GROUNDWATER COLLOIDS
IN TWO ATLANTIC COASTAL PLAIN AQUIFERS:
COLLOID FORMATION AND STABILITY

by

Joseph Nolte Ryan Jr.
B.S.E., Civil Engineering
Princeton University
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Submitted in partial fulfillment
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ABSTRACT

Colloids play a significant role in the enhancement of transport of hazardous pollutants in the subsurface environment, yet very little is known about their nature and distribution in groundwater. The difficulty in sampling for groundwater colloids is a major hindrance in understanding their behavior.

In this investigation, groundwater was sampled from two pristine aquifers in New Jersey and Delaware Coastal Plain sediments to characterize the colloidal population. The methods of groundwater sampling for colloids developed by Backhus et al. (1986) were refined by monitoring the stabilization of colloid concentration in the field using light scattering analysis. The importance of removing groundwater from the well at low pumping rates (100 mL/min) was demonstrated by calculations of the pumping-induced shear stress on particles in the aquifer and by comparison of the particle size distribution produced by high (1 L/min) and low pumping rates.

The nature and distribution of the groundwater colloidal matter was characterized by scanning electron microscopy and energy-dispersive X-ray analysis, light scattering, and metals and organic carbon determination. The inorganic colloids observed were mainly dispersed clay particles in the <100 nm to 3 μm size range at concentrations as high as 60 mg/L. Colloidal hydrous oxides of iron, aluminum, and titanium were also detected and appeared to be formed by both dispersion and in situ precipitation. Colloidal organic carbon was present in all groundwaters; but in groundwaters containing inorganic colloids, one-third to one-half of the organic carbon was associated with inorganic particles.

Wide variations of colloid abundance observed between groundwaters sampled from nearby wells were attributed to the effects of local geology and hydrology on groundwater chemistry, colloid formation, and colloid stability. The results indicate that anoxic conditions induce colloid formation by reducing the Fe(III) that apparently binds clay particles to aquifer surfaces, and organic carbon coatings stabilize the inorganic colloidal suspension in the groundwater.

The results suggest that the typical geochemical conditions in pollutant plumes may promote colloid formation and stability, leading to enhanced migration of hazardous pollutants.

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CHAPTER 1. THE IMPORTANCE OF COLLOIDS IN GROUNDWATER

1.1. Introduction

Only recently has it become apparent that the transport of organic pollutants, heavy metals, and radioactive materials in groundwater is enhanced by the presence of particles suspended in the groundwater. The suspended particles consist of a diverse group of mobile colloidal organic and inorganic materials that are capable of sorbing contaminants to their surfaces, similar to the sorption of contaminants to immobile aquifer sediments. Many contaminants, particularly hydrophobic organic compounds and low-solubility metal and radionuclide species, are strongly sorbed to aquifer sediments. The fate of these contaminants is often predicted by assessing the partitioning of the contaminant between the dissolved, mobile phase and the sorbed, stationary phase; thus, sorption mitigates the potential hazard of these contaminants in groundwater by the retardation of their transport. In the presence of colloids, a portion of the contaminant is partitioned to a sorbed, mobile phase. The environmental significance of groundwater colloids lies in their ability to enhance the transport of hydrophobic and insoluble contaminants that are expected to be immobile in the aquifer.

The nature of colloidal material in groundwater is poorly understood. The standard methods of collection and preservation of groundwater produce samples that are not representative of the natural colloidal distribution. The composition, size, shape, and surface properties of the colloidal material are difficult to characterize due to the diversity of colloidal material and the limitations of standard analytical procedures, including filtration and microscopy.

Groundwater colloids can be distinguished as particles that remain suspended in the natural groundwater flow, in the parlance of this investigation. Such
particles cover a size range spanning from the upper limits of truly dissolved molecules, 1 to 2 nanometers, to the size of particles that readily settle out of the groundwater flow, a few micrometers. A variety of organic and inorganic materials exist as colloids in groundwater (Stumm and Morgan, 1981; Thurman, 1986), including:

- Components of "dissolved" organic carbon (1 nm to 0.45 μm), including proteins, humic substances, and other organic polymers;
- Organisms, including bacteria (0.5 μm to 2 μm) and viruses (20 to 200 nm);
- Microemulsions of immiscible fluids in water (10 nm to 1 μm);
- Mineral precipitates (10 nm to 1 μm), most notably iron, aluminum, and calcium hydroxides, carbonates, silicates, and phosphates; and
- Rock and mineral fragments (10 nm to a few μm), including clays, oxides, silica, and other weatherable rocks and minerals.

The components of dissolved organic carbon in the 1 to 2 nm range behave in many ways as true dissolved components; however, dispersed humic substances fall into this size range and they are considered colloidal based on their coagulation behavior in the presence of Ca\(^{2+}\) and Mg\(^{2+}\) (Stumm and Morgan, 1981). Furthermore, humic substances frequently interact with the surfaces of inorganic particles to form organic coatings; thus, the surface properties of humic substances must be considered in determining the effect of colloids on contaminant transport.

Colloids can be grouped as hydrophilic and hydrophobic colloids, although a gradual transition exists between the two classes. Hydrophilic colloids have a strong affinity for water; humic substances, proteins, bacteria, and viruses are hydrophilic colloids. Hydrophobic colloids have a negligible affinity for water; nonhydrated metal oxides are typical hydrophobic colloid systems. Many colloids in aqueous systems contain bound H\(_2\)O at their surfaces. Amorphous silica and metal
hydroxides are at least partially solvated, thus they are intermediate between hydrophilic and hydrophobic (Stumm and Morgan, 1981).

The goal of this investigation is to evaluate the natural colloidal load of relatively pristine groundwater. Our criteria for selecting sampling sites led us to two Atlantic Coastal Plain aquifers in New Jersey's Pine Barrens and central Delaware to study the nature and distribution of colloids in groundwater. In this chapter, we will first outline the theory of colloid stability in natural waters by examining the forces of interaction between particle surfaces. Colloid mobility will next be addressed by reviewing the theory of colloid transport with respect to coagulation and filtration. We will then draw on a number of field observations and laboratory experiments that elucidate the factors affecting colloid mobility in groundwater. Next, we will review the environmental fate of two important types of pollutants, hydrophobic organic compounds and long-lived radionuclides, in groundwater. The colloidal transport of these pollutants has been documented in a number of field and laboratory studies. Finally, we will present the goals of this investigation in detail in the final section of this chapter.
1.2. **Colloid Stability and Colloid Transport Theory**

The stability of colloids in groundwater depends on forces of interaction between similar particles, between particles and the aquifer solids, and between particles and gravity. The first interaction controls aggregation and disaggregation, or coagulation and peptization, of the suspended particles. The second interaction governs the attachment and detachment of particles to the immobile aquifer surfaces. The third interaction dictates the removal of particles from suspension by sedimentation. Particle coagulation and attachment are influenced by forces of repulsion and attraction between approaching surfaces. The DLVO theory of colloid stability, developed independently by two groups of researchers, Derjagin and Landau and Verwey and Overbeek (1948), evaluates the balance of attractive and repulsive forces between surfaces. The DLVO theory considers London–van der Waals' attractive forces between particles and coulombic repulsive forces generated by the diffuse double layers of charge surrounding the particles. The total energy of interaction between particles, or between particles and aquifer surfaces, is calculated by determining the amount of work necessary to bring two surfaces closer together, from an infinite distance to some distance \( h \), the interaction distance between the surfaces. The total potential energy \( V_T \) is the sum of the repulsive potential energy \( V_R \) and the attractive potential energy \( V_A \):

\[
V_T = V_R + V_A
\]  

(1.1)

The potential energies of repulsion and attraction have been derived for many model systems of surfaces, such as flat plates, spheres, flat plate–sphere, flat plate–cylinder, and others. The plate–plate model is a good approximation of many surface geometries because the particle dimensions are usually much larger than the distances of separation between particles. The repulsive energy between two flat
plates, $V_R$ ($J/m^2$), assuming a constant surface potential condition, is (Hogg et al., 1966)

$$V_R = \frac{\varepsilon \kappa}{8 \pi} [(\psi_1^2 + \psi_2^2) (1 - \coth \kappa h) + 2 \psi_1 \psi_2 \operatorname{csch} \kappa h]$$  \hspace{1cm} (1.2)

where $\varepsilon$ is the dielectric constant of the solution (for water at 25°C, $\varepsilon = 78.54$), $\kappa$ is the reciprocal of the double layer thickness (m$^{-1}$), approximated by $\kappa^{-1} = 2.8 \times 10^{-8}$ m$^{-1}$ in dilute solutions at 25°C, where $I$ is the ionic strength of the solution (M), $\psi_1$ and $\psi_2$ are the surface potentials of the interacting plates (V), and $h$ is the interaction distance between the two plates. The repulsive energy decreases with increasing separation distance and increases roughly in proportion to the surface potentials.

The separation distance characterizing the maximum repulsive interaction is similar in magnitude to the thickness of the double layer ($\kappa^{-1}$); thus, the range of repulsion depends primarily on the ionic strength of the solution (Stumm and Morgan, 1981). The attractive energy between two flat plates, $V_A$ ($J/m^2$), is (Verwey and Overbeek, 1948)

$$V_A = -\frac{A}{12 \pi h^2}$$  \hspace{1cm} (1.3)

where $A$ is the Hamaker constant (J). The Hamaker constant varies between $10^{-20}$ and $10^{-19}$ J, depending on the density and polarizability of the particles. It is essentially independent of the ionic composition of the solution. The criteria for determining colloidal stability is defined by $V_T = 0$ and $\partial V_T / \partial h = 0$, where $\partial V_T / \partial h$ is the total force acting on the particles. At total potential energies greater than $V_T = 0$, colloids are stable because a repulsive energy barrier exists between the particles that inhibits the approach of the surfaces. If that energy barrier is overcome by forces driving the motion of the particles in suspension, destabilization of the colloidal suspension occurs as particles move into a region of strong attractive energy at short separation distances.

As an example of the application of the DLVO theory, the interaction energy between kaolinite particles and quartz grains in the aquifer calculated by Kia et al.
(1987) is shown in Figure 1.1 for four different ionic strengths. The surface potentials were estimated by measuring the electrophoretic mobilities of kaolinite and quartz particles at different ionic strengths. The attractive potential energy was calculated using a value of $A = 4.4 \cdot 10^{-20} \text{J}$, taken from Flegmann et al. (1969).

At small separations, the attractive energy greatly exceeds the repulsive energy between the particle surfaces. At high ionic strengths, the range of the repulsion is reduced and the attractive energy dominates at all distances, hence the kaolinite particles would be expected to adhere to the quartz grains. At lower ionic strengths, a repulsive energy barrier arises that inhibits the attachment of kaolinite to quartz. Kia et al. (1987) were studying the case of kaolinite detachment from quartz grains. Based on these potential energy calculations, they predicted that decreasing the ionic strength to $I < 0.038 \text{ M}$ (for which the maximum total potential energy just reached $V_T = 0$) would cause the kaolinite particles to detach from the quartz grains. In their laboratory columns, they observed kaolinite detachment at ionic strengths of $I = 0.03$ to $0.04 \text{ M}$, similar to the predicted value.

The effects of chemical factors on colloid stability must also be considered for particles in natural waters. The concentration and valency of electrolytes in solution strongly affect the electrostatic interaction between surfaces of charged particles. Adsorption of multivalent cations, in particular $\text{Fe}^{3+}$ and $\text{Al}^{3+}$ and their hydrolysis products, can reduce and actually reverse the charge of hydrophilic surfaces. The response of colloids with different surface functional groups to the presence of multivalent cations is varied because the coordination chemistry of the different surface groups toward cations can be dramatically different. The adsorption of anions, such as phosphates, silicates, and organic substances containing hydroxyl or carboxyl groups, can also alter the surface charge of hydrophilic surfaces. The reduction of surface charge by the adsorption of various electrolytes can substantially increase the coagulation rate of colloids and decrease
Figure 1.1. Total Potential Energy vs. Distance of Separation between Two Flat Plates at Different Ionic Strengths (after Kia et al., 1987)
the critical coagulation concentration (Stumm and Morgan, 1981).

The DLVO theory of colloid stability is commonly applied to the behavior of suspended particle coagulation and transport through porous media. The coagulation and transport of particles is governed by the frequency of particle–particle and particle–aquifer surface collisions and the interactions between the particles' surfaces. The DLVO theory is used to estimate the collision efficiency \( \alpha \), a parameter that describes the "stickiness" of the collisions. The collision efficiency is a ratio of the number of particle collisions that result in aggregation of particles to the total number of particle collisions. For fresh waters, \( \alpha \) typically ranges from \( 10^{-6} \) to \( 10^{-4} \), while in salt water, \( \alpha \) is in the range of 0.1 to 1 as the double layers of the particles are compressed (Stumm, 1977).

The transport of colloids through porous media can be examined by applying the theoretical concepts developed for analyzing the performance of waste water filtration beds. The removal of particles from suspension depends on the frequency of collisions between particles and the aquifer surface and the collision efficiency factor \( \alpha \). The frequency of collisions between particles and surfaces is controlled by three processes: interception, sedimentation, and diffusion (Yao et al., 1971). Interception is contact between the particle and the aquifer surface as the particle diverges from the streamline of the flow path due to its inertia. Sedimentation is the influence of gravity on the path of particles more dense than water. Diffusion is the transport of particles by thermal agitation.

The general equation describing the variation of suspended particle concentration in a porous medium is derived by Yao et al. (1971) from a mass balance of the particle concentration \( C \) about an elemental volume of suspension:

\[
\frac{\partial C}{\partial t} + \nu \nabla C = D_B \nabla^2 C + \left( 1 - \frac{\rho_f}{\rho_p} \right) \frac{mg}{3 \pi \mu f_d p} \frac{\partial C}{\partial z}
\]  

(1.4)

where \( t \) is the time, \( \nu \) is the groundwater velocity, \( D_B \) is the Brownian diffusion
coefficient of the particles, \( \rho_f \) is the fluid density \((g/cm^3)\), \( \rho_p \) is the particle density \((g/cm^3)\), \( m \) is the particle mass, \( g \) is the gravitational acceleration \((cm/sec^2)\), \( \mu_f \) is the fluid dynamic viscosity \((g/cm\cdot sec, or poise)\), \( d_p \) is the particle diameter, and \( z \) is the coordinate in the direction of the gravitational force. The second term of the left hand side of equation (1.4) describes the effects of advection on the particle concentration. The first term of the right hand side of equation (1.4) describes the effects of diffusion and the second term characterizes sedimentation. The effects of interception are included in the boundary conditions used to numerically integrate the equation.

The efficiency of a porous medium for particle removal (the goal of wastewater filtration) is quantified by the number of contacts between particles and the aquifer surface in a term called the single-collector efficiency, \( \eta \). The single-collector is a single grain of the aquifer unaffected by its neighbors and stationary in space. Yao et al. (1971) defined the single-collector efficiency as

\[
\eta = \frac{\text{rate at which particles strike the collector}}{v_o C_o (\pi d_c^2/4)}
\]

where \( v_o \) and \( C_o \) are the groundwater velocity and suspended particle concentration where the flow pattern is undisturbed by the presence of the collector, and \( d_c \) is the diameter of the collector grain. To determine the rate at which particles strike the collector, the distribution of particles near the surface is evaluated by integrating (1.4) numerically, assuming steady state concentration \((\partial C/\partial t = 0)\), laminar flow around the collector, and boundary conditions of \( C = C_o \) at infinite distance from the collector and \( C = 0 \) at a distance of \((d_c + d_p)/2\), where \( d_p \) is the suspended particle diameter, from the center of the collector. Particle fluxes are determined across the surface of the collector from the concentration gradients to assess the rate at which particles strike the collector.
The analytical determinations of $\eta$ for single transport mechanisms given by Yao et al. (1971) can be used to illustrate the contribution of each mechanism to the overall single-collector efficiency. The contribution of diffusion, $\eta_D$, to the total single-collector efficiency $\eta_T$ is

$$\eta_D = 0.9 \left( \frac{kT}{\mu_f \rho_p d_c v_o} \right)^{2/3}$$  \hspace{1cm} (1.5)

where $k$ is the Boltzmann constant (1.381·10^{-16} erg/K) and $T$ is the absolute temperature. For the contribution of interception, $\eta_I$,

$$\eta_I = \frac{3}{2} \left( \frac{d_p}{d_c} \right)^2$$  \hspace{1cm} (1.6)

and for sedimentation, $\eta_G$,

$$\eta_G = \frac{(\rho_p - \rho_f) g d_p^2}{18 \mu_f v_o}$$  \hspace{1cm} (1.7)

The total single-collector efficiency can be approximated by a sum of the analytical expressions:

$$\eta_T = \eta_D + \eta_I + \eta_G$$  \hspace{1cm} (1.8)

The single-collector efficiency of a typical unconsolidated sandy aquifer as a function of particle size is shown in Figure 1.2. The aquifer grain diameter $d_c = 0.25$ mm, the groundwater velocity $v_o = 10^{-4}$ cm/sec, particle density $\rho_p = 2.6$ gm/cm³ for typical clay particles, fluid density $\rho_f = 0.9991$ g/cm³ and fluid viscosity $\mu_f = 0.01139$ poise at $T = 288.15$ K, and the acceleration due to gravity $g = 980$ cm/sec². The prominent feature of Figure 1.2 is low single-collector efficiency for particles in the 100 to 500 nm range. Below this range, particle transport is dominated by Brownian diffusion, and above this range, sedimentation is the important transport mechanism, similar to the analysis of transport processes leading to coagulation. Assuming that the interactions of particles of all sizes with the aquifer surface are similar, colloids in the 100 to 500 nm range are expected to be the most mobile under typical aquifer conditions. If the density of the particles...
Figure 1.2. Analytical Determination of Single-Collector Efficiency vs. Particle Diameter (after Yao et al., 1971)

- \( \eta = 10^{-4} \text{ cm/sec} \)
- \( d_c = 0.25 \text{ mm} \)
- \( \rho_p = 2.6 \text{ g/cm}^3 \)
is reduced, then the importance of sedimentation as a transport process diminishes and the minimum $\eta_T$ shifts to larger particles.

From these considerations of the theories of colloid stability and transport in groundwater, we have gained an understanding of the factors that influence the fate of suspended particles. Colloid stability is controlled primarily by the London–van der Waals forces of attraction, the electrostatic repulsion caused by the charge of the diffuse double layer, the ionic strength, and the electrolyte composition of the solution. The transport of colloids through porous media depends on the frequency of collisions between particles and the aquifer surface and the efficiency, or "stickiness" of collisions. Collision frequency is primarily determined by Brownian diffusion for smaller particles and sedimentation for larger particles, while interception plays a minor role for large particles. The particle–aquifer surface interactions described by the DLVO theory determine the collision efficiency. Collision frequency is lowest for relatively dense particles (2.6 g/cm$^3$) in the 100 to 500 nm size range; thus, they are most likely to remain suspended in groundwater. Less dense particles of larger diameters (up to about 1 $\mu$m for $\rho_p = 1.05$ g/cm$^3$) are also more mobile.
1.3. **Colloid Mobility in Field Observations and Laboratory Experiments**

The occurrence of organic and inorganic colloids in groundwater has been noted in the various fields of literature for some time; however, the difficulty of securing representative samples and analyzing them with standard procedures has hindered the accurate characterization of colloid nature and distribution. In this section, we will review a number of investigations of the occurrence and effects of colloids in groundwater.

The distribution of "dissolved" (0.45 μm–filtered) organic carbon (DOC) in groundwaters throughout the United States was measured by Leenheer et al. (1974) and they reported a median concentration of 0.7 mg C/L. These measurements include organic carbon present as coatings of inorganic particles that passed through the membrane filters. Groundwaters of the Southeastern Coastal Plain aquifers generally contain much higher DOC concentrations, 6 to 15 mg C/L, because the low-lying, swampy terrain common in the region generates large quantities of DOC (Leenheer et al., 1974; Feder and Lee, 1981). In groundwaters below swampy areas, the predominant components of DOC are humic and fulvic acids (Oliver et al., 1983; McKnight et al., 1985; Thurman, 1986). Other significant components of groundwater DOC are proteins and amino acids, carbohydrates, hydrocarbons, and carboxylic and phenolic acids. The DOC in shallow groundwaters comes from surface waters and plant degradation in the soil zone; in deep groundwaters, DOC may be formed by the bacterial degradation of kerogen, the fossilized organic matter present in sediments. Deep groundwaters contain less DOC than shallow groundwaters because the source of organic carbon, kerogen, is fairly sparse and because much of the organic carbon in the groundwater has been oxidized during the long residence time in the aquifer (Thurman, 1986).
The mobility of colloidal organic carbon is evident in the dissolved nature of
the smaller organic macromolecules and polyelectrolytes (< 1000 m.w.). The
mobility of larger macromolecules was observed by Robertson et al. (1984) in a
plume of contaminants generated by a waste pulp liquor pit in Quebec. The plume
contained high concentrations of total organic carbon (2000 mg/L) and tannins and
lignins (780 mg/L). The tannins and lignins, which are relatively resistant to
degradation in groundwater, were transported over 800 meters to a discharge point
in a stream. Reinhard (1984) also observed transport of large components of
dissolved organic carbon at a water reclamation facility in California. Over a period
of one and a half years, the organic carbon had achieved a 50 percent breakthrough
at a well 40 meters downstream from the injection point. Enfield and Bengtsson
(1988) studied the mobility of a large organic macromolecule, blue dextran,
approximating the size (2·10^6 m.w.) and hydrophilicity of many natural microbial
polymers in groundwater. Soil column tests showed that blue dextran eluted before
the tritiated water used as a conservative tracer, as expected from experiences with
size exclusion gel chromatography. The inclusion of clay in the sandy soil column
further increased the relative velocity of the blue dextran through the soil column.

The occurrence of bacteria and viruses in groundwater is of great concern to
public health officials because about half of the outbreaks of water-borne diseases
reported every year are caused by bacteria and viruses in groundwater. Keswick et
al. (1982) reviewed the use of microorganisms as tracers in groundwater and
reported bacteria transport of up to 900 meters and virus transport of up to 1600
meters in groundwater. The transport of viruses in groundwater depends on virus
survival rates and migration properties, but these factors are not well understood
(Keswick and Gerba, 1980). Yates et al. (1987) attempted to model the transport of
viruses in groundwater, but their efforts were constrained by the lack of
quantitative data on virus survival and migration. Harvey et al. (1984) studied the
bacterial abundance and distribution in glacial outwash unconfined aquifer on Cape Cod, Massachusetts, contaminated by a plume of treated sewage. The bacteria were about 10 to 50 times more abundant in the contaminated groundwater than in the uncontaminated groundwater. Bacterial counts in the contaminated groundwater ranged from about $1.9 \cdot 10^6$ to $0.25 \cdot 10^6$ ml$^{-1}$ at distances of 0.21 and 0.93 km from the source of the plume. Most of the bacteria (> 97 percent) were attached to aquifer solids. Wilson et al. (1983) characterized the bacterial population of a shallow unconfined aquifer in a floodplain in Oklahoma. They found 3 to $9 \cdot 10^6$ microbes/g dry material, but they did not distinguish between mobile and attached bacteria. The predominant bacteria were small Gram-positive coccoid forms. From these studies, it is apparent that bacteria and viruses are quite mobile in the subsurface, although many of the factors affecting their transport are not well understood.

Historically, the mobility of inorganic colloids in aquifers and soils has concerned hydrologists and petroleum engineers investigating reductions of aquifer permeability, soil scientists studying the effects of soil formation on crop production, and geologists interested in the depositional history of sediments.

Nightingale and Bianchi (1977) observed an increase in groundwater turbidity following recharge of relatively dilute, aerated water (about 50 $\mu$S specific conductivity) into spreading basins in a sandy aquifer in California. The increased turbidity was caused by the dispersion of poorly-crystallized submicron-sized particles in the aquifer. The high turbidity levels were well-correlated with groundwater of low specific conductivity. Nightingale and Bianchi (1977) worried that increased dispersion might reduce the aquifer permeability, thus limiting the usefulness of the recharge basin.

The reduction of aquifer permeability by the mobilization of clay particles is an important concern of petroleum engineers using high-pressure injections of
dilute, aerated water and steam to increase the yield of mature oil fields. Lin (1985) observed an unexpected decrease in the permeability of an Alberta, Canada oil-sand formation during a simulation of steam injection. In a column test, Lin (1985) determined that increased temperatures caused the dispersion of clay particles, which led to the plugging of pores in the formation. The effect of temperature is evident in the full equation describing the reciprocal of the double layer thickness (Stumm and Morgan, 1981):

\[ \kappa = \left( \frac{e^2 \sum_i n_i z_i^2}{\epsilon k T} \right)^{\frac{1}{4}} \]

where \( e \) is the elementary charge of an electron (1.6 \times 10^{-19} \text{ C}) and \( n_i \) and \( z_i \) are the concentration (number/cm³) and valence of the ions in solution. The increase in temperature decreases \( \kappa \), which causes a reduction of the repulsive energy between the surfaces; thus the adhered clay particles are resuspended (Khilar and Fogler, 1984).

Khilar and Fogler (1984) and Kia et al. (1987) performed detailed experiments on the effects of salt concentration and composition and pH on the release of clay particles from sandstone in laboratory columns. The clay particle release was measured by reductions in the hydraulic conductivity of the sandstone core. As discussed in the preceding section, they applied the DLVO theory to predict the critical salt concentration that would cause the release of clay particles. Khilar and Fogler (1984) determined that multivalent cations prevented the release of clay particles due to the strong ion-exchange affinity of the clays—the electrostatic repulsion was substantially reduced by the adsorption of Ca²⁺. The effects of temperature increase were also examined, for which particle release was observed at elevated salt concentrations, indicating the reduction of electrostatic repulsion by an decrease in \( \kappa \), as discussed above. The detachment of particles by the hydrodynamic forces incident on the particles at flow rates of 8.9 \times 10^{-4} \text{ to } 1.6 \times 10^{-1}
cm/sec were determined to be negligible. The calculations of the hydrodynamic force were negligible compared to the London—van der Waals attractive force and the actual increase in flow rates produced no reduction in hydraulic conductivity. Kia et al. (1987) concentrated on the effect of pH on the release of clay particles from the sandstone. At pH < 4.8, the clay particles remain adhered to the quartz surfaces because the electrostatic repulsion between the surfaces is substantially reduced by the adsorption of hydrogen ions.

Champlin (1971) observed the relative transport of a dissolved radionuclide tracer and radio-labeled kaolinite particles in a large test bed of sand. In a solution of distilled water, the transport of the kaolinite particles was stalled by attachment to the quartz surfaces, probably due to the electrostatic attraction of the positively—charged edges of the kaolinite for the negatively—charged quartz surfaces (although little information on the solution chemistry was supplied). The addition of phosphate salts to the solution (in an unspecified amount) greatly enhanced the mobility of the kaolinite particles, presumably by adsorption of the phosphate anions to the positively—charged edges of the kaolinite.

The transport of clay particles through soil formations is referred to as illuviation. Illuviation often produces accumulations of bands, or lamellae, of clay in many soils (Dijkerman et al., 1967). These clay bands increase the cation exchange capacity of the soil, thus increasing soil fertility for deep—rooted crops. The formation of the clay bands may be caused by the evaporation of the wetting front, mechanical sieving by low permeability soil zones, or coagulation of clay colloids in response to high concentrations of clay suspensions or changes in soil water chemistry. Folks and Riecken (1956) noted the association of iron with clay bands. They postulated that iron is periodically precipitated as ferric hydroxide after being complexed and transported through the soil by organic ligands, especially oxalic acid. The precipitation of ferric hydroxide may reduce the
permeability of the formation so that it sieves out illuviating clay particles, or the ferric hydroxide may enhance the coagulation of the clay particles. Bond (1986) studied illuvial band formation in a laboratory column of sand. He noted that the band formation required very small amounts of clay in the soil (< 1 percent) and that clays were transported through soils at very slow velocities and very low water contents ($\theta < 0.2$).

The effect of chemistry of infiltrating irrigation water on the stability and clay content of agricultural soils has been the subject of many recent studies. Generally, laboratory columns of soil are used to determine the effect of ionic strength, electrolyte composition, and $pH$ on the hydraulic conductivity of the soil. The reduction of soil permeability is commonly caused by the release of clay particles, although clay swelling and soil slaking, or physical disintegration, are also thought to contribute (Abu-Sharar et al., 1987). Ali et al. (1987) and Yousaf et al. (1987) observed that clay release increased and hydraulic conductivity decreased as the electrolyte concentration decreased and the concentrations of $Ca^{2+}$ and $Mg^{2+}$ relative to $Na^{+}$ increased. Suarez et al. (1984) found that infiltrating water of higher $pH$ reduced soil hydraulic conductivity to a greater extent than water of lower $pH$ for a $pH$ range of 6 to 9. The compression of the double layer by increased ionic strength and the reduction of surface charge by the bivalent cations predicted by the DLVO theory explains these trends well.

The mechanical infiltration of clays into coarse-grained desert alluvium has been documented by Walker et al. (1978). Stream flows depositing the alluvium, which consists of sand and gravel, are extremely effective at sorting out the clay fraction; however, the interstitial voids of these sediments commonly contain clays. The clay is transported to the alluvial basins by runoff from adjacent highlands and it infiltrates into the formation. The infiltrated clays are distinguished from authigenic clays by a diagnostic clastic texture: plates of mixed size and composition
are aligned parallel to the surface of the framework grains. Layers of sediments containing infiltrated clays are generally located above low permeability sediments that bar further infiltration.

