HYDROGEOCHEMISTRY OF THE NEW JERSEY PINE BARRENS

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As part of our state's service to New Jersey citizens and municipalities, this report has been published by the Geological Survey of the Department of Environmental Protection.

This document is a technical publication which establishes the current level of hydrogeochemical knowledge in a significant portion of the Pine Barrens region. Most importantly, it identifies and proposes some basic geochemical processes that are unique in type and degree to the Pine Barrens' type of ecosystem. It provides a technical basis for further research in planning by those who are familiar with soil chemistry, geochemistry and water chemistry. In this way, the "Hydrogeochemistry of the New Jersey Pine Barrens" will help lead to decisions which protect this fragile ecosystem.

Your comments are earnestly solicited and we appreciate the opportunity to serve you.

Very truly yours,

JERRY FITZGERALD ENGLISH
Commissioner

TABLE OF CONTENTS

Page

ACKNOWLEDGMENTS

CHAPTER 1 INTRODUCTION

CHAPTER 2 GEOCHEMISTRY OF PRECIPITATION

CHAPTER 3 RIVER WATER: MAJOR ELEMENT GEOCHEMISTRY AND MASS BALANCES

CHAPTER 4 STREAM AND GROUND WATER: TRACE METAL GEOCHEMISTRY

CHAPTER 5 ORGANICS AND ORGANO-METALLICS IN PINE BARRENS WATERS

CHAPTER 6 ESTUARY WATER: TRACE METAL GEOCHEMISTRY

LIST OF FIGURES

LIST OF TABLES

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Chapter 1

INTRODUCTION

This report summarizes the results of research on the hydrogeochemistry of the New Jersey Pine Barrens carried out over the past ten years at the authors' laboratories.

The following subjects have been studied: major element geochemistry of precipitation and stream water; trace metal compositon of stream, estuary and groundwater; aqueous chemistry of humic substances and organo-metallic interactions in stream and estuary water; genesis of bog iron and the role of iron-oxidizing bacteria; and finally, Al and Fe solubility in stream ground and estuary water and flocculation of Al, Fe, Mn, and humates at the stream-estuary interface.

Pine Barrens ecology, hydrology, and geochemistry have been the subjects of some 6 senior and 4 junior undergraduate theses at the Department of Geological and Geophysical Sciences at Princeton University since 1970. In addition, a summer NSF grant was awarded to fourteen undergraduates to study the Pine Barrens ecology in 1971. Three graduate students and three faculty advisors have also been involved in the research. NSF Grant No. GA-31061 was awarded from 1971 to 1973 to D. Kinsman for research on the chemical composition of surface and shallow groundwaters of the area. Parts of the present study constitute a portion of the Ph.D. research of the primary co-author.

Research has focused primarily on the drainage basins of two rivers: Cedar Creek and the Mullica River (fig. 1-1). The Cedar Creek basin, comprising 144 km² (56 mi²) of land, has not yet been significantly disturbed by development or farming. Most of the area is forested and in 1974 the population density was only 84.6 per square mile (in Lacey municipality, Anonymous, 1974). Cranberry cultivation is the principal agricultural acitivity. The Mullica River Basin drains 1476km² (570 mi²) of land, almost a third of the area of the entire Pine Barrens. In 1967 the population density was approximately 66 people per square mile. Here there is much farming, including cranberry, blueberry, peach, and apple cultivation, especially in the western and southern parts of the basin. Forest dominates the remainder of the region (Rhodehamel, 1973).

GEOLOGY*

New Jersey may be subdivided into three main geologic provinces as illustrated in fig. 1-2 after Olsson (1963). In the Piedmont Lowland Province the sediments of the non-marine late Triassic to early Jurassic Newark Group nonconformably overlie Precambrian and Paleozoic basement. Late Cretaceous through Eocene sediments outcrop in a narrow belt bordering the Piedmont. This belt and the more southerly Miocene—Pliocene (?) sediments constitute the New Jersey Coastal Plain—essentially the northernmost exposure of the Atlantic Coastal Plain (barring small outcrops on Long Island and Nantucket).

The region known locally as the Pine Barrens or Pinelands occupies a major part of the New Jersey Coastal Plain and is defined largely by its unique pine-dominated vegetation. While originally occupying some 5800km² (2250 mi²), pressures of land development have decreased this coverage today to approximately 3900km² (1500mi²) (Bartlett et al., 1978).

Topographically, the New Jersey Coastal Plain is flat and low-lying, with poor drainage, many swamps, and slow-flowing streams. The two major rivers, the Mullica and the Great Egg Harbor River fall only 1.5m in 25 km (5 ft in 16 mi), and 1.5m in 37 km (5 ft in 23 mi), respectively (Starkey, 1962).

The stratigraphy of the Coastal Plain has been detailed elsewhere (Owens and Minard, 1960; Olsson, 1963; Richards, 1967; Minard et al., 1969; Anderson and Appel, 1969; Owens and Sohl, 1969; Rhodehamel, 1973; Minard et al., 1974), and is only briefly outlined here. Dipping seaward at usually less than 10m/km (50 ft/mi), the sediments are roughly 300m thick in outcrop (Olsson, 1963), and thicken to roughly 1300m both seward and to the south. Fig. 1-3, from Owens and Sohl (1969) is a schematic cross-section approximately along strike, and fig. 1-4, from Anderson and Appel (1969) illustrates the downdip seaward thickening of strata and the underlying succession of aquifers and aquitards. The sediments, which are uncosolidated or partly consolidated, consist of interlayered marine, marginal marine, and nonmarine formations. Sediment types vary from the beach sands and alluvial gravels and clays of the overlying Cohansey and Kirkwood formations to the highly glauconitic Hornerstown, Merchantville, Marshalltown, and Navesink formations. Carbonaceous and glauconitic silty clays are interbedded in the Magothy, Merchantville, and Woodbury formations. The entire region is overlain by a discontinuous veneer of Quaternary sand, gravel, and clay—the Bridgeton, Pensauken, and Cape May Formations in order of decreasing age. Owens and Sohl (1969) have concluded that the Coastal Plain section represents a cyclical pattern of marginal marine transgression and regression with outer-shelf greensands in any cycle being overlain by near shore silty units, and finally by beach sands and gravels.

Iron occurs throughout the section predominantly as glauconite in the greensands and glauconitic clays (fig. 1-3). It is also locally abundant in silts and clays as siderite concretions. Pyrite and vivianite have also been

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* Portions of the following sections of Chapter 1 are reprinted from Crerar et al. (1979) by permission of Elsevier Scientific Publishing Company.

described in interbedded glauconitic marls and shales (Braddock-Rogers, 1930; Starkey, 1962). These ironstones, which are found below and to the west of the Pine Barrens are believed to be the source of the iron oxide stains and cements in the upper Cohansey and Kirkwood Formations and of the bog iron that is found along many of the streams in the area.

HYDROLOGY

Water is one of the principal resources of the New Jersey Coastal Plain. Despite its proximity to the major east coast cities, the Pine Barrens remains almost totally undeveloped and its waters are pristine and unpolluted. In 1954-1955, the Wharton Tract, consisting of some 385 km^2 (95,000 acres), was set aside by the State of New Jersey as a groundwater reserve to meet future water requirements in the Camden and Atlantic City areas.

As illustrated in fig. 1-4, the New Jersey Coastal Plain is underlain by a succession of aquifers and aquitards, the latter becoming increasingly glauconitic and clay-rich downdip. The principal aquifers of the Pine Barrens region are the Magothy, Raritan, Kirkwood and Cohansey Formations. Rhodehamel (1970) has estimated the usable standing water reserves of the Cohansey Sand alone in this region at 40.9×10^{12}l (10.8×10^{12} gallons). The uppermost aquifers are hydraulically interconnected. To the south and east, an increase in the silt and clay content of the Cohansey Sand and upper Kirkwood forces groundwater to the surface (Rhodehamel, 1970).

The streams in this region are fed largely by groundwater baseflow. Rhodehamel (1970) developed a hydrologic budget for the Pine Barrens based on the relationship:

$$P = R + ET$$

where

P = average annual precipitation, as cm (in) depth over the area [113 cm (45 in)]

R = average annual stream runoff, measured as cm (in) depth over the area [56.5 cm (22.5 in)] and

ET = the average annual evapotranspiration, as cm (in) depth over the area [56.5 cm (22.5 in)].

The model presumes no groundwater baseflow to the ocean due to the seaward decrease in aquifer permeability noted above. Because P and R are determined from rain and stream gauging stations, and ET is computed, then any groundwater discharge to the ocean would simply decrease ET. Most importantly for the present purpose, Rhodehamel also estimated that groundwater baseflow supplies roughly 89% of all river water, the remainder coming from direct surface runoff. Hence rivers in this region are almost entirely fed by underlying aquifers.

The Cohansey Sand, which is the uppermost aquifer, is relatively unreactive chemically, consisting primarily of quartz sands and gravels with local clay lenses. Rainfall in the Pine Barrens is acidic, with an average pH of around 4.4, caused by atmospheric pollution. Unaltered Pine Barrens river and groundwaters are also acidic, attributed to the low pH of the rainfall, CO_2 from plant respiration and decay and the prevalence of natural organic acids from the swamplands. Both river and ground waters contain extremely low total dissolved solid contents (15-30 ppm). Owing to the inert nature of the Cohansey Sand, the principal difference between precipitation chemistry and ground/river water chemistry is the addition of SiO_2, Fe, and in some cases, organic carbon to the latter.

ECOLOGY

Unique geological, hydrological, and geochemical conditions have combined to provide habitats for many unusual forms of vegetation in the Pine Barrens. The area is rather inappropriately named as it actually supports at least 800 plant species and varieties, and 400 animal species (McCormick, 1970; Bartlett et al., 1978). Two distinct phases of vegetation are present: upland and lowland (McCormick, 1970). Upland areas are dominated by a forest of pygmy pitch pine 60 to 150 cm tall (2 to 5 feet) and blackjack and post oak. Because of the high permeability of the Cohansey Sand and corresponding rapid infiltration, surficial conditions are arid, and organic decompostion is slow. Flammable plant remains accumulate, and the area is prone to frequent fires. Pitch pine has the ability to stemsprout after a fire. Also this species exhibits a polymorphism of open and closed cones; pitch pines in the lowlands are largely open-coned while those in the highlands typically have closed cones that open during fire. Post and blackjack oak are more fire resistant than several other related species in the Barrens such as scarlet, black, white, and chestnut oaks which occur in more protected areas. Pitch pine and post and blackjack oaks show marked adaptation for survival through fires, and because of this they have evolved to dominate much of the upland area (Givnish, 1971; McCormick, 1970).

Adjacent to the fire-swept, desert-like conditions of the uplands are the water-saturated bogs and swamps of the lowlands. Such swamps are dominated by Atlantic White Cedar, red maple, black gum, sweet bay magnolia, pitch pine and some twenty-five species of sphagnum moss (Givnish, 1971; Givnish and Kinsman, 1972; Harshberger, 1916; McCormick, 1970). The soil of the swamps has an acidic peat-like composition and both soil and waters are relatively poor in nutrients. These swamps afford some of the best remaining habitats on the east coast for many rare and unusual plants characteristic of an oligothrophic or ombrotrophic environment. Among these are various insectivorous plants, adapted to low nitrogen, high acid conditions. They include: pitcher plant, roundleaf sundew, spatulate-leaf sundew, threadleaf sundew, horned bladderwort, and swollen bladderwort (Givnish, 1971). Also suited to the moist, acid, swamp environment are 26 species of wild orchids, including: arethusa, grasspink, pink ladyslipper, white-fringed orchid, orange-fringed orchid, green woodland orchid, yellow-crested orchid, and rose poponia. Other rareties include carolina clubmoss and the federally endangered curly grass fern, which grow in both sphagnum bogs and cedar swamps (Givnish, 1971). The lowlands environment also supports large scale commercial cultivation of cranberries and blueberries.

An exceptionally large number of plant and animal species reach their northern and southern limits within the Pine Barrens (Bartlett et al., 1978, pp. 19-33; McCormick, 1970). Hence the area serves as a natural laboratory for biologists interested in the habitat and range of such species.

Survival of the rare and unusual biota of Pine Barrens upland and lowland areas is dependent upon the hydrology, geochemistry, and fire-controlled ecology of the area. Any significant change from present conditions may result in the destruction of habitat and extinction of many unique plants. For example, excessive water removal may cause a drop in the water table in bogs. This would in turn kill plants requiring a saturated root environment and also increase fire frequency resulting in destruction of habitat. Pine Barrens surface and ground water chemistry is poorly buffered and may be significantly altered through even minor amounts of pollution. For example relatively high pH's are observed in stream waters during spring and summer months and are likely attributable to agricultural activities such as liming although the photosynthetic activity of algae and water plants might also cause a slight rise in pH. Agricultural activity may also increase the concentrations of certain ions such as calcium in Pine Barrens waters. Numerous Pine Barrens plants require low pH and very low ionic strengths for survival (for example, sphagnum moss is calciphobic, Givnish, 1971). Consequently relatively unobtrusive practices such as liming fields may alter natural water chemistry enough to affect biota. Pollution from urban or industrial activities would likely have even greater effects.

The Pine Barrens ecology is in delicate balance with water geochemistry and hydrology. The results of the present study underline the fragility of this ecosystem.

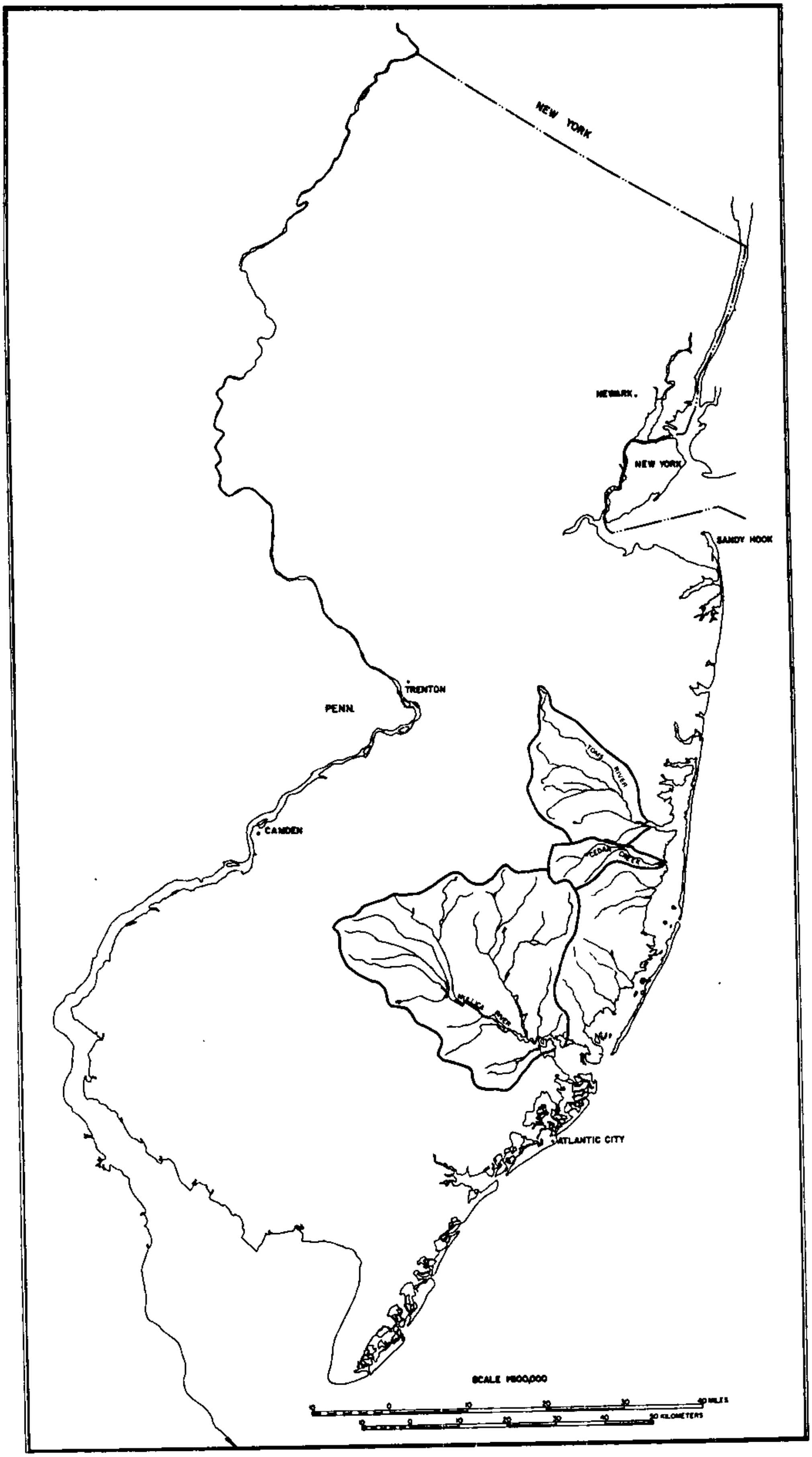


Fig. 1-1. Drainage basins of rivers in the New Jersey Pine Barrens which were monitored during this study.

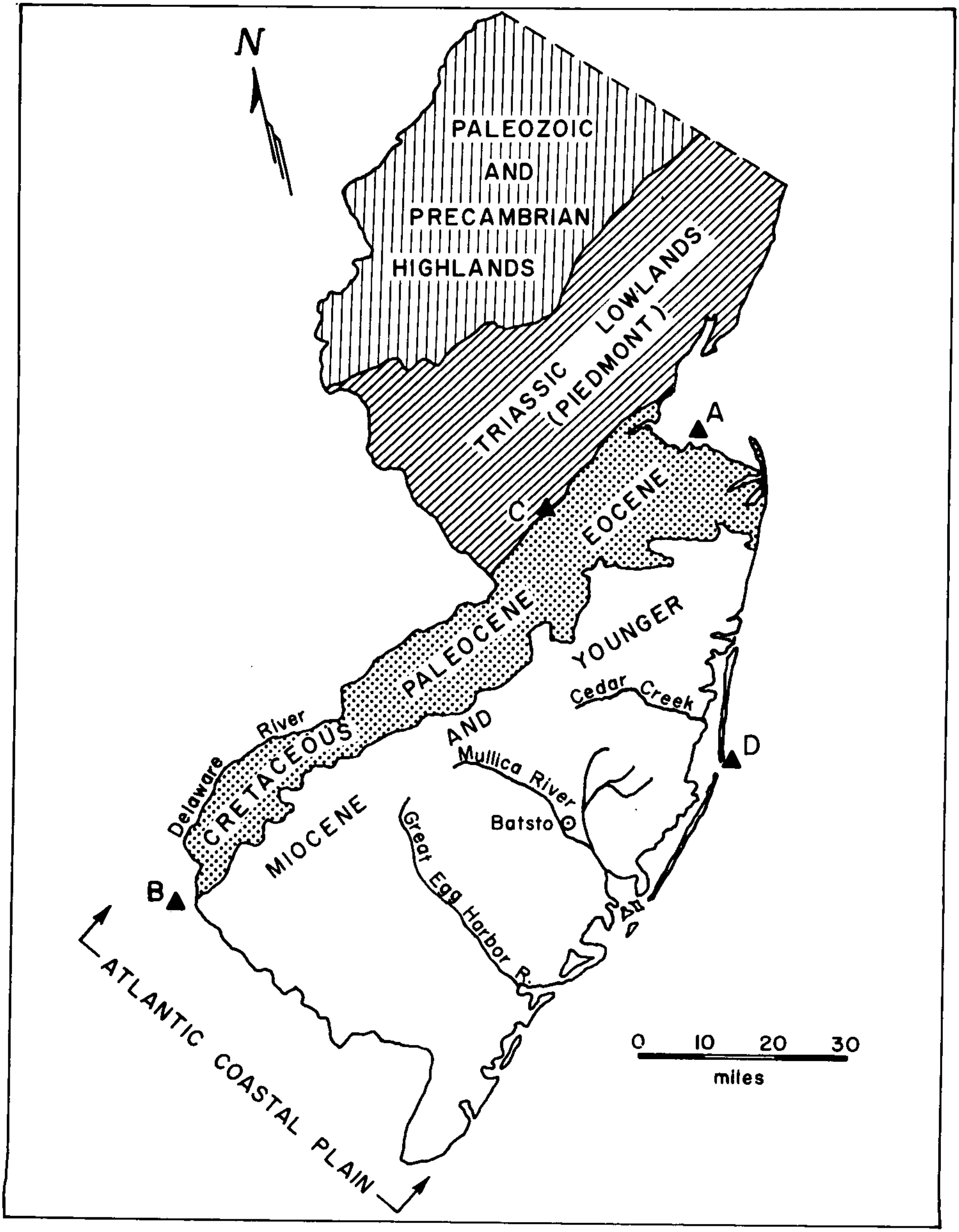


Fig. 1-2. Major geologic provinces of New Jersey. Reprinted with permission of Elsevier Scientific Publishing Co.

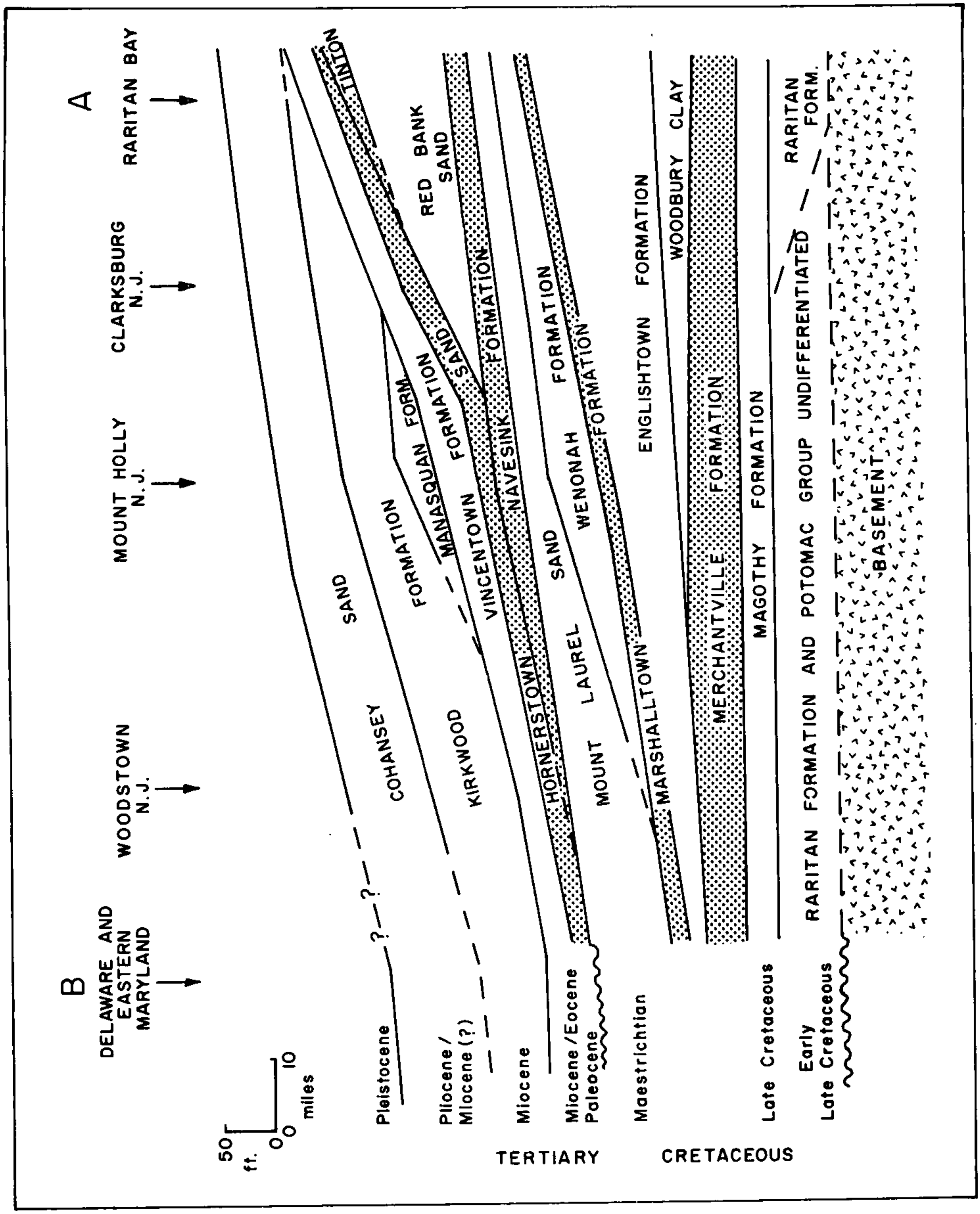


Fig. 1-3 Generalized cross section from A to B on fig. 1-2 showing the approximate thickness and lateral relations of the Coastal Plain formations. Glauconitic units are stippled. Reprinted with permission of Elsevier Scientific Publishing Co.

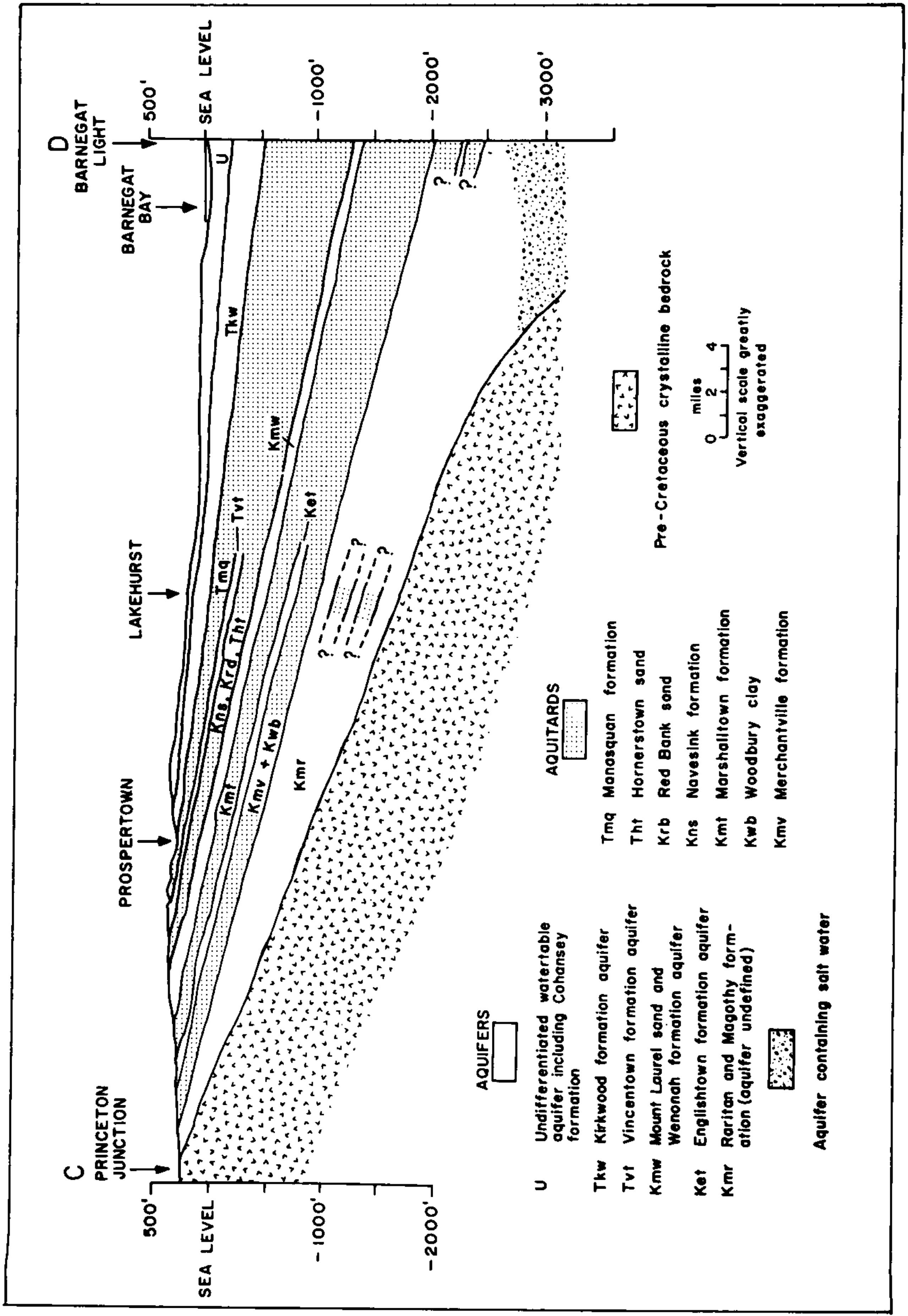


Fig. 1-4. Geohydrologic section across the New Jersey Coastal Plain from C to D on fig. 1-2 showing aquifers and aquitards. Reprinted with permission of Elsevier Scientific Publishing Co.

Chapter 2

GEOCHEMISTRY OF PRECIPITATION

INTRODUCTION

Precipitation chemistry plays a major role in the overall hydrogeochemistry of the Pine Barrens. The soluble and particulate matter which enters a drainage basin in precipitation usually has a minor effect on the geochemistry of streams—this is typically controlled by soils, lithology, and vegetation. However, this generalization does not hold for the Pine Barrens. Here, soils are thin and poorly developed; the quartz sands and gravels of the Cohansey Formation are chemically unreactive and highly permeable. The ion exchange and adsorption capacities of these uppermost sediments are exceptionally low. Consequently, it is conceivable that the chemistry of ground waters and streams in the region might reflect the rainfall composition (Kelsey and Kinsman, 1971).

Precipitation chemistry is itself quite variable, changing as a function of time and place, and these variations were also investigated systematically.

METHODS

In order to achieve maximum control on geochemical inputs and outputs, a single drainage basin, Cedar Creek, was extensively monitored. Five of the Princeton rain gauges (Rwa-Rwe) were located near various tributaries of this stream (fig. 2-1). These gauges were arranged from source to mouth of Cedar Creek to provide samples of rainfall ranging from near the coastline to the drainage divide between the Delaware River and Atlantic Ocean. These gauges were sampled during the period December 1970 to December 1972, inclusive.

To provide a further check on precipitation chemistry, three more gauges (Rwf to Rwh) were established in June, 1971 (fig. 2-1). These provide an additional cross-section of the Pine Barrens, and help monitor inputs to drainage basins of the Mullica River and the smaller coastal streams. These gauges were also terminated at the end of December 1972.

The basic Princeton rain gauge consisted of a one liter polyethylene bottle with the top cut off and inverted in the remaining part to form a collecting funnel. The area of the funnel was 65.28 cm^2 (10.11 in^2). The bottom of the funnel was covered with a piece of heavy plastic sheet in which a slit was cut to minimize evaporation losses. Drainage of the water through the slit into the main reservoir was facilitated by a small air hole punched into the side of the gauge near its top. The collector was mounted on a 2m high pole in an area as far away from trees and human interference as possible.

Precipitation samples were collected from the gauges at approximately two week intervals, although during periods of low rainfall, gauges were left unsampled for up to four weeks. The average length of the sampling intervals was 19.2 days, and a total of 39 precipitation samples was obtained from each gauge.

The rain gauges were open to the atmosphere throughout the sampling period. Accordingly, the samples represent bulk precipitation or the total sum of rainfall, snowfall and dry particulate matter from the atmosphere. Throughout this paper, the term "precipitation" shall refer to this total contribution. This study focuses on the longer term variations in precipitation chemistry, and no attempts were made to sample precipitation from individual storm systems.

ANALYTICAL PROCEDURES

Rainwater samples were filtered (Whatman No. 5) and weighed immediately after collection. The mass of water was recalculated into a volume and thence into inches and centimeters of precipitation. Some pH measurements were made at this time. Concentrations of major cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) were measured by atomic absorption spectrophotometry at accuracies of ± 1% except for K^+ which is reliable to ± 3%. Cl^- was determined using a specific ion electrode (± 3%). The quantitative analysis of these constituents was usually completed within a few weeks of the sample collection.

SO_4^{2-} analyses were carried out by adding 20 ppm $BaCl_2$ to the samples. The SO_4^{2-} was precipitated as $BaSO_4$ and the solution was analyzed for residual Ba^{2+} by atomic absorption spectrophotometry at ± 5%. NO_3^- determinations were made by UV spectrophotometry using the brucine method (Rand et al., 1976) with an accuracy of ± 7%. Total PO_4^{3-} analyses were also performed on several samples. After acid digestion, the PO_4^{3-} was determined by spectrophotometric analysis using the molybdate yellow method (Rand et al., 1976) at ± 5% accuracy. All of these analyses, together with a complete redetermination of pH, were performed at a later date (Gay, 1975). In the interim the samples were stored in polyethylene bottles in a dark closet, there being no evidence of significant chemical alteration.

AMOUNT OF PRECIPITATION

Fig. 2-2 is a map of the average yearly precipitation in southern New Jersey during 1971 and 1972. Precipitation contour lines are based on information gathered by cooperating observers of the U.S. Weather Service and published in "Climatological Data—New Jersey" (Anonymous, 1971a, 1972a). For both years, the average rainfall across the state was well above the normal of 115 cm/yr (45.6 in/yr). The average yearly precipitation recorded by Weather Service gauges over the study period was 134.5 cm (53.4 in) in southern New Jersey and 132.8 cm (52.7 in) in the Pine Barrens region.

The published data also allowed us to compute the collecting efficiency of the Princeton gauges. The average precipitation collected per sampling period compared favorably with that determined from the six nearest Weather Service stations (see Appendix I). The notable exception occurred during times of heavy rainfall (>8 cm) when the Princeton gauges overflowed; as a result, the yearly average precipitation recorded by our gauges was about 15 to 20% less than that reported by the Weather Service. In addition, Gambell and Fisher (1966) and Eriksson (1959; 1960) have shown that similar samplers established for chemical analyses of precipitation collected 10-25% less water than neighboring rain gauges. They attributed this to two factors: 1) the funnel diameters of the chemical collectors were smaller and 2) they were higher off the ground than the volume-measuring devices. As such, the chemical collectors were more exposed to atmospheric turbulence and were less effective in collecting snow and light rainfall. The conclusion of Gambell and Fisher (1966) suggests that the collection inefficiency of the Princeton gauges should have no effect on the observed concentration of the chemical components. However, volumetric information used in subsequent calculations is taken from the Weather Service gauges.

GEOCHEMISTRY OF PRECIPITATION

The average composition of precipitation in our study area reflects the proximity of the ocean. For example, the content of total dissolved solids is more than twice that reported for precipitation throughout North Carolina and Virginia (Gambell and Fisher, 1966). Sodium is the dominant cationic species as opposed to calcium, which is generally more abundant in rainfall over inland areas. Chloride concentration is also notably higher than observed inland.

The average concentrations of major components in Pine Barrens precipitation are listed in table 2-1 along with Gambell and Fisher's (1966) observations for North Carolina and Virginia. In the sections that follow, fluctuations in the input rate of these constituents (except PO_4^{3-}) are examined with respect to precipitation volume, seasonal changes and geographic distribution. The PO_4^{3-} data are insufficient for detailed analysis at this time.

INPUT OF CHEMICAL CONSTITUENTS

The average input of each constituent per square meter for individual sampling periods is plotted as a function of precipitation in fig. 2-3. The constituents are divisible into two groups. Na^+, Cl^-, Mg^{2+} and SO_4^{2-} show a definite tendency toward higher mass inputs during periods of high rainfall while K^+, Ca^{2+} and NO_3^- are much less dependent upon the amount of precipitation. These data indicate that members of the first group are carried in the atmosphere largely as soluble salts. Generally speaking, soluble salts in precipitation originate as marine aerosols derived from the bursting of bubbles in the foam of waves (Junge, 1958). These aerosols, which reflect seawater composition, become further concentrated by evaporation. Being hygroscopic, they wash out in greater amounts with increasing precipitation.

Marine aerosols constitute only a minor source of SO_4^{2-}, usually less than 10% of the total SO_4^{2-} in precipitation (Gambell and Fisher, 1966). Other natural sources are also insignificant, and most of the abundant sulfate in the Pine Barrens precipitation originates as SO_2 from the combusion of fossil fuels (Nakai and Jensen, 1967). This excess SO_4^{2-} is balanced by H^+, which gives rise to the acidic rain in the Pine Barrens and throughout the northeast (Cogbill and Likens, 1974; Gay, 1975).

The second group contains those constituents that enter the collectors predominantly as dry fallout. Dry fallout tends to be derived as aerosols from continental source areas. The composition of these aerosols depends upon the soil type, rock exposure, vegetation and climate of the regions over which the air mass has passed (Delany et al., 1973). This material accompanies precipitation, but it is not dissolved in the water so the total inputs are not as dependent on the amount of rainfall. An earlier study of precipitation over a large area of the northeastern United States showed effects similar to those outlined above, particularly in coastal locations (Pearson and Fisher, 1971).

In their study, Pearson and Fisher found that magnesium behaved as a dry particle, but the Pine Barrens data show a definite correlation between the mass of Mg^{2+} and precipitation (Fig. 2-3(d)). This is reasonable in light of the different study areas considered. Most of the stations of Pearson and Fisher (1971) are located well inland, far removed from the immediate effects of marine aerosols. Accordingly, the bulk of Mg^{2+} contained in the precipitation in these areas is derived from continental sources. By contrast, the inland-most rain gauge in this study is only 45 km (28 mi.) from the coast and much of the Mg^{2+} is derived from soluble marine aerosols. The coastal stations of Pearson and Fisher (1971) also contain significantly higher amounts of Mg^{2+} than the other locations.

The minimum amount of each component introduced per square meter as dry fallout during an average sampling period (19.2 days) can be determined from the y-intercept on fig. 2-3. Thus Ca^{2+} exhibits a dry fallout rate of 292 mg $m^{-2}yr^{-1}$, and K^+ has a fallout rate of 219 mg $m^{-2}yr^{-1}$. The widely scattered nature of the NO_3^- data make it difficult to determine a baseline input.

SEASONAL VARIATIONS

The concentration of each chemical constituent in the precipitation can vary significantly over time (fig. 2-4).

Although the short-term changes are a function of complex meteorological variables, variations over longer periods of time illustrate systematic relationships. The concentration of Na^+ and Cl^- is substantially reduced during the summer months as compared to the rest of the year. In contrast, both K^+ and SO_4^{2-} show strong maxima during the spring and summer. The SO_4^{2-} maxima are balanced by the low pH which also occurs at these times. Spring and summer maxima are also exhibited by Ca^{2+} and NO_3^-, whereas Mg^{2+} seems to be unaffected by the change in seasons. These observations were substantiated by computer-generated Fourier analyses of the data which demonstrated principal periodicities of six months to a year for all constituents except Mg^{2+}.

The studies of Fisher (1968) and Gambell and Fisher (1966) in North Carolina and Virginia revealed similar seasonal variations which were attributed to changes in the pattern of storm activity. During the winter, the majority of storm systems tend to pass off the coast. These pick up water vapor laden with marine aerosols enriched in Na^+ and Cl^-. Easterly winds blow these aerosols ashore where they are washed out by precipitation. In contrast, during the summer months storms originate more frequently in the mid-continent region and move eastward towards the coast. These storm centers typically carry continental aerosols (enriched in Ca^{2+}, K^+, NO_3^- and SO_4^{2-}) which influence the composition of the rainfall. These same meteorological influences are responsible for the changes in the Pine Barrens precipitation (fig. 2-5).

In a detailed study of the pH, SO_4^{2-} and NO_3^- contents of Pine Barrens precipitation, Gay (1975) concluded that precipitation with low pH and high SO_4^{2-} occurred during periods when a) storms passed over heavily industrialized areas or b) when prolonged stagnation of the air mass concentrated SO_2 in the atmosphere. This effect is particularly common during the summer months.

GEOGRAPHIC DISTRIBUTION

The Princeton rain gauges were arranged in two transects across the coastal plain (fig. 2-1). Both the total dissolved solids and the chemical composition of the precipitation change noticeably along this transect (fig. 2-6). Cl^- and Na^+ show a very prominent decrease in concentration with increasing distance inland from the ocean. This provides additional evidence that both ions originate as marine aerosols. Conversely, the concentrations of Ca^{2+} and K^+ increase inland reflecting their principal derivation from continental particulate matter. The behavior of Mg^{2+} is somewhat anomalous here as it is with respect to seasonal variations. There is an initial decline away from the coast, and then a slight rise in the concentrations further inland. Although Mg^{2+} in the Pine Barrens precipitation is principally a soluble aerosol, this tendency together with its insensitivity to meteorological changes indicates that the ion must have both marine and continental sources.

The change in total dissolved solids (TDS) is even more remarkable considering the short distance of the transect. At gauge Rwa (33-12-377) which is 0.2 km (0.1 mi.) inland, the precipitation is dominantly a NaCl solution and total dissolved solids (excluding SO_4^{2-} and NO_3^-) are 9.2 ppm. At Rwg (32-25-434), which is 24 km (15 mi.) from the coast, the TDS have dropped to 6.4 ppm, Ca^{2+} has become the dominant cation and the Cl^- concentration has decreased substantially.

IONIC RATIOS

Further evidence as to the sources of the ionic species can be obtained from ion ratios. Assuming that Na^+ is entirely oceanic in origin (as the data suggest), a plot of each constituent as a function of Na^+ should parallel the ratio in sea water if a marine source is indeed significant. Fig. 2-7 shows that only for K^+ and Ca^{2+} can an origin from sea water aerosols be considered relatively unimportant. Most ion ratios are enriched in Na^+ relative to their sea water compositions. For the "continental" ions (K^+ and Ca^{2+}), the sea water ratios provide a base level below which the rainfall values never fall. The average SO_4^{2-}/Na^+ ratio (not plotted) is 3.67, well above the sea water value of 0.25, which confirms the predominantly continental origin of SO_4^{2-}.

These data permit the establishment of an "hierarchy of ions" based on their importance in sea water aerosols:

$$Cl^- = Na^+ > Mg^{2+} > K^+ > Ca^{2+} > SO_4^{2-}$$

$$\text{mostly marine} \dashrightarrow \text{mostly continental}$$

The Cl^-/Na^+ ratio in the precipitation averages 2.03 which is noticeably higher than the ratio 1.8 of sea water. Accordingly, in contrast to other studies (Eriksson, 1959; Junge, 1958; Fisher, 1968), there is no excess Na^+, but rather a Cl^- superabundance. The excess Cl^- averages 0.31 mg l^{-1} or about 11% of the total Cl- in the rainwater.

A similar Cl^- excess was observed by Pearson and Fisher (1971) in some of their coastal precipitation samples. Eriksson (1960) proposed a mechanism for aerosol fractionation in the atmosphere which produces HCl:

$$SO_3 + H_2O = H_2SO_4$$

$$H_2SO_4 + 2NaCl = 2HCl + Na_2SO_4$$

A preferential "washout" of the HCl could produce excess Cl^-.

Atmospheric pollution is a prime source for the additional SO_3 required for the production of HCl in the atmosphere. Cogbill and Likens (1974) document the increasing H^+ concentration in precipitation over the last several years and maintain that, at present, some

5% of this H^+ is balanced by Cl^-. At an average pH of 4.4:

$$[H^+] = 4.0 \times 10^{-2} \text{ meq } l^{-1}$$

Balanced by $Cl^- = (4.0 \times 10^{-2})\ (5\%) = 0.2 \times 10^{-2}$ meq l^{-1} $[Cl^-]$ balanced by $H^+ = (0.2 \times 10^{-2})\ (35.5) = 7.1 \times 10^{-2}$ mg l^{-1}. This accounts for approximately 25% of the excess Cl^- in Pine Barrens precipitation. The remainder must be balanced by other cations, perhaps Mg^{2+}.

IONIC BUDGET AND MASS INPUT

The data generated from this study permit the calculation of both charge balance in the rainwater (table 2-2) and mass input of all major constituents into the Pine Barrens for 1971-72 (table 2-3).

The total equivalents of anions and cations balance within the limits of analytical error indicating that these components constitute the bulk of precipitation chemistry.

Note that SO_4^{2-}, which is derived principally from pollution, constitutes some 45% of the total mass of chemical components in Pine Barrens precipitation.

CONCLUSION

1) The precipitation in the New Jersey Pine Barrens has a relatively high average content of total dissolved solids with a particular enrichment of Cl^- and Na^+ compared to other locations.

2) The overall composition of the precipitation is particularly influenced by its location near the coast. Total dissolved solids decrease by 30% some 24 km (15 mi.) inland from the coast, and the rainfall changes from a predominantly NaCl to a $CaSO_4$ solution.

3) Na^+, Cl^-, SO_4^{2-} and some Mg^{2+} enter the rainfall as soluble salts and their mass input increases with greater amounts of precipitation. Ca^{2+}, K^+ and NO_3^- apparently enter the gauges as dry fallout with a mass input relatively independent of precipitation.

4) All ions other than Mg^{2+} exhibit seasonal variations in concentration. Na^+ and Cl^- are low during the summer months, but K^+, Ca^{2+}, H^+, SO_4^{2-} and NO_3^- reach their maxima in the spring and summer. These fluctuations correlate with principal storm movements: winter storms move up the coast from the Gulf of Mexico whereas summer storms frequently move east from the mid-continent.

5) Na^+ and Cl^- are derived principally from marine aerosols, other ions have a continental or mixed source. Comparison of ion ratios suggests the following sequence:

$$\begin{array}{c} Cl^- = Na^+ > Mg^{2+} > K^+ > Ca^{2+} > SO_4^{2-} \\ \text{mostly marine} \xrightarrow{\hspace{6em}} \text{mostly continental} \end{array}$$

NO_3^- and PO_4^{3-} are also predominantly continental in origin. The SO_4^{2-} is principally a by-product of fossil fuel combustion, and is balanced by H^+ which causes the acidic rain conditions prevalent in the Pine Barrens. NO_3^- and PO_4^{3-} are derived principally from soil dust.

6) An average of 15.08± 1.19 metric tons km^{-2} yr^{-1} of all ions fell on the Pine Barrens during 1971-72. SO_4^{2-}, which has a primarily industrial source, represents some 45% of this total.

Table 2-1. Chemical composition of precipitation

Species	Pine Barrens (ppm)	North Carolina[1] and Virginia (ppm)
Na^+	1.39	0.56
Ca^{2+}	1.10	0.65
Mg^{2+}	0.23	0.14
K^+	0.32	0.18
Cl^-	2.82	0.57
SO_4^{2-}	5.09	2.26
NO_3^-	0.39	0.62
PO_4^{3-}	0.74	n.d.
Total	11.41	4.98

(1) from Gambell and Fisher (1966)

Table 2-2. Ionic budget for Pine Barrens precipitation

Cations		
Na^+	= 1.39 mg l^{-1}/23 g equivalent^{-1}	= 6.04 ± 0.06 x 10^{-2} meq l^{-1}
K^+	= 0.32/39	= 0.82 ± 0.02 x " "
Mg^{2+}	= 0.23/12	= 1.92 ± 0.02 x " "
Ca^{2+}	= 1.10/20	= 5.50 ± 0.05 x " "
H^+	= $10^{-4.41}$	= 3.89 ± 0.80 x " "
Total Cations		= 18.17 ± 0.95 x 10^{-2} meq l^{-1}
Anions		
Cl^-	= 2.82 mg l^{-1}/35.5 g equivalent^{-1}	= 7.94 ± 0.08 x 10^{-2} meq l^{-1}
SO_4^{2-}	= 5.09/48	= 10.60 ± 0.50 x " "
NO_3^-	= 0.39/62	= 0.63 ± 0.04 x " "
PO_4^{3-}	= 0.074/79	= 0.01 ± 0.001 x " "
Total Anions		= 19.18 ± 0.62 x 10^{-2} meq $^{-1}$

Table 2-3. Annual average mass input for 1971-72*

Cations			
Na^+	= 1.85 ± 0.13	metric tons km^{-2}yr^{-1}	(4.54 tons mi^2 yr^{-1})
K^+	= 0.42 ± 0.04	"	(1.03 " ")
Mg^{2+}	= 0.31 ± 0.02	"	(0.76 " ")
Ca^{2+}	= 1.46 ± 0.01	"	(4.58 " ")
H^+	= 0.052 ± 0.004	"	(0.15 " ")
Anions			
Cl^-	= 3.73 ± 0.26	"	(9.14 " ")
SO_4^{2-}	= 6.72 ± 0.70	"	(16.47 " ")
NO_3^-	= 0.52 ± 0.03	"	(1.28 " ")
PO_4^{3-}	= 0.074 ± 0.001	"	(0.02 " ")
Total	= 15.08 ± 1.19	"	(36.97 " ")

*Computed from 1971-72 average of 132 ± 8.0 cm of precipitation.

