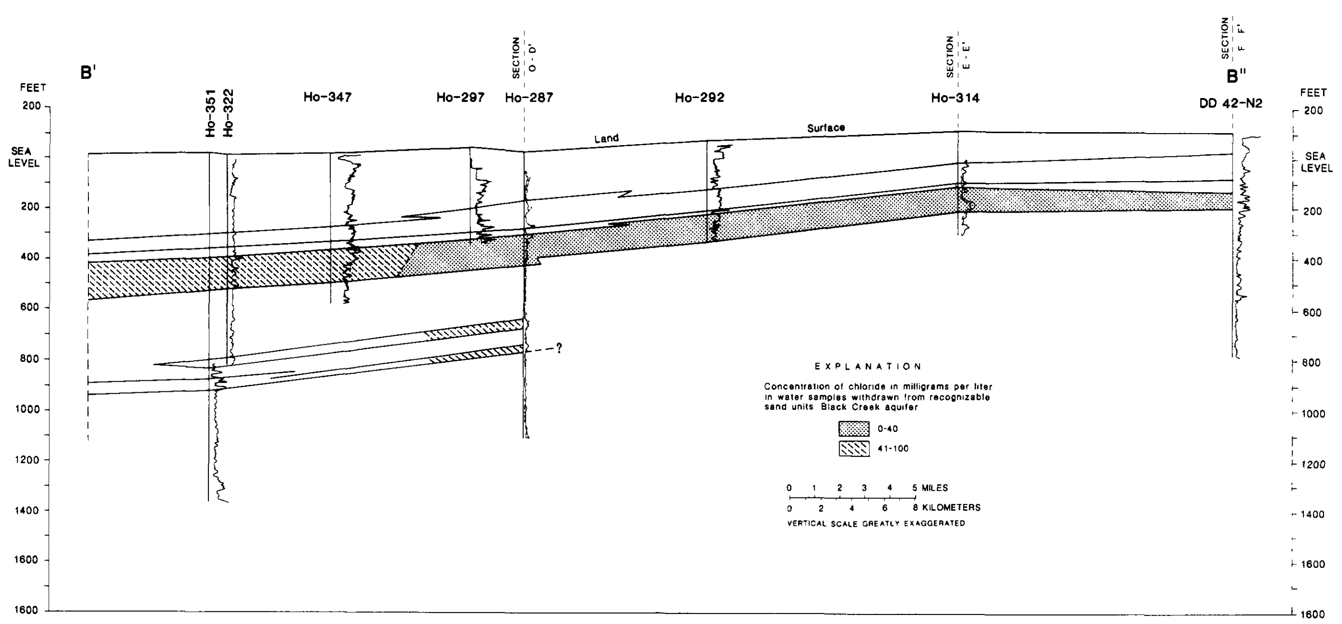

Figure 9. Geohydrologic cross section B'–B'' showing the known and inferred locations of the zone of dispersion and diffusion in the Black Creek aquifer of Horry and Georgetown Counties, South Carolina, and vicinity.