The mobility of clay particles in groundwater and soil water is well established by the studies cited above; however, the colloidal behavior of other inorganic colloids in groundwater is not well-documented. An investigation of the iron geochemistry of the New Jersey Coastal Plain groundwater near Camden, New Jersey led to the observation of suspended ferric oxyhydroxide in a zone of the confined aquifer containing very high iron concentrations and near-neutral pH (Langmuir, 1969). The ferric oxyhydroxide was probably composed of amorphous material and goethite, but characterization of the suspended material by X-ray diffraction or electron microscopy was not performed. The stability of the colloidal ferric hydroxide was probably reduced by increased sedimentation as the particle size increased. These colloids were produced by the natural, steady-state evolution of the groundwater chemistry in the aquifer, as opposed to many of the other cases of colloid mobilization caused by some disturbance of the groundwater or soil water chemistry or the infiltration of water with high particle concentrations.

The detachment of colloidal metal hydroxide particles from metal and glass surfaces was observed in a series of studies by Matijevic and his co-workers and summarized by Kallay et al. (1987). The effects of a number of parameters (time of contact, pH, ionic strength, temperature, addition of surfactants, and the surface characteristics of the adsorbent) on the detachment of particles by diffusion alone were observed in column experiments. The theoretical aspects of the detachment were described by a summation of the electrostatic, London–van der Waals, and short–range repulsion forces (from solvation effects, electron cloud repulsion, Brownian motion of attached particles, etc.). The variation of ionic strength in the detachment experiments gave an unexpected result: particle detachment increased
with increasing ionic strength. The unusual behavior was explained by the inclusion of the short-range repulsion energy in the determination of the total potential energy profile and the relaxation of the electrical double layer interactions for constant potential cases. The probability of particle detachment depends in part on the depth of the energy well near the distance of minimum separation. The applicability of these results to colloids in natural groundwaters may be limited because of the elaborate preparation of the particle surfaces performed for these experiments. The adsorption of cations, organic films, and solvation of natural colloids may inhibit their approach to the minimum separation distance, where the effects of the short-range repulsive forces are important.

In this section, we have reviewed the documented cases of mobility of organic and inorganic colloids in groundwater. The mobile organic colloids and the biocolloids were generally released into aquifers following waste disposal and their mobility is shown by the distance they have travelled from their source. Most of the cases of colloid mobility are caused by a change in the aquifer chemistry: the injection of dilute, aerated water or steam to an aquifer and the infiltration of dilute rainwater or saline irrigation water into soils and the subsequent suspension of adhered particles. The effects of solution chemistry on colloid stability have been explained by the variations in the electrostatic repulsive energy caused by changes in the ionic strength and the electrolyte composition. The effect of pH on the colloid stability primarily affects the surface charge of hydrophilic colloids, although the importance of the hydrogen ion in determining the ionic strength at low pH cannot be neglected. In other cases, such as illuviation and infiltration of clays into soils and geologic formations, the mechanisms of clay release are less clear; however, the soil column and geologic record provide evidence of the colloid mobility. Finally, the case of the suspended ferric oxyhydroxide particles shows that mobile colloids can be produced in natural, stable aquifers.
1.4. **Colloids and the Enhancement of Contaminant Transport**

The primary motivation for investigating the nature and distribution of colloids in groundwater is to determine the effect of colloids on the transport of contaminants in the aquifers and soils. We will focus on the transport of two types of contaminants: 1) hydrophobic organic compounds, such as pesticides, polynuclear aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB), and other halogenated hydrocarbons; and 2) long-lived radionuclides. The fate of these compounds in natural waters is generally predicted by a partitioning between soluble and sorbed phases. The partitioning is described by a partition coefficient, $K_p$, or a distribution coefficient, $K_d$. Both parameters are defined as a ratio of the concentration of the compound in the sorbed phase, $C_s$ (mole solute/g sorbent), to the concentration of the compound in the dissolved phase, $C_w$ (mole solute/mL water). Hydrophobic organic compounds and many species of radionuclides are extensively sorbed to aquifer solids; therefore, the velocity of their transport in groundwater is effectively retarded relative to the velocity of groundwater flow.

The retardation of a compound is described by the ratio of the total amount of the compound in all phases to the amount of the compound in mobile phases. For the simple case of a compound partitioned between soluble and immobile sorbed phases, the expression for the retardation factor, $R_f$, reduces to

$$R_f = \frac{v}{v_c} = 1 + \frac{\rho_b}{n} K_p$$  \hspace{1cm} (1.10)

where $v$ is the average linear velocity of the groundwater (cm/sec), $v_c$ is the velocity of the transport of the compound (cm/sec), $n$ is the saturated porosity of the aquifer, and $\rho_b$ is the bulk density of the sediment (g/cm³), defined by $\rho_g (1-n)$, where $\rho_g$ is the density of the aquifer grains (g/cm³). Thus, the transport of a compound with a high $K_p$ can be substantially reduced by sorption.
The use of partition coefficients in determining retardation is based on some assumptions concerning sorption equilibria. The sorption isotherm is assumed to be linear, meaning that the $K_p$ describing the sorption must be constant over the concentration range of interest. The sorption isotherm is also assumed to represent a completely reversible reaction; that is, desorption must release the same amount of the compound as was adsorbed. Finally, the kinetics of the sorption reaction must be fast relative to the groundwater residence time to allow the sorption reaction time to reach equilibrium. Reardon (1981) warned that these conditions are not always met in the case of pollutant migration in a contaminated groundwater.

The presence of mobile colloidal material modifies the expression for retardation. The mobile forms of the compound now include some of the compound sorbed to colloidal material. If we assume that the same $K_p$ can describe the partitioning of the compound to both the aquifer solid and the colloidal material, the expression for the retardation coefficient is now

$$R_f = \frac{v}{v_c} = 1 + \left[ \frac{K_p \rho_b}{n + n K_p C} \right]$$

(1.11)

where $C$ is the concentration of colloidal material (g/mL). The transport of the compound by colloidal material thus decreases the retardation of the compound in groundwater.

1.4.1. Colloids and Hydrophobic Organic Compounds

The partitioning of hydrophobic organic compounds, such as aromatic and chlorinated hydrocarbons, depends primarily on the fraction of organic carbon in the sorbent (Karickhoff et al., 1979). $K_p$ can be related to the fraction of organic carbon, $f_{OC}$, of a sediment or soil to determine a partition coefficient $K_{OC}$ based on
the organic carbon content of the sorbent:

\[ K_{OC} = \frac{K_p}{f_{OC}} \]  

(1.12)

Reasonable estimates of \( K_{OC} \) for a compound can be made from its octanol/water partition coefficient, \( K_{OW} \). The results of Means et al. (1980) and Chiou et al. (1983) emphasized the dependence of sorption of hydrophobic organic compounds on the organic carbon fraction of the sorbent. The partitioning of a wide range of compounds can be accurately estimated with only a knowledge of the \( f_{OC} \) of the sediment or soil. The \( K_{OC} \) of a compound can also be estimated from its water solubility (Chiou et al., 1979).

The importance of the organic carbon fraction of sediments in the sorption of hydrophobic organic compounds suggested that various components of dissolved organic carbon, which are suspected of coating many particle surfaces in groundwater, may also bind hydrophobic organic compounds in solution. Carter and Suffet (1982) observed the binding of DDT to dissolved humic materials extracted from pond water from the New Jersey Pine Barrens and sediments from a northern New Jersey reservoir. The DDT–humic substance binding constants were measured by equilibrium dialysis techniques. DDT would normally be expected to strongly partition into the suspended particulate phase, but Carter and Suffet (1982) concluded that a significant fraction of DDT in natural waters may be bound to dissolved and mobile humic substances. The \( K_{OC} \) determined for the DDT–humic substance binding was very close to the \( K_{OC} \) determined for sorption to sediments by Chiou et al. (1979).

Landrum et al. (1984) used reverse–phase separation to determine the binding of PAHs, PCBs, and DDT to commercial humic acids. The humic acids bound major portions; however, the partition coefficients of these compounds for natural dissolved organic matter was about 1 order of magnitude lower at similar
DOC concentrations. McCarthy and Jiminez (1985) measured the rate of binding of benzo[a]pyrene to commercial humic acids. They determined that binding was reversible and complete within 5 to 10 minutes. The correlations observed by these researchers between \( K_{oc} \) and \( K_{ow} \) or water solubility were similar to those observed for the sorption of the same compounds to many different sediments and soils. 

Chiou et al. (1986) compared the binding of hydrophobic organic compounds to humic substances and to polyacrylic acids. The humic substances substantially increased the apparent water solubility of the compounds, but the high-polarity extended-chain structures of the polyacrylic acids did not, suggesting that humic substances contain sizable intramolecular nonpolar environments favorable for association with hydrophobic organic contaminants. Wershaw (1986) extended these ideas by proposing that humic substances act like micelles with hydrophobic interiors able to provide a nonpolar "harbor" for compounds with low water solubility and hydrophilic exteriors that enable them to remain dissolved and mobile at the ionic strength and \( pH \) of most fresh waters.

The \( K_{oc} \)'s determined for sorption of hydrophobic organic compounds to sediments and binding to dissolved humic substances are quite similar, suggesting that the organic fraction of sediments is composed of compounds similar to, and probable including, humic substances. Table 1.1 lists a number of correlations observed between \( \log K_{oc} \) vs. \( \log K_{ow} \) for comparison. \( K_{oc} \) was often found to correlate better with water solubility of the compounds for sorption to sediments (Chiou et al., 1979; Means et al., 1980).

Evidence reported by Means and Wijayaratne (1982) and Garbarini and Lion (1985) indicates that partition coefficients are different for sorption to sediments and colloidal matter. The sorption of two nitrogen-containing compounds, atrazine and linuron, was observed to be 10 to 35 times stronger onto natural colloids as onto sediments (Means and Wijayaratne, 1982). These investigators postulated that the
Table 1.1. Correlation of $K_{oc}$ with $K_{oc}$ for hydrophobic organic compounds by least-squares regression fitting of log-log plots.

Sorption to Soils and Sediments

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Regression</th>
<th>$R^2$</th>
<th>Study</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAH, CH</td>
<td>$\log K_{oc} = 1.00 \log K_{ow} - 0.21$</td>
<td>1.00</td>
<td>(1)</td>
</tr>
<tr>
<td>PAH</td>
<td>$\log K_{oc} = 1.00 \log K_{ow} - 0.317$</td>
<td>0.98</td>
<td>(2)</td>
</tr>
<tr>
<td>AH, CAH</td>
<td>$\log K_{oc} = 0.72 \log K_{ow} + 0.49$</td>
<td>0.95</td>
<td>(3)</td>
</tr>
</tbody>
</table>

Binding to Humic Substances

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Regression</th>
<th>$R^2$</th>
<th>Study</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAH, PCB</td>
<td>$\log K_{oc} = 0.77 \log K_{ow} + 0.52$</td>
<td>0.75</td>
<td>(4)</td>
</tr>
<tr>
<td>PAH</td>
<td>$\log K_{oc} = 0.89 \log K_{ow} + 0.24$</td>
<td>0.92</td>
<td>(5)</td>
</tr>
<tr>
<td>PCB, AH</td>
<td>$\log K_{oc} = 0.91 \log K_{ow} - 0.71$</td>
<td>1.00</td>
<td>(6)</td>
</tr>
</tbody>
</table>

AH  Aromatic Hydrocarbons  
CAH Chlorinated Aromatic Hydrocarbons  
CH  Chlorinated Hydrocarbons  
PAH Polycyclic Aromatic Hydrocarbons  
PCB Polychlorinated Biphenyls  

(1) Karickhoff et al. (1979); (2) Means et al. (1980); (3) Schwarzenbach and Westall (1981); (4) Landrum et al. (1984); (5) McCarthy and Jiminez (1985); (6) Chiou et al. (1986)
increased surface area of the colloids was responsible for the increased sorption; however, the nitrogen-containing compounds are also able to associate with surfaces by ion exchange and condensation reactions. Gschwend and Wu (1985) noted that the variation of the atrazine and linuron sorption with pH indicated these other sorption reactions were involved. Garbarini and Lion (1985) observed that the sorption of trichloroethene and toluene by dissolved humic acid is nearly 3 times as strong as the sorption to alumina coated by humic acid. The humic acid associated with the alumina surface apparently loses some of its ability to sorb trichloroethene and toluene, perhaps because the sites involved in binding with the alumina surface groups are important for sorption of hydrophobic organic compounds. However, several problems with this work restrict its application to natural waters. The commercial humic acids used in the experiment were not purified prior to use. The method used to attach the humic acid to the alumina included drying the coated particles at 105°C. The effects of these experimental procedures on the results are unclear, but they do not portray processes occurring in natural waters. Finally, the behavior of trichloroethene and toluene, which are appreciably soluble in water, may not be easily extrapolated to less soluble hydrophobic organic contaminants.

The observation of some irreversibility in the sorption and desorption of some hydrophobic organic compounds and the dependence of the partition coefficients on the solid-to-solution ratio in experiments (DiToro and Horzempa, 1982; Voice et al., 1983) led Gschwend and Wu (1985) to investigate the effects of a colloidal sorbent phase on the determination of sediment-water partition coefficients for some PCBs. Precautions were taken to eliminate or account for the presence of suspended particles or organic macromolecules, resulting in the determination of consistent partition coefficients over a wide range of solid-to-solution ratios and completely reversible and linear sorption–desorption isotherms. Baker et al. (1986) extended the concepts advanced by Gschwend and
Wu (1985) to determine partition coefficients for PCB congeners in Lake Superior. The $K_p$'s measured in the lake water did not correlate well with the compounds' $K_{ow}$'s or the suspended solid particle (> 0.6 μm–filtered) concentration or organic content. The association of PCBs with nonfilterable microparticles and organic macromolecules was hypothesized to explain the distribution of the compounds in the lake water. Baker et al. (1986) concluded that the dominant phase of hydrophobic organic compounds in most surface waters may be the colloidally–associated phase. Both Gschwend and Wu (1985) and Baker et al. (1986) used the same partition coefficients to describe the sorption of hydrophobic organic compounds to colloidal matter and sediments.

Methods have been developed to prevent the interference of colloidal material in the determination of partition coefficients: equilibrium headspace analysis for relatively volatile compounds (Garbarini and Lion, 1985; Brownawell, 1986), and fluorescence quenching by sorption of compounds that fluoresce in water, such as aromatic hydrocarbons (Gauthier et al., 1986).

Vinten et al. (1983) examined the effect of colloid transport on the vertical infiltration of two pesticides, DDT and paraquat. Paraquat, with two secondary amine groups attached to a biphenyl double ring, is an ionizable compound. Both pesticides have very high sediment–water partition coefficients, thus their transport in soil is expected to be drastically retarded. Suspensions of montmorillonite particles (30 mg/L) spiked with paraquat and sewage effluent solids (about 100 mg/L) spiked with DDT were allowed to infiltrate through a 12 cm column. In a distilled water solution, about 50 percent of the paraquat was transported the entire length of the column, but in a CaCl$_2$ solution, the paraquat transport was confined to the upper 2 cm. The mobility of paraquat, which is strongly adsorbed by ion exchange to the clay, was thus linked to the mobility of the clay particles, which were mobile in the distilled water, but coagulated and attached to the pore surfaces.
in the CaCl₂ solution. The affinity of clay particles for hydrophobic organic compounds is expected to depend on their organic carbon fraction; therefore, it is likely that the clay colloids were coated to some degree by organic carbon. Most sewage effluent is composed primarily of organic matter; thus, the major portion of the DDT is expected to partition to the abundant colloidal organic carbon. The permeability of the soils was shown to assert primary control over the transport of the DDT–sewage particles.

As an example of the potential effects of colloidal material on the transport of hydrophobic contaminants, we will predict the fate of three pollutants, tetrachloroethene (4CE), pyrene, and 2,4,5,2',4',5'-hexachlorobiphenyl (PCB), in groundwater. For our setting, we will use the sewage effluent plume emanating from rapid infiltration beds at Otis Air Force Base, Cape Cod, Massachusetts. We will assume that the three pollutants have been present in the sewage effluent since disposal began in 1936 (Barber et al., 1988). The unconfined glacial outwash aquifer has an average hydraulic conductivity of about 1.3×10⁻³ m/sec, a porosity of \( n = 0.35 \), and a hydraulic gradient of 1.5 m/km, resulting in a groundwater velocity of about 0.5 m/day, or about 200 m/yr. The bulk density of the sediments is about 1.8 g/cm³ and the average organic carbon fraction of the sediment is \( f_{\text{soc}} = 0.001 \), although near the sewage beds \( f_{\text{soc}} \) is as high as 0.0075. The dissolved organic carbon concentration of the plume varies from about 3 to 11 mg C/L. About half of the organic carbon is composed of detergents and surfactants, branched- and long-chain alkylbenzenesulfonic acids (Barber et al., 1988), that are not expected to contribute to the binding of the pollutants significantly, but may increase their solubility slightly by a cosolute effect. The dissolved carbon concentration active in binding the pollutants is estimated to be \( C_{\text{doc}} = 2 \) mg C/L for which \( f_{\text{doc}} = 1 \). The presence of typical inorganic colloids is not expected in this aquifer due to the very low content of clays and other minerals; however, Gschwend and Reynolds (1987)
reported the presence of about 4 mg/L of ferrous phosphate colloids formed by \textit{in situ} precipitation near the disposal beds. The ferrous phosphate colloids will contribute to the sorption of the pollutants if they are organically coated. We will use a concentration of inorganic colloids \( C_{ic} = 4 \text{ mg/L} \) and estimate the fraction of organic carbon on the inorganic colloids at \( f_{ic} = 0.01 \).

The measured \( K_{oc} \)'s and the aquifer information are used with equations (1.10) and (1.11), adapted to accommodate \( K_p = K_{oc} f_{oc} \) and two mobile sorbed phases, the dissolved organic carbon and the ferrous phosphate colloids. \( R_{2ph} \) represents soluble/stationary sorbed partitioning of the pollutants and \( R_{3ph} \) represents soluble/mobile sorbed/stationary sorbed partitioning:

\[
R_{2ph} = 1 + \frac{\rho_b \ K_{oc} f_{soc}}{n} \tag{1.13}
\]

\[
R_{3ph} = 1 + \frac{\rho_b \ K_{oc} f_{soc}}{n + nC_{doc} K_{oc} f_{doc} + nC_{ic} K_{oc} f_{ic}} \tag{1.14}
\]

We are assuming that a single \( K_{oc} \) (mL/g) describes partitioning of the pollutants to each of the sorbed phases, and that the \( K_{oc} \)'s apply to these aquifer conditions, although they were measured under other conditions. In determining the distances traversed over 52 years, we will assume that other losses of the pollutants, such as biodegradation, are unimportant. A conservative groundwater tracer would have traveled about 10.4 km since 1936. The results of this analysis are shown in Table 1.2.

The retardation of the PCB decreased by about 30 percent, but the predicted distance of migration increased from 9 to 13 meters—hardly an environmentally significant result. However, it must be remembered that the retardation coefficient is defined by the ratio of groundwater velocity to the velocity of the breakthrough of 50 percent of the mass of the pollutant; thus, it may be possible for small quantities of the pollutant to move far ahead of the center of mass of the plume.
<table>
<thead>
<tr>
<th>Compound</th>
<th>measured $K_{oc}$</th>
<th>$R_{2ph}$</th>
<th>distance travelled</th>
<th>$R_{3ph}$</th>
<th>distance travelled</th>
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<tr>
<td>Tracer</td>
<td>0</td>
<td>1</td>
<td>10.4 km</td>
<td>1</td>
<td>10.4 km</td>
</tr>
<tr>
<td>4CE</td>
<td>210</td>
<td>2.13</td>
<td>4.7 km</td>
<td>2.13</td>
<td>4.7 km</td>
</tr>
<tr>
<td>pyrene</td>
<td>84,000</td>
<td>432</td>
<td>240 m</td>
<td>370</td>
<td>280 m</td>
</tr>
<tr>
<td>PCB</td>
<td>220,000</td>
<td>1,130</td>
<td>9.0 m</td>
<td>787</td>
<td>13 m</td>
</tr>
</tbody>
</table>

4CE tetrachloroethene $K_{oc}$ from Chiou et al. (1979)
pyrene $K_{oc}$ from Karickhoff et al. (1979)
PCB 2,4,5,2',4',5'-hexachlorobiphenyl $K_{oc}$ from Chiou et al. (1979)
Indeed, Barber et al. (1988) observed that a number of compounds were present at detectable levels far ahead of the main body of organic pollutants.

The retardation of pyrene is reduced by only 15 percent, while the transport of 4CE is not affected at all by the presence of colloidal matter. This example illustrates that only compounds with very high $K_{\text{ow}}$'s or very low water solubility will be significantly affected by colloidal transport at normal concentrations of DOC in groundwater (0.5 to 5 mg C/L). However, locations where hydrophobic organic pollutants exist in the groundwater frequently have elevated colloidal organic carbon concentrations (landfill leachate plumes, coal tar sites, etc.). Also, it is clear that the inorganic colloid load would have to be very high to affect retardation because the sorption to inorganic colloids is controlled by their $f_{\text{oc}}$.

In this section, we have presented evidence that indicates that colloidal material significantly increases the transport of hydrophobic organic compounds in groundwater. The importance of organic carbon in the sorption of hydrophobic compounds suggests that inorganic colloids coated by organic matter will sorb hydrophobic organic compounds. The binding of hydrophobic organic compounds to humic substance establishes the existence of sorbed mobile phases. The retardation factors of only very high $K_{\text{ow}}$ and very low water solubility compounds will be significantly affected by colloidal transport at normal concentrations of colloidal matter; however, the transport of a small fraction of the pollutant in the groundwater will greatly enhanced if the assumptions regarding equilibrium and linear, reversible sorption are not followed. In heterogeneous aquifers, where groundwater flows preferentially through high permeability zones, such as gravel beds or fractures, groundwater flow may be too rapid to allow for sorption equilibrium. Also, if the majority of the pollutant is transported through such zones, the available sites may be filled. For PCBs and PAHs, the enhanced transport of even a very small fraction of the pollutant can be significant.
1.4.2. Colloids and Long-Lived Radionuclides

In this section, we will evaluate the enhancement of radionuclide transport in groundwater. A number of field and laboratory investigations indicate that the presence of colloidal matter significantly decreases the sorption of radionuclides to aquifer sediments and mobilizes them in the groundwater. The fate of radionuclides is controlled by many of the same processes that control trace metal distributions in natural waters. The most important of these is adsorption of radionuclides onto solid phases. Radionuclides, and metals in general, are adsorbed primarily to two mineral phases in groundwater: hydrous oxides (of iron, aluminum, and manganese), and clay minerals. Cationic radionuclides are specifically adsorbed to surface hydroxyl groups on hydrous oxides. Adsorption usually occurs over a narrow pH range, below which there is essentially no adsorption and above which adsorption is complete. The adsorption of metals to hydrous oxides is analogous to the hydrolysis of the metals in solution (Dugger et al., 1964; James and Healy, 1972). Clays adsorb metals by ion exchange of interlayer cations for cations in solution. Isomorphic substitutions in the clay structure result in overall negative charges balanced by the incorporation of exchangeable interlayer cations. Highly substituted clays, such as montmorillonite and vermiculite have high cation exchange capacities (CEC), while the more weathered clays, such as illites, chlorites, and kaolinite have low CECs. The ion exchange mechanism is selective for cations of high solution concentration, high valence, and low ionic radius; thus, in typical groundwaters, it may not be very important for trace concentrations of radionuclides. The binding of radionuclides, and of all metals, to humic substances and other components of organic carbon, also must be considered in evaluating the adsorption of radionuclides to stationary phases. Organic coatings are thought to be important in natural waters, especially
on positively-charged surfaces such as hydrous oxides. The adsorption of anion radionuclide species is expected to be controlled by electrostatic attraction to positively-charged surfaces in the aquifer.

The adsorption of radionuclides and metals is quantified by a distribution coefficient $K_d$, defined in the same way as the partition coefficient $K_p$ for organic compounds as the ratio of solute mass adsorbed per unit mass of aquifer solid to the solute concentration in solution. The determination of $K_d$ for a radionuclide depends strongly on the solution chemistry and the sorbent medium. The solution chemistry determines the oxidative state and speciation of the radionuclide. The redox chemistry of some radionuclides is quite complex; for example, actinides exist in four redox states (III, IV, V, and VI). Usually, the speciation and affinity for adsorption of each of these redox states are considerably different.

The equilibrium speciation of uranium is a good example of the complexity of actinide chemistry. Three oxidation states occur in natural waters: U(IV), U(V), and U(VI). U(IV) tends to precipitate as uraninite (UO$_2$) and coffinite (USiO$_4$), while U(V) and U(VI) are stable in natural waters as various species. The solution speciation depends on the redox potential and pH of the solution and the concentrations of carbonate, chloride, fluoride, phosphate, and sulfate anions. Based on the existing thermodynamic data and typical groundwater concentrations for the anions, U(OH)$_5^-$ is stable only at low Eh ($-0.4$ to $-0.1$) and pH above 5. At intermediate Eh ($-0.1$ to $+0.2$) and pH below 7, UO$_2^+$ predominates. In more oxidizing waters, the uranyl ion (UO$_2^{2+}$) and uranyl fluoride complexes predominate below pH 5; from pH 4.5 to 7, the UO$_2$(HPO$_4$)$_2^{2-}$ ion is the principal species. At higher pH, UO$_2$CO$_3^0$ and di- and tri-carbonate complexes predominate at all redox potentials (Langmuir, 1978).

The adsorption of radionuclides has been measured under a wide variety of conditions. Usually, the experimental conditions are designed to simulate particular
geologic media where nuclear waste disposal is practiced or planned. This results in determinations of $K_d$'s that are applicable only to those specific situations. Unfortunately, there is no easily measured normalizing parameter to relate the sorption character of the diverse geologic media as there is for the sorption of organic compounds, the organic carbon fraction of the sediment. The variation of redox states and speciation of the radionuclides with solution chemistry further restricts the application of $K_d$'s to situations with similar chemistry. To avoid this problem, Meyer et al. (1984) suggested a model to estimate the adsorption characteristics of different geologic formations based on the mixture of adsorbents in the formation. They used the adsorption isotherms of $\text{Cs}^+$, $\text{Sr}^{2+}$, $\text{Eu}^{3+}$, and $\text{TcO}_4^-$ on several hydrous oxides and clays to develop theoretical isotherms for natural minerals and rocks based on their oxide content. The application of this model to various minerals produced isotherms similar to experimentally—observed isotherms, suggesting that such a model could provide useful estimates of the adsorption nature of many formations.

Many estimates of radionuclide speciation and experimental determinations of $K_d$ neglect the effect of the binding of radionuclides with humic substances and other organic macromolecules. As for most metals (Schnitzer and Khan, 1972), radionuclides form very stable complexes with natural and synthetic organic ligands. Bertha and Choppin (1978) and Nash and Choppin (1980) reported the formation of very stable complexes between $\text{Eu(III)}$, $\text{Am(III)}$, and $\text{Th(IV)}$ and natural humic substances. The adsorption of strongly complexed radionuclides may be significantly decreased by concentrations of organic carbon common in groundwater, as indicated by the results of Boggs and Sietz (1984). They investigated the effect on humic substance binding on $\text{Am}$ and $\text{Np}$ adsorption to crushed basalt rock samples. The $K_d$'s determined for adsorption of $\text{Am}$ and $\text{Np}$ decreased by 25 to 50 percent upon the addition of as little as 1 mg C/L humic substances (a mixture of
commercial humic acid and soil fulvic acid). The $K_d$'s decreased by as much as 1 to 2 orders of magnitude when 200 mg C/L were added to the solution. Nelson et al. (1985) also observed that colloidal organic carbon inhibited the adsorption of Pu(III) and Pu(IV) to suspended lake bed sediment particles. They determined $K_d$'s at varying sediment-to-solution ratios by correcting for the presence of colloidal organic carbon in the same fashion as Gschwend and Wu (1985) did for organic compounds. They determined that the colloidal organic carbon and the sediments had approximately equal affinities for Pu, on a weight basis. It is conceivable that in some systems, the partitioning of radionuclides to the solid phase may actually be increased by adsorption to organically coated aquifer surfaces. The adsorption of metals to organically coated surfaces forms ternary metal–ligand–surface complexes (Davis and Leckie, 1978).

The potential effects of inorganic colloid transport of radionuclides are considered by Avogadro and de Marsily (1983) in a model describing colloid transport in porous media. They accounted for the occurrence of two types of colloids in groundwater: 1) colloids formed by precipitation of supersaturated phases, also known as "true" colloids; and 2) colloids formed by dispersion or fragmentation of aquifer material, also known as "pseudo–colloids." The formation of "true" colloids of radionuclide hydrous oxides would directly increase the mobility of radionuclides strongly sorbed to aquifer solid. Cleveland (1979) noted that the formation of amorphous PuO$_2$ colloids of submicron size may follow the polymerization of Pu(IV) hydrolysis products. Formation of other metal hydrous oxide colloids capable of adsorbing radionuclides would also increase radionuclide mobility. As true colloids age and grow in size, they tend to be settled, coagulated, or attached to aquifer surfaces. Organic coatings may inhibit their growth and stabilize them in suspension. Pseudocolloids are generally composed of clays,
oxides, and other mineral fragments. They tend to be more stable in suspensions because they are not growing in size. They may also be coated by organic matter, which often increases their ability to adsorb radionuclides.