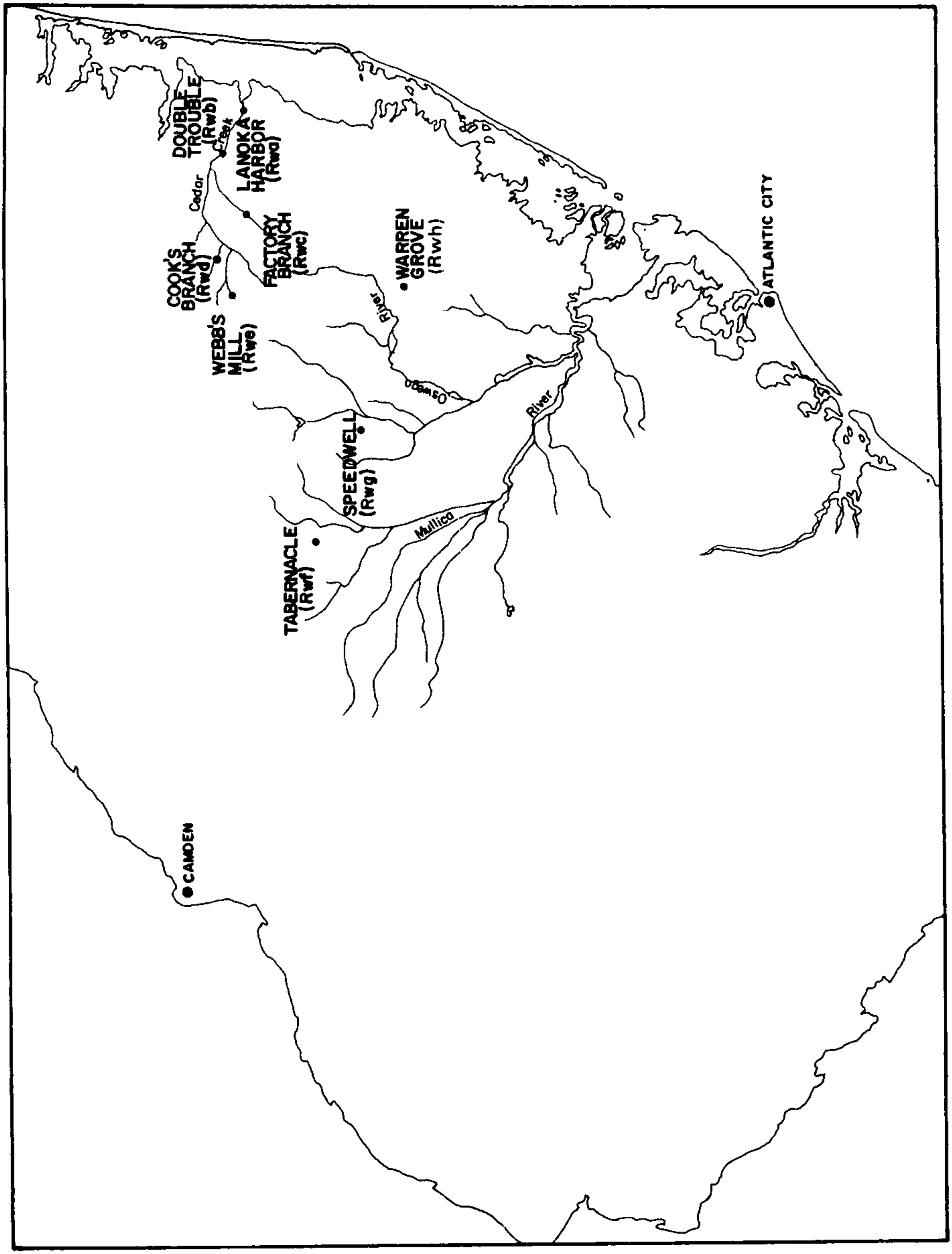


Fig. 2-1. Location of Princeton rain gauges. Land-Oriented Reference Data System (LORDS) coordinates for the gauges are given in Appendix I.

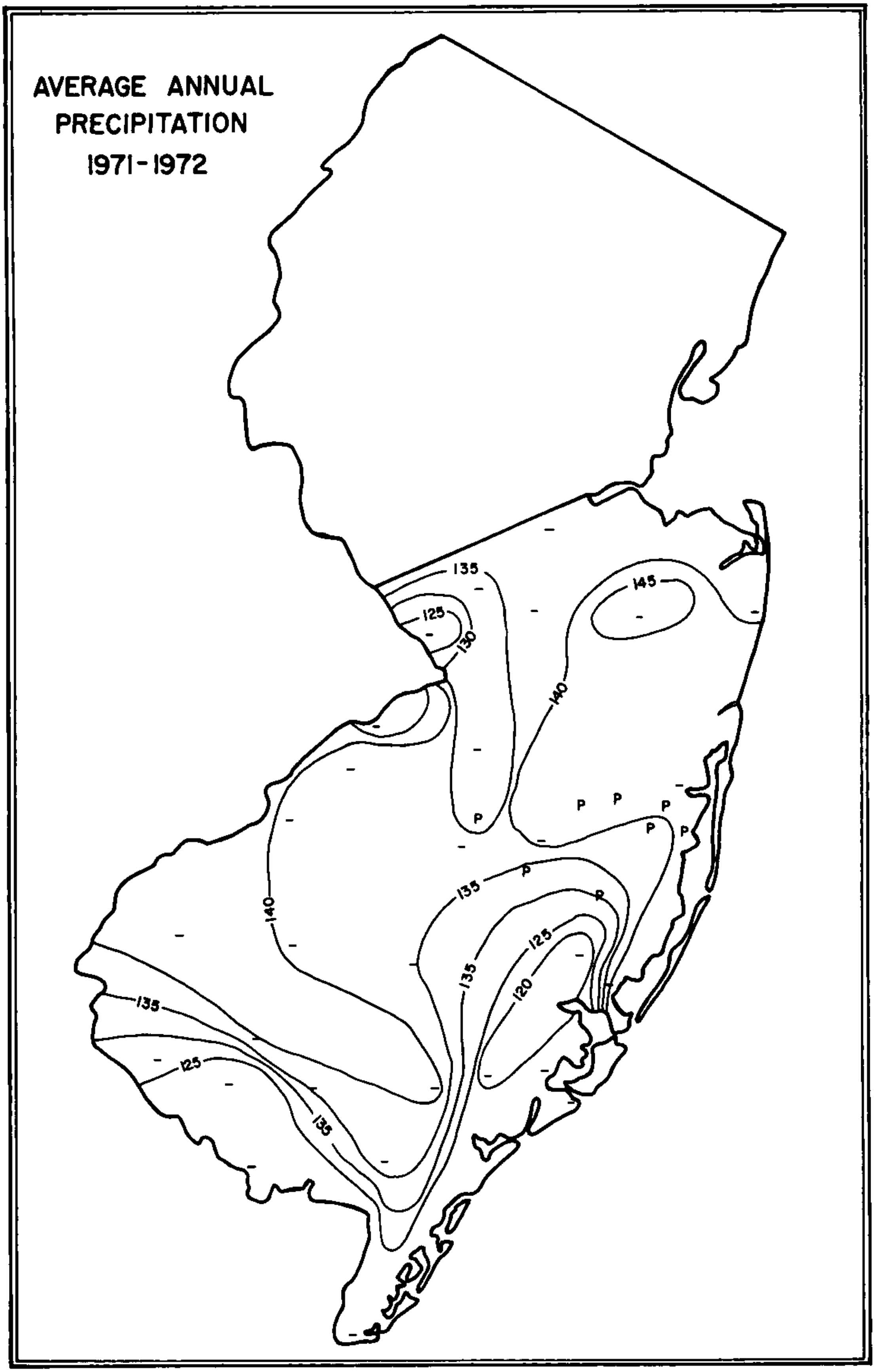


Fig. 2-2. Contour map of average yearly precipitation in southern New Jersey for 1971-72. Statewide precipitation for these years is 15% above normal. P = Princeton rain gauge; – = Weather Service rain gauge; Units in cm/yr.

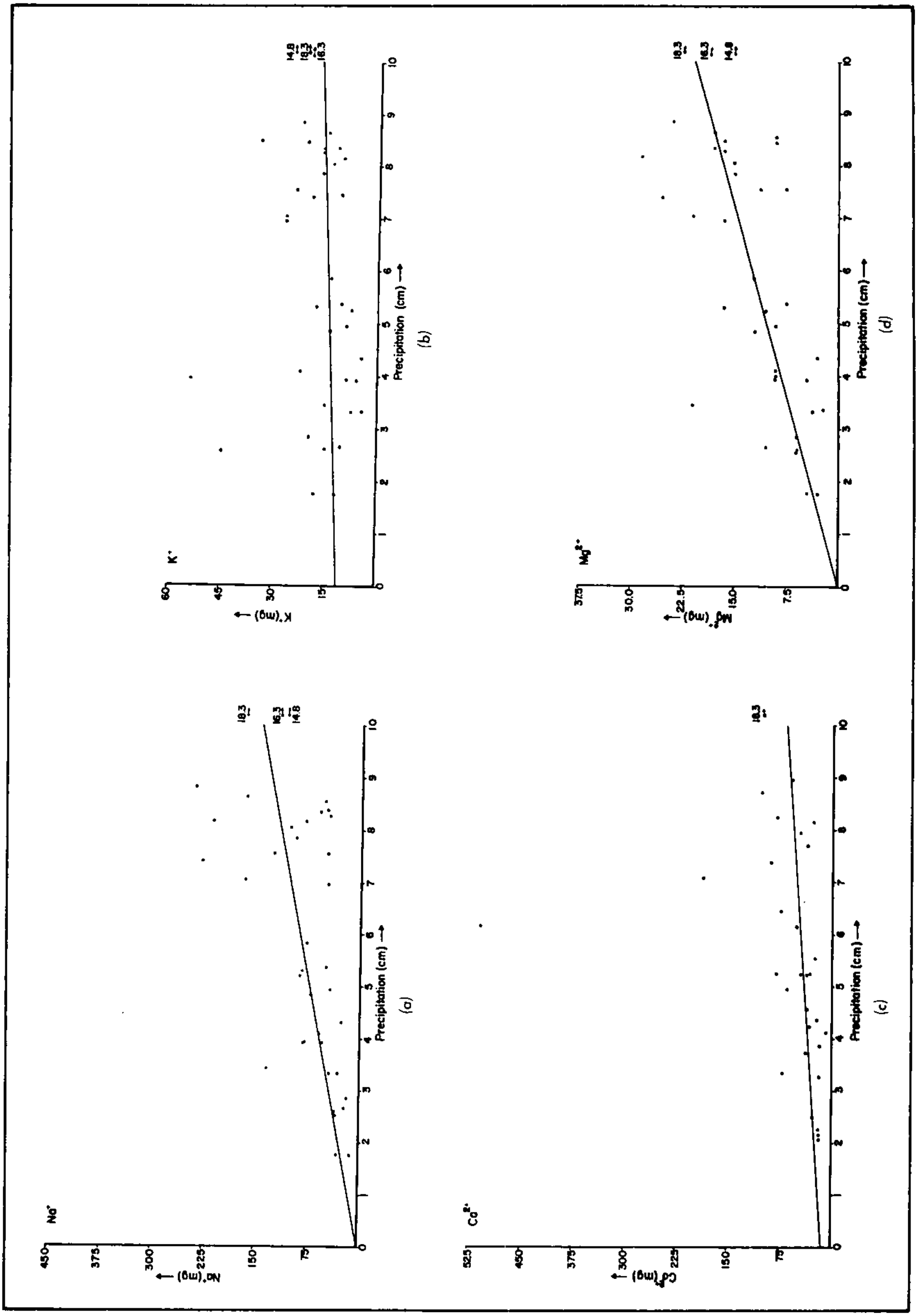


Fig. 2-3. Input of chemical constituents as a function of precipitation amount. Vertical axis shows mass input per m² of land surface.

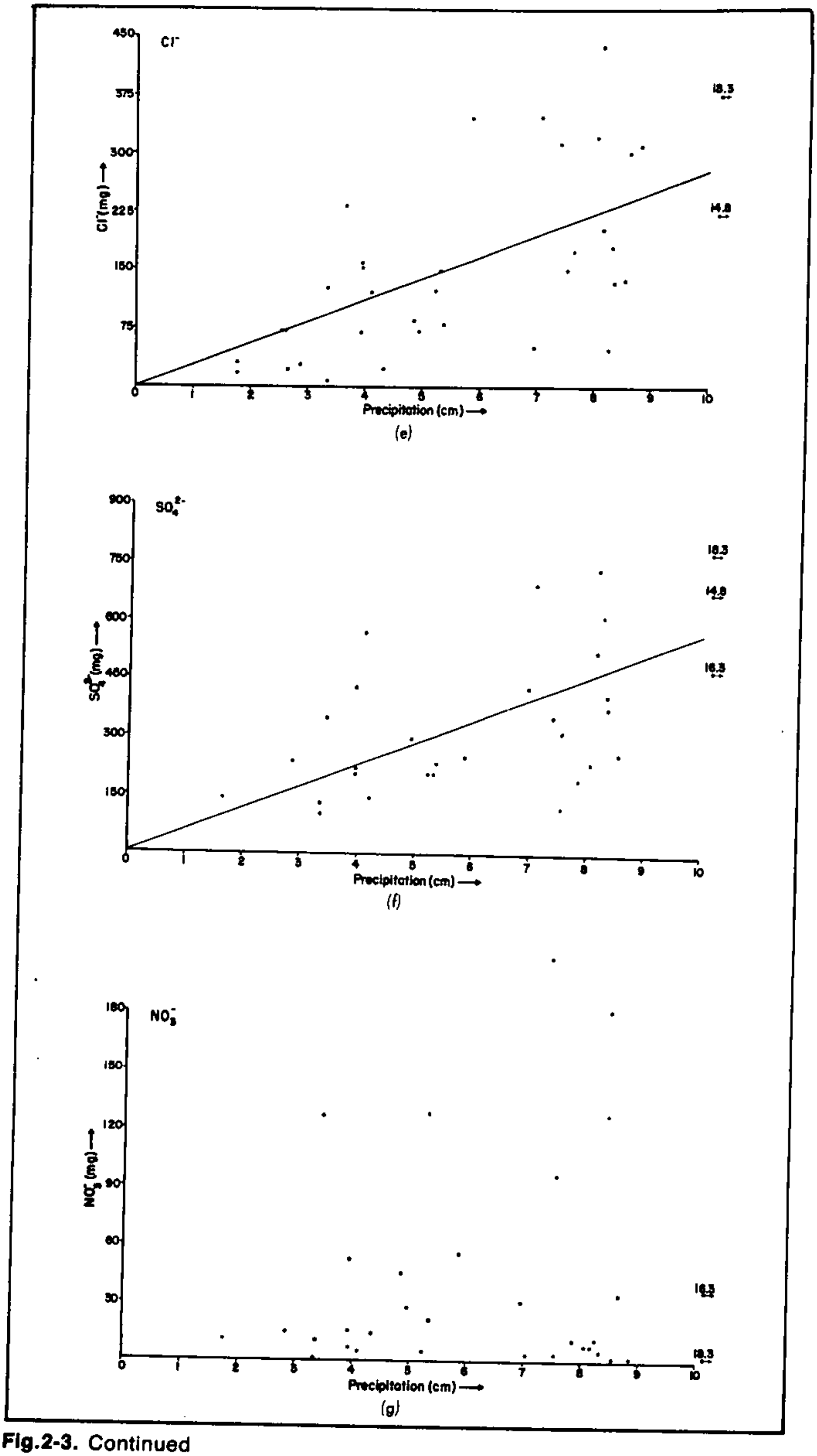
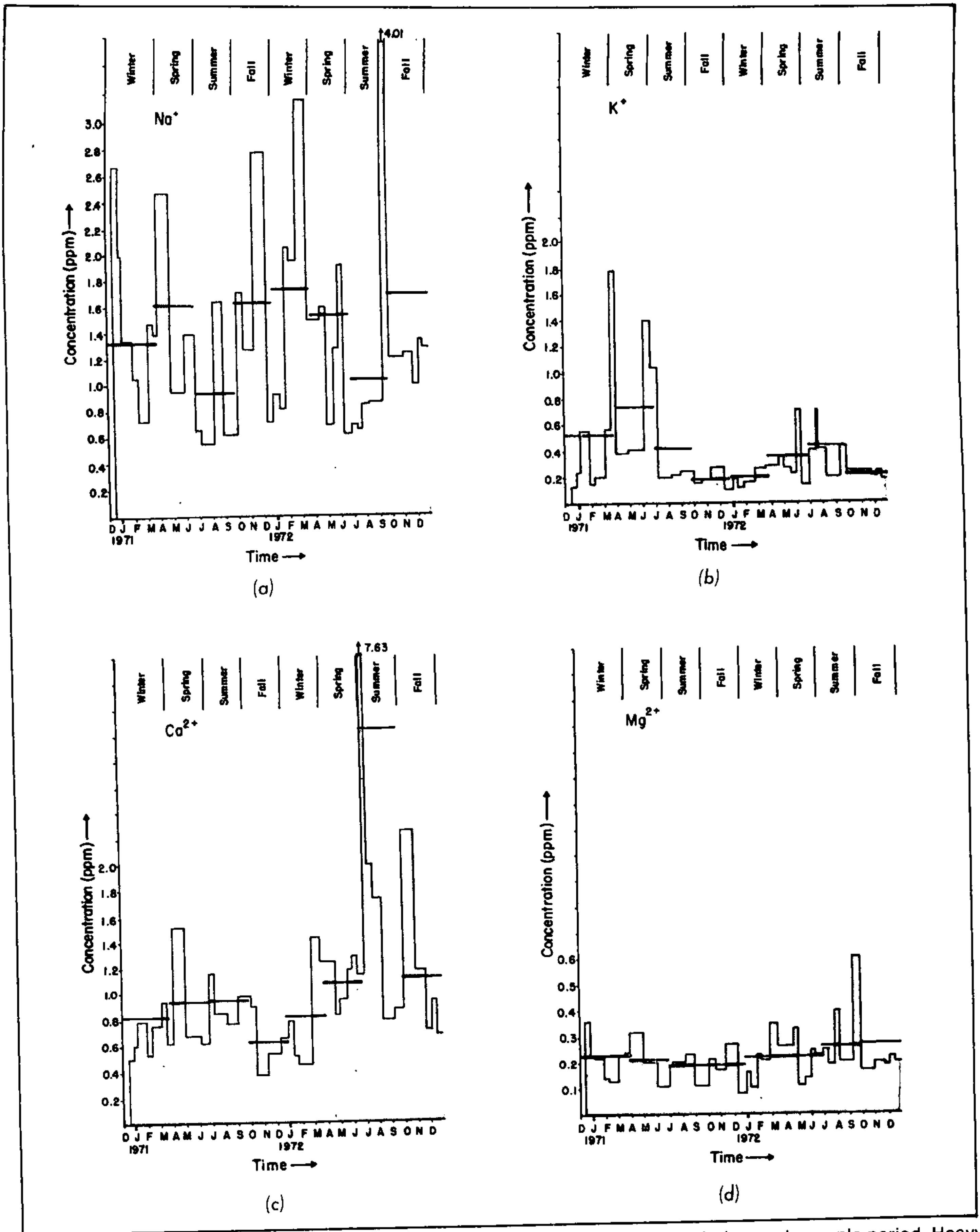


Fig.2-3. Continued



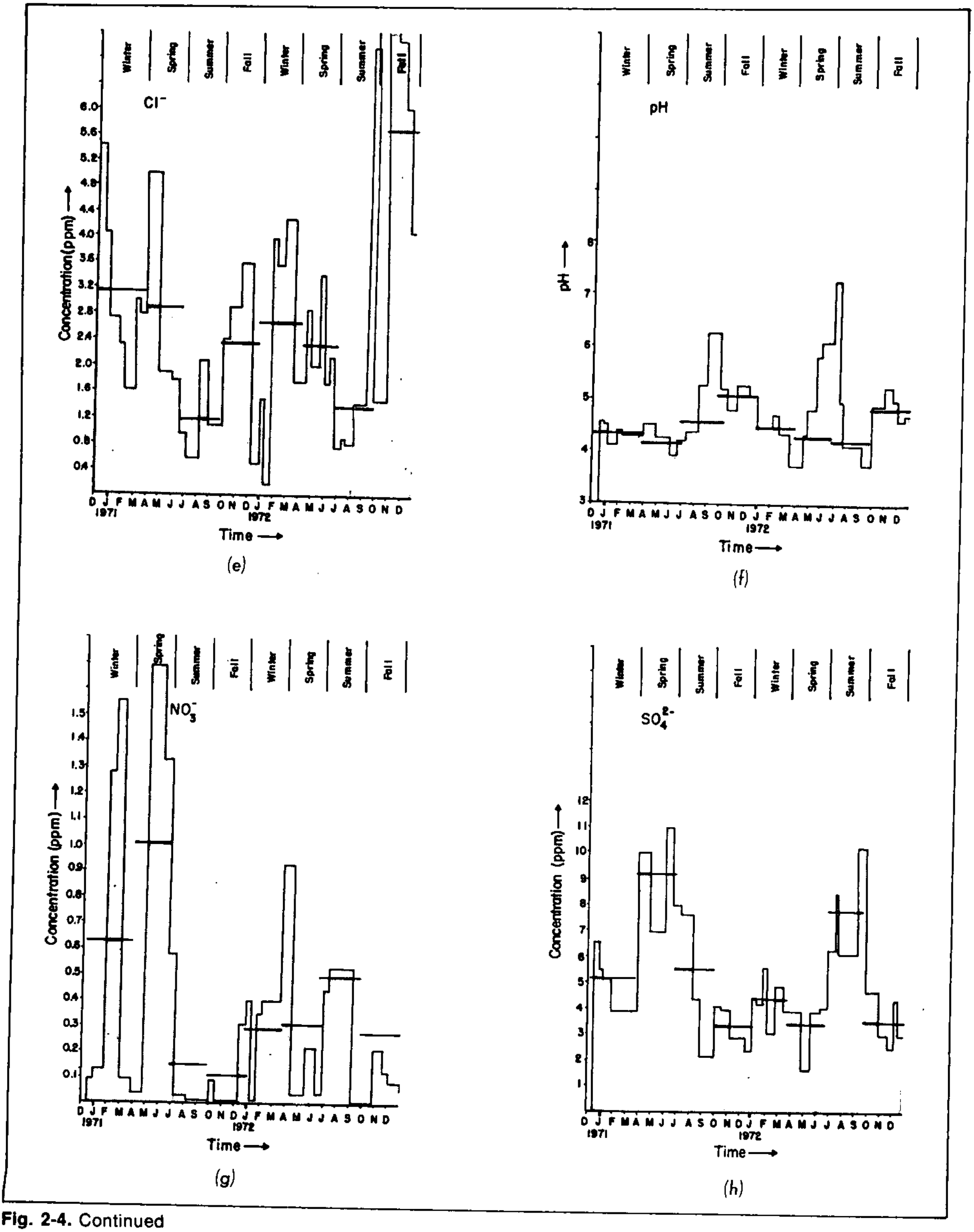
(a)

(b)

(c)

(d)

Fig. 2-4. Histograms showing concentrations of various species in precipitation during each sample period. Heavy lines give seasonal average concentrations.



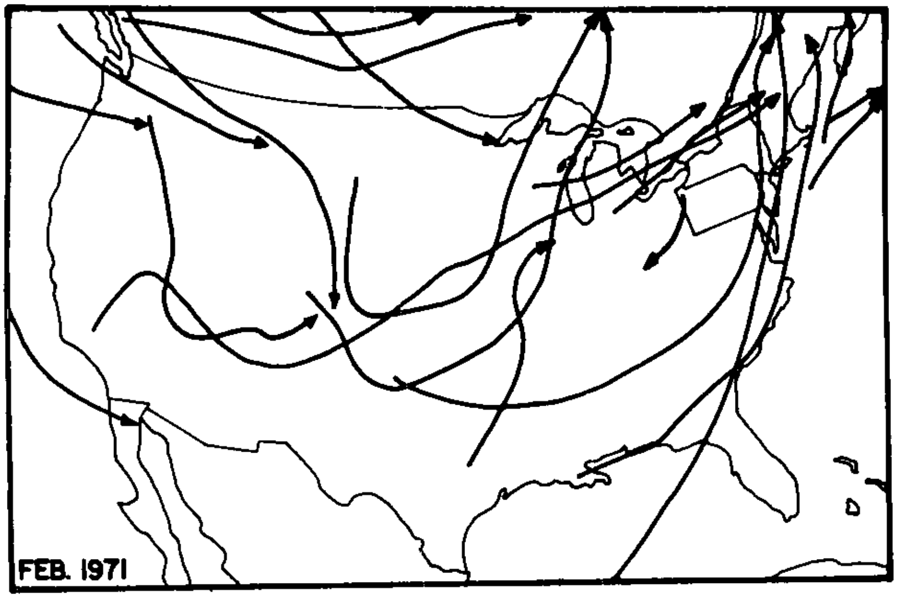
(e)

(f)

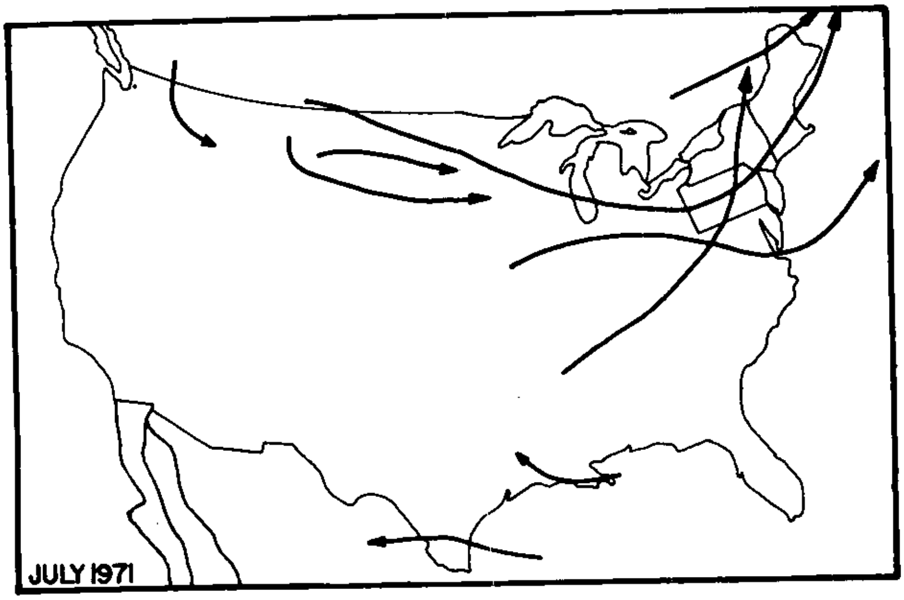
(g)

(h)

Fig. 2-4. Continued



(a)



(b)

Fig. 2-5. Typical storm paths over United States for winter (a) and summer (b).

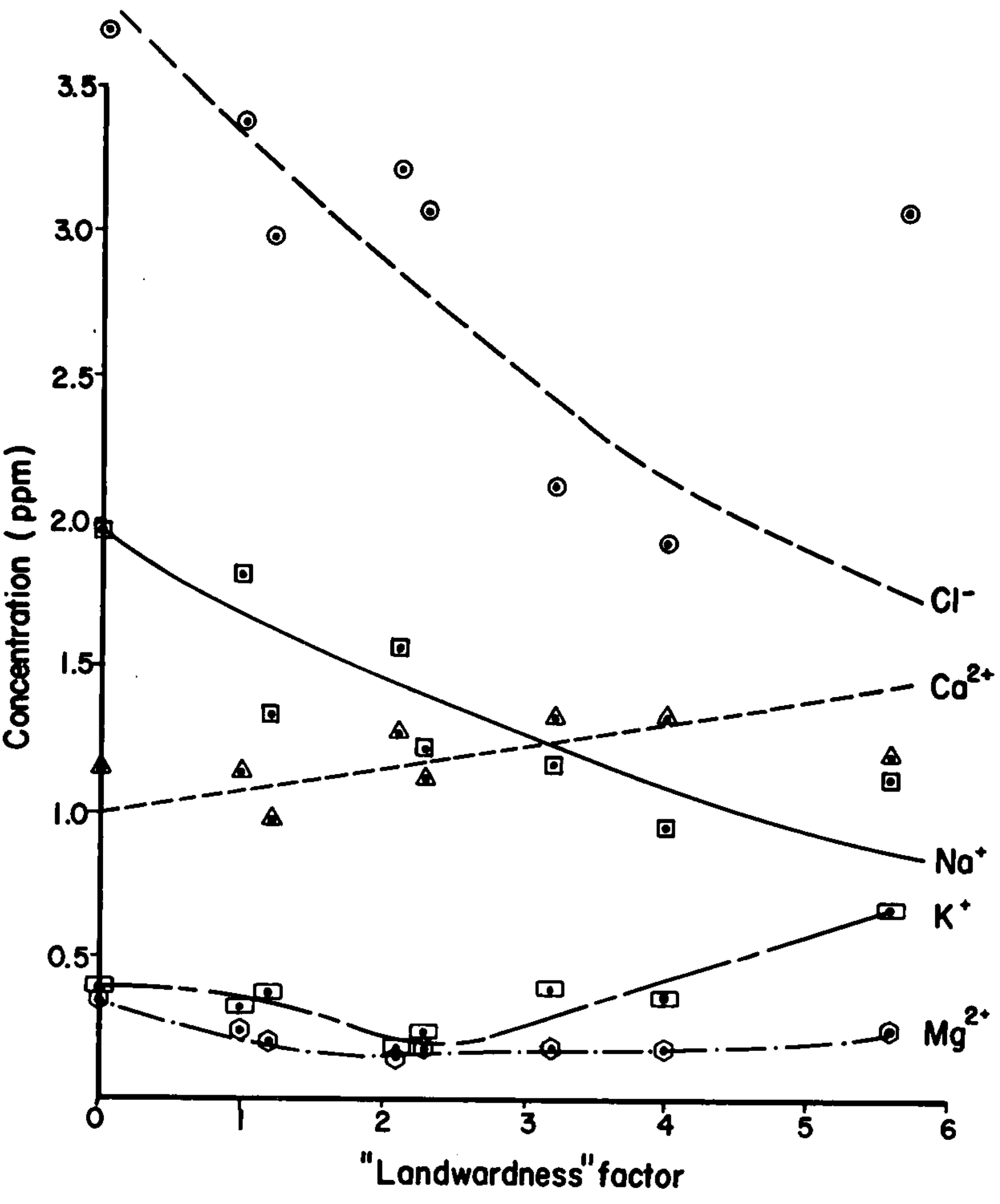


Fig. 2-6. Change in composition of precipitation as a function of distance from coast. The "Landwardness Factor" is a measure of the perpendicular distance to the coastline. One unit is equal to approximately 8 km. Data for SO_4^{2-} and NO_3^- are insufficient and are not plotted.

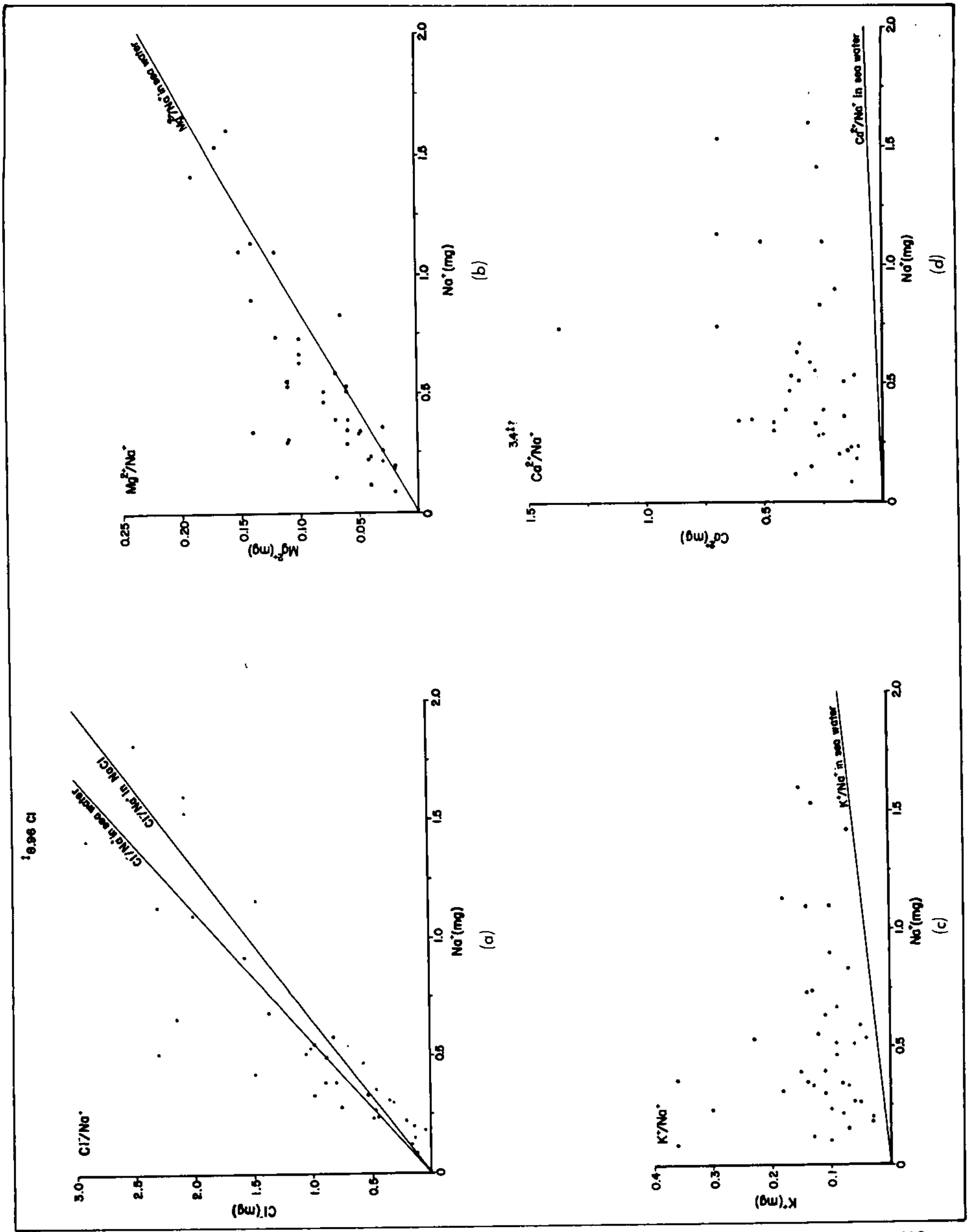


Fig. 2-7. Concentration of ionic species in precipitation plotted as a function of Na^+ Data for SO_4^{2-} and NO_3^- are insufficient and are not plotted.

Chapter 3

RIVER WATER: MAJOR ELEMENT GEOCHEMISTRY AND MASS BALANCES

INTRODUCTION

The geochemistry of precipitation provides some baseline data for the chemical input to the Pine Barrens. By monitoring the chemical composition of the river waters we can then determine the proportion of chemical components derived from sources other than precipitation. We can also gain insight into the behavior of the precipitation constituents within the total hydrogeochemical framework.

METHODS

River water sampling stations were established in two distinct networks (fig. 3-1), and monitored during 1971 and 1972. The first network comprised 11 stations along Cedar Creek and its tributaries, providing a detailed coverage of the changes in water chemistry along its length. These stations were maintained for the first year of the study and subsequently reduced to 5 for the second year, corresponding to the locations of the Princeton rain gauges along the stream. Samples were collected at approximately four-week intervals. In addition, 22 other sites were set up to monitor other rivers in the region (fig. 3-1), five of these at U.S. Geological Survey gauging stations (sites Ga, Gb, Gd, Ge, Gf). All reconnaissance sites were sampled together approximately every four weeks. Detailed information concerning sampling locations and dates is given in Appendix II.

Water samples were collected in 1l polyethylene bottles which were rinsed with river water immediately before sampling. Water temperature was recorded at the same time, and pH measurements were made in the field during several sampling periods. Upon being returned to the laboratory, the water samples were filtered (Whatman #5), and the pH was checked. Analyses were made of Na^+, K^+, Mg^{2+}, Cl^-, SO_4^{2-}, and SiO_2; procedures used were the same as those described in Chapter 2. Except for SO_4^{2-} and PO_4^{3-}, analyses were completed within 3 to 4 weeks after collection. These two anions were analyzed at a later date, but storage of the samples in a cool, dark closet appears to have prevented any significant chemical alteration.

GENERAL HYDROLOGY

Drainage Basins and Discharge

The Pine Barrens comprise some 5800 km² (2250 mi²) of southern New Jersey (Rhodehamel, 1966). The drainage basins of the rivers monitored in this study cover 2116 km² (820 mi²) or approximately 30% of the Pine Barrens. Two large river systems dominate the study area. The Mullica system, at the southern boundary, has an area of 1476 km² (570 mi²) and includes the Batsto, Wading, Oswego and Bass Rivers. The Toms River system in the north contains 494 km² (191 mi²) and includes the drainage basins of Wrangle Brook and Jakes Branch. The remainder of the region is drained by small streams flowing directly into the Atlantic Ocean. The largest of these is Cedar Creek, which has a drainage area of 144 km² (56 mi²). Discharge records from the five U.S. Geological Survey gauging stations at the sampling sites were examined for the period of study (Anonymous 1972b, 1973, 1974b). In addition, Princeton University reactivated a decommissioned USGS gauging station on Cedar Creek during the early part of the investigation (Kelsey, 1971). Pertinent data are listed in table 3-1. The column in the table headed Discharge/Unit Area was obtained by dividing the discharge of each river by the area of the respective drainage basin upstream from the gauging station.

Precipitation over the Pine Barrens region is relatively uniform (cf. fig. 2-2); therefore those streams with a higher discharge per unit area must have a greater baseflow (i.e. deep groundwater contribution). Oyster Creek and the Mullica River both exhibited large groundwater contributions during 1971-72.

Discharges of the rivers vary significantly during the year with periods of low flow occurring in the late summer (fig. 3-2). The annual average surface runoff in the Pine Barrens has been estimated at 6% (Rhodehamel, 1970), yet river response times can be rapid indicating the near-surface permeability of the Cohansey aquifer is very high. Kelsey (1971) recorded the effect of two rainstorms on the gauging station at Cedar Creek, and concluded that 2 to 3 hour response times to local precipitation were typical. Heavy rains fell during August-September, 1971 (Stankowski, 1972) and again in September-November, 1972; both of these are clearly apparent in the discharge records.

Water Temperatures

Temperatures recorded at the reconnaissance sampling sites are listed in table 3-2. Site Ca is also included to represent Cedar Creek. As expected, the river water temperatures show a strong seasonal dependence. The coldest temperature (0°) was measured in the Batsto River (Ge) on December 31, 1970; the warmest water (29.9°) was recorded in Westecunk Creek (Gc) on July 7,

1971. Of greater significance are large temperature differences recorded in different streams on the same day. Although some temperature excursions will be caused by variations in stream size, solar insolation, soil characteristics, etc., significant departures from the regional average can reflect the contribution of deep groundwater to the river discharge. Such groundwater possesses a relatively constant temperature (approximately 13°C) and tends to moderate the seasonal variability of surface water temperatures. Accordingly, rivers fed by a significant amount of deep groundwaters will exhibit higher-than-average temperatures in winter and somewhat lower-than-average in the summer (Kelsey and Kinsman, 1971). This effect is most noticeable at site Gb-Oyster Creek, which shows a two-year temperature range of only 14.2° compared to an average of 21.7° for all streams tested. These data corroborate the conclusions based on discharge per unit area (table 3-1). The Mullica River, which should also show a more moderate temperature cycle, fails to do so. Perhaps the size of the Mullica drainage basin and the river's many tributaries tend to obscure the temperature effects of the groundwater.

GEOCHEMISTRY

The average composition of the Pine Barrens rivers is listed in table 3-3. These figures are based on all samples analyzed, with each site given equal weighing. The total dissolved solids of 20 ppm are very low compared to the 105 ppm of world average river water (Livingstone, 1963). The very acidic pH of the Pine Barrens rivers is also unusual; this phenomenon is discussed in more detail in Chapter 4.

Regional Variations

There are significant regional differences in the two-year average chemical compositions of the various streams (fig. 3-3). In general, the Cedar Creek tributaries have lower concentrations of all constituents than the other rivers. On the other hand, the Mullica and Batsto River sites exhibit the highest concentrations.

Sodium and Chloride

It was determined in Chapter 2 that Na^+ and Cl^- in precipitation are derived principally from marine aerosols. Similar evidence is apparent in the river water data: the highest Na^+ and Cl^- values are found in the small streams which drain directly into the Atlantic Ocean. Na^+ in these streams ranges between 3 and 5 ppm, while Cl^- attains concentrations of 6 to 8 ppm. Further inland, Na^+ is typically about 2 ppm and Cl^- averages 3-5 ppm. The higher values near the coast reflect an increased input of marine aerosols.

Oyster Creek (Gb) contains lower concentrations of Na^+ and Cl^- than the other coastal rivers. This is probably a result of the unusually large groundwater contribution to the stream which dilutes the aerosol component. On the other hand, Hammonton Creek (Rp) and the Mullica River (Gf, Rj) show somewhat elevated Na^+ and Cl^- values. These may be caused by the deep landward penetration of marine aerosols derived from the Mullica River estuary, but an unusual groundwater composition is also a possibility. Pollution may also be a factor in the vicinity of Rp.

Other Cations

Ca^{2+}, Mg^{2+} and K^+ exhibit similar coastal effects but the magnitudes are not as great owing to their mixed continental and marine sources. The Cedar Creek basin provides the best illustration: higher concentrations are found at Lanoka Harbor (site Ca) than at any inland station except Chamberlain's Branch (site Cj). The pattern over the larger Pine Barrens area is less predictable. In general, K^+ and Ca^{2+} concentrations are significantly higher in all other rivers than in Cedar Creek. The reasons for this are not entirely clear, but may be related to a greater development of agriculture in the Mullica-Batsto-Wading River basin. Use of lime and potash fertilizer in the fields would ultimately result in greater amounts of Ca^{2+} and K^+ entering the rivers. The inland increase of Ca^{2+} and K^+ in precipitation is also partly responsible.

The distribution of Mg^{2+} is more uniform than other cations but all exhibit extraordinarily high concentrations at Toms River (site Ga) and along the lower Mullica and Batsto Rivers (sites Ge, Gf, Rp and Rj). The Toms River site is in a populated area and the Toms River Chemical Company is located 250m (800 ft) upstream. Although effluent from the plant is not discharged into the river, these higher concentrations most likely result from human activities. However, in the Mullica River basin, pollution is considerably less important. As indicated by the high discharge per unit area of the stream (table 3-1), deep groundwater apparently provides a large portion of the baseflow. The Cohansey and Kirkwood aquifers are thinner at this distance inland (cf. fig. 1-3) and cross-formational leakage from the aquifers of the Vincentown and Mount Laurel Formations is a distinct possibility. Waters from these aquifers must pass through the clay-rich Manasquan or glauconitic Hornerstown Formations which would increase the TDS of the waters. The Mullica-Batsto River junction may represent the principal locale where these deep waters surface.

Sulfate, Phosphate and Silica

SO_4^{2-} and PO_4^{3-} concentrations behave differently than other constituents. SO_4^{2-} concentrations are usually lower at the coast. This distribution is not surprising in light of the origin of SO_4^{2-} as a pollutant in precipitation (Chapter 2); the principal sources of SO_2 in the atmosphere lie in the industrial regions to the west and north of the Pine Barrens.

The SO_4^{2-} concentrations at Toms River and the Mullica-Batsto River are still anomalously high and presumably the same processes that govern the high cation concentrations at these sites (*water pollution at*

Toms River; deep groundwater and fertilizer leachate at Mullica) are responsible. Although Cedar Creek has somewhat lower SO_4^{2-} concentrations, at Chamberlain Branch (Cj) the value is doubled. Chamberlain Branch also has higher cation and Cl^- concentrations than the other Cedar Creek sites. The reasons for this are not clear, but since contamination is unlikely there may also be an unusual groundwater composition here.

Except for some anomalously high PO_4^{3-} concentrations at Hammonton Creek (site Rp), which may result from contamination, neither PO_4^{3-} nor SiO_2 show any systematic variations in the Pine Barrens rivers. PO_4^{3-}, being a nutrient, is maintained at fairly constant levels by biological metabolic activity. The homogeneity of the Cohansey Formation together with the consistently low pH of the rivers and an abundant diatom population combine to keep SiO_2 at fairly constant levels close to the equilibrium solubility of quartz. There is no measurable input of SiO_2 in precipitation.

Temporal Variations

The concentrations of all the components in the river water vary with time as observed in the Cedar Creek basin (fig. 3-4). Unlike the composition of precipitation, definite seasonal trends are not easily discernible for all ions. The largest changes occur in the anions, Cl^- and SO_4^{2-}. Cl^- reached a maximum in May, 1971, dropped precipitously and then climbed gradually to a second peak in April, 1972. These springtime peaks may be due to storage of Cl^- from winter storms in snow and ice and subsequent release during spring thaw. While this is a reasonable explanation, it is difficult to understand why Na^+ does not exhibit an equivalent seasonal variation; perhaps there is an additional, non-marine source. SO_4^{2-} maxima occurred during the winter months (January, 1971; December, 1971; December, 1972), approximately 6 months out of phase with SO_4^{2-} peaks in rainfall. This also suggests a storage mechanism for SO_4^{2-} during the warmer months of the year, perhaps in the vegetation. The concentration changes of the cations are relatively small in comparison, and do not exhibit any systematic behavior.

Mass Balances in Pine Barrens Rivers

Rhodehamel (1970) estimated that 50% of the precipitation which fell on the Pine Barrens was returned to the atmosphere via evaporation and transpiration. Kelsey (1971) analyzed the long-term data for the Cedar Creek basin and calculated an evapotranspiration of 46(±5)%. According to the information accumulated during this study, the evapotranspiration was slightly less than this. Based on water budget:

Precipitation $= 132.8$ cm $= 13.3 \times 10^8$ l $km^{-2}yr^{-1}$
Discharge rate $= 2.44 \times 10^{-2} m^3 s^{-1} km^{-2} = 7.7 \times 10^8$ l $km^{-2}yr^{-1}$
Evapotranspiration $= 5.6 \times 10^8$ l $km^{-2}yr^{-1}$

This is equivalent to an evapotranspiration of 42% for the Pine Barrens during 1971-72. A similar figure is obtained by comparing the ionic concentrations in precipitation (table 2-1) with those in river water (table 3-3); the average evapotranspiration indicated by Na^+ and Cl^- is 43%.