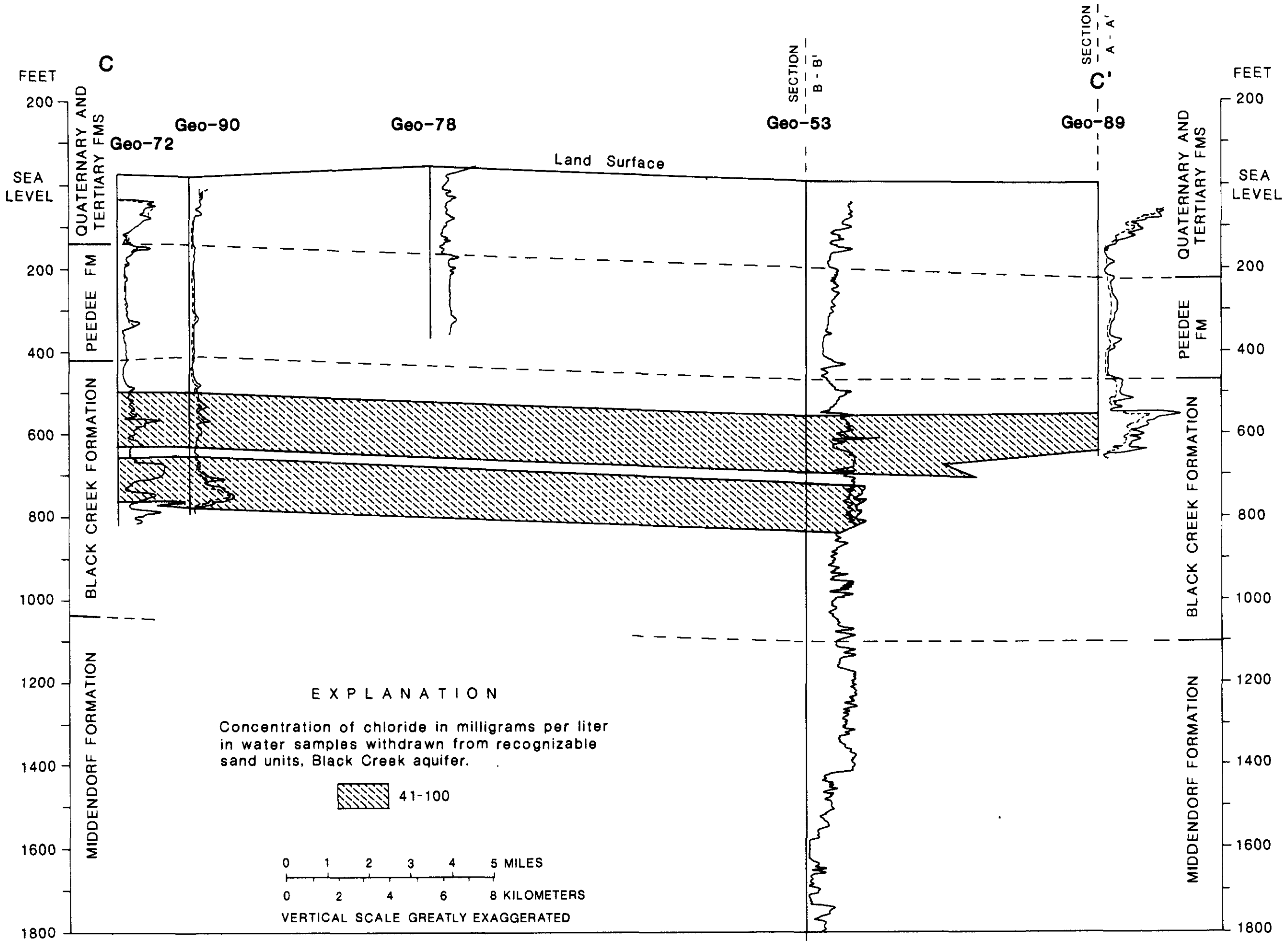

Figure 10. Geohydrologic cross section C–C' showing the known an inferred locations of the zone of dispersion and diffusion in the Black Creek aquifer of Georgetown County, South Carolina.

