

**HYDROGEOCHEMISTRY OF MAJOR AND TRACE ELEMENTS IN GROUND
AND SURFACE WATER IN THE NEW JERSEY PINE BARRENS**

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ABSTRACT

Hydrogeochemistry of Major and Trace Elements of Ground and Surface Water in the New Jersey Pine Barrens

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This study investigates major and trace element geochemistry of ground and surface water in the New Jersey Pine Barrens (around Wharton State Forest). The chemical composition of dissolved species of Cohansey Formation groundwater differs from that of the underlying Kirkwood Formation. The difference implies that groundwater from the two formations has different sources, geochemical processes and flow patterns and that cross-formational flow between them is minor. The source of iron in bog iron deposits in the New Jersey coastal plain is thus not from cross-formational flow from a deeper formation, but from within the Cohansey Formation. Chemistry of Cohansey groundwater is mainly controlled by precipitation (rain and snow) with limited water:rock reactions. Solute in Kirkwood groundwater are mostly derived from water:rock reactions because Kirkwood groundwater is controlled by regional flows that have long residence

time. The presence of clay and other confining layers contributes to the heterogeneity of groundwater composition, even over short distances. Most well waters did not show seasonal variations in composition because groundwater has residence time longer than a year.

Stream water is similar to Cohansey groundwater in major element composition, which shows that stream and shallow groundwater are both dominated by precipitation composition and that there is extensive recharge interchange between them. The low pH values of surface water (average 4.5) and Cohansey groundwater (average pH = 5.3) appear to be affected by acid rain in this region. High pH of Kirkwood groundwater (average 8.3) is caused by water:rock reactions in the Kirkwood Formation. Na^+/Cl^- in the Cohansey groundwater has a ratio (0.577) close to that in seawater (0.55), indicating Na^+ and Cl^- are from marine aerosols. When pH is greater than 4.8, aluminum concentration is consistent with controls by gibbsite or/and kaolinite solubility. However, when pH is less than 4.8, Al is undersaturated with these minerals. At low pH, Al activity is controlled by saturation with organic aluminum phases having low Al/COOH ratios.

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CHAPTER 1

INTRODUCTION

The Pine Barrens of the New Jersey Coastal Plain is a unique place for environmental geochemists who are interested in water quality of relatively pristine and undeveloped areas. Forested mostly with oak and pine trees, the Pine Barrens spans an area about 1500 square miles (3900 km²) and covers seven counties in southeastern New Jersey. Water in the Pine Barrens is one of the major resources of the New Jersey Coastal Plain.

Water chemistry in the Pine Barrens has been the subject of a number of previous studies. Rhodehamel (1970, 1973, 1979) did the most comprehensive investigations of the ground and surface water hydrology in the Pine Barrens. Kelsey and Kinsman (1971) conducted hydrological and geochemical studies of the Cedar and Oyster Creek basin in the northern part of the New Jersey Pine Barrens. Johnson (1979) concluded that the acid precipitation in the Pine Barrens was the cause of acidification of stream waters. Yuretich *et al.* (1981), Crerar *et al.* (1981) and Means *et al.* (1981) carried out a more extensive study of the geochemistry of precipitation and stream water in the Cedar Creek and the Mullica River. They also reported iron and aluminum concentrations and distributions in shallow groundwater in their study area. Recently, Jones (1994) did a detailed study of major element and trace element chemistry in precipitation and surface water of the Mullica River Basin. All these studies have focused on surface water chemistry or

groundwater resource availability. Little has been done on the groundwater chemistry, except a recent water quality investigation in the McDonalds Branch Basin (Johnsson and Barringer, 1993), a small watershed in the northern Pine Barrens.

The purpose of this study is to investigate the solute chemistry of groundwater in the Cohansey and Kirkwood Formations in the Pine Barrens (particularly, in the Mullica River Basin). The specific objectives of the study are:

1. to compare groundwater chemistry of these two stratigraphic units and explain the differences and similarities;
2. to compare groundwater chemistry with surface water and precipitation chemistry to determine groundwater sources and composition controls;
3. to investigate geochemistry of aluminum, an important species in areas affected by acid rain;

Finally, this study will include a geochemical discussion of bog iron, the origin of which is not fully understood, but is at least partially related to the distribution of iron in groundwater.

CHAPTER 2

STUDY AREA

Location

The Wharton State Forest, which occupies most of the Mullica River Basin, is a very sparsely populated area in southern New Jersey's Pine Barrens (Figure 1). It is about 380 km² (150 mile²) in area and lies mostly in Burlington County with small portions in Atlantic and Camden Counties in New Jersey. Topographically, the State Forest is nearly flat and poorly drained with many swamps and slowly flowing rivers. Since the basin is located to the east of the main surface-water drainage divide, the Mullica River flows southeastward to join the Atlantic Ocean. Other rivers in the study area (Batsto River, Wading River and Oswego River (east branch of the Wading River)) are all tributaries to the Mullica River.

A number of factors make the Mullica River Basin an excellent place for hydrogeochemical studies. It is one of the largest drainage basins in the center of the Pine Barrens and contains most of the typical soils, and plant and animal species in the Pinelands. The Mullica River Basin, thus, can represent the Pine Barrens as a whole. Human activities and pollution within the park are minimal except for some recreational activities such as canoeing, camping and hunting. Because of its clean ground and surface waters, the Park was purchased by the State of New Jersey in 1954 as a water reserve. The importance of water quality in the Wharton State Park is self-evident.

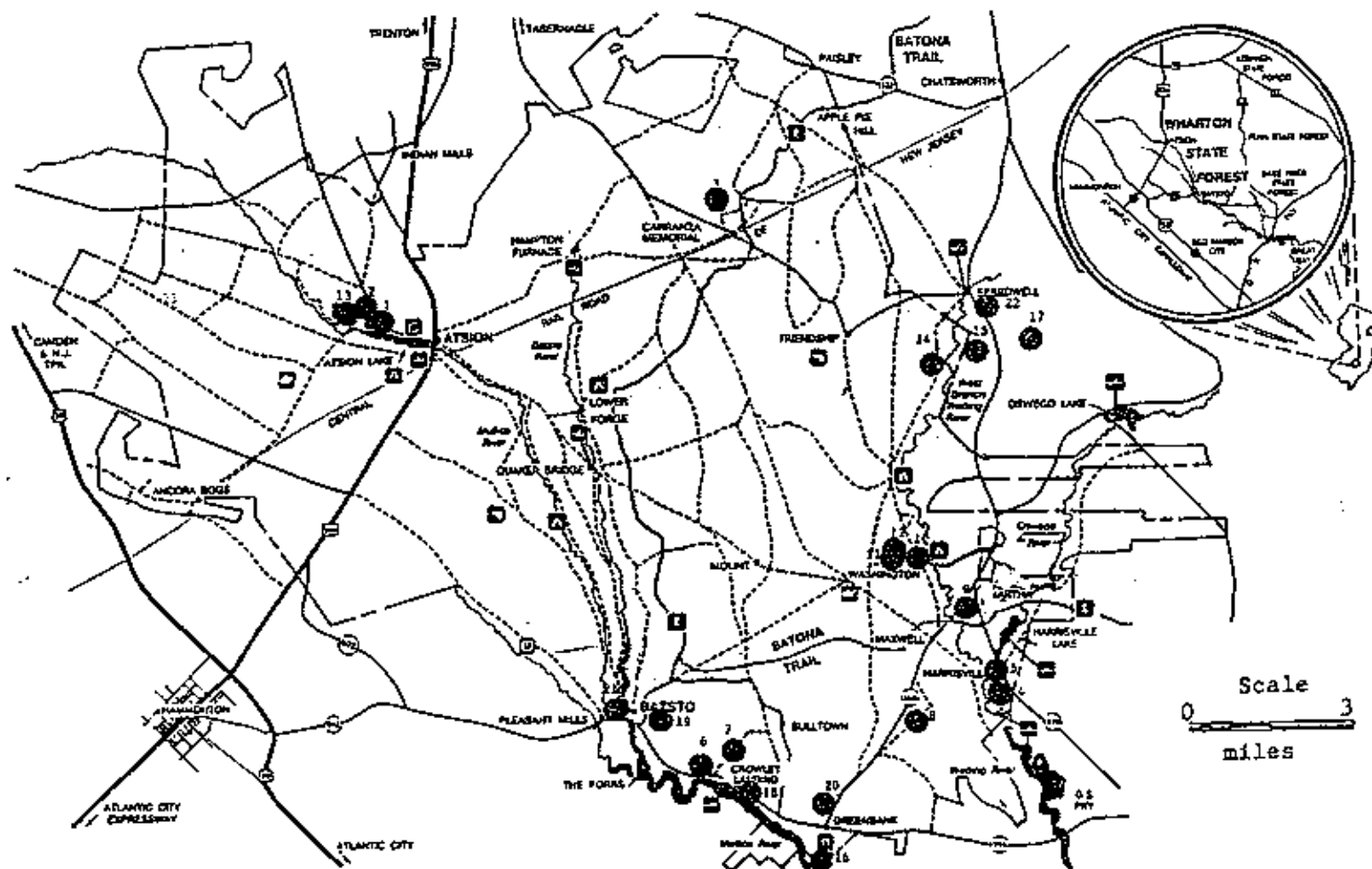


Figure 1. Map of the Wharton State Forest in the New Jersey Pine Barrens. Dots with numbers indicate groundwater sampling sites.

Geology

The stratigraphic unit exposed at the surface of most of the study area is the Cohansey Formation of either Miocene or Pliocene age. The age is not known precisely because of the lack of diagnostic fossils within the Cohansey Formation. The Cohansey is underlain by the Miocene Kirkwood Formation (Table 1). Each formation has a thickness of about 45 meters (150 feet) in the Park and dips and thickens southeastward toward the Atlantic Ocean. Both formations are made up of unlithified quartz sand containing carbonaceous clay and silt lenses and layers which form confining layers. These confining layers have important effects on the hydrogeochemistry of groundwater by altering flow paths and by providing mineral sources for ion exchange and other reactions.

The Cohansey Formation is composed dominantly of quartz sand (90%) with a minor amount of chert and ironstone pebbles and silt. In the laminated carbonaceous clay layers, the minerals are largely kaolinite and a very small amount of ilmenite. According to Rhodehamel (1973), the clay layers in the Cohansey comprise about 11% of the total lithology. The Cohansey sand crops out many places in the Wharton State Park; in other places it is overlain by a veneer of Tertiary Beacon Hill Gravel and Quaternary deposits.

The Kirkwood Formation, which does not crop out within the Park, contains mappable units of gravel, sand, silty sand, feldspathic sand and clay layers (Minard and Owens, 1962). The mineralogy of the Kirkwood Formation is very similar to that of the Cohansey Formation except that feldspar, which is almost absent in the Cohansey, is quite common in the Kirkwood Formation. In texture, the sand fraction in the Cohansey

Table 1. Summary of the stratigraphic section in the Mullica River Basin

System	Series	Formation	Thickness	Lithology	Hydrologic Characteristics
Quaternary	Holocene	undifferentiated deposits in stream channels, marshes, estuaries and bays.	0-3 m	Clay, sand, silt, bog iron and peat	Too thin to tap for water.
	Pleistocene	Cape May Formation	0-5 m	Clay, sand, silt and gravel	Highly permeable, hydrologically connected to underlying formations.
Bridgeton Formation		0-7 m	Clayey, feldspathic sand	hydrologically connected to underlying formations.	
Tertiary	Pliocene	Becon Hill Gravel	0-12 m	Interbedded sand and gravel	hydrologically connected to underlying formations.
	--- ? ---	Cohansey Sand	8-70 m	Coarse-grained sand, silt, thin beds of clay	Major aquifer. Excellent capacity to store and ability to yield water.
	Miocene	Kirkwood Formation	30-200 m	Very fine to coarse-grained sand, gravel and clay	Major aquifer with confining layers. Upper part of formation hydrologically connected to the Cohansey Sand.
	Eocene	Manasquan Formation	0-70 m	Clayey, fine-grained glauconitic quartz sand	Confining unit and minor aquifer.

Formation is usually coarser than that in the Kirkwood. The presence of feldspar, which has a more rapid dissolution rate, makes the Kirkwood groundwater more chemically reactive. On the other hand, the finer grain size of the Kirkwood sand lowers groundwater travelling time and yields a long residence time. Thus, a greater degree of water:rock reactions in the Kirkwood Formation is expected.

The contact between the two stratigraphic units is unconformable (Bascom *et al.*, 1909; Minard and Owens, 1963). In well samples, Rhodehamel (1973) observed a sharp boundary between the yellowish-orange colored oxidized Cohansey strata and the light- to dark-gray Kirkwood strata and suggested a wide spread unconformity between them. A blocky iron-oxide zone was observed at a number of locations at the Cohansey-Kirkwood contact (Rhodehamel, 1973).

Hydrology

Although the hydrologic features of the Kirkwood Formation in the Mullica River basin are poorly understood, it is generally believed that the Cohansey and the upper Kirkwood Formations are hydrologically connected to form a large Kirkwood-Cohansey aquifer system. The aquifer system extends downward to a diatomaceous clay unit (a thick clay bed which dips and thickens southeastward) that separates the upper Kirkwood from the lower Kirkwood. The lower Kirkwood Formation is called the "Atlantic City 800-foot sand", where it is tapped for drinking water by coastal cities.

According to the research of Rhodehamel (1973), the hydraulic conductivity in the Cohansey Formation varied from under 30 cm/day in the clay layers to about 30 m/day

in the fine to medium sand. The hydraulic conductivity in the Kirkwood sand is less known. A laboratory determination (Rhodehamel, 1973) gave a value of 72 cm per day. In the study of Harbaugh and Tilley (1984), the simulated horizontal hydraulic conductivity of the aquifer system is about 15 m/day in most part of the basin, about 10 m/day in the northeastern basin and about 5 m/day in the mid- to eastern part of the basin.

The water table is about 30 meters above sea level in the northwestern part of the Mullica Basin, 50 meters in the northeastern part, and at about sea level in the southeastern of the basin, where the Mullica River drains into the ocean. The potentiometric surface elevation of the Kirkwood Formation is generally less than 30 meters in the north of the basin and reduces to about sea level at the southeast (Rhodehamel, 1973). A detailed comparison between the water-table contour map of the Cohansey Formation (Harbaugh and Tilley, 1984) and the potentiometric surface elevation map of the Kirkwood Formation (Rhodehamel, 1973) reveals that the potentiometric surface is generally 5 meters below the water table. In the absence of major gradients, there is little impetus for cross-formational flow from the Kirkwood to the overlying Cohansey Formation.

CHAPTER 3

METHODS OF INVESTIGATION

Water samples were collected monthly in the Wharton State Forest, New Jersey (Figure 1), starting in May 1995 and ending in April 1996. Surface water samples were collected from the Batsto River, Oswego River, West Wading River and Mullica River (Table 2). Groundwater samples were collected from 10 campsite pumps in the Wharton State Forest, 3 artesian wells, 2 pumphouses in the Park, 3 pumping wells from a cranberry farm northeast of the Park, and 4 household faucets without disinfectant or water softener systems (Table 3). Depths of these wells range from 10 meters to 60 meters. Depths to water table are not generally known for these wells. The estimated depth of the bottom of the Cohansey Formation in this study is 50 meters. Therefore, most of the sampling wells are in the Cohansey Formation.

Table 2. Locations of surface water sampling sites

Stream	Location
Batsto	Rt. 542 at the gauging station
Mullica	Rt. 206 at the Atsion Lake
Wading	Rt. 563 near the bridge
Oswego	Rt. 679 at the gauging station

Table 3. Locations and parameters of the sampling wells

#	Well	Location	Longitude	Latitude	Depth (m)
1	Atsion	Atsion Lake camp	74°43'47.56"	39°44'25.24"	33
2	Atsion2	Atsion Lake camp	74°43'47.56"	39°44'25.24"	M *
3	Batona	Batona camp	M	M	11
4	Bodine	Bodine Field artesian on Rt.679	74°31'19.70"	39°39'45.08"	M
5	Bodine2	Bodine Field camp	74°31'19.70"	39°39'45.08"	11
6	CL1	Clowley's landing camp	74°37'05.15"	39°37'37.39"	50
7	CL2	Clowley's landing pumphouse	74°37'05.15"	39°37'37.39"	M
8	CML	Cookie Monster lane on Rt. 563	74°34'11.04"	39°37'45.40"	15
9	Egghar	in a house on Rt. 563	74°32'47.52"	39°40'09.30"	8
10	GD1	Godfrey bridge camp	74°32'49.07"	39°41'21.52"	11
11	GD2	Godfrey bridge camp	74°32'57.70"	39°41'16.16"	11
12	GD3	Godfrey bridge camp	74°33'03.27"	39°41'17.88"	11
13	Goshen	Goshen Pond camp (Atsion Lake)	M	M	11
14	Hawkin	Hawkins Bridge camp	M	M	38
15	JW	Cranberry farm on Rt. 563	M	M	64
16	Lovers	Lovers' Lane on Rt. 542	74°35'00.58"	39°36'38.38"	12
17	OS	Cranberry farm on Rt. 563	M	M	56
18	S1	an artesian well on Rt. 542	74°36'34.53"	39°37'30.53"	21
19	S2	pumphouse in the Batsto village	74°38'54.91"	39°38'44.08"	60
20	Setter	in a house on Rt. 563	74°34'37.10"	39°37'02.71"	13
21	Super	an artesian well in the Batsto village	74°39'07.85"	39°38'38.67"	M
22	WT	Cranberry farm on Rt. 563	M	M	60

* Note: M - missing measurements.

All water samples were collected in polyethylene bottles which had been cleaned with dilute perchloric acid for 12 hours. The bottles were rinsed thoroughly with distilled, deionized water and then rinsed with river water or groundwater before each filling. Surface water samples were collected below the water surface to avoid the effect of surface films. Groundwater was sampled after flushing the well for several volumes of the well (about 5 minutes) to ensure the samples were from the aquifer, not from water stored within the wells.

At each locality, two bottles of water were collected after being filtered with 0.45 μm Millipore™ filters. One bottle was acidified with 0.5 ml of Ultrex™ grade nitric acid to prevent precipitation of solids. Water samples were stored in a refrigerator and analyzed within days.

Eh, pH, temperature and alkalinity were measured in the field. pH was determined using a Orion® Sure-flow™ combination electrode and Digi-Sense® digital pH/mv/ORP meter. Eh was determined using a Corning redox combination electrode on a Markson model 93 digital pH/mv meter. Alkalinity was determined using the Hech titration package to pH 5.1 when alkalinity was less than 30 ml/l of CaCO_3 , and to pH 4.8 when alkalinity reading exceeded 30 ml/l of CaCO_3 .