Table 3-4 documents the annual chemical input and output of the Pine Barrens drainage areas. The input by precipitation is from table 2-3; the output is calculated from average concentrations in river water (table 3-3) and the discharge rate of 7.7×10^8 l $km^{-2}yr^{-1}$ for 1971-72.

The very good agreement between the geochemical input and output in the Pine Barrens proves the singular importance of precipitation as the controlling influence upon the composition of the rivers.

Some constituents exhibit discrepancies. Ca^{2+} and PO_4^{3-} are significantly more abundant in precipitation than in river water; SO_4^{2-} also exhibits an excess. On the other hand, the mass of Mg^{2+} is slightly greater in river water. The difference in PO_4^{3-} amounts probably represents the consumption of PO_4^{3-} as a nutrient by microorganisms and inorganic precipitation with the bog iron (cf. Chapter 7). The large amount of SO_4^{2-} in precipitation is a relatively recent phenomenon which stems from the increasing combustion of fuels low in particulate matter (e.g. natural gas). Prior to 1950, SO_4^{2-} in rainfall was probably much lower than at present (Likens and Bormann, 1974). The river water SO_4^{2-} content may be influenced by "older" deep ground water (contained within the aquifer for a year or longer) with low SO_4^{2-} which dilutes that in runoff as well as by possible temporary storage in the biomass (Gay, 1975).

The large part of the "missing" Ca^{2+} may also be stored within the Pine Barrens vegetation. Art et al. (1974) have determined that Ca^{2+} is the most abundant cation in plant material. An analysis of several Pine Barrens vegetation samples (Gay, 1975) revealed that Ca^{2+} is at least 3 to 4 times more concentrated than other ions (table 3-5). Accordingly, the plants can serve as a reservoir for Ca^{2+} at least on a short-term basis.

The excess of Mg^{2+} in the river water is comparatively small and may be attributable to analytical discrepancies. However, the glauconitic Tertiary formations underneath the Cohansey Formation are enriched in Mg^{2+} and deep ground water entering the rivers would add to the Mg^{2+} concentration in precipitation. Additional evidence for geochemical contributions by deep groundwater is discussed in subsequent chapters.

CONCLUSIONS

1. River waters in the Pine Barrens are acidic (average pH 4.51) with total dissolved solids of approximately 20 ppm. These are low compared with the 105 ppm found in world average river water.
2. Discharge and temperature data indicate that Oyster Creek and the Mullica River possess a larger ground water baseflow than the other streams.
3. Most of the cations together with Cl^- have higher concentrations in streams near the coast. This is due to (additional) contributions from marine aerosols. SO_4^{2-}

concentrations in the streams increase inland reflecting closer proximity to industrialized regions with a higher atmospheric SO_2 content.

4. PO_4^{3-} and SiO_2 are relatively constant in the river waters. PO_4^{3-} concentrations are probably controlled by consumption as a nutrient whereas SiO_2 levels are near thermodynamic equilibrium with the quartz of the Cohansey Formation.

5. The lower Mullica and Batsto Rivers have higher concentrations of all ions than the other rivers. This may indicate that water from aquifers in Lower Tertiary formations (e.g., Vincentown, Mt. Laurel) is reaching the surface in this locale.

6. Cl^- and SO_4^{2-} in river water show evidence of seasonal variations, but the causes for these are not entirely understood. The cations have few discernible time trends.

7. Geochemical mass balances confirm that river water composition is largely controlled by precipitation with the exception of SiO_2. Only Mg^{2+} shows a slight excess in the streams; this may be a contribution from deep groundwater. The input of Ca^{2+}, PO_4^{3-} and SO_4^{2-} is greater than the output. Ca^{2+} is apparently being stored in vegetation; PO_4^{3-} is metabolized by microogranisms. SO_4^{2-} concentrations in precipitation are a function of SO_2 in the atmosphere. The latter has been increasing in recent years and the river water reflects the large contribution of "older", less-polluted groundwater.

Table 3-1. Pine Barrens rivers: discharge

Gauging Station	Average Discharge 1971-72 m^3s^{-1} (cfs)	Average Discharge Long Term** m^3s^{-1} (cfs)	Discharge/Unit Area 1971-72 $m^3s^{-1}km^{-2}$	Discharge/Unit Area 1971-72 (cfsm)	Discharge/Unit Area Long Term $m^3s^{-1}km^{-2}$	Discharge/Unit Area Long Term (cfsm)
Toms River (Ga)	8.17 (288)	6.06 (214)	2.54 x 10^{-2}	(2.32)	1.89 x 10^{-2}	(1.73)
Oyster Creek (Gb)	0.87 (30.5)	0.80 (28.3)	4.52 "	(4.10)	4.16 "	(3.81)
Oswego River (Gd)	3.07 (108)	2.48 (87.6)	1.85 "	(1.69)	1.50 "	(1.37)
Batsto River (Ge)	4.34 (153)	3.60 (127)	2.38 "	(2.17)	1.97 "	(1.80)
Mullica River (Gf)	4.10 (145)	3.14 (111)	3.43 "	(3.14)	2.63 "	(2.41)
Cedar Creek (Ca)	2.72 (95.5)*	3.04 (107)	1.89 "	(1.71)*	2.11 "	(1.91)
		Weighted Mean	2.44 "	(2.22)	2.01 "	(1.83)

* Cedar Creek data available only for water year 1971 (Oct. 1970-Sept. 1971)

** Long-term data are based on the entire period for which the gauging stations were in operation: Ga = 45 yr; Gb = 8 yr; Gd = 43 yr; Ge = 46 yr; Gf = 16 yr; Ca = 27 yr.

		1971												1972											
	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D
Ca	1.6	–	5.4	5.5	11.1	12.6	19.3	23.4	20.0	21.5	14.5	–	3.8	5.2	1.4	6.1	7.7	15.3	15.2	24.8	19.5	16.9		5.2	5.8
Ga	0.9	–	1.4	2.9	8.6	11.9	–	23.0	22.7	–	17.5	–	3.4	7.1	3.5	8.5	–	16.0	16.4	19.7	22.1	19.7	10.2	–	5.7
Gb	7.2	–	4.2	5.8	7.4	13.4	–	19.4	19.2	18.2	–	9.8	5.8	8.7	–	–	–	–	–	–	19.5	16.4	–	5.2	8.5
Gc	3.1	–	3.9	4.9	6.4	16.4	21.1	29.9	24.0	22.7	–	9.4	3.4	8.2	4.8	9.7	10.1	15.6	16.7	21.6	23.8	19.6	11.0	–	7.1
Gd	0.4	–	3.4	2.9	6.9	16.0	23.8	23.2	20.4	22.5	–	8.5	3.6	7.4	4.5	8.5	9.6	15.4	14.5	19.7	22.4	17.4	10.0	–	5.3
Ge	0.0	–	3.1	2.9	8.1	15.1	21.8	24.4	22.9	21.2	–	7.7	3.9	6.9	4.5	8.3	11.3	15.8	16.9	20.0	22.4	18.3	10.8	–	5.0
Gf	–	–	2.0	–	–	–	21.7	24.4	–	21.8	–	7.8	2.5	6.3	4.9	8.7	10.5	15.6	15.8	20.0	22.5	17.9	10.5	–	4.8
Rf	0.1		1.6	2.4	7.6	14.9	21.6	22.4	20.8	22.2	–	7.9	3.1	6.9	3.9	8.5	10.8	15.4	15.0	19.8	22.0	17.7	9.5	–	5.0
Rg	2.4	–	2.1	3.4	5.9	12.6	–	20.9	18.6	19.8	–	9.6	5.4	7.7	6.0	8.0	8.4	14.0	16.2	18.7	26.3	16.8	10.2	–	–
Rh	–	–	3.0	4.4	6.4	13.9	23.1	19.6	–	19.4	–	8.9	5.1	7.5	4.8	8.5	9.6	14.4	15.3	18.6	19.5	16.8	10.1	–	6.0
Ri	–	–	–	4.4	6.9	17.4	17.7	27.9	26.4	22.8	–	8.2	4.0	6.8	4.7	9.8	10.1	15.2	17.6	22.0	25.1	22.4	10.9	–	5.8
Ra	0.9	–	2.4	1.6	6.4	13.0	12.8	17.4	16.8	19.6	–	6.3	–	–	–	–	–	–	–	–	–	–	–	–	–
Rb	0.4	–	0.1	1.3	6.4	14.6	23.0	16.4	22.0	20.7	–	6.5	2.4	–	–	–	–	–	–	–	–	–	–	–	–
Rc	0.9	–	3.9	2.0	6.4	12.1	21.6	18.7	17.9	18.9	–	8.1	3.5	7.6	–	–	–	–	–	–	–	–	–	–	–
Rd	0.9	–	3.1	2.4	5.9	17.0	18.3	24.0	21.4	21.2	–	8.6	1.8	–	–	–	–	–	–	–	–	–	–	–	–
Re	0.8	–	0.1	1.4	6.4	15.9	23.9	24.4	22.7	22.3	–	7.2	1.5	–	–	–	–	–	–	–	–	–	–	–	–
Rj	–	–	–	–	–	–	–	22.9	21.7	21.4	–	7.7	3.0	6.4	3.8	8.3	10.6	15.2	15.7	14.6	20.0	17.7	10.0	–	5.4
Rk	–	–	–	–	–	–	21.8	28.4	23.8	23.8	–	7.9	3.0	7.4	4.7	10.0	9.4	16.1	19.9	23.0	25.5	22.2	11.2	–	6.4
Rl	–	–	–	–	–	–	16.8	20.4	22.1	19.9	–	9.8	3.3	8.9	6.9	10.0	9.2	16.7	15.3	18.2	19.2	18.9	9.9	–	7.3
Rm	–	–	–	–	–	–	–	–	26.4	–	23.5	8.9	2.4	8.4	6.1	10.0	10.4	15.5	17.8	21.6	23.0	20.2	11.0	–	6.6
Rn	–	–	–	–	–	–	–	–	22.2	17.1	–	–	5.4	9.3	4.9	9.5	9.9	15.8	17.2	20.6	22.7	18.5	10.1	–	8.5
Ro	–	–	–	–	–	–	–	–	21.2	16.6	–	–	5.6	9.0	3.9	10.0	9.9	15.8	16.9	19.8	21.7	19.9	10.9	–	8.4
Rp	–	–	–	–	–	–	–	–	–	–	–	–	4.8	7.9	3.9	8.0	9.4	14.4	12.7	18.3	19.2	15.9	9.8	–	6.8
AVG	1.0	–	2.7	3.2	7.1	14.5	20.6	22.7	21.7	20.7	18.5	8.3	3.7	7.6	4.5	8.9	9.8	15.4	16.2	20.1	22.0	18.5	10.4	5.2	5.7

Table 3-2. Pine Barrens river temperature

Table 3-3. Average River composition (ppm)

Na^+	K^+	Mg^{2+}	Ca^{2+}	$C1^-$	SO_4^{2-}	PO_4^{3-}	SiO_2
2.58	0.63	0.57	1.05	4.72	6.16	0.037	4.32

pH = 4.51

TDS = 20.07 ppm

Table 3-4. Chemical mass balances of precipitation input versus river output

Species	Precipitation Input metric tons $km^{-2}yr^{-1}$	(tons $mi^{-2}yr^{-1}$)	Output in Rivers metric tons $km^{-2}yr^{-1}$	(tons $mi^{-2}yr^{-1}$)
Na^+	1.85±0.13	(4.54)	1.99±0.15	(4.88)
K^+	0.42±0.04	(1.03)	0.49±0.04	(1.20)
Mg^{2+}	0.31±0.02	(0.76)	0.44±0.03	(1.08)
Ca^{2+}	1.46±0.01	(3.58)	0.81±0.04	(1.98)
H^+	0.052±0.004	(0.15)	0.042±0.007	(0.10)
$C1^-$	3.73±0.26	(9.14)	3.63±0.30	(8.89)
SO_4^{2-}	6.72±0.70	(16.47)	4.74±0.31	(11.61)
PO_4^{3-}	0.074±0.001	(0.18)	0.028±0.001	(0.068)
Total	14.62±1.16	(35.85)	11.441±0.89	(29.81)

Table 3-5. Chemical Composition of Vegetation (ppm in ash)

Na^+	K^+	Ca^{2+}	Mg^{2+}	SO_4^{2-}
26	1151	3921	419	32

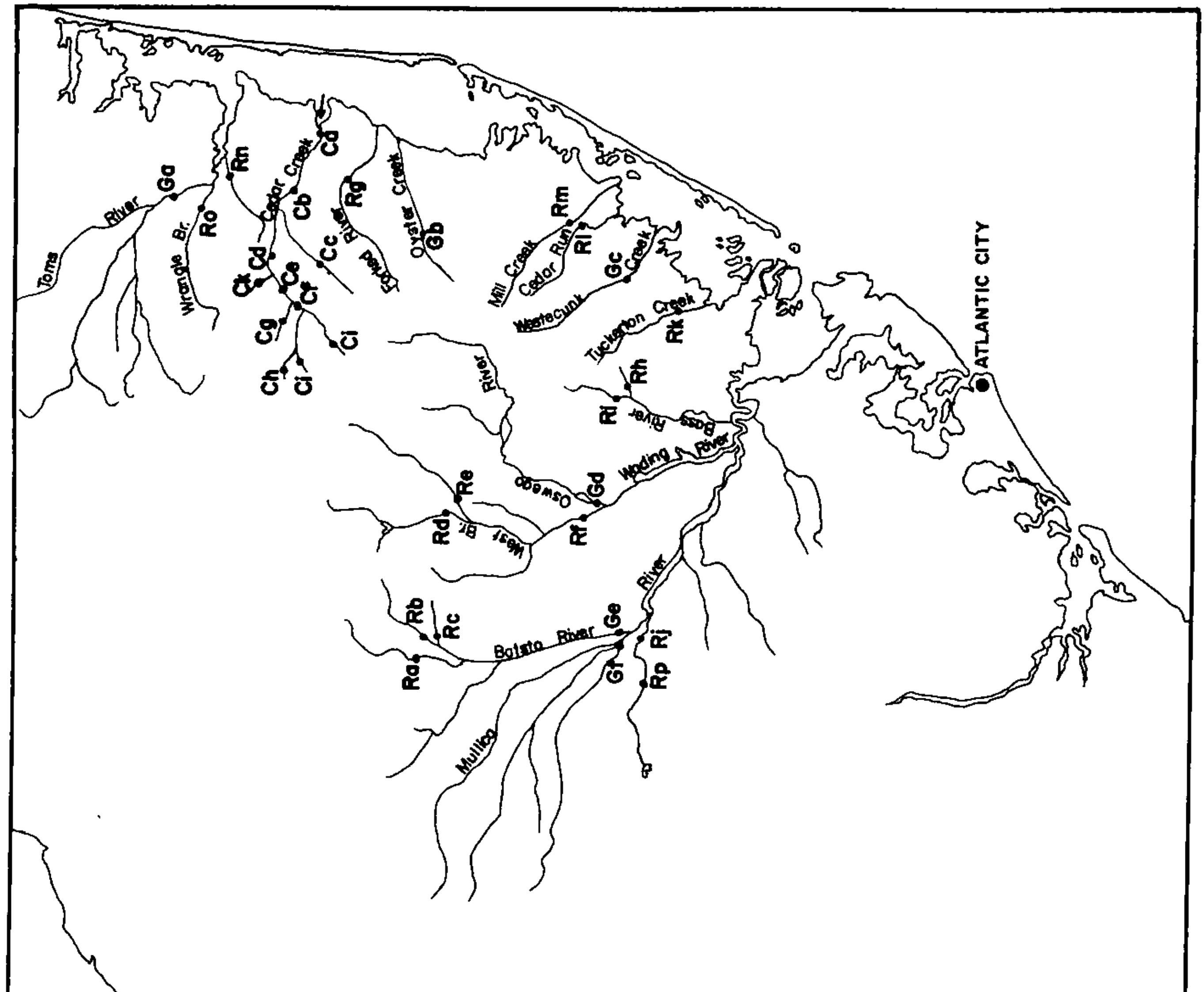


Fig. 3-1. River water sampling sites monitored during 1971-72.

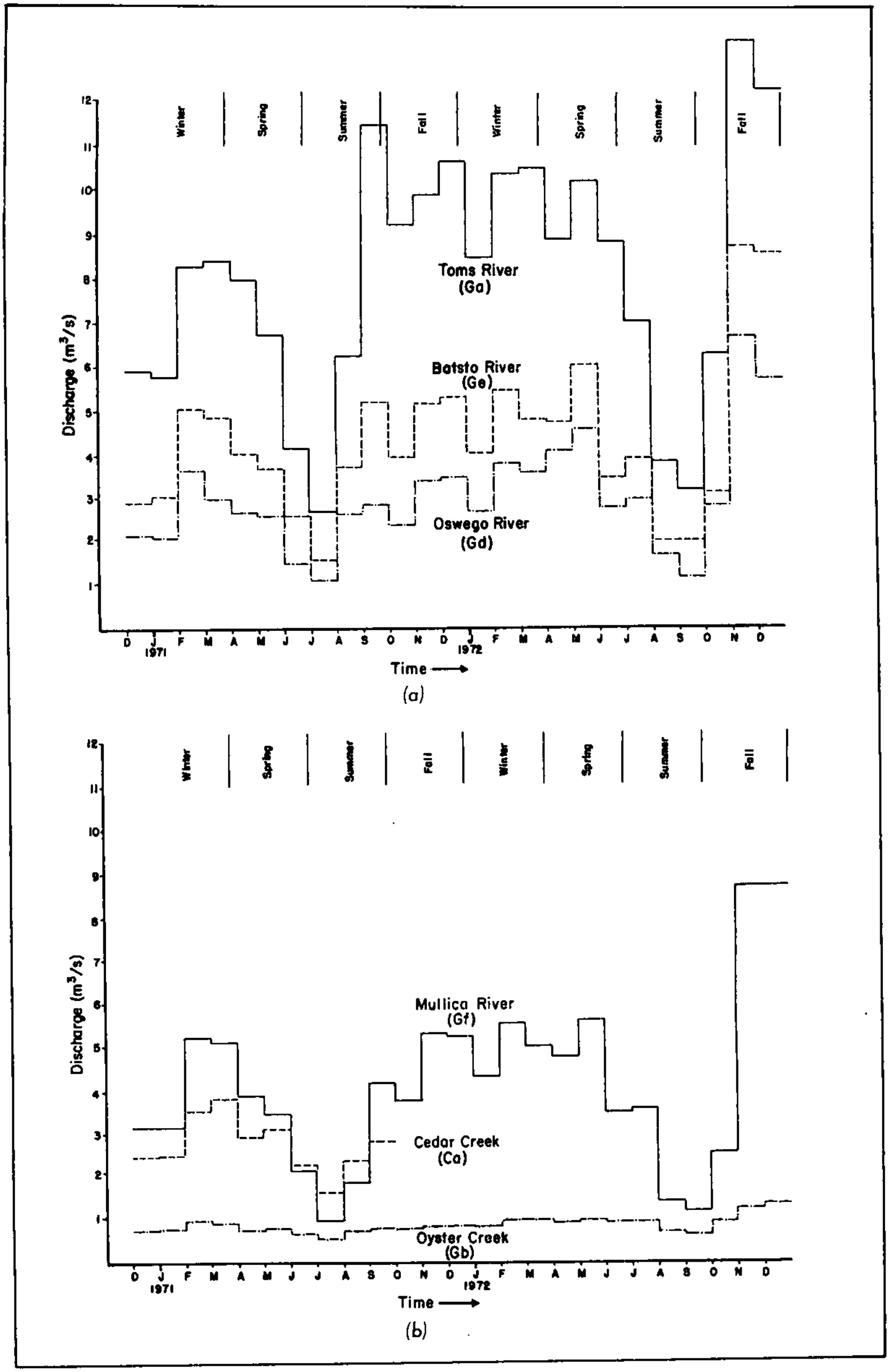


Fig. 3-2. Average monthly discharges recorded at U.S. Geological Survey gauging stations on Pine Barrens rivers for 1971-72.

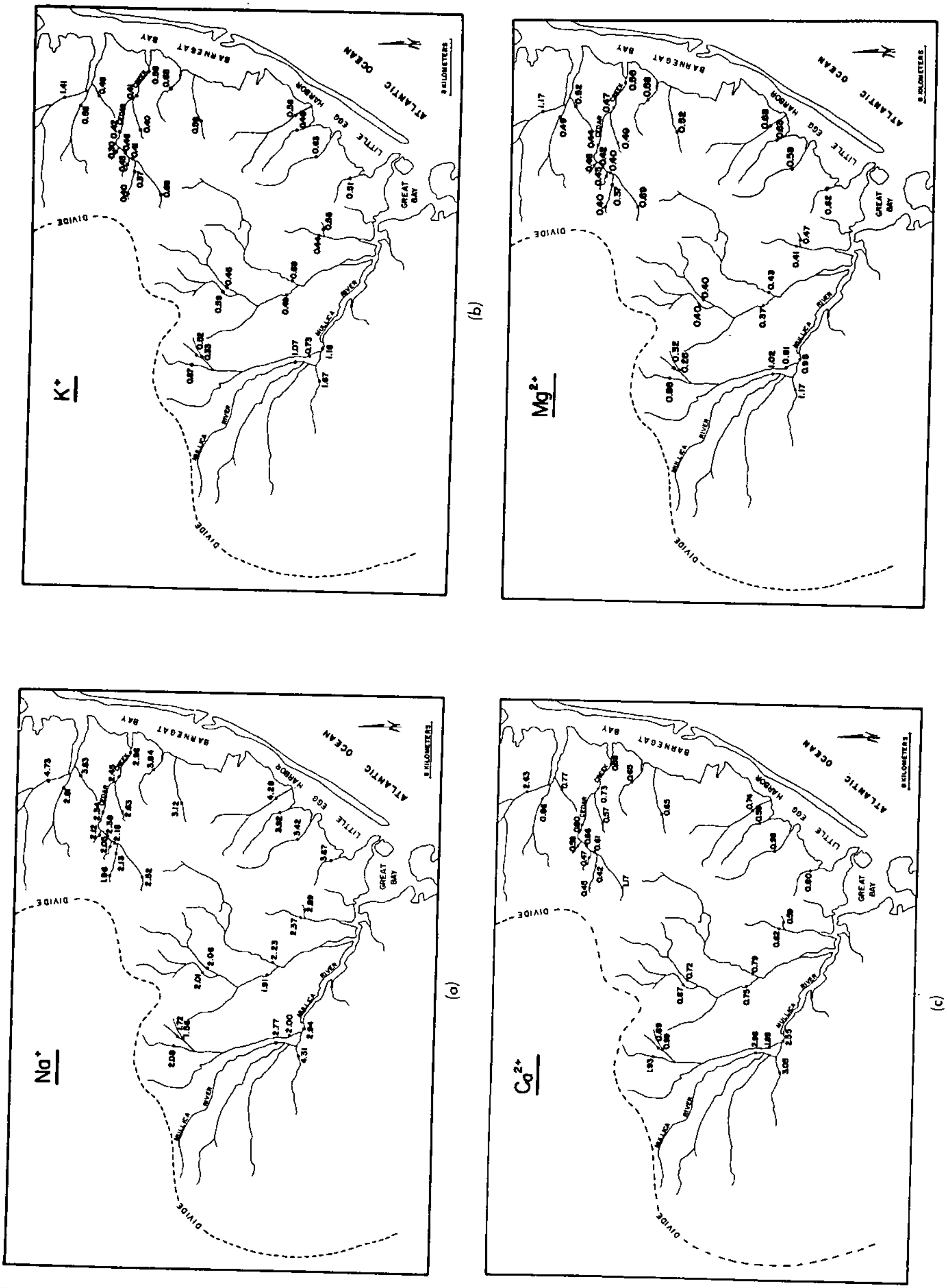


Fig. 3-3. Average concentrations of major chemical components in Pine Barrens rivers during 1971-72.

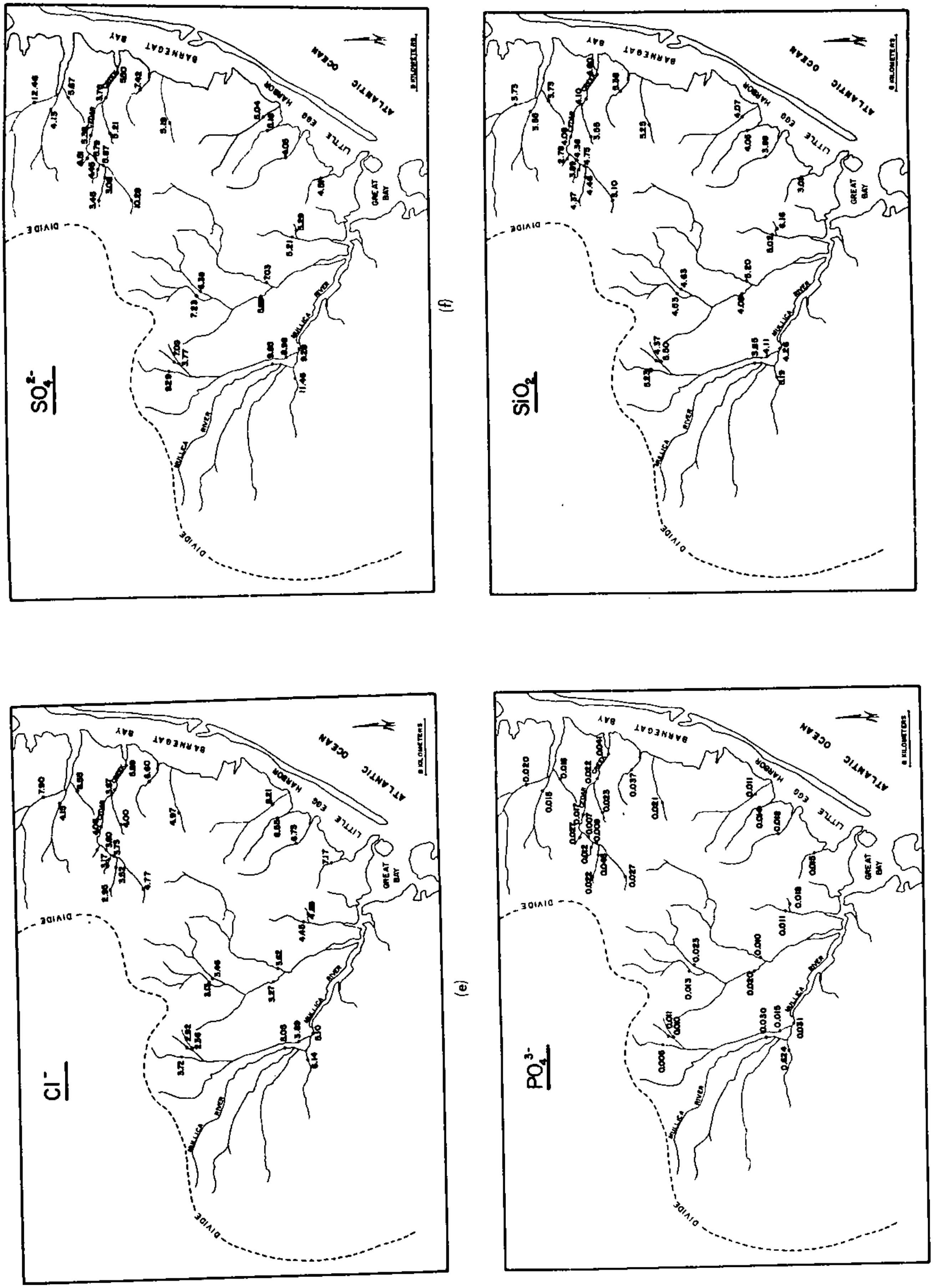


Fig. 3-3. Continued

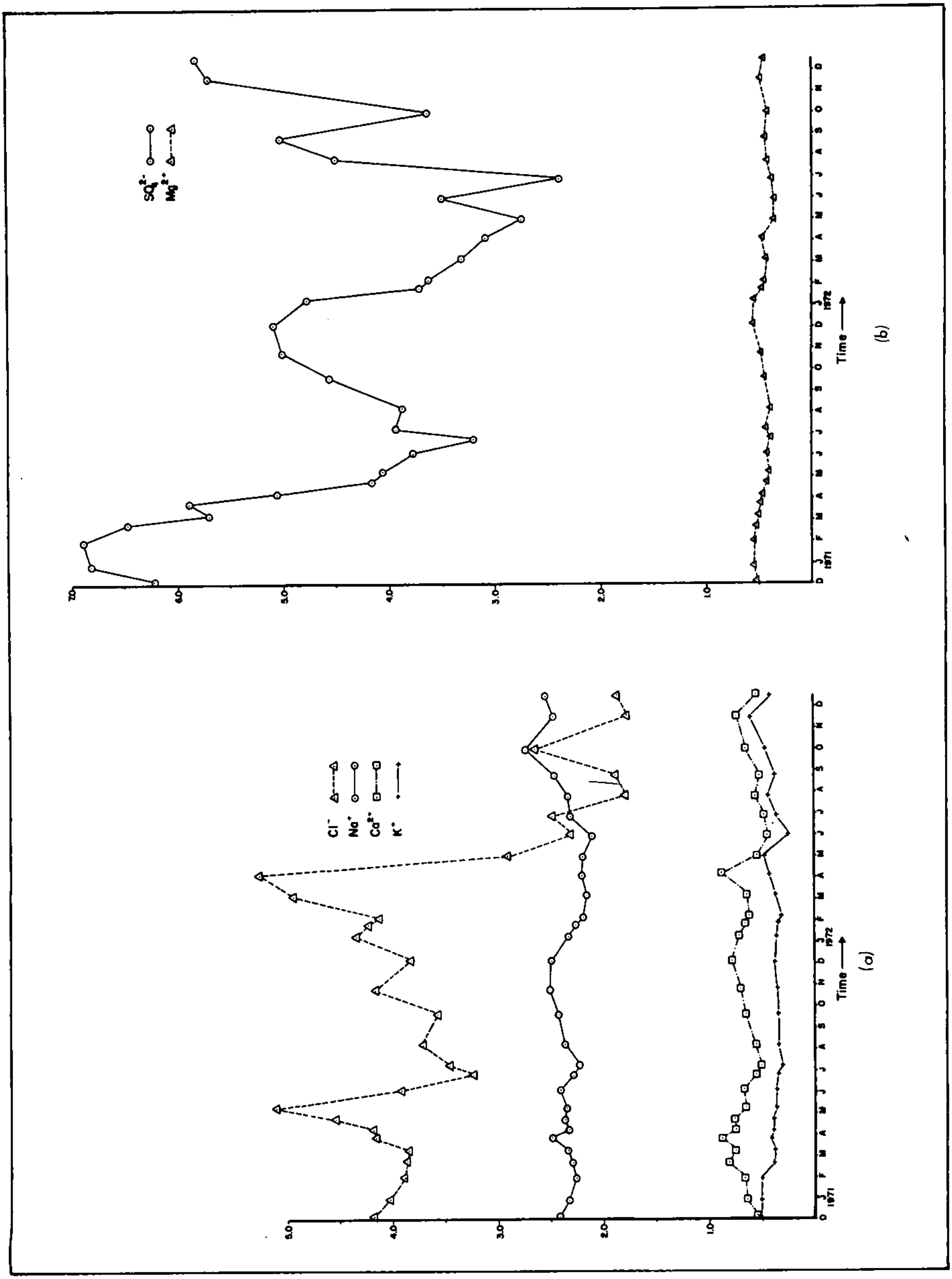


Fig. 3-4. Seasonal variations in major element chemistry of Cedar Creek during 1971-72. Vertical scale is in ppm.

Chapter 4

STREAM AND GROUNDWATER: TRACE METAL GEOCHEMISTRY

INTRODUCTION

From September, 1976 to April, 1978, we monitored seven different metals: Fe, Al, Mn, Zn, Cu, Pb, and Cd, along with pH, Eh, total dissolved solids, silica, and organic carbon in Pine Barrens stream and groundwater. Analytical results are discussed and tabulated below.

The data have been analyzed from a number of different viewpoints:

1. seasonal fluctuations of stream water trace element geochemistry;
2. comparison of Cedar Creek and Mullica River chemistries;
3. differences between stream water and groundwater chemistry; and
4. chemical differences between Pine Barrens river water (which is in some respects unique) and stream water from other parts of the world.

Chemical mechanisms of trace metal transport in Pine Barrens streams have also been of particular interest; e.g., whether a given trace metal is transported primarily in the dissolved or suspended load, the chemical speciation of various inorganic and organic trace metal complexes, and the chemical equilibria governing trace metal solubility.

METHODS

Water samples were collected in polyethylene bottles that had been purified with 1:10 Ultrex ultrapure concentrated HNO_3. Stream samples were collected from the same location (same depth and distance from bank) at each sampling. Groundwater was sampled using a Gorman-Rupp centrifugal pump with a 7.5 meter long, 5 cm diameter rubber hose and three-horsepower Briggs and Stratton gasoline engine. Wells were flushed 10-20 minutes prior to sampling. The wells themselves are described below.

pH, Eh, and temperature were measured in the field. pH was determined using a combination electrode and Orion model 601 pH/mV meter powered by a Trav-electric model 50-160 12 volt battery with AC converter. Eh was obtained using a platinum electrode coupled with a Ag/AgCl reference electrode on an Orion model 407A field pH/mV meter. True Eh was calculated from temperature and measured Eh using the conversion factors of Langmuir (1971).

Reliable Eh measurements are often difficult to obtain. Langmuir (1971) indicates that some oxygenated rain, stream, shallow lake, ocean, and groundwaters may give irreproducible Eh readings because of the absence of reduced species. Similarly, equilibrium in Eh measurements may never be attained in some heavily polluted, stagnant, or organic-rich waters, water-logged soils, and finer-grained sediments because of the absence of oxidized species. However acidic, oxygenated iron-rich systems, such as the Pine Barrens waters, should be well poised for Eh measurements. When significant concentrations of Fe^{3+} and Fe^{2+} are present, the ferric-ferrous iron couple can give water a high redox capacity (Langmuir, 1971). Eh measurements performed in this study were generally fast and reproducible and therefore appear to have thermodynamic significance.

Aliquots of each sample were filtered through $0.2\mu m$ Nucleopore membranes in the laboratory as soon as possible upon returning from the field. Great care was taken to minimize trace metal contamination. Glassware that was routinely cleaned in an acid bath was in addition soaked in 1:10 Ultrex HNO_3 and rinsed with double distilled H_2O prior to use. Both unfiltered and filtered samples were acidified to $pH < 2.0$ using concentrated Ultrex HNO_3 prior to analysis.

Total dissolved solids were determined by evaporating 1 liter of filtered sample to dryness. Evaporated residue was analyzed for organic carbon on a Leco carbon-sulfur analyzer.

Si was analyzed on a model 603 Perkin-Elmer atomic absorption flame spectrophotometer. Fe, Al, Mn, Zn, Cu, Pb, and Cd values were obtained using the graphite furnace attachment to this instrument.

Two computer programs were written to determine theoretical Fe and Al solubilities in the water samples. Calculated solubilities were then compared with solubilities measured in filtered samples to determine whether samples were undersaturated or supersaturated with respect to certain solids. The calculations are explained, and the Gibbs free energies and stability constants are tabulated in Appendix III.

*STREAM WATER DATA

Eh, pH, TDS, organic carbon, trace element contents, and Fe and Al solubility ratios for stream waters collected at sites shown in Fig. 1 are compiled in table 4-1 and discussed below. New Jersey Geological Survey Land Oriented Reference Data System (LORDS; see Widmer et al., 1974) coordinates for sample sites are given in parentheses for each sample site.

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* Some of the stream water trace metal data is taken from Amster (1977) and Quiett (1977), unpublished undergraduate senior theses for the Depts. of Chemistry and of Geological and Geophysical Sciences, Princeton University.

Cedar Creek

Total dissolved solid (TDS) contents in Cedar Creek are extremely low, generally within 20-25 ppm. Total solids vary little from TDS contents. Cedar Creek water, though tea-colored, is generally very clear. Transport of suspended material such as colloidal organics, Fe and Al oxides, clays, etc., is minor. Dissolved organic carbon averages 2-2.5 ppm. Though these concentrations are not particularly high, organic carbon comprises a relatively large proportion (about 10%) of TDS. Since the dominant organic constituents such as humic and fulvic acids contain about 50% carbon by weight, organic acids comprise an even larger proportion (approximately 20%) of TDS. Organic contents show seasonal fluctuation. Higher values are observed in the summer when microbial activity is most pronounced.

Cedar Creek Eh and pH both demonstrate seasonal trends. Eh is lower in summer than in winter. Pine Barrens stream pH is quite low in comparison to other streams. pH values are generally highest during summer, ranging between 4.5-5.5, and lower in spring and fall. However winter pH varies, with relatively high pH observed during the winter of 1976-77 and low pH's during the winter of 1977-78. Summer pH is higher than fall and spring pH, even though organic acid contents are greatest during the summer; this may in part be attributed to precipitation pH which is somewhat higher during summer (see Chapter 2). Agricultural activities, particularly the liming of fields during growing seasons is probably also responsible for the higher summer pH. Since TDS values are very low, the pH buffering capacity of the waters is slight. Natural stream water pH is therefore easily disrupted.

Iron

Total and 'dissolved' Fe concentrations average 100-400 ppb and 20-200 ppb, respectively. Total Fe is higher during the summer than the winter; suspended Fe is present most likely as mixed organic-Fe and hydroxide colloids. 'Dissolved' Fe is defined as that which passes through a 0.2 μm Nucleopore filter, though it is likely that colloids smaller than 0.2 μm are present in these waters. For example in a study of Fe in New Jersey Coastal Plain ground water, the average size of Fe oxide colloids was 1.0 μm but colloids < 0.01 μm were detected (Langmuir, 1969a; 1969c). Similarly in a study of the Mullica River estuary, Boyle et al. (1977) noted the presence of mixed Fe oxide and organic colloids in 0.45 μm filtered samples. Therefore it is likely that true dissolved Fe is somewhat lower than our filtered Fe concentrations.

Fe solubility ratio calculations using the computer program FESOL (see Appendix III) suggest that Cedar Creek waters are close to saturation with respect to amorphous $Fe(OH)_3$ (based on input values of 10 ppb estimated F^-, 3 ppm SO_4^{2-}, 2 ppm Cl^-, and the appropriate Eh and pH, given in table 4-1). Measured/theoretical Fe ratios average 0.26 with a standard deviation of 0.34. A solubility ratio of 1.0 denotes saturation, less than 1.0, undersaturation, and greater than 1.0, supersaturation.

The theoretical solubility of major inorganic Fe species vs. pH at typical Pine Barrens stream water conditions is shown in fig. 4-2. Note that the dominant inorganic solution species at $pH < 5$ is Fe^{2+}. In the higher pH (5.0-5.5) samples, the ferric species $Fe(OH)^{2+}$ and $Fe(OH)_2^+$ become increasingly important. With the exception of $FeHSO_4^+$, Fe chloride, fluoride and sulfate species are quantitatively almost negligible at the pH, Eh, and low ligand concentrations of these samples. The occurrence of organic Fe species is discussed in the following chapter. Seasonal patterns in Fe solubility correspond roughly to the pH data. Fe solubility is high and therefore measured/theoretical Fe solubility ratios are low in the relatively low pH spring and fall samples. Waters are relatively more saturated in summer months when pH is higher. During the winter, Cedar Creek was slightly supersaturated with respect to amorphous $Fe(OH)_3$ in 1976-77 when pH was higher, and undersaturated in 1977-78 when pH values were much lower.

Aluminum

Total and dissolved Al concentrations average 50-120 ppb and 20-80 ppb, respectively. Therefore roughly 50% of the total Al present in these waters is colloidal. No seasonal trends in total or filtered Al concentrations were observed.

Al solubility ratio calculations using the computer program ALSOL (see Appendix III) suggest that Cedar Creek waters are undersaturated with respect to halloysite, nearly saturated with respect to gibbsite, and supersaturated with respect to kaolinite (based on input values of 2.0 ppm dissolved Si, 10 ppb total F, 3 ppm SO_4^{2-}, and appropriate pH, as given in table 4-1). Al solubility ratios average 0.17 (std. dev. = 0.19) with respect to halloysite, 0.66 (std. dev. = 0.73) with respect to gibbsite, and 5.06 (std. dev. = 7.17) with respect to kaolinite.

Predicted inorganic Al solubility and complex speciation at typical stream water conditions is illustrated in fig. 4-3. As an example, solubility shown is relative to gibbsite. At low pH, Al solubility is maximum and is comprised largely of Al^{3+}. At $4.3 < pH < 5.4$ Al solubility is lower and consists of various hydroxy species such as $Al(OH)^{2+}$, $Al(OH)_2^+$, and $Al(OH)_3^\circ$. Al sulfate and fluoride species become quantitatively important only at much greater SO_4^{2-} and F concentrations.

Though Cedar Creek Al contents exhibit no seasonal patterns, Al solubility ratios do. These trends, as with Fe solubility, are largely a function of pH. Higher pH summer and winter samples are relatively more saturated with respect to all three solids than the lower pH winter and moderately low pH spring and fall samples.

Trace Elements

Trace elments other than Fe and Al which have been analyzed include Mn, Zn, Cu, Pb, and Cd (table 4-1). With the exceptions noted below these analyses were performed on unfiltered samples. Mn in Cedar Creek ranges from 3-9 ppb and averages about 6 ppb. Zn concentrations are slightly more variable, ranging from 1-10 ppb and averaging 4-5 ppb. Cu rarely exceeds 1.5 ppb and averages about 0.75 ppb. Pb and Cd, at approximately 0.35 and 0.12 ppb respectively, are almost below the detection limits of the graphite furnace.

Data from filtered samples (not listed in table 4-1) indicate that total Mn is approximately equal to dissolved Mn, suggesting that Mn transport occurs predominantly in the dissolved state. In some cases total Zn slightly exceeds 'dissolved' (filtered) Zn, suggesting some colloidal transport. Cu, Pb, and Cd concentrations are so low in these samples that contamination during filtration prevents collection of reliable dissolved state concentrations.

Mullica River

The Mullica River is chemically very similar to Cedar Creek, the main exception being greater concentrations of Fe and certain trace metals in the former (table 4-1). In Chapter 3 it was noted that the Mullica River generally also contained higher concentrations of major components. TDS contents in the Mullica River, at approximately 30 ppm, are greater than in Cedar Creek, yet are still low compared to average stream water (Turekian, 1969). Dissolved organic carbon values, ranging up to 5 ppm, are also slightly greater than in Cedar Creek. Unlike Cedar Creek, total solid content of Mullica River water, at 35-45 ppm is significantly greater than TDS. The 5-15 ppm of filterable solids is predominantly flocculated organics and amorphous Fe oxyhydroxides. In addition total solid and organic carbon contents in summer are higher than winter values.

Eh and pH in the Mullica River both demonstrate seasonal trends similar to those observed at Cedar Creek. Eh is relatively lower in the summer and higher during winter. During summer, Mullica River Eh is usually lower than Cedar Creek Eh, but pH is highest in the summer in both rivers. These pH fluctuations are probably attributable at least in part to agricultural activity. The highest pH values are observed at Pleasant Mills, which is about 16 km (10 mi.) downstream from Atsion. The Mullica River has drained much more agricultural acreage at Pleasant Mills than at Atsion.

Iron

A major difference in the chemistries of the two rivers is that Mullica River waters contain more Fe than Cedar Creek. Total Fe in the Mullica River ranges from 0.5 to over 4 ppm, which is about an order of magnitude greater than in Cedar Creek. Coonley et al. (1971) also noted large amounts of filterable Fe in Mullica River waters. Total Fe is higher during summer, and colloidal Fe occurs predominantly as mixed organic and oxyhydroxide floccules. 'Dissolved' Fe ranges from 0.1 to 1.0 ppm.

Fe solubility ratios indicate that Mullica River waters are generally supersaturated with respect to amorphous $Fe(OH)_3$ (based on input values of 100 ppb F^-, 3 ppm SO_4^{2-}, 2 ppm Cl^-, and the appropriate Eh and pH data, as given in table 4-1; see Appendix III for calculations). Measured/theoretical Fe ratios average 2.98 (std. dev. = 4.35) as opposed to 0.26 for Cedar Creek. Reasons for this significant difference in Fe saturation state for the two streams are: 1) the generally higher Mullica water pH and consequently lower Fe solubility; and 2) the higher 'dissolved' Fe concentrations in the Mullica River. This latter factor may in part be attributed to the presence of small colloidal Fe and organic Fe complexes that are not retained by the filters and consequently are included in the 'dissolved' Fe analyses. From the Fe solubility ratios in table 4-1, no distinct seasonal pattern in Fe saturation is apparent. The increase in theoretical Fe solubility due to low summer Eh is cancelled by the higher summer pH. 'Dissolved' Fe shows no distinct seasonal fluctuation.

Aluminum

Total and "dissolved" Al contents average 100-300 and 20-140 ppb, respectively. Roughly 65% of the total Al present is colloidal. No seasonal trends in Al content are observed. ALSOL solubility calculations indicate that Al solubility ratios, like Fe, are generally much greater in Mullica River than in Cedar Creek. Mullica River is nearly saturated with respect to halloysite, supersaturated with respect to gibbsite, and extremely supersaturated with respect to kaolinite (based on input values of 2.0 ppm dissolved Si, 10 ppb total F, 3 ppm SO_4^{2-}, and appropriate pH, as given in table 4-1). Al solubility ratios average 0.81 (std. dev. = 0.78) for halloysite, 3.26 (std. dev. = 3.21) for gibbsite, and 31.6 (std. dev. = 33.8) for kaolinite. Higher solubility ratios are observed in the summer because of the higher pH.

Trace Elements

Total trace element concentrations are slightly greater in the Mullica River than in Cedar Creek (table 4-1). Mn ranges from 13-30 ppb and averages 20 ppb. Zn is generally 4-5 ppb, but sometimes reaches 30 ppb. Cu averages a little less than 1 ppb. Pb ranges up to 3 ppb, and Cd is barely detectable at 0.1-0.2 ppb. Pb concentrations are reduced somewhat by filtration whereas Mn contents are not (data not in table 4-1). Mn transport therefore occurs predominantly in the dissolved state, whereas some Pb is colloidal, possibly absorbed to organic-Fe oxyhydroxide floccules. Reliable 'dissolved' Zn, Cu, and Cd determinations could not be obtained because of contamination during filtration.

The above analyses pertain to the non-estuarine section of the Mullica River, which has the largest drainage basin in the Pine Barrens. Smaller creeks draining bogs and swamps possess even lower pH and higher organic and trace metal contents than those reported for Cedar Creek and the Mullica River. Small creeks may have pH's as low as 3.5, dissolved organic acid contents as high as 50 ppm, and dissolved Fe and Al contents as high as 10 and 5 ppm, respectively. TDS and pH of Pine Barrens streams are quite low, and organics, Fe, and Al comprise an unusually high proportion of TDS compared to average stream water (Turekian, 1969; Livingstone, 1963).

*GROUNDWATER DATA

Geochemical data for 15 groundwater samples from 11 different wells are given in table 4-2. Sample site locations are indicated in fig. 4-4. Groundwaters were obtained from polyvinyl chloride observation wells installed by the U.S. Geological Survey in the Wharton Tract. Three of the 11 wells are deep, with intake screens set between 115-250 feet. The other 8 are screened between 10-50 feet. Most wells tap the Cohansey aquifer, except for one of the deep wells, 6D, which may be from the Kirkwood (Lyon, 1977).