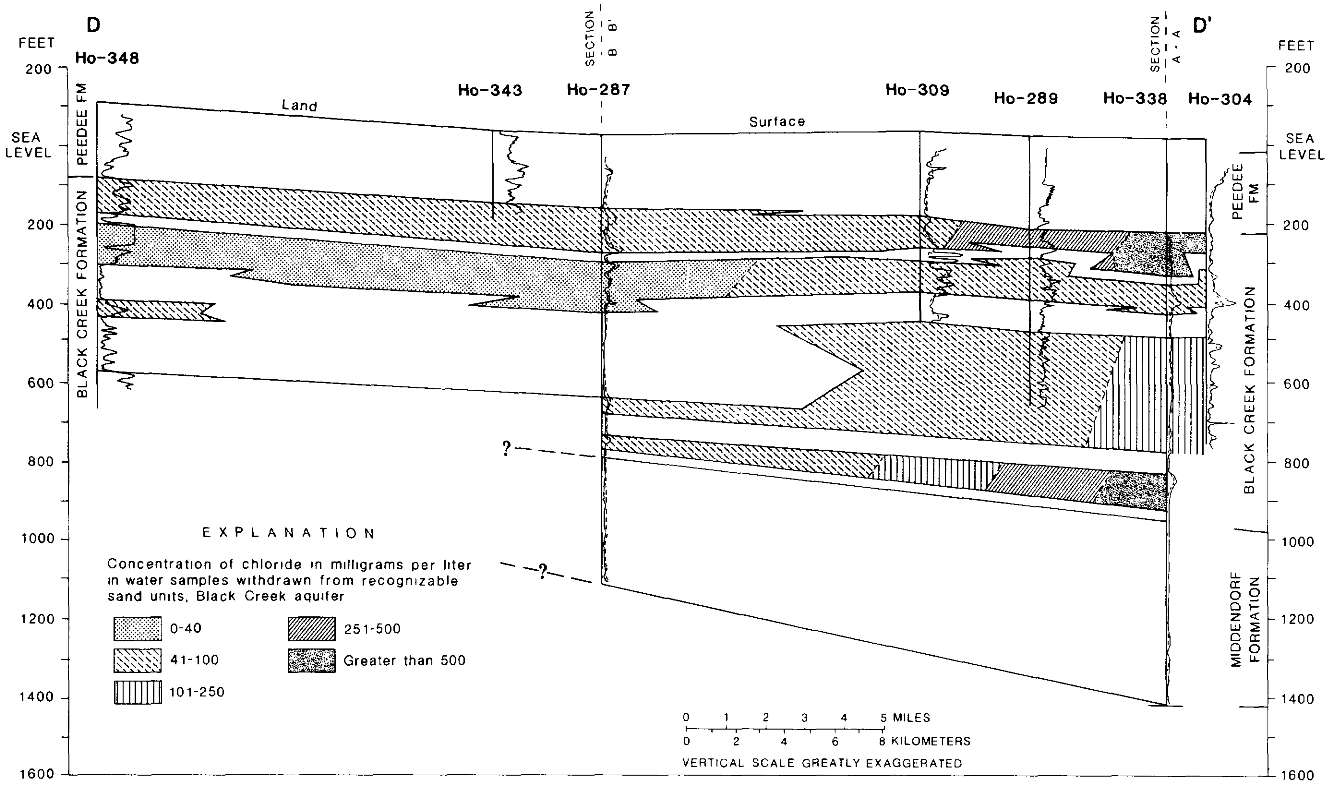

Figure 11. Geohydrologic cross section D-D′ showing the known and inferred locations of the zone of dispersion and diffusion in the Black Creek aquifer of Horry County, South Carolina.

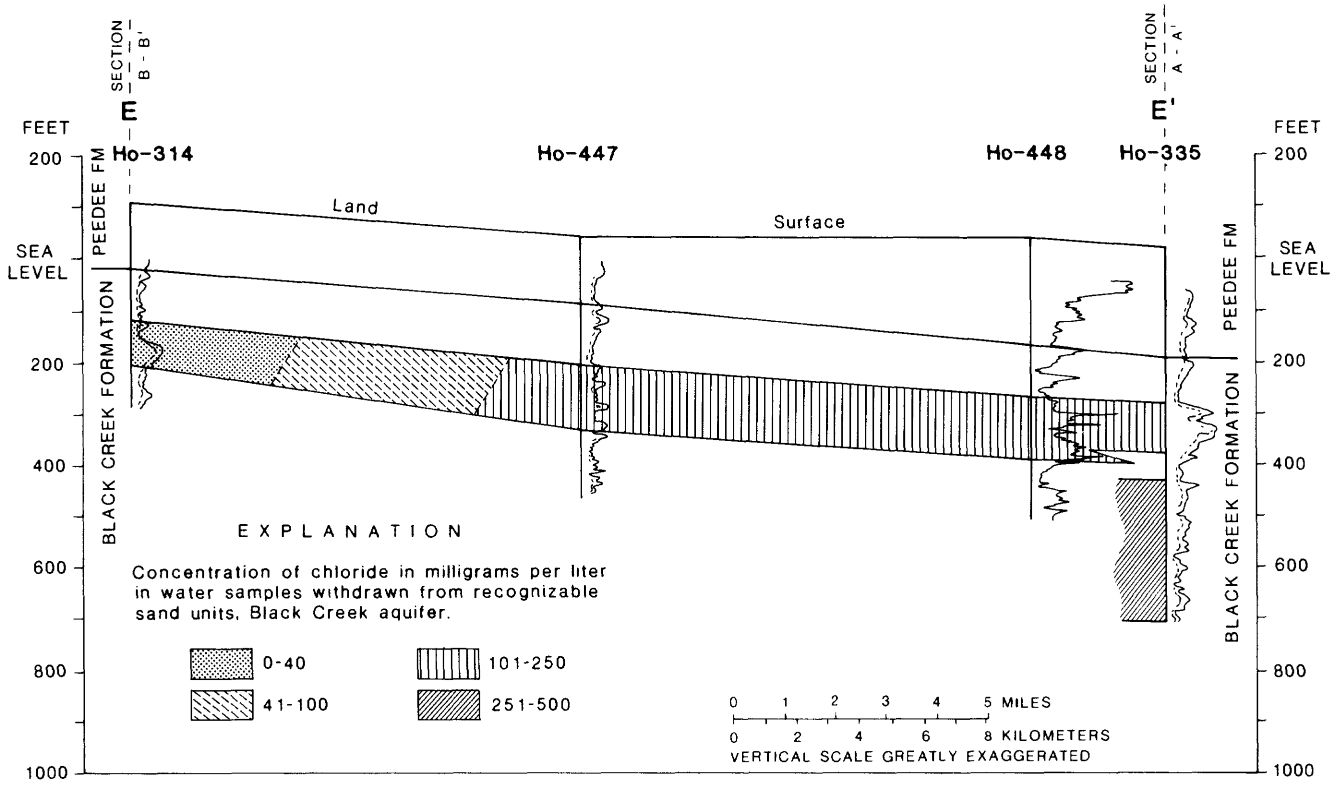

Figure 12. Geohydrologic cross section E-E′ showing the known and inferred locations of the zone of dispersion and diffusion in the Black Creek aquifer of Horry County, South Carolina.