In the lab, major cations, Na^+ , Mg^{2+} , Ca^{2+} , K^+ , total Fe and Mn, and silica concentrations in water were determined using a Perkin-Elmer Model 3030 Atomic Absorption flame Spectrophotometer. Dissolved aluminum was determined using the HGA graphite furnace attached to this instrument.

Major anions (Cl^- , SO_4^{2-} , NO_3^- , PO_4^{3-} and F^-) were determined in the unacidified

water samples using a Dionex Model 14 Ion Chromatograph (IC). The eluent solution used for IC was four liters of NaHCO_3 - Na_2CO_3 solution (prepared by dissolving 0.9 grams of NaHCO_3 and Na_2CO_3 in 4 liters of double distilled water). The regenerant solution for IC was dilute sulfuric acid (1 ml of concentrated sulfuric acid per liter of double distilled water). Cl^- , SO_4^{2-} and F^- were measured using a strip chart recorder with 0.2 volt scale; NO_3^- and PO_4^{3-} were determined under 20 mv scale. Since F concentrations were so low in water samples that the water dip totally covered the fluoride peak, 50 μl of NaHCO_3 - Na_2CO_3 solution (concentration same as the eluent) was used for every 10 ml of samples to cancelled the water dip.

Dissolved Organic Carbon (DOC) were determined using a Dohrmann-Xertex IR Carbon Analyzer. The eluent solution for DOC Analyzer was 20 grams of potassium persulfate and 1 ml of concentrated H_3PO_4 dissolved in one liter of double distilled water. The 10 ppm carbon standard solution was made from potassium acid phthalate (KAP) by dissolving 0.212 g of KAP in 100 ml water followed by 1:100 dilution. In total, 25 samples of surface water and 75 samples of groundwater were collected. Altogether 1700 analyses of water quality were done. Results are in Appendix II and III.

Discharge data of rivers in the study area were obtained from the U.S. Geological Survey, Water Resources Division, Trenton, New Jersey. The geochemical computer program WATEQ4F2.0 (Ball & Nordstrom, 1991) was used to calculate concentrations of various dissolved ions and saturation indices of different minerals.

Experiments were done to determine the bound aluminum ratios (defined as the equivalents of organically bound aluminum per unit organic matter divided by the

equivalents of RCOOH per unit organic matter). Samples of humic muck were collected from seven sites in the Wharton State Forest (Table 4).

Table 4. Sampling sites for humic muck

Name	Location
Batsto	from the streambed of the Batsto River at the Batsto visitors' center on Rt. 542
Batsto 2	from a swamp near the Batsto visitors' center
Mullica	from a creekbed near the Mullica River at Batsto on Rt. 542
Wading	from the streambed of the Wading River on Rt. 563
Oswego	from the streambed of the Oswego River on Rt. 679
Bodine	from a swamp near an artesian well at the Bodine field camp on Rt. 679
Atsion	from the lakebed of the Atsion Lake on Rt. 206

To extract organic matter from the muck, samples were screened with water to pass through a 0.246 mm sieve (sieve #60). The residues were collected and were let stand for several minutes for them to separate into different density layers. The top layer was light-colored water with little suspended organic matter. The middle layer was black or brown (caused by the color of cedar trees) and rich in organic matter; the bottom layer was gray fine sand. To obtain the organics from muck samples, the top two layers were separated by decanting and filtrated through 0.25 mm filter paper. The separated organic matter was air-dried and divided into two fractions which were saved for analyses of organic aluminum and RCOOH. Organically bound aluminum was determined by extraction of 1.00 gram of organic matter with 50 ml of 0.5 M CuCl_2 (Hargrove *et al.*,

1984), followed by AAS analysis. To determine the RCOOH groups, the organic matter was treated with 2 M HCl acid for 24 hours to remove metallic cations and other soluble inorganic components, then rinsed repeatedly with deionized distilled water until no Cl ion was left in the filtrate, and was again allowed to air dry. The RCOOH groups were measured by titration of 1.00 g of HCl-treated organic matter in 100 ml 0.002 M CaCl₂ with 0.1 N NaOH to pH 7 under Argon (Cronan *et al.*, 1986). Titration was conducted in a round-bottom flask with three arms. One arm contained a pH electrode, another the buret tip, the third the Argon line. The sample was stirred during the titration using a magnetic stir bar. Base was added after the reading on the pH meter was stabilized (approximately at 1 ml per 7 minutes).

CHAPTER 4
MAJOR ELEMENT CHEMISTRY OF GROUND AND SURFACE
WATER IN THE PINE BARRENS

This chapter presents the solute chemistry of major species. Trace elements will be discussed in Chapters 5 and 6. Compositions of surface water and groundwater from the two stratigraphic units (the Cohansey and Kirkwood Formations) are discussed separately and then compared. Analyses of surface water and groundwater compositions are in Appendix II and III.

Cohansey Groundwater

Compositional Variation

Although the Cohansey Sand is often considered to be a fairly uniform coarse sand with minor clay (ca 10%), Cohansey groundwater has variable composition (Table 5). Solute sources and chemical reactions are the two major factors affecting variation in groundwater composition. More specifically, groundwater composition is controlled by composition of precipitation (containing marine and continental aerosols and pollution), by weathering processes (water:rock reactions), and by biochemical reactions in soil horizons.

Concentration of total dissolved solids (TDS) in the Cohansey Formation is as low

as 21.3 ppm, a value which is only slightly higher than the TDS composition in rivers in the Pine Barrens (around 20 ppm). The low TDS suggests that the amounts of chemical weathering and mineral dissolution in the Cohansey Formation is very limited, due to the inertness of quartz sand and the lack of weatherable minerals in the Cohansey Formation.

Table 5. Concentration ranges of major dissolved constituents in Cohansey groundwater

Constituents	Minimum	Maximum	Median
pH	3.83	6.10	5.30
TOC (ppm)	1.53	11.6	4.38
Na ⁺ (ppm)	0.87	9.34	2.02
Ca ²⁺ (ppm)	0.18	8.43	0.79
K ⁺ (ppm)	0.21	4.23	1.20
Mg ²⁺ (ppm)	0.05	2.66	0.55
SiO ₂ (ppm)	1.26	23.0	5.15
Cl ⁻ (ppm)	2.03	12.5	3.50
NO ₃ ⁻ (ppm)	< 0.001	4.25	0.02
SO ₄ ²⁻ (ppm)	0.35	11.7	6.58
PO ₄ ³⁻ (ppm)	< 0.004	0.04	0.01
F ⁻ (ppm)	< 0.01	0.55	0.07
Mn (ppm)	< 0.001	0.55	0.03

Precipitation carries marine aerosols, continental aerosols (soil dust), biological emissions and anthropogenic pollution in the Pine Barrens (Jones, 1994). Na⁺/Cl⁻ in rainwater is close to the ratio in seawater (Table 6), indicating that Na⁺ and Cl⁻ in rainwater come from marine aerosols. Other dissolved species in rainwater have much

higher ratios to Cl^- than those in seawater (Table 6), which suggests those species come mostly from soil dust, biological emission and air pollution.

Solute chemistry of Cohansey groundwater is mainly controlled by precipitation since most major dissolved species, such as Na^+ , Mg^{2+} , K^+ , SO_4^{2-} and PO_4^{3-} , have similar ratios to Cl^- in the groundwater as in the rainwater (Table 6). The Cl^- is used as reference because it does not usually participate in chemical reactions at these concentrations.

Table 6. Compositional comparison of Cohansey groundwater, rainwater in the Pine Barren and the average sea water, expressed as weight ratios to Cl^-

Items	Cohansey Groundwater	Rainwater (Jones, 1994)	Seawater*
Na^+/Cl^-	0.577	0.554	0.556
$\text{Mg}^{2+}/\text{Cl}^-$	0.157	0.152	0.067
K^+/Cl^-	0.343	0.393	0.021
$\text{Ca}^{2+}/\text{Cl}^-$	0.226	0.107	0.024
$\text{SO}_4^{2-}/\text{Cl}^-$	1.880	1.518	0.140
$\text{NO}_3^-/\text{Cl}^-$	0.0057	0.295	2E-7
$\text{PO}_4^{3-}/\text{Cl}^-$	0.003	< 0.001	5E-8
SiO_2/Cl^-	1.471	0.277	2E-5
TOC/Cl^-	1.251	0.982	2E-5

* Source: Drever, 1988.

The Na^+/Cl^- ratio in Cohansey groundwater is very similar to that of seawater and follows the marine aerosol trend (Figure 2). Therefore, the source of Na^+ and Cl^- appears to be largely sea salt that is brought in by precipitation. Sample data plotted above the marine aerosol trend line in Figure 2 contain excess Na^+ and may indicate a small amount

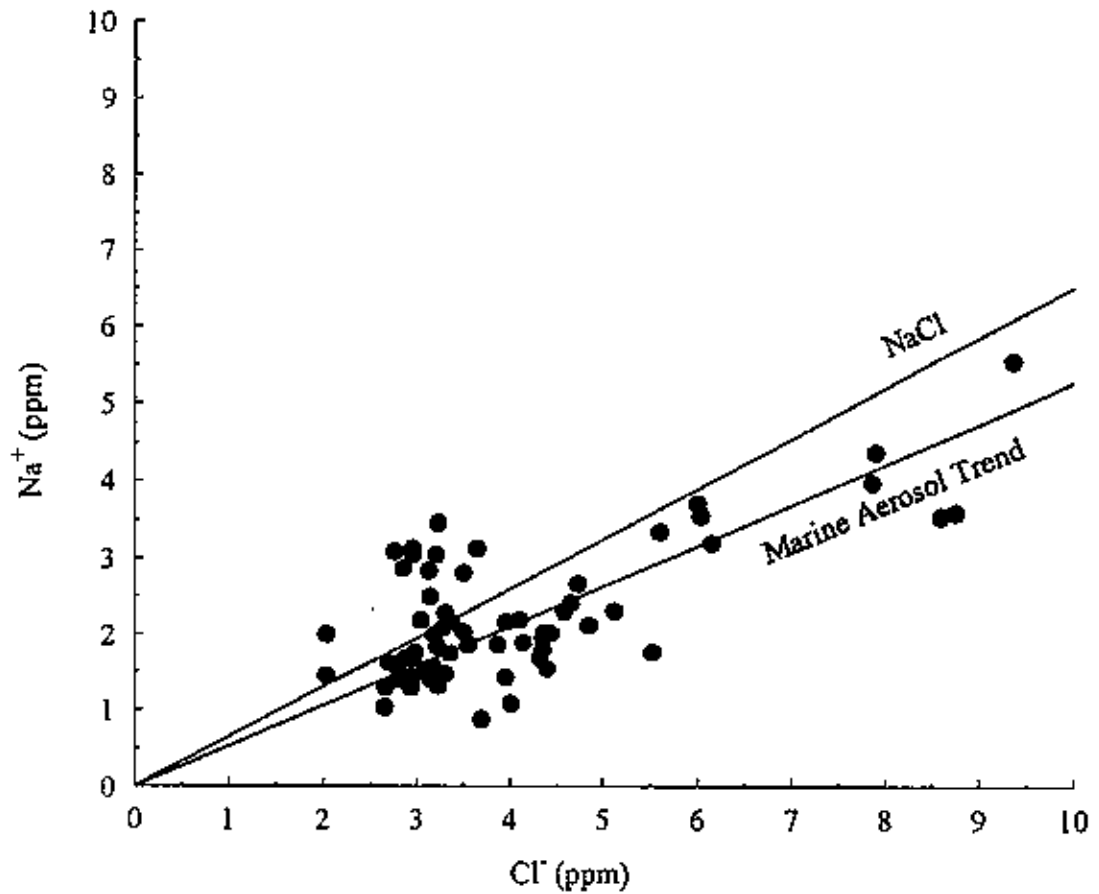
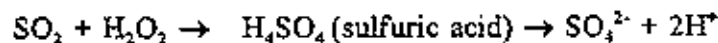
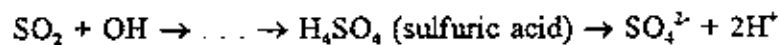


Figure 2. Na⁺ vs. Cl⁻ in Cohansey groundwater in the New Jersey Pine Barrens. Most data fall along the marine aerosol trend, indicating that the source of Na⁺ and Cl⁻ is from sea salt. Sample points that spread vertically above the marine aerosol trend at Cl⁻ concentration about 3 ppm demonstrate a small amount of water:rock reactions in the Cohansey Formation. Sample data are in Appendix II.

of water:rock reactions in the Cohansey Formation. The amount of Na^+ and Cl^- from marine aerosols usually shows geographic variations in precipitation and is usually greatest near the coast (e.g. Berner and Berner, 1987). In the Pine Barrens, Na^+ and Cl^- concentrations in Cohansey groundwater are highest near the coast (Figures 3 and 4), similar to concentration trends in precipitation (Yuretich *et al.*, 1981; Jones, 1994).

Other major dissolved species in Cohansey groundwater do not seem to be derived from sea-salt aerosols. The ratios of these ions to Cl^- are much higher than those in seawater (Table 6), suggesting other sources in precipitation contribute more to groundwater composition. Mg^{2+} and K^+ in the groundwater are derived mainly from continental aerosols and biogenic aerosols. K^+ is proved to be an important element emit from plants in the study area (M. Mandel, personal communication). Because this area is strongly affected by acid rain (pH = 4.3, Jones, 1994), both $\text{SO}_4^{2-}/\text{Cl}^-$ and $\text{NO}_3^-/\text{Cl}^-$ ratios are high in rainwater in the Pine Barrens. SO_2 , NO and NO_2 gases, which are emitted to the atmosphere during the combustion of fossil fuels (coal and oil), react with OH gas radicals or dissolve with H_2O_2 in cloud droplets and are rapidly converted to sulfuric acid or nitric acid (Berner and Berner, 1987). Since both sulfuric acid and nitric acid are strong acids, they dissociate quickly in rain water to form SO_4^{2-} , NO_3^- and H^+ :



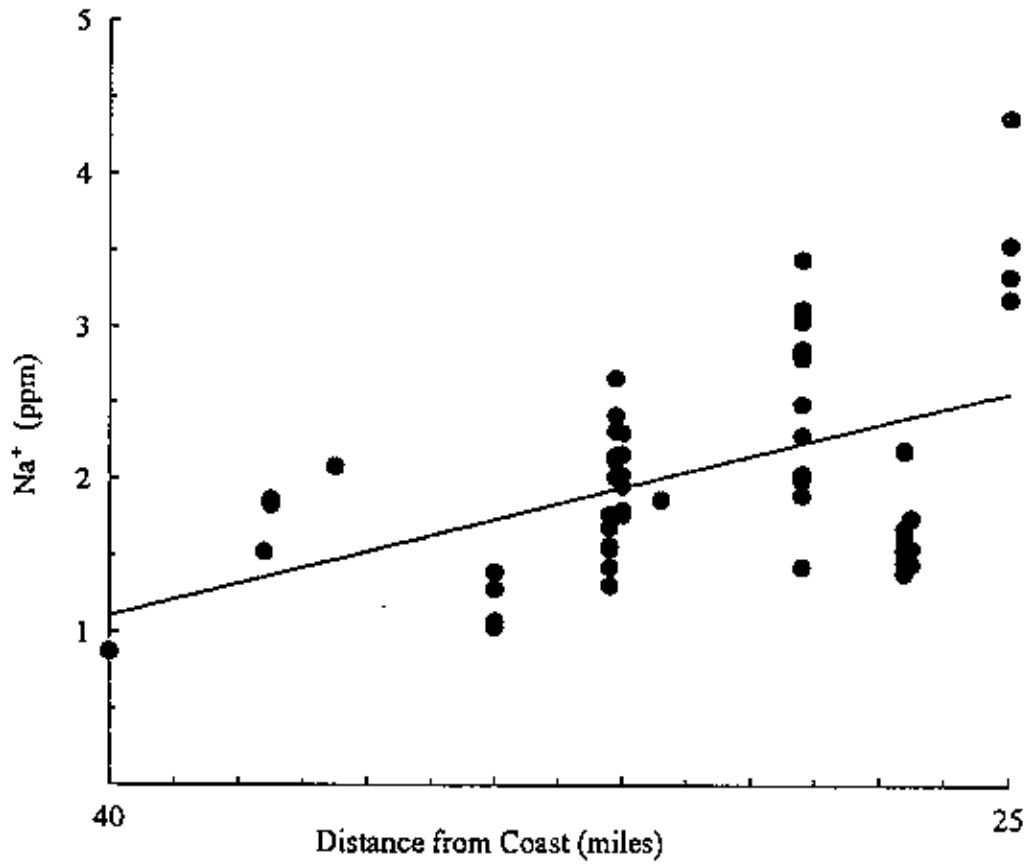


Figure 3. Na⁺ geographic distribution in Cohansey Groundwater in the New Jersey Pine Barrens. Na⁺ concentration increases from the west to the east toward the Atlantic Ocean. It confirms that the source of Na⁺ is marine aerosols. The variation in data is caused by spatial variation of Cohansey groundwater. See Figure 5.