Colloids are expected to form near the nuclear waste packages sealed in high-level radioactive waste repositories. Sietz et al. (1979) suggested that colloid formation and adsorption to colloids may explain transport of small quantities of highly retarded radionuclides, such as Cs and some actinides, at the velocity of the groundwater flow in their column experiments. The fast-moving components may cause radiologic hazards, even though they represent only a small fraction of the activity escaping from a breached repository. Shade et al. (1984) reported that actinide adsorption to iron-silicate and bentonite colloids was quite high at near-neutral pH. Iron-silicate and bentonite colloids may be generated by the disintegration of the high-level waste package components. The experiments of Rees et al. (1985) showed that Pu(IV) transport was significantly enhanced by adsorption to colloidal material originating from the glass matrix used to contain the high-level nuclear waste.

In low-level waste disposal, the adsorption to natural colloids is more likely to affect the transport of radionuclides. Sheppard et al. (1979; 1980) identified the 2 to 3 nm component of soils as the primary adsorbent of radionuclides in a variety of soils in column experiments. They presumed that the 2 to 3 nm fraction was composed of humic substance polymers. Significant adsorption and enhancement of mobility was reported for Cs, Sr, Am, Cm, and U. Eichholz et al. (1982) observed that cationic radionuclides were competitively adsorbed onto clay colloids in the presence of various geologic media. These clay particles passed through columns of the geologic media at the velocity of the groundwater flow. The clay particle stability was shown to depend on the salt concentration of the solution—at high salt concentrations, the clay colloids were substantially retained in the columns.
Champ and Merritt (1981) observed that Cs was transported on 0.2 to 1.0 \( \mu m \) particles in columns containing sediments collected near the Chalk River National Laboratory (CRNL) in Ontario, Canada. They determined that micro-organisms were involved in the release or formation of the particles by irradiating the columns with \(^{60}\)Co gamma rays. After radiation, bacterial cell counts were greatly reduced and Cs transport was increased, suggesting that the Cs was transported on the dead cells released from the soil grains. Champ et al. (1982) observed that Pu transport through CRNL soils was dominated by Pu associated with the >0.45 \( \mu m \) fraction at steady state. Pu transport with the >0.45 \( \mu m \) fraction was initially only about 20 percent, but it increased to nearly 50 percent. Nearly 30 percent of the steady state effluent was associated with the 500 to 10,000 m.w. fraction separated by ultrafiltration. This fraction is commonly considered to be the molecular weight range of humic substances and their aggregates. The investigations of radionuclide mobility at CRNL were summarized by Champ et al. (1984). They determined that anionic species were the predominant form of most radionuclides in the groundwater of 4 contaminant plumes. They concluded that the anionic species were mainly organic ligands of the radionuclides. The DOC concentrations in the plumes ranged from about 2 to 7 mg C/L, suggesting that natural organic ligands were mobilizing a large fraction of the radionuclides.

The study of the mobilization of radionuclides from low-level waste pits at Oak Ridge National Laboratory (ORNL) in Tennessee (Means et al., 1978a) concluded that complexation by organic ligands could drastically enhance the migration of radionuclides in groundwater. Means et al. (1978) determined that the formation of very stable radionuclide–EDTA and humic substances complexes reduced the adsorption of the cobalt and uranium to the aquifer sediments. Groundwater samples were separated by gel filtration chromatography. Greater than 90 percent of the Co was associated with organic compounds of <700 m.w. in
the groundwater. The major compound in this fraction was EDTA. The distribution of U in the groundwater, which was detected at much lower levels that $^{60}$Co, was about 70 percent with the <700 m.w. fraction and 30 percent with the >700 m.w. fraction. With infrared spectroscopy, the major component of the >700 m.w. fraction was identified as natural humic substances.

As an example of the enhancement of radionuclide transport by colloidal matter, we will consider a hypothetical high-level nuclear waste repository in a shale formation buried deep underground. The effects of colloidal transport will be evaluated by the comparing the soluble/stationary sorbed and soluble/mobile sorbed/stationary sorbed partitioning for Co and Pu as we did in the previous section for some hydrophobic organic compounds. High-level nuclear waste must be isolated from the biosphere for at least 10,000 years because of the extreme environmental hazards of even small quantities of long-lived radionuclides, according to the requirements of the Nuclear Waste Policy Act of 1982.

For this aquifer, we will estimate a groundwater velocity of 0.5 m/day, a porosity of $n=0.1$, and a bulk density of 2.2 g/cm$^3$. We will assume this shale formation is similar to the shale at ORNL investigated by Means et al. (1978a; 1978b). This shale has strong affinity for radionuclides because it contains Mn and Fe oxides. The smallest size fraction of the soil particles (0.2 $\mu$m to 2.0 $\mu$m) adsorbed radionuclides especially well. We will assume that the fragmentation of the small fraction of soil particles has produced a colloidal concentration of $C_{ic}=5$ mg/L. The groundwater chemistry, which determines the redox state and speciation of the radionuclide, is assumed to be a predominantly Ca–HCO$_3^-$–SO$_4^{2-}$ ionic composition; pH is 7.5 and the Eh is about 0.1 V. Considering only inorganic ligands, cobalt will occur primarily as Co$^{2+}$ and plutonium will occur in the Pu(IV) oxidation state. The speciation of Pu(VI) is predicted to be Pu(OH)$_5^-$, but Cleveland (1979) cautions that this species never occurs in natural waters even
though it is thermodynamically stable. The groundwater is assumed to have $C_{org} = 2$ mg C/L available to bind radionuclides.

The constants used to describe the uptake and binding of the radionuclides are listed in Table 1.3. The adsorption of Co to the aquifer solids and the inorganic colloids is described by the $K_d$ determined by Means et al. (1978a). This $K_d$ inherently reflects the speciation of Co in the groundwater because the experiment was performed under the aquifer conditions. The adsorption of Pu(IV) to the shale will be described by a $K_d$ measured for the adsorption of Pu(III,IV) to lake sediments by Nelson et al. (1985). The binding of Co$^{2+}$ to humic substances is described by the overall binding constant $K_{HS}^O$ determined for Ni$^{2+}$ binding to humic substances from lake water by McKnight (1979). The Ni$^{2+}$ binding constant should be a good estimate for Co$^{2+}$ because the OH$^{-}$ and citrate binding constants of the two ions are very close. For Pu(IV), the binding constant determined for Th(IV) by Nash and Choppin (1980) was used as an estimate, assuming that the stability of the Pu(IV)–humic substance binding constant is similar. The humic substance binding constants apply to the reaction $R + HS \rightarrow R-HS$, for which

$$K_{HS}^O = \frac{[R-HS]}{[R][HS]}$$

(1.15)

where $[R]$ is the activity of the radionuclide (M), $[HS]$ is the concentration of the ionized humic substance, and $[R-HS]$ is the concentration of the complex (M).

Assuming that the 2 mg C/L DOC contain about 5 meq/g of ionized carboxylic functional groups, $[HS] = 10 \, \mu$eq/L.

The retardation factors were estimated by modifying equations (1.10) and (1.11) to reflect the use of $K_d$'s describing partitioning and binding constants $K_{HS}^O$ describing complexation by humic substances:

$$R_{2ph} = 1 + \frac{\rho_b K_d}{n}$$

(1.16)

$$R_{3ph} = 1 + \frac{\rho_b K_d}{n + nK_{HS}^O[HS] + nC_{ic}K_d}$$

(1.17)
The travel distances shown in Table 1.3 are based on 10,000 years of groundwater flow at 0.5 m/day.

The dramatic reduction in the retardation factor for Pu(IV) results directly from the humic substance complexing predicted by the large $K_{HS}^0$. The distance travelled in the 10,000 year lifetime of the repository is still very small relative to the distance travelled by a conservative tracer, but we must remember that the retardation factor reflects the average transport velocity of the radionuclide and does not account for rapid transport in fractures and other high permeability zones. The strong binding of Pu(IV) and other actinides to colloidal organic carbon substantially increases their mobility even at normal groundwater DOC concentrations.

The review of the many investigations of speciation, sorption, and transport of radionuclides indicates that colloidal matter enhances the mobility of many radionuclides quite substantially. As for organic compounds, components of dissolved organic carbon, especially humic substances, played a major role in the binding and mobilizing of radionuclides. The importance of inorganic colloidal matter must also be considered due to the organic coatings commonly found on these particles in natural waters.

<table>
<thead>
<tr>
<th>Table 1.3. Prediction of the retardation of two radionuclides released from a nuclear waste repository.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nuclide</td>
</tr>
<tr>
<td>--------</td>
</tr>
<tr>
<td>Tracer</td>
</tr>
<tr>
<td>Co(II)</td>
</tr>
<tr>
<td>Pu(IV)</td>
</tr>
</tbody>
</table>
1.5. **Goals of the Investigation**

The most pressing motivation for assessing the nature and distribution of colloids in groundwaters is to evaluate the potential for enhancement of pollutant transport. The goals of this investigation were to assess whether groundwater in relatively pristine aquifers contains colloidal matter, to determine the nature and size distribution of the colloids present, and to explain their presence in terms of the geology and groundwater geochemistry. The focus of the investigation was on inorganic colloids, which were expected to be present in size ranges that we could analyze by light scattering, photon correlation spectroscopy, and electron microscopy. The importance of colloidal organic carbon in the enhancement of pollutant transport, as recognized in the preceding sections, was not easily characterized by the analytical techniques available.

To choose sites to sample groundwater for colloids, four criteria were followed: 1) properly designed, constructed, and developed wells were installed at the site; 2) the groundwater at the site was considered uncontaminated; 3) previous sampling revealed the presence of high levels of organic carbon ( > 1 mg C/L); and 4) high levels of total iron. Dissolved organic carbon and iron were expected to play important roles in colloid stability and chemistry. Components of organic carbon are known to play an important role in the adsorption of organic compounds and trace metals in natural water. They are also capable of changing the surface properties of inorganic surfaces, which has a profound effect on adsorption (Davis, 1982) and stability of particles in natural waters (Hunter and Liss, 1979; Tipping and Cooke, 1982). The effect of coatings of organic carbon were of primary interest in this investigation. Iron was expected to be important in the *in situ* formation of colloids, based on the results of Langmuir (1969) in a natural groundwater and Gschwend and Reynolds (1987) in a contaminated plume. In these cases, Fe(III)
hydrolyzed to form colloidal ferric hydroxides and ferrous iron precipitated with phosphate to form ferrous phosphate colloids. The redox potential of the groundwater was also suspected of influencing colloid formation and stability; thus, the iron content of the water was thought to be important because iron is capable of controlling the redox state of the system (Langmuir, 1971a).

The second major goal of this investigation was the further development of groundwater sampling procedures to obtain samples representative of the natural colloid load. The major refinement over the sampling techniques developed by Reynolds (1985) and Backhus et al. (1986) is the measurement of colloid concentration in the groundwater during sampling. The colloid concentration was determined by measuring the light scattering intensity of the groundwater in the field. The light scattering data was used to evaluate the effectiveness of purging the standing water from the well and to determine when the groundwater colloid concentration had stabilized at a representative level.

Groundwaters from two regions of Atlantic Coastal Plain surficial aquifers were chosen for this investigation based on these criteria. The first region is the Pine Barrens, located in southern New Jersey, and so named because of the dominant type of vegetation. The Pine Barrens are the northern—most surface expression of the Atlantic Coastal Plain (except for some isolated outcroppings on Long Island and Nantucket). The second region is the geologically younger sediments of the Atlantic Coastal Plain in Kent County, central Delaware. The region is dominated by agricultural land use. The following chapters of this report contain the details of the groundwater sampling procedure used to obtain representative samples for colloids and the results of the analyses of the colloidal samples taken from the groundwater. The formation and stability of the colloids found in these groundwaters were found to be closely related to the criteria used to select sampling sites—the organic carbon and iron content of the groundwaters.
CHAPTER 2. GROUNDWATER SAMPLING FOR COLLOIDS

2.1. Introduction

Many studies have shown that appropriate sampling methods and materials are essential for accurate characterization of the various compounds of interest in groundwater (Gibb et al., 1981; Barcelona et al., 1984; Nielsen and Yeates, 1985). From these studies, it is well known that specific sampling and storage procedures must be devised and followed to obtain representative samples. For example, samples to be analyzed for volatile organic compounds must not be exposed to the atmosphere; and trace metal samples will be contaminated by galvanized steel wells. But comparatively little care has been taken to insure that groundwater samples are representative of aquifer conditions with respect to the nature and size distribution of colloids (Buddemeier, 1986). The importance of obtaining representative samples for groundwater colloids has only recently been recognized, and the proper materials, equipment, sampling methods, and laboratory analytical instruments necessary for sampling are not widely understood or utilized.

In this chapter, the crucial factors affecting groundwater sampling for colloids will be discussed: well design, well construction and development, groundwater pumping rate, pump selection, removal of standing water, and preservation of sample chemistry. The effect of disturbing natural groundwater flow patterns by pumping to obtain samples will be examined by calculating the increase in shear on particles in the aquifer produced by various pumping rates. The groundwater sampling methods and materials designed and developed to sample groundwater for colloids by Reynolds (1985) and Backhus et al. (1986) and used in this investigation will be reviewed. Field investigations testing the sampling methods were conducted as part of obtaining groundwater samples for colloids in
two unconfined aquifers of the Atlantic Coastal Plain in New Jersey and Delaware. The abundance and nature of colloids was determined by measurements of light scattering intensity and density of particles on filters examined by scanning electron microscopy. The discussion will explain how these results demonstrate that the sampling methods used in this investigation provide groundwater samples representative of the natural colloid distribution.
2.2. **Factors Affecting Groundwater Sampling for Colloids**

Groundwater samples for colloid nature and size distribution is significantly affected by many facets of groundwater monitoring. Well design, well materials, well construction and development, pump materials and mechanism, purging and sampling flow rate, purging of the well, and sample handling and storage methods all play important roles in determining the integrity, or the representativeness, of a groundwater sample for colloids.

2.2.1. **Well Construction and Materials**

The monitoring well will be considered first. A properly designed, constructed, and developed monitoring well made of inert materials should not change the nature or size distribution of the natural colloids. Well design must facilitate the collection of representative groundwater samples from a discrete portion of the aquifer formation in a reasonable amount of time. The well should be screened over a short interval for two reasons: 1) to provide adequate resolution of the location of groundwater flow containing the colloids; and 2) to reduce the time necessary to purge standing water from the well. The adequate assessment of the geochemical origin of the colloids requires resolution to match the small-scale geologic heterogeneities detectable by borehole logging (on the order of decimeters). Such small heterogeneities are known to provide high permeability pathways for groundwater flow (Childs et al., 1974; Freeze and Cherry, 1979). Also, the practical matter of purging time is an important consideration for sampling. A short screened interval allows the use of an inflatable packer to isolate the well screen from the overlying standing water. Purging time, even at very low flow rates, can be reduced to enable the sampling of as many as four wells in one day. For
example, a 5 cm–diameter well with a screened interval of 1 meter drilled to a depth of 10 meters where the depth to the water table is 3 meters contains approximately 14 liters of standing water. The placement of a packer above the well screen reduces the volume to approximately 2 liters. The time required to remove three well volumes at a pumping rate of 100 mL/min is reduced from about 7 hours to 1 hour.

Well construction is an important factor in obtaining groundwater samples for colloids. All well drilling techniques disrupt the aquifer formation by redistributing material and creating suspended particles as a result of abrasion (Buddemeier, 1986); however, some techniques are notoriously disruptive to the groundwater colloid distribution. Some drilling techniques using drilling muds, organic–rich slurries of bentonitic clays and other synthetic materials, to drill wells deep into solid rock. Drilling muds lubricate the drill bit and carry cuttings to the surface. The result is a zone around the well that is contaminated with respect to colloids and fine particles. Wells drilled by water–rotary and cable–tool methods are considerably cleaner than mud–rotary, but the large quantities of "tap" water pumped into the formation under pressure probably alter the existing groundwater chemistry and hydrology significantly.

Augering is the least disruptive drilling method because foreign materials are not introduced to the subsurface environment and the formation is not excessively churned by high–speed drilling or hammering. Augering is most useful in shallow, unconsolidated sediments where it is not necessary to drill more than a few meters below the water table. Below the water table, saturated sands tend to collapse and flow into the auger. To drill deeper than the water table, the auger method can be supplemented by the drilling of casing (with a casing drill bit attached to the bottom of the casing string) directly into the unconsolidated sediments. If it is necessary to drill into indurated sediments, the air–rotary method provides a
relatively clean technique. Compressed air carries the cuttings to the surface along with a stream of the formation groundwater. The injection of compressed air may significantly change the aquifer redox conditions, but the duration and distance of oxygen infiltration into the aquifer is unknown. Of course, the well itself is a permanent conduit to the aquifer that allows an oxic zone to persist next to the well indefinitely.

Some indurated sediments require the placement of a well packing around the well screen. Saturated unconsolidated sediments will usually collapse around the screen when the well casing or auger is withdrawn, but in hard rock, a packing of porous material (usually sand and gravel) must be placed around the screen to provide support. Obviously, it is important that this material does not contribute colloids to the groundwater sample; furthermore, the well packing should not remove colloids from the groundwater. The well packing may operate as a filtering medium with surface properties different from those of the aquifer material (Buddemeier, 1986).

The void left around the well riser pipe after the auger or drilling casing is installed is usually filled by cuttings brought up from the subsurface. The repacking of the borehole leaves a zone of high permeability for rapid vertical transport of groundwater and the mixing of groundwaters from different layers in the aquifer. Therefore, a seal is usually placed around the well in two places: just above the screen and at the land surface. It important to remember that the seal may not prevent vertical mixing and that the seal materials (usually expanding bentonite clay pellets) may generate foreign colloids.

Relatively inert materials must be used for the well screen and riser pipe. The well screen should be constructed of Teflon or stainless steel because it is direct contact with the groundwater to be sampled. The potential for sample contamination by leaching of the well screen and riser pipe must be considered if
certain materials are used. Galvanized steel risers can contaminate the groundwater with colloids, as rusted iron may flake off the pipe as pumps or bailers are lowered into the well. Also, the surface properties of the well material must be considered for possible removal of colloids, as for the well screen material.

Well development is an important step in the preparation of a monitoring well for groundwater sampling. New wells usually must be pumped to remove particles that accumulate in the well or block the well screen. Rigorous procedures are used for the development of large–capacity water supply wells, but for small–diameter monitoring wells, such procedures are not be followed because submersible pumps that fit in a 5 cm–diameter well are not capable of the high flow rates that would normally be recommended for development. Well development is usually performed by pumping at the maximum flow rate (about 4 L/min) until the groundwater turbidity is low and constant. Also, occasional reversal of pumping is effective in dislodging particles trapped in the well screen, analogous to the effect of reversing the flow in filtration beds (Herzig et al., 1970). Finally, the newly installed and developed well should be allowed to equilibrate with the formation groundwater for some period of time. It is difficult to determine when a well is ready to produce representative groundwater samples. Monitoring of the stabilization of chemical parameters and particle abundance in the field is probably the best criteria short of a complete analysis of the groundwater chemistry. Longer times should probably be allowed for wells drilled by more disruptive techniques and wells in low permeability formations.

2.2.2. Sampling Procedures

At many sites, wells are already in the ground; all that can be done about shortcomings in well design and construction is to account for them in considering
the sampling results. However, sampling and storage methods can be carefully tailored to sample groundwater from wells without significantly altering the chemistry or colloid distribution of the sample.

Removing groundwater through a well necessitates disturbance of the natural groundwater flow. The increased flow velocities and shear stresses may suspend particles into the groundwater. In the sampling procedure (Backhus et al., 1986), a very low pumping rate (approximately 100 mL/min) is used to minimize the disturbance of the groundwater flow and to collect samples representative of the natural colloid population. Typical small-diameter pumps produce flow rates of 1 to 4 L/min in shallow wells and these flow rates will produce groundwater velocities far in excess of natural groundwater velocities. The sudden increase in groundwater velocity may resuspend settled particles in the 1 to 3 μm range and detach adhered particles in the submicron range (Herzig et al., 1970). Larger particles (up to 30 μm) can be suspended by the reversal of the natural groundwater flow direction produced downstream of the well by high flow rate pumping. The average linear groundwater velocities produced by pumping at 100 mL/min, 1000 mL/min, and 4000 mL/min as a function of distance from the well screen can be estimated by dividing the pumping rate by the area through which the groundwater is passing, similar to the analysis of Reynolds (1985). The calculated groundwater velocities are shown in Figure 2.1 for a 5 cm—diameter well screened over a 1.0 meter interval in an aquifer with porosity of 0.4. The groundwater velocity \( u \) (cm/sec) can be represented by

\[
    u = \frac{Q}{2\pi n(R + r)h}
\]

(2.1)

where \( Q \) is the pumping rate (cm³/sec), \( n \) is the porosity, \( R \) is the distance from the well screen (cm), \( r \) is the radius of the well (cm), and \( h \) is the length of the screened interval (cm). This analysis assumes that the groundwater flow is horizontal, thus the effects of drawdown are ignored, and the groundwater enters the well along the
Figure 2.1. Calculated Pumping-induced Groundwater Velocities at Three Flow Rates

Figure 2.1a. Decrease to Natural Groundwater Velocity for All Pumping Rates

<table>
<thead>
<tr>
<th>Flow Rates</th>
<th>Pumping-induced velocity (cm/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4,000 mL/min</td>
<td>dashed line</td>
</tr>
<tr>
<td>1,000 mL/min</td>
<td>solid line</td>
</tr>
<tr>
<td>100 mL/min</td>
<td>dotted line</td>
</tr>
</tbody>
</table>

Natural Groundwater Velocity \(9.8 \times 10^{-5}\) cm/sec

Distance from Well Screen (m)

Well diameter 5 cm   Well screen length 1.0 m   Porosity 0.4

Figure 2.1b. Groundwater Velocities within 100 cm of the Well Screen

<table>
<thead>
<tr>
<th>Flow Rates</th>
<th>Pumping-induced velocity (cm/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4,000 mL/min</td>
<td>dashed line</td>
</tr>
<tr>
<td>1,000 mL/min</td>
<td>solid line</td>
</tr>
<tr>
<td>100 mL/min</td>
<td>dotted line</td>
</tr>
</tbody>
</table>

Natural Groundwater Velocity \(9.8 \times 10^{-5}\) cm/sec

Distance from Well Screen (cm)
entire length of the screen. The effects of drawdown in the unconfined aquifer are assumed to be negligible when the pumping rates are low and the well is screened substantially below the water table. At these relatively low flow rates, the groundwater is expected to enter the well along the length of the screen and then flow toward the pump inlet inside the well. At higher flow rates, groundwater might be drawn more directly to the pump inlet; thus, the flow would be drawn through a smaller area, causing higher groundwater velocities. The analysis also assumes that the groundwater around the well is stationary and that the radial influence of pumping will be felt equally in all directions. This assumption is acceptable when the pumping-induced velocities are significantly greater than the natural groundwater velocities, but when the pumping-induced velocities are comparable to the natural groundwater velocities, the direction of natural groundwater flow will significantly affect the resulting groundwater flow velocities. Finally, the analysis calculates the average linear velocity of the groundwater, not the actual pore velocity, which is greater because the water must follow the tortuous paths around the aquifer grains.

Figure 2.1 shows the decrease of pumping-induced velocities with distance until the flow is equal to the natural groundwater velocity. The natural groundwater velocity, $9.8 \times 10^{-5}$ cm/sec, is calculated for an aquifer with a hydraulic conductivity of $4.2 \times 10^{-2}$ cm/sec, a hydraulic gradient of 0.93 m/km, and a porosity of 0.4, typical for the New Jersey Coastal Plains surficial aquifer. The natural groundwater velocities calculated for the Delaware Coastal Plain aquifer are similar.

Increased groundwater velocities are expected to mobilize particles that were settled and attached to the aquifer substrate. A comparative assessment of the resuspension of settled particles and the detachment of adsorbed particles by increased groundwater velocities is possible by determining the increase in shear stress incident on the particles. We will calculate the shear rates produced in the
aquifer by the natural groundwater velocity and the pumping-induced velocities for
100, 1000, and 4000 mL/min pumping rates and compare them to shear rates known
to disaggregate and detach particles in experiments. Using an experimental
arrangement physically analogous to particles attached to much larger aquifer
grains, Hubbe (1985a; 1985b) determined the shear stress necessary to remove TiO₂
particles of size range 150 nm to 700 nm from a glass plate. The corresponding
shear rates ranged from about 1.0 to 25 sec⁻¹, with the lowest shear rate

corresponding to the largest particle size. The shear stress necessary to remove
particles from the plate depends on the balance between an adhesive torque due to
van der Waals attractive forces and a hydrodynamic torque due to the shear flow.
Shiga et al. (1985) observed the removal of red blood cells from a
polymethylmethacrylate plate at median shear rates as low as 10 to 20 sec⁻¹. Shear
rates as low as 4 sec⁻¹ broke up aggregates of montmorillonite in seawater and
kaolinite aggregates were peptized at shear rates between 16 and 32 sec⁻¹ (Hunt,
1982). The size range of particles studied by Shiga et al. (1985) and Hunt (1982) is
considerably larger than the size range of suspended particles in groundwater.
Other studies have examined the breakup of clay aggregates coagulated by alumina
(Matsuo and Unno, 1981), ferric hydroxide (Pandya and Spielman, 1982), and
cationic polymers (Lu and Spielman, 1985). The range of shear rates necessary for
peptization of the aggregated clays is much higher: 70 to 200 sec⁻¹.

The average shear rate \( G \) (sec⁻¹) is expressed as

\[
G = \left( \frac{\epsilon}{\nu_f} \right)^{1/2}
\]  

(2.2)

where \( \epsilon \) is the mean energy dissipation rate (cm⁻²·sec⁻¹), and \( \nu_f \) is the kinematic
viscosity of the fluid (cm²/sec). In terms of flow through porous media, the energy
dissipation rate can be equated to the the energy of head loss and expressed as

\[
\epsilon = g u \frac{dh}{dT}
\]  

(2.3)
where $g$ is the acceleration due to gravity (980 cm/sec$^2$), $u$ is the average linear velocity of the groundwater (cm/sec), and $dh/dl$ is the hydraulic gradient. The groundwater velocity can be replaced by

$$u = \frac{K}{n} \frac{dh}{dl}$$  \hspace{1cm} (2.4)

according to Darcy's Law, where $K$ is the hydraulic conductivity (cm/sec) and $n$ is the porosity, assuming the groundwater flow is laminar (Freeze and Cherry, 1979). If the Reynolds number of the flow is less than 1 to 10, the groundwater flow is laminar (Bear, 1972). The Reynolds number for flow through porous media, $R_e$, is expressed as

$$R_e = \frac{\rho_f u_s d}{\mu_f}$$

where $\rho_f$ is the fluid density (0.9991 g/cm$^3$ at 15°C), $\mu_f$ is the dynamic viscosity of the fluid (0.01139 poise at 15°C), $u_s$ is the specific discharge (cm/sec), and $d$ is a representative length dimension for the porous medium, usually the mean grain diameter. For the maximum groundwater velocity produced by pumping at 4000 mL/min, 0.11 cm/sec at the well screen, $u_s = 4.4 \times 10^{-2}$ cm/sec, and the mean grain size is estimated at $d = 0.025$ cm for a medium-grained unconsolidated sand (Freeze and Cherry, 1979). The resulting $R_e \approx 0.1$, so the groundwater flow is laminar and Darcy's Law applies.

The result for the mean energy dissipation rate is

$$\epsilon = g \frac{K}{n} \left[ \frac{dh}{dl} \right]^2.$$  \hspace{1cm} (2.5)

Finally, replacing $\nu_f$ with $\mu_f / \rho_f$, and substituting the expression for $\epsilon$ into Equation (2.2), we arrive at the average shear rate $G$ for groundwater flow:

$$G = \left[ \frac{g \rho_f K}{\mu_f n} \right]^{1/2} \frac{dh}{dl}.$$  \hspace{1cm} (2.6)

To determine the shear rates produced by pumping, a hydraulic gradient is inferred through Darcy's Law using the groundwater velocity at a distance of 2.5 cm from the well screen. At 2.5 cm from the well screen, the groundwater velocity is near
the maximum velocity produced by pumping, but the aquifer is less disturbed by well installation. The resulting shear rates are tabulated in Table 2.1.

From this analysis of shear, we can see that the shear rate produced at a distance of 2.5 cm from the well screen by pumping at 1000 and 4000 mL/min approaches and exceeds the shear rates that remove TiO₂ particles from glass (1 to 25 sec⁻¹) and blood cells from an acrylic surface (about 10 to 20 sec⁻¹) and break up clay aggregates (4 to 32 sec⁻¹). The 100 mL/min pumping rate does not produce shear rates that just approach the lower limit of shear rates observed by Hubbe (1985a; 1985b), but only at this relatively short distance from the well screen. Further away from the well screen, shear rates capable of removing particles from surfaces are never felt. Therefore, the calculations of groundwater velocities and shear rates induced by pumping indicate that pumping at 100 mL/min should produce samples that contain only colloids naturally suspended in the groundwater.