Groundwaters contain generally higher TDS than the stream waters. TDS values range from 28-99 ppm, as opposed to 20-35 for the streams. The groundwaters are generally very clear with little filterable solids. At 0.5-2.0 ppm, organic carbon concentrations in groundwaters are distinctly lower than in the streams. However, very shallow groundwaters close to bogs and swamps may contain much higher organic concentrations.

Silica analyses were performed on groundwaters; deep samples (2D, 6D, 7D, and 56S) contain higher Si contents than shallow samples (table 4-2).

Though it is difficult to generalize from only 3 deep groundwater samples, mild differences between Eh and pH of shallow and deep groundwaters are suggested. Eh of deep samples averages about +455 mV. The Eh of shallow samples, excluding the low value of well 51S on 6/1/77 (which was believed to be obstructed), averages +520mV. This trend of increasing Eh with decreasing depth is consistent with oxygenation of the shallow samples. The pH of deep samples averages 4.65, which is slightly higher than the average pH of the shallow samples, 4.43. Perhaps shallow shamples are slightly more acidic because of the presence of organic acids and/or the addition of CO_2 from the soil or root respiration. In general, groundwater pH is essentially the same as precipitation pH (Chapter 2, this study).

Iron

Deep and shallow groundwaters also vary in Fe content. Fe concentrations of deeper samples range from 0.5 to 1.5 ppm. Fe contents of shallow samples are less, ranging from 0.05-0.30 ppm. One exception is sample 51S which had a low Eh and contained nearly 3 ppm Fe.

Filtration made little difference in the Fe content of the groundwaters. This contrasts with stream waters, particularly those of the Mullica River, in which large amounts of colloidal Fe are present.

Fe solubility calculations indicate that the groundwaters are uniformly undersaturated with respect to $Fe(OH)_3$ (based on input values of 100 ppb F^-, 3 ppm SO_4^{2-}, 2 ppm Cl^-, and the appropriate Eh and pH data, given in table 4-2). Measured/theoretical Fe ratios average 0.060 (std. dev. = 0.060). Shallow samples are generally even more undersaturated than the deep samples, a consequence of the higher dissolved Fe contents and pH of the latter.

Aluminum

Groundwater Al concentrations are rather high, ranging from 0.02-5.0 ppm. Al contents of both filtered and unfiltered samples are very similar. Therefore most of the Al is probably dissolved.

ALSOL solubility calculations indicate that groundwaters are supersaturated with respect to all three minerals considered: halloysite, gibbsite, and kaolinite (based on input values of 10 ppb total F, 3 ppm SO_4^{2-}, and appropriate pH and Si content, as indicated in table 4-2). Measured/theoretical Al solubility ratios average 1.42 (std. dev.= 1.52) for halloysite, 4.14 (std. dev. = 3.26) for gibbsite, and 40.26 (std. dev. = 41.02) for kaolinite. Al solubility in general decreases with decreasing depth, particularly solubility with respect to gibbsite.

Trace Metals

Total trace metal concentrations in groundwater are greater and more variable than in stream water. Ratios of individual trace metal contents /TDS, however, are similar for both ground and surface waters. These chemical similarities further support our contention in Chapter 3 that some groundwater migration from deep aquifers to the surface is occurring. Mn ranges from 8-210 ppb in groundwater as opposed to 5-30 ppb in the streams. Zn varies from 1-80 ppb, and compares with 1-30 ppb in the streams. Cu, Pb, and Cd concentrations, averaging 1.7, 1.2, and 0.4 ppb, respectively, are slightly greater than stream water contents.

Further groundwater data from the Pine Barrens and surrounding areas are available from a number of sources (e.g. see Anderson and Appel, 1969; Clark et al., 1968; Farlekas et al., 1976; Rhodehamel, 1973; Rush, 1962; Anonymous, 1976; data compiled in Lyon, 1977).

DISCUSSION

Comparison of Pine Barrens Water Chemistry with Federal Drinking Water Standards

Stream water geochemical analyses given in this report are in general agreement with those of several previous investigators (Toth and Ott, 1972; Anderson, 1970; Anonymous, 1976a). In a few cases, our metal concentrations are lower than those of others (e.g. Cu, Pb, and Zn of the Mullica River at Pleasant Mills, p. 296, Anonymous, 1976a; and Fe in the Mullica groundwater , Rhodehamel, 1973). Since painstaking care was taken to prevent contamination, which is most

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* Some of the groundwater data is taken from Lyon (1977), an unpublished undergraduate senior thesis for the Dept. of Geological and Geophysical Sciences, Princeton University.

always a problem in low-level trace metal analysis, the lower trace element concentrations reported here are probably the most reliable.

Trace metal contents of Pine Barrens ground and stream waters are low compared to present national drinking water standards. Maximum permissible concentrations (MPC's) of pH, total dissolved solids, and selected trace metals based on primary and secondary national drinking water standards are compared to observed concentrations in Pine Barrens waters (table 4-3). Primary drinking water standards include toxic elements such as Cd and Pb (Anonymous, 1976b). Secondary standards, which are less strict than primary regulations, deal with substances that are not as toxic but possess other undesirable qualities such as taste or color (Anonymous, 1977). Concentrations of Cd and Pb in the Pine Barrens waters sampled are 1 to 2 orders of magnitude lower than national drinking water standards (table 4-3). Cu, Zn, and total dissolved solids, which are included among secondary standards, are well below MPC's. However Fe and pH fall outside recommended limits in both stream and groundwater, and Mn exceeds MPC in certain groundwaters. Color of surface waters is commonly high, ranging from 3 to 150 Pt-Co units, particularly during the growing season (Rhodehamel, 1973). In general this exceeds the secondary drinking water standard of 15 Pt-Co units (Anonymous 1976a; 1977). Much of the color and Fe, particularly in Mullica stream waters, can be removed by filtration. This might prove useful in water treatment.

The groundwaters analyzed are low in organic and colloidal Fe content and therefore have little color. Dissolved Fe is quite high in certain groundwaters. Some of this Fe can be precipitated by aeration. Groundwater trace metal contents are variable, and Mn in some of the groundwaters is higher than suggested secondary standards for drinking water. Mn contents of the groundwaters are not significantly reduced by filtration.

In summary, pH, Fe, Mn and color fall outside recommended federal secondary limits in some Pine Barrens stream and/or groundwaters. Prior to long-term human consumption of Pine Barrens waters, further purification of these four chemical parameters may be desired.

Discussion of Fe and Al Solubility Calculations

Fe solubility calculations indicate significant differences in the measured /theoretical Fe solubility ratios of Cedar Creek, Mullica River, and groundwater (see tables 4-1 and 4-2). Of these, groundwater is the least saturated with an average Fe solubility ratio of 0.060 (table 4-1). At the low pH and relatively low Eh conditions observed, theoretical Fe solubility is rather high (1 to 24,000 ppm; see fig. 4-2), and an Fe source adequate for creating Fe supersaturation may not be available in the groundwater environment. On the other hand, pH and Eh are generally higher in the surface water environment, and therefore theoretical Fe solubility is somewhat lower. Also stream waters are in contact with abundant Fe oxyhydroxide flocculant. Accordingly, solubility ratios are higher in surface waters than in groundwater, the average being 0.26 for Cedar Creek and 2.98 for the Mullica River (table 4-1). The higher solubility ratios of Mullica River waters probably reflect the inclusion of < 0.2 μm Fe oxyhydroxide colloids and organic Fe species in the "dissolved" Fe analyses in table 4-1. This interpretation is substantiated by data on organometallic interactions in Chapter 5 of this study and by the results of Jones et al. (1974) who observed abnormally high Fe solubility ratios in streams with highly organic sediment.

Al solubility calculations on the same samples suggest that both ground and stream waters are in approximate equilibrium with halloysite, slightly supersaturated relative to gibbsite, and very supersaturated with respect to kaolinite (table 4-2). This is in contrast to the results of Jenne and Truesdell (1973) and Jones et al. (1974) who found that ground and river waters studied were approximately saturated with respect to kaolinite. However, their results were based on earlier free energy data that differ from those used here.

Our results bear greater similarity to those of Paces (1978); still, his calculations were based on different thermodynamic data. Solubility ratios for Cedar Creek, the Mullica River, and the groundwater samples are: 5.06, 31.6, and 40.26 for kaolinite; 0.17, 0.81, and 1.42 with respect to halloysite; and 0.66, 3.26, and 4.14 for gibbsite, respectively. Al solubility is much lower in Cedar Creek than in Mullica River ground and stream waters. The high organic content of the Mullica River and therefore the presence of dissolved organic Al complexes may be contributing to the high Al solubility ratios in these samples. But this cannot account for the even higher solubility ratios of Mullica groundwaters because they have a much lower organic content.

Al in Mullica River ground and stream waters probably originates from the weathering of glauconite in early Tertiary and late Cretaceous formations buried below and exposed to the west of the Mullica drainage basin (see Chapter 1). It is probable that the Fe in the massive bog iron deposits of the Pine Barrens also originates from this source. It is also possible that one of the reasons the Mullica River basin is more highly enriched with bog iron than other basins is that there are more glauconite deposits near the Mullica River and therefore a greater source of iron. The same arguments may be applied to the high Al contents (glauconite being an aluminosilicate) of Mullica River ground and stream waters. Also, perhaps Al contents of these waters are supersaturated with respect to kaolinite and more nearly in equilibrium with halloysite and gibbsite because formation of gibbsite and halloysite is relatively fast (Wilson, 1969; Parham, 1969) but precipitation of kaolinite is kinetically slow. Alternatively, Paces (1978) suggests that a reversible metastable aluminosilicate solid of variable composition (not gibbsite, halloysite, or kaolinite) controls Al solubility in many natural waters.

CONCLUSIONS

1. From September, 1976 to April, 1978 we monitored stream and groundwater concentrations of seven different trace metals: Fe, Al, Mn, Zn, Cu, Pb, and Cd, along with pH, Eh, total dissolved solids and organic carbon. Owing to the low pH of precipitation, CO_2 from plant decay and respiration, and the presence of organic acids, Pine Barrens waters are unusually acidic, ranging from pH 3.5—5.5. Anomalously high pH's have been observed during certain summer months and are attributed to agricultural activities such as liming. Total dissolved solids are very low, ranging between 20-35 ppm in stream water and 25-100 ppm in groundwater. Fe, Al, and natural organic acids comprise unusually large proportions of the TDS. Early Tertiary and late Cretaceous glauconites buried below and exposed to the west of the Pine Barrens serve as likely sources of Fe, Al and other trace elements in surface and groundwaters. Trace element contents of Pine Barrens waters follow their order of abundance in glauconite, the general trend being: Fe = Al > Zn = Mn > Cu, Pb, Cd.

2. Fe solubility calculations suggest that a) Cedar Creek waters are close to saturation; b) Mullica River waters are slightly supersaturated; and c) groundwaters are uniformly undersaturated with respect to amorphous $Fe(OH)_3$. Apparent supersaturated conditions in stream water may indicate the presence of organically-bound Fe or small Fe oxyhydroxide colloids that are not retained during sample filtration.

3. Al solubility calculations suggest that a) Cedar Creek waters are undersaturated with respect to halloysite, slightly supersaturated relative to gibbsite, and supersaturated with respect to kaolinite; b) Mullica River and groundwaters are approximately saturated with respect to halloysite, supersaturated with respect to gibbsite, and very supersaturated with respect to kaolinite.

			mV	ppm		ppb		measured Fe: theoretical Fe solubility ratio	ppb		measured Al: theoretical Al solubility ratio			total unfiltered ppb				
Sample Sites	Date	pH	Eh	TDS	[1]dissolved org. carbon	total Fe	[1]dissolved Fe	[2]amorphous Fe $(OH)_3$	total Al	[1]dissolved Al	[3]kaolinite	[4]halloysite	[5]gibbsite	Mn	Zn	Cu	Pb	Cd
Cedar Creek: Lanoka Harbor [9](33-12 377)	9/29/76	4.10	+516	20.0	[6]—	—	113	0.0025	96.7	50.6	0.24	0.0059	0.024	4.7	—	—	—	—
	12/1/76	4.70	515	24.6	1.65	—	134	0.14	—	92.7	6.40	0.28	1.02	8.0	—	—	—	—
	2/8/77	4.80	713	26.4	0.77	—	120	0.78	—	71.7	7.21	0.31	1.12	7.0	5.2	—	0.6	—
	3/31/77	4.25	545	16.2	2.32	—	238	0.041	—	109	1.18	0.032	0.13	8.2	—	—	—	—
	6/1/77	4.54	569	24.8	2.25	342	99	0.17	94.9	50.2	1.91	0.073	0.28	6.5	1.6	1.6	0.2	0.1
	7/28/77	4.92	515	22.9	—	243	38	0.14	111	50.4	8.23	0.32	1.14	4.1	1.4	1.2	0.7	0.1
	9/22/77	4.44	561	25.1	2.07	324	32	0.29	123	79.8	2.07	0.070	0.28	6.4	4.8	0.5	0.4	0.1
	1/5/78	3.90	564	25.6	—	163	—	[7]0.0056	110	—	[8]0.15	[8]0.0035	[8]0.015	8.4	10.1	0.1	0.2	<0.1
	4/28/78	—	—	—	—	255	230	—	125	107	—	—	—	5.0	7.0	0.4	0.8	0.2
Double Trouble (33-12-116)	6/1/77	4.70	544	25.6	3.70	383	152	0.34	342	35.0	2.42	0.10	0.39	9.3	2.8	1.5	0.2	0.2
	7/28/77	5.23	480	21.0	—	262	21	0.16	62.7	16.4	8.65	0.23	0.89	3.5	1.2	0.6	0.9	0.1
	9/22/77	4.56	556	27.5	2.70	370	55	0.082	87.7	75.7	3.11	0.12	0.47	6.1	8.7	0.6	0.5	0.2
	2/4/78	4.15	569	—	—	175	—	[7]0.036	83.0	—	[8]0.52	[8]0.013	[8]0.055	—	—	—	—	—
Dover (33-01-849)	12/1/76	5.00	496	19.6	1.22	—	57	0.20	—	18.4	4.17	0.15	0.53	7.6	—	—	—	—
	2/8/77	5.40	672	21.3	1.17	—	26	0.75	—	18.0	15.09	0.37	1.48	6.0	5.3	1.6	0.5	—
	3/31/77	4.67	532	21.2	2.33	—	106	0.16	—	38.1	2.34	0.098	0.37	7.4	—	—	—	—
	6/1/77	5.30	562	20.5	2.64	139	66	1.35	49.0	—	[8]31.84	[8]0.81	[8]3.18	5.9	1.6	—	0.1	0.2
	9/22/77	4.84	517	23.4	2.42	94	30	0.074	46.5	44.3	5.20	0.22	0.78	5.8	6.6	0.5	0.2	0.1
	1/5/78	4.35	573	23.1	2.25	66	—	[7]0.049	43.9	—	[8]0.78	[8]0.023	[8]0.094	7.0	7.4	0.1	<0.1	0.1
	4/28/78	—	—	—	—	90	84	—	67.0	58.9	—	—	—	4.2	5.0	0.4	0.8	0.1
Bamber (33-11-125)	7/28/77	5.55	441	20.4	—	88	41	0.65	49.7	9.7	1.11	0.26	1.07	2.6	0.4	0.2	0.1	0.1
	9/22/77	4.68	505	24.8	2.90	148	50	0.034	54.2	—	[8]3.44	[8]0.15	[8]0.55	5.9	4.0	0.4	0.4	0.1
	1/5/78	4.10	568	23.0	2.40	95	—	[7]0.014	45.8	—	[8]0.21	[8]0.0054	[8]0.022	6.5	6.9	0.1	0.2	—
	4/28/78	—	—	—	—	111	105	—	58.4	49.6	—	—	—	3.6	5.8	0.5	0.7	0.2
Mullica River: Pleasant Mills (32-32-473)	10/4/76	5.70	590	—	—	—	177	9.32	—	73.7	106.33	2.49	10.31	14.8	—	—	—	—
	12/1/76	5.40	461	—	2.66	—	746	6.67	—	88.3	73.98	1.80	7.25	—	—	—	—	—
	2/8/77	5.20	583	—	2.04	—	844	13.84	—	52.0	24.88	0.69	2.60	—	—	0.3	0.6	—
	3/31/77	4.47	541	23.8	2.34	—	448	0.27	—	134	3.95	0.14	0.54	—	—	—	1.4	—
	5/28/77	5.75	—	—	—	3,320	600		154	57.5	88.59	2.08	8.59	16.4	3.7	1.4	1.5	0.1
	6/1/77	5.73	375	34.3	4.81	3,830	445	2.90	122	23.4	35.15	0.82	3.41	16.4	6.0	1.2	0.8	0.1
	7/28/77	5.93	352	30.2	2.56	4,210	30	0.31	157	21.2	39.65	0.93	3.84	13.0	1.5	0.2	1.3	0.1
	9/22/77	5.79	384	29.5	1.85	3,000	12	0.15	98	18.3	29.60	0.69	2.87	15.2	4.8	0.7	0.8	0.1
	1/5/78	4.34	567	—	—	695	—	[7]0.42	312	—	[8]5.26	[8]0.16	[8]0.63	30.2	25.1	0.1	0.4	0.1
	4/2/78	4.25	561	—	—	624	251	0.074	251	—	[8]2.73	[8]0.074	[8]0.30	—	—	—	—	—
	4/28/78	—	—	—	—	1,058	509	—	227	152	—	—	—	17.9	15.0	1.7	1.8	0.2
Atsion (32-21-576)	10/4/76	5.40	635	—	—	—	380	10.27	—	120	100.56	2.45	9.95	21.3	—	—	—	—
	12/1/76	4.80	558	27.2	1.82	—	247	1.10	—	70.8	7.11	0.31	1.10	25.5	—	—	—	—
	2/8/77	4.80	603	28.8	1.06	—	499	3.00	—	94.2	9.44	0.41	1.46	25.6	—	0.8	2.0	—
	5/28/77	4.70	—	—	—	1,990	70	—	164	—	[8]11.30	[8]0.49	[8]1.80	18.8	5.1	0.8	1.9	0.1
	6/1/77	4.93	548	30.3	4.78	3,330	220	1.34	275	137	23.29	0.90	3.17	18.2	3.4	1.4	1.2	0.2
	7/14/77	4.75	422	—	—	3,110	—	[7]0.16	182	51.5	4.29	0.19	0.68	16.2	2.6	1.1	2.8	0.2
	7/28/77	5.34	428	28.5	2.94	3,020	116	0.38	221	41.5	30.01	0.75	2.97	15.6	2.0	0.6	2.5	0.1
	9/22/77	5.55	513	20.2	1.97	3,000	30	1.04	98	26.3	30.04	0.71	2.92	15.2	4.8	0.7	0.8	0.1
	1/5/78	4.21	570	—	—	590	—	[7]0.18	271	—	[8]2.38	[8]0.063	[8]0.26	29.6	29.0	0.2	0.7	0.2
	4/2/78	4.35	551	—	—	1,400	373	0.15	243	—	[8]4.29	[8]0.13	[8]0.52	25.5	—	—	—	—
	4/28/78	—	—	—	—	1,697	—	—	914	142	—	—	—	17.9	21.0	2.3	7.3	0.3

[1] samples filtered through 0.2 μm Nucleopore membranes

[2] theoretical solubility of Fe calculated using amorphous Fe $(OH)_3$ as solid

[3] theoretical solubility of Al calculated using kaolinite as solid

[4] halloysite as solid

[5] gibbsite as solid

[6] — = not analyzed

[7] total Fe analysis used in solubility ratio calculation

[8] total Al analysis used in solubility ratio calculation

[9] LORDS coordinates listed in parentheses with sample site name

Table 4-1. Trace metal chemistry of stream water samples from Cedar Creek and the Mullica River.

		feet		mV	ppm			ppb		measured Fe: theoretical Fe solubility ratio	ppb		measured Al: theoretical Al			total unfiltered ppb				
Well Code	Date	Depth Well Screen	pH	Eh	TDS	[1]diss.org. carbon	Si	total Fe	[1]diss. Fe	[2]amorphous $Fe(OH)_3$	total Al	[1]diss. Al	[3]kaolinite	[4]halloysite	[5]gibbsite	Mn	Zn	Cu	Pb	Cd
2D (31-35-192)[7]	6/1/77	145-150	4.29	483	37	0.6	6.15	755	750	0.017	1063	1061	33.02	1.20	1.61	10.0	3.8	2.0	0.9	0.2
6D (32-33-189)	6/1/77	245-250	4.89	415	40	0.6	8.30	1370	1330	0.13	493	19	10.12	0.39	0.39	16.2	22.1	1.6	0.9	0.6
7D (31-24-896)	6/1/77	115-120	4.75	474	[6]—	—	2.93	650	550	0.20	516	18	2.01	0.09	0.24	7.9	5.8	—	1.6	0.2
16S (31-24-896)	6/1/77	24-29	4.70	501	32	1.8	1.43	67	65	0.044	330	202	10.76	0.43	2.22	15.0	2.0	1.8	1.4	0.2
19S (32-31-122)	5/27/77	20-25	4.20	—	—	—	1.50	71	62	—	1611	1531	9.53	0.24	1.37	24.4	1.2	2.6	0.7	0.2
19S (32-31-122)	6/1/77	20-25	4.30	568	29	2.1	1.46	117	110	0.054	1751	1523	16.59	0.45	2.46	23.7	1.4	0.8	1.0	0.2
22S (32-21-763)	6/1/77	10-15	4.33	566	41	0.8	1.00	181	155	0.072	2683	2831	25.27	0.67	5.44	25.6	73.9	1.4	1.6	0.4
42S (32-32-593)	5/27/77	25-35	4.30	—	—	—	2.93	290	271	—	4661	3710	57.00	1.66	6.02	210.5	56.2	2.1	3.0	1.2
42S (32-32-593)	6/1/77	25-35	4.30	535	88	1.6	2.25	181	180	0.031	4985	4983	94.13	2.88	6.08	211.5	80.3	2.1	1.5	1.0
43S (32-33-478)	5/27/77	20-25	4.40	—	—	—	1.50	61	56	—	1511	1306	22.34	0.67	3.69	42.9	3.2	1.7	0.9	0.3
43S (32-33-478)	6/1/77	20-25	4.27	593	40	1.9	1.45	109	105	0.082	3163	1715	16.02	0.43	2.33	43.0	6.4	2.9	0.4	0.5
51S (31-35-192)	6/1/77	15-25	4.55	274	99	—	2.75	2875	2871	0.00012	1960	1959	96.46	4.07	11.62	40.6	3.5	0.4	1.4	0.1
52S (32-21-517)	5/27/77	21-26	4.80	—	—	—	2.60	60	57	—	210	199	24.52	1.09	3.10	34.0	0.9	0.8	0.6	0.1
52S (32-21-517)	6/1/77	21-26	4.70	493	28	1.0	2.58	50	50	0.026	500	499	40.75	1.87	5.40	33.4	26.0	1.6	1.4	0.4
56S (32-33-189)	6/1/77	45-50	4.31	385	34	0.7	5.23	1040	1025	0.0006	3710	3699	145.32	5.23	8.23	8.4	8.0	1.4	0.3	0.5

[1] samples filtered through 0.2 μm Nucleopore membranes

[2] theoretical solubility of Fe calculated using amorphous $Fe(OH)_3$ as solid.

[3] theoretical solubility of Al calculated using kaolinite as solid

[4] halloysite as solid

[5] gibbsite as solid

[6] — not analyzed

[7] LORDS coordinates given in parentheses with well code

Table 4-2. Trace metal geochemistry of groundwater from the Mullica River drainage basin

Table 4-3. Maximum permissible concentrations of selected chemical parameters based on national drinking water standards compared to range of observed trace metal contents of Pine Barrens stream and groundwater

Contaminant	[1]MPC(mg/l)	Total Stream Water Content(mg/l)	Total Groundwater Content (mg/l)
Cadmium	[2]0.010	<0.0001 to 0.0003	0.0001 to 0.0012
Copper	[3]1.0	0.0001 to 0.0023	0.0004 to 0.0029
Iron	[3]0.30	0.06 to 4.2	0.050 to 2.9
Lead	[2]0.050	<0.0001 to 0.0073	0.0003 to 0.0030
Manganese	[3]0.050	0.0026 to 0.0300	0.0079 to 0.212
pH	[3]6.5-8.5 pH units	3.9—5.9	4.20 to 4.90
Total Dissolved Solids	[3]500	16—35	28—99
Zinc	[3]5.0	0.0004 to 0.0290	0.0009 to 0.080

[1] maximum permissible concentration based on national drinking water standards
[2] primary drinking water standard (see Anonymous, 1976b)
[3] secondary drinking water standard (see Anonymous, 1977)

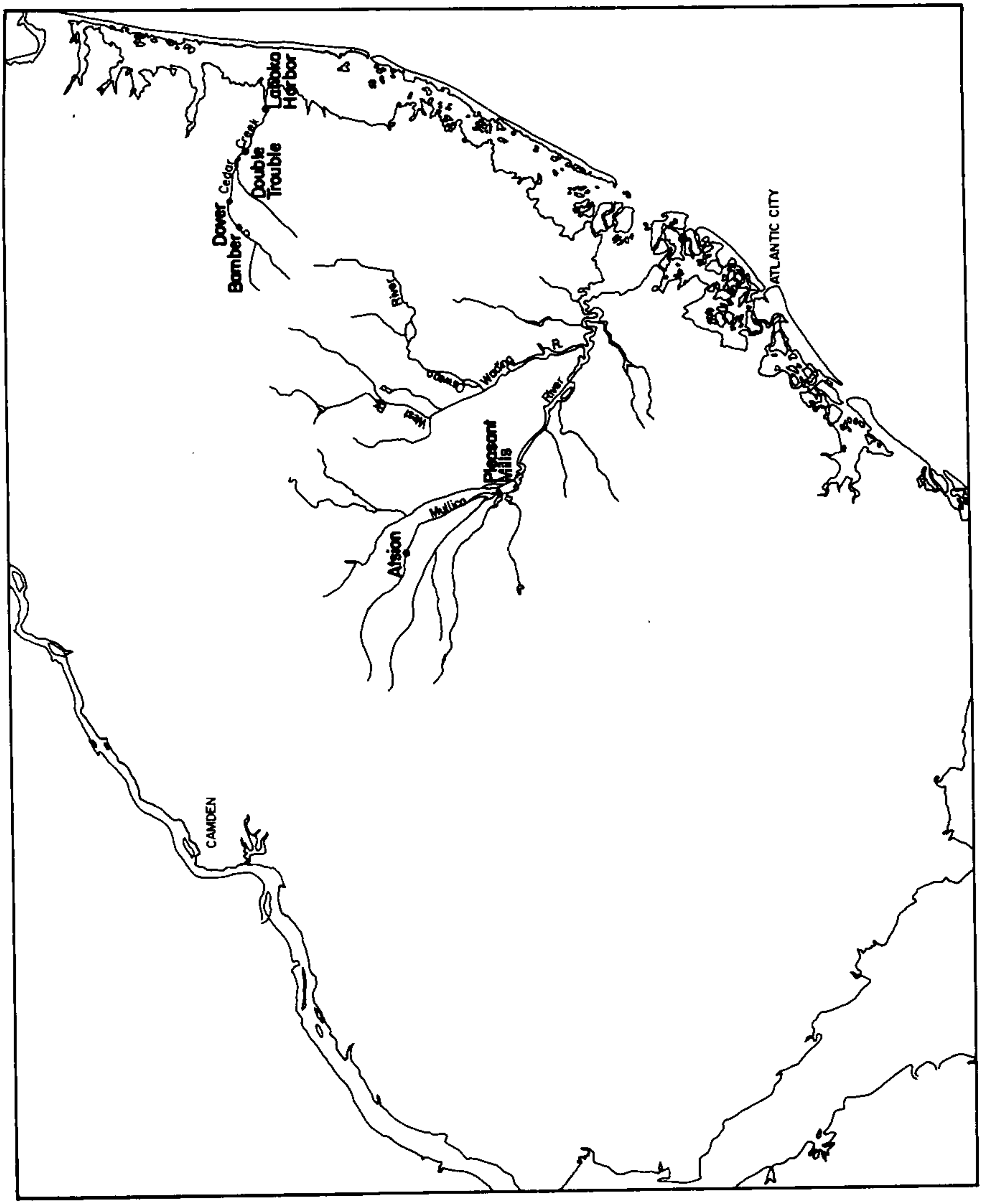

Fig. 4-1. Cedar Creek and Mullica River sampling sites for trace metal analyses.

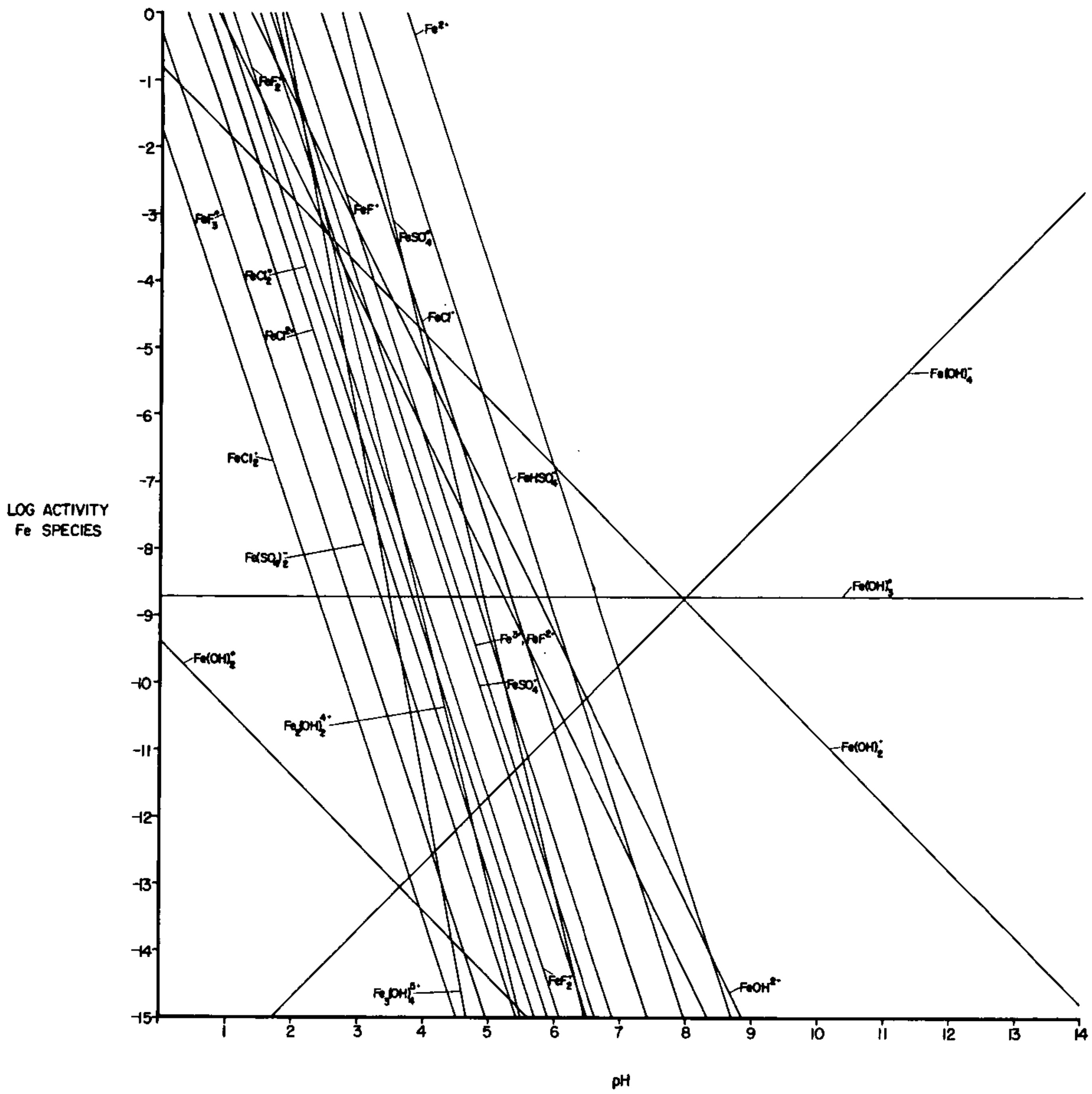

Fig. 4-2. Theoretical solubility of major inorganic Fe species vs. pH at Eh and ligand concentrations typical of Pine Barrens stream or groundwater (Eh =400 mV, 3 ppm SO_4^{2-}, 2 ppm Cl^-, 10 ppb F^-).

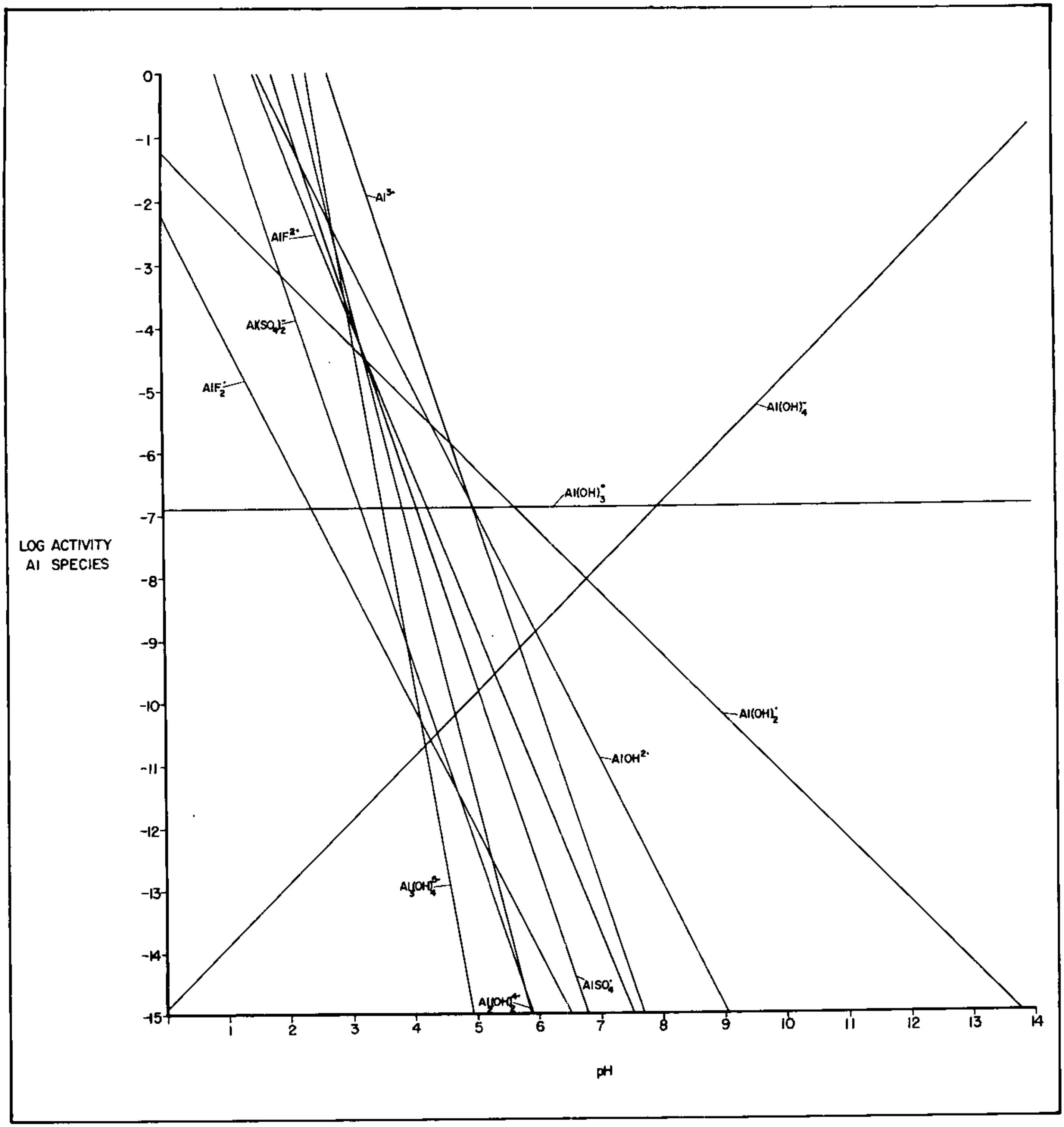

Fig. 4-3. Theoretical solubility of major inorganic Al complexes relative to gibbsite vs. pH at ligand concentrations typical of Pine Barrens stream or groundwater (3 ppm SO_4^{2-}, 10 ppb total F).

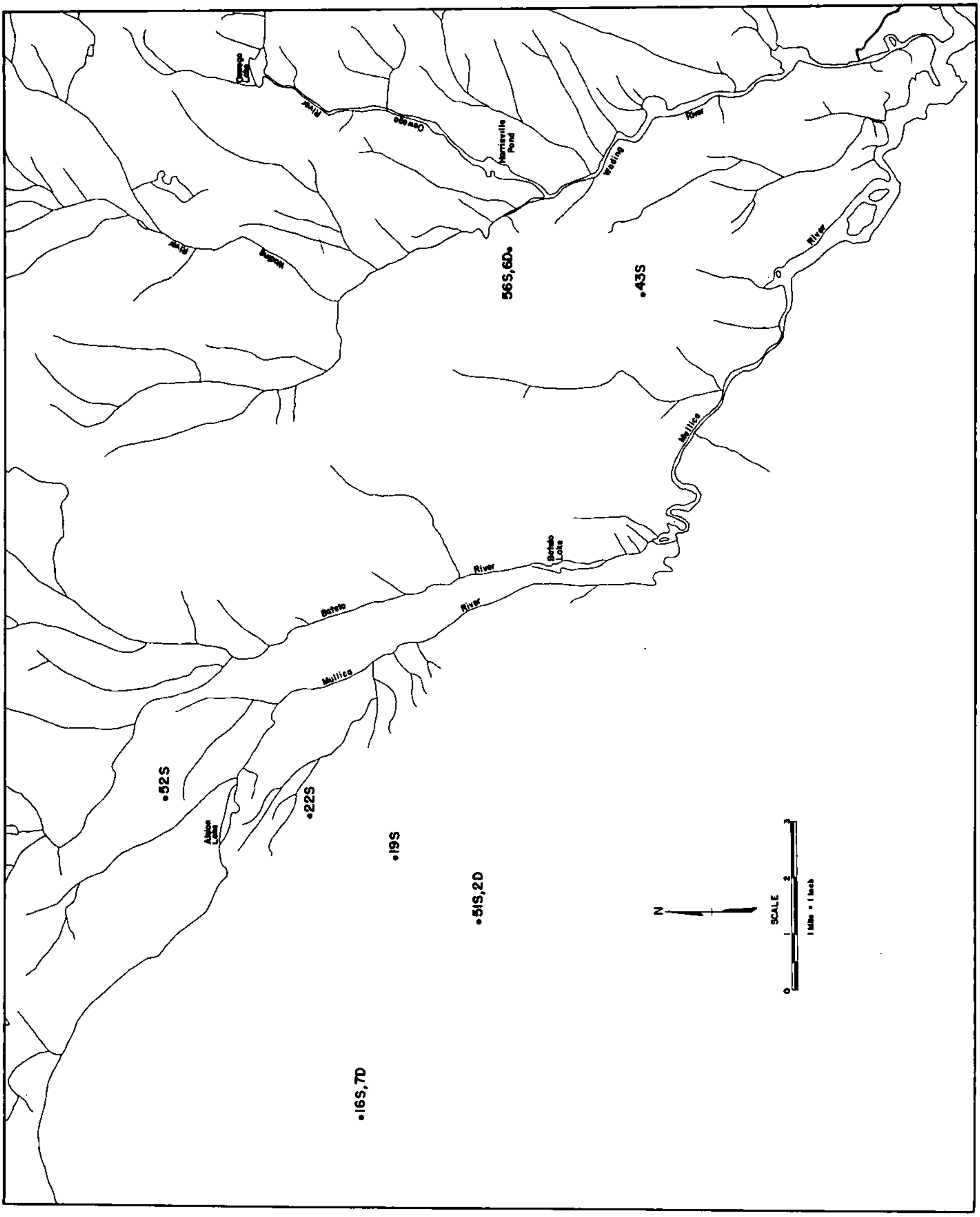

Fig. 4-4. Locations of U.S. Geological Survey polyvinyl chloride groundwater observation wells sampled.

Chapter 5

ORGANICS AND ORGANO-METALLICS IN PINE BARRENS WATERS

INTRODUCTION

Pine Barrens waters are particularly appropriate for study of dissolved organic constituents and organo-metallic interactions. Surface waters are clear and tea-colored, containing up to 30 ppm soluble organic carbon and 10 ppm total Fe. Significant concentrations of trace metals such as Al (up to 5 ppm) and Mn, Zn, Cu, Pb, and Cd (up to 30 ppb) have also been measured (see table 4-1).

The prime objective of this aspect of the study has been to characterize the surface water organics present and evaluate interactions between organic acids and trace metals, particularly Fe. Organics have been analyzed using elemental analysis, functional group titrations, infrared spectrophotometry (IR), and gel filtration chromatography (GFC). Organo-metallic associations have been investigated primarily through GFC. The results and implications of these and other analyses are presented following a brief review of the origin of humic substances and organo-metallic interactions in the natural environment.

REVIEW: ORGANIC MATTER IN NATURAL WATERS

Studies on natural water systems indicate the presence of a complex and heterogeneous mixture of organic materials. Amino acids and various lipids, especially fatty acids, are common constituents in ground, river, and sea water (Prashnowsky et al., 1972; Cranwell, 1974; Degens, 1970; Hare, 1969; Parker, 1969; Jeffrey, 1970; and Slowey et al., 1962). Additional diverse organic compounds such as uronic acids (Mopper and Larsson, 1978), carbohydrates, sterols (Prashnowsky et al., 1972), pheophytins, chlorin pigments (Peake et al., 1972), aliphatic and aromatic hydrocarbons, pristane, and phytane (Ishiwatari and Hanya, 1974) may also be present in natural waters. However humic substances, such as humic and fulvic acids, are quantitatively the most important (Kononova, 1966).

Humic substances are widely distributed in soils, natural waters, marine and lake sediments, peat bogs, carbonaceous shales, lignites, brown coals, etc. These organic substances give a characteristic tea-brown color to stream, lake, or soil water, and are largely derived by leaching of decaying plant materials, or humus, near the surface. There is no specific chemical formula for a humic substance. Its composition varies with vegetative source and geographical location. But humics in general contain high phenolic hydroxy and carboxylic acid contents, which give these compounds strong metal complexing capacities.

Humic substance is actually a general name for at least four different kinds of organic molecules: humic acid, fulvic acid, hymatomelanic acid, and humin. These groups may be differentiated by their respective solubilities. Humic acid is soluble in alkali, but insoluble in acid; fulvic acid is soluble in both alkali and acid; hymatomelanic acid is the alcohol-soluble fraction of the humic acid; and humin is insoluble in alkali (Stevenson and Butler, 1969). The humic acid fraction can be subdivided into two groups using solubility in an electrolyte under alkaline conditions as the criterion. So-called "brown" humic acid is not coagulated in the presence of an electrolyte whereas "grey" humic acid is.

The mechanism of formation of humic substances has been the subject of several recent reviews (Kononova, 1966; Stevenson and Butler, 1969). The traditional theory states that humic substances are direct decomposition products of oxidized lignin that has undergone condensation reactions in the presence or absence of amino compounds. According to this idea, the role of cellulose in humus generation is minor because of its rapid decomposition in soils. Support for this view is provided by chemical degradation studies which show similarities in the basic structural units of both lignin and humics.

A second theory states that humic substances result from the degradation of plant and animal tissues by microorganisms into monomolecular reactive components, which later undergo resynthesis and condensation (Kononova, 1966). Flaig (1972) and Harder et al. (1973) believe that microbially synthesized polyphenols and quinones are the principal reactive components. Welte (1974) emphasizes the role of amino acids and carbohydrates, which polymerize via Maillard-type reactions.

A completely satisfactory scheme for the synthesis of humic substances has clearly not yet been provided. A lignin pathway may predominate in anaerobic terrestial environments such as swamps. Biosynthesis from phenol and quinones may be of considerable importance in certain forest soils (Stevenson and Butler, 1969). On the other hand, the lignin-depleted marine environment may lead to humus synthesis from Maillard-type condensation and polymerization of plankton and algal exudates, especially amino acids and polysaccharides (Nissenbaum, 1974; Welte, 1974).

Since humification may occur on different source materials under different environmental circumstances, variations in the chemistry of the resulting humic substances are expected. For example, marine humics have

(1) higher molecular weights, (2) higher carbonyl and quinone contents, and (3) lower phenolic and hydroxyl contents than soil humics. Lake and marine humics are more aliphatic and possess higher H/C and N/C ratios than soil humics (Ishiwatari, 1970; 1973; Shapiro, 1957). As a result the cation exchange capacity, total acidity, and trace metal complexing capacity of soil humics are generally greater (Rashid, 1969; 1971). These differences are consistent with the more aliphatic, less acidic, lipid-rich algal source of marine and lake humics. Soil humics originate from more aromatic and acidic, lignin-rich higher plants.

Studies on humics formed in different soil environments also reveal systematic chemical variations. For example, the chernozem environment favors the formation of "grey" humic acid. Podzols are characterized by the more hydrophilic "brown" humics and fulvics. Chernozem humics have higher carbon and lower oxygen and hydrogen contents, and are more aromatic in character than those from podzolic environments (Kononova, 1966).

Fulvic acid is a less highly crosslinked and polymerized form of humic acid. Fulvic acids generally have lower molecular weights and contain more oxygen than humic acids, and the hydroxyl and carboxyl contents of fulvic acids are higher. This accounts for the greater solubility of fulvic acids in water and suggests that the metal-chelating capacities of the two should differ (Stevenson and Butler, 1969).

Finally, variations in chemistry may also occur between different molecular weight fractions of humic substances from the same setting. Lower molecular weight humics and fulvics contain less carbon and more oxygen and are therefore more acidic and better metal-complexers than the higher molecular weight species (Rashid, 1971; Beck et al., 1974; Reuter and Perdue, 1977). This may be attributed to the fact that functional groups are consumed during the condensation and polymerization reactions giving rise to the higher molecular weight fractions.

REVIEW: ORGANO-METALLIC INTERACTIONS IN THE NATURAL ENVIRONMENT

The strong affinity of humic materials such as peat and coal for trace elements is well documented. Numerous coals, peats, and black shales are enriched in uranium (Breger, 1974), vanadium, molybdenum, arsenic, selenium (Szalay and Szilagyi, 1968; Szalay, 1969), yttrium and many of the rare earths (Chuveleva et al., 1962), mercury (Hem, 1970; Jenne, 1970; Lindberg and Harriss, 1974), and transition metals (Zubovic, 1961a, b; Rashid, 1974; Cheshire et al., 1977; Griffith and Schnitzer, 1977). It is generally agreed that trace element enrichment occurs primarily during diagenesis. Trace elements from groundwater are fixed through reduction, complex formation, or a combination of both.

The dominant role of humic substances in the transport of trace metals in natural water systems has also been established. Organic acids, because of their ability to degrade minerals, are integral to the processes of weathering and podzolization (Huang and Keller, 1972; Schalscha et al., 1967; Dubach et al., 1964; Wright and Schnitzer, 1963). Organic acids modify the chemical properties of metal ions and thus may affect natural processes. For example chelates increase the metal uptake rate of plants (Hale and Wallace, 1970; Wallace, 1972; Lipton and Goldin, 1976) and decrease the accumulation of metals in sediments (Means et al., 1978; Jackson, 1975). The organic associations of Fe in natural waters have been studied intensively (see e.g., Hem, 1960; Shapiro, 1957, 1967; Ghassemi and Christman, 1968; Lamar, 1968; Christman, 1970; Plumb and Lee, 1973; Picard and Felbeck, 1976; Senesi, et al., 1977).