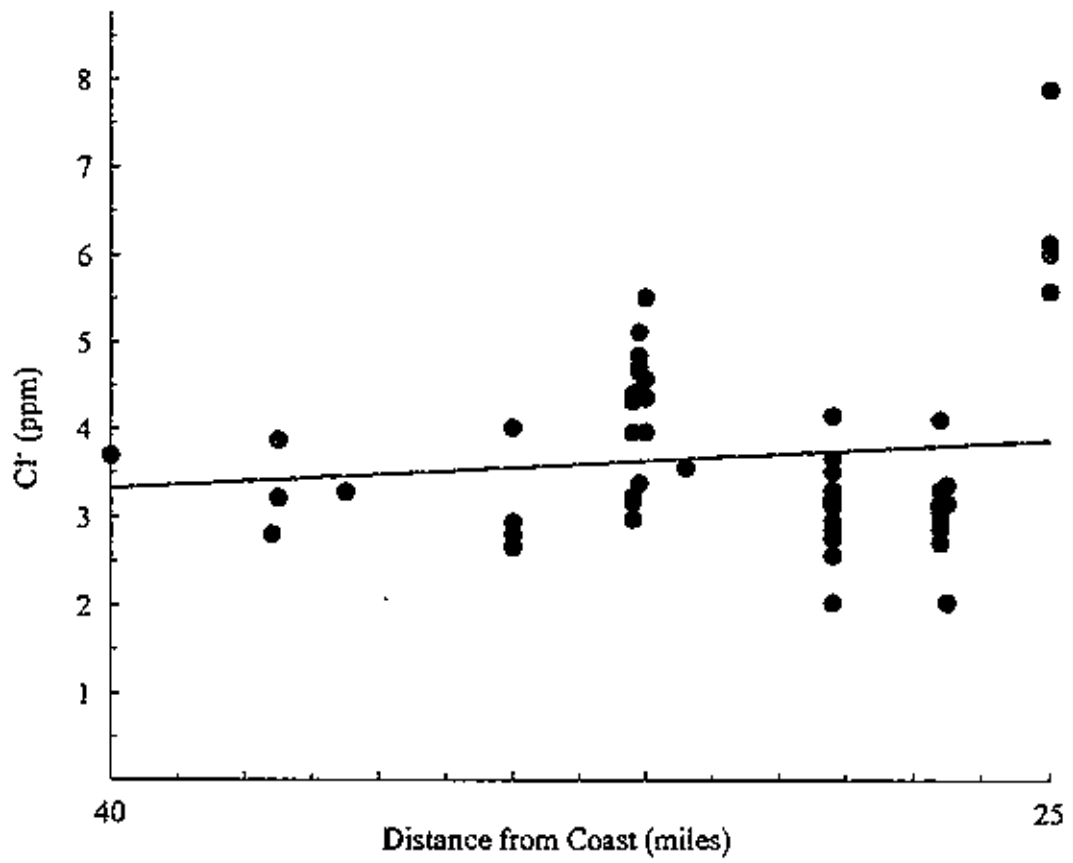


Figure 4. Geographic distribution of Cl⁻ in Colhansey Groundwater in the New Jersey Pine Barrens. See Figure 3.

SO_4^{2-} in precipitation has remained in groundwater as shown by the similar $\text{SO}_4^{2-}/\text{Cl}^-$ ratio between groundwater and rain; however, much of the NO_3^- in rain is removed by biological activities in soil (denitrification processes) so that groundwater has a low $\text{NO}_3^-/\text{Cl}^-$ ratio. Like the acid stream waters in the study area (average pH = 4.5), the low pH of groundwater (pH = 5.3, Table 5) also results from anthropogenic acid rain pollution (average pH = 4.3, Jones, 1994).

Ratios of $\text{Ca}^{2+}/\text{Cl}^-$, SiO_2/Cl^- and TOC/Cl^- in Cohansey groundwater are higher than in precipitation, indicating that other inputs besides precipitation also play an important part. Dissolved silica (SiO_2) is from water:rock reactions, in which quartz reacts with acid groundwater releasing SiO_2 into groundwater. $\text{Ca}^{2+}/\text{Cl}^-$ in groundwater is about twice the amount of the ratio in precipitation. Besides precipitation, Ca^{2+} could come from ion exchange or dissolution of calcite in the clay layers. However, there is little to no calcite in the Cohansey Formation. Ca^{2+} could be from soil horizons. TOC concentrations in the groundwater are not unusually high (Table 5). Groundwater typically has TOC concentrations between zero and 20 ppm. TOC comes mostly from rain, organic-rich upper soils and carbonaceous confining layers.

Temporal Variation

Temporal variation may also add to the variation in groundwater composition. However, water sampled from individual wells within the Cohansey Formation shows little seasonal variation (Figures 5 and 6). For example, given an analytical uncertainty of ± 0.1 ppm for Na^+ and K^+ , groundwater composition was fairly stable during the one

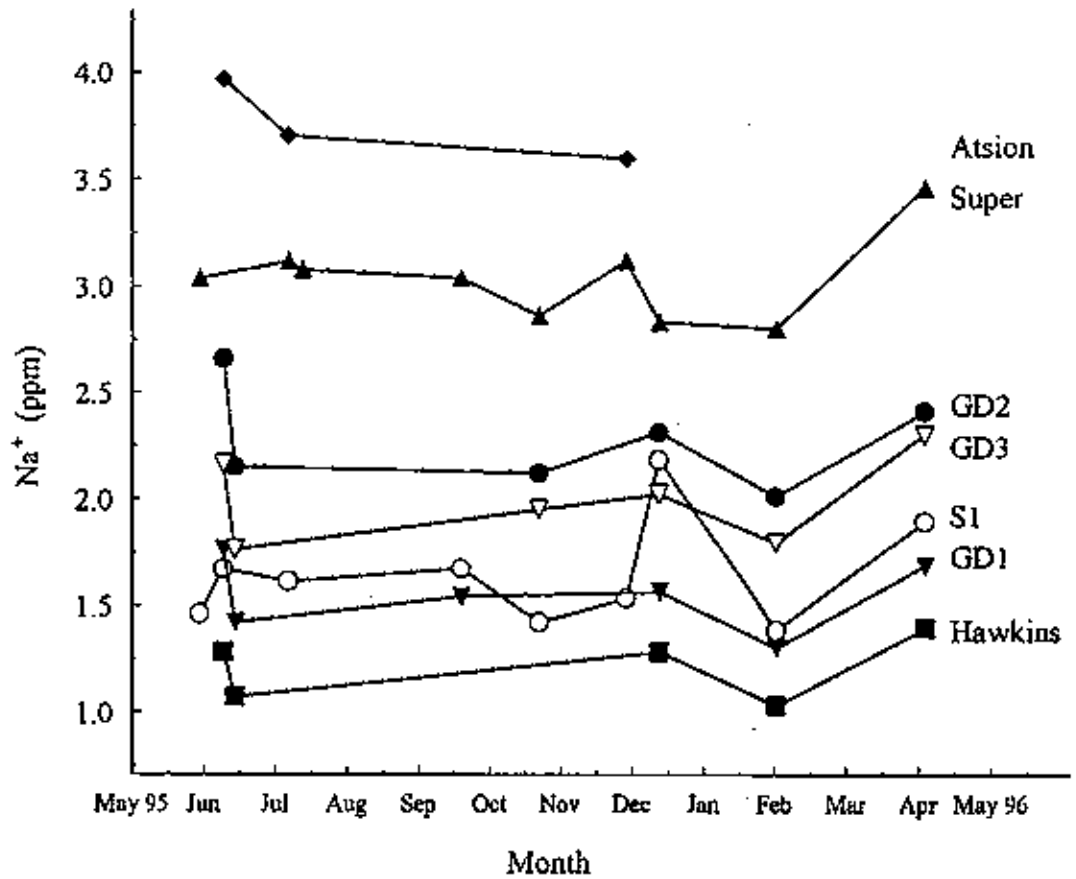


Figure 5. Temporal and spatial variations of Na^+ in Cohansey groundwater in the New Jersey Pine Barrens. Na^+ concentrations show little seasonal variation from May 1995 to April 1996. However, spatial variation in groundwater composition is distinctive.

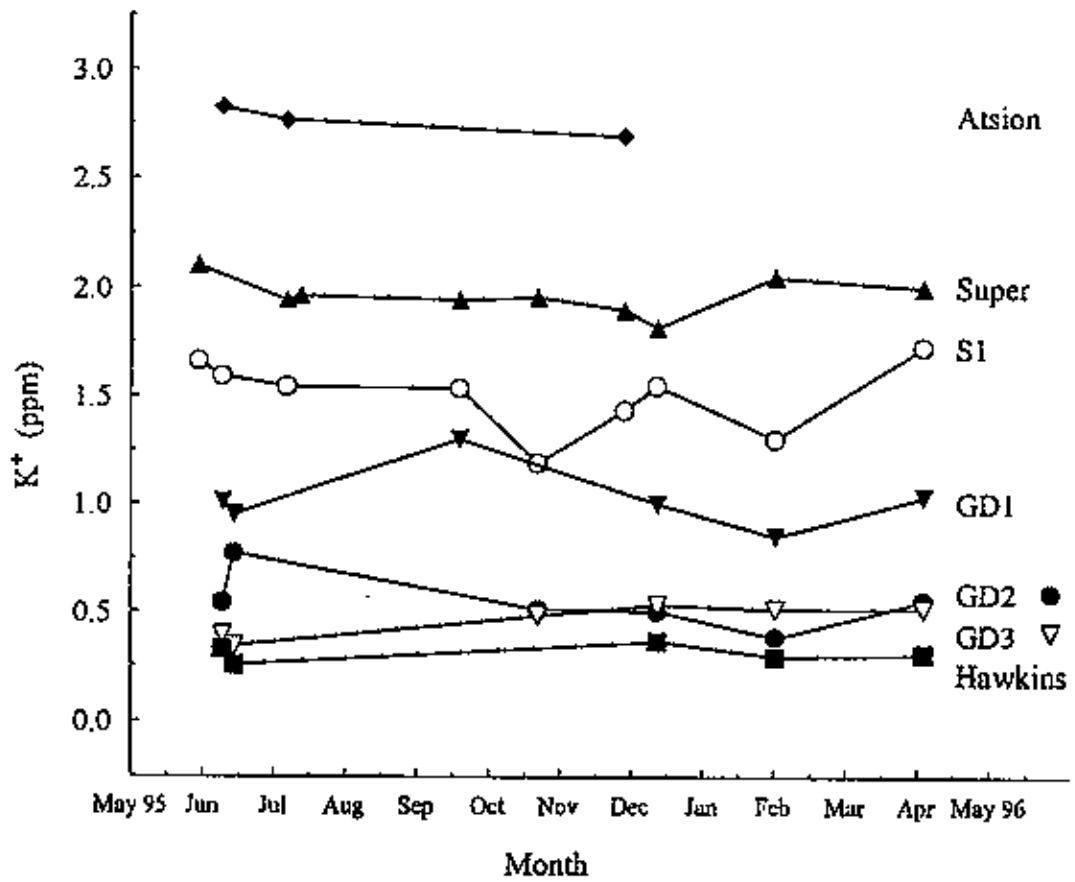


Figure 6. Temporal and spatial variations of K^+ in Cohansey groundwater in the New Jersey Pine Barrens. See also Figure 5.

year sampling period. In contrast, surface water in the same area showed seasonal variation (Jones, 1994). Groundwater generally has residence time greater than one year so that seasonal change was not observed. However, Na^+ showed a jump in concentration in April, 1996 (Figure 5). The high Na concentrations might have been caused by the use of a new standard solution in analyses or might be an indication of road salt pollution in the study area since a considerable amount of road salt was used in the past severe winter and most of the sampling sites are close to highways.

Spatial Variation

In addition to general compositional gradients (Figures 2, 3 and 4), highly localized variations within Cohansey groundwater are also observed (Figures 5 and 6). Concentrations of Na^+ and K^+ are quite different in seven wells that spread over the study area. Three wells (GD1, GD2 and GD3, refer to Figure 1 and Table 3 for location) which are very close to one another (less than 20 meters separate the wells) and have the same depth (ca. 10 meters) show distinctly different water compositions. The clay confining layers within the Cohansey Formation, which have low permeability, restrict vertical mixing of groundwater and contribute to the heterogeneity of Cohansey groundwater. However, the presence of clay layers in the Cohansey Formation does not render much influence to its water chemistry, as shown by the low ion contents in Cohansey groundwater. Since Cohansey sand is coarse, and thus quite permeable, groundwater does not have really long residence time in the Cohansey Formation for water-rock reactions.

In conclusion, Cohansey groundwater is acid water with low TDS in a sand

aquifer. Its composition is controlled mostly by precipitation, among which marine and continental aerosols and acid rain pollution are most important because the New Jersey Pine Barrens is near the ocean and close to the major metropolitan areas (source of acid-rain pollution) of the east coast.

Kirkwood Groundwater

Kirkwood groundwater, compared with Cohansey groundwater, is significantly different in composition (Table 7). Because there are not enough deep wells in the study area, data from several USGS wells in and around the Wharton State Park are also employed for the comparison (Table 7). USGS well parameters are listed in Table 8.

Although there are differences between data obtained from wells in the Wharton State Forest and that from USGS wells, indicating compositional variation within the Kirkwood, concentrations of major dissolved species differ greatly from those of Cohansey groundwater. For instance, the concentration of total dissolved solids, which averages about 200 ppm, is ten times that of Cohansey groundwater. Since the Kirkwood Formation is about 40 to 70 meters below surface, surface sources and biochemical reactions are no longer most important as they seem to be in the Cohansey. Instead, water:rock reactions are more significant. The Kirkwood Formation has a higher portion of more weatherable minerals, such as feldspar and clay minerals. These components provide sources for water:rock reactions and contribute to the high pH, high ion and TOC concentrations in Kirkwood groundwater. Take the following possible water:rock reaction as an example:

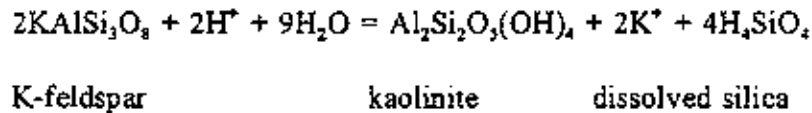
Table 7. Average composition of groundwater from the Kirkwood Formation (USGS data included)

Items	This Study (5/95-4/96)	USGS Well Data
pH	8.28	6.90
TOC	8.63	N/A*
Na ⁺	63.7	25.0
Ca ²⁺	6.77	5.35
K ⁺	5.10	3.80
Mg ²⁺	2.68	0.75
SiO ₂	5.05	15.0
Cl ⁻	1.51	2.00
NO ₃ ⁻	0.01	N/A
SO ₄ ²⁻	14.8	7.75
PO ₄ ³⁻	0.06	N/A
F ⁻	0.59	0.33
HCO ₃ ⁻	103.4	98.0
Mn	0.01	0.02

Note: N/A - not analyzed

Table 8. USGS Kirkwood well parameters

Longitude	Latitude	Date Data Recorded	Depth (meters)
74°46'04"	39°40'41"	09/81, 08/84, 09/91, 09/87	30
74°40'31"	39°48'12"	09/83, 09/90, 09/94	43
74°35'42"	39°45'36"	08/84, 09/91	51
74°39'58"	39°40'38"	09/59, 11/63, 07/64	60
74°52'08"	39°40'46"	08/61	81
74°51'57"	39°41'00"	02/64, 04/69	100



During the dissolution of K-feldspar, dissolved K^+ and dissolved silica enter the groundwater to raise the TDS concentration. Hydrogen ion is consumed which raises the groundwater pH value. Reactions between plagioclase and water release Na^+ and Ca^{2+} ions. The Ca^{2+} can also be obtained from dissolution of calcite. The HCO_3^- is mainly from silicate and calcite weathering. The Mg^{2+} may come from biotite or glauconite weathering. The SO_4^{2-} and F^- come from sulfuric and fluorite-bearing minerals in minor quantities. However, Cl^- concentration in Kirkwood groundwater is very low, averaging 1.5 ppm, even lower than that in Cohansey groundwater (average 3.5 ppm). Since there are no Cl^- minerals in the Kirkwood Formation, Cl^- retains its original concentration from its source. The low Cl^- concentration indicates an inland source of Cl^- , which may be at the place where the Kirkwood Formation crops out approximately 30 km northwest of the Wharton State Forest. Kirkwood groundwater apparently has travelled a great distance and a long time from its origin. This kind of groundwater flow is called regional flow.

Little seasonal variation of Kirkwood water composition was observed. Even larger degrees of heterogeneity of Kirkwood water may be expected since the Kirkwood sand is much less permeable than the overlying Cohansey sand (Chapter 2). Overall, Kirkwood groundwater is slightly alkaline, and its chemical composition is controlled largely by water-rock reactions because Kirkwood groundwater is controlled by regional flows that have long residence time.

Surface Water

Surface water chemistry in the Pine barrens was previously studied by Kelsey and Kinsman (1971), Yuretich *et al.* (1981) and Jones (1994). Results from these studies (Table 9) are not strictly comparable because of different sampling locations, sampling time periods and analytical techniques used. Also, concentrations are affected by river discharge. For example, concentrations of Na^+ and K^+ increase with discharge (Please refer to a later explanation on Figures 9 and 10.) Data in Table 9 have not been corrected for differences in discharge. Nevertheless, the major element compositions do not differ very much between these studies. The stable surface water composition may indicate that the surface geo-, bio- and hydro- systems in the Pine Barrens did not change much during the past twenty-five years.

Jones (1994) found that Na^+ and Cl^- in stream water came mostly from marine aerosols and pollution. This conclusion is confirmed in this study (Figure 7). Unlike groundwater, seasonal variation is very distinctive in the Pine Barrens' surface water (Figure 8). Most species show lower concentrations in the summer, and higher concentrations in the fall and winter. This difference is associated with the amount of precipitation and consequent runoff in the study area.

Table 9. Comparison of average stream water compositions in several studies in the New Jersey Pine Barrens

Species	Kelsey and Kinsman (1971)	Yuretich <i>et al.</i> (1981)	Jones (1994)	This study (1995-1996)
Na ⁺ (ppm)	3.30	2.73	2.51	2.30
Ca ²⁺ (ppm)	0.80	1.05	0.94	1.07
K ⁺ (ppm)	0.60	0.63	1.45	0.85
Mg ²⁺ (ppm)	0.70	0.57	0.57	0.63
SiO ₂ (ppm)	5.00	4.32	2.75	3.06
Cl ⁻ (ppm)	6.50	4.72	4.55	5.08
NO ₃ ⁻ (ppm)	N/A*	N/A	0.11	0.02
SO ₄ ²⁻ (ppm)	N/A	6.36	6.73	6.33
PO ₄ ³⁻ (ppm)	N/A	0.04	0.01	0.01
DOC (ppm)	N/A	N/A	3.36	6.79
TDS (ppm)	N/A	20.4	23.9	20.0
pH	4.50	4.51	3.97	4.52

*Note: N/A - not analyzed.