Pumping groundwater at such low flow rates is not a trivial matter. Very few reliable pumps are capable of steady, continuous withdrawal of groundwater at 100 mL/min without substantial modification. The few pumps that are capable of low flow rate pumping without modification are unacceptable for other reasons. The pump should minimize exposure of the groundwater to the atmosphere to prevent sample degassing and changes in redox chemistry. Also, the components of the pump that come into contact with the groundwater must have low surface area and must be made of relatively inert materials (e.g., Teflon, stainless steel 304, polypropylene) to reduce sample contamination and losses due to solute and particle adsorption. An unknown factor of pump suitability is the amount of turbulent energy imparted to the water by the various pumping mechanisms and the effect of increased shear on the colloid distribution.

The purging of the groundwater standing in the well and in the aquifer near the well is important because that water has been in contact with the atmosphere
Table 2.1. Shear rates produced by natural and pumping-induced groundwater flow at a distance of 2.5 cm from the well screen.

<table>
<thead>
<tr>
<th>Groundwater velocity $u$ (cm/sec)</th>
<th>Shear Rate $G$ (sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural</td>
<td>9.8·10$^{-5}$</td>
</tr>
<tr>
<td>100 mL/min</td>
<td>1.3·10$^{-3}$</td>
</tr>
<tr>
<td>1000 mL/min</td>
<td>1.3·10$^{-2}$</td>
</tr>
<tr>
<td>4000 mL/min</td>
<td>5.3·10$^{-2}$</td>
</tr>
</tbody>
</table>
and the well materials for a prolonged period (Barcelona and Helfrich, 1986). The well is an unnatural conduit to the atmosphere that introduces oxygen to the aquifer and allows carbon dioxide to escape. The extent of the zone altered by atmospheric exposure is not known; therefore, the chemistry of the pumped groundwater should be monitored for the stabilization of field-measurable parameters (pH, Eh, specific conductivity, dissolved oxygen, temperature, and colloid abundance) indicative of unperturbed groundwater. As mentioned before, a short screened interval that can be isolated by an inflatable packer can reduce the volume necessary to purge from the well.

The well purging must also remove particles resuspended into the standing water from the bottom of the well and dislodged from the well casing. Usually, the bottom of the well is coated by a layer of particles that settle out of the groundwater entering the well. These particles are often disturbed and resuspended by placing the pump in the well. The monitoring of the suspended particle concentration in essential in determining when the pumped water has reached a steady level representative of the groundwater.

Once the groundwater is pumped to the surface, it must be properly handled to preserve the chemical integrity of the samples until analysis. Sample exposure to the atmosphere, elevated temperatures, and light must be minimized. Exposure of the sample to the atmosphere allows for degassing of carbon dioxide and an increase in pH. The redox chemistry of samples with low dissolved oxygen can also be drastically affected by addition of oxygen. Many metals are far more soluble in reducing groundwaters and the oxidation of these metals often results in the formation of hydrous oxides of the metals. For example, Troup et al. (1974) and Reynolds (1985) observed the oxidation of dissolved Fe(II) to ferric hydroxide precipitates in sediment and groundwater samples. Furthermore, the oxidation of Fe(II) to Fe(III) can reduce the concentrations of phosphate and other anions and
trace metals by precipitation of ferric phosphates and adsorption to ferric hydroxide surfaces (Bray et al., 1973).

Exposure of the sample to light affects the nature and abundance of various organic macromolecules, especially humic and fulvic acids, as well as the redox chemistry. Possible photochemical processes that might act on the sample include the photoreductive dissolution of iron oxide colloids (Waite and Morel, 1984), the photoreduction of Fe(III) to Fe(II) by humic substances and subsequent oxidation of Fe(II) back to Fe(III) by dissolved oxygen (Miles and Brezonick, 1981; Madsen et al., 1986), the transformation of various trace organic chemicals by transfer of absorbed light energy from humic substances (Zepp et al., 1985), and the production of singlet oxygen by humic substances subject to light (Cooper and Zika, 1983; Frimmel et al., 1987).

Finally, the samples should be stored and analyzed at or a few degrees below the ambient groundwater temperature. Low temperatures slow metal oxidation, gas exchange, the nucleation of precipitates, and bacterial metabolism.
2.3. **Sampling Materials and Methods**

The groundwater sampling and handling procedures used in this investigation were developed by Reynolds (1985) and Backhus *et al.* (1986). These procedures, along with certain modifications of equipment, address the concerns raised in the preceding section: suspension of colloids by high pumping rates; modification of colloid size distributions by excessive pump turbulence; purging of the standing water in the well; and exposure of the sample to the atmosphere, light, and elevated temperatures. The design, construction, and development of the wells already installed at the sites will be considered in the interpretation of the sampling results.

The groundwater sampled for this investigation was collected during two sampling expeditions: April, 1987 and October, 1987. During the April sampling trip, four wells in the watershed of the McDonalds Branch in Lebanon State Forest, New Jersey, in an region known as the Pine Barrens, and three wells scattered throughout Delaware were sampled to reconnoiter for colloids in groundwater. The four Pine Barrens wells sampled are designated QWH–1A, QWH–1B, QWH–4A, and QWH–4B ("Swamp Shallow," "Swamp Deep," "Upland Shallow," and "Upland Deep," respectively, are the informal names used in this investigation; see Figure 3.1 for the locations of the wells). In Delaware, the three wells sampled are called Db24–17, located southeast of Newark, Delaware; well Lc42–01, located about 2 km west of Harrington, Delaware; and well Qe44–01, located a few kilometers west of Trap Rock State Park (see Figure 4.1 for the locations of the wells).

Results gathered from the April sampling and analysis indicated that significant amounts of colloids existed in the Swamp Deep (QWH–1B) groundwater in the Pine Barrens and in the well Lc42–01 groundwater near Harrington, Delaware. A focused sampling program was devised to fully examine these wells, as well as surrounding wells, to define the geological, hydrological, and geochemical
conditions that produced these colloids during the October sampling. A means of estimating colloid concentrations, analysis of samples by light scattering intensity, was brought into the field to provide instantaneous data regarding colloid abundance in the groundwater. In the Pine Barrens, the Swamp Deep well was purged for 6 hours at low flow rates before samples were collected, and the Swamp Shallow and Upland Deep wells (QWH–1A and QWH–4B, respectively) were sampled again to provide comparisons of groundwater chemistry and colloid abundance. In Delaware, a well located a few kilometers southeast of Harrington, Delaware, that had not been sampled during the April sampling, well Md22–01, was included in the investigation to examine the local contrast in groundwater chemistry. Well Lc42–01 was purged for 7 hours before being sampled. At the conclusion of sampling in some of the wells, the pumping rate was increased to the maximum rate, about 1 L/min, to examine the response of the colloids in the formation. Data on the colloid abundance, as measured by light scattering analysis and SEM/EDX analysis of suspended sediment collected on filters, will be discussed in the final section of this chapter as justification of the sampling procedures discussed in this section.

2.3.1. Sampling Equipment

The equipment used to withdraw groundwater from the wells included four main components: 1) the pump; 2) the inflatable packer; 3) the AC-to-DC adjustable power supply; and 4) the gasoline-powered AC generator. The pump (model SP–202, Fultz, Inc., Lewistown, PA) is a submersible, gear-driven, DC-powered model, 17.8 centimeters long and 4.45 centimeters in diameter. The Teflon gears induce the flow of groundwater through a stainless steel (304) mesh screen and pump body. The water is pushed to the surface in a continuous stream
through a 0.5 cm–diameter polypropylene discharge tube. The pump motor is powered by an AC–to–DC adjustable filtered power supply (Model EFB, Electro Products Laboratory, Chicago, IL). The power supply is capable of supplying and varying the voltage necessary to maintain a 100 mL/min pumping rate. The AC power is supplied by a gasoline–driven generator that also provides power for other field instruments. The pump can also be powered by a 24 volt battery pack and controlled by a variable rheostat, allowing for increased portability at the expense of greatly reduced pumping duration and reliability. The inflatable packer (manufactured and modified by QED Environmental Systems, Inc., Ann Arbor, MI) is placed about 0.7 meters above the pump. The pump power lines and discharge tube run through the packer body. The packer is made of polyvinyl chloride, with stainless steel fittings and an inflatable bladder made of viton. A plastic–coated pressure tube connects the packer to the pressurized gas supply and a steel cable provides support for lowering and hoisting the pump. The packer pressure tube is fitted with a pressure gauge and one–way check valve for operation by a hand pump for increased portability, or it can be attached directly to a pressurized gas cylinder (argon is used). Figure 2.2 schematically shows the arrangement of the pumping system in the well. The pump and discharge tube were rinsed thoroughly with distilled water between wells.

At the surface, the pH, Eh, specific conductivity, dissolved oxygen, and temperature of the groundwater were measured in a Plexiglas flow–through cell that prevented exposure of the groundwater to the atmosphere (Figure 2.2). The pH and Eh were measured using a Horizons Ecology (Chicago, IL) Model 5996 pH/mV meter with an Orion combination pH electrode and a Cole–Parmer Pt electrode with 4N Ag/AgCl reference electrode. The pH electrode was calibrated with pH 4.00 and pH 7.00 buffers, and the Eh electrode was calibrated with solutions of quinhydrone in pH buffers. The solutions were kept at groundwater temperature in
Figure 2.2. Sampling Setup (developed by Backhus et al., 1986).
the calibration cell (of the flow-through cell) to properly calibrate the electrodes with respect to temperature. Eh measurements were corrected for the potential difference between the Ag/AgCl reference electrode and the hydrogen half-cell using the correction factor listed by Langmuir (1971a). Eh measurements were stable and reproducible within ±5 mV after prolonged pumping. Specific conductivity was measured on a Hanna Instruments (Italy) model HI 8333 conductivity meter, calibrated in 40% NaNO₃, 40% NaHCO₃, and 20% NaCl solutions of known conductivity. Dissolved oxygen and temperature were measured using a Y.S.I. (Yellow Springs, OH) Model 54 dissolved oxygen meter. The meter was calibrated to an oxygen-saturated solution at air temperature. The accuracy of the meter and the exclusion of oxygen from the flow cell are questionable at DO concentrations below 30 μM. All instruments were rinsed between wells using deionized distilled water (ddH₂O) prepared on a Milli-Q system (Millipore Corp., Bedford, MA).

The light-scattering intensity of the groundwater was measured at a fixed angle of 90° in a Coulter (Hialeah, FL) model N4 submicron particle analyzer equipped with a 4 mW HeNe laser generating coherent radiation at λ=632.8 nm. The standard Coulter N4 is burdened by a background scattering intensity of about 10⁴ counts/sec, so the instrument was modified to provide a background low enough to measure the scattering intensity of very dilute solutions: a low dark counts (<10 counts/sec), high gain photomultiplier (model 9893, Thorn EMI Gencom, Fairfield, NJ) and high voltage power supply (model S502, Products for Research, Danvers, MA) were added to the particle analyzer. The sample chamber temperature was set to the groundwater temperature and is precise to ±0.2°C. In the field, samples were collected in polystyrene 1-cm path length cells, filled to overflowing, and then capped tightly and placed in the sample chamber of the particle analyzer. Samples were equilibrated for 3 minutes to relax turbulent fluid motions caused by sample handling and temperature differences.
The light scattering intensity was measured for approximately 3 minutes and the mean scattering intensity and standard deviation were reported for the sample. The computation of the arithmetic mean occasionally produced results skewed toward a few scattering intensity measurements that were 1 to 2 orders of magnitude larger than majority of the measurements made for a sample. The high measurements are probably caused by the settling of a few large particles through the sample volume, which increases the light scattering intensity far above the intensity scattered by the more abundant, but smaller, particles. The standard deviations of these samples are often larger than the means themselves for the more dilute samples. The light scattering intensity of field blanks of ddH$_2$O was also measured—a range of 125 to 175 counts/sec was recorded for the polystyrene sample cells. Samples were also taken in the field in 60 mL BOD bottles to measure scattering intensity in the lab to evaluate the effect of storage on colloid size distribution.

Based on the SEM/EDX analysis of groundwater particles collected on filters during the reconnaissance sampling, it was determined that the vast majority of particles were clays of some sort, kaolinite being one of the most likely candidates for both Pine Barrens and Delaware groundwaters. Therefore, scattering intensities of the groundwaters were compared to scattering intensities of kaolinite solutions of known concentrations to estimate the groundwater colloid weight concentrations were estimated (Kerker, 1969). The kaolinite solutions were made up with colloidal kaolin powder (EM Science, Cherry Hill, NJ) and ddH$_2$O and a standard curve was established (Figure 2.3) by measuring the light scattering intensities of at least 4 samples at a number of concentrations from 1 to 100 mg/L. The scattering intensities of the ddH$_2$O background samples were reduced to a mean of 25 counts/sec using fluorescence-grade quartz sample cells.
Figure 2.3. Kaolinite Scattering Intensity Standard Curve

Figure 2.3a. Kaolinite 1 to 100 mg/L

Figure 2.3b. Kaolinite 1 to 10 mg/L
Photon correlation spectroscopy was also performed on the field samples to attempt to determine the size distribution of the particles immediately after withdrawal from the well. The resulting autocorrelation curves showing the decay of correlated scattering intensity were analyzed using the method of cumulants (Koppel, 1972) and the Size Distribution Processor (a proprietary version of the CONTIN program developed by Provencher (1979)). These data analysis programs reside in the memory of the built-in computer of the N4 particle analyzer. Experimental parameters (duration, sample time $\tau$, and the upper limit of the size range) were varied extensively, but the heterogeneity of the samples' colloid distribution and the presence of large, slow-moving particles ("dust") prevented the determination of reliable and reproducible results.

Samples were taken and stored in containers for various analyses in the laboratory. All sample containers, syringes, filters, and filter holders were cleaned by soaking in 2 N HNO$_3$ solution and rinsing at least three times with ddH$_2$O, then sealed until use.

Groundwater was collected on filters for analysis by scanning electron microscopy/energy dispersive X-ray (SEM/EDX) analysis. Five milliliters of groundwater were sampled directly from the discharge tube into polyethylene disposable syringes and force-filtered through in-line 15 nm pore diameter Nuclepore polycarbonate filters in 25 mm-diameter Millipore Swinnex filter holders. Nuclepore polycarbonate filters were used throughout the investigation based on the results of Jay (1985) and Jardine et al. (1986). The filters were loaded into the filter holders in the lab and sealed until use. The filters and particles were rinsed with 5 mL of ddH$_2$O to rinse away ions that might precipitate during evaporation of water on the filter. Filters were left in filter holders and placed in a desiccator to promote filter drying. In the lab, filters were removed from the filter holders, placed in covered polystyrene petri dishes, and returned to the desiccator until the SEM/EDX
analysis.

Samples for analysis of iron, aluminum, silicon, and organic carbon in the laboratory were collected in 60 mL and 300 mL glass BOD bottles sealed in plastic zipper-lock bags. The use of glass containers was not expected to significantly change the silicon concentrations because the groundwaters were already saturated with respect to quartz. Prior to sampling, the BOD bottles and plastic bags were flushed and filled with argon, then sealed until sampling. During sampling, the ground-glass stopper was shaken off, the plastic bag was opened slightly, the discharge tube was inserted into the BOD bottle, and the bottle was filled from the bottom to overflowing. The tube was removed, the bag was quickly sealed, and the stopper was maneuvered into the neck of the BOD bottle, sealing the sample with no headspace. In the field, samples were stored in a cooler filled with ice packs. Upon return to the laboratory, samples were stored until analysis in a refrigerator at a temperature just below the average groundwater temperature. Samples to be filtered for the dissolved concentration of various parameters were filtered within 1 week of sample collection.

2.3.2. Sampling Procedure

The typical sampling procedure began with the placement of the pump in the well. The pump was placed so that the inflatable packer was set just above the well screen. After the packer was inflated, the discharge tube was submerged in a container filled with water and the pump was started by initially applying a low voltage and gradually increasing the voltage until a slow flow of bubbles appeared in the container (in this manner, surging was avoided during the start—up). When the groundwater reached the surface, the flow rate was quickly measured in a graduated cylinder and the voltage adjusted to maintain a 100 mL/min pumping rate. A field
light scattering intensity sample was taken and inserted in the N4 particle analyzer and a laboratory light scattering intensity sample was collected in a 60 mL BOD bottle. The field chemistry meters were then calibrated in solutions maintained at groundwater temperatures in the flow cell. The groundwater flow, electrodes, and probes were switched to the measurement cell and a set of groundwater chemistry parameters were measured. Groundwater chemistry and flow rate was measured every 20 minutes or whenever there was an abrupt change in flow rate (the pump operating at reduced voltage is susceptible to jamming by sand and grit in the gears). Light scattering intensity was measured in the field every 40 minutes, but more frequently as pumping progressed, to provide more statistical certainty of the results.

Purging of the well continued in this manner for at least 150 minutes at each well and at least 15 liters of water were removed. In a 5 cm–diameter well with a 1.0 meter screened interval in a aquifer with porosity of 0.4, this corresponds to the removal of the groundwater within about 8.0 cm of the well screen. One well (Swamp Deep) was purged for 420 minutes and all the groundwater within a distance of 15.5 cm was removed. For wells purged for an extended period of time, intermediate filter and groundwater samples were taken for SEM/EDX and light scattering analysis in the lab.

At the completion of sampling in some wells, the pumping rate was increased to the pump's maximum rate, normally about 1 L/min, to examine the effects of high flow rate pumping on colloid sampling. Samples were collected for field light scattering measurement, lab light scattering measurement (in a 60 mL BOD bottle), and for SEM/EDX analysis (on a 15 nm filter).
2.4. **Pumping Results**

During the October sampling, the light scattering intensity of the groundwater was closely monitored in the field during the pumping of the five wells. Colloid concentration, as measured by light scattering intensity, was one of the criteria used to evaluate the effectiveness of purging the wells. As with the various chemical parameters measured in the field, the wells were purged until the colloid concentration stabilized. Scattering intensity was also measured in the laboratory to check the effects of sample storage on colloid stability. The particles in the groundwater larger than 15 nm were carefully collected on filters for SEM/EDX analysis. After sampling in some wells, the pumping rate was boosted from 100 mL/min to 1 L/min to examine the effect of increased flow velocity and shear stress on aquifer surfaces after prolonged pumping at the low flow rate.

Light scattering and pumping rate data are presented in a pair of graphs for each well, the first showing the scattering intensity of field- and lab-analyzed samples against the pumping time, and the second showing variations in the pumping rate against time. The field-measured chemical data are also presented as a function of pumping time for some wells. Relevant results of the SEM/EDX analysis will also be described to illustrate the effects of purging and increasing the pumping rate.

**2.4.1. Swamp Deep Pine Barrens**

The Swamp Deep well (QWH-1B) was pumped for nearly 7 hours at an average flow rate of slightly less than 100 mL/min (Figure 2.4). Water reached the surface 30 minutes after the pump was started. The flow rate was monitored during that time by observing the flow of bubbles from the discharge line. The unusual
Figure 2.4. Scattering Intensity and Pumping Rate Variations

Well QWH-1B "Swamp Deep"

Scattering Intensity (counts/sec)

Pumping Rate (mL/min)

- Water reached surface
- Sampling period

Temporary Flow Reversal
feature in the pumping rate graph, labelled "temporary flow reversal," was caused by a sudden jamming of the pump gears. The pump motor was susceptible to jamming by large particles while it was being operated at the low voltages necessary to achieve low flow rates. The water in the discharge line began flowing backward into the well until sufficient voltage was applied to free the pump gears. The voltage was then quickly decreased to return to the 100 mL/min pumping rate. The jamming and subsequent unclogging did not cause any increase in colloid concentration measurable by scattering intensity, but an increase in the dissolved oxygen and Eh was measured during the flow reversal.

The variations of the chemical parameters during the purging and sampling of the Swamp Deep well are shown in Figure 2.5. The chemical parameters appear to be changing with time and not stabilized at any particular value by the end of purging; however, the graphs actually show quite minor changes that may be even be affected by other factors over the 6 hour purging period (meter drift in changing temperatures). The Eh and DO gradually decrease and the pH gradually increases as the standing water and groundwater exposed to the atmosphere is purged. The groundwater temperature follows the daily trend of the air temperature because the water in the pump discharge line is exposed to the air temperature for about 25 minutes at the low flow rate.

The initial samples brought up from the Swamp Deep well were quite turbid and orange—brown in color. They scattered more than five times as much light as the 100 mg/L kaolinite standard. In the groundwater sampled into small BOD bottles, particles quickly settled and covered the bottom. Vigorous shaking was necessary to resuspend them for lab analysis of scattering intensity. The scattering intensities steadily declined until about 340 minutes after the start of pumping, when the scattering intensity stabilized at about 2.0·10^4 counts/sec (equal to the scattering intensity of about 60 mg/L kaolinite). Sample collection commenced
Figure 2.5. Variation of Chemical Parameters Measured in the Field vs. Pumping Time for the Swamp Deep Well
after nearly 420 minutes of purging. After sampling was completed, a final field determination of scattering intensity showed that the colloid abundance had decreased slightly in the final hour of sampling. Whether this slight decrease represents a small variation in a stable colloid concentration or a continued decrease over a much longer time scale is uncertain; however, the scattering intensity remained at about $2.0 \times 10^4$ counts/sec for about 2 hours. The samples collected in small BOD bottles and analyzed for scattering intensity upon return to the lab (in all cases, within 1 week of taking the samples) generally show lower scattering intensities than those measured in the field. Particles were probably adhered to the clean walls of the bottles and could not be resuspended by vigorous shaking.

Four samples of suspended sediments from the Swamp Deep well were trapped on 15 nm filters and analyzed by SEM/EDX. The results, shown in detail in Table A.1 in the Appendix, revealed that each of the four filters were heavily covered with particles. No correlation could be made between filter coverage and scattering intensity because each of the filters were completely covered by particles. The particles ranged in size from $<100$ nm to $20$ $\mu$m; the majority of the particles were in the $500$ nm to $2$ $\mu$m range.

Three distinct types of particles were identified in each of the filter samples. On the SEM/EDX instrument, particles were identified by structure and relative elemental abundance: 1) high–iron clays composed of about 46.4 percent Si, 40.6 percent Al, and 11.1 percent Fe; 2) low–iron clays composed of about 52.4 percent Si, 43.2 percent Al, and 3.5 percent Fe; and 3) iron–rich crystalline minerals, composed of greater than 50 percent iron. The suspended sediment was predominantly composed of the clays, which spanned the entire size range and appeared as individual flat plates of random geometry and as booklets of plates. The largest clay plates were generally the high–iron clays. The iron–rich minerals were smaller, in the $<100$ nm to $500$ nm size range, and situated in clumps of
rectangular fragments (Figures 3.3 and 3.6). The filters taken at different purging times were examined for changes in particle nature or size distribution as purging progressed, but no change could be discerned.

2.4.2. Swamp Shallow Pine Barrens

The Swamp Shallow well was sampled after purging for nearly 3 hours at an average flow rate of about 100 mL/min (Figure 2.6). The water remained deeply tea-colored throughout pumping, but there was no visible turbidity after the first hour of purging. The flow rate was 210 mL/min when the water reached the surface, but it was quickly reduced to about 85 mL/min. Following the collection of samples, the flow rate was briefly boosted to about 1.0 L/min to monitor the effects of high flow rate pumping on particle concentration.

The chemical parameters showed some variations during purging related to the purging of standing water in and around the well. The Eh and DO quickly decreased during purging to levels of 0.285 V and 30 µM O₂. The high flow rate measurements were slightly lower due to the reduced exposure of the groundwater to the atmosphere. The pH and specific conductivity remained quite steady throughout the purging and high flow rate pumping. The groundwater temperature followed the trend of the air temperature and the lowest groundwater temperature was recorded during the high flow rate pumping. Thus, the high flow rate measurements were reported for Eh, DO, and temperature and the means of the measurements were reported for pH and specific conductivity in Table 3.6.

The scattering intensity of the first sample was about 1.6 \cdot 10^4 \text{ counts/sec} just after the water reached the surface (about 47 mg/L in terms of the kaolinite standards). The groundwater scattering intensity dropped to a steady level of about 570 counts/sec (or 2.6 mg/L kaolinite) after nearly 3 hours of purging, despite deep
Figure 2.6. Scattering Intensity and Pumping Rate Variations

Well QWH-1A "Swamp Shallow"

Scattering Intensity (counts/sec)

Pumping Rate (mL/min)

- Field
- Lab

Background Intensity ~150 counts/sec

Water reached surface

Sampling period

Pumping Time (min)
tea—color that persisted in the water. The organic compounds present in the groundwater are poor light scatterers relative to kaolinite and other clays due to the lower indices of refraction and the smaller size of the organic compounds. At the end of sampling, the light scattering level was essentially the same; however, one of the two lab samples analyzed scattered about three times as much light as the field—measured samples. Atmospheric exposure during sample handling in the lab may have allowed oxidation of dissolved ferrous iron to ferric hydroxide prior to the light scattering analysis, but at the low pH of the Swamp Shallow groundwater, the hydrolysis of dissolved iron is very slow (Stumm and Lee, 1961; Sung and Morgan, 1980; Davison and Seed, 1987).

The particles collected from the groundwater at the Swamp Shallow well very lightly covered the filter taken at the end of the purging, in agreement with the low scattering intensities. The EDX analysis, which measures the energy of X-rays from an volume of sample about 1.5 μm in diameter and about 1.5 μm deep, was marked by high backgrounds of Au and Zn, but excellent isolation of individual particles was possible. The particles spanned a size range of about 300 nm to 3 μm. The largest, but least abundant, particles were rounded, framboidal grains that ranged in size from about 1 μm to 3 μm, and were composed of ≥ 97 percent silicon—probably quartz fragments. Other particles detected in small numbers included 1) small (300 nm to 600 nm) clumpy, crystalline particles composed of about 98 percent Al; and 2) slightly larger (around 1 μm) crystalline clumps of blocky plates composed of about 88 percent iron. Details on the SEM/EDX results are listed in Table A.1.
2.4.3. Upland Deep Pine Barrens

The Upland Deep well was sampled in October, 1987 to examine the processes contributing to the formation of colloids in the Pine Barrens groundwater. The reconnaissance sampling of April, 1987 revealed that the groundwater at the Upland Deep well had a very low colloid concentration (about 500 counts/sec). Similar results were obtained during the October sampling. The Upland Deep well was purged for 150 minutes at an average flow rate of about 100 mL/min and sampled, then the pumping rate was increased to 1.0 L/min to determine the effects of increased groundwater velocity on the colloid distribution (Figure 2.7).

The chemical parameters showed trends that the standing water in and around the well was purged and groundwater not exposed to the atmosphere was sampled. The Eh and DO quickly decreased and pH increased to stable levels over the first hour of purging. The specific conductivity increased slightly after the first hour to the level reported in Table 3.6. The groundwater temperature responded to changes in air temperature and decreased by about 2°C during the high flow rate pumping.

The first sample for field light scattering measurement was collected immediately after the water reached the surface. An intensity of about $3.2 \times 10^4$ counts/sec, or about 90 mg/L kaolinite, was registered. All of the following samples had scattering intensities of less than $2 \times 10^3$ counts/sec. For the last hour of purging, the scattering intensity diminished to less than $10^3$ counts/sec, or <4 mg/L kaolinite concentration. During the sampling, the pump jammed and positive flow was suddenly lost. The efforts to restore flow may have caused the slight increase in scattering intensity measured in the field at the 175 minute mark ($1.8 \times 10^3$ counts/sec).
Figure 2.7. Scattering Intensity and Pumping Rate Variations

Well QWH-4B "Upland Deep"

Scattering Intensity (counts/sec)

Background Intensity
~150 counts/sec

Water reached surface
Sampling period
High pumping rate
Flow reversal

Pumping Rate (mL/min)

Pumping Time (min)
After sampling, the pumping rate was abruptly increased to 1.0 L/min. The resulting flow was quite turbid and orangish-brown in color, even after three hours of low flow pumping. Two samples were taken for light scattering measurement, one in the field and one in the lab. Both showed substantial increases in scattering intensity, to colloid concentrations as high as 40 mg/L kaolinite. The sample measured in the lab after storage scattered slightly less light than the field sample.

One filter sample was collected at the Upland Deep well, at the end of purging, for SEM/EDX analysis. The particles were very sparsely distributed on the filter, as expected from the low scattering intensity. The predominant particles were rounded plates ranging in diameter from 500 nm to 2 μm. The plates were composed of silicon and aluminum in a 1.1:1.0 atomic ratio along with trace amounts (<1 percent) of potassium and iron. Other particles detected on the Upland Deep filter were similar to particles on the field blank filter. These particles may be present in the ddH₂O or added as airborne contamination in the field.

2.4.4. Well Lc42-01 Harrington, Delaware

Well Lc42-01 was purged for 6 hours at an average flow rate of about 100 mL/min. The pumping rate was much more variable at well Lc42-01 than in the Pine Barrens wells, as can be seen in Figure 2.8. Two temporary flow reversals occurred, one just before the completion of purging and one during sampling. Corrections to the flow rate were performed as smoothly as possible and apparently had no effect on the colloid composition.