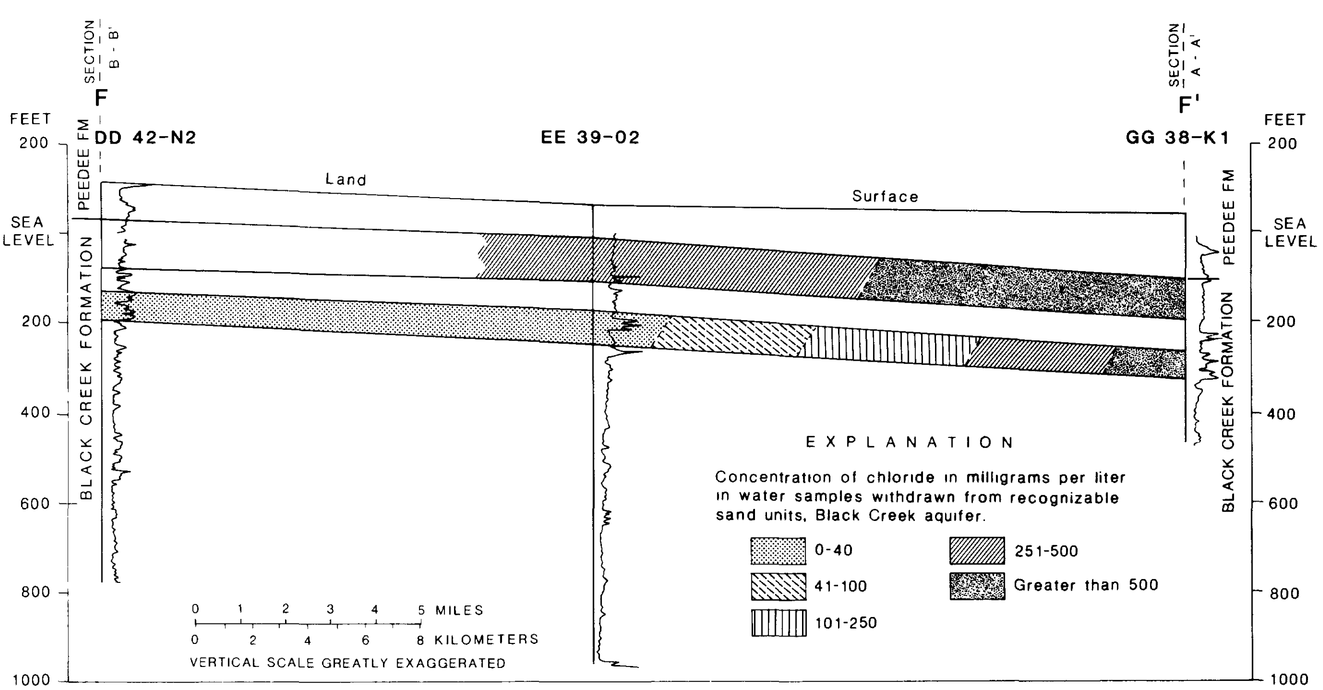

Figure 13. Geohydrologic cross section F–F′ showing the known and inferred locations of the zone of dispersion and diffusion in the Black Creek aquifer in adjacent counties in North Carolina.

marine clays, common throughout the Black Creek Formation, exchange sodium for calcium ions. The clays originally were in geochemical equilibrium with the ancient seawater that occupied the pore spaces. It is presumed that both the ancient seawater and the clay had a sodium to calcium ratio near that of modern seawater, 26:1 in milligrams per liter. The following reaction includes both the calcium carbonate dissolution reaction and the prevailing exchange reaction where sodium-rich clays are present:

$$CaCO_3 + Na_2(clay) + CO_2 + H_2O \rightarrow 2Na^+ + 2HCO_3^- + Ca(clay) \qquad (2)$$

The mole ratio of sodium to bicarbonate produced by these reactions is 1:1, nearly the same as that observed from chemical analyses (fig. 16).