Before November 1995, when the discharge of the Batsto River was less than 2.7 meter³ (100 cubic feet) per second, the concentrations of major dissolved species varied positively with discharge (Figure 8). In the examples of Na⁺ and K⁺ in the Batsto and the Mullica Rivers (Figures 9 and 10), ion concentrations are in linear relationship with discharge. When discharge is linearly and positively correlated with ion concentrations in stream water, it indicates that solutes in streams come from precipitation or from runoff (soil inflow) or both. Runoff, which does not seem important to the chemistry of Cohansey groundwater, is significant in the composition of rivers. In each precipitation event, most of water entering soil zone will flow laterally through the organic-rich root

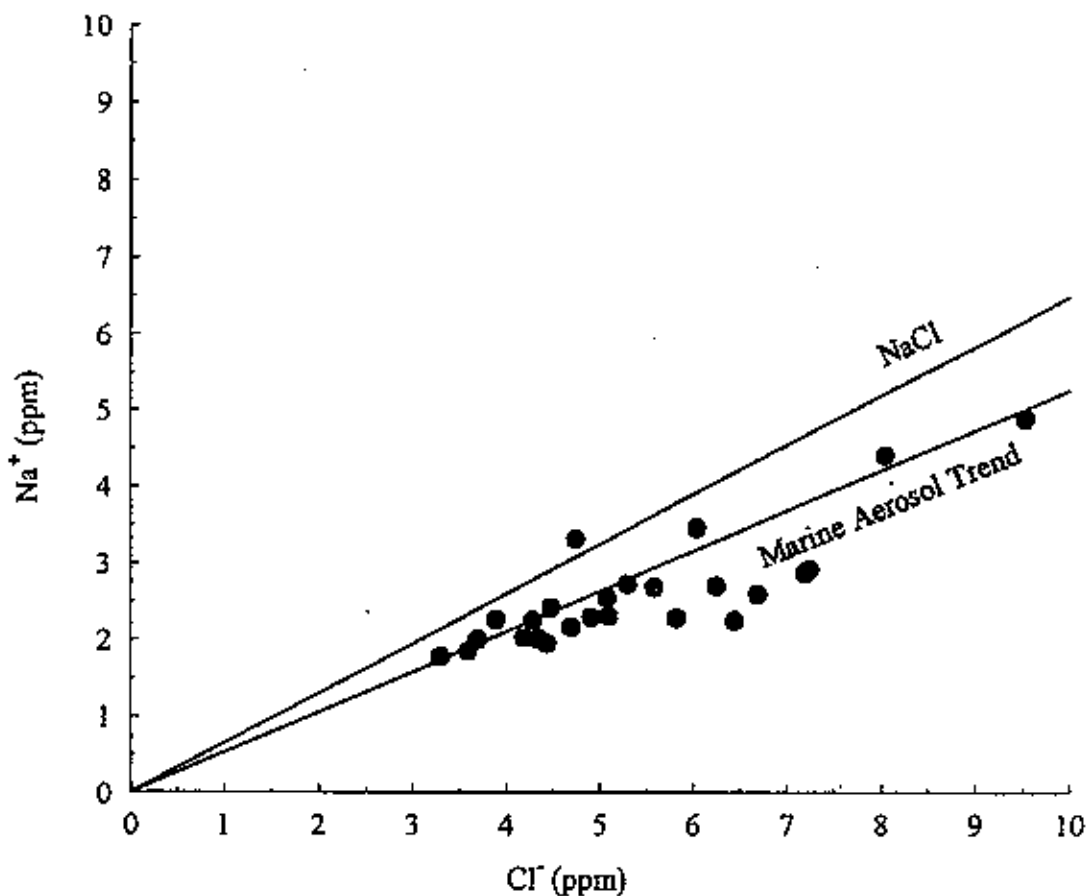


Figure 7. Na⁺ vs. Cl⁻ in surface water in the New Jersey Pine Barrens. Most data fall on the marine aerosol trend, which indicates the source of Na⁺ and Cl⁻ is mainly from marine aerosols through precipitation. Some data which fall below the trend suggest human pollution (salt or HCl gas) adding excessive Cl⁻ in water.

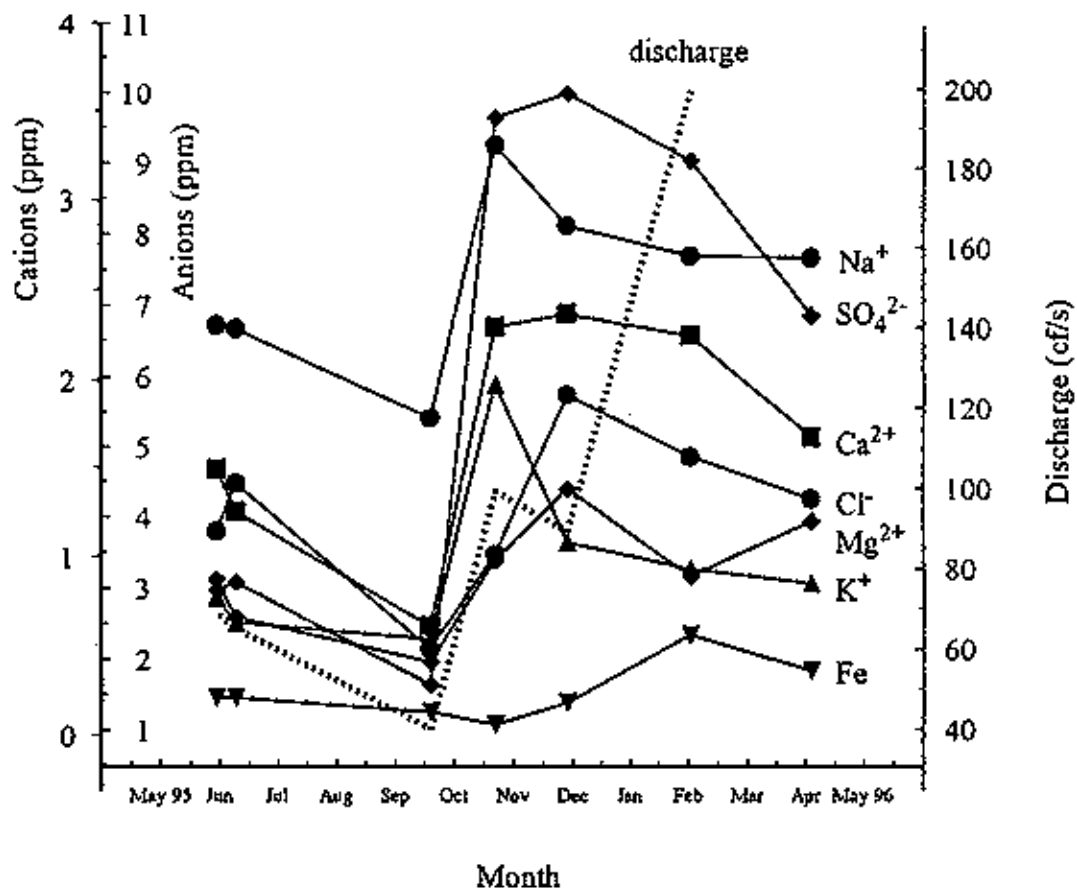


Figure 8. Seasonal variation of major element concentrations in the Batsto River in the New Jersey Pine Barrens. Major element concentrations were lower during May to October and higher from October to February. Major element concentrations increase with increasing discharge at discharge less than 100 cubic feet per second (27 m³/second).

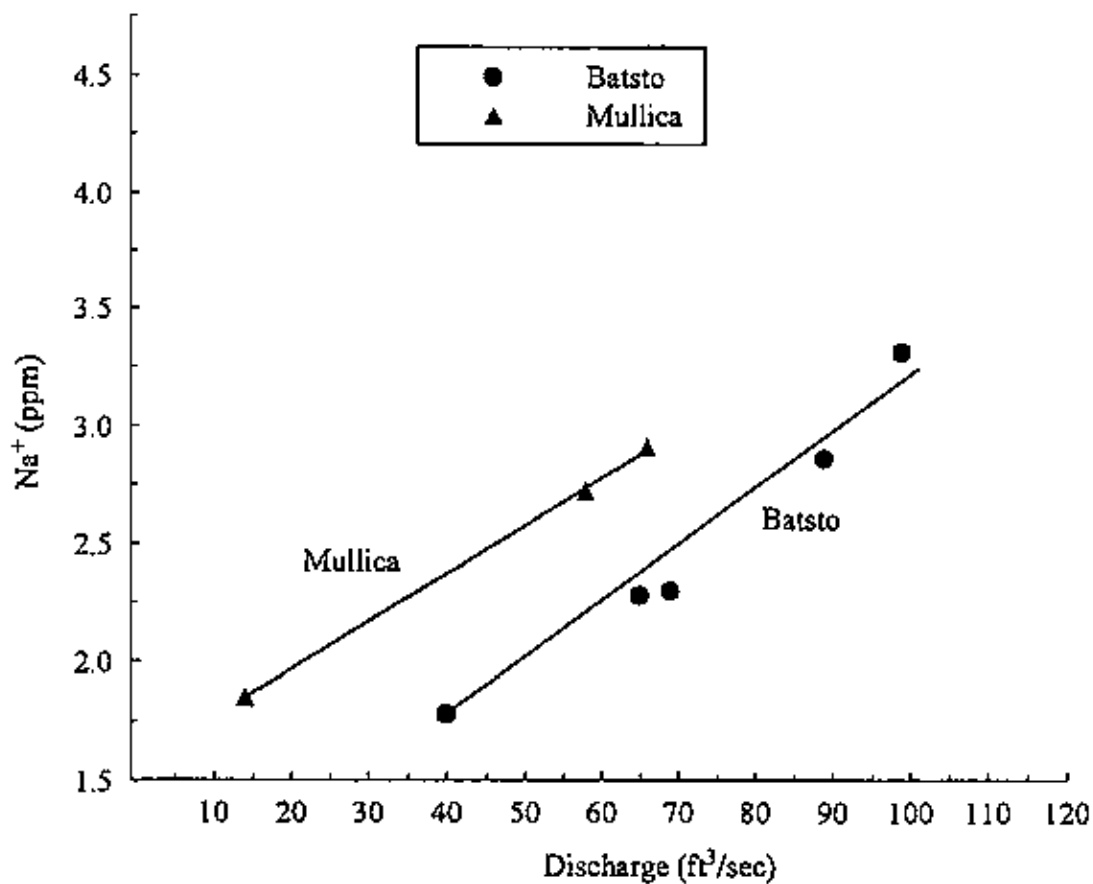


Figure 9. Na⁺ concentrations vs. discharge in the Batsto and Mullica Rivers in the New Jersey Pine Barrens. Na⁺ increases with increasing discharge at discharge less than 100 ft³/second (2.7 m³/sec).

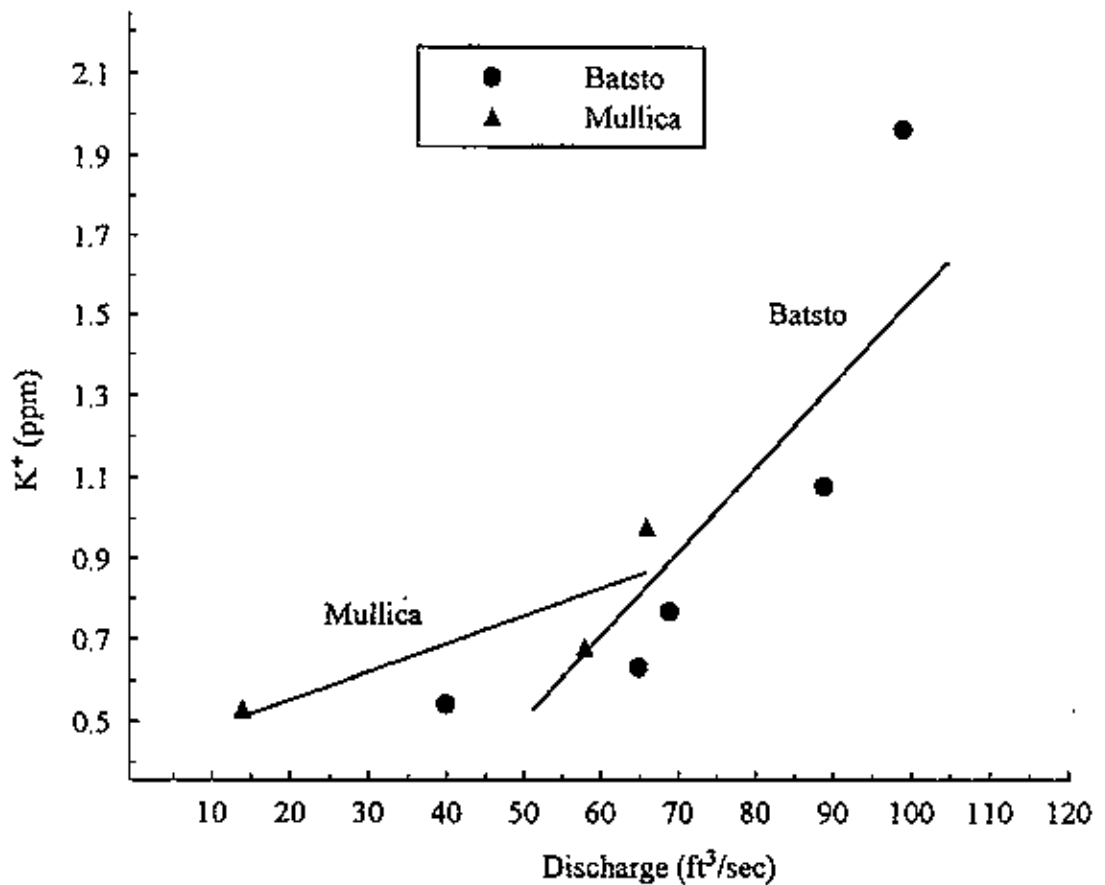


Figure 10. K⁺ concentrations vs. discharge in the Batsto and Mullica Rivers in the New Jersey Pine Barrens. K⁺ also show positive correlation with discharge at discharge less than 100 ft³/second (2.7 m³/sec).

zone to supply streams rather than percolate vertically to groundwater table. Horizontal permeability is usually assumed to be ten times that of vertical permeability in computer modelling (Osgood, 1995). Thus, species that are abundant in runoff will show a difference in chemical composition between river water and Cohasset groundwater. The differences will be discussed later in this chapter.

When discharge increased rapidly in the winter months, water moved so rapidly through the system that major species were diluted by rainfall and snowfall. However, it is not very reasonable for those species, such as Na^+ and Cl^- , which were previously confirmed as coming primarily from precipitation, to be diluted by precipitation itself. Actually, precipitation contains very low amounts of ions. For example, Na^+ averages only about 0.62 ppm (Jones, 1994). Dry deposition and the process of evaporation add to ion concentrations in river water. Since the low temperature is generally below 0°C during the winter in the Pine Barrens, evaporation can not be as efficient because of the low temperature.

It is worthwhile to point out that only H^+ (expressed using pH, Figure 11) and Al (Figure 23 in Chapter 6) show no dilution by discharge at extremely high discharge periods. The positive correlations between ion concentrations and discharge indicate very abundant sources for H ion and Al ion in precipitation and/or in runoff in the winter. In the Pine Barrens, the acid rain is worst in winter (pH around 3.6, Jones, 1994) because more fossil fuels have been used for heating. Much higher SO_4^{2-} concentration (Figure 8) in the winter (about 10 ppm) than in the summer (2-3 ppm) also demonstrates that precipitation is much more acid in winter.

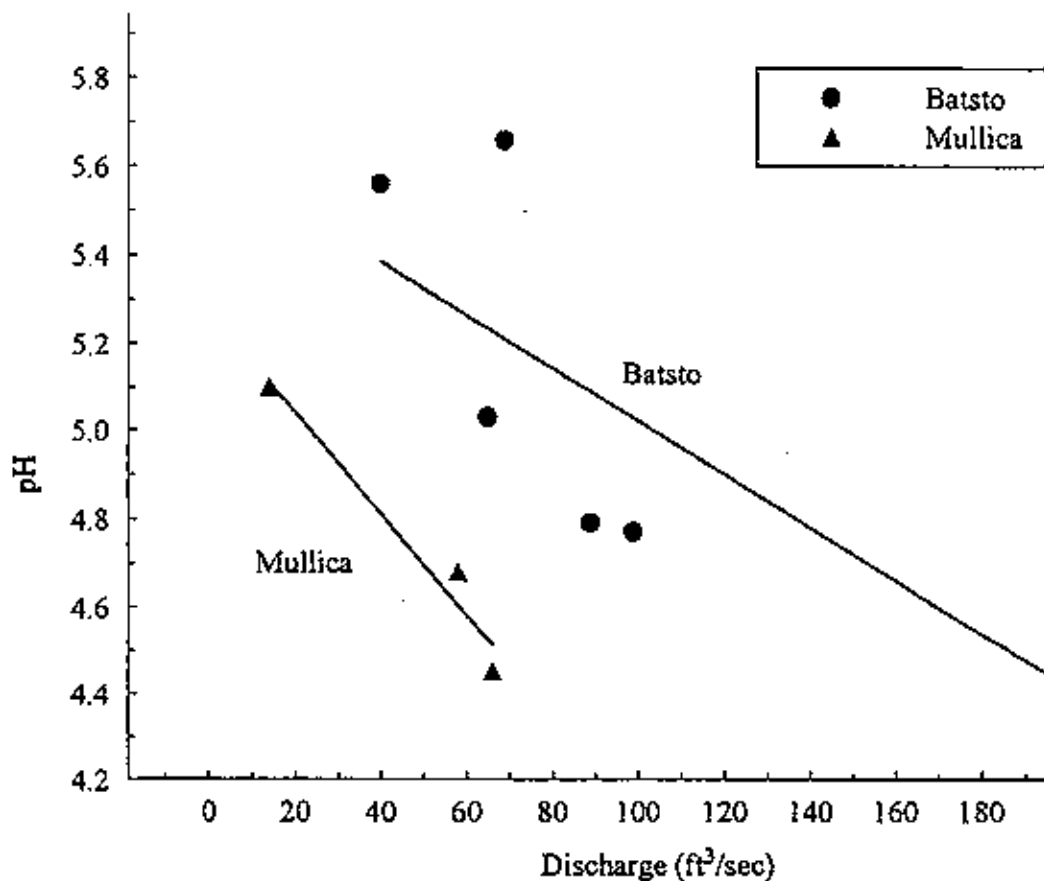


Figure 11. pH vs. discharge in the Batsto and Mullica Rivers in the New Jersey Pine Barrens. pH decreases with increasing discharge throughout the sampling period, indicating the acidity of stream water comes from acid precipitation and organic acids from soil. That there is no dilution effect for pH at high discharge suggests abundant source of H^+ at high discharge.

Chemical Comparison Between Surface Water and Groundwater

Based on previous accounts, the similarities and differences in water chemistry between surface water and groundwater in the Pine Barrens may already be seen. A more detailed source- and process-oriented comparison below yields some interesting results.