The variations of the chemical parameters measured in the field are shown in Figure 2.9. The Eh remained steady during the purging until it unexpectedly rose during the high flow rate pumping. The DO initially declined and stabilized during purging, then decreased further during sampling, and finally dipped to its minimum
Figure 2.8. Scattering Intensity and Pumping Rate Variations

Well Lc42-01

Scattering Intensity (counts/sec)

Background Intensity ~150 counts/sec

Pumping Rate (mL/min)

Water reached surface
Sampling period
High pumping rate
Figure 2.9. Variation of Chemical Parameters Measured in the Field vs. Pumping Time for Well Lc42-01

- **Pumping Rate vs. Pumping Time**
- **Temperature vs. Pumping Time**
- **Eh vs. Pumping Time**
- **pH vs. Pumping Time**
- **Dissolved Oxygen vs. Pumping Time**
- **Specific Conductivity vs. Pumping Time**
during the high flow rate pumping. The pH was relatively constant throughout the purging and high flow rate pumping, while the specific conductivity rose gradually and then declined during the sampling and high flow rate pumping. The groundwater temperature also rose gradually during the day and then decreased in the evening, following the air temperature. The gradual rise and fall of the specific conductivity may be caused by the concurrent change in groundwater temperature. The final chemical parameters are listed in Table 4.5.

The first light scattering sample, taken 3 minutes after groundwater reached the surface, scattered $1.4 \times 10^5$ counts/sec of light, or about four times as much as the 100 mg/L kaolinite standard. The scattering intensities abruptly decreased in the groundwater during purging until a relatively steady level of about $2 \times 10^3$ counts/sec was reached after three hours of pumping. This level persisted for three more hours until sampling. Three anomalously high scattering samples, one taken at the 285 minute mark and two taken during sampling, were measured in the lab and may have been affected by sample handling (exposure to the atmosphere). Fairly rapid ferric hydroxide precipitation is likely given the near-neutral pH and high dissolved iron content of the Lc42–01 groundwater.

At the conclusion of sampling, the pumping rate was turned up to 1 L/min and two groundwater samples were taken for light scattering measurement. The field measurement showed a 75 percent increase over the steady scattering intensity, to about $3.5 \times 10^3$ counts/sec, but the lab–measured scattering intensity was slightly lower than the steady level, at $1.8 \times 10^3$ counts/sec.

Four filter samples were taken during purging and one filter sample was taken during the high flow rate pumping. The filter coverage decreases with purging time, as can be seen in the series of SEM photographs shown in Figure 2.10, in agreement with the light scattering results. The high flow rate filter sample shows approximately the same filter density as the filter sample taken at the end of
Figure 2.10.  Scanning electron micrographs of groundwater particles collected on 15 nm filters during pumping of well Lc42–01.

SEM Micrographs on following page.

Figure 2.10a.  Photo No. 13, upper left, Pumping Time 105 minutes, pumping rate ~100 mL/min.

Figure 2.10b.  Photo No. 18, upper right, Pumping Time 205 minutes.

Figure 2.10c.  Photo No. 21, lower left, Pumping Time 295 minutes.

Figure 2.10d.  Photo No. 26, lower right, Pumping Time 360 minutes, sampling commenced.

Scale bars shown on micrographs; filters magnified 500 times.
purging; however, the nature of the large particles on the high flow rate filter is
different than the last purging filter sample. This difference will be explained in the
following description of the filter particles.

The filter sample taken after 105 minutes (Figure 2.10a) is densely covered
with a wide size range of particles varying from ≤100 nm to nearly 40 μm. The most
abundant particles are rounded plates, spanning the entire size range. These
particles are divided into two groups: 1) high-K clay with an average composition
of 53.4 percent Si, 36.8 percent Al, and 5.8 percent K, and 2) low-K clay, composed
of 53.0 percent Si, 43.2 percent Al, and trace amounts of Fe, Ca, and K. Less
abundant are large (2 μm to 5 μm) quartz fragments, composed of ≥ 97 percent
silicon (detailed information on the particle compositions appear in Table A.2 in the
Appendix).

The second filter sample (Figure 2.10b), collected at well Lc42–01 after 205
minutes of purging, is less densely covered by particles. The most abundant
particles are the iron–potassium clays, but the plates of clay are smaller, ranging in
size from ≤100 nm to 3 μm.

The third filter sample (Figure 2.10c), collected after 295 minutes of purging,
showed a continued decrease in the density of particle coverage even though the
scattering intensities did not change significantly. There are fewer large particles (1
μm to 3 μm), but the smaller particles (< 1 μm) are still quite abundant. Clays are
the primary type of particle, corresponding to the common compositions detected on
the first filter sample. A small number of mineral fragments composed of silicon,
aluminum, and trace amounts of iron and calcium were also detected, as well as a
single, large (about 2 μm × 5 μm) amorphous clump of iron-rich minerals (≥ 80
percent Fe). This filter also contains some large aggregations (2 μm to 4 μm) of
organic material, as well as a pair of 300 nm to 400 nm spheres composed of greater
than 90 percent titanium.
The fourth filter sample from well Lc42–01 was collected after 6 hours of purging. It appears quite similar to the previous filter with the notable exception of a few very large plates (up to 20 μm) in one area of the filter, shown in Figure 2.10d. These large plates have compositions similar to the clays described above, but generally they had much more potassium (up to 10 percent K instead of the mean 5.8 percent for the high–K clays). The most abundant particles are smaller plates of the low–K clay in the ≤ 100 nm to 2 μm size range.

The final filter sample was collected at high flow rate after purging and sampling for nearly 7 hours at about 100 mL/min. The coverage of the filter is approximately the same as the previous filter and the size distribution of the colloid load is similar, but a major difference exists in the nature of the largest particles (5 μm to 10 μm). The large particles are primarily quartz fragments and not thin plates of clay. The majority of particles less than 1 μm across are clay plates. The significance of the appearance of large quartz fragments in the first filter sample and in this high flow rate sample will be discussed after the results of pumping well Md22–01 are presented.

2.4.5. Well Md22–01  Harrington, Delaware

Well Md22–01 was purged for nearly 3 hours at a low flow rate, sampled, and then pumped briefly at a high flow rate. The data presented in Figure 2.11 show the pumping rates and light scattering intensities for well Md22–01. As in the other wells, the scattering intensity is quite high initially, 7.0 × 10^4 counts/sec, but after about 100 minutes of purging, it had decreased to a very low and steady level of less than 500 counts/sec. This corresponds to a decrease from about 200 mg/L to less than 2.5 mg/L in terms of kaolinite standards. Two temporary flow reversals occurred, probably due to large suspended sediments jamming the pump gears.
Figure 2.11. Scattering Intensity and Pumping Rate Variations

Well Md22-01

Scattering Intensity (counts/sec)

- Background Intensity
- ~150 counts/sec

Pumping Rate (mL/min)

- Water reached surface
- Sampling period
- High pumping rate
The final chemical parameters are presented in Table 4.5. The Eh and DO decreased slightly and pH increased slightly after the first few minutes of pumping, reflecting the removal of groundwater influenced by atmospheric exposure. The groundwater temperature closely followed the trend of the air temperature. The specific conductivity gradually increased during purging and sampling, but decreased slightly during the high flow rate pumping.

At the end of purging and sampling, the flow rate was increased to about 1.1 L/min and the scattering intensity quickly rose to the initial levels. The large difference between the field- and lab-measured samples may be attributed to a real increase in turbidity between the samplings.

Two filter samples were collected at well Md22–01. The first filter (Figure 2.12), taken after 170 minutes of purging, shows a wide size range (≤ 100 nm to 40 μm) of relatively dispersed particles. Every particle analyzed by EDX revealed a similar composition: about 52.7 percent Si, 36.4 percent Al, 8.1 percent potassium, and 1.5 percent iron, along with trace amounts of calcium and titanium. These particles appear as booklets, single plates, and rounded clumps of aggregated plates. The larger clay plates contain a greater proportion of potassium than the smaller plates.

The filter sample taken during high flow rate pumping is densely covered with two types of particles (Figure 2.12b). Most of the larger grains, in the 1 μm to 10 μm range, are quartz fragments—they are composed of greater than 80 percent silicon. The second type of particles are clays similar to those described for the first filter sample, covering a size range of ≤ 100 nm to 5 μm. Again, the larger clay plates contain more potassium than the smaller clay plates.
Figure 2.12. Scanning electron micrographs of groundwater particles collected on 15 nm filters during pumping of well Md22–01.

SEM Micrographs on following page.

Figure 2.12a. Photo No. 34, left,
Pumping Time 170 minutes, pumping rate ~100 mL/min.

Figure 2.12b. Photo No. 37, right,
After Sampling, High Pumping Rate ~1.1 L/min.

Scale bars shown on micrographs; filters magnified about 5,000 times.
2.5. **Discussion of Pumping Results**

The results presented in this chapter focus on the methods and materials used to collect groundwater samples containing natural distributions of colloids. The effects of various aspects of monitoring well design and construction on the natural colloid distribution must be considered in determining the integrity of groundwater sampled for colloids. The sampling methods developed by Reynolds (1985) and Backhus *et al.* (1986) were used to assure that the disturbance of the natural colloid distribution would be minimized during sampling. The results indicate that the low flow rate pumping for well purging and sampling and the monitoring of the particle concentration during purging are the most crucial factors in preserving the natural colloid distribution in the groundwater samples.

The monitoring of the light scattering intensity of the groundwater in the field was used to determine the effectiveness of purging of the standing water in the well. The field–measured scattering intensities were generally higher than those measured in the lab. The particles probably settled or were adhered to the clean walls of the container and were not resuspended by shaking when the scattering intensities were measured about a week after the samples were collected. Some of the lab–measured scattering intensities were anomalously high; exposure to the atmosphere could have caused the formation of colloids not present in the groundwater (*e.g.*, ferric hydroxides).

The initial groundwater samples from each well had very high scattering intensities. The high particle concentration can be attributed to the resuspension of sediments settled in the bottom of the wells. The placement of the pump inevitably includes striking the well bottom in an effort to find the proper depth to set the packer. The predominance of clays in the initial particle load indicates that the bulk of particles in the water standing in and around the well are not the result of
exposure to the atmosphere (e.g., ferric hydroxides). Instead, the particles have been transported into the wells by natural groundwater flow or high-flow rate pumping (performed by other samplers) and have settled there in the lower velocity flow. During the low flow rate purging, the light scattering levels decreased to steady scattering intensities much lower than those of the initial samples. Further resuspension of particles settled to the bottom of the well by pumping at 100 mL/min is not likely because the pump inlet is located above the body of the pump, as shown in Figure 2.2. There is only about 0.25 cm clearance between the pump and the well screen.

The time required to purge the standing water that contains the high concentration of resuspended particles from the bottom of the well can be estimated by assuming a first order flushing of the standing water and the inflow of groundwater at some stable particle concentration representative of the natural colloid distribution. The change in the particle concentration of the pumped groundwater with time, as measured by scattering intensity, can be expressed by

$$\frac{dC}{dt} = - \frac{Q}{V} (C - C_i)$$  \hspace{1cm} (2.6)

where $C$ is the particle concentration (or scattering intensity), $C_i$ is the particle concentration of the natural groundwater that flows into the well after the standing water is purged, $Q$ is the pumping rate (cm$^3$/min), and $V$ is the volume of the standing water in the well (cm$^3$). The solution of this first order differential equation is

$$C = (C_o - C_i) \exp \left( - \frac{Q}{V} t \right) + C_i$$  \hspace{1cm} (2.7)

where $C_o$ is the initial particle concentration in the standing water. Three examples presented below will illustrate the various factors affecting the purging of the standing water in and around the well with respect to the particle concentration.

The first order flushing of the standing water in the Swamp Deep well is calculated using these parameters: $V = 2000$ cm$^3$, based on a 5 cm-diameter well
with a 1 meter screened interval isolated by the packer, \( Q = 100 \text{ cm}^3/\text{min} \), \( C_0 = 1.88 \times 10^5 \text{ counts/sec} \), and \( C_1 = 2.00 \times 10^4 \text{ counts/sec} \). These calculations are based on the assumption that the water in the well will be removed throughout the length of the screened interval without further resuspension of particles from the bottom of the well by pumping. It is uncertain whether this assumption is correct due to the isolation of the pump inlet above the pump body.

The calculated particle concentration based on the first order flushing of the standing water in the well is shown by the solid line in Figure 2.13a. The calculated decrease in particle concentration is much more rapid than the actual decrease in particle concentration. Two possibilities may explain this discrepancy: 1) a larger volume of water containing a particle concentration of \( C_0 \) exists around the well due to disturbance of the aquifer sediments by well installation; or 2) the pumping is resuspending more particles from the bottom of the well, thus keeping the pumped groundwater particle concentration higher for a longer period of time. It is difficult to ascertain the effect of the second possibility, but the first possibility can be further examined by determining the effect of a larger volume of water with high initial particle concentration due to the release of particles caused by well installation. The typical auger used to install wells is 19.4 cm in diameter overall. Assuming that another 1 cm of the aquifer around the edge of the auger is also disturbed, the total diameter of the disturbed zone is 21.4 cm. After the well is installed, this zone contains about 15 liters of water (for an aquifer with porosity of 0.4), which we will assume contains a uniform particle concentration of \( C_0 = 1.88 \times 10^5 \text{ counts/sec} \).

The first order flushing curve with \( V = 15 \text{ liters} \) is shown by the dashed line in Figure 2.13a. The particle concentrations calculated for flushing the standing water in the well and the disturbed zone of the aquifer initially follow the actual concentrations, but after the third and fourth hour of purging, the calculated
Figure 2.13. Flushing of Particles in Standing Water Compared to Actual Scattering Intensities

**Figure 2.13a.** Well QWH-1B "Swamp Deep"

Scattering intensity (counts/sec)

- Flushing of Particles in Well (2 L)
- Flushing of Particles in Well and Aquifer (15 L)

Field Intensity
Lab Intensity

Background Intensity ~150 counts/sec

**Figure 2.13b.** Well Lc42-01

Scattering intensity (counts/sec)

- Flushing of Particles in Well (2 L)

Field Intensity
Lab Intensity

Background Intensity ~150 counts/sec

**Figure 2.13c.** Well Md22-01

Scattering intensity (counts/sec)

- Flushing of Particles from Well

Field Intensity
Lab Intensity

Background Intensity ~150 counts/sec

Pumping Time (min)
particle concentrations are too high and they do not decrease to the stabilized particle concentration measured in the field by scattering intensity. These bounding flushing curves suggest that the purging of groundwater from the Swamp Deep well initially involves removing standing water with high concentrations of particles resuspended from the bottom of the well. Next, the purging of groundwater from a disturbed zone with some particle concentration between the standing well water and the natural groundwater may maintain the relatively high particle concentrations. Finally, natural groundwater containing the background particle concentration of about $2.00 \cdot 10^4$ counts/sec is pumped from the well. The further resuspension of particles from the bottom of the well may also affect the particle concentration.

The first order flushing calculation was applied to well Lc42–01 (Figure 2.13b) using $C_0 = 1.40 \cdot 10^5$ counts/sec, $C_i = 2.05 \cdot 10^3$ counts/sec, and $V = 3$ liters because the Delaware wells are screened over a 1.5 meter interval. The calculated flushing curve follows the decrease of the actual groundwater particle concentration quite closely, although the assumptions involved do not assure that the calculated flushing curve actually describes the purging dynamics. Nevertheless, the good match suggests that the purging of the standing water in the well at a high particle concentration is directly followed by the pumping of natural groundwater with the background particle concentration of $2.05 \cdot 10^3$ counts/sec. The effect of the disturbed zone or further resuspension of particles in the well is not apparent in well Lc42–01.

At well Md22–01, the flushing curve calculated using $C_0 = 7.04 \cdot 10^4$ counts/sec, $C_i = 2.63 \cdot 10^2$ counts/sec, and $V = 3$ liters underestimates the actual decrease in particle concentration. Somehow, the standing water in the well decreased more rapidly than predicted by the flushing curve. It is possible that very large particles (such as the quartz fragments observed on the high flow rate
groundwater filter collected from Md22–01) were resuspended when the pump was placed in the well, then quickly resettled before being removed with the purged water.

The importance of low flow rate pumping (100 mL/min) was emphasized by increasing the flow rate to 1 L/min after purging and sampling in three wells. The high pumping rate produced drastic increases in scattering intensity in two of the wells (Upland Deep and Md22–01). After purging and sampling for 7 hours, the scattering increase was less noticeable in well Lc42–01. Comparison of the filter samples collected during low pumping rates and high pumping rates revealed that the large increase in scattering intensity in well Md22–01 was indeed caused by an increase in colloid concentration. Furthermore, the high flow rate filter sample contained large quartz fragments that were not present in the low flow rate filter sample. Large quartz fragments also appeared in the high flow rate filter sample of well Lc42–01, as well as the initial filter sample (collected after 105 minutes of low flow rate purging); however, none of the filter samples collected during the last 3 hours of purging show any detectable trace of quartz particles.

The large quartz fragments have settling velocities on the same order as the maximum groundwater velocities produced by pumping at 100 mL/min, assuming that their shapes can be approximated by spheres (Gibbs et al., 1971). With such large settling velocities relative to the groundwater velocities, the large quartz fragments settled out of the groundwater pumped at 100 mL/min (Herzig et al., 1970). However, pumping at 1000 mL/min apparently produced groundwater velocities sufficient to suspend the large quartz particles and transport them to the surface.

There still remains the question of how these large particles are resuspended into the groundwater flow. The calculation of the shear rates occurring at the groundwater velocities produced by a range of pumping rates indicated that 1000
and 4000 mL/min pumping rates can detach and disaggregate particles in the aquifer, based on comparison of the calculated shear rates to shear rates observed to produce the same effects in experiments (Hubbe, 1985a; 1985b; Shiga et al., 1985; Hunt, 1982). Furthermore, the sudden imposition of groundwater flow in the direction opposite the natural groundwater flow (downstream of the well) can temporarily resuspend large particles (up to 30 μm) trapped in small pores (Herzig et al., 1970). The area affected by the flow reversal in much larger for a 1000 mL/min pumping rate than it is for a 100 mL/min pumping rate. The high flow rates may resuspend more particles from the bottom of the well, which would also lead to higher particle concentrations after the low flow rate pumping. These observations lead to the conclusion that the increase in pumping rate is responsible for the large quartz fragments found on the high pumping rate filters. The pumping rate of 1000 mL/min, commonly used in groundwater sampling, alters the nature and size distribution of the colloid in the samples.

The stabilization of the particle concentration, as measured by light scattering intensity and calibrated by standard suspensions of kaolinite colloids, as well as various chemical parameters, measured the effectiveness of the purging of the standing water in and around the well. The particle concentration proved to be the most valuable indicator of the purging effectiveness. Some chemical parameters measured in the field stabilized quickly relative to the particle concentration, while other were stable throughout the purging period. Dissolved oxygen and Eh usually declined quickly during the initial stages of purging and dipped to their lowest levels during the high flow rate pumping. The pH occasionally increased slightly, possibly in response to reduced degassing of CO₂ as exposure of the groundwater to the atmosphere decreased. The specific conductivity was usually stable throughout pumping or varied slightly in response to changes in the groundwater temperature. The groundwater temperature responded directly to the air temperature because the
slowly pumped groundwater spent 20 to 25 minutes in the pump discharge tube. In summation, the DO and Eh measurements may provide some indication of the effectiveness of purging, but they usually decreased to steady values long before the particles concentrations stabilized.

The plots of scattering intensity against pumping time revealed that 120 minutes (Md22–01) to 330 minutes (Swamp Deep) of purging at 100 mL/min were required to reach stabilized particle concentrations in terms of light scattering intensity. The volume of water purged from the wells before stabilization corresponds to at least 4 well volumes for well Md22–01 to about 16 well volumes for the Swamp Deep well. The "three–well–volume and steady chemistry" criteria generally applied to well purging would not serve well for groundwater sampling for colloids. Some sensitive measure of particle concentration should also be performed in the field to assure that the groundwater sampled contains a natural distribution of colloids, not artifacts from the resuspension of particles in the well or the chemically and physically disturbed region around the well.

In summary, the very low pumping rate (100 mL/min) reduces the disturbance of groundwater flow to levels that are not expected to resuspend settled particles or detach adhered particles. Higher flow rates (1000 mL/min and greater) are expected to significantly alter the groundwater particle distribution. The monitoring of light scattering intensity during purging provides a reliable measure of the colloid concentration of the groundwater and the best measure of effectiveness of purging for groundwater sampling for colloids. The sampling methods and materials used in this investigation produce groundwater samples that are faithful to the actual colloid distribution in the groundwater and allow for confident interpretations of the analyses.
CHAPTER 3. GROUNDWATER COLLOIDS IN THE PINE BARRENS

3.1. Site Description: Geology, Hydrology, and Geochemistry

The first stop on the search for groundwater suspected of containing colloidal matter is the surficial aquifer of the New Jersey Coastal Plain. The groundwater of this aquifer is known to contain high levels of iron and organic carbon beneath the many lowland areas of the region. Furthermore, the presence of colloidal iron oxyhydroxide was detected by Langmuir (1969) in deeper aquifers near the Delaware River. Crerar et al. (1979; 1981) attributed the high concentrations of dissolved iron and aluminum in the groundwater to complexation by the colloidal organic carbon and possibly to formation of colloidal oxyhydroxides. Pristine groundwater still exists New Jersey beneath the protected reserves of the Pine Barrens in the southern part of the state. We found sampling sites in a small watershed in Lebanon State Forest where the U.S. Geological Survey is conducting a comprehensive study of the effects of acid deposition on the geochemistry of the system.

3.1.1. Regional Setting

New Jersey can be divided into three principal geologic and physiographic provinces, as illustrated in Figure 3.1, after Olsson (1963). The narrow belt of Late Cretaceous through Eocene sediments and the more southerly Miocene to Pliocene sediments constitute the New Jersey Coastal Plain, an area covering about 5,500 km² in the southern half of the state. These sediments represent the northernmost expression of the Atlantic Coastal Plain with the exception of small isolated
Figure 3.1. Location of Wells in McDonalds Branch Watershed.
remnants rising above the sea (Long Island and Nantucket). The Coastal Plain sediments are about 300 meters thick and dip seaward usually less than 10 meters per kilometer, thickening to roughly 1,300 meters far offshore. Topographically, the region is flat and low-lying, with many swamps and slow-flowing streams that drain into the Delaware River to the west and into the Atlantic Ocean to the east.

The uppermost unit of the New Jersey Coastal Plain sediments is the Late Miocene Cohansey Sand, a blanket of quartz arenite ranging in thickness from a featheredge to greater than 70 meters at the coast. The Cohansey Sand is a regressive barrier beach and barrier-protected deposit composed of iron-stained beach sands, alluvial gravels, and multi-colored laminated clays with sporadic peat lenses formed in surf zones, backshore dunes, and freshwater and saltwater marshes (Carter, 1978). Rhodehamel (1979a) reports that the Cohansey is composed of about 76 percent sand and gravel, 13 percent silt, and 11 percent clay and indurated layers in the inland region. Nearer to the coast, the clay fraction increases to about 24 percent. Primarily kaolinitic clay beds, ranging in thickness from laminated seams (3 to 6 cm) to massive beds as thick as 1 meter, extend over large areas of the Cohansey within 6 meters of the surface. Iron is abundant in the Cohansey Sand as goethite and limonite coatings on sand grains and as pyrite, siderite, glauconite, and vivianite in bogs near streams (Braddock-Rogers, 1930; Rhodehamel, 1979a). Glauconite is the dominant matrix mineral in sands and silts of the deeper Hornerstown Sand, Tinton, and Navesink Formations (Carter, 1978).

A unique region of pine-dominated vegetation known locally as the Pine Barrens occupies about 3,900 km² of the New Jersey Coastal Plain (Bartlett et al., 1978). Two types of ecosystems are present in the Pine Barrens—uplands and lowlands (McCormick, 1970). The upland terrain is characterized by excessively well-drained sandy soils and pine, pine-oak, and oak-pine vegetation. The upland soils are acidic (pH 3.4 to 4.6), very low in cation exchange capacity (0 to 4
meq/100 g), highly leached, and rapidly permeable (Markley, 1979). Some clay minerals and hydroxides have been identified in the sandy soil, including kaolinite, Al–interlayered vermiculite and smectite (montmorillonite) and gibbsite, and their abundances increase with depth in the soil (Douglas and Trela, 1979). The canopy vegetation is dominated by the pitch pine (Pinus rigida), the blackjack oak (Quercus marilandica), and the post oak (Q. stellata). These species show marked adaptation to the frequent wild and prescribed forest fires in the Pine Barrens: the normally closed cones of the pitch pine open when subjected to the heat of fire to spread seeds, and the oaks are more fire–resistant than several other related species in the area (McCormick, 1970). The understory is largely lowbush blueberry (Vaccinium vacillans), sheep laurel (Kalmia angustifolia), and scrub oak (Q. ilicifolia) (Little, 1979).

The lowland communities in the Pine Barrens include hardwood swamps and nearly monospecific cedar swamps. Lowlands are also distinguished by seasonally high water tables. The soils are similar to those in the uplands, but often a layer of histosols (nutrient–poor muck and peat) overlays the sandy soils near streams (Markley, 1979). The cedar swamps are dominated by Atlantic white cedar (Chamaecyparis thyoides) and the hardwood swamps contain primarily red maple (Acer rubrum) and black gum (Nyssa sylvatica). Both types of swamps have an ericaceous understory and thick mats of Sphagnum moss (McCormick, 1970; Little, 1979). The lowlands are also home to several types of insectivorous plants, 26 species of wild orchids, and some endangered mosses and ferns, as well as large–scale commercial cranberry and blueberry cultivation (McCormick, 1970).

In the late eighteenth century, during the American Revolution, the swamps and bogs of the Pine Barrens were an important source of iron ore for the fledgling colonies. Today, groundwater has replaced iron as the chief resource of the region. Rhodehamel (1970) estimated that $40.9 \times 10^{12}$ liters of potable water are contained in
the Cohansey Sand alone. The Cohansey is essentially a water table aquifer, but low-pressure confined conditions exist over large areas in the lower parts of the aquifer. A mean hydraulic conductivity of $4.2 \times 10^{-2}$ cm/sec was measured in the Cohansey Sand during a series of pumping tests in Lebanon State Forest (site of this investigation). The average hydraulic gradient in the area is 0.93 m/km (Rhodehamel, 1979b). The aquifers and streams are fed by an average annual precipitation of about 114 cm, of which some 40 to 60 percent is lost to evapotranspiration (Rhodehamel, 1970; Swanson and Johnson, 1980; and Johansson and Lord, 1987). Most of the remainder, nearly 90 percent, infiltrates into the ground (Rhodehamel, 1970) because the highly permeable soils and flat topography greatly reduce the amount of surface runoff. A large portion of the precipitation that enters the soils feeds the streamflow; only a small portion is lost to deep groundwater flow in most areas. Most of the streams and rivers of the Pine Barrens are fed primarily by groundwater inflow (Rhodehamel, 1970).

The degree of hydraulic continuity between the Cohansey aquifer and the major river of the Pine Barrens, the Mullica River, was examined by Lang (1961) and Lang and Rhodehamel (1962). They measured water levels in a network of observation wells in and near the river during a six-day pumping test and found that the underlying aquifer was poorly connected with the river, probably because of a thin deposit of relatively impermeable bog iron which had formed in the bed of the river. The swamps adjacent to the Mullica were well-connected to the aquifer—they dried up during the pumping test. Crerar et al. (1979) confirmed this conclusion by measuring water levels in adjacent deep and shallow wells screened in the Cohansey Sand and the underlying Kirkwood Formation, a hydraulically connected aquifer composed of similar sediments. They found evidence for upward flow of groundwater near the Mullica River and proposed that the upward flow is transporting iron from the underlying glauconitic formations to the swamps.
surrounding surface streams, where it is deposited as bog iron.

The precipitation of the Pine Barrens is quite acidic (mean pH 4.41 measured by Yuretich et al. (1981)). The average chemical composition of precipitation (Table 3.1) is controlled by the abundance of aerosols released from the surf zone. Seasonal changes in wind direction and distance from the coast substantially alter the ionic composition of the precipitation. The average composition of two major Pine Barrens rivers, the Mullica River and Cedar Creek, is also listed in Table 3.1. The paucity of weatherable minerals in the Cohansey Sand and the corresponding lack of alkalinity—producing weathering reactions are responsible for the acidic pH (4.51) and very low total dissolved solids (about 20 mg/L) measured by Yuretich et al. (1981). Using a mass balance of ions in precipitation and river water (Table 3.2), they demonstrated that the precipitation has a controlling influence on the chemical composition of the rivers due to the relative inertness of the Cohansey Sand.