Ground water in upgradient areas is relatively low in sodium. As the water moves downdip, carbon dioxide is encountered in the system dissolving calcite and producing bicarbonate and calcium ions. The calcium ions are exchanged for sodium ions on clay surfaces. As the calcium concentration is diminished by exchange, the solution becomes undersaturated with respect to calcite causing more calcite to dissolve, increasing bicarbonate concentrations, and more sodium to be released from clays through further cation exchange. The amount of calcium in solution is not controlled solely by the solubility of calcium carbonate because the water is undersaturated

Table 1. Selected anions and cations and the saturation indices (SI) for calcite calculated from WATEQ

[Analyses are for water samples withdrawn from the Black Creek aquifer]

Well	Anion and cation concentrations, in milligrams per liter				pH	Saturation index of calcite[1]
	Chloride	Sodium	Calcium	Bicarbonate		
HO-305, Pirate Cove	67	300	2.0	710	8.2	-0.22
GEO-108, Pawleys Island	35	270	2.2	700	8.3	- .11
GEO-63, Georgetown fire tower	27	210	2.0	480	8.4	- .18
HO-334, Baytree	280	460	4.8	750	8.1	- .10
HO-287, Conway no. 4	88	240	1.9	480	8.3	- .30
HO-431, Loris, John Deere	15	130	2.4	330	8.2	- .50
Little River	440	560	6.3	714	8.0	0

[1] Saturation index is log $I_{ap}/K_{(T)}$ where I_{ap} is the ionic activity product and $K_{(T)}$ is the mineral solubility product at the specified temperature.

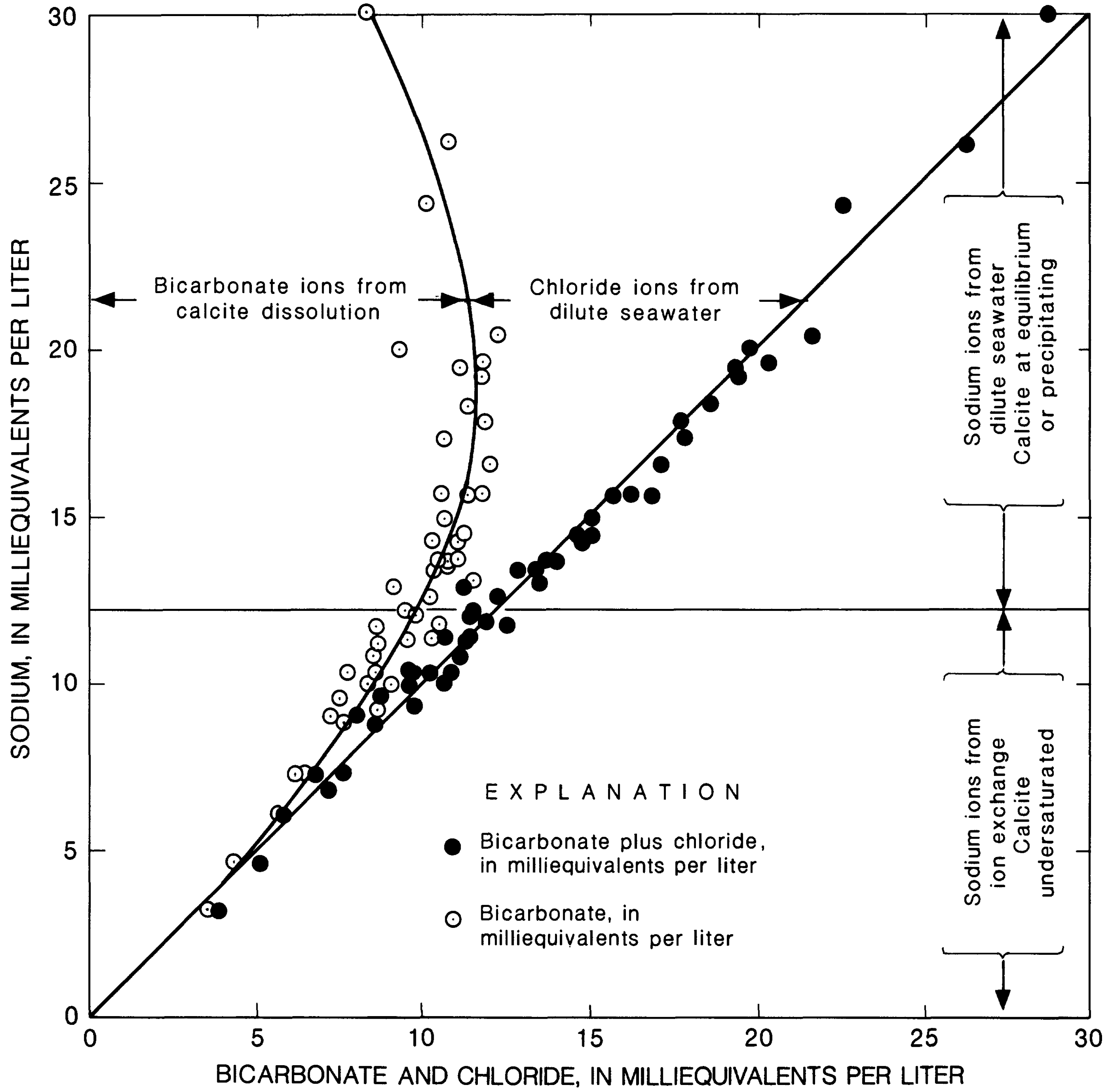

Figure 14. Relation of equivalent concentrations of bicarbonate and chloride to sodium in water samples withdrawn from the Black Creek aquifer.