Most studies on organo-metallic interactions in natural waters fall into three categories: 1) the theoretical approach, in which chelation is inferred from comparison of observed metal contents with calculated metal solubilities; 2) laboratory analyses of the mineral-dissolving and complex-forming capacities of natural organic acids; and 3) determination of organo-metallic associations as they exist in field samples. The theoretical approach has been employed to infer organic associations with Fe in stream water (Jones et al., 1974). Numerous laboratory studies on the metal-solubilizing and complexing capacities of organics have been undertaken (e.g. Huang and Keller, 1970; Rashid and Leonard, 1973; Rashid, 1971; Buffle et al. 1977; Chau and Lum-Shue-Chan, 1973). The order of stability of organo-metallic complexes has been observed to generally follow the Irving-Williams series: (trivalent ions) > $Pb^{2+} > Cu^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+} > Cd^{2+} > Fe^{2+} Mn^{2+} > Mg^{2+}$ (Schnitzer, 1969; Schnitzer and Khan, 1972; Irving and Williams, 1948). Most desirable, however, are studies in which organo-metallic associations are analyzed as they occur in the field because of the elimination of possible error in extrapolating laboratory results to field situations. There is abundant evidence from dialysis, correlation, and solvent extraction analysis that various metals in sea water (Siegel, 1971; Rona et al., 1962; Slowey et al., 1967), lake water (Barsdate, 1970), and river water (Nesterova, 1960; Perdue et al, 1976; Beck et al., 1974) are to a large extent organically-bound. Data on organo-metallic associations have been greatly improved by the relatively recent development of better analytical techniques, such as anodic-stripping voltametry (Chau and Lum-Shue-Chan, 1974), ultrafiltration (Schindler et al., 1973) and gel filtration chromatography (Means et al., 1977). Ultrafiltration has been employed to demonstrate organic-Hg complexes in estuary water (Andren and Harriss, 1975) and associations between organics and numerous trace metals in swamp waters (Schindler et al., 1973; Giesy and Briese, 1977). Gel filtration chromatography has been similarly applied to demonstrate associations between Fe and organics in natural waters (Ghassemi and Christman, 1968; Christman, 1970; Plumb and Lee, 1973; Means et al., 1977).

Though humic substances and trace metals are known to be commonly associated, the mechanism of fixation or bonding between metals and humic substances is still poorly understood. The three most popular concepts are (1) metal ions are brought into solution by reduction to a more soluble lower valence state; (2) metals join in colloidal suspensions with organic acids; (3) metals and organics form soluble complexes. While metal reduction by organic matter has often been postulated, in many instances it is not certain whether the reduction reaction is inherent to the humus or is the result of bacterial action. Theis and Singer (1974) report that oxidation of Fe^{2+} in well-aerated waters is inhibited totally in the presence of tannic acid, gallic acid, and pyrogallol, and is partially inhibited in the presence of glutamic acid, tartaric acid, and glutamine. They also describe the simultaneous reduction of dissolved Fe^{3+} by tannic acid, gallic acid, and pyrogallol. However, in both cases, the reduced Fe forms stable complexes with the organic matter. Similarly, Szilagyi (1971) reports reduction of Fe^{3+} to Fe^{2+} and subsequent fixation of both by humic acid. Apparently reduction is not the ultimate solubilization mechanism, but, rather, is a side effect of chelation.

Studies by Shapiro (1964) and Stumm (1967) have suggested that metals and organics become associated either in the form of insoluble complexes or as peptized colloidal species. Shapiro found that extracts of natural organics tended to influence the size of $Fe(OH)_3$ floccules. The majority of these floccules took on a size in the range 0.1-0.45 μm in the presence of organic matter. In the absence of organics, the sizes were larger, and the bulk of the precipitate or flocs could be removed on 0.45 μm filters. Organics apparently played a dominant role in the peptization of Fe species.

The formation of soluble chemical complexes is the most popular model for metal-organic interactions. This approach has been summarized by Theis and Singer (1974), Wright and Schnitzer (1963), Stevenson (1976), and many others. Other studies, however, have suggested that metal-organic interactions possess both qualities of chelation and colloid formation. For example, Hall and Lee (1973) have shown that natural organics remain in true solution at low Fe concentrations; at increased Fe^{3+} concentrations, the same organics and Fe associate to form larger particles of colloidal dimensions. A similar study with Cu and humic acids yielded almost identical results (Kononova, 1966). Whether or not organic material is in true solution depends directly on the amounts of heavy metal present in the system.

A study by Ong and Bisque (1968) also illustrates the dual nature of metal-organic associations, although these authors offer a slightly different explanation. According to this model, metal-organic pairs possess qualities of hydrophobic colloids (a physical phenomenon) in addition to properties of chemical chelation. According to the Fuoss effect, the addition of a salt to a polyelectrolyte (such as a natural organic acid) causes the stretched configuration of the molecule to coil, this being statistically the most probable configuration. The initial stretched configuration is caused by the mutual repulsion of negative charges on dissociated or ionized functional groups. With the addition of salt, cations are attracted to the carboxylate and phenoxide anions (complex formation), thereby reducing the intermolecular repulsion of the chain and allowing coiling. This coiling causes some of the water of hydration to be expelled from the structure. Therefore, the molecule is less solvated and has transformed from a hydrophilic to a hydrophobic type of colloid or macromolecule that subsequently precipitates (Ong et al., 1970). Ong's ideas are similar to those of Hall and Lee. In both models, organic molecules become less soluble in the presence of high concentrations of complexing cations.

METHODS

Humic (HA) and fulvic (FA) acids from Pine Barrens water samples were separated and purified using a procedure adapted from Rashid and King (1969). Unfiltered field samples, either unconcentrated or preconcentrated on a rotoevaporator or by lyophilization, were acidified to pH 1 with concentrated HCl. HA precipitated out of solution overnight and was separated from FA by filtration through a 0.2 μm Nucleopore membrane. HA was air dried, and FA was evaporated to dryness, during which the HCl added earlier was volatilized. HA and FA were then purified through dialysis against Rexyn 101 H^+-form cation exchange resin for several days to several weeks. This removed both small molecular weight inorganics and organics as well as complexed cationic contaminants. High molecular weight organic species were retained within the dialysis bag. HA and FA were then evaporated to dryness and weighed to obtain approximate HA/FA ratios. Reported FA contents are lower than true FA content because of the removal of the low molecular weight fraction during dialysis. Low molecular weight HA was not lost because of its insolubility in the low pH dialysis environment.

Purified HA and FA were then analyzed for elemental and functional group content. Functional group analyses were performed using a procedure described elsewhere (Rashid and King, 1970). The infrared absorption of unpurified HA and FA was analyzed using a Perkin-Elmer model 237B Grating Infrared Spectophotometer.

Molecular weight distributions and organo-metallic associations were investigated using gel filtration chromatography (GFC), a process which desalts and physically separates organic solutes on a column according to size and shape. Using GFC, specific molecular weight organic fractions and their trace metal contents can be isolated from initially heterogeneous solutions (Means et al., 1977).

The GFC separations used 1.6 × 40 cm and 5.0 × 100 cm columns packed with Sephadex gels G-10, G-15, G-25, and G-50. Samples filtered through 0.2 μm Nucleopore filters, either unconcentrated or lyophilized and re-extracted with double distilled water, were eluted through the columns. Column flow rates were maintained with a peristaltic pump at 20 ml hr^{-1} for small and 200 ml hr^{-1} for large columns. Doubly-distilled, degassed water was employed as eluant. 20-50 ml aliquots of unconcentrated or preconcentrated samples were fed into the large columns. 0.5-2 ml portions of preconcentrated samples were introduced into the small columns. Upon elution samples were analyzed for uv absorbance at 254 nm (measuring mostly organic carbon in these waters) using an in-line spectrophotometer. Upon discharge from the spectrophotometer, samples were collected in aliquots for subsequent metal (mostly Fe) determinations, which were obtained using a Model 603 Perkin-Elmer Atomic Absorption Spectrophotometer and the graphite furnace attachment.

*ORGANIC AND ORGANO-METALLIC ANALYSES

The most striking characteristic of Pine Barrens stream water is the abundance of organic carbon, present mainly in the form of humic substances. Dissolved organic carbon ranges up to 30 ppm in swamp and bog water and averages 2.25 and 2.75 ppm in Cedar Creek and Mullica River waters, respectively (see table 4-1). Thus organic carbon constitutes a relatively large proportion (approximately 10%) of the total dissolved solids in these waters. Organic compounds such as humic and fulvic acids contain only about 50% carbon by weight. Therefore approximately 20% of the total dissolved solids present is composed of organic acids. Humic substances also comprise a substantial proportion of the filterable solids in Pine Barrens river waters.

Stream humics likely originate from two different sources: soils or swamps. Soil-derived organics probably predominate in upstream locations, with swamps becoming increasingly important downstream. Soil and swamp organics are ultimately derived from pitch pine *(Pinus rigida)*, Atlantic white cedar *(Chamaecyparis thyoides)* and several species of sphagnum moss, which are the dominant types of vegetation in the Pine Barrens (Kelsey, 1971).

Stream water organics were fractionated into humic (HA) and fulvic (FA) acids, which were then purified and analyzed for elemental and functional group composition (as explained in *Methods*). HA/FA ratios from both the Mullica and Cedar drainage basins indicate that humics and fulvics are present in nearly equal proportions with fulvics predominating slightly (table 5-1).

Elemental Analysis

HA and FA from above were next analyzed for elemental composition (see table 5-2). Elemental (or ultimate) analysis provides a useful inventory of the distribution of major elements in humic substances. The carbon content of Pine Barrens stream water HA averages 50%; the oxygen content averages 43%, and hydrogen and nitrogen range from 3.8-4.6% and 2.3-2.8%, respectively. Pine Barrens FA contains less carbon and nitrogen but more oxygen than HA. The higher oxygen content of FA accounts for its greater aqueous solubility relative to HA.

Compared to HA and FA from other podzolic environments (table 5-2), Pine Barrens HA and FA are lower in carbon, slightly lower in hydrogen and nitrogen, and higher in oxygen. C/H ratios of both Pine Barrens HA and FA are generally higher than those of humic substances from corresponding environments. Kononova (1966) indicates that there may be great compositional variability in humics from similar settings. The degree of aromatization is indicated by the C/H ratio, more aromatized substances possessing higher C/H ratios. Therefore the relatively high C/H ratios of Pine Barrens HA and FA discussed above may be indicative of a greater than normal degree of aromatization.

Functional Group Titrations

The principal oxygen-bearing functional groups in humic substances are carboxyls, phenolic and alcoholic hydroxyls, carbonyls, and methoxyls (Schnitzer and Kahn, 1972). The major acidic functional groups include carboxyls and phenolic hydroxyls. Pine Barrens river water HA and FA have been analyzed for total acidity and carboxyl content, using the titration method outlined by Rashid and King (1970). Phenolic hydroxyl functions have been calculated by difference (total acidity minus carboxyl).

Our results are compared with previously reported acidic functional group contents of soil humic and fulvic acids in soils and river water (table 5-3). Total acidity of Pine Barrens HA and FA is in general higher than that of soil HA and FA tabulated by Schnitzer and Kahn (1972) and are more consistent with that of total unfractionated river water organics reported by Beck et al., (1974). Apparently river water organics are more acidic than humic substances in soil (Beck et al., 1974). The high phenolic hydroxyl/carboxylic acid ratios of humic and fulvic acids in the Pine Barrens are particularly significant.

The wide scatter in the total acidities (8.9-27.1) of Pine Barrens organics may be attributed partly to sample preparation. All HA and FA were dialyzed against Rexyn 101 H^+-form cation exchange resin to remove complexed metals and to restore functional groups to acid form prior to analysis. The experimental procedure detects functional groups in their acid forms only; metal salts are not recorded. Consequently samples that have not been sufficiently dialyzed, i.e. that contain metal-complexed functional groups, will give apparently low total acidity, carboxyl, and phenolic hydroxyl values. The Cedar Creek Dover FA fraction was dialyzed for 3 weeks whereas the other 3 samples were purified for only several days. The longer dialysis period probably accounts for the greater acidity of the Dover sample, in

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*Some of the organic analyses are taken from Amster (1977) an unpublished undergraduate senior thesis from the Dept. of Chemistry, Princeton University.

that more functional groups were converted to acid form. The acidity of the Dover sample is therefore the most reliable and the other 3 samples are probably low. In view of the relatively low acidity of humics from areas other than the Pine Barrens (table 5-3), it is proposed that many previous investigators have not taken the above problem into account.

Infrared-Spectrophotometric Analysis

Infrared spectrophotometry (IR) gives further information about the chemistry of organic matter in Pine Barrens river water. IR spectra of unpurified HA and FA from both the Mullica River and Cedar Creek basins resemble those reported by Schnitzer and Kahn (1972), Beck et al., (1974), and Stevenson and Goh (1971). The prominent bands in the IR spectra may be assigned as follows: broad band at 3400 cm^{-1}, O-H and to a lesser extent N-H stretching; shoulder peak at 2850-2950 cm^{-1}, aliphatic C-H stretching; strong band at 1700-1720 cm^{-1}, C = O stretching in carboxyl and ketone groups; peak at 1640 cm^{-1}, aromatic C = C, hydrogen bonded quinone carbonyl C=O stretching, also COO^- carboxylate; small peak at 1375 cm^{-1}, COO^- carboxylate or aliphatic C-H; and broad peak around 1200 cm^{-1}, C-O stretch of alcohol, phenol, carboxyl acids, etc. (Beck et al., 1974; Schnitzer and Kahn, 1972; Rashid, 1971).

Comparison of the IR spectra of Pine Barrens humics and fulvics suggests some compositional differences (see fig. 5-1). Humic acid spectra show greater absorption at 2850 to 2950 cm^{-1} than fulvic acid. This indicates that Pine Barrens HA is more aliphatic than FA, which is consistent with previous findings on HA from other areas (Stevenson and Goh, 1971; Beck et al., 1974). In addition, Pine Barrens FA has proportionately greater absorption in the 1600-1650 cm^{-1} and 1350-1375 cm^{-1} and less absorption in the 1700-1720 cm^{-1} regions of the spectrum (fig. 5-1). This suggests that a greater proportion of total C = O functional groups in FA are present as quinone or carboxylate metal complexes whereas relatively more of the C = O in HA occurs as ketone or acid-form carboxylic functions (Rashid, 1971; Schnitzer, 1968; Levesque and Schnitzer, 1967). This interpretation is supported by the data of Schnitzer and Kahn (1972), which illustrates much higher ketone C = O/total C = O ratios in soil HA than in FA. Furthermore, a greater proportion of carboxyl groups in FA may occur as carboxylate-metal complexes because of the greater metal-holding capacity of FA relative to HA (Stevenson and Butler, 1969).

Gel Filtration Chromatography of Organo-Metallics

Molecular weight distributions and organo-Fe associations in both Cedar Creek and Mullica River water have been investigated by gel filtration chromatography (GFC), as outlined in *Methods.*

In the GFC process all solute species with molecular weights below the exclusion limit of a selected gel are proportionately retarded by the column. For example, Sephadex gel G-10 has an approximate exclusion limit of molecular weight 700; all molecules with molecular weight greater than 700 are therefore eluted unimpeded by this gel. Smaller molecules are proportionately retarded and fractionated, the smallest emerging from the column last. Inorganic complexes of metal cations are strongly retarded or sorbed by Sephadex gels (Plumb and Lee, 1973). Hence organic substances are effectively "desalted" or isolated from smaller inorganic species. The occurrence of a trace metal with an organic fraction in an elution profile therefore suggests a chemical association between the organics and the trace metal.

Approximate molecular weight exclusion limits for Sephadex gels G-15, G-25, and G-50 also used in this study are 1,500, 5,000, and 10,000, respectively. These molecular weight cutoffs are calibrated according to dextrans and do not necessarily apply to humic substances, which have different chemical structures and shapes. Unfortunately it is not yet possible to calibrate GFC columns exactly for humic substances, because of the lack of appropriately characterized standards. However GFC can reveal relative molecular weight differences within a given group of compounds.

Elution profiles of Pine Barrens water samples passed through gels G-10, G-15, G-25, and/or G-50 are illustrated in figs. 5-2 through 5-6. In each graph, the blue dextran peak denotes the gel exclusion limit (highest molecular weight fraction). At constant flow rate, the abscissa represents the time required for the various fractions of the sample to pass through the column. From left to right, progressively smaller molecular weight fractions are encountered.

Typical GFC elution profiles for Pine Barrens surface water are exhibited in fig. 5-2. Note that an absorbance at 254 nm represents primarily organic matter in these profiles. The elution profile of this sample for gel G-10 shows no fractionation (fig. 5-2), therefore indicating that all of the organics were greater than 700 in molecular weight (calibrated according to dextrans). When passed through gel G-15, the sample exhibited some fractionation. The elution profile for gel G-25 shows four distinct molecular weight fractions. Finally, when the sample was eluted through gel G-50, most of the organic matter was fractionated. In all of these graphs and those of figs. 5-3 through 5-6, the Fe profile closely correlates with that of the organic content. This points to a definite association between 'dissolved' (filtered) Fe and humic substances in Pine Barrens surface waters. In the samples that contain 20-30 ppm organic carbon, 60-70% of the original 'dissolved' Fe content is recovered in the organic peaks and is present as organo-metallic complexes. In the samples that contain relatively little (2-5 ppm) organic carbon, organically-complexed Fe accounts for approximately 10-20% of the total 'dissolved' Fe present.

Associations between organics and other trace metals such as Al, Pb, Cu, Mn, Zn, and Cd could not be properly evaluated because of their low concentrations in filtered samples. Dilution and contamination during chromatographic analyses were additional problems. However on the basis of the above literature review there is good reason to suspect such associations, particularly in the case of Al, Pb, and Cu, which possess especially strong complexing affinities for organic acids (Irving and Williams, 1948; Schnitzer and Kahn, 1972).

CONCLUSIONS

1. Natural organic substances which together with Fe give Pine Barrens stream waters their striking tea-brown color consist largely of humic and fulvic acids (HA and FA). Compared to humic substances from other podzolic environments, Pine Barrens HA and FA are lower in carbon, hydrogen, and nitrogen and higher in oxygen. FA has a greater total acidity and therefore metal-binding capacity than HA. Infrared spectrophotometric data suggest that Pine Barrens HA is more aliphatic than FA. Also a greater proportion of carboxyl groups in FA is present as quinone or carboxylate metal complexes whereas relatively more of the carboxyl in HA occurs as ketone or acid-form carboxylic functions.

2. Gel filtration chromatography analysis demonstrates an association between "dissolved" Fe and organics in Pine Barrens stream waters. Approximately 10-20% of the Fe in water with little organic matter (4-10 ppm humic content) appears to be associated with organics. This figure increases to 60-70% in waters that contain about 40-60 ppm humic substances.

Table 5-1. Humic and fulvic acid as % total humus

Sample, Date	Humic acid content % of total humus	Fulvic acid content % of total humus
Mullica River: tributary, 6/76	42.0	58.0
Cedar Creek:		
Dover, 6/76	34.0	66.0
Lanoka Harbor, 6/76	32.8	67.2
Lanoka Harbor, 9/76	51.5	48.5

Table 5-2. Elemental composition of humic and fulvic acids from Pine Barrens waters and other sources

Sample	[4]%C	[4]%H	[4]%N	[4]%O	C:H	Reference
Mullica River: Tributary	50.3	3.8	2.8	42.0	13.2	this study
Cedar Creek: Dover	49.2	3.9	2.4	44.5	12.5	this study
Cedar Creek: Lanoka Harbor	50.5	4.6	2.3	42.6	10.9	this study
[1]podzolic soil	57.3	5.1	2.8	34.4	11.2	compiled by Schnitzer & Kahn (1972)
[2]podzolic soil	54.5	4.8	4.4	36.2	11.4	compiled by Kononova (1966)
ordinary chernozem	62.5	2.8	3.3	31.3	22.5	compiled by Kononova (1966)
Fulvic acids						
Mullica River: Tributary	48.5	3.8	1.0	46.6	12.7	this study
Cedar Creek: Dover	41.6	3.0	0.7	54.6	13.9	this study
Cedar Creek: Lanoka Harbor	44.0	5.8	2.5	47.7	7.6	this study
[3]podzolic soil	47.0	4.4	1.5	46.4	10.7	compiled by Schnitzer & Kahn (1972)
natural water	46.2	5.9	2.6	45.3	7.8	compiled by Schnitzer & Kahn (1972)

[1] averaged from 6 analyses, p. 30, Schnitzer and Kahn (1972); 0.5% sulfur present

[2] averaged from 2 analyses, p. 60, Kononova (1966)

[3] averaged from 3 analyses, p. 31, Schnitzer and Kahn; 0.7% sulfur present

[4] all analyses adjusted to 0.0% ash

Table 5-3. Total acidity and distribution of acidic functional groups in humic and fulvic acids from Pine Barrens waters and other sources

Sample	Total acidity (meq/g)	Carboxyl (meq/g)	Phenolic hydroxyl (meq/g)	Reference
Humic acids				
Mullica River: Tributary	12.4	5.2	7.2	this study
Soil Humic	6.6	4.5	2.1	compiled by Schnitzer & Kahn (1972)
"	8.7	3.0	5.7	"
"	5.7	1.5	4.2	"
"	10.2	4.7	5.5	"
"	8.2	4.7	3.6	"
Fulvic acid				
Mullica River: Tributary	8.9	2.2	6.7	this study
Cedar Creek: Dover	10.3	1.9	8.4	"
Cedar Creek: Lanoka Harbor	27.1	6.5	20.6	"
Soil fulvic	14.2	8.5	5.7	compiled by Schnitzer & Kahn (1972)
"	12.4	9.1	3.3	"
"	11.8	9.1	2.7	"
[1]River water organic	16.6	8.3	8.3	Beck et al. (1974)
[2]River water organic	12.2	8.4	3.8	"
[3]River water organic	12.4	9.6	2.8	"

[1] chemically resembles fulvic acid, sample RS-11 in Beck et al. (1974)

[2] chemically resembles fulvic acid, sample RS-30 in Beck et al. (1974)

[3] chemically resembles fulvic acid, sample RS-34 in Beck et al. (1974)

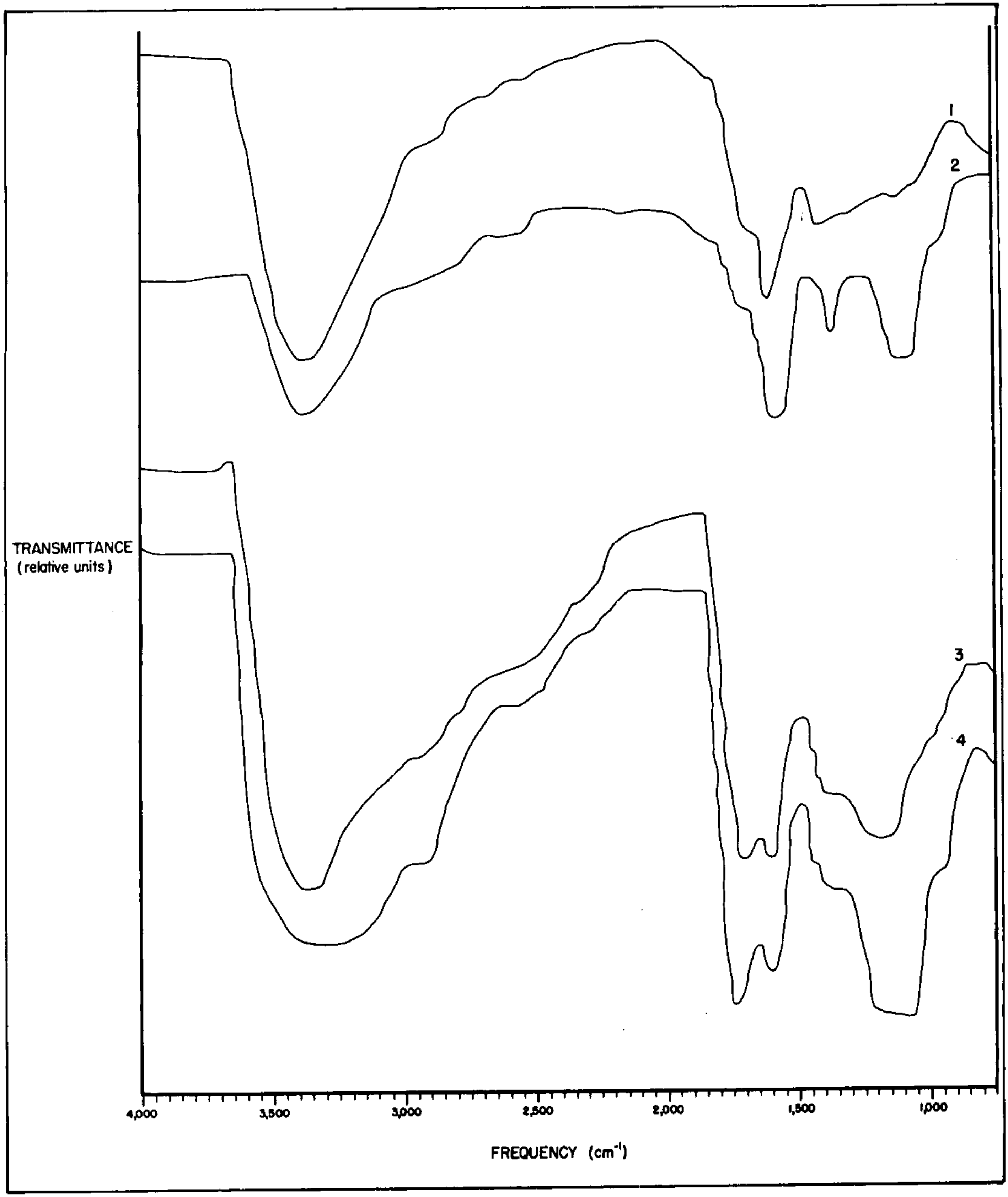

Fig. 5-1. Infrared spectrograms of Pine Barrens fulvic (1 and 2) and humic (3 and 4) acids.

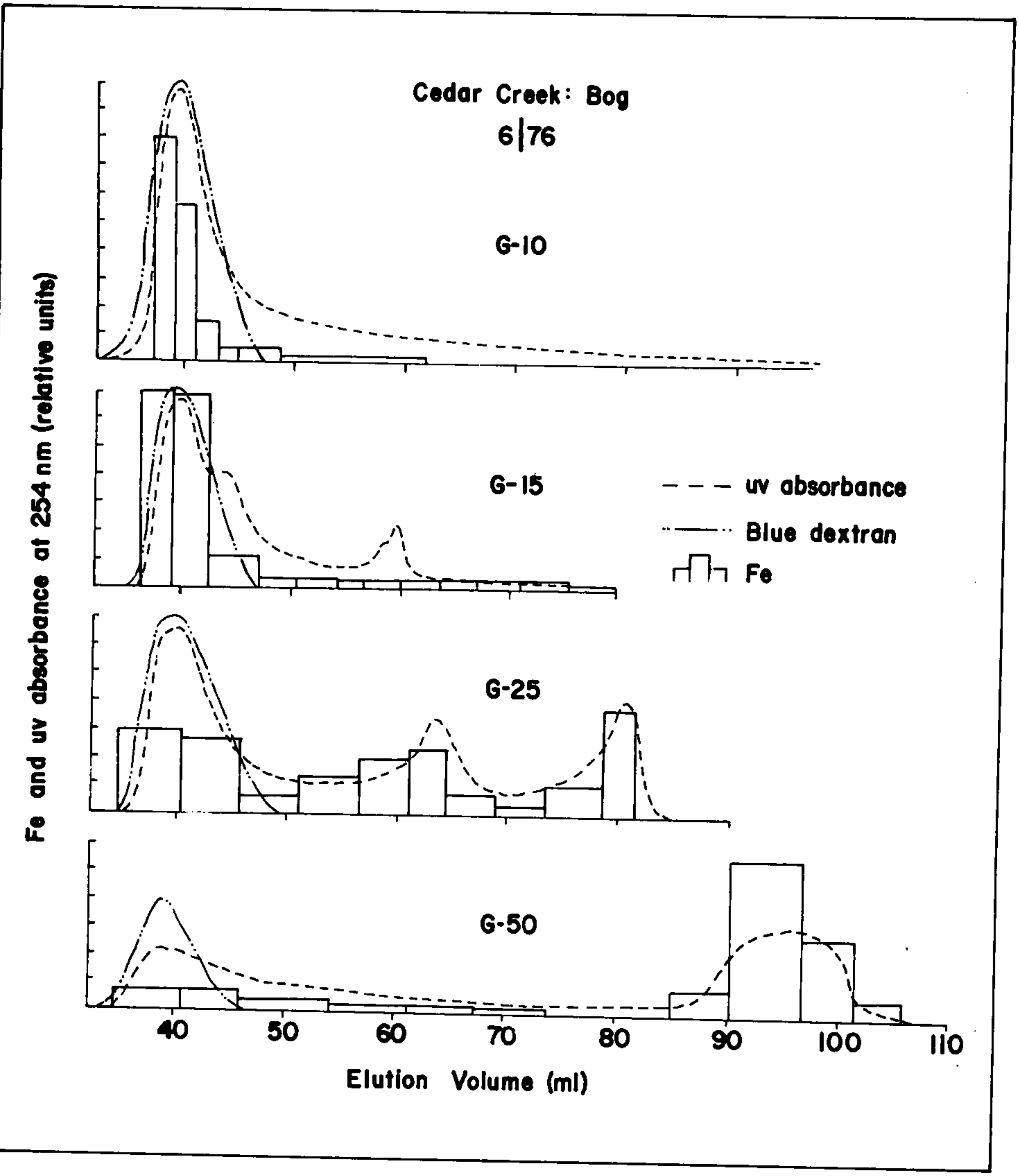

Fig. 5-2. Gel filtration chromatography elution profiles for Cedar Creek bog water.

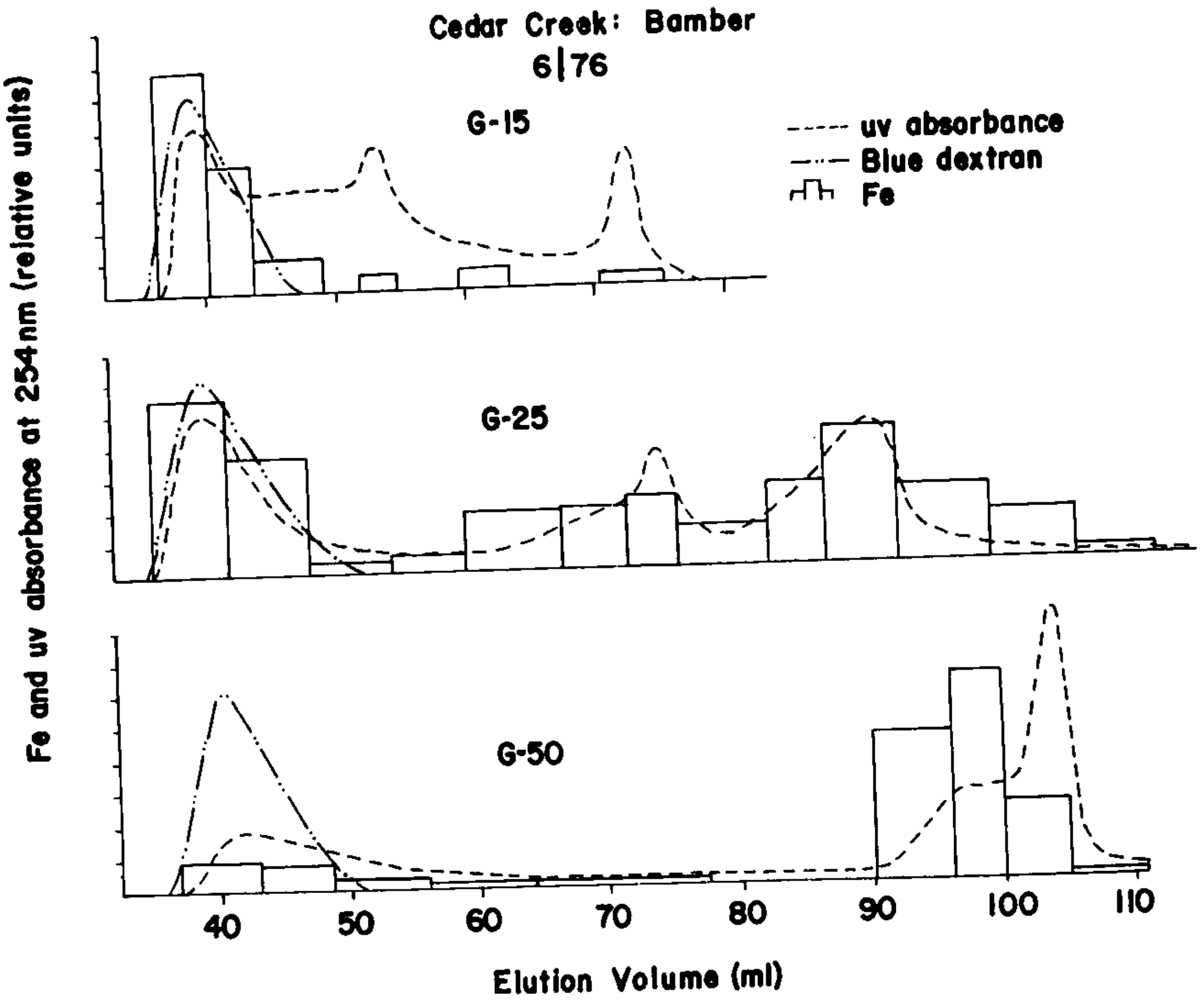

Fig. 5-3. Gel filtration chromatography elution profiles for Cedar Creek stream water.

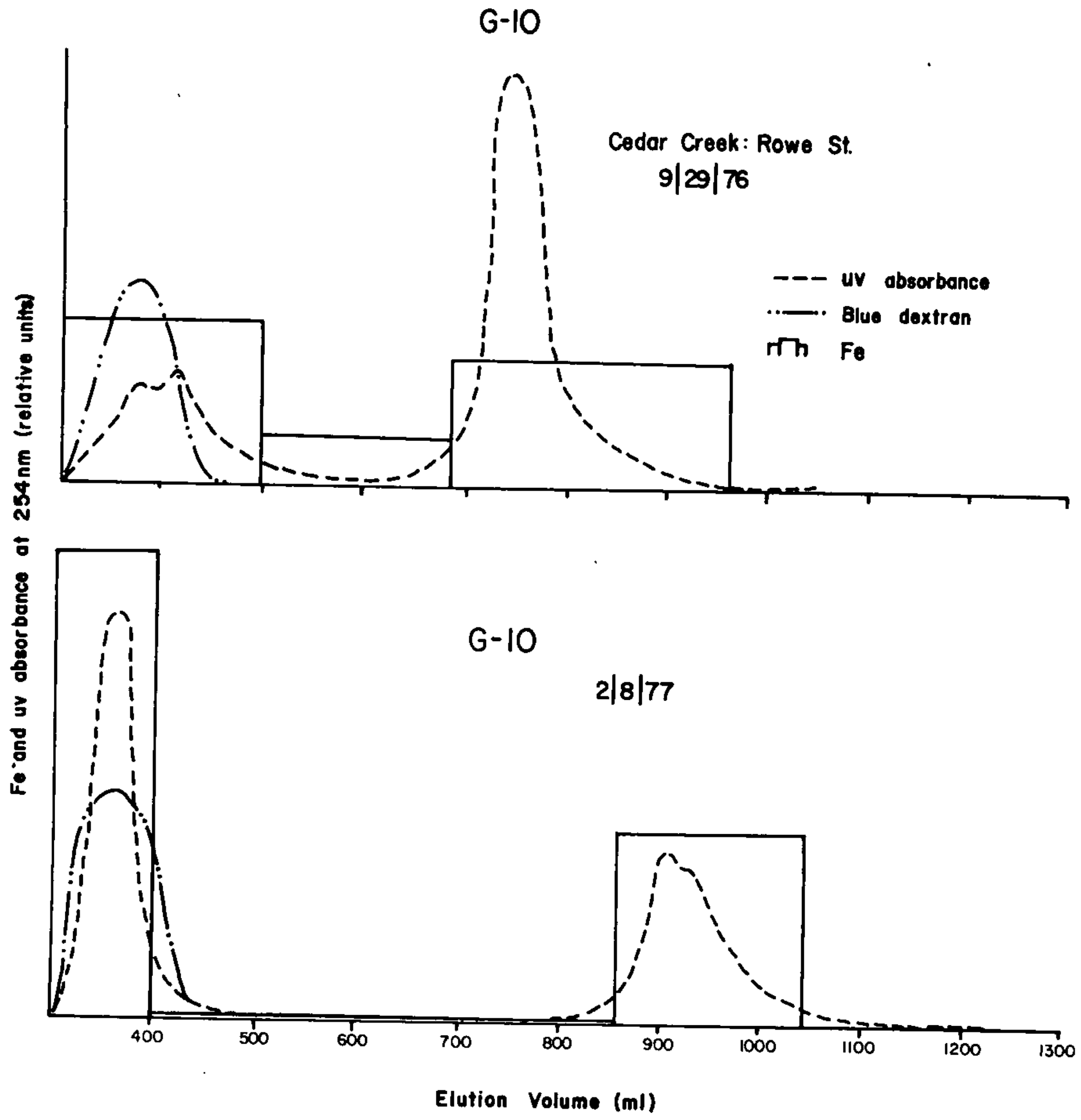

Fig. 5-4. Gel filtration chromatography elution profiles for Cedar Creek inner estuary water.

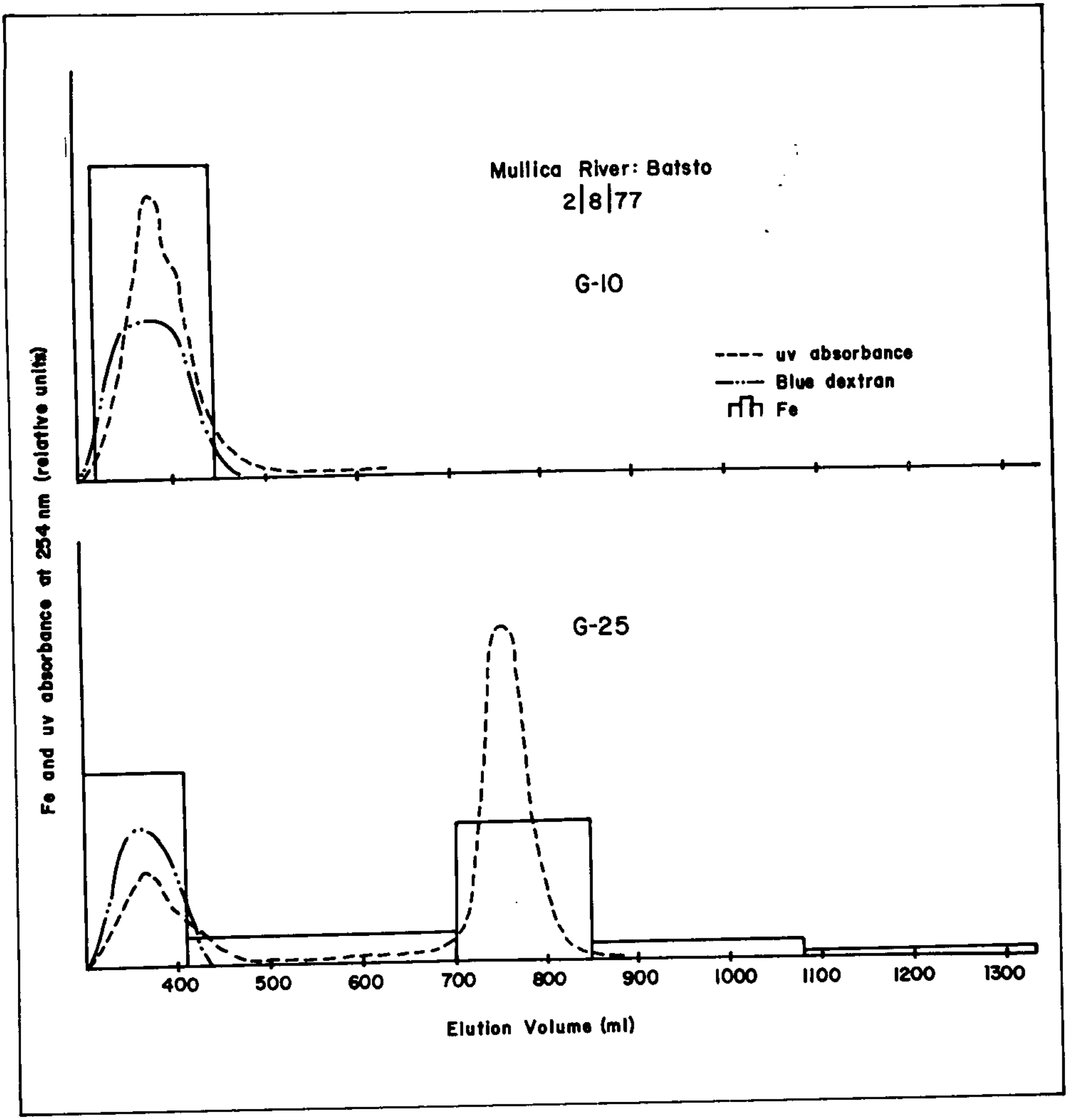

Fig. 5-5. Gel filtration chromatography elution profiles for Mullica River stream water.

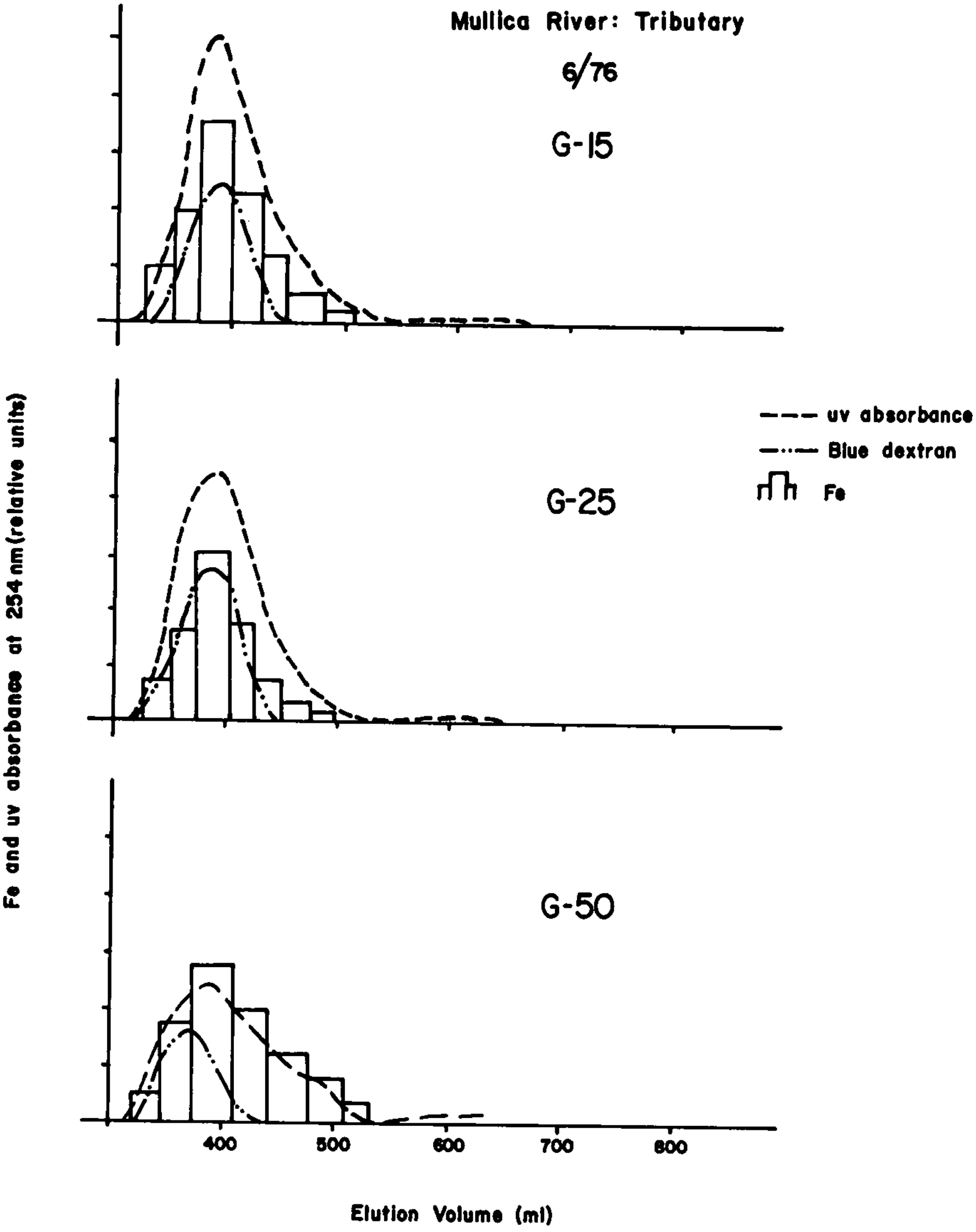

Fig. 5-6. Gel filtration chromatography elution profiles for Mullica River bog water.

Chapter 6

ESTUARY WATER: TRACE METAL GEOCHEMISTRY

INTRODUCTION

Many of the analyses and calculations performed on stream and groundwater samples have also been done on samples from the Cedar Creek and Mullica River estuaries. Fe, Al, Mn, Zn, Cu, Pb, Cl, and Si along with Eh and pH were monitored at 5 different stations in the Cedar Creek estuary (fig. 6-1) and at 3 sites in the Mullica River estuary (see fig. 6-2) between September, 1976 and April, 1978. The saturation states of Fe with respect to amorphous $Fe(OH)_3$ and of Al relative to gibbsite, halloysite, and kaolinite in these waters have also been calculated.

Particular attention was focused on the behavior of organics and trace metals in the region of stream water—estuary water mixing. At this point, stream water with a very low pH and ionic strength (and therefore poorly buffered) mixes with sea water which has a much greater pH and ionic strength. In the quieter estuarine environment colloidal substances in stream water settle to the bottom. Because of the higher pH of sea water, the aqueous solubility of Fe and Al is greatly reduced, and Fe and Al oxides precipitate. In addition, dispersed inorganic and organic colloids are flocculated by the higher electrolyte concentration of sea water. Field and laboratory evidence for the various chemical reactions occurring in this unique geochemical setting are presented below.

*ESTUARY WATER DATA

Estuary water pH, Eh, Cl, trace metal contents, and Fe and Al solubility ratios are compiled in table 6-1. LORDS coordinates are given for each sample site (Widmer et al., 1974). Sampling sites are listed in order of increasing distance from the stream (see figs. 6-1 and 6-2). pH and Cl increase with increasing sea water influence. Estuary Eh is generally lower than stream water values. Si concentrations, though not recorded in table 6-1, range from 1 to 2.5 ppm.

Iron

'Dissolved Fe', again defined as that passing through a 0.2 μm Nucleopore filter, decreases with increasing sea water influence. Indeed, a certain amount of decrease is expected with mixing of the two water masses, in that sea water possesses an average dissolved Fe concentration of only 3-4 ppb (Turkeian, 1969). However, the observed decrease greatly exceeds that predicted by a simple dilution model.