Some major ions in the mass balance exhibit notable discrepancies. Phosphate is significantly more abundant in precipitation than in river water because it is consumed as a nutrient by microorganisms. Phosphate may also be precipitated as vivianite in bog iron deposits (Crerar et al., 1979). The decrease in calcium abundance is attributed to storage in vegetation. Art et al. (1974) determined that calcium is the most abundant cation in plant material and Gay (1975) confirmed this result in vegetation in the Pine Barrens—calcium was three times more abundant in plants than any other cation. The large decrease in sulfate abundance, which accounts for greater than 80 percent of the mass difference between precipitation input and river output, is more difficult to explain. Sulfate may be lost to deep groundwater flow or anaerobically reduced to sulfide in the presence of sulfate—reducing bacteria and precipitated as iron sulfide in bog iron (Yuretich et al., 1981). The FeS precipitates are diagenetically altered to pyrite.
Table 3.1. Average composition of precipitation and stream water in the Pine Barrens (after Yuretich et al., 1981).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Precipitation¹</th>
<th>Stream Water²</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td></td>
<td>4.41</td>
<td>4.51</td>
</tr>
<tr>
<td>Na⁺</td>
<td>μM</td>
<td>60.4 (±33.5)*</td>
<td>119.0 (±36)</td>
</tr>
<tr>
<td>K⁺</td>
<td>μM</td>
<td>9.5 (±9.0)</td>
<td>16.2 (±9.2)</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>μM</td>
<td>27.5 (±28.8)</td>
<td>26.3 (±18.5)</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>μM</td>
<td>9.5 (±4.1)</td>
<td>23.5 (±9.5)</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>μM</td>
<td>79.4 (±55.2)</td>
<td>133.0 (±43.7)</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>μM</td>
<td>53.0 (±24.9)</td>
<td>66.3 (±24.5)</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>μM</td>
<td>6.3 (±7.9)</td>
<td>n.a.</td>
</tr>
<tr>
<td>PO₄⁻</td>
<td>μM</td>
<td>0.8 (±0.3)</td>
<td>0.4 (±0.1)</td>
</tr>
<tr>
<td>H₄SiO₄</td>
<td>μM</td>
<td>n.a.</td>
<td>72.0 (±13.2)</td>
</tr>
<tr>
<td>TDS</td>
<td>mg/L</td>
<td>11.5 (±7.2)</td>
<td>20.4 (±6.9)</td>
</tr>
</tbody>
</table>

¹ sampled every 2 weeks from 12/70 to 12/72 at 8 sites in eastern Pine Barrens.
² sampled every month from 12/70 to 12/72 at 33 sites in eastern Pine Barrens.
* standard deviation of the mean
TDS = Total Dissolved Solids
n.a. = not analyzed
Table 3.2. Chemical mass balance of precipitation input and river output in the Pine Barrens (after Yuretich *et al.*, 1981).

<table>
<thead>
<tr>
<th>Element</th>
<th>Precipitation Input (t/km²·yr)(^1)</th>
<th>Stream Output (t/km²·yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(^+)</td>
<td>0.05 ± 0.004(^*)</td>
<td>0.04 ± 0.01</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>1.85 ± 0.13</td>
<td>2.11 ± 0.15</td>
</tr>
<tr>
<td>K(^+)</td>
<td>0.49 ± 0.04</td>
<td>0.49 ± 0.04</td>
</tr>
<tr>
<td>Ca(^{2+})</td>
<td>1.46 ± 0.01</td>
<td>0.81 ± 0.04</td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>0.31 ± 0.02</td>
<td>0.44 ± 0.03</td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>3.73 ± 0.26</td>
<td>3.63 ± 0.30</td>
</tr>
<tr>
<td>SO(_4^{2-})</td>
<td>6.72 ± 0.70</td>
<td>4.89 ± 0.31</td>
</tr>
<tr>
<td>PO(_4^{3-})</td>
<td>0.07 ± 0.001</td>
<td>0.03 ± 0.001</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>14.69 ± 1.16</strong></td>
<td><strong>12.44 ± 0.89</strong></td>
</tr>
</tbody>
</table>

\(^1\) t/km²·yr = metric tons per square kilometer per year (1 t = 10\(^3\) kg)

\(^*\) standard deviation of the mean
after burial (Berner, 1984). Magnesium output was slightly greater than input, perhaps because deep groundwaters, rich in cations from glauconitic sediments, contribute magnesium to the river waters (Crerar et al., 1979).

The main difference between precipitation and groundwater chemistry is the addition of organic carbon, silica, iron, and aluminum to the water (Crerar et al., 1981). Organic carbon, composed mainly of humic and fulvic acids, is slowly generated by the decay of plant matter in the dry, nutrient-poor soil of the uplands areas. In the lowland swamps, organic carbon is rapidly leached from the matted organic layer at the surface by the standing water and is slowly decomposed. The high organic carbon levels, common to Atlantic Coastal Plain swamps and streams (Beck et al., 1974), produce dark brown to orange color in waters that remains after 0.2 μm—filtration (Crerar et al., 1981). The organic carbon input is highest in autumn when leaf fall is heavy. Dissolved H₄SiO₄, derived primarily from the weathering of clay minerals, exceeds saturation relative to quartz solubility, but is undersaturated with respect to amorphous silica in the groundwater. Iron and aluminum are derived primarily from deep groundwater near major streams and rivers. In the uplands, dissolution of the clay minerals in the sediments contribute most of the iron and aluminum.
3.1.2. Site–specific Description

For this investigation, groundwater was sampled for colloids at four wells located near the headwaters of the McDonalds Branch watershed in Lebanon State Forest, southern New Jersey. McDonalds Branch watershed is a small (6 km²), pristine, forested catchment representative of the geology and ecology of the Pine Barrens. Wells QWH–4A and QWH–4B (Upland Shallow and Upland Deep, respectively) are located side–by–side in a typical upland environment. About 60 meters to the southwest, wells QWH–1A and QWH–1B (Swamp Shallow and Swamp Deep) are located side–by–side in a typical hardwood swamp bordering on McDonalds Branch, at the transition between upland and lowland environment. In April and October, 1987, the swamp wells were surrounded by about 0.7 meters of standing water on the surface. The surface elevation at the upland wells is about 1.3 meters above the swamp wells. The well locations are shown in Figure 3.1 and the well construction details and the groundwater hydraulic head are listed in Table 3.3. Figures 3.2a and 3.2b show the sediment lithology at the Upland and Swamp wells, respectively.

McDonalds Branch and its watershed has been the site of a number of investigations concerning the budget and biogeochemistry of trace metals (Swanson and Johnson, 1980; Turner et al., 1985), the acidification of headwater streams (Johnson, 1979; Morgan, 1984; and Lord et al., 1986), the soil adsorption of sulfate (Schuster and Uchrin, 1985), and the photoreduction of iron oxides (Madsen et al., 1986). The U.S. Geological Survey is currently conducting a long–term study of the behavior of major ions and trace metals to determine the effects of acidic deposition in the watershed (Johnsson and Lord, 1987; Lord et al., 1988). Streamflow and water quality data have been collected at this site since 1953 and 1963, respectively, as part of routine USGS monitoring programs. These studies provided some
Table 3.3. Well construction details for McDonalds Branch monitoring wells (after field data supplied by D.G. Lord, USGS, WRD, West Trenton, NJ).

<table>
<thead>
<tr>
<th></th>
<th>QWH–1A Swamp Shallow</th>
<th>QWH–1B Swamp Deep</th>
<th>QWH–4A Upland Shallow</th>
<th>QWH–4B Upland Deep</th>
</tr>
</thead>
<tbody>
<tr>
<td>Land Elevation(^1) (m)</td>
<td>40.4</td>
<td>40.4</td>
<td>41.3</td>
<td>41.3</td>
</tr>
<tr>
<td>Hydraulic Head(^1) (m)</td>
<td>40.15</td>
<td>39.57</td>
<td>39.34</td>
<td>39.34</td>
</tr>
<tr>
<td>Well Depth (m)</td>
<td>1.7</td>
<td>9.2</td>
<td>4.9</td>
<td>10.9</td>
</tr>
<tr>
<td>Screened Interval (m)</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
</tr>
<tr>
<td>Well Diameter (cm)</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Screen Slot Width (mm)</td>
<td>0.64</td>
<td>0.25</td>
<td>0.25</td>
<td>0.64</td>
</tr>
<tr>
<td>Date Installed</td>
<td>August, 1984</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^1\) reference to National Geodetic vertical datum of 1929.
Figure 3.2a. Well Construction and Lithology at the Swamp Site.

(swamp Shallow QWH-1A Swamp Deep QWH-1B)

- dark brown mulch with gravel.
- very coarse gravel.
- coarse gravel.
- brown, med. to coarse sand with some gravel.
- no return from sampler.
- med. to very coarse sand.
- brown, med. sand.
- no return from sampler.
- tan, med. sand.

(from well log data supplied by D.G. Lord, USGS, WRD, West Trenton, NJ)
Figure 3.2b. Well Construction and Lithology at the Upland Site.

(from well log data supplied by D.G. Lord, USGS, WRD, West Trenton, NJ)
significant details on the hydrology and geochemistry of the watershed, which will be drawn upon during discussions of the results.

According to groundwater levels measured in shallow wells by the U.S. Geological Survey (Lord et al., 1986), the groundwater flow paths are roughly parallel to McDonalds Branch at the study site (as shown in Figure 3.1b). Hydraulic head levels in the Swamp wells indicate that the border of the swamp is a recharge zone; therefore, the stream and the ephemeral surface water in the swamp contribute to the groundwater flow. The headwaters of McDonalds Branch are located in the uplands that define the topographic divide between waters that flow westward into the Delaware River and waters that flow eastward to the Atlantic Ocean. Even in the uplands, swampy areas are common due to the low relief. According to regional groundwater flow models (Toth, 1962), the uplands that form a topographic divide are recharge zones—groundwater flows downward at such a divide and not laterally across the divide. In areas of low relief, surface runoff is minimal and the meandering streams drain watersheds slowly; thus, infiltration of precipitation to the water table is increased. Based on the hydrology of the McDonalds Branch watershed, Lord et al. (1986) contend that iron and aluminum are supplied by clay minerals in the Cohansey Sand via the shallow groundwater flow paths. The upward vertical flow of deep groundwaters and transport of iron and aluminum from the underlying glauconitic sediments as suggested by Crerar et al. (1979) is only characteristic of the peripheral discharge areas near the lower reaches of major rivers.
3.2. Laboratory Methods and Materials

The groundwaters returned to the lab were analyzed for various parameters designed to elucidate the nature and size distribution of the colloids. Each of the analyses performed required different sample handling and preparation, labware cleaning, standards, and blanks. As mentioned in Chapter 2, Nuclepore polycarbonate membrane filters were chosen for this investigation, based on the results of Jay (1985) and Jardine et al. (1986).

Groundwaters were analyzed for "total" and "dissolved" iron, aluminum, and silicon by atomic absorption spectroscopy (AAS). Total element measurements determined the concentration of the element in the dissolved, organically complexed, and hydrous oxides form, as well as dissolved forms derived from partial dissolution of clays and other minerals after acidification. Dissolved element measurements determined the concentration in forms that passed through a 15 nm pore size filter, the dissolved and organically-complexed forms. Therefore, the difference between the total and dissolved concentrations of the element correspond to the element in colloidal oxide and hydroxide form. Labware used in the analyses were made of polyethylene or polycarbonate, washed by soaking in 2 N HNO₃, and rinsed at least three times with ddH₂O. Samples were removed from Biochemical Oxygen Demand (BOD) bottles under an argon atmosphere by disposable syringes. "Dissolved" samples were filtered through 15 nm filters without exposure to the atmosphere prior to filtration.

All samples were acidified to pH 1.0 with concentrated HNO₃ Ultrex before analysis on the Perkin–Elmer model 372 AAS equipped with a model HGA 400 graphite furnace atomizer. Standards were prepared from stock solutions of FeCl₃, Al metal, and NH₄SiF₆ and the range of linear response was determined for each element. Three replicates of samples and blanks (ddH₂O) were analyzed for total
and dissolved concentrations for each element to determine the error associated with the entire sample handling and analysis procedure. The total element blanks were negligible for each element, but the iron and aluminum concentrations measured for the filtered blanks were on the same order as those measured for the least-concentrated samples, so corrections were made in the sample concentrations for the blanks. The filtered blanks for silicon were also significantly above zero, but were less than one percent of the dissolved silicon levels measured. The main source of error between replicates is probably traceable to the removal of sample aliquots from the BOD bottles. Vigorous shaking and inversion of the bottles did not always insure a homogeneous mixture of particles throughout the bottle. Another possible source of error was the dilution of sample aliquots to concentrations within the linear range of absorption for the AAS. Dilutions made with adjustable automatic pipettes to as little as 0.01 mL in 1 mL were necessary for some samples.

"Total" and "dissolved" organic carbon was measured for the groundwater following a method similar to that outlined in Menzel and Vaccaro (1964). "Total" samples measure the organic carbon in a unaltered sample; "dissolved" samples measure the organic carbon that passes through 30 nm pore size filters. The dissolved samples should measure organic carbon in the form of various organic macromolecules, including humic substances. The total samples measure the dissolved organic carbon as well as the organic carbon associated with particles larger than 30 nm (which includes organic carbon coating on inorganic colloids). Labware used for organic carbon analysis was made of glass, with the exception of disposable syringes, filters, and filter holders used to filter the dissolved samples. All labware was rinsed at least three times in water doubly-distilled and stored in glass containers (gdH₂O). Sample aliquots for total organic carbon were transferred to ampoules in pipettes under an argon atmosphere. For the dissolved organic carbon, sample aliquots were taken in disposable syringes under an argon
atmosphere and filtered through 30 nm filters. Straight and filtered blanks of 
gdH₂O and standards of potassium biphthalate dissolved in gdH₂O were prepared 
using the same methods. Potassium persulfate and phosphoric acid solutions were 
added to the samples, blanks, and standards, and then inorganic carbon was purged 
out of the ampoules with O₂ and the ampoules were sealed and heated at 121°C for 
30 minutes in an autoclave. The CO₂ evolved from the oxidation of organic carbon 
was measured on an O.I.C. (College Station, TX) Model 524 total carbon system. 
Three to five replicates of each sample, blank, and standard were analyzed. The 
detection limit of the method was determined by the amount of organic carbon in 
the blanks, which was averaged approximately 0.2 mg C/L. The 30 nm–filtered 
blanks were not significantly different than the unfiltered blanks. The error 
associated with the sample preparation and measurement was about ± 10 percent, 
mainly due to the removal of replicate aliquots from the BOD bottle.

Light scattering intensities were measured in the laboratory using the N4 
particle analyzer described in the previous section to determine the effect of sample 
storage on colloid size distribution. Samples were transferred to a ddH₂O–rinsed 
quartz cell, filled to overflowing, and capped with teflon plugs under argon 
atmosphere to exclude oxygen. The samples placed in the sample chamber were 
equilibrated for 5 minutes at groundwater temperatures. Scattering intensity was 
determined by recording the varying intensity for 3 minutes and computing the 
arithmetic mean intensity and standard deviation. The scattering intensity 
measured for the blanks, ddH₂O in quartz cells, ranged from 25 to 40 counts/second.

The effect of filtration on the light scattering results was determined by 
filtering aliquots of a sample through a 3.0 µm and a 1.0 µm filter and a nominal 500 
m.w. cutoff Diaflo ultrafilter membrane (Amicon Div., W.R. Grace, Danvers, MA). 
The ultrafiltration was performed under argon pressure in a glove box. The Light 
scattering intensity of the samples was measured immediately after filtration.
Based on the scanning electron microscopy/energy-dispersive X-ray (SEM/EDX) analysis of groundwater particles collected on filters during the reconnaissance sampling, it was determined that the vast majority of particles were clays of some sort, kaolinite being one of the most likely candidates for both McDonalds Branch and Delaware groundwaters. Therefore, scattering intensities of the groundwaters were compared to scattering intensities of kaolinite suspensions of known concentrations, and the colloid weight concentrations were estimated (Kerker, 1969). The kaolinite suspensions were made up with colloidal kaolin powder (EM Science, Cherry Hill, NJ) and ddH₂O and a standard curve was established (Figure 2.2).

Photon correlation spectroscopy was attempted on the samples in the same manner as the light scattering intensities were determined. A number of experimental parameters, including duration, sample time \( \tau \), and the upper limit of the size range, were varied extensively. The samples were also filtered through 3.0 \( \mu m \) and 1.0 \( \mu m \) filters to remove "dust," but no reliable or reproducible results were achieved.

Scanning electron microscopy (SEM) and energy-dispersive X-ray analysis (EDX) were performed on both the April and October samples. The April samples were collected on 100 nm filters, plated with a mixture of gold and palladium, and analyzed at an electron beam accelerating voltage of 30 kV on an ARM model 1000 SEM instrument and at 15 kV on a JEOL model JSM–840 SEM/ETEC Autoscan semi-quantitative EDX instrument. The October samples, collected on 15 nm filters, were gold-plated and analyzed at 20 kV on a Cambridge Stereoscan 250 Mk III SEM equipped with a Tracor–Northern model 5400 fully-quantitative, calibrated EDX analyzer. The EDX results are corrected for the presence of two large peaks originating in the sample mounting: the gold plating and the zinc in the double-sided tape used to attach the filter to the stub. The filters were
systematically scanned and EDX analyses were conducted on "representative" particles; however, perhaps only one–tenth of the total filter area was scanned.

SEM/EDX analyses of individual particles can be used to identify some minerals, particularly clays, by morphology and elemental composition (Bassin, 1975; Mudroch et al., 1977). Ranges of clay composition were determined from mineral formulae and EDX analysis of standard clay minerals and the average abundances of the constituent elements were normalized to silicon.

X–ray powder diffraction was performed on two samples from the April sampling trip, one from the Upland Shallow groundwater in the Pine Barrens and one from the Lc42–01 groundwater in Delaware. Sediments were collected from samples with very high suspended loads by evaporating the samples to dryness in an oven at 180°C. The sediments were resuspended in a solution of nitrocellulose binder, mounted on glass microscope slides, and analyzed using a Rigaku RU300 X–ray diffractometer equipped with an 18 kW Cu–Kα X–ray generator operating at 60 kV. The resulting X–ray diffraction patterns were identified using a computer–based peak identification routine and the Joint Committee Powder Diffraction Series minerals index. Sediments were collected from less–concentrated samples by filtering through 0.45 μm Nuclepore silver membrane filters, but the amount of sediments collected from 300 mL of groundwater was insufficient to obtain satisfactory diffraction peaks.
3.3. **Results**

3.3.1. **April 1987 Sampling**

The results of the limited analyses performed on groundwater collected during the April, 1987 sampling excursion are summarized in Table 3.4. Because of the difficulties encountered during the pumping of the wells, these measurements may not truly reflect the chemistry and colloid content of the groundwaters. In retrospect, the lack of a method to monitor the colloid concentration in the field makes it impossible to determine when the groundwater purging is sufficient; therefore, the groundwater may have been sampled before the colloid concentration decreased to a stable level. However, the April results were useful in planning future sampling and analytical strategies.

The April, 1987 field-measured parameters are the stabilized values determined during the purging of the wells. They compare favorably with the averages and ranges of a series of past measurements performed by the U.S. Geological Survey during the period January, 1987 to February, 1987 (and shown in Table 3.5). The pH measurements in the Upland Deep and Swamp Shallow groundwaters are the same as the mean values measured by the USGS (Lord *et al.*, 1988); however, the pH measurements recorded in the Upland Shallow and Swamp Deep groundwaters are both below the pH range measured by the USGS. The dissolved oxygen concentrations measured at the the Upland Deep groundwater are significantly higher the the range measured by the USGS, but the dissolved oxygen measurements in the other groundwaters agree well with the USGS data. The specific conductivities measured in the Swamp Shallow and Swamp Deep groundwaters are slightly below and above, respectively, of the ranges measured by the USGS and quite different from the mean value; in the other groundwaters, the
Table 3.4. Summary of results for McDonalds Branch groundwater collected in April, 1987.

<table>
<thead>
<tr>
<th>Field Parameters</th>
<th>QWH–1A Swamp</th>
<th>QWH–1B Swamp</th>
<th>QWH–4A Upland</th>
<th>QWH–4B Upland</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shallow = shallow</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Deep</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature, °C</td>
<td>12.5</td>
<td>13.0</td>
<td>13.5</td>
<td>14.0</td>
</tr>
<tr>
<td>pH</td>
<td>3.8</td>
<td>4.0</td>
<td>4.4</td>
<td>5.1</td>
</tr>
<tr>
<td>Eh, V</td>
<td>0.370</td>
<td>0.430</td>
<td>0.340</td>
<td>0.445</td>
</tr>
<tr>
<td>Dissolved, O₂, μM</td>
<td>34</td>
<td>30</td>
<td>270</td>
<td>260</td>
</tr>
<tr>
<td>Specific Conductivity, μS</td>
<td>73.</td>
<td>48.</td>
<td>39.</td>
<td>28.</td>
</tr>
</tbody>
</table>

Laboratory Parameters

Average Light Scattering Intensity (± σ) counts/sec

<table>
<thead>
<tr>
<th>Filtered Type</th>
<th>unfiltered</th>
<th>3 μm–filtered</th>
<th>1 μm–filtered</th>
<th>ultrafiltered¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(±1720)</td>
<td>(±1180)</td>
<td>(±1130)</td>
<td>(±23.0)</td>
</tr>
<tr>
<td></td>
<td>3930</td>
<td>3760</td>
<td>n.a.</td>
<td>50.0</td>
</tr>
<tr>
<td></td>
<td>(±1870)</td>
<td>(±2380)</td>
<td></td>
<td>(±14.6)</td>
</tr>
<tr>
<td></td>
<td>28880</td>
<td>n.a.</td>
<td></td>
<td>126</td>
</tr>
<tr>
<td></td>
<td>(±1500)</td>
<td></td>
<td></td>
<td>(±14.6)</td>
</tr>
<tr>
<td></td>
<td>3500</td>
<td></td>
<td></td>
<td>55.1</td>
</tr>
<tr>
<td></td>
<td>(±350)</td>
<td></td>
<td></td>
<td>(±14.4)</td>
</tr>
<tr>
<td></td>
<td>867</td>
<td></td>
<td></td>
<td>136</td>
</tr>
<tr>
<td></td>
<td>(±268)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

¹ ultrafiltered = nominal 500 m.w. cutoff filters (Amicon Diaflo).

n.a. = not analyzed.
Table 3.5. Groundwater chemistry of McDonalds Branch groundwater for January, 1985 to February, 1986 (after Lord et al., 1988).

<table>
<thead>
<tr>
<th></th>
<th>QWH–1A Swamp</th>
<th>QWH–1B Swamp</th>
<th>QWH–4A Upland</th>
<th>QWH–4B Upland</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Shallow</td>
<td>Deep</td>
<td>Shallow</td>
<td>Deep</td>
</tr>
<tr>
<td>Temperature, °C</td>
<td>8.9 (3.7–18.0)</td>
<td>11.4 (10.7–13.0)</td>
<td>11.5 (10.3–14.0)</td>
<td>11.8 (10.3–13.0)</td>
</tr>
<tr>
<td>pH</td>
<td>3.8 (3.4–4.1)</td>
<td>4.9 (4.6–5.1)</td>
<td>4.9 (4.7–5.1)</td>
<td>5.1 (4.9–5.1)</td>
</tr>
<tr>
<td>Dissolved O₂¹, µM</td>
<td>19 (3–75)</td>
<td>34 (16–53)</td>
<td>250 (230–270)</td>
<td>180 (170–210)</td>
</tr>
<tr>
<td>Specific Conductivity, µS</td>
<td>112 (74–268)</td>
<td>28 (23–41)</td>
<td>36 (33–38)</td>
<td>32 (31–34)</td>
</tr>
<tr>
<td>Alkalinity, meq/L</td>
<td>−0.21</td>
<td>0.009</td>
<td>−0.001</td>
<td>n.a.</td>
</tr>
<tr>
<td>Na⁺, µM</td>
<td>107</td>
<td>79</td>
<td>81</td>
<td>67</td>
</tr>
<tr>
<td>K⁺, µM</td>
<td>5.0</td>
<td>5.0</td>
<td>7.0</td>
<td>8.0</td>
</tr>
<tr>
<td>Ca²⁺, µM</td>
<td>13</td>
<td>10</td>
<td>45</td>
<td>39</td>
</tr>
<tr>
<td>Mg²⁺, µM</td>
<td>13</td>
<td>12</td>
<td>29</td>
<td>42</td>
</tr>
<tr>
<td>NH₄⁺, µM</td>
<td>3.0</td>
<td>1.0</td>
<td>&lt;1.0</td>
<td>&lt;1.0</td>
</tr>
<tr>
<td>Cl⁻, µM</td>
<td>160</td>
<td>95</td>
<td>95</td>
<td>81</td>
</tr>
<tr>
<td>SO₄²⁻, µM</td>
<td>170</td>
<td>31</td>
<td>77</td>
<td>68</td>
</tr>
<tr>
<td>NO₃⁻, µM</td>
<td>&lt;1.0</td>
<td>&lt;1.0</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>PO₄³⁻, µM</td>
<td>&lt;1.0</td>
<td>&lt;1.0</td>
<td>&lt;1.0</td>
<td>&lt;1.0</td>
</tr>
<tr>
<td>Dissolved² H₄SiO₄, µM</td>
<td>90 (67–123)</td>
<td>82 (80–83)</td>
<td>46 (45–50)</td>
<td>52 (50–54)</td>
</tr>
<tr>
<td>Dissolved Fe, µM</td>
<td>68 (52–90)</td>
<td>37 (18–48)</td>
<td>&lt;0.2 (0.1–0.4)</td>
<td>&lt;0.1 (0.1–0.2)</td>
</tr>
<tr>
<td>Dissolved Al, µM</td>
<td>36 (33–44)</td>
<td>4.0 (2.6–5.2)</td>
<td>7.0 (4.0–14)</td>
<td>1.0 (0.7–2.0)</td>
</tr>
<tr>
<td>DOC², mg C/L</td>
<td>19 (13–25)</td>
<td>1.2 (0.7–2.0)</td>
<td>1.0 (0.3–2.0)</td>
<td>0.9 (0.3–1.5)</td>
</tr>
</tbody>
</table>

¹ Dissolved Oxygen determined in laboratory measurements.
² Dissolved = 0.45 µm–filtered in the field.
specific conductivity is outside the range measured, but still within 15 percent of the
mean values.

The light scattering intensity data measured in the laboratory reveals the
effect of differential filtering on the population of colloids in the samples; although
the actual concentrations are not indicative of the true groundwater colloid load. In
the Upland Shallow groundwater, the particles responsible for light scattering
(corresponding to about 8 mg/L kaolinite) passed through a 3 μm filter, but were
essentially removed by ultrafiltration (nominal 500 m.w. cutoff). The Upland Deep
groundwater scattered the least light. After ultrafiltration, the scattering intensity
remained at about three times the background level. The Swamp Shallow
groundwater scattered light at about the same intensity as the Upland Shallow
groundwater, and again, 3 μm–filtering did not remove a significant amount (given
the error associated with the measurement). The dark orange–brown color of the
water remained after ultrafiltration, but the light scattering was reduced to
background levels. The Swamp Deep groundwater scattered the most light,
corresponding to about 80 mg/L kaolinite. About 80 percent of the light scattering
particles were removed by 1 μm–filtering. Ultrafiltration reduced the light
scattering to about 2½ times the background level.

The size distribution and nature of the groundwater particles trapped on a
100 nm filters were revealed by SEM and semi–quantitative EDX analysis. These
particles may indicate the geologic composition of the aquifer, but we do not feel
they are representative of the groundwater colloid population due to the sampling
problems experienced in April. The Upland Shallow groundwater contained mainly
smooth, platy particles composed of about 48 percent Si, 45 percent Al, and 7
percent Fe. Most of the plates were randomly shaped, but somewhat round, ranging
from about 100 nm to 10 μm in diameter. The plates were approximately 25 nm
thick on the edges. They were caught on the filters as individual plates, as large
disorganized clumps, and as accordion-like booklets of attached plates. Very few particles were greater than 3 \( \mu m \) in diameter, therefore the scattering intensity remained after 3 \( \mu m \)-filtering.

The filter containing the particles from the Upland Deep groundwater was sparsely covered compared to the Upland Shallow filter. The particles were primarily clay plates similar in size, shape, and composition to those in the Upland Shallow groundwater. The particles in the 3 \( \mu m \) to 10 \( \mu m \) size range comprise a slightly greater fraction of the particle distribution, therefore the 3 \( \mu m \)-filtering may have reduced the scattering intensity slightly. Some small clay plates (\(<100 \) nm to 1 \( \mu m \)) were attached to the largest clay plates.

The Swamp Shallow groundwater covered the filter with about the same density of particles as the Upland Shallow groundwater, confirming the similar scattering intensities measured for each groundwater. Particles trapped on the filter include clay plates similar to those present in the Upland groundwaters. The Swamp Shallow clays appeared somewhat more weathered than those in the Upland groundwaters. In addition, some small, isolated clumps of spherical 100 to 300 nm particles rich in Fe were detected. Some primarily organic particles (long thin rods, lumpy branches, and spiked spheroids) could be biogenic structures, bacteria, and pollen spores.

The Swamp Deep groundwater filter was heavily covered with particles, in agreement with the light scattering results. The most abundant particles were the ubiquitous clays containing about 1 to 3 percent Fe, ranging in size from less than 100 nm to 10 \( \mu m \). It is evident from Figure 3.3a, which shows the typical shapes and sizes of the clay plates as well as a booklet of plates, that 1 \( \mu m \)-filtering would remove a large portion of the light scattering particles. Some of the clay plates were heavily covered with smaller particles that were rich in Fe (Figure 3.3b).
Figure 3.3. Scanning electron micrographs of Swamp Deep groundwater particles collected on 100 nm filters in April, 1987.

SEM Photos on following page.