with respect to calcium carbonate. The amount of calcium in solution is limited by the mass action of the system which includes both calcite dissolution and cation exchange. In fact, the cation-exchange reaction/calcite-dissolution process has been shown to be dominant based on enrichment of $\delta^{13}C$ isotope values of the inorganic carbon in solution which is attributable to dissolved calcite (R.W. Lee, written commun., 1983).

The passage of calcium-rich water downgradient through sediments containing sodium-rich clay has increased calcium and reduced sodium on clay surfaces. If the exchange reaction would be permitted to go to completion without being fueled by calcium from subsequent dissolution of calcium carbonate, the exchange reaction between the solution and the clays would reach equilibrium (fig. 17); the proportion of sodium and calcium in

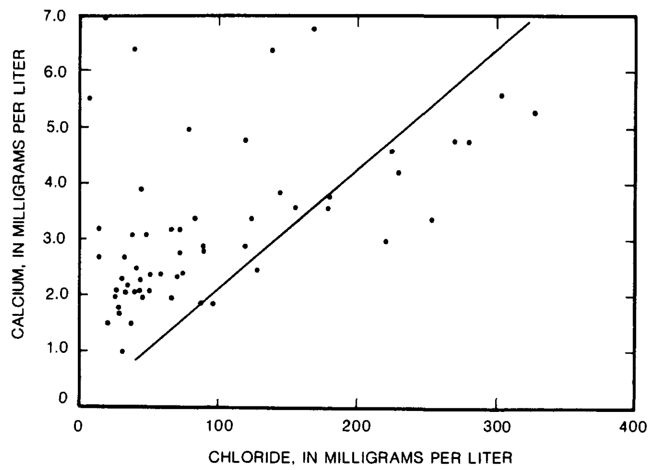

Figure 15. Relation of calcium to chloride in water from the Black Creek aquifer.

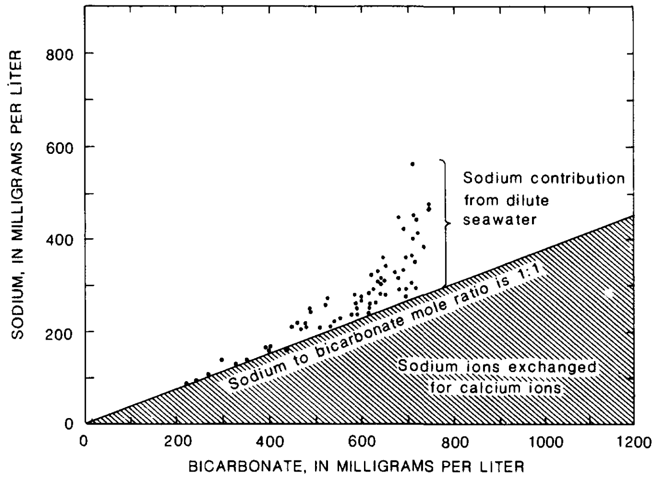

Figure 16. Relation of sodium to bicarbonate in water from the Black Creek aquifer and the mole ratio of sodium to bicarbonate produced by calcium carbonate dissolution and subsequent cation-exchange reactions.