Fe solubility ratio calculations determined using the computer program FESOL suggest that both Cedar Creek and Mullica River estuary waters are supersaturated with respect to $Fe(OH)_3$ (calculations based on Eh, pH, and Cl^- activity given in table 6-1; ionic strength, SO_4^{2-} and F^- concentrations were estimated). The degree of supersaturation increases even though 'dissolved' Fe concentrations decrease with increasing sea water influence. Some outer estuary waters are supersaturated by more than two orders of magnitude. Stream waters, on the other hand, are close to saturation or are slightly undersaturated (see table 4-1). These high degrees of supersaturation in the estuaries indicate that most of the Fe is either organically-complexed and/or in the form of very small oxyhydroxide colloids that are not deposited at the fresh/saline water interface. This conclusion is supported by the data of Boyle et al. (1977), which demonstrates that about 75% of the Fe in Mullica estuary waters was removable through ultracentrifugation or filtering down to 0.05 μm.

Fig. 6-3 shows the theoretical solubility of inorganic Fe solution species relative to amorphous $Fe(OH)_3$ at conditions approximating those of the Bay Way sampling locality. Whereas Fe^{2+} dominates in stream water and some low pH estuary samples (fig. 4-2), $Fe(OH)_2^+$ is dominant in the other estuary. Several chloride and sulfate species, including $FeCl^+$, $FeHSO_4^+$, $FeCl_2^0$, and $FeSO_4^0$ also contribute to total solubility (fig. 6-3). At pH 8.0 - 8.3, characteristic of open ocean water, the principal inorganic Fe species are $Fe(OH)_3^0$ and $Fe(OH)_4^-$ (fig. 6-3). Fe fluoride complexes are relatively unimportant over the entire range of environmental conditions considered.

Aluminum

The behavior of Al in estuary waters resembles that of Fe. In the Mullica River estuary, dissolved Al generally decreases with increasing sea water influence. Nevertheless, Al solubility calculations suggest that outer estuary waters from both settings (i.e. Dolan St., Bay Way, Lower Bank) are supersaturated with respect to all three minerals considered: halloysite, gibbsite, and kaolinite (calculations based on input values of 2.0 ppm Si, pH as given in table 6-1; ionic strength, SO_4^{2-}, and total F concentrations estimated).

Both Cedar Creek and the Mullica River show supersaturation levels in the outer estuary that are even greater than those in the inner estuary and stream. The high supersaturation values may in part originate because precipitation of clays such as kaolinite is kinetically slow. However, gibbsite formation is relatively fast (Hem and Roberson, 1967; Smith and Hem, 1972). Therefore, it would be unlikely to observe such large Al

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* Some of the estuary data and Fe vs. Cl graphs are taken from Quiett (1977) an unpublished undergraduate senior thesis from the Dept. of Geological and Geophysical Sciences, Princeton University.

supersaturation values relative to gibbsite unless some of the Al is present as organic complexes or very small colloids.

The theoretical solubilities of inorganic Al solution species relative to gibbsite (as an example) at chemical conditions approximating the Bay Way sampling site are illustrated in fig. 6-4. At the low pH typical of stream water, soluble species are largely Al^{3+} and the mono- and di-hydroxy complexes, $Al(OH)^{2+}$ and $Al(OH)_2^+$ (fig. 4-3). At ligand concentrations typical of Cedar Creek and outer estuary water, however, Al fluoride and sulfate complexes such as AlF^{2+} and $AlSO_4^+$ may contribute to total Al solubility, especially at $pH<5$ (fig. 6-4). At higher pH, Al hydroxy complexes such as $Al(OH)_3^0$ and $Al(OH)_4^-$ dominate total solubility, even in the presence of higher SO_4^{2-} and F^- ligand concentrations.

Trace Metals

Trace metals other than Fe and Al which have been analyzed include Mn, Zn, Cu, and Pb. These four elements are generally more abundant in the estuaries than in the streams. Consistent with the pattern observed in the stream water, Mn and Zn concentrations are slightly higher in the estuary of the Mullica River than in the Cedar Creek estuary. In the Cedar Creek estuary, higher Mn values are observed in the lower Eh samples. Cu and Pb concentrations are quite low and similar in both estuaries. Cd, though not listed in table 6-1, averages 0.1-0.5 ppb at both localities.

In a few samples that were filtered (data not in table 6-1), total Mn was approximately equal to dissolved Mn, suggesting that Mn transport occurs predominantly in the dissolved state. Similar to results obtained from stream water analyses, the concentrations of Fe, Al, and Pb were generally greater in unfiltered than in filtered estuary water, indicating the presence of colloids < 0.2 µm. Reliable dissolved Cu, Zn, and Cd concentrations could not be obtained because of contamination during filtration.

FLOCCULATION OF FE, AL, AND ORGANICS DURING MIXING OF STREAM WATER AND SEA WATER

Review

The flocculation of dissolved organic and inorganic substances which occurs when river water mixes with sea water has been the subject of several recent investigations. By plotting Fe vs. Cl contents of numerous estuary water samples, Coonley et al. (1971) showed that up to 95% of the river water Fe is being flocculated in the Mullica River estuary. Sholkovitz (1976) used mixing experiments to illustrate removal of Fe, Mn, Al, P, and humic substances from Scottish river water when mixed with sea water. Boyle et al. (1977) employed a combination of Fe vs. salinity plots and mixing experiments to demonstrate flocculation of Fe and organic matter in several U.S. east coast estuaries, including that of the Mullica River. Flocculation of Fe and/or Mn in estuarine environments has also been observed in the Gulf of St. Lawrence (Bewers et al., 1975), Chesapeake Bay (Carpenter et al., 1975), and in several southeastern U.S. localties (Windom et al., 1971; Windom, 1975). The role of organic substances in the absorption of trace metals on estuarine sediments and in depleting the trace metal contents of estuarine waters has also been emphasized (Swanson and Palacas, 1965; Schutz and Turekian, 1965; and Szalay and Szilagyi, 1967). In Scottish river water maximum removal of Fe, Al, and humates was induced by $CaCl_2$. Equimolar concentrations of $MgCl_2$ also promoted flocculation, but to progressively lesser extents (Eckert and Sholkovitz, 1976).

While there is abundant evidence for the removal of Fe, Al, Mn, P, humates and possibly other trace metals in estuaries, there is little general agreement as to the flocculation mechanism. Windom et al. (1971) suggest that dissolved Fe is precipitated as Fe oxyhydroxides resulting from the increase in pH in sea water. Ong et al. (1970), Sholkovitz (1976), and Boyle et al. (1977) suggest that coagulation of organo-metallics promoted by the higher ionic strength of sea water is the primary mechanism.

The chemical composition of the flocculant is apparently quite variable. Fe oxides were the principal flocculants identified in studies by Coonley et al. (1971), Windom et al. (1971), and Murray and Gill (1978). Sholkovitz (1976) and Boyle et al. (1977) have identified humates in flocculants and suggested that organic matter must play an important role in controlling the removal of Fe, Al, and other trace elements. Higher molecular weight organics, because of their higher C/O content, are less soluble and therefore more susceptible to flocculation than the lower molecular weight species (Sieberth and Jensen, 1968; Andren and Harriss; 1975; Reuter and Perdue, 1977).

Field Evidence

Our data are consistent with that of Coonley et al. (1971) and Boyle et al. (1977) in demonstrating the flocculation of Fe in the Mullica River estuary. 'Dissolved' Fe plotted against Cl^- for samples collected on different sampling trips show that the decrease in Fe content in the inner estuary is much more rapid than predicted by dilution (fig. 6-5). A similar relationship holds for Fe in Cedar Creek (fig. 6-6). Additional data for Al in both the Mullica River and Cedar Creek estuaries indicate the same general trend (figs. 6-7 and 6-8).

Laboratory Evidence

In order to further investigate the chemical mechanisms of Fe and Al removal, laboratory flocculation experiments similar to those of Eckert and Sholkovitz (1976) were performed on stream water collected at Batsto on 4/28/78. Eleven different aliquots of unfiltered stream water were treated with either $CaCl_2$, $MgCl_2$, or NaCl so that resulting solutions had compositions of 0.01M, 0.02M, 0.04M, and 0.1M $CaCl_2$; 0.01M, 0.02M, 0.05M, and 0.10M $MgCl_2$, or 0.1M, 0.2M and 0.5M NaCl. Additional samples containing no electrolytes were adjusted to pH 8.3 using 1.0M NaOH in order to compare the effects of electrolytes and the pH of sea water on flocculation. After several days Fe, Al, Mn and, in a few cases, organic carbon contents were determined on these solutions and on a blank to which no pH or electrolyte adjustment had been made. Our results (figs. 6-9, 6-10, and 6-11) show that flocculation of Fe, Al, and also Mn occurred in all samples containing electrolyte. Flocculation of organics was also observed. However, only 10-20% of the total organics present were removed, whereas Fe, Al, and Mn flocculation in general exceeded 80%. Figs. 6-9 through 6-11 show that $CaCl_2$ and $MgCl_2$ cause greater trace element removal than equal concentrations of NaCl. Fe is in general removed by all electrolytes to a greater extent than Al or Mn. Removal of all three metals increases rapidly at relatively low ionic strengths and levels out at higher electrolyte contents (figs. 6-5 through 6-8). Precipitation of Fe, Al and Mn continues at Na, Mg, and Ca molarities greater than those in sea water (sea water Ca = 0.01M, Mg = 0.05M, Na = 0.5M), a point that is also emphasized by Eckert and Sholkovitz (1976). Little flocculation of organics or trace metals in the pH 8.3 samples without additional electrolyte was observed.

DISCUSSION

Both laboratory mixing experiments and analyses of field samples demonstrate that Fe, Al, Mn, and a small amount of organic carbon in Pine Barrens river water are flocculated upon mixing with sea water. Coagulation by electrolytes is the principal removal mechanism. In this setting pH appears to play a lesser role.

Similar to Boyle et al. (1977), we found that a small amount of the humic material present is flocculated along with a larger proportion of the Fe, Al, and Mn. Precipitation of Fe, Al, and Mn continues at ionic strengths greater than that of sea water (figs. 6-9 through 6-11, this study; also confirmed by Eckert and Sholkovitz, 1976). We conclude that in the Pine Barrens much of the Fe and Al precipitates at the stream/estuary interface as oxides and/or hydroxides and that the high electrolyte content of sea water catalyzes the flocculation. The small amounts of organics removed from solution are likely the less soluble higher molecular weight species (Rashid, 1971; Beck, et al., 1974). Small amounts of Fe and Al may also be removed by this mechanism as complexes of the organic flocculants. Fe, Al, and trace metals associated with the larger proportion of humic and fulvic acids that are not flocculated will remain in solution in the estuary environment. This estuarine precipitation of only small amounts of organics is consistent with the humic/fulvic acid compositional data of Chapter 5. Fulvic acid, which is the most soluble form of humic substances and by definition not precipitated by electrolytes, comprises on the average at least 50% of the total Pine Barrens river humic content (table 5-1). In addition, the humic acid present is characterized by higher than average oxygen contents and therefore greater aqueous solubility (table 5-2). Flocculation of a greater proportion of organics might be anticipated in an estuary receiving drainage from, for example, chernozem or chestnut soils. Humic acids from these soil types possess higher C/O ratios than those from podzols and are therefore less soluble. "Grey" humic acid, which is by definition precipitated by electrolyte (Stevenson and Butler, 1969), is more prevalent in a chernozem or chestnut than in a podzol soil environment (Kononova, 1966).

Organics that resist flocculation because of their high oxygen contents also possess the strongest metal-complexing capacity for the same reason (Rashid, 1971; Beck et al., 1974). Since the inorganic solubility of both Fe and Al at near neutral pH and moderate Eh is quite low (fig. 4-2), the Fe and Al in filtered estuary samples are likely present as either small oxyhydroxide colloids or associated with organic acids. This is important in that the chemical form of these metals affects their sorptive interactions with sediments and their utilization by biota.

IMPLICATIONS OF REMOVAL OF FE AND AL IN ESTUARIES

Most cations have marine residence times that are very much smaller than the age of the earth. For example, the oceanic residence time of dissolved Fe relative to average water input appears to be only several hundred years (Garrels and Mackenzie, 1971). This is less than the mixing time of the ocean (Boyle et al., 1977) and suggests that removal of river-borne iron must be localized to a high degree. The data presented in this chapter along with that of Boyle et al. (1977), Sholkovitz (1976), and many others suggest that much Fe and Al is removed in estuaries. The removal of organics, Fe, Al, and other trace metals has now been observed in at least 10 estuaries on 17 occasions (Boyle et al., 1977). Estuarine flocculation reactions appear to be common phenomena. Therefore if these reactions are sufficiently widespread, the input of certain metals to the open ocean must be less than previous estimates (Livingstone, 1963). A certain proportion of the Fe and Al precipitated in estuaries may of course be later remobilized to overlying waters. It is therefore difficult to quantify the amount of Fe and Al that is delivered to the open oceans, though this amount is almost certainly less than the total dissolved Fe and Al content of river water. Boyle et al. (1977) estimate that the amount of 'dissolved' Fe actually delivered to the oceans is about an order of magnitude less than the primary river value. Estuarine removal of Al appears to be significant but somewhat less than that observed for Fe (this study; Sholkovitz, 1976).

Removal of Fe, Al, and organics in estuaries may also affect the geochemical cycles of other trace metals. Fe oxides and insoluble humic materials possess strong adsorption capacities for numerous trace elements, including most of the transition metals, transuranic elements, and heavy metals such as Ag, Au, Hg, Cd, and Pb (e.g. see Jenne, 1968). Flocculated Fe oxyhydroxides, Al hydroxides, and humic materials may act as depositional sinks for many other trace elements and lead to trace element enrichment in estuary sediments (Sholkovitz, 1976; Turekian, 1977). It has even been suggested that trace metals are transported by fine-grained iron and managanese oxides originating in estuaries, giving rise to the observed enrichment of trace metals in deep-sea sediments relative to continental sources (Bender and Schultz, 1969; Turekian, 1968). An understanding of the reactivity of Fe, Al, and humics in estuaries is clearly essential to the understanding of marine geochemical cycles of numerous elements.

CONCLUSIONS

1. Fe, Al, Mn, Zn, Cu, and Pb along with Eh and pH were monitored at 5 different sites in the Cedar Creek estuary and at 3 sites in the Mullica River estuary between September, 1976 and April, 1978. 'Dissolved' Fe and Al decrease with increasing sea water influence at a rate faster than that predicted by simple dilution. Mn, Zn, Cu, and Pb concentrations are in general slightly higher than their stream water values.

2. The saturation states of 'dissolved' Fe with respect to amorphous $Fe(OH)_3$ and of 'dissolved' Al relative to gibbsite, halloysite, and kaolinite in estuary waters have been calculated. Both Cedar Creek and Mullica River estuary waters are supersaturated with respect to all of the above solid phases, and the degree of supersaturation increases even though Fe and Al contents decrease with increasing sea water influence. The high degree of supersaturation observed probably indicates that much of the "dissolved" Fe and Al in estuary water is either organically-complexed or in the form of <0.2 µm oxyhydroxide colloids.

3. A combination of laboratory mixing experiments and analyses of field samples demonstrates that Fe, Al, Mn, and a small amount of organic carbon in Pine Barrens river water are flocculated upon mixing with sea water. Coagulation by electrolytes such as NaCl, $MgCl_2$, and $CaCl_2$ is the principal removal mechanism. $CaCl_2$ and $MgCl_2$ cause greater trace element removal than equal concentrations of NaCl. It is concluded that much of the flocculated Fe and Al is precipitated as oxides and/or hydroxides. The small amount of organics removed from solution are likely higher molecular weight species, which have higher C/O ratios than smaller molecular weight species and are consequently less soluble.

			mV	ppm	ppb	measured Fe: theoretical Fe solubility ratio	ppb	measured Al: theoretical Al solubility ratio			total unfiltered ppb			
Sample Site	Date	pH	Eh	[1]Cl	[2]dissolved Fe	[3]amorphous $Fe(OH)_3$	[2]dissolved Al	[4]kaolinite	[5]halloysite	[6]gibbsite	Mn	Zn	Cu	Pb
Cedar Creek: Rowe St. [7](33-12-377)	9/29/76	5.30	420	816	66	0.067	22	6.34	0.22	0.72	9.1	–	–	0.9
	12/1/76	4.70	512	30	143	0.12	97	5.61	0.25	0.91	7.9	–	–	–
	2/8/77	5.20	653	74	159	2.50	72	29.1	0.84	3.10	7.7	–	–	1.2
	3/31/77	4.67	504	106	–	–	102	4.20	0.20	0.72	8.6	–	2.6	1.9
	4/28/78	–	–	62	–	–	117	–	–	–	6.0	9.4	3.6	1.3
Sand Bar (33-12-378)	9/29/76	6.40	384	2765	40	5.14	42	97.1	2.28	9.41	10.2	4.8	3.3	0.9
	12/1/76	5.90	403	886	126	2.92	59	94.8	2.23	9.18	9.6	–	–	–
	2/8/77	5.70	633	227	123	5.98	68	89.3	2.10	8.66	7.2	–	–	1.2
	3/31/77	6.26	400	1454	–	–	65	143.7	3.37	13.9	10.1	–	3.4	1.5
	4/28/78	–	–	993	–	–	–	–	–	–	10.1	6.5	1.9	1.2
Dolan St. (33-12-379)	9/29/76	7.20	410	11346	7	6.90	–	344.6	8.08	33.4	18.8	5.0	–	2.0
	12/1/76	7.70	406	2198	90	215.3	–	155.0	3.63	15.0	10.0	–	–	–
	2/8/77	6.10	593	674	107	12.4	41	82.7	1.94	8.01	8.2	–	–	1.4
	3/31/77	7.05	430	5319	110	86.7	63	158.2	3.71	15.3	16.5	–	–	2.9
	4/28/78	–	–	4396	–	–	–	–	–	–	25.9	7.4	3.0	2.2
Bay Way (33-12-387)	9/29/76	7.60	382	11340	5	9.47	–	146.7	3.44	14.2	16.6	8.6	–	1.8
	12/1/76	6.30	395	3120	75	7.38	–	–	–	–	11.1	–	–	–
	2/8/77	6.20	603	780	107	15.4	43	92.6	2.17	8.98	8.8	–	–	1.0
	3/31/77	7.55	455	7446	83	154.3	69	137.0	3.21	13.3	18.5	–	–	2.8
	4/28/78	–	–	5212	–	–	–	–	–	–	26.0	7.2	3.2	2.0
Barnegat Bay (33-12-174)	4/28/78	–	–	17727	–	–	69	–	–	–	–	9.2	14.2	2.5
Mullica River: Green Bank (32-32-949)	10/4/76	5.60	582	340	331	12.5	85	89.4	2.13	8.71	17.9	16.4	–	–
	12/1/76	5.10	499	14	254	1.46	84	26.2	0.82	2.96	22.2	–	–	–
	2/8/77	4.90	643	6	349	2.80	99	14.1	0.56	1.99	22.1	17.4	–	1.1
	3/31/77	4.63	526	4	422	0.39	183	9.1	0.38	1.44	27.5	–	–	–
	4/28/78	–	–	106	–	–	–	–	–	–	20.1	27.9	1.2	1.0
Lower Bank (32-43-125)	10/4/76	6.10	533	2796	196	20.2	16	28.7	0.67	2.78	26.1	24.7	–	–
	12/1/76	5.90	405	326	63	1.83	32	54.8	1.28	5.31	24.7	–	–	2.7
	2/8/77	6.00	603	425	163	15.4	46	85.5	2.00	8.28	26.9	17.6	1.4	2.1
	4/28/78	–	–	2411	–	–	–	–	–	–	36.0	22.5	2.6	1.8
Great Bay (33-44-441)	4/28/78	–	–	14181	–	–	–	–	–	–	–	27.0	12.2	3.5

[1] Cl determined using specific ion electrode

[2] samples filtered through 0.2 μm Nucleopore membranes

[3] theoretical solubility of Fe calculated using amorphous $Fe(OH)_3$ as solid

[4] theoretical solubility of Al calculated using kaolinite as solid

[5] halloysite as solid

[6] gibbsite as solid

[7] LORDS coordinates given in parentheses with sample site name

Table 6-1. Trace metal geochemistry of Cedar Creek and Mullica River estuary waters

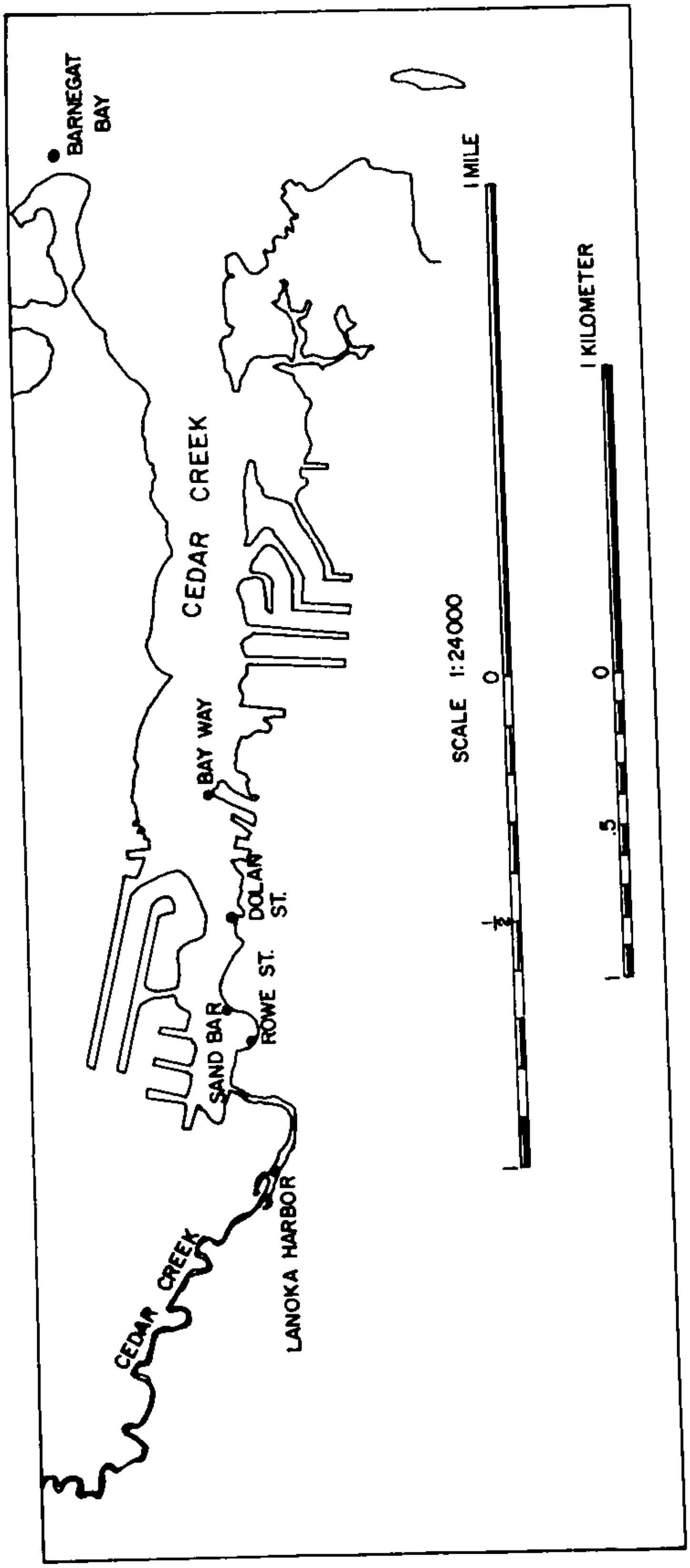

Fig. 6-1. Cedar Creek estuary sampling site locations.

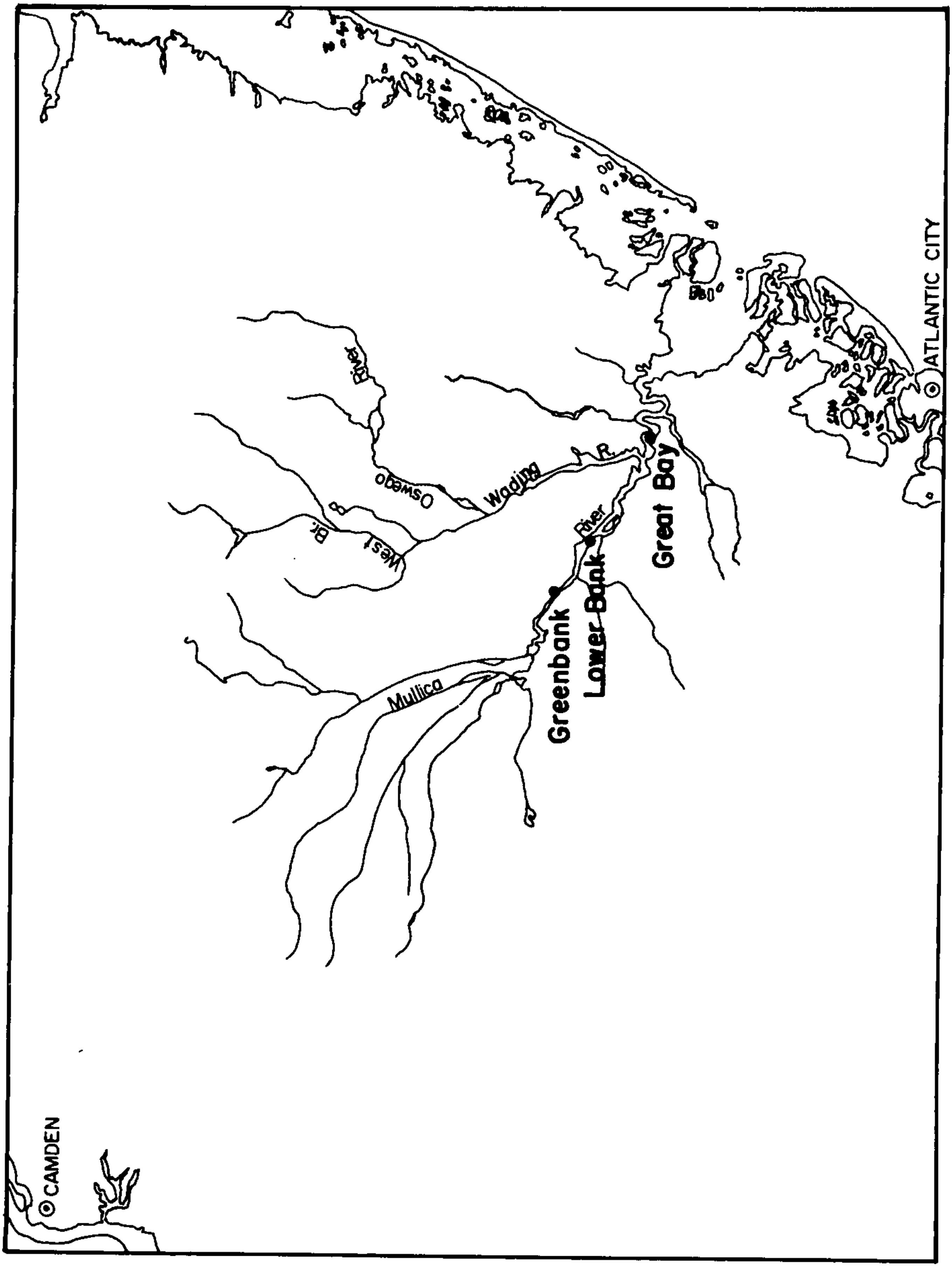

Fig. 6-2. Mullica River estuary sampling site locations.

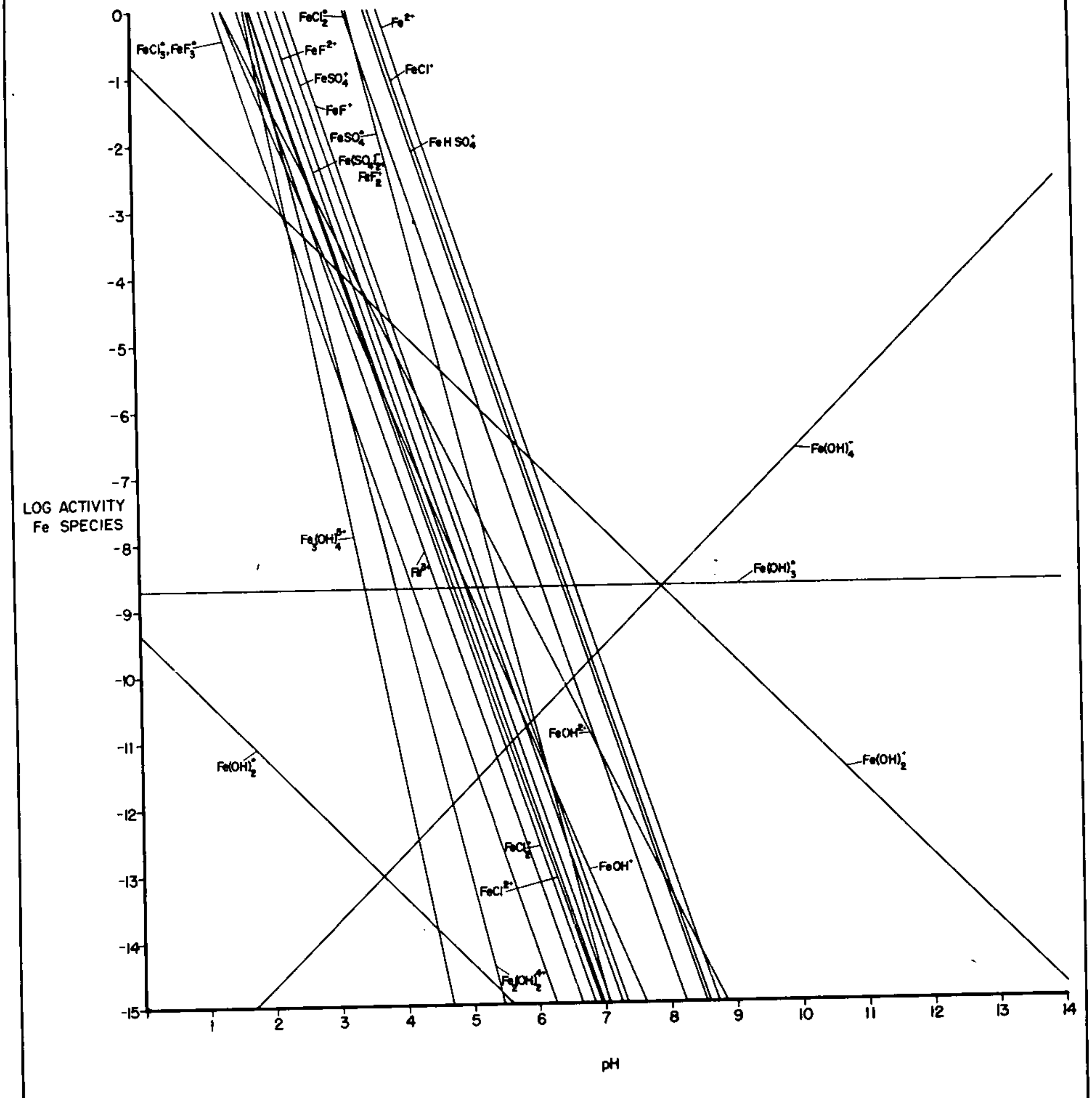

Fig. 6-3. Theoretical solubility of major inorganic Fe complexes vs. pH at Eh and ligand concentrations typical of Pine Barrens outer estuary water (Eh = 400 mV, 6000 ppm Cl^-, 514 ppm SO_4^{2-}, 294 ppb F^-).

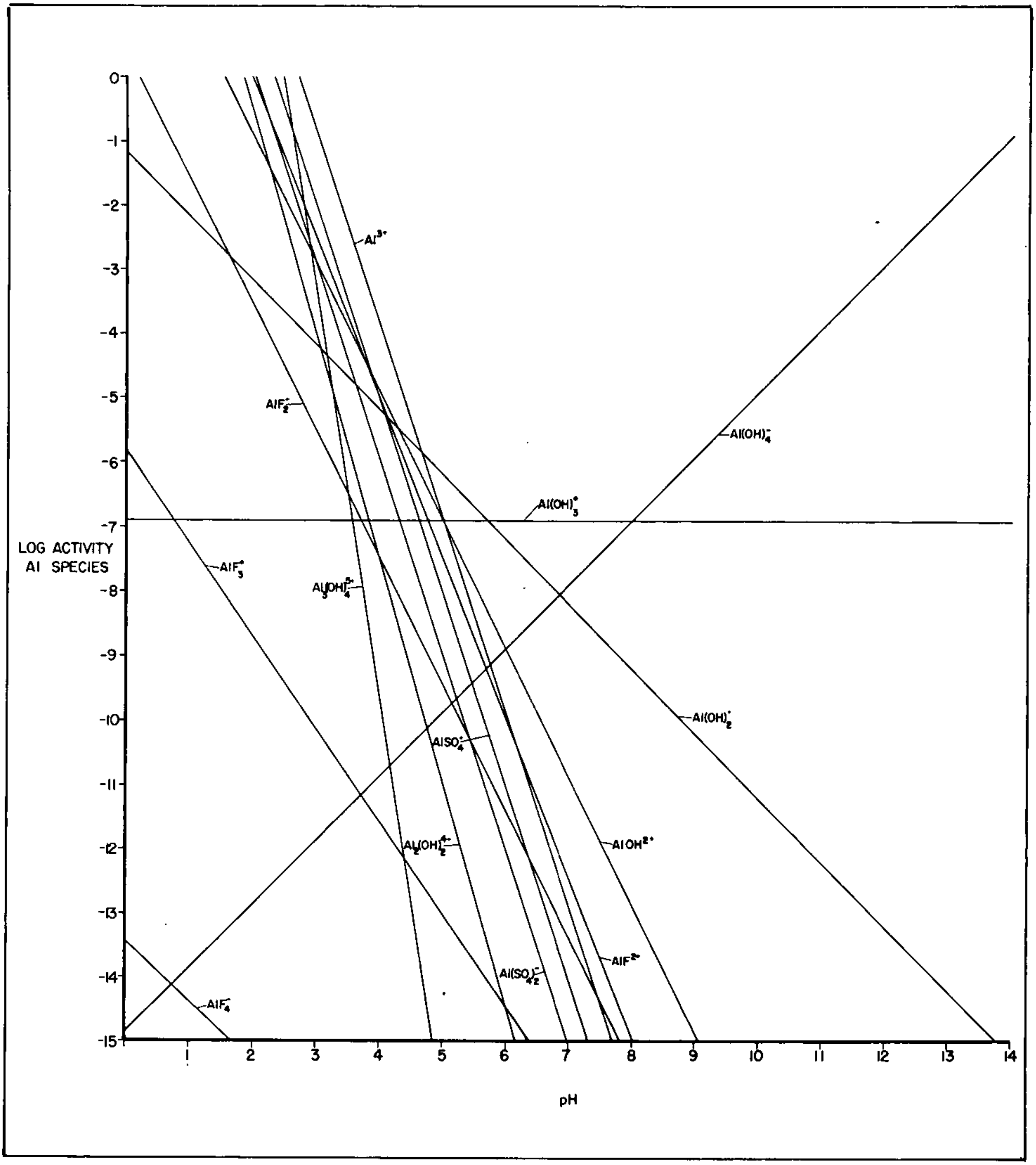

Fig. 6-4. Theoretical solubility of major inorganic Al complexes relative to gibbsite vs. pH at ligand concentrations typical of Pine Barrens outer estuary water (514 ppm SO_4^{2-}, 294 ppb total F).

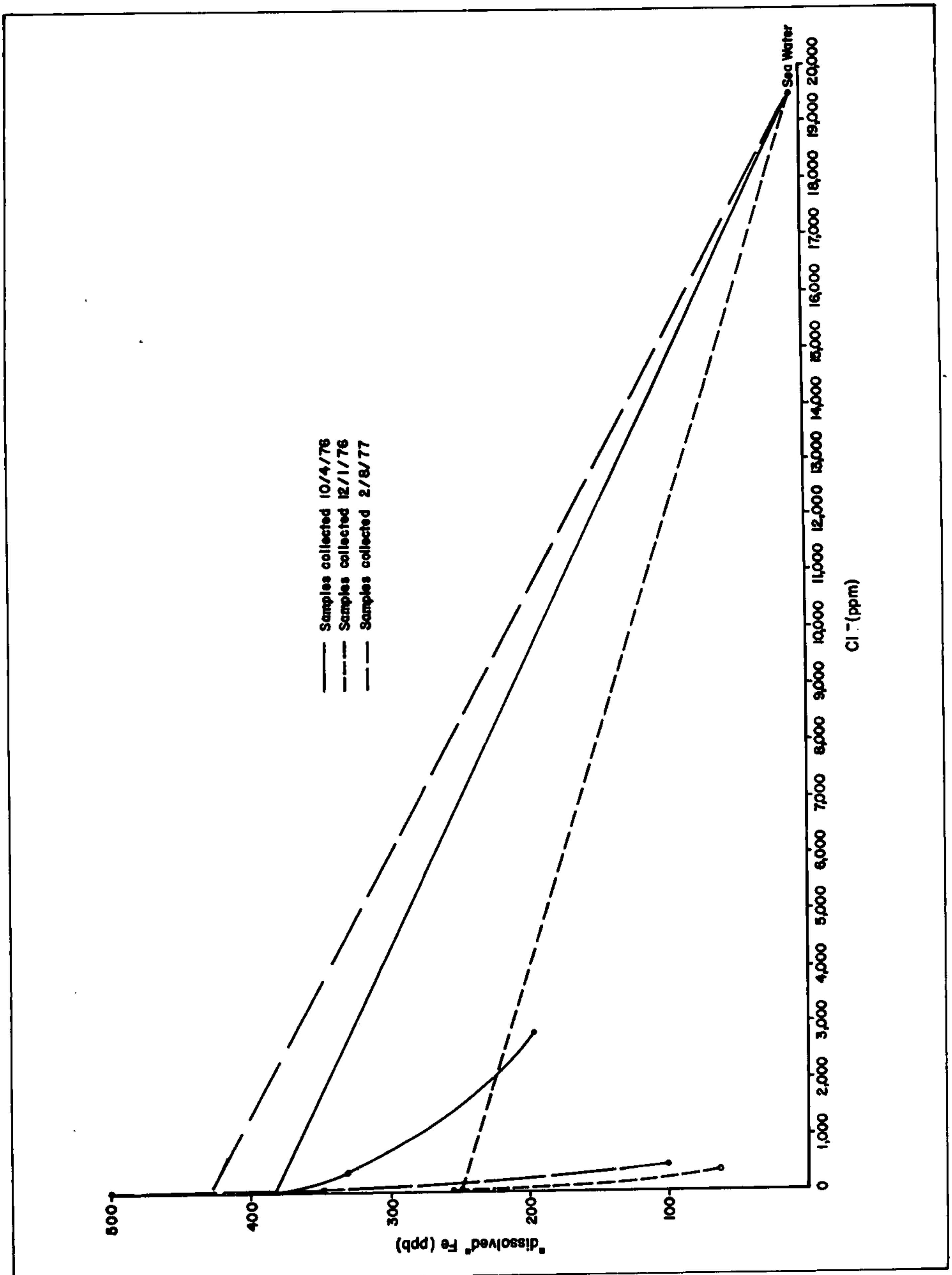

Fig. 6-5. Fe vs. Cl⁻ content of Mullica River estuary water. Straight lines show Fe concentrations predicted by simple dilution model.

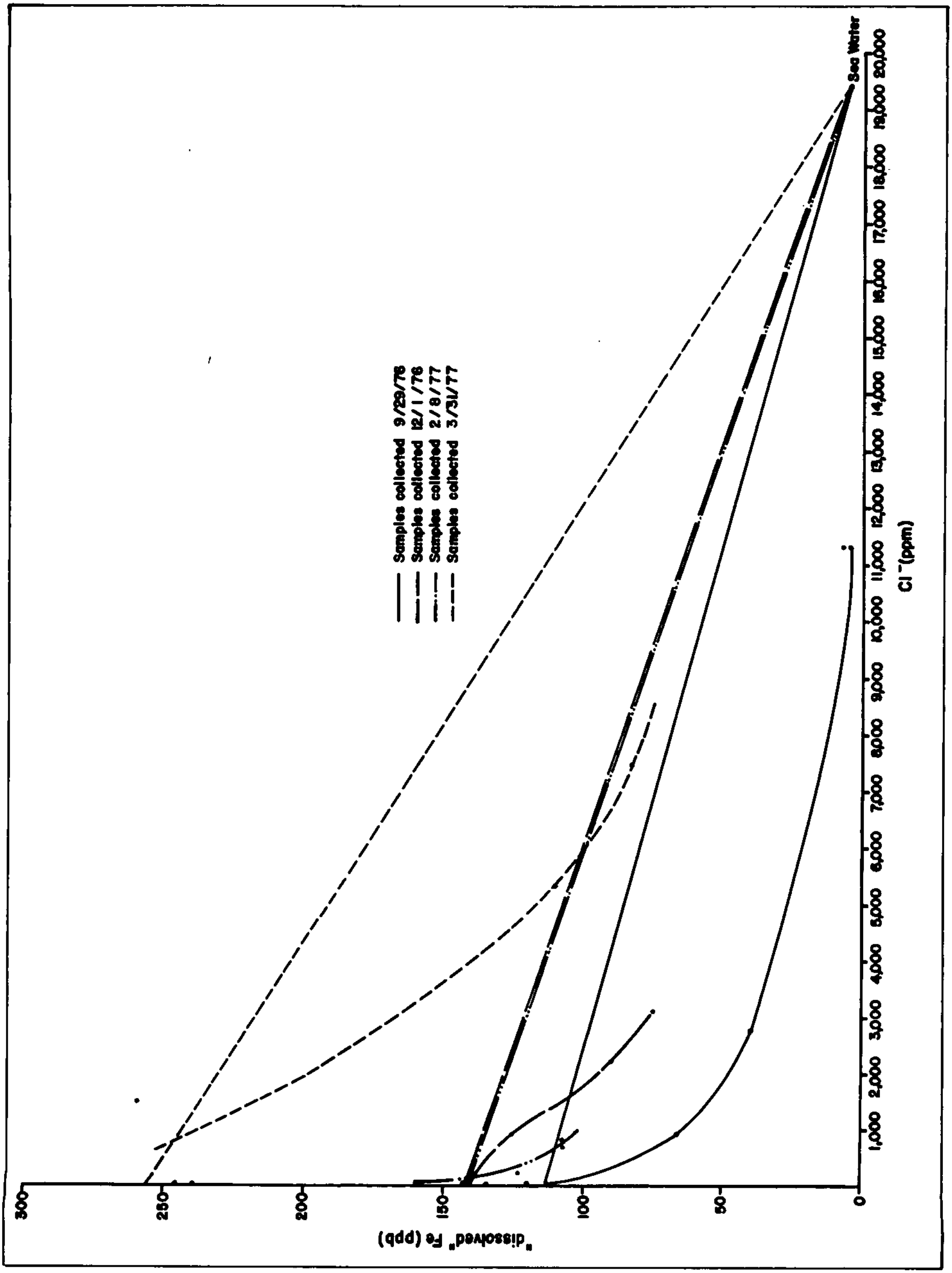

Fig. 6-6. Fe vs. Cl- content of Cedar Creek estuary water. Straight lines show Fe concentrations predicted by simple dilution model.

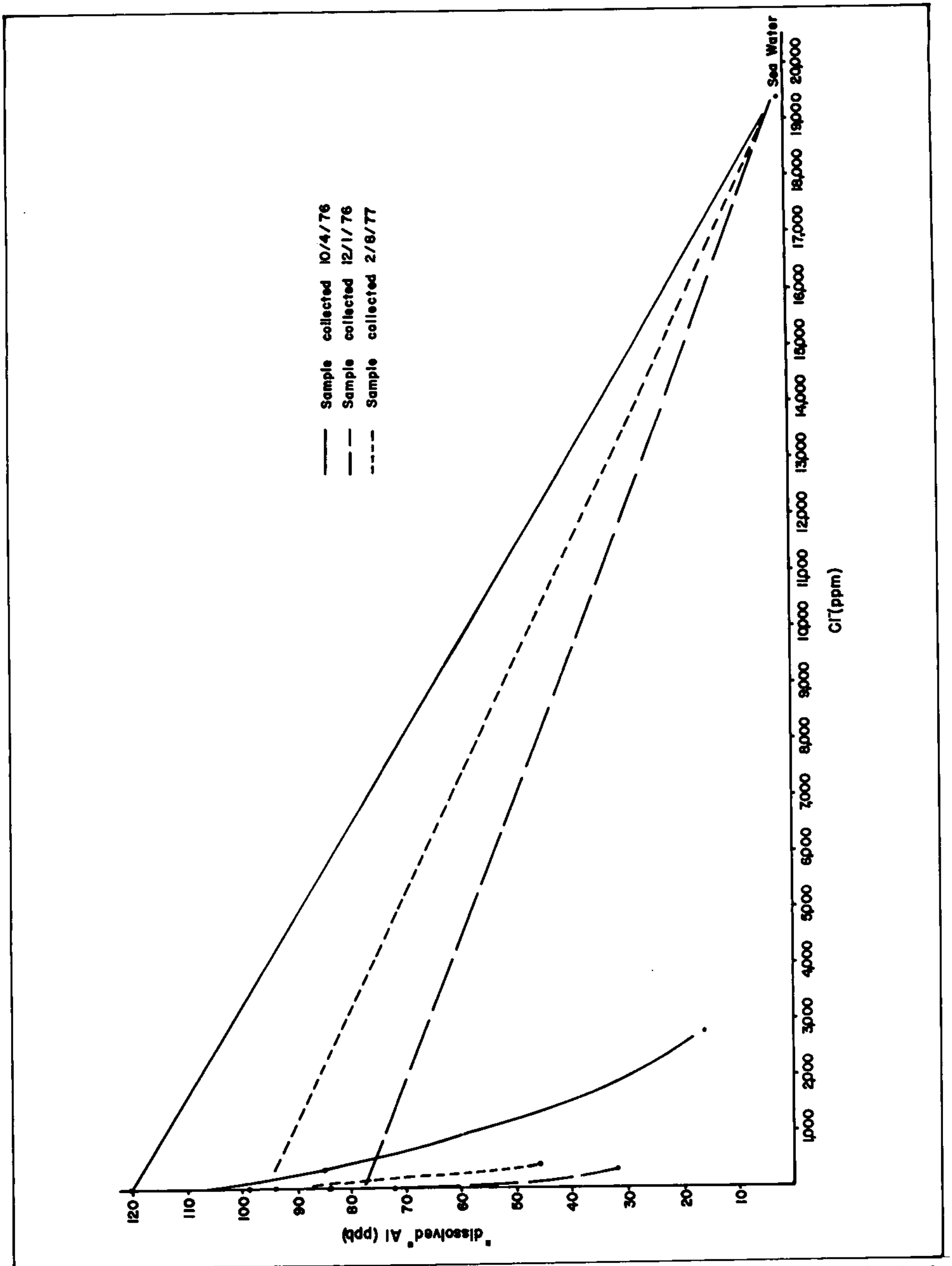

Fig. 6-7. Al vs. Cl- content of Mullica River estuary water. Straight lines show Al concentration predicted by simple dilution model.