Surface Water and Cohansey Groundwater

It is generally believed that Cohansey groundwater serves as base flow for rivers in the study area. Differences in composition between river water and Cohansey groundwater are expected since surface water is highly influenced by discharge, as previously shown. However, for the concentrations of most major species, stream water does not differ much from Cohansey groundwater (Table 10). The close resemblance suggests they have similar geochemical sources (e.g. marine aerosols, Figures 2 and 7) and chemical reactions in the study area. As previously concluded, the chemistry of Cohansey groundwater is actually dominated by precipitation. Similarly, the water chemistry of streams in the Pine Barrens is also controlled by precipitation. Chemical reactions in sand and soil are minor in contributing to both ground and surface water chemistry. On the other hand, the similarity in water composition may indicate extensive recharge between rivers and groundwater.

Table 10. Comparison of average compositions of stream water and groundwater from the Cohansey and the Kirkwood Formations in the Pine Barrens

Items	Stream Water	Cohansey Groundwater	Kirkwood Groundwater
pH	4.52	5.30	8.28
TOC (ppm)	6.79	4.38	8.63
Na ⁺ (ppm)	2.30	2.02	63.7
Ca ²⁺ (ppm)	1.07	0.79	6.77
K ⁺ (ppm)	0.85	1.20	5.10
Mg ²⁺ (ppm)	0.63	0.55	2.68
SiO ₂ (ppm)	3.06	5.15	5.05
Cl ⁻ (ppm)	5.08	3.50	1.51
NO ₃ ⁻ (ppm)	0.02	0.02	0.01
SO ₄ ²⁻ (ppm)	6.33	6.58	14.8
PO ₄ ³⁻ (ppm)	0.01	0.01	0.06
F ⁻ (ppm)	0.06	0.07	0.59
HCO ₃ ⁻ (ppm)	0.00	1.10	103.4
Mn (ppm)	0.03	0.03	0.01
Al (ppb)	205.1	20.2	10.15
Fe (ppm)	0.38	0.73	0.09

Discrepancies in composition between surface water and Cohansey groundwater do exist. Besides precipitation, surface water chemistry can be modified by runoff which includes reactions in soil. However, for Cohansey groundwater, reactions in soil are not very significant since the water table is generally below soil zone and only a small amount of soil water percolates down to the groundwater table. Species that are abundant in runoff will show higher concentrations in stream water than in groundwater. Similarly, composition of groundwater can be altered when there are reactions between water and porous media. Although water:rock reactions are minor in the Cohansey Formation, some do occur (see Figure 2). Ions that are strongly influenced by water:rock reactions in groundwater will be diluted by river water as groundwater meets the surface.

pH in stream is lower than pH in Cohansey groundwater (Table 10). The higher concentration of hydrogen ion in stream is caused by organic acids infiltrated from soil. Water:rock reactions in the Cohansey sand also somewhat neutralize the low pH in its groundwater. Similarly, soil organic matter contributes to an extra amount of TOC in river waters. Also, high aluminum concentration in stream is caused by dissolution reactions in soil horizons. Since the Cohansey sand is very inert and is mostly quartz, the only prominent result of water:rock reaction is silica dissolution. Dissolved silica is lower in stream than in Cohansey groundwater because silica comes solely from water:rock reaction and is diluted by precipitation in rivers.

Cohansey Groundwater and Kirkwood Groundwater

Groundwater from the two formations differs considerably in major element concentrations. The difference is caused by differences in their sources, geochemical reactions and groundwater flow systems. The great differences in water chemistry suggest little cross-formational flow between the two formations. In other words, vertical flow is minor between the two formations. The clay confining layers and iron beds between the two units may restrict cross-formational flow.

Unlike Cohansey groundwater, whose composition is mainly controlled by its source (precipitation), the composition of Kirkwood groundwater, which has a much longer residence time, has been greatly altered from its original composition source. The composition of Kirkwood groundwater is almost totally modified by water:rock reactions with sand and clay. For Na^+ and Cl^- (Figure 12), Cohansey groundwater follows the marine aerosol trend, whereas Na^+ in Kirkwood groundwater follows the trend of water:rock reactions. In Kirkwood groundwater, Na^+ concentrations vary from below 5 ppm to about 70 ppm indicating that the amount of water:rock reactions varies within the formation. The stable and low Cl^- concentrations in Kirkwood groundwater, even much lower than those in Cohansey groundwater, suggest that Cl^- in Kirkwood groundwater does not come from water:rock reactions. There are no minerals that can produce Cl^- in the Kirkwood Formation. In fact, Cl^- is the only major species whose concentration is not modified by water:rock reactions, and thus can indicate the source of Kirkwood groundwater. Assuming that all Cl^- in Kirkwood groundwater (average 1.5 ppm) is originally from precipitation, its source can be inferred to be much more inland, according

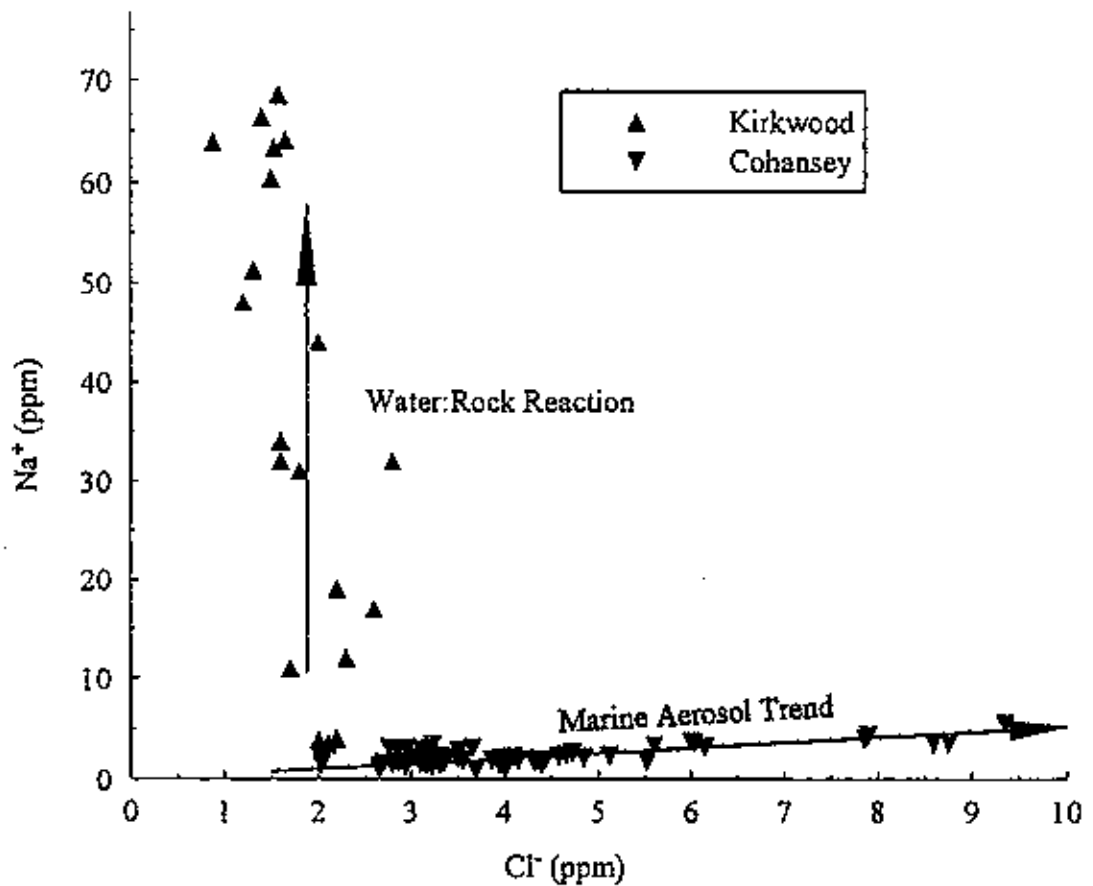


Figure 12. A source- and process- oriented comparison of groundwater from the Cohansey and Kirkwood Formations in the New Jersey Pine Barrens. Na^+ and Cl^- in Cohansey groundwater are derived from marine aerosols through precipitation. Na^+ in Kirkwood groundwater is controlled by water:rock reactions; the low Cl^- concentration indicates that Kirkwood groundwater comes from more inland.

to the concentration gradient in Figure 4. Therefore, Kirkwood groundwater has traveled a great distance and a long time in the sand aquifer. The Kirkwood Formation crops out about 30 km northwest of the Wharton State Forest. The Cl⁻ concentration in river water in Homerstown, NJ, where the Kirkwood sand is exposed, is about 2 ppm (J. Betts, personal communication).

Regional flow dominates Kirkwood groundwater flow (Figure 13). Regional flow that has residence time as long as several hundred thousand or even million years is the major condition ensuring water:rock reactions that result in high TDS content in Kirkwood groundwater. In contrast, the flow system in the Cohansey Formation is dominated by local flows (Figure 13) because only local groundwater mixing can preserve the marine aerosol trend and geographic distribution that were observed in Cohansey groundwater (Figures 2, 3 and 4). Marine aerosols, which come from the ocean, precipitate with rain, mix with groundwater and then are redistributed within the aquifer. If the redistribution of the cyclic sea salt followed the regional flow system, then regional flows would move waters hundreds of miles away from their origins and modify their composition by retaining waters in a series of chemical reactions for thousands or even millions of years. Local groundwater flows have much shorter residence time than do the regional flows so that water:rock reactions in the Cohansey are much less prominent than in the Kirkwood. Despite the similarity in mineral contents between the two formations (The only difference is in feldspar; Chapter 2.), different flow systems give different residence time and thus result in very different degrees of water:rock reactions in the two formations.

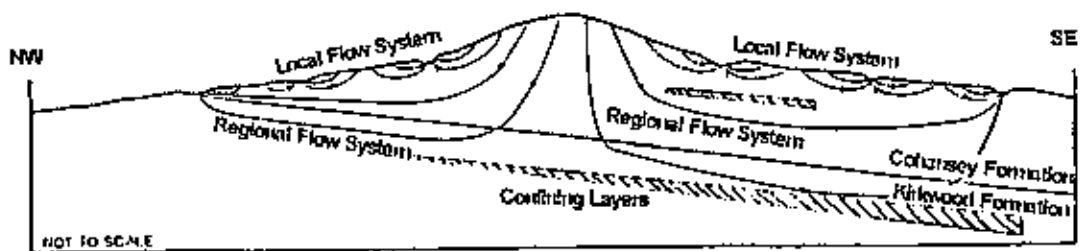


Figure 13. A schematic diagram of flow systems in the New Jersey Pine Barrens (modified after Rhodehamel, 1973). Local flow system dominates the Cohamsey Formation. Regional flow system dominates the Kirkwood Formation.

Phase Stability Diagram

Despite the different residence time alluded to above, water in both formations is near saturation with quartz (Figures 14 and 15), the most prevalent mineral in the Pine Barrens. Dissolved silica is the only species that has similar concentration in both formations (Table 10). In the stability diagrams (Figures 14 and 15), data for groundwater from both formations cluster around the quartz saturation line. However, surface water is undersaturated with respect to quartz and lies to the left of the quartz saturation line.

In the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ system (Figure 14), surface water equilibrates with gibbsite and kaolinite. Cohansey groundwater is mostly in the kaolinite field, with a small number of data points in the gibbsite field. Kirkwood groundwater is exclusively in the upper kaolinite field. ($a_{\text{Na}^+}/a_{\text{H}^+}$) of Kirkwood groundwater is about six orders of magnitude higher than that in river and Cohansey groundwater. The stability diagram shows the degree of water:rock reactions. Theoretically, a possible path of solute composition as albite or analcite reacts with water is from gibbsite field to kaolinite to Na-beidellite and to analcite or albite. The values of $a_{\text{Na}^+}/a_{\text{H}^+}$ from the Pine Barrens indicate very little water:rock reactions in surface water, only a little in Cohansey groundwater, and a greater amount in Kirkwood groundwater since the data points are much closer to the field of Na-beidellite. Water chemistry of Kirkwood groundwater will proceed further along the path of water:rock reactions given more time.

In the $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ system (Figure 15), different degrees of water:rock reactions are more obvious. The possible path of solution composition as K-feldspar reacts with water is from gibbsite field to kaolinite to muscovite and to K-feldspar. The possible

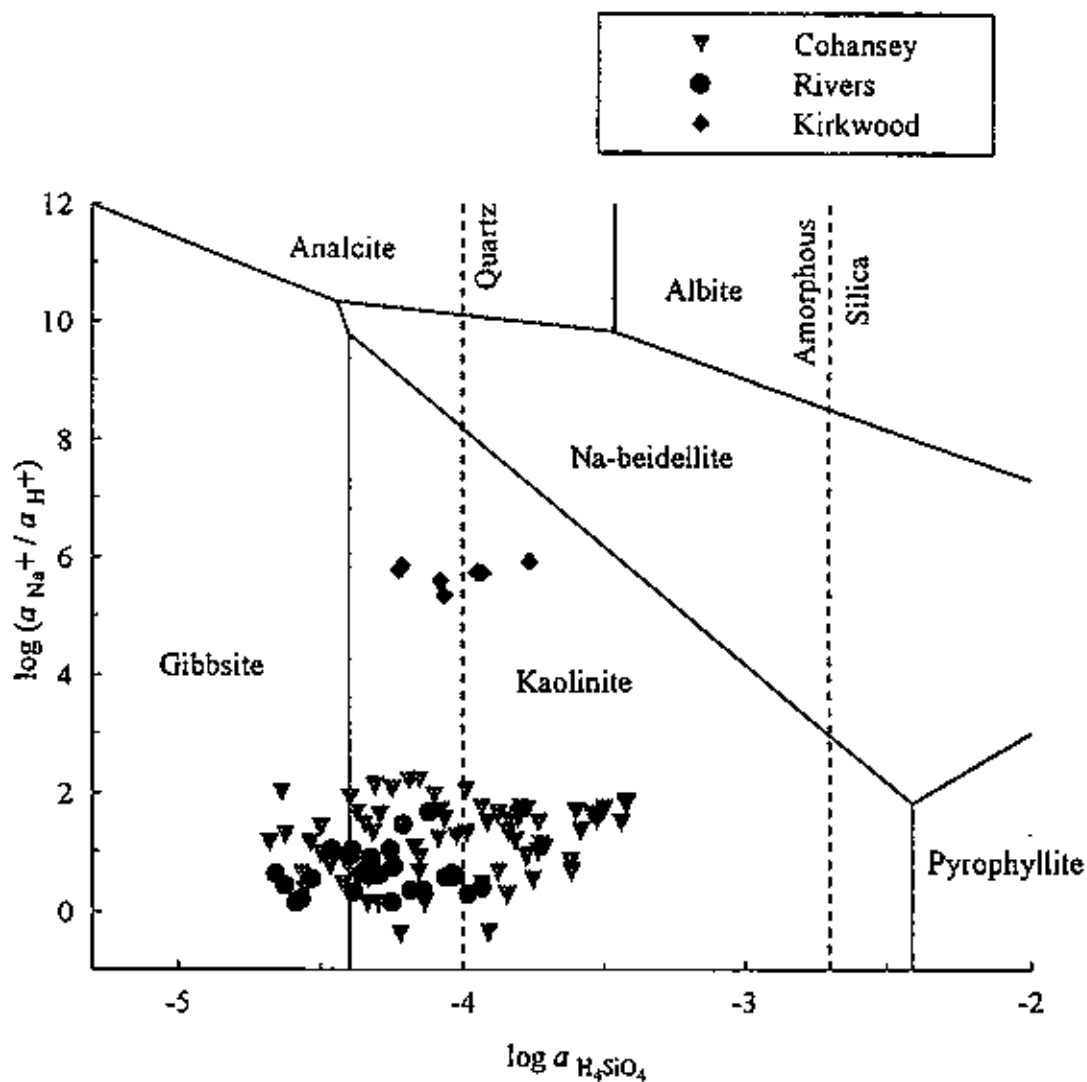


Figure 14. Pine Barrens' water data in phase diagram in system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$. Surface water and Cohansey groundwater data fall in the gibbsite and kaolinite fields, showing little to only slight amount of water:rock reactions. Kirkwood groundwater data plot high above in the kaolinite field, indicating a greater degree of water:rock reactions and groundwater evolution. The composition of Kirkwood groundwater would ultimately evolve to albite field.