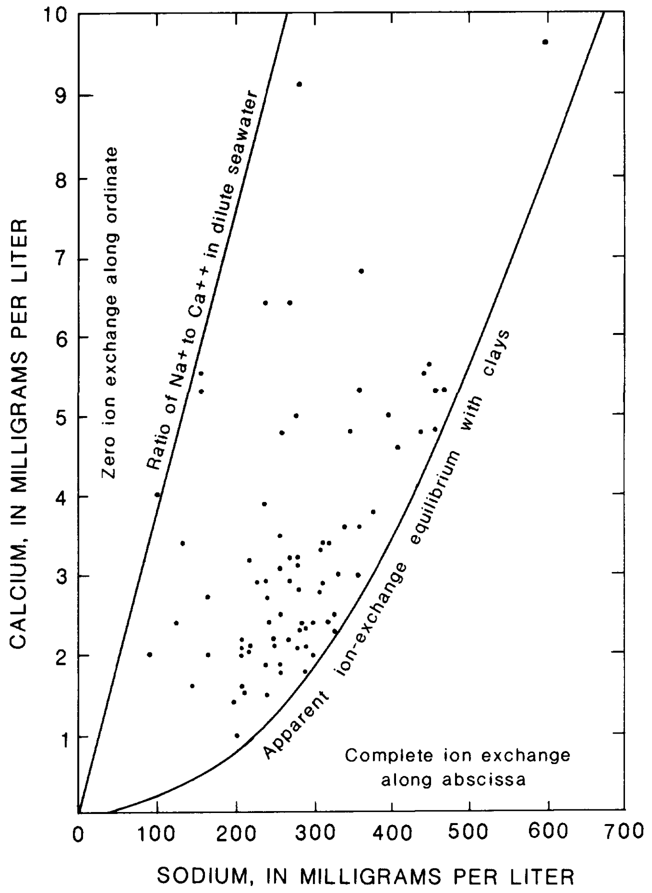

Figure 17. Relation of calcium to sodium in water samples withdrawn from the Black Creek aquifer, showing control on concentration limits imposed by cation-exchange equilibrium.

solution would balance the proportion of exchangeable sodium and calcium ions on the clay surfaces. The dynamic sodium bicarbonate enrichment process continues downgradient until seawater is encountered in the aquifer sands. As the amount of seawater increases downgradient, the slope of the cation-exchange equilibrium boundary approaches the slope representing the approximate ratio of sodium to calcium in seawater (26:1, in milligrams per liter) (fig. 15). The shift in the ion-exchange equilibrium line from that of modern dilute seawater results from the exchange of sodium for calcium upgradient of the study area. Downgradient, where dilute seawater occurs, the proportion of sodium to calcium at exchange sites on the clays (previously at equilibrium with the original pore fluids) now is in contact with water having a larger ratio of sodium to calcium. Accordingly, calcium ions are released from the clays to the aquifer and sodium ions removed from the water through the following "reverse" cation-exchange reaction:

$$2Na^{+} + Ca(clay) \rightarrow Ca^{++} + Na_2(clay) \qquad (3)$$

The reaction proceeds until the sodium to calcium ratio of the aqueous solution balances the sodium to calcium ratio of the clays along the cation-exchange equilibrium curve of figure 17.

The cation-exchange reaction thus approaches an equilibrium which represents a mass-action limit; change in the concentration of sodium and calcium due to exchange is insignificant. The calcium ions in solution increase according to equation 3. As the solution approaches calcite equilibrium, aqueous calcium ion no longer increases because calcite dissolution ceases, and bicarbonate concentration reaches an approximate upper limit of 750 mg/L. Accordingly, the Na:HCO_3 mole ratio of 1:1 produced by the calcite dissolution and cation-exchange process (equation 2) suggests that cation exchange is diminished at approximately 280 mg/L of sodium (figs. 2, 14, and 17), the molar equivalent of

750 mg/L bicarbonate. Therefore, sodium concentrations greater than 280 mg/L are considered to be derived from dilute seawater.

If seawater simply mixes with the ground water, concentrations of sodium and calcium that are higher than those observed should result. Mineral solubilities applied to the available water-quality data for the Black Creek aquifer indicate that such an increase of aqueous calcium ion would exceed calcite saturation under these conditions, even with the higher ionic strength of the mixture. The observed concentrations of both calcium and bicarbonate are lower than calculated in the freshwater-seawater mixtures, apparently because of precipitation of calcite. The approximate locations of the cation exchange and calcite solubility boundaries in terms of concentration of bicarbonate and calcium at constant pH in the Black Creek aquifer are shown in figure 18.

The dissolution of calcite cement in the Black Creek aquifer exposes fossil shark teeth to interstitial waters. Fluoride ions contained in the shark teeth are released to the ground water through anion exchange with hydroxyl ions (Zack, 1980, p. 31):

$$\underset{\substack{\text{(fluorapatite)}\\ \text{(fossil shark teeth)}}}{Ca_5(PO_4)_3F} + OH^- \rightarrow \underset{\text{(hydroxylapatite)}}{Ca_5(PO_4)_3OH} + F^- \qquad (4)$$

In the Black Creek aquifer, ion exchange (sodium for calcium and fluoride for hydroxyl) proceeds concurrently with dissolution reactions (producing calcium, bicarbonate, and hydroxyl). Calcite saturation occurs in those parts of the Black Creek aquifer where dilute seawater permits a higher concentration of calcium ions to remain in the water because of increased ionic strength. Therefore, no additional calcite dissolves. The sequence of geochemical reactions is:

Where $Na^+ < 280$ mg/L; $Na^+/Ca^{++} <$ clay Na/Ca ,

$$CaCO_3 + Na_2(\text{clay}) + CO_2 + H_2O \rightarrow 2Na^+ + 2HCO_3^- + Ca(\text{clay}),$$

and $$Ca_5(PO_4)_3F + OH^- \rightarrow Ca_5(PO_4)_3OH + F^-.$$

Where $Na^+ = 280$ mg/L; $Na^+/Ca^{++} =$ clay Na/Ca,

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca^{++} + 2HCO_3^-,$$

and $$Ca_5(PO_4)_3F + OH^- \rightarrow Ca_5(PO_4)_3OH + F^-.$$

Where $Na^+ > 280$ mg/L; $Na^+/Ca^{++} >$ clay Na/Ca,

$$2Na^+ + Ca(\text{clay}) \rightarrow Ca^{++} + Na_2(\text{clay}),$$
$$Ca^{++} + 2HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O,$$

and $$Ca_5(PO_4)_3OH + F^- \rightarrow Ca_5(PO_4)_3F + OH^-.$$

In areas where dilute seawater occurs ($Na^+ > 280$ mg/L), higher calcium concentrations limit calcium carbonate dissolution, thus limiting exposure of fossil shark teeth to interstitial waters. Therefore, in the Black Creek aquifer, areas which have never been completely flushed of ancient seawater (parts of North and South Carolina) contain less fluoride than areas of the aquifer which have been flushed by freshwater.

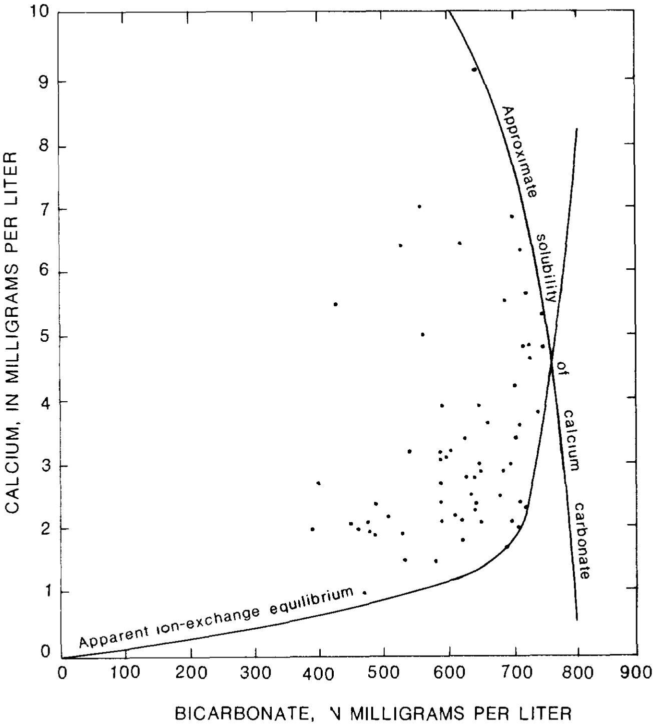

Figure 18. Relation of calcium to bicarbonate in water from the Black Creek aquifer.

SUMMARY

Water containing relatively high concentrations of sodium and chloride occurs in parts of the Black Creek aquifer of Horry and Georgetown Counties, South Carolina. In these areas, the aquifer contains incompletely flushed seawater, diluted by advancing meteoric water into a wide zone of dispersion and diffusion.

Ion-exchange reactions (sodium for calcium and fluoride for hydroxyl), which occur with the calcium carbonate dissolution reaction, proceed at or near their respective phase boundaries, producing calcium, bicarbonate, and hydroxyl ions. The reaction sequence and stoichiometry result in an aqueous solution in which the sum of bicarbonate and chloride in equivalents per liter is equal to the equivalents per liter of sodium.

Calcium ions are exchanged for sodium ions from sodium-rich clays until dilute seawater is encountered in the aquifer. The cation-exchange reaction attains equilibrium at a sodium concentration of 280 mg/L. Amounts of sodium greater than 280 mg/L are contributed from seawater. In these areas of the aquifer, a "reverse" cation-exchange reaction proceeds in which calcium ions are released from clays and sodium ions removed from solution. Both forward and "reverse" cation-exchange reactions approach an equilibrium which represents a mass-action limit in terms of the ratio of sodium to calcium in solution versus the ratio of exchangeable sodium to calcium on clay surfaces. In areas where the aquifer contains dilute seawater, calcium carbonate saturation is reached, calcite dissolution ceases, and precipitation of calcite is likely.

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