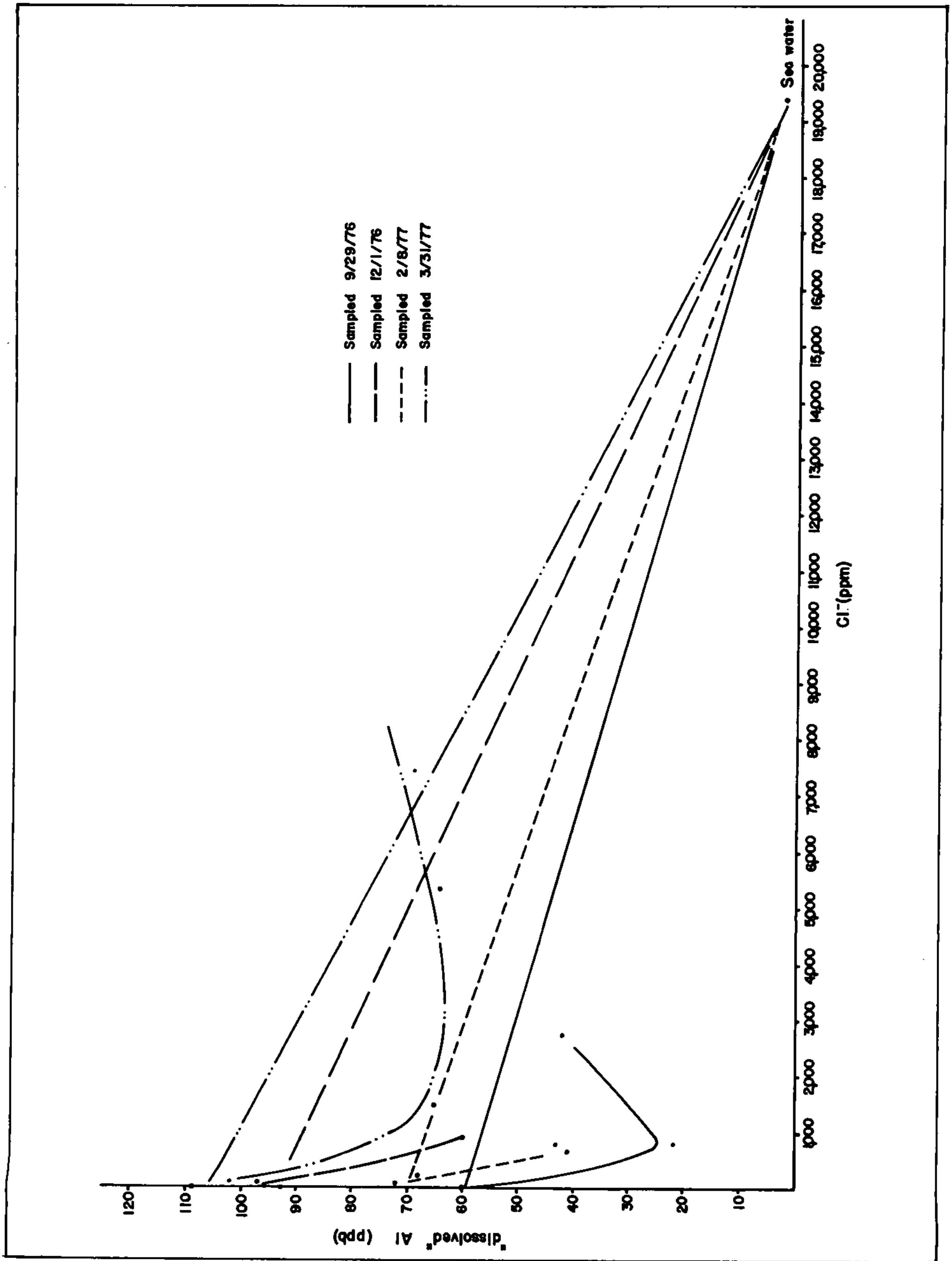

Fig. 6-8. Al vs. Cl⁻ content of Cedar Creek estuary water. Straight lines show Al concentration predicted by simple dilution model.

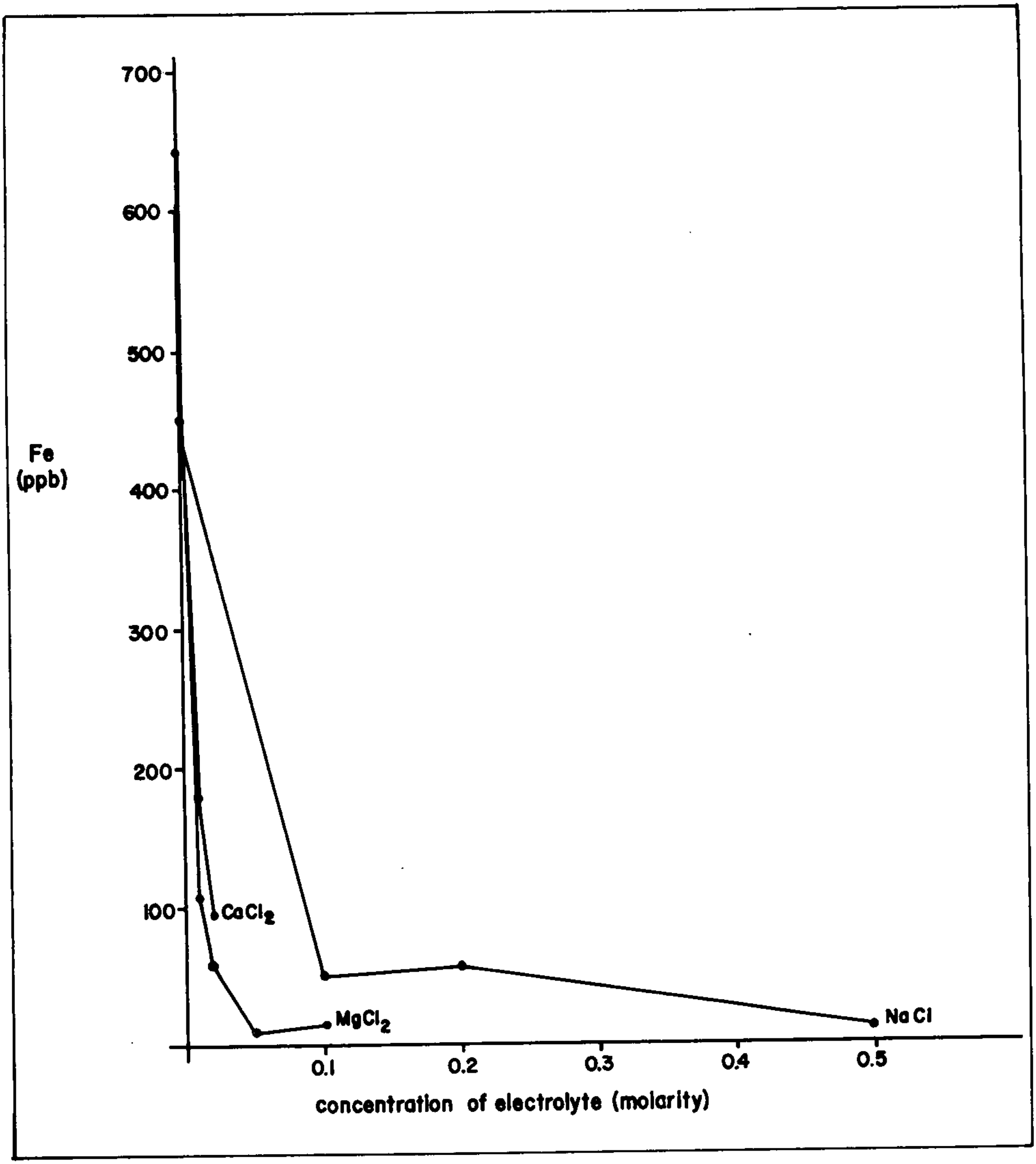

Fig. 6-9. Results of laboratory mixing experiments showing effect of electrolyte on precipitating Fe in Batsto River water.

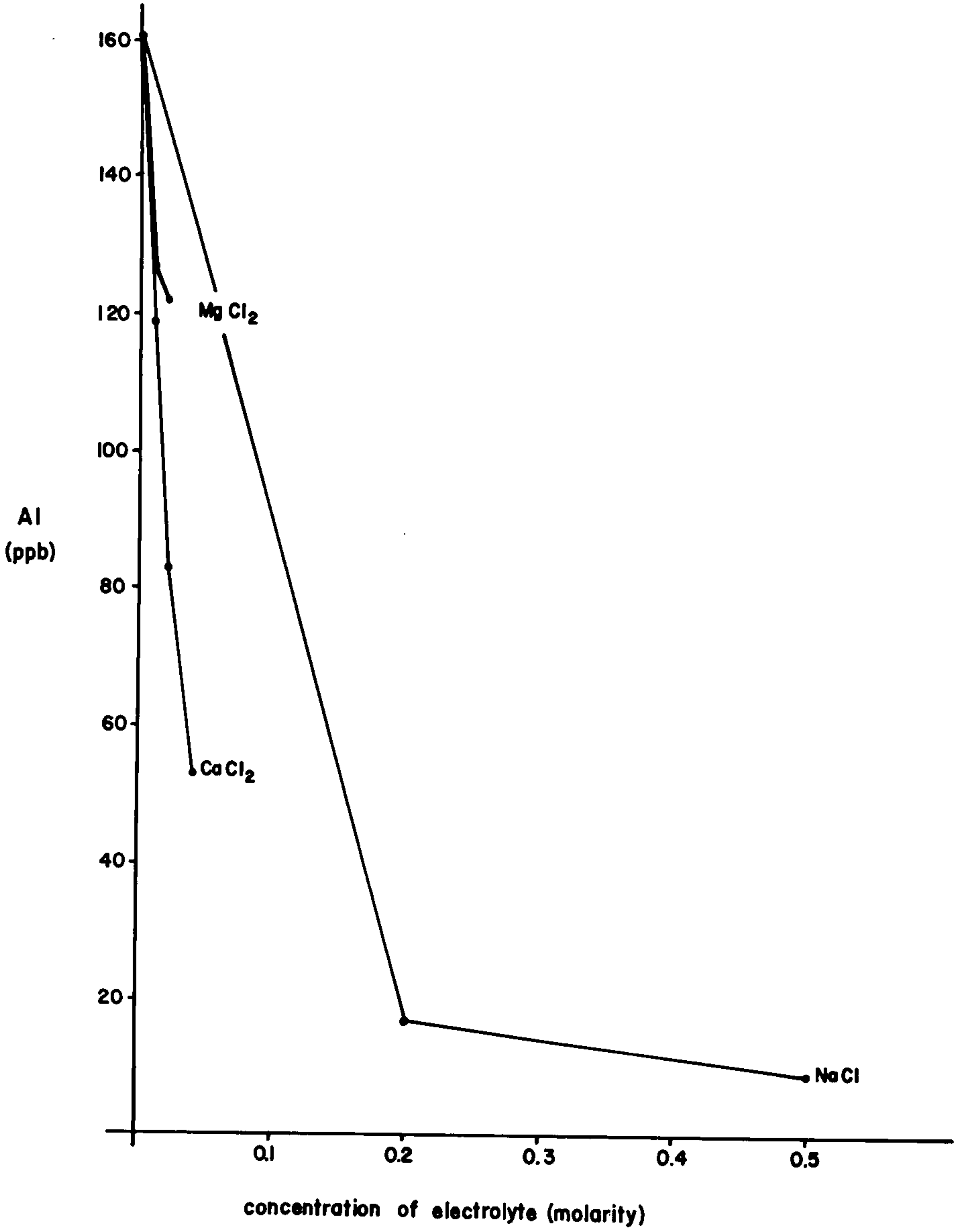

Fig. 6-10. Results of laboratory mixing experiments showing effect of electrolyte on precipitating Al in Batsto River water.

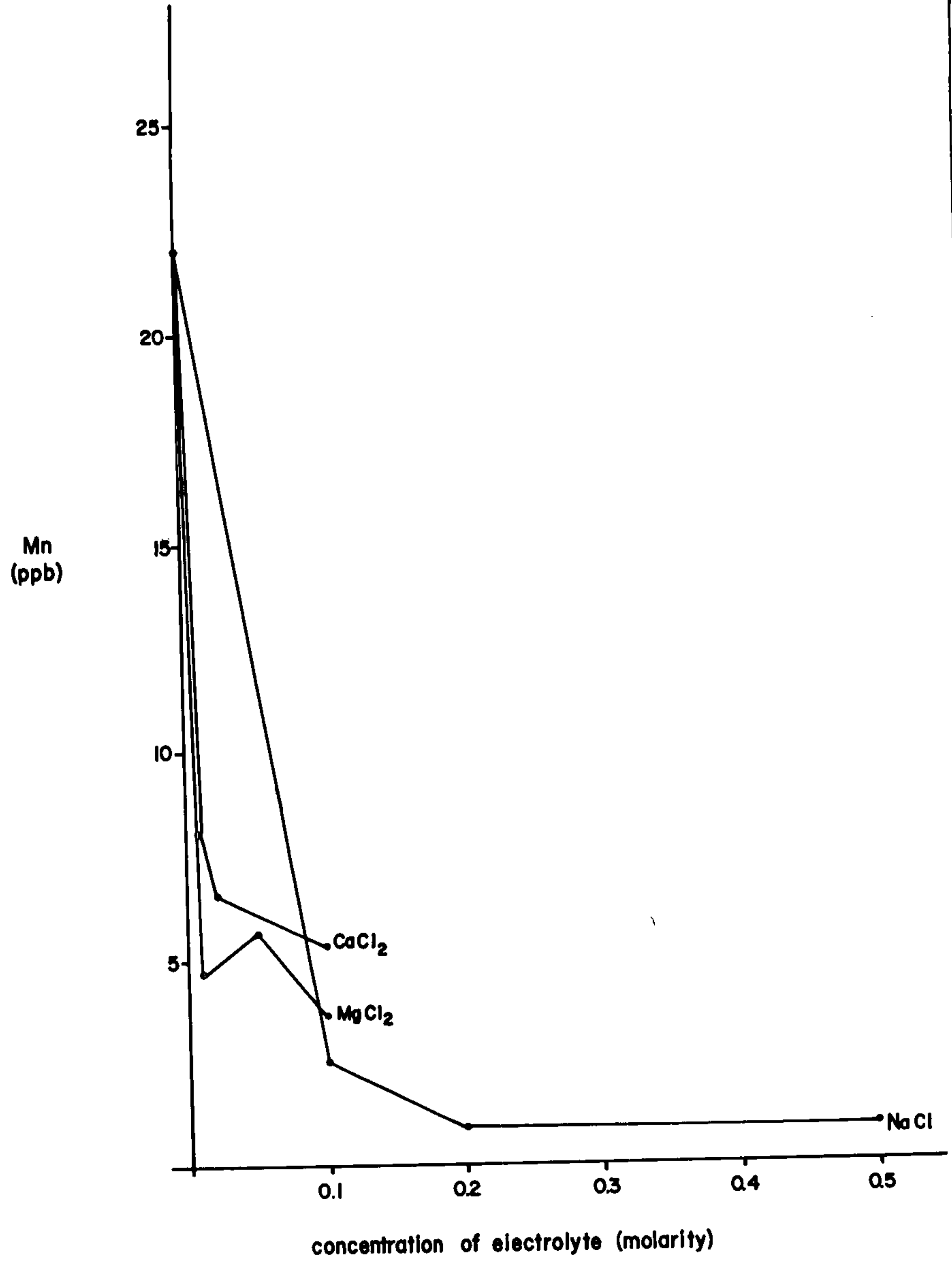

Fig. 6-11. Results of laboratory mixing experiments showing removal of Mn by electrolyte in Batsto River water.

Chapter 7

*BIOGEOCHEMISTRY OF BOG IRON

INTRODUCTION

From the early 1700's to the mid 1850's southern New Jersey was the site of a flourishing iron industry (Starkey, 1962; Pierce, 1957; Braddock-Rodgers, 1930; Bayley, 1910). Rivers and swamps of the southern New Jersey Coastal Plain contain sporadic but quantitatively important deposits of bog iron, which consist of unconsolidated to massive limonite impregnating sands, silts, and gravels. These local bog iron deposits provided raw material for some thirty furnaces and forges in the area (Braddock-Rodgers, 1930; Pierce, 1957). Oyster and clam shells were commonly used as flux, and charcoal made from pitch pine served as both reducing agent and fuel. The industry, which boomed for almost a century, produced many tons of cast iron pipe, stoves, tools, cooking utensils, and other items for east coast cities. In addition it served as the principal source of munitions for the Revolutionary War and the War of 1812.

The discovery of anthracite near the magnetite ores of Pennsylvania and northern New Jersey along with the dwindling supply of bog iron in southern New Jersey eventually doomed the bog iron industry. It has also been suggested that bog ores contain high concentrations of phosphorus and sulfur, making them undesirable for the production of steel (Bayley, 1910). As a result, the South Jersey industry declined rapidly after 1840. Within twenty-five years most of the region had returned to the wild and remains largely unpopulated to this day.

BACKGROUND

Probably because such deposits are no longer economic, there have been few modern studies of true bog iron occurrences either in New Jersey or elsewhere. This chapter describes the stream and groundwater chemistry of the South Jersey locality and focuses on the microbiota which appear to catalyze bog iron deposition.

While reconnaissance surveys were made on all major streams in the Pine Barrens area over a three year period, attention was focused primarily on the region around Batsto, shown in fig. 1-2. This town on the Mullica River was a center of bog iron activity for nearly a century. Streambeds in the area are coated with freshly precipitated iron oxides, and massive deposits, which are scattered in distribution, occur under river banks and in adjoining bogs. The ochre to red precipitate is ubiquitous, coating plants, pebbles, and stream bed detritus, and collecting as flocculent masses in more stagnant waters. All forms of ore were originally exploited, these being defined according to texture as "loam ore" (loose precipitate plus soil or sand), "seed ore" (partly consolidated) or rock-like "massive ore." "Massive ore" is presumably an older more consolidated form of "loam ore" (Rogers, 1840; Braddock-Rogers, 1930). It has been said that the ore, once mined, took twenty years to regenerate (Starkey, 1962), although this growth rate has not been accurately measured. In fact, the bog iron industry began importing ore in the early 1800's, and surprisingly little bog iron remains in the Pine Barrens today, suggesting much slower growth. We have observed a significant accumulation of bog iron ("massive" type) which has grown into slag from the Martha furnace along the Oswego River (east branch of the Wading River). This indicates that bog iron deposits of significant proportions are capable of accumulating within about 150 years, the probable age of the slag.

Between June 1976 and July 1977, we sampled the Batsto site on a bimonthly basis. Surface and ground water samples were collected from the Mullica River and Cedar Creek drainage basins and chemically analyzed as described in Chapter 4. Samples to be analyzed for bacteria were collected from the air-water interface, from subsurface bog waters, and from flocculent gels coating submerged plants or floating on the surface. Massive bog iron samples were collected from the bottom of Atsion Lake (when it was drained), from several locations along the Batsto and Oswego rivers, and from a bog about 2 miles north of Washington. The mineralogy and trace element content of selected bog iron samples were analyzed using X-ray and wet chemical techniques. Bog iron was also analyzed for microfossil content using a scanning electron microscope.

Bog iron is usually friable, containing admixed sand, silt and/or clay. Oolitic or concretionary structures are rare or absent. Fig. 7-1 shows the typical texture of massive bog iron, with rounded, well-sorted quartz grains thickly cemented by limonite. The ore composition itself is that of an impure limonite, with assays ranging from 12-60%, but rarely exceeding 30% Fe (Bayley, 1910). The only iron mineral identifiable by X-ray diffraction was goethite, the bulk of the ore consisting of amorphous iron oxyhydroxides.

We analyzed four different bog iron samples for Fe and several trace elements and found only 4-14% Fe (table 7-1). Trace element contents such as Mn, Al, Zn, Cu, Pb, and Cd were generally very low at several ppm to several ppb. Our phosphorous analyses indicated a maximum of 204 ppm (or 0.02%). Comparison of trace metal: Fe ratios in bog iron with those typical of stream and groundwater show that bog iron is very depleted in trace

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* Portions of Chapter 7 have been taken from Crerar et al. (1979) by permission of Elsevier Scientific Publishing Company.

metals relative to the water from which it is precipitating (see table 7-2). This suggests that the mechanism responsible for the bog iron formation is very selective towards Fe.

The traditional explanation for the mechanism of bog iron deposition is a variation on the following theme: CO_2 - enriched, O_2 - depleted deep groundwater containing soluble Fe rises towards ground level. CO_2 is lost and O_2 is gained; and consequently pH and Eh increase. Because iron oxide is less soluble under these conditions, it flocculates out as limonite at the surface. The resulting precipitate is deposited along the banks of streams, swamps, lakes, and coves. The deposits accumulate and mix with sand and mud and gradually harden into ore (Rhodehamel, 1973; Coonley et al., 1971; Pierce, 1957; Braddock-Rogers, 1930; Bayley, 1910).

Our data discussed below emphasize the role of iron-oxidizing bacteria in bog iron deposition.

WATER CHEMISTRY

Stream Water

Chemical characteristics of Pine Barrens stream water, such as pH, Eh, organic carbon, TDS, Fe, Al and other trace elements are presented and discussed in Chapter 4 (see table 4-1). An interesting characteristic of Pine Barrens streams is that during the summer, stream bottoms become coated with a red amorphous $Fe(OH)_3$ precipitate that is not present during the winter. Because of the similarities between this precipitate and bog iron, a study was undertaken to determine why deposition occurred predominantly in the summer. Our objective was to evaluate whether flocculation can be explained by inorganic chemical considerations alone. By comparing seasonal Fe saturation levels provided by the computer program FESOL, seasonal changes on Fe solubility can be detected.

As discussed in Chapter 4, Eh and pH at both Cedar Creek and the Mullica River demonstrate seasonal trends. Eh is lower in summer than in winter. pH in summer is generally higher than in fall and spring. Winter pH varies, with relatively high values observed during the winter of 1976-77 and lower values occurring during the winter of 1977-78 (see table 2-1). Measured: theoretical Fe solubility ratios generally follow the pH trend, higher solubility ratios being measured at times of higher pH. Solubility ratios are therefore higher during the summer when dominant $Fe(OH)_3$ precipitation is observed, but are also equally high during some winter months, during which little $Fe(OH)_3$ flocculation occurs. Natural pH trends in the Pine Barrens are thought to be now obscured by agricultural activity. In coastal plain environments with less agriculture, summer pH is typically lower than winter pH because of the higher organic acid contents in summer waters (Beck et al., 1974). Low summer pH relative to winter pH promotes $Fe(OH)_3$ dissolution rather than precipitation.

Inorganic Fe equilibria consequently do not account for the observed temporal distribution of $Fe(OH)_3$ precipitation on stream bottoms in either the Cedar Creek or Mullica River drainage basins. In both drainage basins precipitation of $Fe(OH)_3$ during certain winter months is predicted. On the other hand, Fe-oxidizing bacteria are abundant in Pine Barrens surface waters only during the summer and are metabolically most active during this period. While this does not prove that Fe precipitation is organically catalyzed, bacterial oxidation presents an attractive explanation.

Groundwater

Chemical data for Pine Barrens groundwaters were presented and discussed in Chapter 4 (table 4-2). Calculations similar to those performed on stream waters were also applied to the groundwater. Whereas the prior objective was to evaluate the seasonal precipitation of Fe on stream bottoms, the goal in applying the program to groundwater was to determine whether Fe solubility decreases with decreasing depth of groundwater, a condition of the traditional theory of inorganic bog iron deposition. Theoretical Fe solubilities obtained on some 10 to 15 groundwater samples in table 4-2 were all undersaturated in $Fe(OH)_3$ (amor.) and showed no consistent pattern of decreasing solubility of Fe with decreasing depth. Though deep groundwaters generally had lower Eh than shallow waters, the pH of shallow samples was significantly lower than that of the deep. The increased solubility of Fe resulting from the relatively lower pH of the shallow waters outweighed the decrease in solubility caused by their slightly higher Eh. That is, Fe solubility was actually higher in shallow groundwater than in deep, although it is the shallow groundwater from which bog iron is precipitating. The traditional explanation of bog iron formation, that of $Fe(OH)_3$ precipitating from groundwater that becomes progressively supersaturated in Fe with decreasing depth, is therefore not corroborated by these calculations. However, locales of bog iron precipitation all possess Fe-oxidizing bacteria, which are capable of providing the necessary catalyst for bog iron formation.

*BACTERIOLOGY OF SURFACE WATERS

Samples of water and freshly precipitated oxides were analyzed for bacteria both microscopically, and, in two instances, using species-specific culture media. Microscopic examinations were performed at 1200 power using Nomarski interference optics. Known iron-oxidizing bacteria which were positively identified in our samples included *Thiobacillus ferrooxidans, Leptothrix ochracea, Crenothrix polyspora, Siderocapsa geminata* and *Metallogenium* sp. *Naumaniella* sp. was tentatively identified, as were *Toxothrix* and *Gallionella* which could also be possible polymorphs of *Metallogenium* induced in laboratory culture.

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* Much of the bacteriology was performed by G.W. Knox and reported in his (1977) unpublished undergraduate senior thesis for the Dept. of Geological and Geophysical Sciences, Princeton University.

Thiobacillus ferrooxidans is a small (0.6 by 1.6 μm) rod-shaped organism (Levy et al., 1973). It is exceptionally acidophilic with a typical viable pH range from 1 to 4.6, growth being poor above pH 4 (Lundgren et al., 1974). It is an obligate chemolithotroph; that is, it must produce metabolically useful energy from iron or sulfur oxidation (Walsh, 1977). This organism, though rare, was positively identified in a few subsurface water samples from the New Jersey locality by growth in the species-specific "9K" medium of Silverman and Lundgren (1959).

Crenothrix polyspora is characterized by unbranched filaments up to 1 cm long and 1-6 μm in diameter surrounded by very thin colorless sheaths often encrusted with iron or manganese oxides at the base (Hirsch, 1974; Wolfe, 1960). Cells within the filament are roughly rectangular, and approximately 5 μm in diameter. The organism is found in waters containing organic matter and dissolved iron (Hirsch, 1974). At the New Jersey locality, *Crenothrix* is commonly attached to submerged plants. Fig. 7-2A is an example in an untreated water sample from the Batsto site.

Leptothrix ochracea displays sheathed straight rods (0.6-1.5 by 3-12 μm), often coated with iron or manganese oxides (Mulder, 1974). Natural growth in iron-containing waters is accompanied by voluminous, flocculent masses of ferric oxyhydroxide containing numerous yellow-brown, short, smooth empty sheaths (Harder, 1919; Mulder, 1974). Fig. 7-2B is a photomicrograph of an untreated water sample from the Batsto site, showing an empty *Leptothrix* sheath, common in both surface and subsurface samples.

Siderocapsa geminata typically occurs as capsulated paired cells, the capsule being 7 to 11 μm in diameter and often stained brown by iron and manganese oxides (Skuja, 1974). Fig. 7-2C, a photomicrograph of an untreated subsurface water sample, shows a high concentration of this organism.

Naumaniella, like *Siderocapsa,* is capsulated and stained yellow, but contains single, rod-shaped cells (Zavarzin, 1974). According to Zavarzin (1974) this organism can decompose organic complexes of both iron and manganese. *Naumaniella* was tentatively identified in subsurface water samples from this locality.

Walsh and Mitchell (1972a, 1973) have isolated an iron-oxidizing organism they termed *Metallogenium* which is morphologically similar to *Gallionella ferruginea* as described by Balashova (1968) and Zavarzin and Hirsch (1974). These organisms grow as twisted filaments encrusted with ferric oxides, and lack conventional cell walls. The Walsh and Mitchell iron-oxidizing *Metallogenium* grows in flocculent ferric precipitates and tolerates pH values from 3.5 to 6.8 with an optimum at 4.1. Fig. 7-2D, again of an untreated surface water sample from our locality, shows organisms corresponding morphologically to either *G. ferruginea* or to the iron-oxidizing *Metallogenium,* although terminal cells often described on *Gallionella* are absent. The same water samples were used to inoculate Walsh and Mitchell's (1972a) *Metallogenium* isolation medium. A 1 ml inoculum was added to 30 ml of culture medium, and serial transfers were made at 72 hour intervals. After five transfers the surviving organisms were photographed as in 7-3C. Addition of 100 units/ml of penicillin G to this medium did not affect growth, and we conclude, following Walsh and Mitchell (1972a, 1973) that the organism is *Metallogenium* and not *G. ferruginea.*

SCANNING ELECTRON MICROSCOPE STUDY OF BOG IRON

Small chips of bog iron ore approximately 0.5 cm square were gold plated for scanning electron microscopy (SEM). Textures and structures strongly resembling bacterial morphologies were common on almost all samples examined. For example fig. 7-3A, taken at 20,000 X, reveals a structure approximately 0.65 μm in diameter which could be a fossilized *Lepthothrix* sheath. Similarly, figures 7-3B and D show structures resembling the twisted filament and "rose-garland" morphologies of *Metallogenium.*

Microfossils of *Leptothrix* morphology, such as that in fig. 7-3A, have been noted in bog iron from other localities as early as 1910 (Molisch, 1910). However, the bog iron microfossils of figures 7-3B and 7-3D represent a new discovery. The presence of these microfossils and the profusion of bacteria-like structures in the limonite matrix suggests a strong association between bacteria and ore deposition.

DISCUSSION

Source of Iron

The first problem to be addressed is the source of the anomalously high surface concentrations of iron in the study area. As shown in fig. 4-2, the topmost Cohansey and Kirkwood Formations are predominantly composed of chemically inert quartz sands. Soil horizons, where present at all, are thin and poorly developed. Hence one must look to a deeper source for the iron, and this is likely provided by the underlying glauconites and beds enriched in pyrite, siderite, and vivianite.

As previously noted, streams and bogs in this region are fed largely by groundwater baseflow. At a number of the groundwater well sites sampled, water levels were higher in wells screened at greater depths (150 feet) than in adjacent wells screened at lesser depths (25 feet), indicating a tendency towards net upward flow. Water levels from an earlier network of observation wells in the Cohansey Formation near Batsto were reported by Lang (1961) and Lang and Rhodehamel (1962) and support this conclusion—that groundwater flows both laterally and vertically into the Mullica River basin.

As discussed previously, groundwaters sampled in the present study within the Mullica River drainage basin were consistently acidic, ranging from pH 4.3—4.4 for shallow wells (5-25 feet) to pH 4.7—4.8 for deeper wells

(<200 feet). Sources of this acidity could include sulfate from rainwater and pyrite oxidation, trace organic acids, and carbon dioxide from organic decay and plant respiration, the latter presumably being most important in the shallower, more acidic waters. These acidic, corrosive groundwaters are undersaturated in $Fe(OH)_3$ (amor.) while carrying up to several ppm of the metal. These waters ascend from underlying iron-rich strata, providing the most likely source of the iron in surface streams and bogs. Glauconite probably also serves as one source of Al, Mn, Zn and other trace metals in bog Fe and stream and groundwater. Table 7-3 shows the trace metal composition of two glauconite samples from the Hornerstown formation. Note that trace element abundances in glauconite are approximately the same as in typical Pine Barrens stream and groundwater following the general order: $Fe \doteq Al > Zn \doteq Mn > Cu \doteq Pb \doteq Cd$. The significant phosphorous content of the glauconite may serve as the source of the reputed (Bayley, 1910) high phosphorous content of bog iron.

Iron Oxidation Kinetics

While sampled groundwaters are undersaturated in $Fe(OH)_3$(amor.), surface waters are approximately saturated in the metal at first sight. Thus, it would appear that iron oxides simply precipitate as undersaturated groundwaters become aerated in surface streams and bogs—this is the traditional model of bog ore formation. However, there is a kinetic difficulty here owing to the acidity of the surface waters. The measured pH of river, bog, and shallow groundwaters averages about 4.3-4.5 during the summer when oxide accumulation is greatest and concentrations of humic and fulvic acids are high. The problem arises because the oxidation of the ferrous iron, Fe^{2+}, is inordinately slow below pH 6 (Stumm and Morgan, 1970, p. 534).

For pH values greater than 4.5, the rate of oxidation of Fe^{2+} in abiotic systems follows the kinetic relationship:

$$-d[Fe^{2+}]/dt = k\ [Fe^{2+}]\ [OH^-]^2 P_{O_2} \qquad (1)$$

where $k = 8.0\ (\pm\ 2.5) \times 10^{13}$ liter^2 mole^{-2} atm^{-1} min^{-1} at 25°C. Below pH 3.5, the rate law is independent of pH:

$$-d[Fe^{2+}]/dt = k'\ [Fe^{2+}] P_{O_2} \qquad (2)$$

where $k' = 1.0 \times 10^{-7}$ atm^{-1} min^{-1} at 25°C (Singer and Stumm, 1970; Stumm and Lee, 1961). Note that according to (1), a 100-fold increase in the oxidation rate occurs with a unit increase in pH. Assuming rate law (1) and pH = 4.5, P_{O_2} = 0.2 atm, and $[Fe^{2+}] = 8.9 \times 10^{-5}$M (or 5 ppm), gives the impossibly slow rate $d[Fe^{2+}]/dt = 8.0 \times 10^{-6}$ ppm/min., or a halftime for Fe^{2+} oxidation of 300 days. (Half-time is the time required to oxidize one half of the ferrous ion at any given starting concentration.) By contrast, at pH 7 Fe^{2+} oxidation occurs at 0.8 ppm/min., with a half-time of 4.3 minutes, all else being the same. Thus, it would appear that Fe^{2+} oxidation should be too slow in the acid waters of the study area to permit significant accumulation of bog iron. An additional mechanism is clearly required.

Much the same argument applies to the problem of acid mine drainage. In this case the oxidation of pyrite follows a four-step cyclical sequence (Stumm and Morgan, 1970, p. 540):

$$FeS_2(s) + 7/2\ O_2 + H_2O = Fe^{2+} + 2SO_4^{2-} + 2H^+ \qquad (3)$$

$$Fe^{2+} + 1/4\ O_2 + H^+ = Fe^{3+} + 1/2\ H_2O \qquad (4)$$

$$Fe^{3+} + 3H_2O = Fe\ (OH)_3(s) + 3H^+ \qquad (5)$$

$$FeS_2(s) + 14\ Fe^{3+} + 8H_2O = 15\ Fe^{2+} + 2SO_4^{2-}\ 16\ H^+ \qquad (6)$$

Here, reaction (3) initially triggers the process, (5) precipitates amorphous iron oxides, and (6) dissolves additional pyrite by Fe^{3+} reduction. Steps (3), (5) and (6) release acidity, often creating pH values as low as 2 or 3. Under such acid conditions, reaction (4), or the oxidation of Fe^{2+}, is exceedingly slow once again and becomes the overall rate-limiting step. Reaction (4) may be catalyzed by light, but only by a factor of 2-3 times; it may also be catalyzed by surface area concentrations exceeding 100 m^2 liter^{-1}, by soluble Fe^{3+}, Cu^{2+}, Mn^{2+}, Co^{2+} and Al^{3+}, and by microbial activity. These catalysts have been tested by Singer and Stumm (1970) who showed that the effect of bacteria far outweighed all others under natural conditions. In fact, they found that microbial activity could accelerate Fe^{2+} oxidation by more than six orders of magnitude at acid pH.

Bacteriological Controls

In rivers polluted by acid mine drainage, *Thiobacillus ferrooxidans* exerts the prime control on reaction (4), and without this organism the acid mine problem would be far less severe (Lundgren et al., 1972; Walsh and Mitchell, 1975; Walsh, 1977). However, *T. ferrooxidans* is extremely acidophilic, growth being poor above pH 4. In the less acidic waters of the New Jersey Pine Barrens *Thiobacillus* is present but rare. On the other hand, *Metallogenium*, with a growth optimum at pH 4.1 is common, as are *Siderocapsa* and *Leptothrix*. In addition, structures resembling *Metallogenium* and *Leptothrix* are preserved in the bog iron itself (figs. 7-3A, B,D). Finally as discussed previously, the streambed precipitation of iron shows a strong seasonal dependence, being far more pronounced in the warmer months and almost negligible in the winter when bacterial counts are also at a minimum. This all suggests that bacteria serve as the necessary catalyst for reaction (4)—the rate-limiting oxidation of ferrous to ferric iron. Amorphous ferric hydroxides would then precipitate according to reaction (5) with a net gain of two moles of H^+ for every mole of Fe^{2+} oxidized. Iron precipitation thus contributes, along with soluble organic acids and CO_2, to the observed acidity of surface and shallow groundwaters. In the Pine Barrens locality, reactions (3) and (6) are less important, except as a possible local source of soluble iron and sulfate where underlying strata contain traces of pyrite.

The conclusion that bacteria serve as catalysts for iron oxidation may also be reached by a process of elimination. Aside from the iron-oxidizing bacteria, no other suitable catalysts seem to be available at this locality. Unlike manganese oxides, freshly precipitated amorphous iron hydroxides are not autocatalytic (see review by Crear et al., 1980). Surface area concentrations exceeding 100 m²/liter of catalyzing materials such as clays are not available on stream beds or at shallow depths in the Cohansey Formation which, instead, consists of well rounded pebbles and sands. As shown in fig. 7-1, typical bog ores collected from swamps in the region consist of relatively coarse quartz sands (rather than clays) thickly cemented by limonite. Stumm and Lee (1961) showed that concentrations of transition metal ions such as Cu^{2+}, Mn^{2+}, and Co^{2+} on the order of one ppm can significantly accelerate Fe^{2+} oxidation. However, concentrations of metals other than iron are too low in these surface and ground waters to effect the orders of magnitude changes required—(see tables 4-1 and 4-2). Stumm and Lee also showed that concentrations of chloride and sulfate on the order of 100 ppm had no measurable effect on the oxidation rate. The major dissolved components of these waters are humic and fulvic acids at concentrations ranging from 1 to about 60 ppm. Theis and Singer (1974) have demonstrated experimentally that similar concentrations of humic and related acids such as tannic acid, glutamine, vanillic and citric acids will notably retard the oxidation of ferrous ion. This is probably attributable to the formation of kinetically stable ferrous-organo complexes such as those predominating in this region. In addition, Theis and Singer showed that the same organic acids will reduce rapidly any ferric iron which might be formed by reaction (4). This underscores the need for additional biological catalysts.

According to Harder (1919), the association of iron-oxidizing bacteria with bog ore deposits has been recognized since 1836. There is also a discussion on the relation between bacteria and bog iron by Dake (1915). In a study of bog iron deposits in swamps at the head of the Snake River, Colorado, Deul (1942) identified abundant growth of the iron oxidizing bacteria *Gallionella, Lepthothrix, Crenothrix,* and *Sphaerotilus.* Deul concluded that these deposits were biogenic because of their visible association with large bacterial colonies.

Historically, the term "bog ore" has been applied to a wide range of freshwater iron-rich deposits. As summarized by Callender and Bowser (1976) these include deposits in soils, springs, bogs, rivers, and lakes. These may vary in texture from the coatings and encrusted sands studied here, to the thick crusts and concretions characteristic of northern lakes. Bacteria associated with the latter lake deposits have been discussed extensively by Perfil'ev et al. (1965) who showed that *Siderococcus, Gallionella* and similar iron-specific organisms precipitate iron, while manganese-oxidizing genera such as *Metallogenium, Caulococcus,* and *Kusnezovia* accelerate precipitation of associated manganese oxides. A thermodynamic model for the biogenic deposition of manganese has been developed by Crerar et al. (1981) and may be applied by simple analogy to the iron oxides.

Metabolic Considerations

It is not known in all cases whether iron-oxidizing bacteria derive metabolically useful energy from the precipitation of iron. Silverman and Ehrlich (1964) have proposed that such bacteria might oxidize iron by 1) direct enzymatic activity, 2) digestion of organo-metallic complexes leaving behind the metallic precipitate as waste, and 3) interaction with end products of metabolic activity such as ammonia and organic bases which raise local pH and precipitate metal hydroxides. Of the bacteria observed in the Pine Barrens samples, *T. ferrooxidans* is an obligate chemolithotroph—that is, it derives all its metabolic energy from the enzymatic oxidation of iron and sulfur; it will grow, but only with extreme reluctance, in purely organic media (Kelly, 1971; Lundgren et al., 1972, 1974). *Gallionella, Leptothrix* and *Metallogenium* have been described as facultative autotrophs in that they appear capable of deriving energy either from the oxidation of organic matter or of iron (Ehrlich, 1972; Walsh and Mitchell, 1972a).

It is believed that *Crenothrix* and *Siderocapsa* may not oxidize iron directly, but will either adsorb ferric ion on their cell surfaces or sheaths, or may oxidize the organic moiety of an organo-iron complex (Ehrlich, 1972).

Direct enzymatic oxidation of Fe^{2+} is a surprisingly inefficient source of energy relative to the more usual heterotrophic oxidation of organics. For example, the oxidation of Fe^{2+} via the summation reaction:

$$Fe^{2+} + 1/4\ 0_2\ (g) + 5/2\ H_2O = 2H^+ + Fe(OH)_3(\text{amor.}) \qquad (7)$$

releases only about 10.4 kcal of energy per mole of Fe^{2+} (assuming $PO_2 = 0.2$ atm, pH = 4.5, and Fe = 5 ppm). In contrast, the heterotrophic oxidation of glucose,

$$C_6H_{12}0_6 + 60_2 = 6CO_2 + 6H_2O\ (1) \qquad (8)$$

releases 677 kcal per mole of glucose (assuming roughly equal CO_2 and 0_2 concentrations). Following Stumm and Morgan (1970, p. 557) and assuming a 36% efficiency in microbial energy conversion, then 140 grams of Fe^{2+} must be oxidized to convert one gram of CO_2 to cellular carbohydrate (by reversing reaction (8)). Hence chemolithotrophs such as *Thiobacillus* must necessarily oxidize great quantities of iron—quantities sufficient to produce limonitic bog ores or thick streambed deposits at acid pH.

There is no direct evidence that any of the bacteria described in the Pine Barrens deposits can oxidize iron by either of the two remaining mechanisms—digestion of organo-metallic complexes or interaction with end products of metabolic activity. In view of the high concentration of organo-iron complexes in the Pine Barrens streams, the first alternative seems particularly attractive. This mechanism was first proposed by Harder in 1919 for the biogenic origin of bog iron. However humic and fulvic acids, which are the prime organic components in the study area, are themselves the end products of decay reactions and are highly resistant to further bacterial attack (Kononova, 1966). In addition, the data of Walsh and Mitchell (1972a) suggest that mild complexing agents such as K,H-phthalate effectively isolate ferrous iron from the metabolic activity of *Metallogenium*. Walsh (personal communication, 1977) has observed similar inhibition with formic and tannic acids and ethylenediaminetetraacetic acid (EDTA), all suggesting that *Metallogenium*, at least, does not precipitate iron by Harder's mechanism.

The organism *T. ferrooxidans*, which displays optimal activity at pH < 3.5, is not as important in the study area as is *Metallogenium* with a growth optimum at pH 4.1. Walsh and Mitchell (1972b) have suggested that acid mine waters are produced by a pH-dependent succession of iron bacteria, with *Metallogenium* first catalyzing Fe^{2+} oxidation in the pH range 3.5-5.0. As the system becomes more acidic due to activity of this organism, *T. ferrooxidans* takes over creating pH values less than 3.5. Walsh and Mitchell (1972b) showed that *Metallogenium* increases Fe^{2+} oxidation rates and resultant acid production by a factor exceeding 200 over the pH range 3.5 to 4.5. The succession to a more acidic *Thiobacillus*-dominated environment does not occur in the Pine Barrens owing to the scarcity of sulfide minerals.

The trace metal analyses of bog iron previously quoted show that the processes precipitating ore are highly specific for Fe. For example, the Fe/Mn ratio of filtered Mullica River water averages roughly 15/1 while that of the bog iron averages 177,000/1. It has been argued that freshwater ferromanganese deposits typically contain much lower trace element concentrations than their marine counterparts because the former are deposited much more rapidly. This leaves less time for the selective adsorption of trace metals onto growing surfaces of freshwater deposits (Callender and Bowser, 1976; Crerar et al., 1980). This effect might also be amplified by the activity of Fe-specific enzymes. For example, the Mn-oxidizing bacterium *Metallogenium personatum* selectively precipitates Mn even when Fe concentrations are significantly higher (Perfil'ev et al., 1965; Crerar et al., 1980). This suggests that *Metallogenium* oxidizes metals enzymatically rather than by an alternative nonselective mechanism.

Microfossils strongly resembling *Metallogenium personatum* have been discovered in the cherts of banded iron formations as old as 1.9 billion years (see review by Crerar et al., 1981). Other microfossils resembling *Sphaerotilus*, *Gallionella*, and *Crenothrix* have been described in the same formations (Barghoorn and Tyler, 1965; Cloud, 1965). It is possible that these organisms or their precursors actively precipitated iron oxides throughout the early history of life on this planet much as they do today.

CONCLUSIONS

1. Several species of iron-oxidizing bacteria have been identified in surface water from the Batsto, New Jersey area. They include: *Thiobacillus ferrooxidans*, *Leptothrix ochracea*, *Crenothrix polyspora*, *Gallionella ferruginea*, *Siderococcus geminata*, and an iron-oxidizing type of *Metallogenium* sp. *Naumaniella* sp. was also tentatively identified.
2. Scanning electron microscopy of the iron deposits reveal the presence of microfossils resembling *Leptothrix* and *Metallogenium*.
3. Seasonal patterns of inorganic Fe solubility in stream water suggest that periods of observed Fe oxide precipitation correlate poorly with the times of lowest theoretical Fe solubility.
4. Solubility of Fe increases with decreasing depth in groundwaters examined, whereas the traditional theory of bog iron deposition would predict the opposite trend.
5. Theoretical calculations based on the rate law of Fe^{2+} oxidation suggest that abiotic oxidation is too slow at pH 4.5, which is typical of Pine Barrens waters, to account for quantitatively significant deposits of bog iron.
6. Conclusions 1) through 5) lend support to the final conclusion which is that the above iron-oxidizing bacteria are promoting bog iron deposition in the Pine Barrens.

Table 7-1. Fe and trace element composition of bog iron samples

	%	ppm						
Sample	[1]**Fe**	**P**	**Mn**	**Al**	**Zn**	**Cu**	**Pb**	**Cd**
#1	4.41	15.2	0.18	5.30	<0.3	0.38	0.75	0.005
#2	4.52	24.0	0.16	6.42	<0.3	0.38	0.74	0.002
#3	12.52	204.5	0.96	21.74	0.51	1.19	2.00	0.013
#4	13.95	70.7	0.97	42.51	6.31	0.69	2.62	0.108

[1] Bog iron samples were digested in conc. HF and HNO_3 in a heated sand bath. Fe and other trace element analyses were then obtained using atomic absorption spectrophotometry. P was analyzed using a colorimetric procedure adapted from Jeffrey (1970).

Table 7-2. Trace metal: Fe ratios in bog iron and average filtered stream and groundwater

Samples	**Mn/Fe**	**Al/Fe**	**Zn/Fe**	**Cu/Fe**	**Pb/Fe**	**Cd/Fe**
[1]bog iron #1 & #2	3.9×10^{-6}	2.7×10^{-4}	$<1.9 \times 10^{-6}$	7.5×10^{-6}	4.5×10^{-6}	4.2×10^{-8}
[2]bog iron #3 & #4	7.4×10^{-6}	$3.4\text{-}6.7 \times 10^{-4}$	3.2×10^{-6} -4.1×10^{-5}	4.7×10^{-6}	4.7×10^{-6}	4.9×10^{-8} -4.1×10^{-7}
[3]Cedar Creek water	6.1×10^{-2}	1.0×10^{0}	4.3×10^{-2}	4.4×10^{-3}	8.1×10^{-4}	5.0×10^{-4}
[3]Mullica River water	6.7×10^{-2}	1.4×10^{0}	2.8×10^{-2}	2.9×10^{-3}	9.0×10^{-4}	2.5×10^{-4}
[4]average groundwater	1.4×10^{-1}	1.0×10^{1}	4.3×10^{-2}	5.9×10^{-3}	9.0×10^{-4}	5.0×10^{-4}

[1] averaged composition of bog iron samples #1 & #2 from table 7-1
[2] averaged composition of bog iron samples #3 & #4 from table 7-1
[3] trace metal: Fe ratios of average Cedar Creek and Mullica River water from table 2-1
[4] trace metal: Fe ratios of average groundwater from table 2-2

Table 7-3. Trace element composition of glauconite from the Hornerstown Formation

	%		ppm					
Sample	[1]**Fe**	**Al**	**P**	**Mn**	**Zn**	**Cu**	**Pb**	**Cd**
G-4	9.21	10	0.33	0.59	2.82	<0.3	0.22	<0.002
G-2	9.26	10	0.28	0.63	2.44	<0.3	0.27	<0.002

[1] Similar to bog iron samples in table 7-1. Glauconite samples were digested in conc. HF and HNO_3 in a heated sand bath. Fe and other trace element analyses were then obtained using atomic absorption. P was analyzed using a colorimetric procedure adapted from Jeffrey (1970).