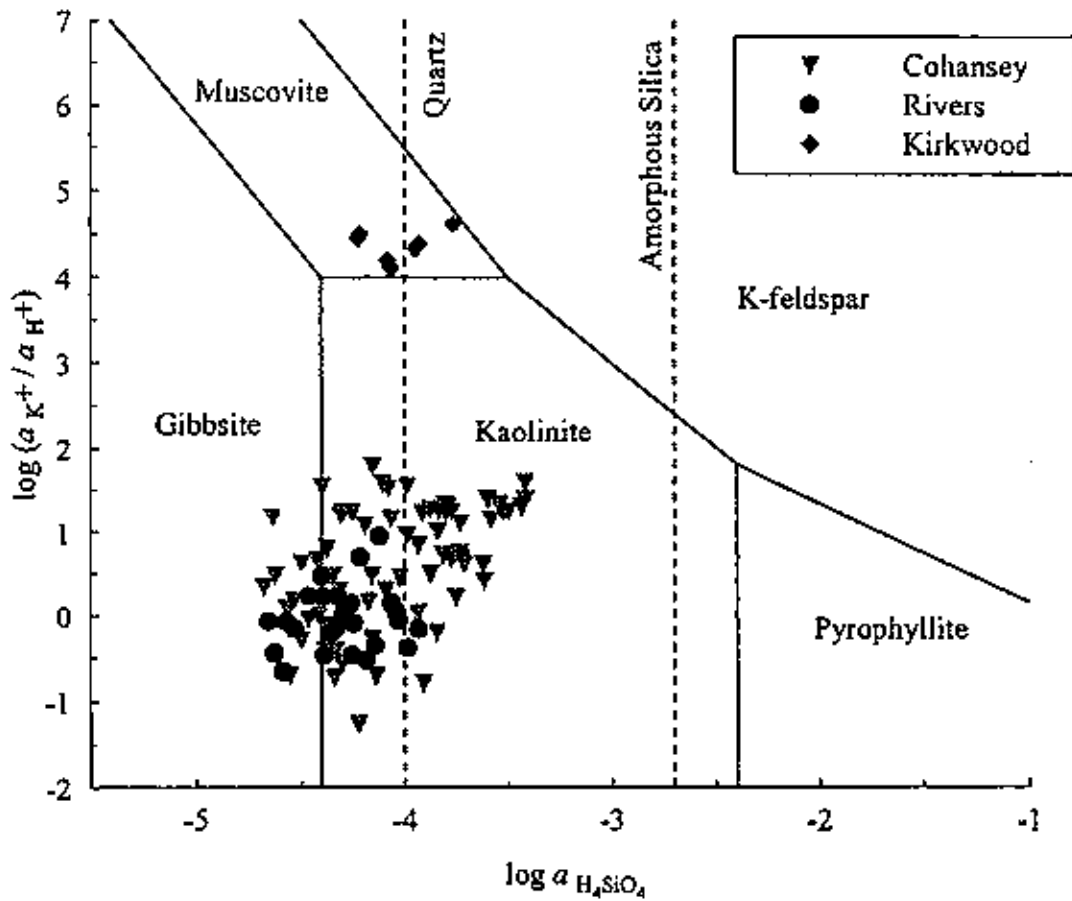
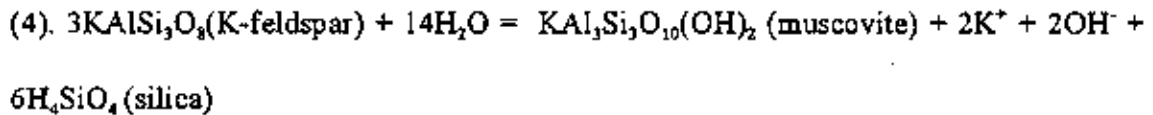
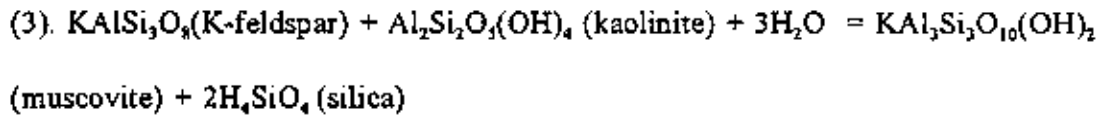
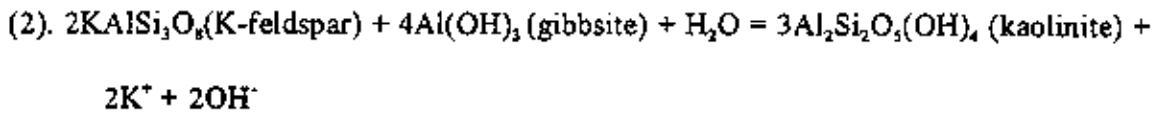
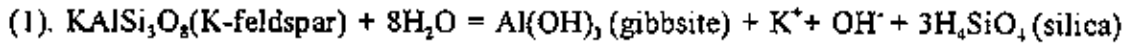


Figure 15. Pine Barrens' water data in phase diagram in system of $K_2O-Al_2O_3-SiO_2-H_2O$. Surface water has little water:rock reactions. Cohansey groundwater shows only a small amount of water:rock reactions. Kirkwood groundwater equilibrates with muscovite or illite, showing a much higher degree of water:rock reactions.

reactions of K-feldspar reacting with water are:



Surface and Cohansey groundwater are in equilibrium with gibbsite or kaolinite phases. Kirkwood groundwater is in equilibrium with muscovite, the phase that has a much higher degree of water:rock reaction. Since K-feldspar, not muscovite, is the abundant mineral in the Kirkwood Formation, more water:rock reaction is expected until the water composition reaches the muscovite - K-feldspar boundary when Kirkwood groundwater would be in equilibrium with K-feldspar and its water chemistry would be stabilized.

CHAPTER 5

ORIGIN OF BOG IRON IN THE PINE BARRENS

Bog-iron deposits in the New Jersey Pine Barrens were a major source of iron in colonial America for more than a century, from the early 16th to the mid- 17th century, until the discovery of magnetite ores in Pennsylvania and northern New Jersey. Geographically, Batsto Village in the Mullica River Basin was the center of the bog-iron industry in the Pine Barrens.

Iron deposits in the Pine Barrens are found in various formations. In the Cohansey and Kirkwood Formations, the bog iron is scattered within the sand aquifers and the river banks as massive Fe-oxides (limonite) admixing in and cementing quartz gravel, sands, and silts. Goethite is the only X-ray identifiable iron mineral (Crerar *et al.*, 1979). One interesting aspect for those bog-iron deposits on the river beds was that the ore could regenerate in about 20 years once it was mined (Starkey, 1962). In the underlying formations, Fe occurs abundantly throughout several formations (Homerstown sand, Navesink Formation, Marshalltown Formation and Merchantville Formation) as glauconite in the sands and glauconitic clays. Siderite, pyrite and vivianite were also described (Braddock-Rogers, 1930; Starkey, 1962).

Ferric Iron Equilibria

Total calculated ferric iron ($\Sigma\text{Fe(III)}$), defined as $\text{Fe}^{3+} + \text{Fe(OH)}^{2+} + \text{Fe(OH)}_2^+ +$

$\text{Fe}(\text{OH})_3^0 + \text{Fe}(\text{OH})_4^-$) in river water and groundwater from the Cohansey and Kirkwood Formations is highly supersaturated with respect to goethite and hematite, and roughly at saturation with amorphous $\text{Fe}(\text{OH})_3$ (Figure 16). Values in Figure 16 are maximal because dissolved organic-iron complexes in water were neglected in the calculation of total ferric iron. As indicated by Means *et al.* (1977), up to 60 - 70% of the dissolved Fe present in the Pine Barrens was associated with organics during the summer months, whereas during the winter, the association decreased to 5 - 10%. Assuming that 70% of the total Fe is in forms of various organic iron, the total ferric iron calculated in Figure 16 would decrease only about 0.5 on the $\log \Sigma \text{Fe}(\text{III})$ axis. Iron would still be generally at saturation with amorphous $\text{Fe}(\text{OH})_3$, which suggests that amorphous $\text{Fe}(\text{OH})_3$ is controlling iron solubility in water. However, the dilemma is that miners found that the bog iron grew faster in the summer, when the waters might be more undersaturated (or less supersaturated) with amorphous $\text{Fe}(\text{OH})_3$, than in the winter months, when the waters were at saturation or oversaturated with amorphous $\text{Fe}(\text{OH})_3$. The iron equilibria were not enough to give a satisfactory explanation on Fe precipitation. On the other hand, kinetic forces play an important role. There was evidence showing that bacterial catalysis may affect the rate of iron precipitation in bog iron (Dake, 1916; Harder 1919; Deul, 1942; Perfil'ev *et al.*, 1965). This effect was confirmed by the study of Crerar *et al.* (1979) and Jones (1994) in the Pine Barrens.

Iron Source in the Bog Iron Deposits

Why these rich bog iron deposits occur in the inert quartz sand is still an unsolved

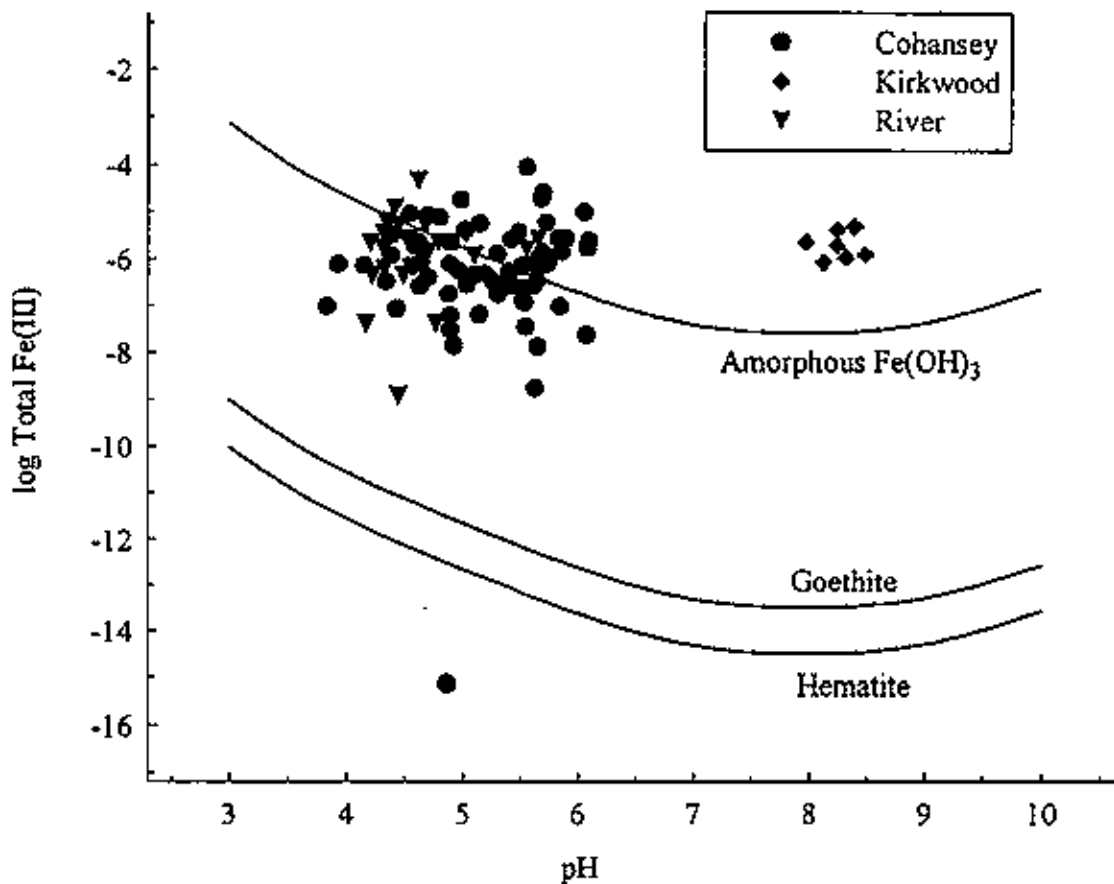


Figure 16. Total ferric iron concentration vs. pH in surface water and groundwater in the New Jersey Pine Barrens. Also shown are solubility lines of hematite, goethite and amorphous Fe(OH)₃. Data indicate that ferric iron is supersaturated with goethite and hematite. Iron activity is controlled by saturation with amorphous Fe(OH)₃. Calculations were done using WATEQ4F (Ball and Nordstrom, 1991).

question. The classic model, as reviewed recently by Crerar *et al.* (1979), was that iron in the Cohansey and Kirkwood bog irons was transported in groundwater from the underlying iron-rich glauconitic formations, and that $\text{Fe}(\text{OH})_3$ was precipitated from the groundwater as it became progressively supersaturated with decreasing depth when it eventually entered oxidizing surface environments.

The classic model assumed that there was abundant cross-formational flow from the underlying Kirkwood Formation to the Cohansey Formation. However, as this study revealed in Chapter 2, the potentiometric surface in the Kirkwood Formation is actually lower than the free water table in the Cohansey Formation, making it impossible for water from a deeper aquifer to come to the surface on a large scale. The differences in solvent water chemistry between the two formations, as well as within the Cohansey Formation, also suggest that there is very little vertical flow between the two formations (Chapter 4).

The other assumption in the classic model was that the iron concentrations increased with increasing depth. However, in both Crerar *et al.* (1979) and this study (Figure 17) there is no obvious relationship between dissolved Fe concentrations and depth. This study finds that iron concentration in the Kirkwood Formation is actually less than in the Cohansey because pH value is as high as 8 in Kirkwood groundwater and iron minerals are least soluble at pH around 8. Degrees of supersaturation/undersaturation with respect to amorphous $\text{Fe}(\text{OH})_3$ is very similar in Cohansey and Kirkwood groundwater (Figure 18).

Stream water and the Cohansey groundwater (from intermittent wells) have very similar total iron concentrations (around 0.3 ppm) (Figure 19). Groundwater from the

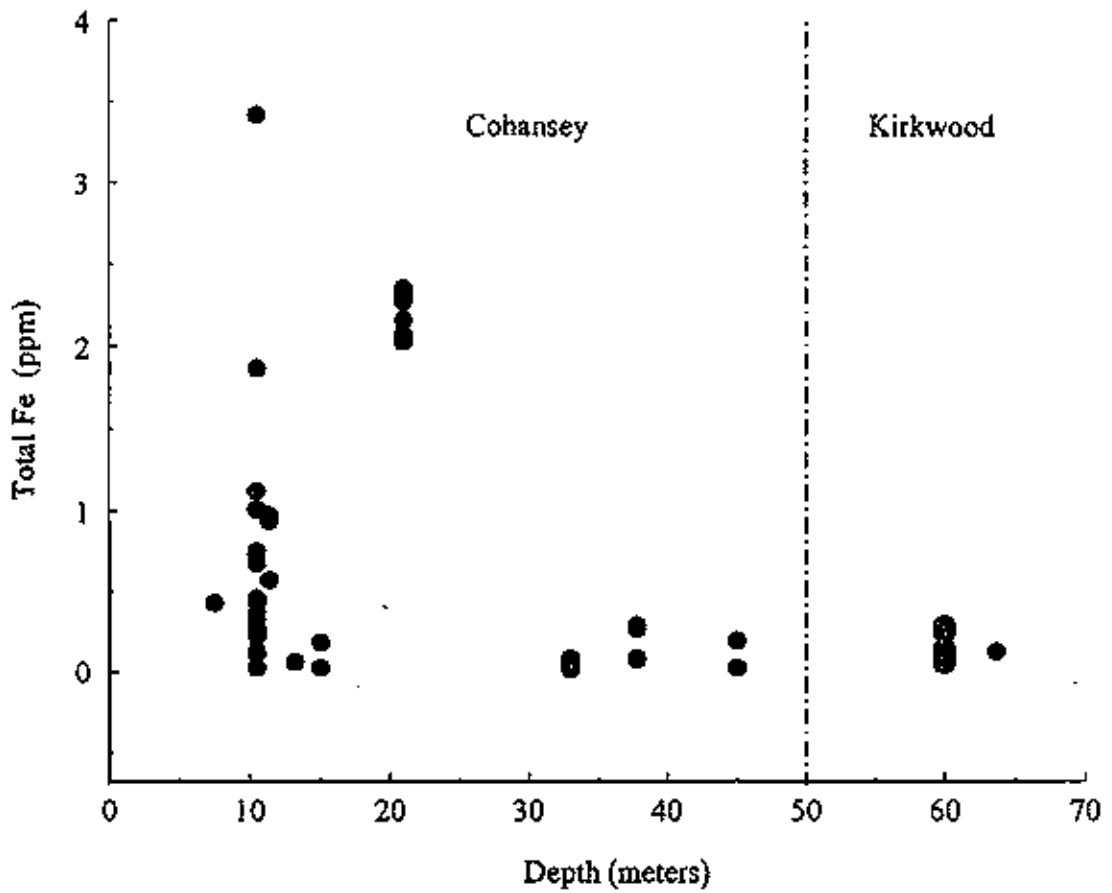


Figure 17. Total dissolved iron vs. depth in groundwater in the New Jersey Pine Barrens. Total iron concentration does not show an increase with depth. On the contrary, wells that have high iron concentrations are all in the Cohansey Formation. Kirkwood groundwater have low iron concentrations because of its high pH.

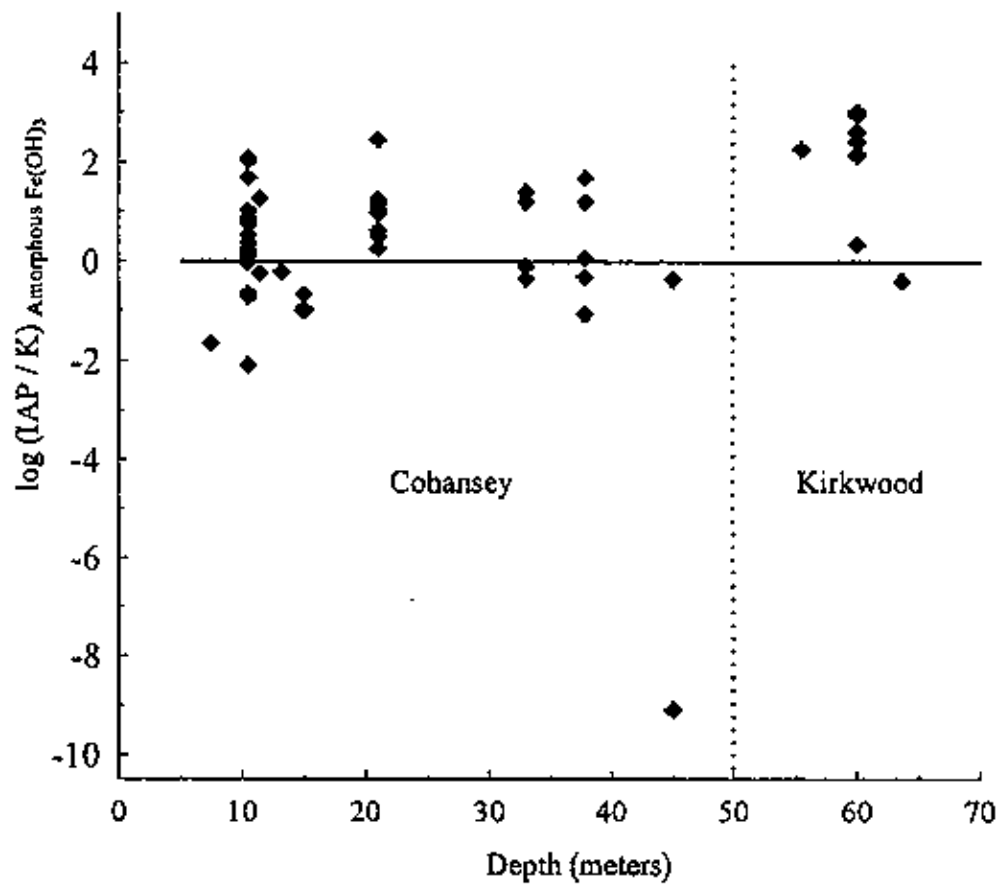


Figure 18. Saturation index vs. depth for amorphous Fe(OH)₃ in groundwater in the New Jersey Pine Barrens. Data indicate little relation between degrees of supersaturation/undersaturation and depth.