Figure 3.3a. Photo No. 12, top of page. Kaolinite "booklet" in center, plus typical clay plates. Filter pores, 100 nm in gaps between particles. Scale bar 10 μm, magnification 6,300 times.

Figure 3.3b. Photo No. 11, bottom of page. Clay plate in lower left corner covered by Fe–rich particles. Other clay plates not covered. Scale bar 1 μm, magnification 12,000 times.
3.3.2. **October 1987 Sampling**

The results from the October, 1987 sampling are summarized in Table 3.6. As before, the field parameters, including light scattering intensities, are the stabilized values determined during the well purging. The laboratory analyses for total and dissolved iron, aluminum, silicon, and organic carbon are also shown in Table 3.6. These sampling results are comparable to those measured by the USGS for the period January, 1985 to February, 1986, shown in Table 3.5. The EDX results are compiled in Appendix Table A.1.

The field-measured pH in the Upland Deep and Swamp Deep groundwaters indicate slightly more acidic water than that measured by the USGS throughout January, 1985 to February, 1986, but the relative acidity of the groundwaters follows the same trend: Swamp Shallow > Swamp Deep > Upland Deep (where Swamp Shallow is the most acidic). The dissolved oxygen measurements closely agree with those performed by the USGS in the laboratory. Specific conductivity measured in the Upland Deep groundwater is just above the range measured by the USGS, but still within 10 percent of the mean. The Eh measurements follow the trend of the dissolved oxygen concentrations—the most oxidizing groundwater, Upland Deep had the highest dissolved oxygen concentration and the least oxidizing groundwater had the lowest dissolved oxygen concentration. The redox—buffering capacities of the Upland Deep groundwater should be high because the groundwaters are acidic and high in iron (Langmuir, 1971a). Eh measurements were stable and reproducible after the purging of a few well volumes. However, the redox potential of the high organic carbon, low dissolved oxygen Swamp groundwaters probably depend on a number of redox couples that are not at equilibrium, such as \( H_2S - SO_4^{2-} \). Measurement of one redox potential for the groundwater probably is not possible for the Swamp Shallow groundwater because of the various states of
Table 3.6. Summary of results for McDonalds Branch groundwater collected in October, 1987.

<table>
<thead>
<tr>
<th>Field Parameters</th>
<th>QWH–1A Swamp Shallow</th>
<th>QWH–1B Swamp Deep</th>
<th>QWH–4B Upland Deep</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature, °C</td>
<td>12.0</td>
<td>10.0</td>
<td>13.0</td>
</tr>
<tr>
<td>pH</td>
<td>3.7</td>
<td>4.5</td>
<td>4.8</td>
</tr>
<tr>
<td>Eh, V</td>
<td>0.275</td>
<td>0.290</td>
<td>0.340</td>
</tr>
<tr>
<td>Dissolved O₂, μM</td>
<td>25</td>
<td>30</td>
<td>190</td>
</tr>
<tr>
<td>Specific Conductivity, μS</td>
<td>93</td>
<td>37</td>
<td>39</td>
</tr>
<tr>
<td>Average Scattering Intensity, c/s</td>
<td>559 (±408)*</td>
<td>20000 (±5440)</td>
<td>325 (±240)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Laboratory Parameters</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>TOC¹, mg C/L</td>
<td>52</td>
<td>1.4</td>
<td>0.8</td>
</tr>
<tr>
<td>DOC², mg C/L</td>
<td>46</td>
<td>0.7</td>
<td>n.a.</td>
</tr>
<tr>
<td>Total Fe, μM</td>
<td>44.3 (±7.1)*</td>
<td>22.3 (±0.1)</td>
<td>0.55 (±0.04)</td>
</tr>
<tr>
<td>Diss.³ Fe, μM</td>
<td>36.6 (±3.2)</td>
<td>7.70 (±0.91)</td>
<td>0.19 (±0.09)</td>
</tr>
<tr>
<td>Total Al, μM</td>
<td>53.5 (±6.2)</td>
<td>58.3 (±5.8)</td>
<td>1.95 (±0.10)</td>
</tr>
<tr>
<td>Diss. Al, μM</td>
<td>43.8 (±3.1)</td>
<td>4.37 (±1.9)</td>
<td>1.56 (±0.26)</td>
</tr>
<tr>
<td>Total Si, μM</td>
<td>133. (±9)</td>
<td>138. (±7)</td>
<td>67.8 (±3.0)</td>
</tr>
<tr>
<td>Diss. Si, μM</td>
<td>105. (±11)</td>
<td>61.7 (±11.2)</td>
<td>56.3 (±3.5)</td>
</tr>
</tbody>
</table>

¹ TOC = Total Organic Carbon.
² DOC = Dissolved Organic Carbon, 30 nm–filtered.
³ Dissolved = 15 nm–filtered.
† c/s = counts/sec.
* standard deviation of the mean.

The light scattering intensities measured in the field are significantly lower than those measured in April, 1987. The decrease may be attributed to better sampling techniques (e.g., lower flow rates, better flow rate control, and better isolation of the screened interval by the packer). The Swamp Deep groundwater has a substantial colloidal load (about 60 mg/L kaolinite equivalent), even after seven hours of purging and sampling.

The total and dissolved concentrations of iron, aluminum, and silicon are shown in Figure 3.4, with each of the three replicates shown to illustrate the magnitude of error associated with the entire analysis. The difference between the total and dissolved concentrations is the concentration of the colloidal fraction larger than 15 nm diameter that is measured by the graphite furnace AAS—primarily the amorphous Fe and Al oxyhydroxides plus some Fe, Si, and Al from the partially dissolved clays. The colloidal concentration of each element is shown in Figure 3.5.

Differences between the Fe, Al, and Si concentrations measured in this investigation and those measured by the USGS may be the result of the sampling methods. The USGS procedures include purging and sampling at 4 L/min and filtering by 0.45 μm filters to determine the "dissolved" concentration of each element, despite the admonitions of Kennedy et al. (1974). The light scattering and SEM/EDX results from this investigation show that some groundwaters contain sizable amounts of clay and oxyhydroxide colloids smaller than 0.45 μm, and pumping at 4 L/min may significantly increase the amount of colloids. Fe, Al, and Si concentrations are substantially increased by the dissolution of the colloidal load. Filtration through 15 nm filters reduces the load of inorganic colloids to negligible amounts. Fe and Al bound in organic complexes (primarily humic substances) still
Figure 3.4. Fe, Si, and Al in McDonalds Branch Groundwater

Well QWH-1B "Swamp Deep"
- Total
- Dissolved (< 15 nm)

Well QWH-1A "Swamp Shallow"
- Total
- Dissolved (< 15 nm)

Well QWH-4B "Upland Deep"
- Total
- Dissolved (< 15 nm)
Figure 3.5. Suspended Fe, Si, and Al in McDonalds Branch Groundwater

Well QWH–1B  "Swamp Deep"

Well QWH–1A  "Swamp Shallow"

Well QWH–4B  "Upland Deep"
pass through the 15 nm filters (indeed, most of the orange–brown color remained after filtration); therefore, even the 15 nm filters are not a true measure of the aqueous species of iron and aluminum.

Other factors may account for the differences between the measurements made for this investigation and those recorded by the USGS. Seasonal variations are discernible for iron and silicon in some wells over the one–year period of monitoring. Iron concentrations are lower in the autumn in the Swamp groundwaters and silicon increased in concentration in the Swamp Shallow groundwater. Some differences may simply reflect real fluctuations or changes in the groundwater chemistry.

The total and dissolved organic carbon results are listed in Table 3.6. The Swamp Deep groundwater has twice as much total organic carbon as dissolved organic carbon, indicating that about 0.7 mg C/L is associated with inorganic particles larger than 30 nm. The organic carbon concentrations in the Swamp Deep groundwater compare well with those measured by the USGS. The Upland Deep groundwater was only measured for total organic carbon because the light scattering and SEM/EDX results indicated there would be very few particles retained on the 30 nm filters. The Swamp Shallow groundwater contained higher organic carbon concentrations in both total and dissolved measurements than the dissolved (0.45 μm–filtered) measurements reported by the USGS. The apparent large difference between the total and dissolved concentrations may not be significant given the error associated with the method (± 10 percent). Based on tests with bipthalate standards, the filters themselves did not adsorb a measurable portion of the organic carbon, although the actual components of the organic carbon may have different surface sorption properties. The large difference may also represent physical obstruction of the pores by the abundant organic carbon.
The results of the SEM/EDX analysis were discussed in Chapter 2 to illustrate the importance of low flow rate pumping and a lengthy purging period. In this chapter, the SEM/EDX results, along with the X-ray diffraction results, will be examined to determine the size distribution and nature of the colloids and to provide some insight into why colloids are present in the Swamp Deep groundwater and not in others.

The particles from the Swamp Deep groundwater can be categorized into three types by their shape and composition: 1) low-Fe sheet particles (mean of about 52.4 percent Si, 43.2 percent Al, and ~5.2 percent Fe); 2) high-Fe sheet particles (46.4 percent Si, 40.6 percent Al, and 11.1 percent Fe); and 3) Fe-rich subhedral lath-shaped particles (53.8 percent Fe, 22.5 percent Si, and 22.7 percent Al).

The low-Fe sheet particles in the Swamp Deep groundwater, shown in Figures 3.6a and 3.6b, have a high Al/Si ratio distinctive of kaolinite (Bassin, 1975; Mudroch et al., 1977) and the typical appearance of clay plates and booklets; however, the Fe/Si ratio is nearly double the maximum Fe/Si ratio expected in the kaolinite structure (Grim, 1968). The excess Fe may be present as ferrous iron substitutions for the Al$^{3+}$ in the octahedral layers or as iron adsorbed to the surface of the clays (as observed in the April filter sample, Figure 3.3b). The clay faces occasionally appear desiccated and rough (see Figure 3.6b), similar to the appearance of clays covered with iron oxyhydroxides presented by Greenland (1975).

The high-Fe sheet particles in the Swamp Deep groundwater, shown in Figures 3.6a and 3.6b, have high Al/Si and Fe/Si ratios and the appearance of clay plates. Only the Fe-chlorite minerals have both high Al/Si and Fe/Si ratios and chamosite is the most common of these minerals in nature. The Fe/Si ratio of chamosite is much higher than the Fe/Si ratio detected for these particles, indicating the possibility of some dissolution and loss of ferrous iron. Chamosite is
Figure 3.6. Scanning electron micrographs of Swamp Deep groundwater particles collected on 15 nm filters in October, 1987.

SEM Photos on following page.

Figure 3.6a. Photo No. 77, top of page.
Chamosite plate in center (Si 47%, Al 40%, Fe 13%).
Kaolinite plate to the right and slightly below center
(Si 52%, Al 45%, Fe 3%).
Scale bar 2 μm, magnification ~10,000 times.

Figure 3.6b. Photo No. 90, bottom of page.
Kaolinite plate in upper left (Si 50%, Al 42%, Fe 5%).
Clump of goethite crystals to right of center
(Si 23%, Al 20%, Fe 55%)
Scale bar 1 μm, magnification ~15,000 times.
known to be a major constituent of iron-rich sediments and some sedimentary iron ores and it weathers to kaolinite, goethite, and limonite (Phillips and Griffen, 1981). Kaolinite and chlorite, as well as vermiculite, are reported as major constituents of the Cohansey Sand in the vicinity of the site by Rhodehamel (1979a) and in nearby borings (Lord et al., 1986).

The Fe-rich lath-shaped particles are identified as goethite based on their morphology and high iron content. The high Si and Al content may indicate surface adsorption and incorporation of these elements into the goethite structure or clay minerals in the area surrounding the goethite crystals on the filter. The crystallinity of the Fe-rich particles discourages the notion that they may have oxidized and precipitated from dissolved ferrous iron on the filters—such rapidly precipitated iron would be present as amorphous iron hydroxide (Langmuir and Whittemore, 1971) and would not formed rapidly at the low pH of the groundwater (Stumm and Lee, 1961; Sung and Morgan, 1980; and Davison and Seed, 1987). The presence of fine-grained goethite indicates oxidation and subsequent hydrolysis of ferrous iron minerals (such as Fe-rich clays, pyrite, and siderite) and ferrous iron-rich groundwater. Goethite is the stable iron oxyhydroxide mineral in humid soil environments instead of hematite because the kinetics of dehydration are very slow at groundwater temperatures and pressures (Langmuir, 1971). The presence of organic matter may further inhibit the crystallization of hematite from less stable oxyhydroxides (Schwertmann, 1966; Kodama and Schnitzer, 1977). Crear et al. (1979) identified goethite as the only XRD-identifiable Fe mineral in the Pine Barrens sediments.

The Upland Deep groundwater contained primarily alumino-silicate sheets composed of about 50.7 percent Si and 46.8 percent Al. The sheet particles have the high Al/Si ratio, trace levels of other cations, and appearance typical of kaolinite. The smooth edges, rounded corners, and etched faces suggest that the
kaolinite plates are considerably more weathered than those in the Swamp Deep groundwater. Also listed in Table A.1 were particles that were similar in size, shape, and composition to particles on the field blanks.

The Swamp Shallow groundwater filter was devoid of sheet alumino–silicates, unlike the April, 1987 filter sample. The dominant particles were Si–rich sub-rounded to very angular grains (average composition 96.4 percent Si and 2.8 percent Al). Some small Al–rich (98.0 percent Al, 2.0 percent) sub-rounded particles and Fe–rich (87.6 percent Fe, 8.2 percent Si, and 4.2 percent Al) weathered, platy particles were also detected. The remaining mineral components must be elements that cannot be detected by EDX, elements of atomic number less than 11, such as oxygen and carbon (Russ, 1971). The Si–rich particles appear to be fragments of quartz grains weathered to varying degrees. The Al–rich particles are probably gibbsite, a product of intense chemical weathering of aluminous minerals, particularly kaolinite. Gibbsite commonly occurs with ferric hydroxides (Phillips and Griffen, 1981) and Pine Barrens soils are known to contain significant amounts of gibbsite (Douglas and Trela, 1979). The weathered Fe–rich particles scanned in the Swamp Shallow groundwater does not have the distinctive lath–like morphology of the goethite colloids observed in the Swamp Deep groundwater; the Swamp Shallow particle also has a much higher percentage of Fe. The particle is probably an aged ferric hydroxide. Siderite is not expected in this groundwater because the bicarbonate concentration (estimated from the alkalinity) is so low.

X–ray diffraction (XRD) analysis of the pinkish–orange sediment collected from a sample of Upland Shallow groundwater collected in April, 1987, indicated the presence of chamosite and halloysite, a hydrated kaolinite, in the sediment. The diffraction peaks were not reproducible enough to estimate the abundance of the clays in the sediment. The diffraction patterns of a number of other clays, including
nontronite and clinochlore, a magnesium analog of chamosite, partially matched the Upland Shallow sediment diffractogram. The heavy sediment load collected at the initiation of pumping in the well does not reflect the colloidal load of the groundwater; however, these clays are expected to be present in the aquifer. These XRD results support the qualitative identifications made by SEM/EDX analyses.
3.4. **Discussion and Interpretation of Results**

Remarkable contrasts in colloid mobility and groundwater chemistry were revealed by careful sampling and analysis of three groundwaters from the McDonalds Branch watershed. The colloid load and organic carbon, iron, aluminum, and dissolved oxygen concentrations varied widely in samples taken from groundwaters representing two major ecological regions of the Pine Barrens, the uplands and the hardwood swamp.

Many of the factors that influence colloid mobility in groundwater depend on the groundwater chemistry. We will first examine the effects of the geology and hydrology on the chemistry of the Swamp and Upland groundwaters, concentrating on the features that influence colloid mobility: pH, ionic strength, organic carbon and dissolved oxygen content, redox state, and iron and aluminum behavior. In particular, the geochemical implications of clay layers in the Cohansey Sand and the swamp bordering the McDonalds Branch will be discussed. Second, the inherent surface properties of the aquifer substrate and the various colloids will be reviewed in terms of surface chemistry, surface charge and points of zero charge. Finally, the effect of the McDonalds Branch watershed groundwater chemistry on the aquifer substrate and colloids will be detailed, complete with the support of a wide range of investigations on the coagulation of clays, inorganic and organic coatings on natural particles, and actual field studies on natural waters.

3.4.1. **Effects of Geology and Hydrology on Groundwater Chemistry**

The salient feature of the geology of the soils and the aquifer in the McDonalds Branch watershed is the presence of clay layers. Such layers are common in the Cohansey Sand and they often cover areas of hundreds of hectares.
Distinct clay layers were found near the surface (at a depth of about 1 to 2 meters) in the Upland Deep boring and in other borings near the site: 1) about 700 meters to the northeast of the site; and 2) on the south side of McDonalds Branch (D.G. Lord, USGS, WRD, West Trenton, NJ, personal communication, 1988). The weathering of clays, which contributes Fe, Al, and Mg to the groundwater, is accelerated in the acidic groundwater. Iron-staining is evident in the Upland Deep sediments (see Figure 3.3). The "pinkish-orange" clay layer at 1 to 2 meters depths indicates the presence of iron-bearing minerals (Schluger and Roberson, 1975) and apparently contributes to the color of the thick layer of "pinkish-tan" sand below 5 meters depth. In the Swamp Deep boring, no clay layer is detected and the deeper sand layers are brown and tan in color.

The clay layers are also sources of clay colloids to the groundwater. Clay particle breakdown and colloid size are controlled by lattice tensions in the clays. Lattice tensions are produced by isomorphic substitutions and by misfits between the superimposed oxygen-sharing octahedral and tetrahedral sheets. Two layer clays, such as kaolinite, generally develop greater lattice tensions than three-layer clays, and hence, they produce more colloids (van Olphen, 1977; Ali et al., 1987).

Infiltrating precipitation and groundwater can transport the clay fragments through sandy soils (Dijkerman et al., 1967) and uncemented sandstones (Walker et al., 1978). This process, known as illuviation, is often associated with the deposition of clay bands enriched in iron (Folks and Riecken, 1956). The clay colloid material can be transported in soil waters at very low velocities and in soils that are quite unsaturated. Bond (1986) observed clay colloid mobilization and banding in sands with water contents of less than 0.2 and clay contents of less than 1 percent. Thus, the groundwater is expected to have an ample supply of clay colloids that are mobile under the geochemical conditions of the Swamp Deep groundwater, although it is uncertain if the areas directly upstream of the site (relative to the groundwater
flow patterns) contain the clay layer detected in the nearby borings.

The hardwood swamp flanking the banks of McDonalds Branch also plays a major role in defining the contrast between the Swamp and Upland groundwaters. The highly acidic, nutrient-poor waters of the swamps contribute heavy loads of organic carbon to the groundwater as it leaches downward through the mulch and peat. The Swamp Shallow groundwater, sampled just below the mulch layer, has organic carbon concentrations as high as what would be expected in the swamp itself. The pH of the groundwater is probably controlled by the dissociation of protons from weak organic acids, especially fulvic acids (Beck et al., 1974; Hemond, 1980). The alkalinity of the groundwater is slightly negative and approximately equal to the hydrogen ion activity. The oxidation of the organic carbon results in anoxic, or nearly anoxic, and reducing conditions in the groundwater, despite its proximity to the surface. Nitrate has also been reduced to ammonium to oxidize the organic carbon, but sulfate levels are very high, more than twice as high as the sulfate levels in the Upland groundwaters, suggesting that the oxidation of organic carbon or the dissolution of pyrite is generating sulfate. Iron reduction is probably occurring in the Swamp Shallow groundwater. The specific conductivity, and hence the ionic strength, of the groundwater is about three times greater than those of the surrounding groundwaters because the reducing, acidic groundwater promotes dissolution of the weatherable minerals. High dissolved iron and aluminum concentrations coexist with remnants of iron hydroxide and gibbsite as products of intense incongruent weathering of clay minerals. The dissolved iron and aluminum is probably largely complexed by humic substances (Koenings, 1976; Crerar et al., 1981). The dissolved H₄SiO₄ concentration is slightly above saturation with respect to quartz, indicating that clay dissolution contributes silicate to the groundwater.

The organic carbon in the Swamp Shallow groundwater is further oxidized as it infiltrates downward to the sampling depth of the Swamp Deep well.
Deep groundwater is still anoxic or nearly anoxic, and the nitrate level is again below the detection limit. The sulfate concentration has been significantly diminished, possibly by reduction to sulfide and subsequent precipitation with Fe(II). Iron reduction must also be contributing to the oxidation of the organic carbon. The Eh and dissolved oxygen measurements indicate that the Swamp Deep groundwater is slightly less reducing than the Swamp Shallow groundwater, which is possible if oxygenated groundwater were to flow laterally toward the well; however, the comparatively low sulfate concentrations in the Swamp Deep groundwater and the hydraulic head measurements of nearby wells do not support this possibility. The pH of the groundwater is significantly higher than that of the Swamp Shallow groundwater due the decrease in abundance of organic acids. Consequently, the specific conductivity and dissolved iron and aluminum concentrations are lower than in the Swamp Shallow groundwater.

The equilibrium geochemistry of iron in the Swamp Deep groundwater can be described by the pe-pH diagram shown in Figure 3.7. Assuming that an Fe(II)—Fe(III) redox couple has the major influence on the redox potential of the groundwater, and that the Pt electrode is measuring that potential, the pe-pH diagram represents stable iron phase at 25°C and atmospheric pressure. The solubility of the major oxidized and reduced iron solids known to exist in the Cohansey Sand, goethite and pyrite (Crerar et al., 1979), probably control the concentration of iron in solution. Total iron in the system is set equal to the measured concentration of dissolved iron, of which Fe\(^{2+}\) is the predominant component. The complexation of iron by inorganic ligands is negligible for Fe\(^{2+}\) under these conditions; however, the chelation of Fe\(^{2+}\) by organic ligands is not accounted for by this analysis. It is expected that Fe(III) and Al(III) occupy most of the humic substance binding sites (Kerndorff and Schnitzer, 1980). Total sulfur is set equal to the average dissolved sulfate concentration (measured by the USGS).
Figure 3.7. $p_e$–$pH$ Diagram for Fe–O–S–H$_2$O system

Swamp Deep groundwater: $Fe_T=7.7 \ \mu$M $S_T=31 \ \mu$M

$\blacklozenge \ \text{pH} = 4.5 \ \ \ \text{pe} = 5.2$

$T=25^\circ C \ P=1 \ \text{atm}$

$FeO(OH)/Fe(OH)_3\cdot S$

$FeS_2$

$pH$

$p_e$

$Q$

$Q$

$Fe^{2+}$

$Fe^{3+}$

$f_{O_2}=1$

$f_{H_2}=1$
at the upper stability limit of pyrite because precipitation of iron sulfides would occur at very low concentrations of dissolved sulfide (Drever, 1982). Siderite is not expected to be an important ferrous iron solid in this groundwater because of the extremely low bicarbonate concentration inferred from the alkalinity measurements made by the USGS. The thermodynamic constants used to construct this diagram were taken from Wagman et al. (1969) and Robie et al. (1978). The effect of activity coefficients in this low ionic strength groundwater is insignificant. The measured Eh was converted to pe by

\[ pe = \frac{F}{2.303RT} \cdot Eh \]

where \( F \) is the Faraday's constant (23.06 kcal/V·g·eq), \( R \) is the gas constant (1.987·10^-3 kcal/deg·mol), \( T \) is the absolute temperature (deg Kelvin), and \( Eh \) is the redox potential (V).

The Swamp Deep groundwater, with \( pe = 5.2 \) and \( pH = 4.5 \), falls in the shaded portion of Figure 3.7 that represents the variability of the stability constant used to describe goethite. The stability constant of goethite depends on two factors: the crystallinity and the particle size (Langmuir and Whittemore, 1971; Langmuir, 1971b). Two free energy of formations (\( \Delta G_f^\circ \)) were used to determine the variability in the equilibrium field of goethite; the first is the published value (Robie et al., 1978) describing the stability of a pure, well-prepared sample. The second is \( \Delta G_f^\circ \) increased by just 5 kcal/mole to describe a less crystalline natural goethite (Drever, 1982) filled with impurities, such as Si, Al, and organic carbon, or a goethite particle of smaller size (Langmuir, 1971b). With this interpretation of goethite stability, the coexistence of goethite colloids and high dissolved iron concentrations at equilibrium is possible in the Swamp Deep groundwater. The position of the stability field of Fe(OH)₃·s, shown by the dashed line in Figure 3.7, indicates that ferric iron precipitation as amorphous ferric hydroxide is not favored in the Swamp Deep groundwater. The stability of colloidal ferric hydroxide is
apparently slightly less than that of amorphous ferric hydroxide; therefore, amorphous ferric hydroxide is expected to be the initial precipitation product (Fox, 1988).

The redox equilibrium approach provides only a qualitative notion of the stability of the various phases because it ignores the possible effects of disequilibrium, kinetics, and biological mediation in redox reactions. The presence of goethite colloids may be temporary; their dissolution may be slowed by organic surface coatings. The low pH and dissolved oxygen concentrations may inhibit oxidation of Fe$^{2+}$, allowing the buildup of ferrous iron in the Swamp Deep groundwater. Iron–oxidizing bacteria, such as *Leptothrix ochracea* and *Metallogenium* sp., are capable of accelerating ferrous iron oxidation in the low pH swamps of the Pine Barrens (Crerar *et al.*, 1979; Madsen *et al.*, 1986).

The Upland Deep groundwater is well-oxygenated because the organic load that develops on the forest floor is relatively light and it usually is oxidized rapidly at the surface. Dissolved oxygen concentrations are within 75 percent of saturation in the Upland Shallow groundwater and within 50 percent in the Upland Deep groundwater. The nitrate concentration is greater than the ammonium concentration and sulfate is one of the major anions in the Upland Deep groundwater. The organic carbon concentration is typical of most oxygenated Pine Barrens groundwaters (Crerar *et al.*, 1981). The pH is slightly higher than that of the Swamp Deep groundwater, perhaps indicating the lesser influence of organic acids on the acidity. The Upland Deep groundwater contains very low concentrations of dissolved iron and aluminum. Dissolved aluminum concentrations may be reduced by precipitation of gibbsite and adsorption to aquifer surfaces, whereas in the Swamp Deep groundwater, dissolved aluminum was probably complexed by humic substances. The dissolved iron in the Upland Deep groundwater is probably present mainly as dissolved Fe$^{2+}$ due to the slow kinetics of
Fe(II) oxidation at low pH. The concentration of dissolved Fe(III) is probably maintained at about $10^{-16}$ M by the dissolution of the goethite present as iron stains on the sand grains. The primary Fe(III) species would be $\text{FeOH}^2+$ at the pH of the Upland Deep groundwater.

The stability of goethite is shown in the $\rho e$–pH diagram in Figure 3.8, which reflects the decreased dissolved iron concentration and the increased sulfate concentration. At $\rho e = 5.7$ and pH = 4.8, the Upland Deep groundwater is within the stability field of goethite, determined in the same manner as for the Swamp Deep groundwater (Figure 3.7). As in the Swamp Deep groundwater, the precipitation of ferric iron is not expected because the groundwater is not near the stability field of $\text{Fe(OH)}_3\cdot s$, shown by the dashed line in Figure 3.8.

The geology and hydrology of the McDonalds Branch watershed produced a sharp contrast in the chemistry of groundwater sampled only 60 meters apart. The chemical differences are clearly related to the contrast in ecological settings on the surface: hardwood swamp and uplands. The concentration of dissolved oxygen, the pH, and the distribution of organic carbon in the aquifer appear to be the crucial factors in controlling the iron and aluminum geochemistry. The colloid abundance in the Swamp Deep groundwater and the presence of iron–stained sand grains in the Upland Deep boring suggest that the groundwater chemistry is affecting the surface properties of the solid phases.

3.4.2. Solid Surface Properties

The chemical and electrostatic forces at the interface between the inorganic colloids, the aquifer substrate, and the groundwater strongly influence the abundance and mobility of the colloids in the solution. These forces depend on the nature of the solid surfaces—their surface coordination chemistry, the distribution
Figure 3.8. pe-pH Diagram for Fe-O-S-H$_2$O system

Upland Deep groundwater: Fe$_T$=0.19 μM  S$_T$=68 μM

$\bullet$ pH = 4.8  pe = 5.8

T=25°C  P=1 atm

FeO(OH)/

FeO(OH)$_3$·s

Fe$_2$S$_2$

$\Phi$

$\Phi$
of surface potential in the diffuse double layer, and the resulting surface charge—and the chemistry of the bulk solution, particularly the pH and ionic strength. In this section, we will review the important features of the solid surfaces of pure compounds relevant to colloid mobility. This will serve as a basis for the evaluation of colloid mobility in the McDonalds Branch groundwater. In the groundwater, of course, the surface properties of the pure compounds may be masked or altered by the adsorption of other materials.

Iron, aluminum, and silicon hydrous oxides are important constituents of the colloid population and the aquifer substrate in the McDonalds Branch groundwater. The iron hydrous oxides found in the Swamp Deep and Swamp Shallow groundwaters were identified as goethite and amorphous Fe(OH)₃. Gibbsite or amorphous Al(OH)₃ was found in the Swamp Shallow groundwater. The Upland Deep contained no suspended iron or aluminum hydrous oxides, but quartz fragments were noted. Quartz is also the dominant aquifer substrate in the Cohansey Sand.