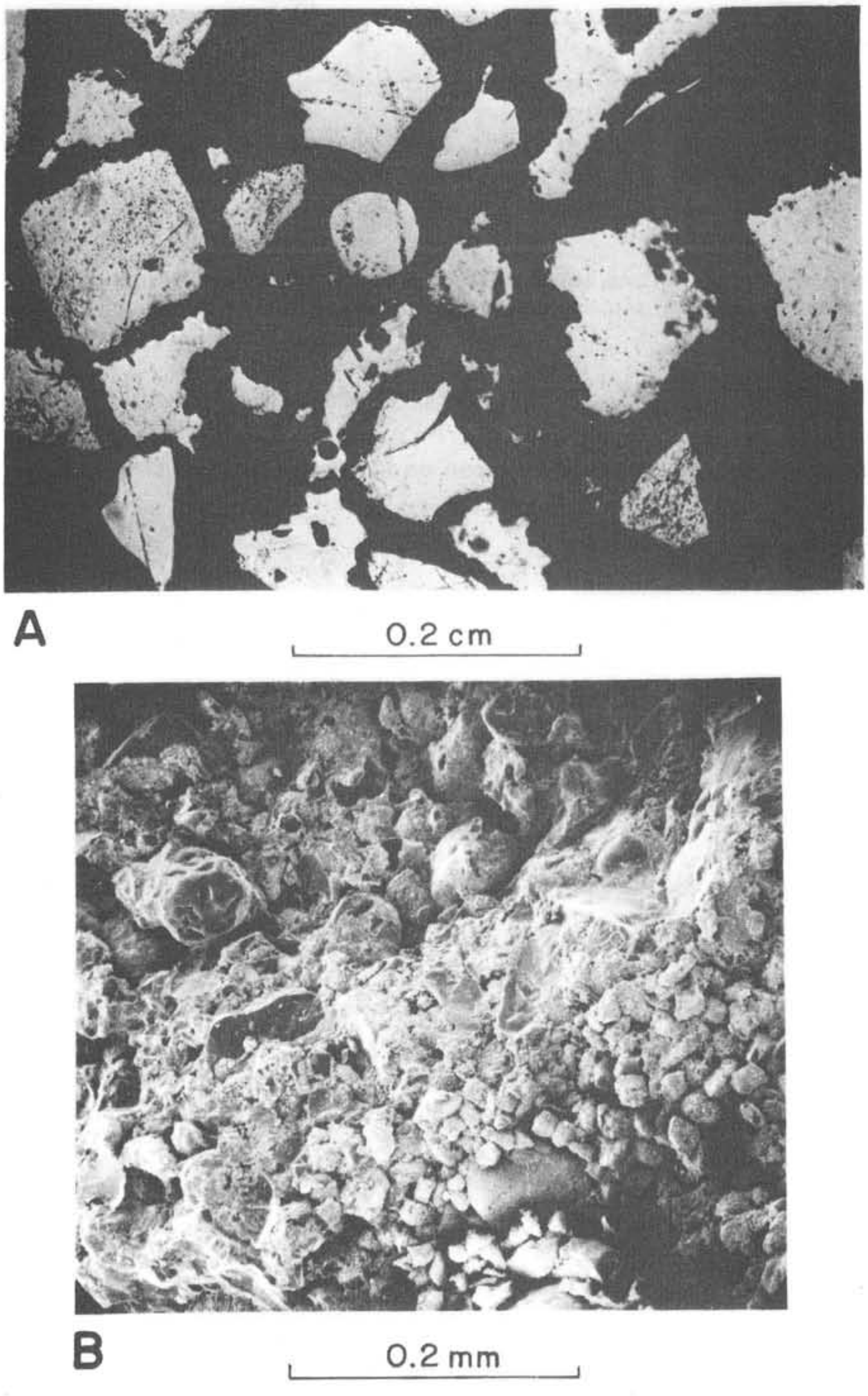

Fig. 7-1. A. Thin section of bog iron showing quartz grains and limonite matrix. B. Scanning electron micrograph of bog iron showing limonite—cemented quartz grains. Reprinted with the permission of Elsevier Scientific Publishing Company.

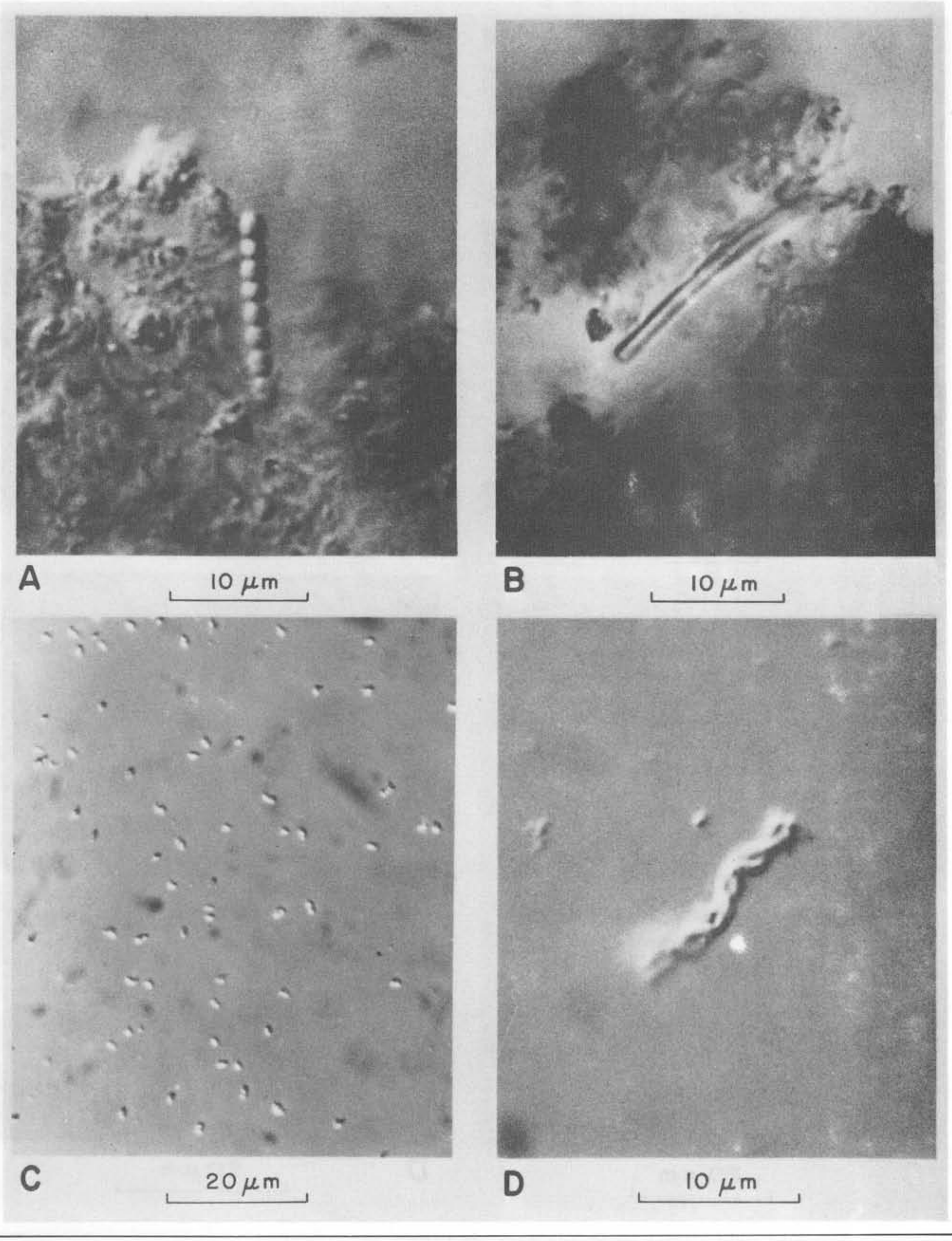

Fig. 7-2. Photomicrographs of A. *Crenothrix polyspora;* B. *Leptothrix ochracea;* C. *Siderocapsa geminata;* and D. iron-oxidizing *Metallogenium* sp. in untreated surface water samples. Reprinted with the permission of Elsevier Scientific Company.

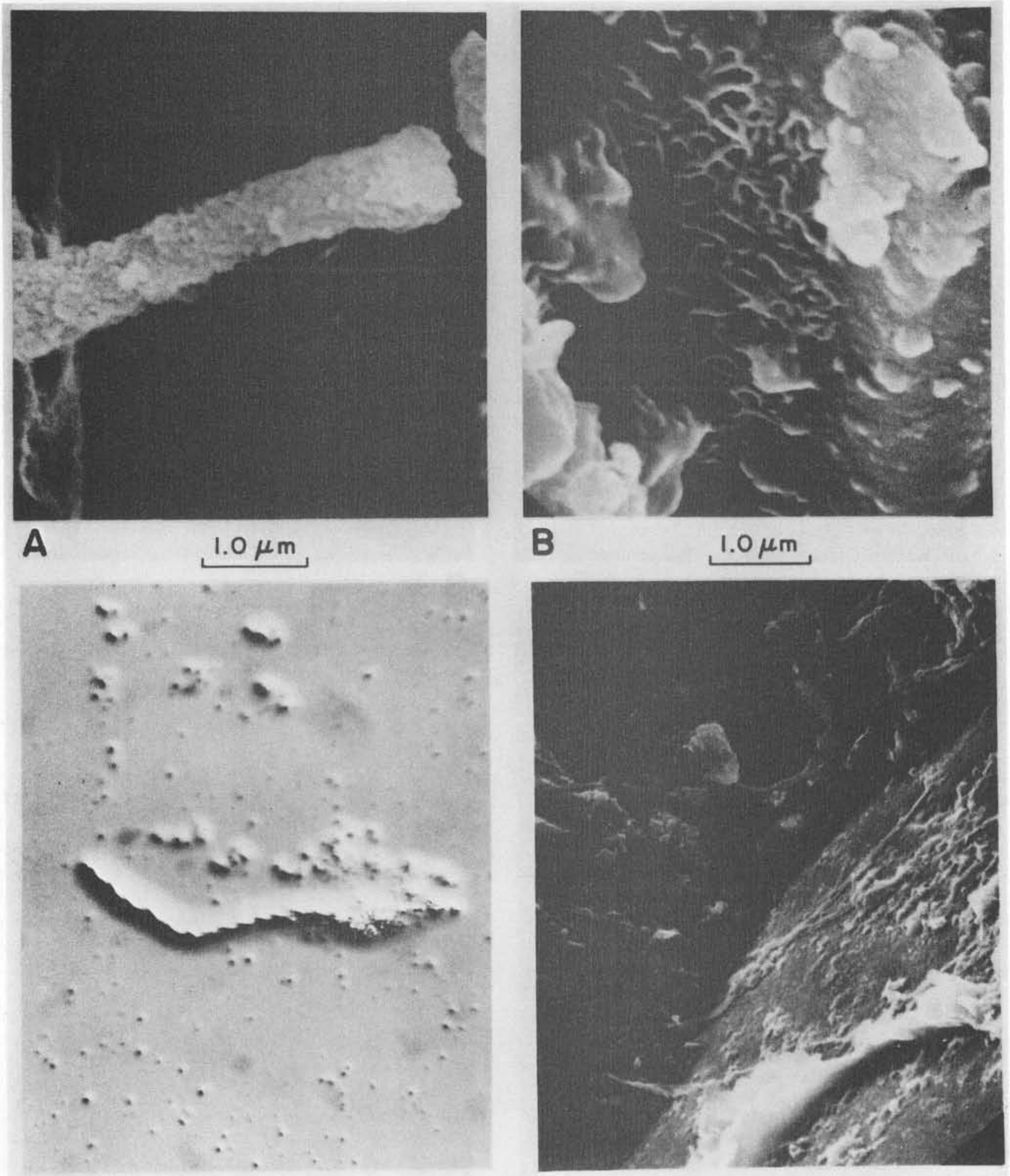

Fig. 7-3. A., B., D. Scanning electron micrographs of bog iron matrix showing probable biogenic structures; C. Photomicrograph of bacteria from surface water samples grown in *Metallogenium* isolation medium. Reprinted with the permission of the Elsevier Scientific Publishing Company.

Chapter 8

CONCLUSIONS AND RECOMMENDATIONS

This report has outlined the chemistry of the major aqueous systems of the New Jersey Pine Barrens. Most phases of the hydrologic cycle have been studied, including precipitation, surface waters, groundwaters, and the estuarine environment. The results may be used as a data base for comparison with the hydrochemistry of the entire Atlantic Coastal Plain. For example, the Coastal Plain rivers of southeast Georgia studied by Beck et al. (1974) bear many striking similarities to the results reported here.

The Pine Barrens rivers are unique in many aspects and differ markedly from the chemistry of the "world average river" reported by Livingstone (1963) and Turekian (1969). For example, the pH of Pine Barrens rivers is considerably lower, while dissolved Fe and organic carbon are significantly higher than values reported for most rivers. The ionic strength of Pine Barrens waters is unusually low, reflecting low total dissolved solids (TDS), about 20% of the average river water. Concomitantly, the ratios of dissolved Fe, Al and organic carbon to TDS are exceptionally high.

Because of their low TDS, Pine Barrens river and ground waters are unusually soft and pure and easily pass primary federal drinking water standards. Unfortunately, many of these same waters contain too much dissolved Fe, Mn, and organic carbon, and are too highly colored to meet secondary federal drinking water standards. In other words, many Pine Barrens waters, while potable, are undesirable in various ways, common problems being slight coloration and iron staining. These difficulties could be corrected by water treatment such as charcoal filtration.

The waters of the Pine Barrens control the entire ecosystem of the area. The results of this study can help predict and measure the effects of encroaching land development. The waters are presently fresh and unpolluted (excepting local contributions from agricultural activity at several sites); thus the reported chemical analyses can serve as a baseline for monitoring any future changes in water quality. Pine Barrens waters are very susceptible to various forms of pollution. First, because of their low TDS and ionic strength, these waters are only weakly buffered, and bear little resistance to chemical change. For example, the addition of only a trace of basic material such as agricultural lime can cause a dramatic rise in pH. Soil profiles are only weakly developed in most regions, and the Cohansey sands which crop out over most of the area are chemically inert and highly permeable. Thus the uppermost soils and sediments have little ion exchange or adsorption capacity and are incapable of effectively filtering out undesirable wastes. In addition, the water table is generally shallow, permitting a rather direct connection between the surface and groundwater (Rhodehamel, 1970). Hence, contaminants introduced at the surface pass rapidly and virtually unimpeded into the underlying aquifer where they may travel long distances in a relatively short period of time. This is borne out by our mass balances on precipitation and river water chemistry: most of the elements and compounds introduced by precipitation are ultimately discharged by rivers. Under more typical geological conditions, soils and sediments exert a far greater control on groundwater chemistry by buffering processes and adsorption of contaminants. Thus there exists a very real threat that the large reservoir of fresh water in the Pine Barrens could become seriously contaminated by municipal, industrial, or agricultural development. Potential sources of pollutants might include leachate from sanitary land fill and septic tanks, industrial waste, broken or leaking sewer lines, and heavy crop fertilization. Streams and bogs of the Pine Barrens are fed predominantly by groundwater base flow. Hence polluted groundwaters would seriously affect the quality of surface waters as well, endangering the overall ecosystem. Many plants which are delicately adapted to present conditions, especially those in the cedar swamps, would not survive a major change in water quality.

Polluted ground and river waters would also adversely influence the chemistry of the estuarine environment. This is particularly critical because many species of fish and shellfish either live or breed in this habitat. For example, in New Jersey, at least 20 species of commercial, sport, and forage food fish representing a multimillion dollar industry, are estuary dependent (Bartlett et al., 1978; Kantor, 1977). In 1977, 3 million dollars worth of estuarine shellfish alone were harvested in New Jersey (Bartlett et al., 1978). This habitat is already seriously endangered: at present, 25% of the state's estuarine waters are partially or fully condemned (Bonsall, 1977).

Bartlett et al. (1978) have proposed the establishment of a "Protection Zone" because of the susceptibility of Pine Barrens waters to pollution and its disastrous effects. This zone would be congruent with the Cohansey Formation aquifer and would essentially encompass most areas considered part of the Pine Barrens. Within this zone water quality would be controlled and protected at both State and local levels. The present study underscores the need for such controls if the integrity of the Pine Barrens and adjacent coastal waters is to be preserved.

The question remains as to whether the groundwater resources of the Pine Barrens should be exploited or left untapped. Rhodehamel (1970) has estimated the total standing water of the Cohansey Formation alone to be 10.8 trillion gallons. This gigantic reserve of unpolluted water is ideally located to supply southern New Jersey communities, as well as industrialized areas along the Delaware River and coastal resort communities.

In 1954, the State of New Jersey purchased the Wharton Tract, 150 square miles located within the Mullica River drainage basin. In addition to providing conservation and recreational facilities, it was expected this area would help meet future water demands of southern New Jersey. Because of the high intrinsic permeability of the Cohansey aquifer, it has been estimated that the Tract could supply a minimum of 150 million gallons of water per day (Rhodehamel, 1973). Rhodehamel (1970, 1973) has proposed that most of this water be drawn from wells of 12 to 15 inch diameter, 100 to 150 feet deep, placed roughly 100 to 150 feet from the downstream reaches of major streams. These would be high-yield wells (500-1,000 gpm) spaced roughly 100 feet apart. It is anticipated that such wells would be fed largely by water drawn down from adjacent streams so that overall depression of the water table would be minimized. During periods of decreased river flow, water would be pumped from wells situated further from the streams.

The danger in pumping large quantities of water from anywhere in the Pine Barrens lies in the possibility of lowering the water table. As noted in Chapter 1, most of the unique flora of the region are adapted to a wetlands or bog environment. This entire ecosystem would be destroyed if the bogs were drained (Givnish and others, 1971). On the economic side, over 10% of the nation's cranberries are harvested from the central Pine Barrens. The maintenance of an extensive network of bogs is essential for cranberry production; therefore, a relatively shallow water table must be preserved. Depression of the water table in lowlands environments would also increase the frequency of fire, creating an ecology of scrub oak and stunted pine resembling that of the desert-like uplands.

With this in mind, Bartlett et al. (1978) have taken a view diametrically opposed to that of Rhodehamel. They state categorically that there is no excess of water in the Pine Barrens and that "any additional removal of water from the aquifer will severely hamper the continued existence of the system."

We recommend that the hydrologic effects of pumping be given serious consideration before any major use is made of Pine Barrens waters, a suggestion also put forth by Givnish and others (1971). A thorough study of this type would combine field pumping tests with theoretical hydrologic modeling. Limits might then be set on the amount of water that could be safely drawn without adversely affecting the environment.

It is also essential that the behavior of pollutants within the hydrologic system be more clearly understood. Our work suggests that soluble pollutants introduced at or near the surface should pass relatively unimpeded into ground waters, and from there to streams and bogs due to the permeability and chemical inertness of uppermost sediments. Further research is needed to establish the dilution rate, direction of flow and degradability of pollutants introduced either at the surface or from shallow sources in this area.

The unique and fragile ecosystem of the New Jersey Pine Barrens is directly dependent upon both the quality and quantity of its ground and surface waters. This delicate balance is now seriously endangered by encroaching suburban sprawl. Strict regulations concerning water quality, water supply and land development are required.

Funding for a preservation plan and limited acquisition of land within the Pine Barrens became available when the National Parks and Recreation Act was signed by President Carter on November 10, 1978. At that time the New Jersey Pine Barrens was designated as the country's first National Reserve. Governor Byrne then issued Executive Order 71 on February 8, 1979 establishing the Pinelands Planning Commission. This was endorsed by the New Jersey Legislature in June of that year with the Pinelands Protection Act. In November of 1980 the Pinelands Commission issued its Comprehensive Management Plan which included: assessment of natural resources, and scenic, aesthetic, cultural, and outdoor recreational resources; land use and management policies; and programs to implement the overall plans and recommendations. The Commission's report stressed the fragility of the Pine Barrens ecosystem and the high susceptibility of the region's surface and ground waters to chemical change. This underscores the need for stringent planning to ensure rational use of the water resources of the Pine Barrens, and to help preserve this unique wilderness area for generations to come.

APPENDIX I: PINE BARRENS RAINFALL AMOUNTS (cm)
Princeton Gauges

	Rwa	Rwb	Rwc	Rwd	Rwe	Rwf	Rwg	Rwh	
	LORDS coordinates								
Sampling Period	(33-12-377)	(33-12-124)	(33-11-282)	(33-11-115)	(32-14-356)	(32-11-589)	(32-23-434)	(32-24-937)	AVG.
1	6.15	7.59	7.80	9.27	9.96				8.15
2	4.37	3.96	4.39	3.58	3.48				3.96
3	2.59	2.67	2.49	2.51	2.74				2.60
4	7.80	7.87	7.11	7.37	7.67				7.56
5	8.23	9.58	8.20	7.95	7.72				8.34
6	4.24	4.22	4.17	3.78	4.09				4.10
7	2.11	2.39	2.77	2.87	2.77				2.58
8	6.43	–	7.26	7.21	7.21				7.03
9	8.71	–	7.65	7.59	9.96				8.48
10	2.31	–	4.10	4.62	4.70				3.93
11	2.26	–	2.06	2.03	1.50	–	1.42	1.91	1.77
12	4.93	–	7.11	9.19	6.88	9.80	9.58	8.97	8.28
13	10.31	10.49	10.49	11.56	9.75	8.79	–	–	10.23
14	8.18	8.36	8.28	9.19	–	8.13	9.30	–	8.55
15	5.23	5.87	3.53	3.86	(9.40)	5.79	9.07	3.15	5.21
16	–	–	–	–	–	–	–	10.97	(10.97)
17	8.97	8.61	8.18	10.87	5.74	–	8.53	10.85	8.82
18	4.11	4.17	3.66	4.72	5.61	–	4.17	3.76	4.31
19	5.56	5.00	5.08	5.79	6.07	5.08	4.75	5.61	5.37
20	3.89	3.10	3.23	3.25	3.48	3.00	3.58	3.28	3.35
21	3.28	2.97	4.27	4.62	5.46	3.28	3.78	4.14	3.98
22	7.98	6.32	8.08	9.32	11.46	7.72	8.18	9.78	8.61
23	10.13	8.10	7.65	6.38	6.88	4.70	7.52	7.85	7.40
24	5.23	3.61	4.90	5.00	5.51	3.91	5.82	4.72	4.84
25	4.57	4.72	5.41	5.41	6.63	5.87	4.52	–	5.30
26	7.09	6.22	8.94	7.57	8.99	6.91	7.11	(8.99)	7.55
27	2.79	1.93	4.22	6.07	5.00	1.47	2.21	2.84	3.32
28	2.03	1.70	2.59	2.16	1.80	1.55	1.65	0.76	1.78
29	8.36	7.82	8.71	9.53	8.71	9.25	8.00	6.07	8.31
30	6.12	7.59	8.74	7.39	8.31	4.06	6.63	7.06	6.99
31	5.23	3.66	3.18	3.81	2.92	–	4.60	3.00	2.85
32	3.33	2.79	2.62	2.54	1.73	3.18	3.18	1.91	2.66
33	5.23	4.45	4.19	3.33	5.72	4.72	5.72	6.20	4.95
34	3.73	2.87	3.07	2.59	3.15	3.43	3.96	4.70	3.44
35	–	8.79	9.53	9.93	11.30	7.77	9.02	9.30	9.38
36	8.94	8.89	9.32	9.86	–	9.32	8.97	9.22	9.22
37	8.46	7.49	8.05	7.24	8.20	7.29	7.90	8.20	7.85
38	5.59	5.11	6.20	6.50	6.83	6.91	4.50	5.08	5.84
39	7.44	7.19	8.71	9.22	8.94	6.12	7.52	9.04	8.02
TOTAL	211.91	186.10	225.94	235.68	226.27	138.05	161.19	157.36	235.88
AVG.	5.73	5.64	5.95	6.20	6.29	5.75	5.97	6.05	6.05
Total Prec./ yr.	112.12	114.55	114.38	119.31	117.31	108.36	116.50	114.64	115.06

Weather Service Gauges

Sampling period	Bass River	Chatsworth	Toms River	Tuckerton	Indian Mills	Pemberton	Avg.	Sample Period Dates
1	NA	2.62	15.44	6.15	7.14	6.73	7.62	12/13/70-12/27/70
2	Inc.	4.75	3.02	4.78	4.62	3.71	4.18	12/27/70-1/7/71
3	1.68	2.46	2.57	2.95	2.44	1.88	2.33	1/7/71-2/1/71
4	5.61	6.96	8.69	4.80	6.83	6.12	6.50	2/1/71-2/10/71
5	5.84	6.96	7.29	9.04	7.75	5.36	7.04	2/10/71-3/3/71
6	4.88	4.55	4.60	4.22	4.88	4.62	4.63	3/3/71-3/17/71
7	2.49	2.11	2.03	2.06	3.66	2.92	2.55	3/17/71-3/31/71
8	6.53	8.05	5.49	6.86	7.87	7.04	6.97	3/31/71-4/29/71
9	8.20	11.51	15.77	8.36	11.66	10.69	11.03	4/29/71-6/3/71
10	3.76	1.12	2.84	3.91	2.57	5.66	3.31	6/3/71-6/23/71
11	0	0	2.51	1.45	1.70	1.65	1.83	6/23/71-7/7/71
12	11.20	7.06	8.25	13.94	6.86	8.33	9.24	7/7/71-8/6/71
13	8.66	24.21	19.51	11.51	19.84	26.31	18.34	8/6/71-8/30/71
14	10.03	13.36	15.93	14.20	11.79	9.37	12.45	8/30/71-10/1/71
15	NA	5.23	5.44	6.10	5.89	5.28	5.59	10/1/71-10/16/71
16	NA	10.44	8.13	11.46	13.64	8.03	10.34	10/16/71-11/13/71
17	Inc.	9.60	10.21	9.02	9.30	9.83	9.59	11/13/71-12/4/71
18	3.66	1.42	4.39	4.09	4.93	4.22	3.79	12/4/71-12/19/71
19	1.40	5.33	5.26	5.49	4.80	5.36	4.61	12/19/71-1/8/72
20	1.73	3.81	2.97	3.33	3.18	2.08	2.85	1/8/72-1/24/72
21	2.82	3.96	4.65	3.89	4.52	3.36	3.91	1/24/72-2/5/72
22	9.78	8.86	7.47	8.51	9.14	6.76	8.42	2/5/72-2/25/72
23	6.86	8.53	10.19	11.02	8.10	7.62	8.72	2/25/72-3/18/72
24	6.60	6.96	5.46	5.44	4.75	4.06	5.55	3/18/72-4/15/72
25	6.88	7.06	7.54	8.97	8.18	7.59	7.70	4/15/72-4/30/72
26	6.15	7.14	6.07	7.29	8.79	9.60	7.51	4/30/72-5/15/72
27	4.55	5.31	6.07	5.00	3.12	4.42	4.75	5/15/72-5/29/72
28	3.02	2.08	3.12	2.90	2.29	2.11	2.59	5/29/72-6/12/72
29	10.46	8.71	11.58	7.95	12.32	12.19	10.54	6/12/72-6/27/72
30	4.06	9.47	7.59	4.52	4.14	4.04	5.64	6/27/72-7/10/72
31	1.60	3.81	3.18	1.12	8.66	4.70	3.85	7/10/71-7/24/72
32	0.91	5.00	0.74	0.96	1.85	1.95	1.90	7/24/72-8/8/72
33	3.33	23.98	6.22	2.36	5.11	2.13	7.19	8/8/72-9/7/72
34	6.20	4.17	2.92	5.84	3.73	5.28	4.69	9/7/72-9/30/72
35	6.60	15.27	20.80	14.02	15.72	16.46	14.81	9/30/72-10/31/72
36	–	15.65	15.62	15.98	17.55	16.84	16.33	10/31/72-11/17/72
37	–	6.25	6.27	8.38	6.73	6.25	6.78	11/17/72-12/1/72
38	–	6.22	9.70	5.92	8.61	8.69	7.83	12/1/72-12/15/72
39	–	8.58	9.80	9.86	8.81	8.05	9.02	12/15/72-12/31/72
Total	155.49	288.56	295.33	263.65	283.47	267.56	272.52	
Avg.	5.18	7.40	7.57	6.76	7.27	6.86	6.99	
Total Precip./ Yr.	99.92	140.62	145.38	128.48	138.14	130.39	132.80	

APPENDIX II: RIVER WATER SAMPLES

Site	Name	LORDS coordinates	Sampling Period	No. Samples
Cedar Creek				
Ca	Lanoka Harbor	33-12-377	11-23-70—12-15-72	31
Cb	Double Trouble	33-12-152	11-29-70—12-15-72	29
Cc	Factory Branch	33-11-282	12-24-70—12-15-72	28
Cd	Dover Forge	33-01-876	12- 5-70— 1- 8-72	16
Ce	Bamber	33-11-125	11-23-70—12- 4-71	16
Cf	Bamber Lake	33-11-143	12- 4-70— 6-23-71	9
Cg	Cooks Branch	33-11-115	12- 4-70—12-15-72	28
Ch	N. Fork, Webbs Mill Br.	32-14-327	12- 4-70—12- 4-71	15
Ci	S. Fork, Webbs Mill Br.	32-14-352	11-23-70—12-15-72	29
Cj	Chamberlain Branch	32-14-661	11-29-70—12- 4-71	15
Ck	Dover Road	33-01-797	12- 4-70—12- 4-71	16
Reconnaissance Sites				
Ra	Batsto River	32-11-998	11-28-70—12- 9-71	12
Rb	Roberts Branch	32-22-119	11-28-70—12- 9-71	13
Rc	Skits Branch	32-22-143	11-28-70— 1-24-72	14
Rd	W. Branch, Wading R.	32-23-435	11-28-70—12- 9-72	12
Re	Shoal Branch, Wading R.	32-23-436	11-28-70—12-19-71	12
Rf	Wading River	32-33-191	11-29-70—12-31-72	24
Rg	N. Branch, Forked R.	33-12-813	11-23-70—12-31-72	24
Rh	E. Branch, Bass R.	32-34-737	2- 7-71—12-31-72	22
Ri	W. Branch, Bass R.	32-34-729	3-10-71—12-31-72	21
Rj	Lower Mullica R.	32-32-729	7- 7-71—12-31-72	17
Rk	Tuckerton Creek	32-35-797	6- 4-71—12-31-72	18
Rl	Cedar Run	33-31-268	6-14-71—12-31-72	18
Rm	Mill Creek	33-31-315	6-14-71—12-31-72	18
Rn	Jakes Branch	33-02-495	7- 8-71—12-31-72	18
Ro	Wrangle Brook	33-02-414	6-14-71—12-31-72	19
Rp	Hammonton Creek	32-31-916	12-19-71—12-31-72	13
Ga	Toms River	33-02-423	12- 5-70—12-31-72	25
Gb	Oyster Creek	33-21-322	12- 4-70—12-31-72	24
Gc	Westecunk Creek	33-21-498	12- 5-7-—12-31-72	24
Gd	Oswego River	32-33-513	11-28-70—12-31-72	24
Ge	Batsto River	32-32-482	11-29-70—12-31-72	24
Gf	Mullica River	32-32-473	2- 7-71—12-31-72	19
			Total	647

APPENDIX III: IRON AND ALUMINUM SOLUBILITY CALCULATIONS

The program to calculate Fe solubility, named FESOL, calculates the solubilities of 24 different Fe solution species, including Fe^{2+}, Fe^{3+}, and 22 ferrous and ferric hydroxy, chloro, sulfate, and fluoro species relative to amorphous Fe $(OH)_3$. Previous work (Hem, 1970; Langmuir and Whittemore, 1971) has established that amorphous Fe $(OH)_3$, goethite, lepidocrocite, and siderite are the most significant solid phases in the solubility range of most natural solutions. Amorphous Fe $(OH)_3$ was chosen for this study because of its ubiquitous presence as particle coatings in the Cohansey Formation, as floccules on Pine Barrens stream bottoms, and in the suspended load of stream waters. Amorphous Fe $(OH)_3$ is also the dominant Fe oxide/hydroxide constituent (except for traces of goethite) of Pine Barrens bog iron.

The program's input variables are pH, Eh, $[Cl^-]$, $[SO_4^{2-}]$, $[F^-]$, ionic strength, and the analytical dissolved Fe concentration. Cl^-, SO_4^{2-}, and F^- may be input as either concentrations or activities. Activity coefficients of all input and output species are calculated from the extended Debye-Huckel equation (Truesdell and Jones, 1974). If input variable is a concentration rather than activity, it is assumed that the free ligand concentration $[L^a]$ is equal to the total input ligand concentration $[\Sigma L]$. That is, in theory the total input ligand concentration $[\Sigma L]$ is equal to the free ligand concentration $[L^a]$ plus the sum of all the Fe-ligand concentrations $[FeL^b] + 2[FeL_2{}^c]$, etc. Here, in order to simplify the computer program, it is assumed that the $[L^a] >> [FeL^b] + 2[FeL_2{}^c]$, etc., and therefore $[L^a] \approx [\Sigma L]$. In several hundred Pine Barrens stream and estuary samples analyzed thus far, this assumption holds true. The solubility calculations are performed as shown below. All calculations were carried out for temperature = 298.15 K.

First, equilibrium activities of the species Fe^{2+} and Fe^{3+} are calculated from the $\Delta G_r{}^o$ of the appropriate species (Garrels and Christ, 1965):

$$Fe^{2+} + 3H_2O(\ell) = 3H^+ + Fe\,(OH)_3\ (amor) + e^-. \qquad (1)$$

$$\Delta G_r^\circ = \Delta G_f^\circ (\text{products} - \text{reactants})$$

$$\Delta G_r^\circ = +\,24.46\ (\text{kcal})$$

$$\Delta G_r^\circ = n\epsilon^\circ F$$

$$\epsilon^\circ = \frac{24.46}{1 \times 23.06} = 1.061$$

From the Nernst equation:

$$Eh = \epsilon^\circ + \frac{RT}{nF}\log K$$

$$Eh = 1.061 + \frac{0.0592}{1}\log\left(\frac{[H^+]^3}{[Fe^{2+}]}\right)$$

which reduces to:

$$\log\,[Fe^{2+}] = \frac{1.061 - Eh - 0.1776\,[pH]}{0.0592} \qquad (2)$$

Given Eh and pH, equation (2) can be easily solved. The calculation for $[Fe^{3+}]$ is similar except that no redox is occurring and consequently Eh is not a factor.

$$Fe^{3+} + 3H_2O\ (\ell) = 3H^+ + Fe\,(OH)_3\ (amor) \qquad (3)$$

$$\Delta G_r^\circ = \Delta G_f^\circ (\text{reactants} - \text{products}) = +6.71\ (\text{kcal})$$

$$\Delta G_r^\circ = -RT\,\ell n\,K$$

$$\Delta G_r^\circ = 1.346\log\left(\frac{[H+]^3}{[Fe^{3+}]}\right)$$

$$\log\,[Fe^{3+}] = (6.71 - 4.092\,pH)/1.364 \qquad (4)$$

The ferrous and ferric hydroxy, chloride, sulfate, and fluoride complex concentrations may then be calculated from $[Fe^{2+}]$ or $[Fe^{3+}]$ and the appropriate stability constant. Using $Fe(OH)^+$ and $Fe(SO_4)^+$ as examples:

$$Fe^{2+} + OH^- = Fe(OH)^+ \tag{5}$$

$$K = 10^{4.5} = \frac{[Fe(OH)^+]}{[Fe^{2+}][OH^-]}$$

$$\log [Fe(OH)^+] = 4.5 + \log [Fe^{2+}] - (14 - pH) \tag{6}$$

and

$$Fe^{3+} + SO_4^{2-} = FeSO_4^+ \tag{7}$$

$$K = 10^{4.04} = \frac{[Fe(SO_4)^+]}{[Fe^{3+}][SO_4^{2-}]}$$

$$\log [Fe(SO_4)^+] = 4.04 + \log [Fe^{3+}] + \log [SO_4{}^{2-}] \tag{8}$$

The cumulative sum of the concentrations of all 24 Fe complexes is the total Fe solubility at a given set of chemical conditions. Comparison of the theoretical Fe solubility with the measured dissolved Fe concentrations indicates the saturation state of the H_2O with respect to amorphous $Fe(OH)_3$.

In the program to calculate Al solubility, named ALSOL, a similar approach is employed to compute equilibrium concentrations of 15 different solution species. The solubilities of Al^{3+} and various hydroxy, fluoro, and sulfate species, are calculated relative to four different solids: kaolinite, halloysite, gibbsite, and amorphous $Al(OH)_3$. Kaolinite, halloysite, and gibbsite were chosen as solid phases because all are common products of chemical weathering (Garrels and MacKenzie, 1971; Parham, 1969; Wilson, 1969; Bricker et al., 1968). Although amorphous $Al(OH)_3$ is the most stable phase, crystallization of gibbsite occurs within a few weeks from supersaturated solutions (Hem and Roberson, 1967; Smith and Hem, 1972).

Input variables in this case are pH, total $[F]$, $[SO_4^{2-}]$, $[H_4SiO_4]$ ionic strength, and the analytical dissolved Al concentration. Eh is not needed because Al is always trivalent in environmental systems. Note that H_4SiO_4 is the dominant solution specie of silica up to pH 9.2, (Stumm and Morgan, 1970) well above the highest pH of any sample evaluated in this study. Activity coefficients of all input and output species, as in FESOL, are calculated from the extended Debye-Huckel equation.

Calculations for Al^{3+}, sulfate, and hydroxy species are based on the same approach used in computing Fe^{3+} and ferric complexes, as illustrated in equations (3), (4), (7), and (8) above. Al^{3+} solubilities relative to kaolinite, halloysite, gibbsite, and amorphous $Al(OH)_3$ are computed from the free energies of formation of reactants and products, pH, and H_4SiO_4 concentrations as illustrated below.

$$Al(OH)_{3\,(amor)} + 3H^+ = Al^{3+} + 3H_2O \tag{9}$$

$$\log [Al^{3+}] = 9.58 - 3pH \tag{10}$$

$$Al(OH)_{3\,(gibb)} + 3H^+ = Al^{3+} + 3H_2O \tag{11}$$

$$\log [Al^{3+}] = 8.10 - 3pH \tag{12}$$

$$Al_2Si_2O_5(OH)_{4\,(hall)} + 6H^+ = 2Al^{3+} + 2H_4SiO_4 + H_2O \tag{13}$$

$$\log [Al^{3+}] = 4.57 - \log [H_4SiO_4] - 3pH \tag{14}$$

$$Al_2Si_2O_5(OH)_{4\,(kaol)} + 6H^+ = 2Al^{3+} + 2H_4SiO_4 + H_2O \tag{15}$$

$$\log [Al^{3+}] = 2.94 - \log [H_4SiO_4] - 3pH \tag{16}$$

The Al hydroxy and sulfate complex concentrations relative to each solid phase may then be calculated from $[Al^{3+}]$, pH, and the appropriate stability constant as shown below, using $Al(OH)_4^-$ and $Al(SO_4)_2^-$ as examples.

$$Al^{3+} + 4(OH)^- = Al(OH)_4^- \tag{17}$$

$$\log[Al(OH)_4^-] = 33.0 + \log[Al^{3+}] - 4(14\text{–pH}) \tag{18}$$

$$Al^{3+} + 2SO_4^{2-} = Al(SO_4)_2^- \tag{19}$$

$$\log[Al(SO_4)_2^-] = -3.61 + \log[Al^{3+}] + 2\log[SO_4^{2-}] \tag{20}$$

As in FESOL, if input SO_4^{2-} value is a concentration rather than activity, it is assumed that the free sulfate concentration $[SO_4^{2-}]$ is equal to the input concentration $[\Sigma SO_4]$, that is, that $[SO_4^{2-}] >> [Al(SO_4)^+] + 2[Al(SO_4)_2^-]$. While this is a good assumption for the Pine Barrens samples analyzed thus far, the same relationship does not hold true for F^- and Al fluoride complexes. The stability constants for AlF^{2+}, AlF_2^+, and AlF_3 are very high. Therefore $[AlF^{2+}] + 2[AlF_2^+] + 3[AlF_3]$ is usually $>> [F^-]$. If $[F^-]$ is input into the program as an activity, astronomical Al fluoride activities are often predicted, throwing doubt on the validity of the input F^- activities. Consequently a different approach is employed in the program to calculate Al fluoride complex solubilities. $[F^-]$ is input as a total concentration value, $[\Sigma F]$. ΣF is iteratively speciated into $[F^-]$, $[AlF^{2+}]$, $[AlF_2^+]$, etc. until the sum of all the species is within ±1% of the input $[\Sigma F]$.

Finally, the total Al solubility is expressed as the cumulative sum of the concentrations of all 15 species. Comparison of the theoretical Al solubility values with the measured dissolved Al content indicates the saturation state of the H_2O with respect to the four solids considered: kaolinite, halloysite, gibbsite, and amorphous $Al(OH)_3$.

Fe reactions		**log K**	**reference**
$Fe^{2+} + OH^-$	$= Fe(OH)^+$	4.5	Smith and Martell (1976)
$Fe^{2+} + 2OH^-$	$= Fe(OH)_2^\circ$	7.4	Smith and Martell (1976)
$Fe^{2+} + 3OH^-$	$= Fe(OH)_3^-$	10.0	Smith and Martell (1976)
$Fe^{2+} + 4(OH)^-$	$= Fe(OH)_4^{2-}$	9.6	Smith and Martell (1976)
$Fe^{2+} + SO_4^{2-}$	$= FeSO_4^\circ$	2.2	Smith and Martell (1976)
$Fe^{2+} + F^-$	$= FeF^+$	0.8	Smith and Martell (1976)
$Fe^{2+} + Cl^-$	$= FeCl^+$	0.36	Sillen and Martell (1964)
$Fe^{2+} + 2Cl^-$	$= FeCl_2^\circ$	0.04	Sillen and Martell (1964)
$Fe^{3+} + OH^-$	$= Fe(OH)^{2+}$	11.81	Smith and Martell (1976)
$Fe^{3+} + 2OH^-$	$= Fe(OH)_2^+$	22.3	Smith and Martell (1976)
$Fe^{3+} + 3OH^-$	$= Fe(OH)_3^\circ$	28.39	calculated from ΔG_f° above
$Fe^{3+} + 4OH^-$	$= Fe(OH)_4^-$	34.4	Smith and Martell (1976)
$2Fe^{3+} + 2OH^-$	$= Fe_2(OH)_2^{4+}$	25.1	Smith and Martell (1976)
$3Fe^{3+} + 4OH^-$	$= Fe\ \ (OH)_4^{5+}$	49.7	Smith and Martell (1976)
$Fe^{3+} + SO_4^{2-}$	$= FeSO_4^+$	4.04	Smith and Martell (1976)
$Fe^{3+} + 2SO_4^{2-}$	$= Fe(SO_4)_2^-$	5.38	Smith and Martell (1976)
$Fe^{3+} + F^-$	$= FeF^{2+}$	6.2	Nordstrom and Jenne (1977)
$Fe^{3+} + 2F^-$	$= FeF_2^+$	10.8	Nordstrom and Jenne (1977)
$Fe^{3+} + 3F^-$	$= FeF_3^\circ$	13.8	Nordstrom and Jenne (1977)
$Fe^{3+} + Cl^-$	$= FeCl^{2+}$	1.48	Smith and Martell (1977b)
$Fe^{3+} + 2Cl^-$	$= FeCl_2^+$	2.13	Smith and Martell (1977b)
$Fe^{3+} + 3Cl^-$	$= FeCl_3^\circ$	1.13	Sillen and Martell (1964)

Gibbs free energies and stability constants for all relevant species are tabulated below.

Gibbs Free Energies ΔG_f°

species		**reference**
H_2O	–56.7 kcal/mole	Wagman et al. (1969)
H^+	0.0 kcal/mole	Wagman et al. (1969)
H_4SiO_4 (aq)	–312.7 kcal/mole	B.S. Hemingway, personal communication, (1978)
Fe^{2+}(aq)	–18.85 kcal/mole	Wagman et al. (1969)
Fe^{3+} (aq)	– 1.1 kcal/mole	Wagman et al. (1969)
$Fe(OH)_3^\circ$	–152.62 kcal/mole	Langmuir (1969)
Al^{3+} (aq)	–117.0 kcal/mole	Hemingway and Robie (1977b)
$AlSO_4^+$(aq)	–296.7 kcal/mole	Hem (1968)
$Al(SO_4)_2^-$ (aq)	–476.6 kcal/mole	Hem (1968)
$Fe(OH)_3$ (amorphous)	–164.49 kcal/mole	Langmuir (1969)
$Al_2Si_2O_5(OH)_4$ (kaolinite)	–908.07 kcal/mole	Hemingway and Robie (1977a)
$Al_2Si_2O_5(OH)_4$ (halloysite)	–903.63 kcal/mole	Hemingway and Robie (1977a)
$Al(OH)_3$ (gibbsite)	–276.02 kcal/mole	Hemingway and Robie (1977a)
$Al(OH)_3$ (amorphous)	–274.00 kcal/mole	estimated

Al reactions	**log K**	**reference**
$Al^{3+} + OH^{-} = Al(OH)^{2+}$	9.01	Smith and Martell (1976)
$Al^{3+} + 2OH^{-} = Al(OH)_2^{+}$	18.7	Smith and Martell (1976)
$Al^{3+} + 3OH^{-} = Al(OH)_3^{\circ}$	27.0	Smith and Martell (1976)
$Al^{3+} + 4(OH)^{-} = Al(OH)_4^{-}$	33.0	Smith and Martell (1976)
$2Al^{3+} + 2(OH)^{-} = Al_2(OH)_2^{4+}$	20.3	Smith and Martell (1976)
$3Al^{3+} + 4(OH)^{-} = Al_3(OH)_4^{5+}$	42.1	Smith and Martell (1976)
$Al^{3+} + F^{-} = AlF^{2+}$	7.0	Smith and Martell (1976)
$Al^{3+} + 2F^{-} = AlF_2^{+}$	12.6	Smith and Martell (1976)
$Al^{3+} + 3F^{-} = AlF_3^{\circ}$	16.7	Smith and Martell (1976)
$Al^{3+} + 4F^{-} = AlF_4^{-}$	19.1	Smith and Martell (1976)
$Al^{3+} + 5F^{-} = AlF_5^{2-}$	19.4	Smith and Martell (1976)
$Al^{3+} + 6F^{-} = AlF_6^{3-}$	19.8	Smith and Martell (1976)
$Al^{3+} + SO_4^{2-} = AlSO_4^{+}$	–1.73	calculated from ΔG_r° above
$Al^{3+} + 2SO_4^{2-} = Al(SO_4)_2^{-}$	–3.61	calculated from ΔG_r° above

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