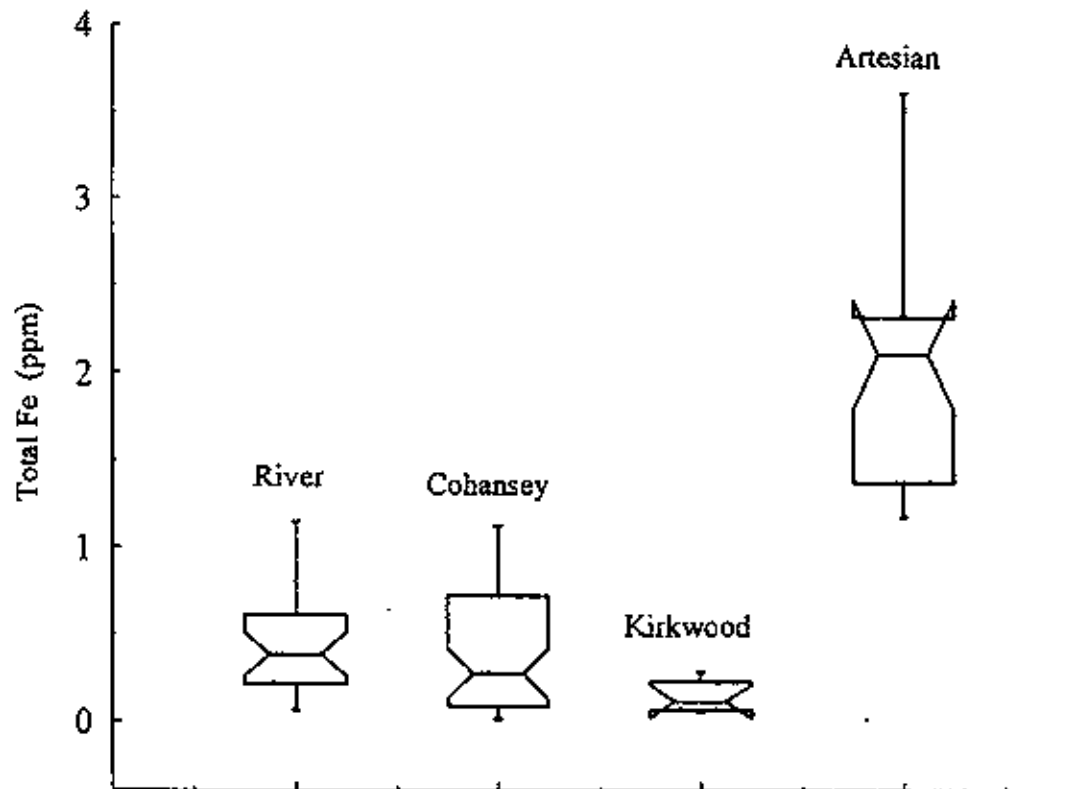


Figure 19. Distribution of total dissolved iron concentrations in river water, Cohansey groundwater (from intermittent wells), Kirkwood groundwater and water from artesian wells in the Cohansey Formation in the New Jersey Pine Barrens. Data indicate that artesian groundwater has the highest Fe concentration (mean = 2.1 ppm) and Kirkwood groundwater has the lowest Fe concentration (mean = 0.09 ppm). River water and Cohansey groundwater (from intermittent wells) have similar Fe levels (mean = 0.3 ppm).

deeper Kirkwood Formation has lower concentrations of total iron, averaging around 0.09 ppm. This is significant since it eliminates the possibility of an iron source from a deeper aquifer. On the other hand, it is very surprising to find that water from all the artesian wells in the Cohansey Formation has the highest iron concentrations, averaging around 2.1 ppm. Since the artesian wells are associated with local confining layers, and the silty and clayey confining layers were observed to be rich in organic matter (Rhodehamel, 1973), it is more likely that the confining layers, which may have high Fe concentration, are the iron source of the bog iron in the sand aquifers and the streambeds. It appears that the glauconite deposits in the underlying formations are not associated with bog-iron deposits in the Cohansey and the Kirkwood Formations.

CHAPTER 6

ALUMINUM GEOCHEMISTRY IN THE PINE BARRENS

Aluminum Concentrations and Toxicity in Natural Waters

Aluminum, which constitutes 8% of the earth's crust, is the most abundant metallic type element and the third most abundant element. However, aluminum is by no means a major component in most natural waters. Stream water and groundwater contain about 50 ppb of total dissolved Al. Seawater and rain water have only about 1 ~ 2 ppb (Berner and Berner, 1987).

The Al in natural waters has received increasing attention because Al concentration increases rapidly in acid waters and causes fish and plants to die. It has been observed that Al is toxic to fish and plants when the total dissolved Al is between 1 ~ 10 μM (about 30 ~ 300 ppb) and at solution pH value between 4 to 5.5 (Baker and Schofield, 1982; Parker *et al.*, 1989; Cleveland *et al.*, 1991; DeLonay *et al.*, 1993). However, numerous surface waters and groundwater are in the aforementioned ranges. Dissolved Al data from surface water and groundwater from the New Jersey Pine Barrens (Table 11 and Figure 20) may indicate the seriousness of the problem. Forty one percent of the data fall into the toxic Al and pH ranges, and most of those in the toxic ranges are stream waters. The toxic aluminum in surface waters poses a direct threat to fishes and water plants. Furthermore, different Al compounds have different toxicity. For instance, it is known that Al complexed with citric acid, fluoride and organics in natural water samples is less

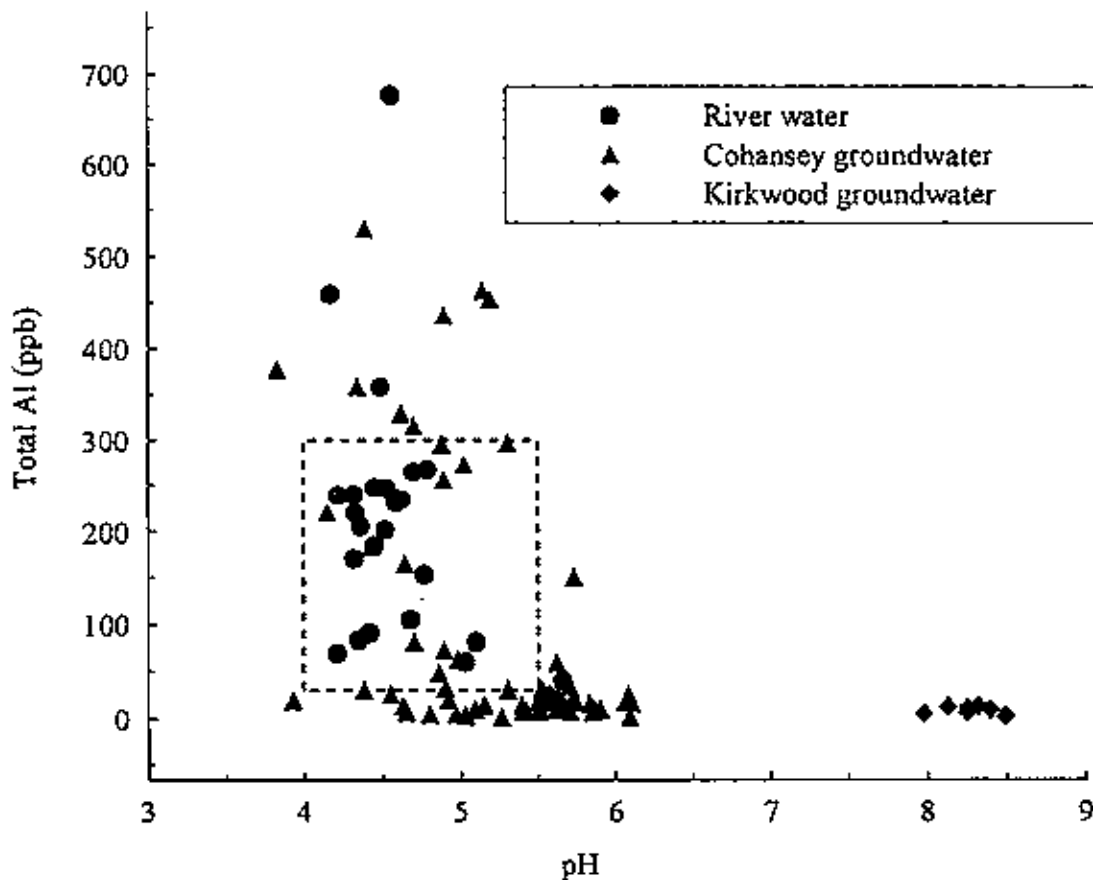


Figure 20. Total dissolved Aluminum vs. pH in the Pine Barren waters. When water has total dissolved aluminum between 30 and 300 ppb and pH between 4 to 5.5, the water is toxic to fishes and water plants. Forty-one percent of the Pine Barrens data, most of which are from the streams, fall into the toxic ranges, shown by the dashed line box above.

toxic than uncomplexed Al (i.e. Al^{3+}) (Dobbs *et al.*, 1989). It is generally known that inorganic aluminum forms are more toxic than organic aluminum forms.

Table 11. Dissolved aluminum concentrations in the Pine Barrens (in ppbs)

	Minimum	Maximum	Median
Stream water	24.9	676.6	205.1
Cohansey water	1.4	529.8	20.2
Kirkwood water	2.5	13.0	9.3

Solubility Controls on Aluminum

It is important to know what processes control the aluminum solubility in natural waters because of the toxicity of uncomplexed Al^{3+} . First, why is high Al concentration associated with acid water? The atmospheric input of sulfuric and nitric acids is believed to contribute to the acidification of waters in the New Jersey Pine Barrens. Waters receiving acid rain (pH approximately 4.3, as reported by Jones, 1994) tend to neutralize the added hydrogen ion by releasing basic cations (Na^+ , K^+ , Mg^{2+} , Ca^{2+}) or retaining acidic anions through ion exchange, adsorption and/or weathering reactions. However, the inert nature of quartz sands and the lack of weatherable minerals in soil of the Pine Barrens give its waters and soil low acid neutralizing capacity (ANC). Under these circumstances, acid neutralization is largely due to dissolution of potentially toxic Al (Driscoll and Newton, 1985; Mulder *et al.*, 1987, 1989). By comparison with groundwater, surface water in the Pine Barrens has much higher aluminum concentrations (Table 11) because surface water is more acidic (Table 10 in Chapter 4).

Concentrations of dissolved Al in natural waters are usually consistent with the solubility of gibbsite and kaolinite, the two most common aluminum minerals in soil. Since the concentrations of dissolved silica in the Pine Barrens are about 3 to 5 ppm, the solubility lines of gibbsite and kaolinite are very close to each other (Drever, 1988). Previous work by Crerar *et al.* (1981) concluded that aluminum concentrations in surface and groundwater in the Pine Barrens were controlled by the solubility of gibbsite and kaolinite. However, this study (combined with that of Jones, 1994) showed that not all of the data fall along the gibbsite saturation line, demonstrated by a -3 slope in Figure 21. Actually, the data form two near-linear trends which intersect at a pH of about 4.8 (Figure 21). At pH > 4.8, activity of aluminum in water (mostly groundwater) is consistent with gibbsite equilibrium (pK = 8.77). At pH < 4.8, activity of aluminum in water (mostly surface water) is undersaturated with gibbsite and is not known to match any common aluminum-hydroxide mineral saturation lines. Aluminum undersaturation in acid waters (pH < 5.0) was also observed by a number of other studies at various locations in North America and Europe (Crouse and Rose, 1976; Nordstrom *et al.*, 1986; Driscoll *et al.*, 1984; Mulder *et al.*, 1994), and has caused a debate on the possible mechanisms.

Aluminum Undersaturation in Acid Waters

One possibility is that there are other aluminum minerals, such as the aluminum sulfate minerals, that might control the aqueous geochemistry of aluminum. However, Jones (1994) showed that surface water in the Pine Barrens is undersaturated with respect to these minerals.

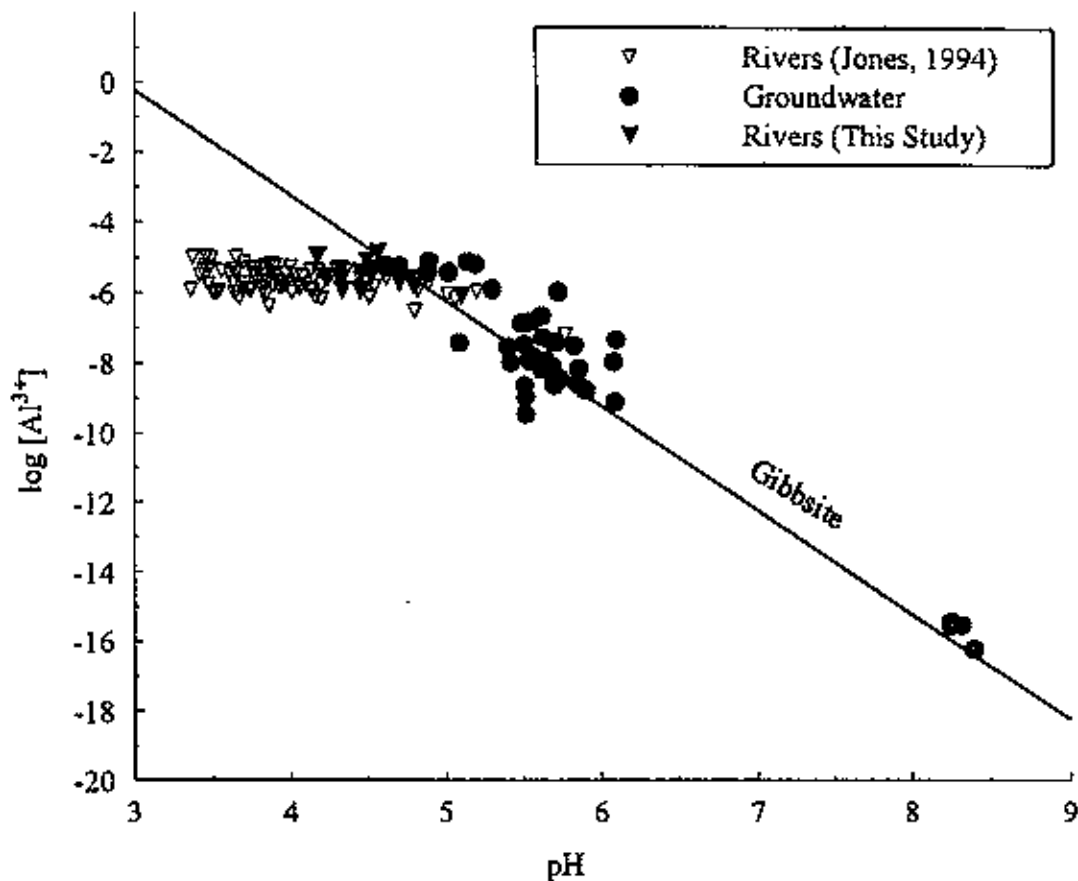


Figure 21. $\log [Al^{3+}]$ vs. pH in the Pine Barrens waters. Two linear trends intersect at pH of 4.8. When $pH > 4.8$, most points fall along the -3 slope line of gibbsite saturation ($pK = 8.77$), indicating activity of Al^{3+} in water (mostly groundwater) is controlled by solubility of gibbsite. At $pH < 4.8$, water samples (mostly from rivers) formed a linear trend that has a more gentle slope than -3. In this case, activity of Al^{3+} in river water is undersaturated with gibbsite.

Aluminum undersaturation was also suggested to be a result of kinetic restraints on the dissolution of aluminous minerals (Nordstrom, 1981; Hooper and Shoemaker, 1985). However, there has been no rigorous effort to test the hypothesis in natural waters. No acceptable explanation is made as to why solutions have low dissolved Al despite pH values less than 4.5 and the elevated concentrations of organic ligands. Furthermore, it is very hard for the kinetic model to quantitatively describe the observed linear relationship between $\log[\text{Al}^{3+}]$ and pH at $\text{pH} < 5.0$.

Another possibility is that Al is controlled by organic aluminum phases. Soil scientists have found that organic Al phases were important sources of pH buffering in acid soils that were low in aluminous-chlorite and relatively low in permanent charge cation exchange capacity, and that organic matter was the most important factor in the control of soil solution Al^{3+} activity (Bloom *et al.*, 1979). Furthermore, the study by Hargrove and Thomas (1980) showed that organic matter could reduce the Al^{3+} activity in soil solution and result in less Al toxicity to plants. Similarly, Mulder *et al.* (1989) demonstrated that only a minor fraction of soil aluminum was readily dissolved in acid soil solutions, and the most soluble fraction consisted largely of non-silicate, organically bound aluminum, which had been formed in the course of soil development. In the system of natural waters, Driscoll (1984) also noticed strong positive correlations between dissolved aluminum and DOC (Dissolved Organic Carbon) in surface waters of the Adirondacks. Progress was made when soil scientists managed to apply what has been found in soil to natural water system.

Cronan *et al.* (1986) developed a model based on their soil equilibration

experiments to predict aqueous Al concentrations in natural waters that have pH values between 3 and 5. The model assumed that, in acid waters, the solubility of aluminum was not controlled by saturation with gibbsite but was controlled by saturation with organic Al. The results of the experiment (Figure 22) indicate that the activity of Al^{3+} in water is affected by pH and the bound Al ratio, which is defined as the equivalents of organically bound Al per organic matter divided by the equivalents of carboxylic (RCOOH) group per organic matter. The solubility of Al decreases with increasing pH, and increases with increasing bound Al ratio. The $\log[Al^{3+}]$ is in a linear relationship with pH given a certain bound aluminum ratio. This linear relationship is exactly what was found in the New Jersey Pine Barrens and what other researchers have found in various places in North America and Europe (Crouse and Rose, 1976; Nordstrom *et al.*, 1986; Driscoll *et al.*, 1984; Mulder *et al.*, 1994).

An attempt to compare the New Jersey data to the organic model was made (Figure 22). Data were plotted onto Cronan's graph of $\log[Al^{3+}]$ vs. pH. The Pine Barrens' data (and also data in other areas which will be discussed later) are almost parallel to the line with the bound Al ratio ranging from 0.0 to 0.1. However, the intercept of the New Jersey data is slightly lower than the line with bound Al ratio of 0.0 - 0.1. The lower intercept may be caused by different kinds of organic matter in the soil of the New Jersey Pine Barrens as compared with what Cronan *et al.* (1986) used in their experiments. It was also observed by Cronan *et al.* (1986) that in places with low mineral content, water could be oversaturated with respect to $Al(OH)_3$ when pH was slightly about 4.8. Thus, the upper limit for the organic model was predicted to pH at about 5.2. Data from the Pine

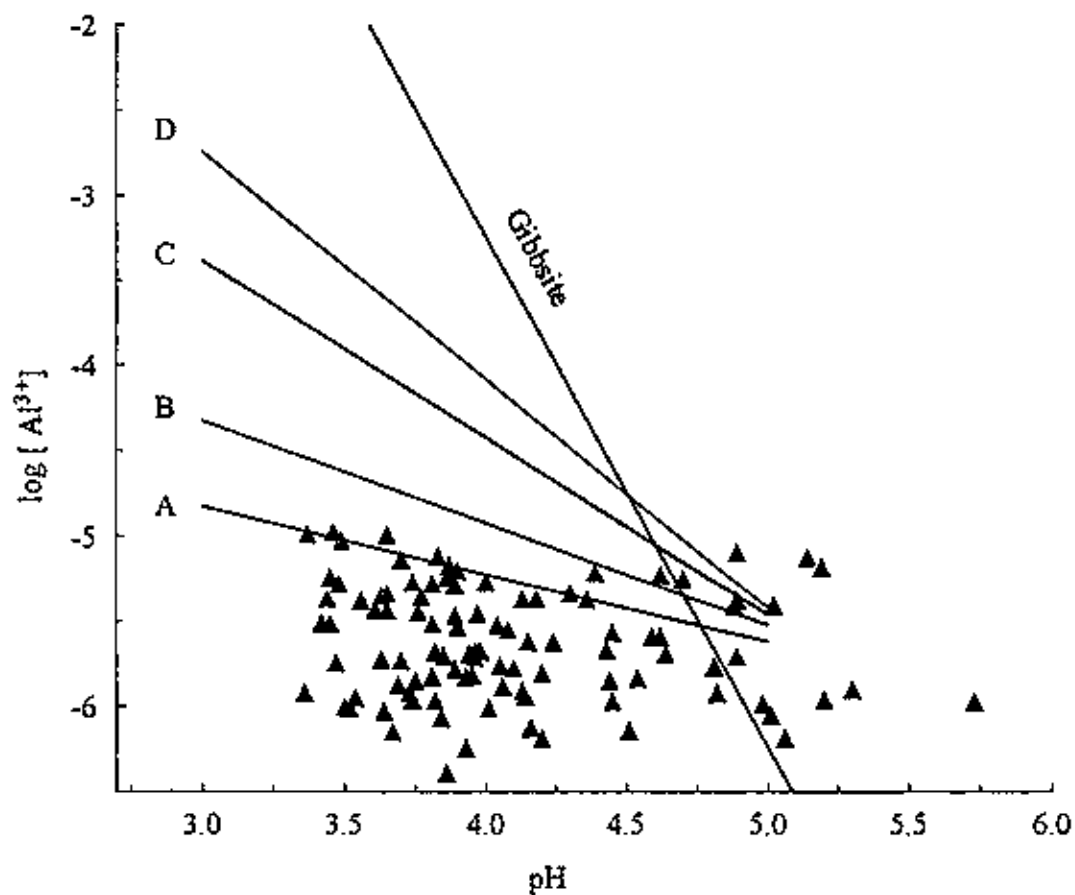


Figure 22. Aluminum solubility in the presence of soil humic matter in the pH range 3.0 to 5.0 (modified after Cronan *et al.*, 1986, Figure 2). The points represent data from the New Jersey Pine Barrens. The four lines marked with A, B, C and D indicate four different ranges of bound aluminum ratios: line A = 0 to 0.1; line B = 0.2 to 0.3; line C = 0.6 to 0.7; and line D = 0.9 to 1.0. The solubility line of gibbsite is shown for reference. The slope of data from the Pine Barrens indicates that the solutions are in equilibrium with Al-organic complexes in soil which have bound aluminum ratio of 0 to 0.1.

Barrens seem to fit this observation (Figure 22), with a pH upper limit at around 5.3.

Evaluations of the Organic Model for Al Undersaturation

1. Bound Aluminum Ratio in the Pine Barrens

To test the organic model for aluminum undersaturation by Cronan *et al.* (1986) in the Pine Barrens area, the bound Al ratios of humic muck in the Pine Barrens were analyzed using techniques by Hargrove *et al.* (1982, 1984) and Cronan *et al.* (1986). The results are shown on Table 12.

Table 12. Bound Aluminum Ratios in the Pine Barrens

Location	Organically Bound Al (meq)	RCOOH (meq)	Weight remained after being treated with HCl (%)	Bound Al Ratios (Organically Bound Al / RCOOH)
Batsto ¹	0.0649	0.45	83.6	0.17
Batsto2 ²	0.0405	0.96	65.5	0.06
Mullica ¹	0.0449	0.37	71.2	0.17
Wading ¹	0.1393	0.68	75.8	0.27
Oswego ¹	0.0279	0.19	71.8	0.18
Atsion ¹	0.0665	1.31	11.1	0.46
Bodine ²	0.0065	0.21	51.3	0.06
Average	0.0557	0.59	61.5	0.19

Note: ¹ - Samples were collected from the streambeds,
² - Samples were collected in the swamps.

The bound Al ratios in the Pine Barrens range from 0.06 to 0.46, and average about 0.19. The range of the bound aluminum ratios in the Pine Barrens is very similar to

that of other soils (Cronan *et al.*, 1986). At equilibrium, the solubility of aluminum is controlled by the least soluble phase in aqueous systems. Since the solubility of Al increases with increase in bound Al ratios (Figure 22), the solubility of aluminum is controlled by the organic aluminum phase with the lowest bound Al ratio, which is about 0.06 in this study. This value corresponds well with what the organic model predicted on the bound Al ratio (between 0.0 and 0.1, Figure 22).

2. Al and Discharge Relations in Surface Water

As this study showed in Chapter 4, major element concentrations in the Batsto River show positive correlations with discharge (Figures 9, 10 and 11). Aluminum behaves similarly. Total dissolved Al concentration increases with increasing discharge in the two major rivers in this region, the Batsto River and the Mullica River (Figure 23). The amount of discharge in rivers in the study area comes from precipitation (and consequent runoff) and groundwater. When precipitation is low, rivers are recharged by groundwater, which has average dissolved Al concentration less than 100 ppb (Table 11). When discharge increases with increasing precipitation, Al in river water can come either from rain or runoff. However, Al concentration in rain is low, averaging about 2 ppb (Jones, 1994) in the Pine Barrens. Therefore, the high aluminum concentrations at high discharge (Figure 23) must come from runoff by dissolution of organic aluminum phases formed during soil development. On the other hand, the dissolution of organic Al solids at high discharge is strongly associated with low water pH in the study area because low water pH appeared also at high discharge periods (Figure 11 in Chapter 4).

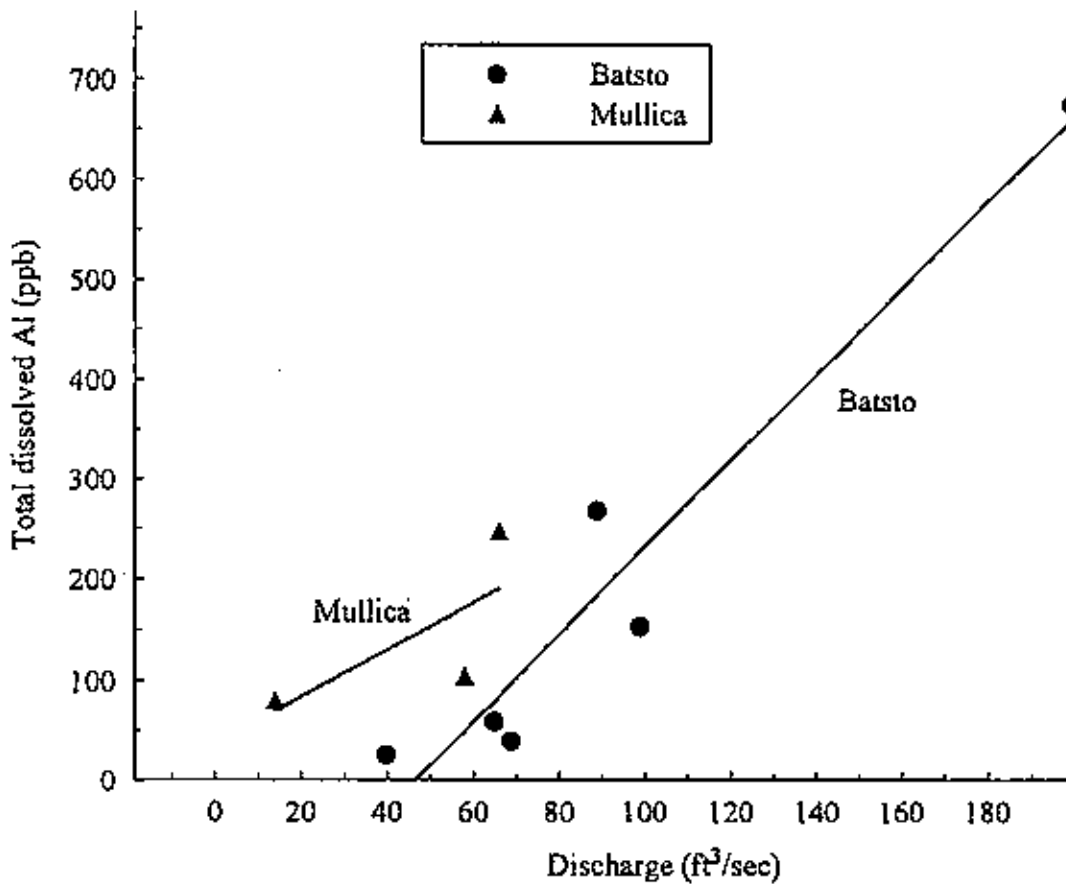


Figure 23. Total dissolved aluminum vs. discharge in the Mullica and Batsto River in the New Jersey Pine Barrens. Aluminum concentration increases with increasing discharge in both rivers. The positive correlation suggests aluminum in rivers comes from groundwater at low discharge and from runoff at high discharge by dissolution of organic Al phases in soil.

To summarize, the gibbsite solubility model is appropriate in the groundwater zone because groundwater has higher pH and low flow speed to ensure attaining mineral saturation. The organic model, or aluminum undersaturation, is applicable to the upper soil horizons. During peak flows of a low order stream (Both the Mullica and the Batsto Rivers are first-order streams.), stream water will be strongly influenced by the "undersaturation" resulted from lateral runoff derived from organic-rich soil horizons, and thus, will demonstrate Al undersaturation in stream water. It is speculated that if Al undersaturation is studied in soil water, the ratio of runoff : base flow (groundwater) can be calculated using a two-endpoint mixing model.

Aluminum Solubility in Other Studies

As mentioned previously, the break in slope on the $\log[Al^{3+}]$ vs. pH diagram (Figure 21) is not unique to the study in the Pine Barrens. Other studies in California (Nordstrom, 1981), the Adirondacks (Driscoll, 1984), and Appalachia (Crouse and Rose, 1976) demonstrated the same phenomenon (Figure 24). It seems that it is a common behavior of aluminum regardless of field conditions, ionic strength, and water qualities.

There is an Al-pH transition zone (defined by Nordstrom and Ball, 1986) at pH between 4.8 and 5.2. When pH is greater than the transition zone, the concentration of aluminum is consistent with the solubility of gibbsite (or kaolinite). When pH is lower than the transition zone, aluminum in water is undersaturated with gibbsite. The undersaturation of aluminum could be controlled by the solubility of organic aluminum phases in soil. The intercepts are different between these datasets. At a higher pH (pH >

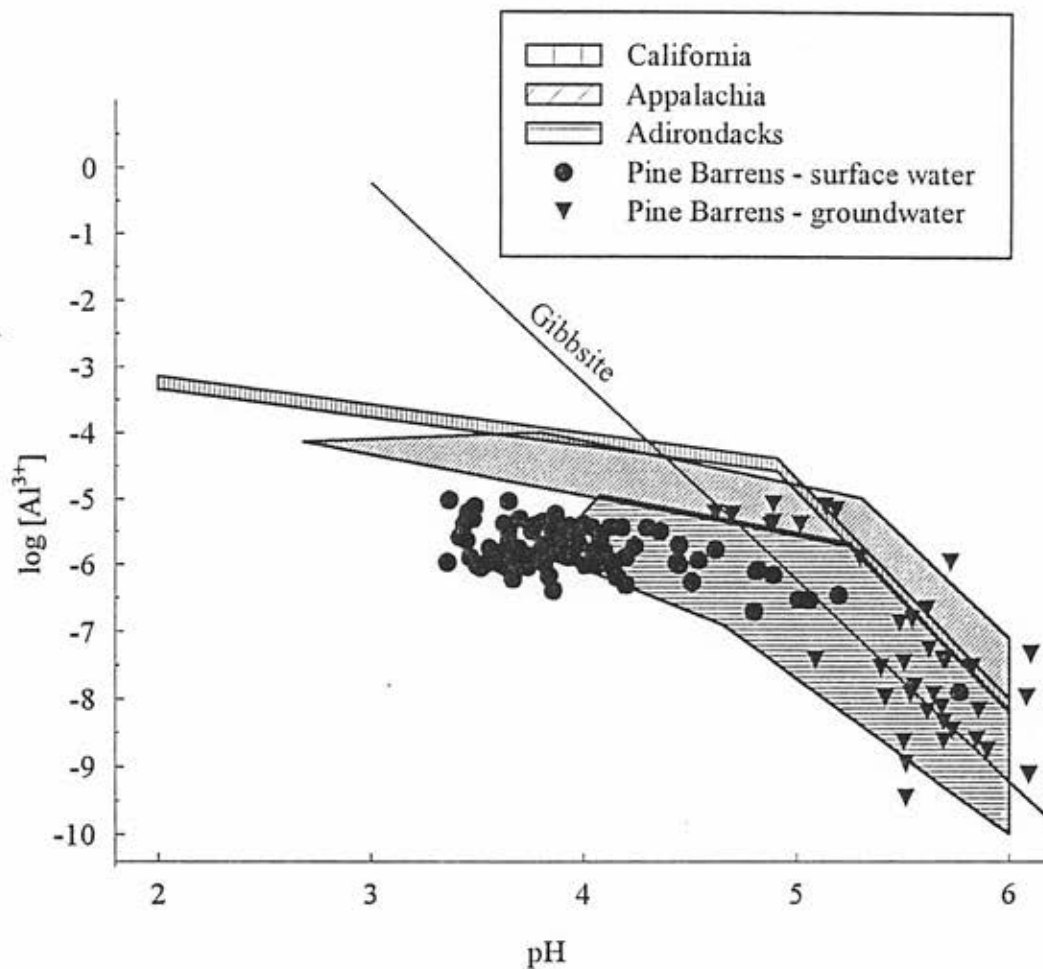


Figure 24. Comparison of $\log[\text{Al}^{3+}]$ vs. pH from California, Appalachia, the Adirondacks (data from Nordstrom and Ball, 1986) and the Pine Barrens (combined with data from Jones, 1994). Each dataset forms two linear trends that intersect at pH between 4.8 and 5.2 (defined as the Al-pH transition zone). At a higher pH (> 4.8 to 5.2), activity of Al is controlled by saturation with gibbsite. At a lower pH (< 4.8 to 5.2), Al in water shows undersaturation with gibbsite and may be controlled by saturation with organic Al phases. The difference in offsets between the datasets at low pH may be caused by different organic matter in various locations.

4.8 - 5.2), it may be caused by different degrees of crystallinity of gibbsite or even different equilibrium constants used; at a lower pH ($\text{pH} < 4.8 - 5.2$), it may be due to different kinds of organic matter presented at various localities. The existence of the transition zone is due to different intercepts.

It is still too early at this point to draw the conclusion that this "two-model theory" is universal for aluminum solubility control. More comparison-and-contrast work on hydrologic, geologic conditions as well as water and soil contents should be done to obtain a range of application.

CHAPTER 7

CONCLUSIONS

Water quality in the New Jersey Pine Barrens is under the threat of acid precipitation because of the low acid buffer capacity of the quartz-rich sands in the aquifers in this region. This study is aimed at providing a better understanding of hydrogeochemical processes in the Pine Barrens and laying a foundation for future research on the potential effects of acid rain in this area. The focus of the research is on the water quality of groundwater and surface water in the Pinelands.

Groundwater chemistry in the Pine Barrens differs significantly between the two stratigraphic units. The difference suggests very little cross-formational flow between them. The difference comes from very different solute sources and chemical reactions in the two formations. Solute chemistry of the overlying Cohansey Formation is controlled mainly by acid precipitation that carries marine and continental aerosols. Chemical reactions in clay layers and sand are minor in the Cohansey because of the shorter residence time that is controlled by local groundwater flows. Water chemistry in the underlying Kirkwood Formation is mainly controlled by water:rock reactions in the sand and clay layers. Since regional flow system controls the Kirkwood groundwater and on the other hand the Kirkwood Formation is much less permeable, Kirkwood groundwater has much slower flow speed and longer residence time to result in a greater degree of water:rock reactions. Surface sources play little part in its composition.

Na⁺ and Cl⁻ in Cohansey groundwater exhibit a Na⁺/Cl⁻ ratio similar to that of sea water and are therefore derived from marine aerosols and distributed by local flow. Kirkwood groundwater contains Na⁺ coming from water:rock reactions, indicating regional flow and long residence time for chemical reactions. Low Cl⁻ concentration in Kirkwood groundwater suggests that the source of Kirkwood groundwater is much further inland.

Cohansey groundwater and surface water are very similar in composition because solute chemistry of both is mainly controlled by precipitation in the region. However, there are some differences which are caused by minor controls in water chemistry. For instance, surface water is also influenced by runoff, and Cohansey groundwater has a small amount of water:rock reactions.

Surface water shows seasonal variation, which is controlled by discharge in rivers. Cohansey groundwater shows little seasonal variation since groundwater has residence time longer than one year. However, in different wells, water chemistry varies, which suggests that groundwater in the Cohansey Formation is quite heterogeneous. The clay confining layers, which has low permeability, contribute to the differences in water composition within the Cohansey Formation as well as between the two stratigraphic units in the Pine Barrens.

The source of bog iron in the Pine Barrens is not associated with the underlying glauconitic formations. The source of bog iron is not transported from the deeper Kirkwood groundwater through cross-formational flow since Kirkwood groundwater has less dissolved iron content. The existence of wide-spread cross-formational flow is questionable because on the one hand, solute water chemistry is quite different between

the two formations; on the other, the potentiometric table of the Kirkwood Formation is observed lower than the water table in the Cohansey Formation, leaving no impetus for water to travel upward. The source of bog iron might be from the iron- and clay-rich confining layers in the Cohansey Formation.

Dissolved aluminum has very high concentration in surface water in the study area because of acid precipitation and low acid neutralizing capacity of quartz sand. The solubility of aluminum in water is found to be consistent with a "two-model theory". When $\text{pH} > 4.8$, activity of aluminum is regulated by solubility of gibbsite or kaolinite. When $\text{pH} < 4.8$, aluminum is undersaturated with these minerals; the activity of aluminum is regulated by solubility of organic aluminum phases with low Al/COOH ratios. The "two-model theory" may apply to acid waters in several places in the United States.

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