The surface charge of hydrous oxides is dependent on the pH of the solution. The charge arises from the association and dissociation of protons on the surface:

\[
\begin{align*}
M^{n+} + \text{H}^+ &\rightleftharpoons M^{n+}\text{OH}^+ \\
M^{n+}\text{OH}^+ &\rightleftharpoons M^{n+}\text{O}^- + \text{H}_2\text{O}
\end{align*}
\]

where \(M\) represents a coordinated metal ion in the surface. The pH at which the surface is uncharged, point of zero charge (PZC) of the oxide, depends primarily on the affinity of the metal ion for electrons. The PZCs for the hydrous oxides important to this investigation are shown in Table 3.7. The hydrous oxides of the least electronegative metal, iron, adsorb protons from solution at the highest pH because of the inability of iron to stabilize the negative charge; therefore, the iron hydrous oxides have the highest PZCs in this group. The more hydrated oxides of a metal generally have more basic PZCs because they have
Table 3.7. PZCs for some hydrous oxides (from Parks, 1965)

<table>
<thead>
<tr>
<th>Hydrous Oxide</th>
<th>PZC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(OH)$_3$</td>
<td>8.5</td>
</tr>
<tr>
<td>geothite</td>
<td>6.7</td>
</tr>
<tr>
<td>Al(OH)$_3$</td>
<td>~8.0</td>
</tr>
<tr>
<td>gibbsite</td>
<td>5.0</td>
</tr>
<tr>
<td>quartz</td>
<td>2.0</td>
</tr>
</tbody>
</table>
a higher ratio of OH⁻/O²⁻ sites on their surfaces (Robinson et al., 1964). The more hydrated minerals are the products of relatively rapid precipitation from a solution with an excess of hydroxyl ions. They are thermodynamically less stable forms of the oxides and will eventually dehydrate to form the more stable oxides (Langmuir, 1971b).

The hydrous oxides strongly adsorb inorganic anions, cations, and organic acids from solution. The large surface areas of hydrous oxides, typically on the order of 200 m²/g, and the high affinity binding sites for heavy metals make them the most important control on heavy metals in the environment (Jenne, 1977). Adsorption of cations on hydrous oxides occurs over a narrow pH range, below which there is no adsorption and above which all cations are strongly absorbed. The narrow pH range of adsorption is different for each adsorbing metal ion. Ligand exchange reactions with silicate and phosphate anions can lower the PZC of the surface by several pH units for an aluminum hydroxide (Parks, 1965). Ligand exchange reactions also occur with humic substances, which can produce negative surface charges at pH below the PZC of the oxide (Tipping, 1981; Tipping and Cooke, 1982, Davis and Gloor, 1981).

The surface properties of the kaolinite and chlorite colloids are complicated by the presence of different double layer structures on the edges and faces of the plates. The structure of kaolinite and chlorite indicate that a siloxane face and a gibbsite face will be exposed on the basal surfaces. On the edges, the primary bonds of the silica tetrahedra and alumina octahedra are disrupted and small amounts of positive charge develop at low pH due to proton acceptance by the alumina groups (Schofield and Samson, 1954). Greenland (1975) examined the surface charge on kaolinite particles as a function of pH by adsorption of Cs⁺ and Cl⁻ and measured 0.2 to 1 meq/100 g of positive charge attributable to the edges. The PZC of the kaolinite edges is estimated to be 7.2 by Williams and Williams (1978) on the basis
of a modeled interpolation of the electrophoretic mobilities of quartz and alumina (\(\alpha-Al_2O_3\)). Tschapek et al. (1974) utilized a similar interpolative approach in measuring the PZC of quartz and alumina mixtures by titration. Alumina dominated the PZC of the mixtures because the lower electronegativity of aluminum forces the alumina group to adsorb protons more strongly to balance the negative charge. Thus, the alumina groups tend to dominate the adsorption of potential–determining ions on the edges.

The surface charge on the faces is generally thought to be caused by the isomorphic substitution of Si\(^{4+}\) by Al\(^{3+}\) in the layers of silicon tetrahedra (Schofield and Samson, 1954; van Olphen, 1977). The resulting negative charge is "permanent" and independent of pH, according to the results of most researchers. The negative charge totals about 2 to 5 meq/100 g, usually measured as the cation exchange capacity. The siloxane group of the exposed silica tetrahedra behaves differently than the silanol group in quartz. The energy of adhesion between a siloxane surface and water is much less than the very large cohesive energy of water, but the strong polarity of the more charged silanol groups is sufficient to overcome the large cohesive energy. Therefore, the silanol surface is much more reactive toward cations in solution because it can overcome the cohesive energy of the hydrating waters (Greenland and Mott, 1978).

The Al–OH groups of the exposed gibbsite face might be expected to behave similarly to the alumina groups exposed at the edges; however, the Al–OH groups have a very high reactivity toward silicate, phosphate, and organic anions. Adsorption of silicate anions, which are plentiful in any weathering environment that produces kaolinite, would cause the surface to develop a pH–dependent negative charge characteristic of silica surfaces (Jepson et al., 1976).

Adsorption of trace metals to clays involves competition with major cations in cation exchange reactions. In most groundwaters, the abundance of Na\(^+\) and Ca\(^{2+}\)
would displace trace metals into solution, but in dilute waters, the selectivity for an trace metal exchanger may be sufficient to remove the trace metal from solution. Hem (1976) observed ion exchange equilibria of lead on halloysite below levels maintained by the solubility of PbCO$_3$. In oxidizing waters, however, adsorption by hydrous oxides would be much more important.

3.4.3. Colloid Formation and Stability in the McDonalds Branch Groundwaters

The interactions of the groundwater chemistry and the solid surfaces that determine the colloid mobility are observed in an equilibrium state of sorts. The sharp contrast in colloid mobility exists and it has probably existed ever since the geologic and hydrologic factors that control groundwater flow and chemistry have been in place. In this analysis, we will attempt to explain the contrast in colloid mobility between the Upland Deep and Swamp Deep groundwaters by starting with new sediments unaffected by clay dissolution, clay colloids, organic carbon, and anoxia. The processes that produced the current situation will be examined. We will begin by evaluating the geochemical processes that affect colloid mobility in the Upland Deep groundwater.

The clay layer detected at 1 to 2 meters depth in the Upland Deep boring is composed primarily of kaolinite and chamosite, according to SEM/EDX and XRD results. The infiltrating groundwater, acidic ($pH < 4$) and low in silica, rapidly dissolves the clay minerals (Garrels and Christ, 1965). The dissolving chamosite, an Fe–chlorite, releases a substantial load of iron into the groundwater. The distribution of iron between Fe(II) and Fe(III) species is controlled by redox reactions in the oxidizing groundwater. At $pH$ 4.8, Fe$^{2+}$ is the major dissolved iron species due to the slow oxidation of Fe$^{2+}$ at low $pH$ and FeOH$^{2+}$ is the major Fe(III) species. As the infiltrating groundwater slowly descends, the dissolved Fe(III)
species, FeOH\(^{2+}\), is strongly adsorbed by the silanol groups of the fresh quartz surfaces (Dugger et al., 1964; Schindler et al., 1976). These researchers noted that the order in which metal ions are adsorbed to the silica surface as pH is increased above the PZC of silica (2.0) corresponds to the hydrolysis constants of the metals. Thus, Fe(III), with a hydrolysis constant exceeded only by H\(^+\), is adsorbed to silica before any other cation.

The adsorption of metal ions can actually reverse the negative charge of the silica surface as the metal hydroxide begins to precipitate on the surface (James and Healy, 1972a). The precipitation on the surface occurs despite undersaturation with respect to the metal hydroxide in the bulk solution, as is the case in the Upland Deep groundwater according to the analysis of the pe–pH diagram. The surface precipitation is possible because the large electric field in the interface region reduces the dielectric constant of the interface relative to that of the bulk solution. The reduced dielectric constant causes a sizable reduction in the solubility product of the metal hydroxide, thus the metal hydroxide is able to precipitate on the surface. The decrease in the solubility product is proportional to the square of the valence of the metal ion, so this effect is quite dramatic for Fe(III). At higher pH, the surface charge again reverses approximately at the PZC of the metal hydroxide forming on the surface. James and Healy (1972b) attributed the pH relationship between metal adsorption and hydrolysis to a lessening of the solvation energy of the free metal ion by the formation of the hydroxy complex. The adsorption of metal–hydroxy complexes proceeds rapidly because the favorable changes in coulombic and chemical energies exceed the unfavorable change in the solvation energy for the metal–hydroxy complex relative to the free metal ion. Another model of adsorption proposed by Schindler (1981) maintains that the surface coordination chemistry is the major factor controlling the adsorption of metal ions to oxide surfaces. Metal–hydroxide complexes that form at the oxide surface are
directly analogous to complexes formed in the bulk solution. The most important point relative to the mobility of colloids in the Upland Deep groundwater is that the intrinsic negative charge of the silica surface can be reversed by adsorption of metal ions and that Fe(III) is the most effective metal at achieving the charge reversal.

The dissolution of the chamosite in the overlying clay layer maintains the supply of Fe(III) to the infiltrating groundwater and the ferric hydroxide continues to build up on the quartz grains of the aquifer until the quartz grains are coated and stained with ferric hydroxide. With time, the ferric hydroxide coating dehydrates and forms goethite, which is the stable ferric oxyhydroxide in shallow sediments under humid conditions (Langmuir, 1971b). The negatively-charged silica surface is converted to a positively-charged goethite surface at the pH of the Upland Deep groundwater. Dissolved iron in the groundwater is controlled by the supply of iron from the clay dissolution, the adsorption of Fe(III) by the silica surfaces, the solubility of the goethite, and the redox chemistry between Fe(II) and Fe(III).

Clay colloids are simultaneously being generated by the physical fragmentation of the clay layer. Dispersion may be accelerated by the infiltration of dilute precipitation with low Ca\(^{2+}\) and Mg\(^{2+}\) concentrations. The released clay colloids are transported downward by infiltrating groundwater until the colloids come into contact with aquifer surfaces by interception, sedimentation, or diffusion and are removed from suspension (Yao et al., 1971). In the Upland Deep groundwater, the clay colloid suspension is probably removed from suspension by two main processes: 1) coagulation; and 2) attachment to the positively-charged ferric oxyhydroxide coatings on the quartz grains.

The coagulation of clays may occur by two processes: self-coagulation and coagulation by Fe(III) and Al(III). The self-coagulation of kaolinites due to the electrostatic attraction of the oppositely-charged edges and faces was first described by Schofield and Samson (1954). Swartzen-Allen and Matijevic (1976) measured
the effect of the pH on the coagulation of kaolinite. Critical coagulation concentrations (CCC), the salt concentration necessary to induce coagulation of a colloid suspension, for dilute kaolinite suspensions (25 mg/L) increased with increasing pH from 2 meq/L NaNO₃ at pH 4.1 to 40 meq/L at pH 10. At low pH, the kaolinite suspension coagulated at very low salt concentrations due to the edge–face attractions. At pH above the estimated PZC of the kaolinite edges, the edges and faces are both negatively–charged and high concentrations of salt are required to compress the double layers sufficiently to induce coagulation.

To examine the possibility of self–coagulation of the clay colloids infiltrating down to the Upland Deep groundwater, the ionic strength of the groundwater can be estimated from the empirical relationship between the ionic strength $I$ (eq/L) and the measured specific conductivity $\mu$ (µS) derived by Langmuir (1969):

$$I = 1.50 \cdot 10^{-5} \mu$$

where the specific conductivity is corrected to 25°C. The result for the Upland Deep groundwater is $I = 0.8$ meq/L, insufficient to cause coagulation at pH 4.8 in NaNO₃ solutions; however, Swartzen–Allen and Matijevic (1976) also measured the CCC in Ca(NO₃)₂ solutions. In the bivalent cation solution, the CCC at pH 4.8 is only 0.13 meq/L because the kaolinite surface selectively exchanges Ca²⁺ for Na⁺, resulting in a lower negative charge on the face and less electrostatic repulsion. The Upland Deep groundwater contains a slightly greater concentration of (Ca²⁺ + Mg²⁺) than Na⁺, thus the clay colloids are expected to self–coagulate and settle out of suspension or be filtered out by small pores.

The adsorption of Al(III) and Fe(III) ions and oxyhydroxides on clay surfaces also induces coagulation rapidly. Packham (1965) observed that kaolinite coagulation was most complete at near–neutral pH, suggesting that the hydrolysis products were important in the coagulation process. Oades (1984) coagulated various clays with Fe(III) and Al(III) polymers and colloids (1 to 10 nm). The
adsorption of the polymers caused coagulation by reducing the charge of the clay surfaces. Goldberg and Glaubig (1987) evaluated the coagulation behavior of the clays affected by the presence of Fe(III) and Al(III) oxides. The oxides lowered the CCCs required to coagulate the clay suspensions most effectively at near-neutral pH.

Clay colloids will also be removed from solution by attachment to the positively-charged goethite surfaces coating the quartz grains. The negatively-charged faces of the clays provide a large surface to interact with the aquifer grains. Clay particles adsorbed to sediments in natural sediments and laboratory columns are typically found with their faces oriented parallel to the surfaces (Walker et al., 1978; Dijkerman et al., 1967). However, in some calcareous sandstones, Walker et al. (1978) observed clay edges adsorbed to quartz grains in a "house of cards" arrangement. The interaction of positively-charged clay edges and negatively-charged silica surfaces may be responsible for this orientation.

Is it reasonable to expect the negatively-charged clay faces to adsorb dissolved Fe$^{3+}$ by selective ion exchange in the Upland Deep groundwater? And could the adsorption of sufficient iron reduce, or even reverse, the negative surface charge of the clay faces such that they would no longer interact with the goethite coatings on the quartz grains? A number of studies report iron oxides coating clay particles and influencing their surface properties. Greenland (1975) analyzed the behavior of the surface charge of clays coated by iron hydrous oxide taken from clay loam sediments and found that the permanent negative charge of the kaolinite face was obscured by the iron hydrous oxide coating. Newton and Liss (1987) examined the electrophoretic mobilities of iron oxyhydroxide-coated clays in an acidic stream and measured uniform positive mobilities on the coated particles. It must be noted that significant amounts of quartz surface were absent from these natural water systems, so the iron hydroxide precipitation found less suitable sites for nucleation.
With silica (or other weakly acidic oxide) and clay surfaces present in the system, the selectivity of one cation over another for each adsorption process must be considered. For selective ion exchange, the selectivity constant for one cation versus another loosely depends on the relative ratios of valence to ionic radius (Freeze and Cherry, 1979). Thus, the clay surface is about three times more selective for Fe\(^{3+}\) than for Ca\(^{2+}\), and about six times more selective than for Na\(^+\). The relative concentrations of the cations in solution also determine how much ends up adsorbed to the clay. For cation adsorption to the silica surface, the first hydrolysis constant indicates the affinity for adsorption. The hydrolysis constant of Fe\(^{3+}\) is approximately ten orders of magnitude larger than that of Ca\(^{2+}\), so Fe(III) species are adsorbed much more strongly to silica surfaces. The observance of kaolinite particles with less than one percent Fe and silica particles with 20 percent Fe in the Upland Deep groundwater supports this contention.

As clay colloids are removed from suspension by coagulation and adsorption, the permeability of the sandy sediment decreases (Champlin, 1971; Khilar and Fogler, 1984; Kia et al., 1987). The decrease in permeability represents a clogging of the pores and increased filtration of clay colloids larger than the pore size. This results in the development of illuvial banding (Bond, 1986) and clay lamellae (Dijkerman et al, 1967). High concentrations of iron are often implicated in such soil structures (Folks and Riecken, 1956). The result may be that clay colloids no longer reach the depth of the Upland Deep groundwater due to pore constriction and filtration. Indeed, the hydraulic heads measured in the Upland Shallow and Upland Deep wells are nearly equal, indicating that infiltration is not significant. The existing low-permeability clay layer and the reduction of the underlying aquifer permeability by illuvial banding may restrict the infiltration of groundwater and clay colloids.

The April, 1987 sampling of the Upland Shallow groundwater produced light
scattering and SEM results that indicate its colloid load was significantly greater than that of the Upland Deep groundwater sampled in April (although the absolute colloid concentrations are not comparable to those obtained in October, 1987 due to sampling difficulties). Given the proximity of the Upland Shallow sampling point to the clay layer, the greater colloid abundance may be related to the distance from their source. Therefore, colloids have not been removed from suspension about 2 to 3 meters from their source. This depth correlates with the occurrence of the "pinkish" sands, which begin at about 5 meters depth. The pink color of the sands indicates the adsorption of Fe(III) and clays.

There are two possible starting points for evaluating the geochemical processes that affect colloid mobility in the Swamp Deep groundwater. The first consists of beginning with a situation similar to the current state of the Upland Deep groundwater: very low colloid abundance caused by coagulation, sedimentation, and adsorption of clay colloids onto positively-charge goethite-coated quartz grains. The second consists of beginning with the introduction of clay-derived iron, clay colloids, and a heavy load of organic carbon to clean sediments beneath a swamp. Thus, in the first case, the colloid mobility in the Swamp Deep groundwater depends on the detachment of adsorbed clay and ferric oxyhydroxide particles from the aquifer substrate; and furthermore, the maintainance of colloid stability in the groundwater after detachment. The second case can be explained by addressing only the second point, the maintainance of colloid mobility.

Initially, we will recall an important observation: the sands at the depth of the Upland Deep are pink in color, but the sands at the depth of the Swamp Deep groundwater are brown and tan, colors not related to ferric iron coatings. Clay must still be an important constituent of the soil and aquifer sediments as evidenced by high iron and aluminum concentrations, especially in the Swamp Shallow
groundwater, and by the substantial amounts of clay retained on the April, 1987 groundwater filter sample. Dissolved iron is being transported to the deeper groundwater, but a significant amount of it is remaining dissolved, as suggested by the analysis of the $p_e$–$p_H$ diagram. The major difference in the chemistry of the Upland and Swamp groundwaters is the abundance of organic carbon and related consumption of dissolved oxygen, nitrate, and sulfate in the Swamp Deep groundwater. The resulting anoxic, reducing conditions result in a zone where ferric oxyhydroxides are not thermodynamically stable.

In the Upland Deep groundwater, the goethite coating on the quartz grains acts as the "glue" that bound the clay colloids to the aquifer substrate. Without the goethite coatings, the clay colloids would not be strongly adsorbed to the quartz grains. Clays would continue to be removed by coagulation–sedimentation and filtration, the collision efficiency factor describing the interaction of the colloids with the surface (Yao et al., 1971) would be greatly reduced. In the Swamp Deep groundwater, Fe(III) in solution is reduced to Fe(II) and the goethite coatings would gradually dissolve to maintain the concentration of Fe(III) in solution. Eventually, the surface of the quartz grains would revert to negative charge at the groundwater $p_H$.

The kinetics of this process can be observed in the advance of a reducing plume of wastewater emanating from a landfill or sewage disposal site. High concentrations of $\text{NH}_4^+$, $\text{Fe}^{2+}$, $\text{H}_2\text{S}$, and $\text{CH}_4$ confirm the presence of a reducing plume. Nicholson et al. (1983) attributed the high ferrous iron concentrations in a leachate plume to the dissolution of ferric iron coating on sand grains. Kimmel and Braid (1980) observed that reducing conditions of leachate plumes removed the orange iron hydrous oxide coating from glacial outwash sediments and turned the sands and gravels to a gray color. Baedecker and Back (1979) noted that the dissolution of Mn– and Fe–oxides in reducing plumes also releases the adsorbed load
of heavy metals—Co, Ni, Cu, and Zn. Finally, Gschwend and Reynolds (1987) detected the formation of 100 nm–diameter ferrous phosphate colloids in a reducing plume. The high dissolved Fe$^{2+}$ concentrations leading to precipitation of the colloids were augmented by dissolution of ferric oxyhydroxide coatings on the aquifer sediments.

A pristine groundwater situation analogous to the reduction of ferric oxyhydroxides in the Swamp Deep groundwater was investigated by Langmuir (1969) in the nearby Raritan and Magothy Formation aquifers that outcrop on the Delaware River in southern New Jersey. His study revealed a connection between the redox potential of the groundwater, the iron geochemistry, and iron oxyhydroxide colloid mobility. As oxygenated groundwater infiltrated into the aquifers and flowed downdip to the east, the pH increased from 5.5 to 8.0, the dissolved (<10 nm–filtered) iron concentration increased from 10 $\mu$M to 120 $\mu$M, and the total iron concentration increased to a maximum of about 280 $\mu$M. The difference between the total and dissolved fractions was assumed to be suspended ferric oxyhydroxides leached from sand grains by the onset of reducing conditions. Langmuir made no attempt to positively identify the suspended particles, so their identification as ferric oxyhydroxides may be incomplete. Also, his samples presumably were collected at high flow rates, thus the suspended loads trapped on filters may not accurately reflect the groundwater colloid load. Back and Barnes (1965) evaluated the iron geochemistry in the Raritan and Magothy aquifers in Maryland by comparing Eh measured in the field and calculated from various iron redox couples. They concluded that reducing conditions diminish the stability of iron oxides in the sediments, but they made no attempt to characterize the suspended load of the groundwater.

In laboratory experiments, Gotoh and Patrick (1974) studied the effect of redox potential and pH on iron in a water–logged soil by measuring the amount of
dissolved iron produced at various Eh and pH conditions. They found that at pH 5 and measured redox potential of +0.300 V, a substantial portion of the ferric iron solid was converted to dissolved Fe$^{2+}$.

It is clear from the observations of this investigation and the results of analogous studies in contaminated and pristine groundwater and laboratory experiments that the onset of anoxic, reducing conditions destabilizes the goethite coatings that bind the clay particles onto the quartz grains. As dissolution of the goethite coatings begins, the clay and goethite colloids detach from the aquifer substrate and move into suspension.

Now we address the second process—the stabilization of the colloidal suspension in the Swamp Deep groundwater. Basically, three types of colloids were observed in the Swamp Deep groundwater: 1) clays with apparently oxide-free surfaces; 2) clays with iron oxyhydroxide coatings; and 3) independent goethite colloids.

The compositions of the oxide-free clays fell into both the low-Fe (kaolinite) and high-Fe (chamosite) categories. For a kaolinite with a "clean" surface, this requires that the 3.5 percent Fe is present as isomorphic substitutions of the Al$^{3+}$ ion. The iron composition is significantly higher than the normal range of structural iron present in kaolinite (Jaynes and Bigham, 1986; Grim, 1968); however, the abundance of iron relative to other bivalent ions that commonly substitute for Al$^{3+}$ in kaolinite increases the feasibility of iron substitution. The surface properties of these clays would be similar to those in the Upland Deep groundwater; therefore, they would be subject to coagulation by edge-face interactions.

The clays with iron oxyhydroxide coatings include particles similar to the clay shown in Figure 3.3b, which was partially covered by relatively crystalline ferric oxyhydroxides, and particles that appear to be completely covered by finely-divided microcrystalline iron oxyhydroxides, comparable in morphology to
those sampled by Greenland (1975). The clays with complete coverage were generally high in iron, so they could be either completely ferric oxyhydroxide-coated kaolinite or less completely covered chamosite. The resolution of the SEM is not sufficient to precisely distinguish the nature of the surfaces. The extent of the ferric hydroxide coating on these clays would dictate their surface charge. As surface coverage increases, the clay would become increasingly positively-charged in the Swamp Deep groundwater and increasingly reactive toward negative surfaces, such as quartz grains freed of their goethite coating or the faces of "clean" clay colloids.

Finally, the independent goethite colloids appeared as lath-like crystals gathered in small clusters. The goethite would possess a positive surface charge in the Swamp Deep groundwater and might be expected to adsorb strongly to the negative silica surfaces. However, their release was prompted by partial dissolution of their structure by the reducing conditions and the continued dissolution and reduction of Fe(III) to Fe(II) is more likely.

The colloids detached from the quartz grains in the Swamp Deep groundwater appear to be unable to remain in suspension due to some of the removal mechanisms operating in the Upland Deep groundwater. Yet the colloids sampled from the groundwater at very low flow rates over long periods of time retain their light scattering intensities over months under anoxic storage conditions—they appear to be truly colloidal. One piece of evidence has not been utilized so far: the amount of organic carbon associated with the suspended (> 30 nm) phase in the Swamp Deep groundwater (0.7 mg/L). The colloids must be coated with organic carbon.

Organic carbon coatings were observed in the studies of Niehof and Loeb (1972; 1974), Hunter and Liss (1979), and Hunter (1980). These investigations established that the surface properties of a wide variety of suspended particles were
masked by ubiquitous coatings of organic matter in estuaries and coastal seawaters. The substantial and uniform negative charge produced by the organic coatings ruled out the hypothesis that coagulation of riverborne particles was caused by neutralization of their charge at the transition to high ionic strength seawater. Tipping (1981) determined that the mechanism of adsorption of humic substances onto iron hydrous oxides in freshwater was consistent with a ligand exchange of the humic anionic groups with the positively-charged hydrous oxide surface. The iron hydrous oxides were converted to negative charge by the adsorption of humic substances. The interactions of organically coated iron hydrous oxides colloids with solutions containing varying concentrations of Ca\(^2+\), Mg\(^2+\), and DOC were tested by Tipping and Cooke (1982) and Tipping and Higgins (1982). Increases in bivalent cation concentrations caused increased coagulation rates of the organically coated particles by reducing the surface, while increased DOC concentrations reduced coagulation rates, apparently by steric stabilization.

Davis and Gloor (1981) isolated the 1000 < \( M_w \) < 3000 range of the organic carbon as the major component adsorbed to aluminum oxide in freshwater. This molecular weight fraction covers the recognized range of humic substance molecular weights. Davis (1982) examined the adsorption of dissolved organic matter by a variety of minerals: aluminum oxide, silica, rutile, and kaolinite. The acidic surface hydroxyls of silica did not react strongly with the organic matter in the pH range 4 to 10, while aluminum oxide adsorbed most strongly with a maximum at pH 5. Aluminum oxide, with its high PZC, presented a positively-charged surface to the organic matter throughout most of the pH range. Kaolinite adsorption decreased with pH as the overall charge of the particles became more negative, but between pH 4 and 5, a unit area of the kaolinite surface adsorbed more DOC from solution than aluminum oxide. The adsorption of organic matter onto kaolinite at low pH probably occurs on the alumina groups on the positively-charged edges and on the
gibbsite basal face, where the adsorption of silicate anions usually dominates.

The humic substances in the Swamp Deep groundwater are expected to pass through the 30 nm filter pores if they are not associated with suspended particles. In dilute Swamp Deep groundwater (especially dilute with respect to bivalent cations), the humic substances would not expected to coagulate to any extent; furthermore, in low pH solutions, the molecules approach a more spherical shape (Gnosh and Schnitzer, 1980). Therefore, their approximate molecular size would be no larger than the 3 to 5 nm diameter estimated by Thurman et al. (1982) and Wershaw and Pinckney (1973).

The stability of the colloids in the Swamp Deep groundwater is maintained by the acquisition of an organic coating comprised mainly of humic substances and the subsequent development of a negatively—charged surface. The organically coated colloids are still removed from suspension by coagulation, but at a very slow rate because of the low Ca$^{2+}$ and Mg$^{2+}$ concentrations and low overall ionic strength of the Swamp Deep groundwater. Furthermore, the organic coating may inhibit the dissolution and reduction of the iron oxyhydroxide colloids and the iron surface coatings on clay colloids (Theis and Singer, 1974).

But what about the time scale of the adsorption of organic carbon to colloids—is it rapid enough to prevent the coagulation and adsorption of unstable colloids? Newton and Liss (1987) studied the effect of organic coatings on a similar colloid population in an analogous geochemical setting—a river and estuary fed by highly acidic, iron—rich mine drainages. Microelectrophoresis and nitrogen adsorption isotherms (Marsh et al., 1984) revealed suspended clay particles coated with a positively—charged ferric oxyhydroxide surface derived from the oxidation and hydrolysis of Fe(II). The river pH varied from 3.4 to 5.0 and total organic carbon was measured at 2.1 mg/L. The positive electrophoretic mobilities of the particles steadily decreased and then became negative as the particles reached the
estuary. The mobilities eventually reached the high negative mobilities measured by Hunter and Liss (1979). These results indicate an increase in control of particle mobility as organic carbon accumulates on the particle and the time scale of the process in surface waters.

Apparently the total organic carbon concentration of the Swamp Deep groundwater is sufficient to control the surface charges of a variety of particles. The Upland Deep groundwater contains more than half as much total organic carbon, yet the colloid population is apparently totally removed from suspension. It is possible that the lower concentration may not sufficiently control the particles' intrinsic surface charge, but the difference is not that great—some surface charge effect would be evident. Another possibility is that the nature of the organic carbon in the Upland Deep makes it less reactive toward oxide surfaces than the Swamp Deep organic carbon, which is probably composed primarily of humic substances that adsorb to oxide surfaces particularly well (Davis and Gloor, 1981). The rapid decomposition of organic matter in the oxygenated Upland groundwater may produce more final oxidation products that contain lower proportions of the acidic functional groups present on humic substances that are involved with the binding to surface hydroxyls. The third possibility, expressed before, is that clay colloids no longer reach the Upland Deep groundwater because illuvial banding has drastically reduced the permeability of the aquifer and blocked the transport of clay colloids.

Finally, a brief analysis of the colloid behavior in the Swamp Shallow groundwater will complete the explanation of colloid mobility in the McDonalds Branch groundwaters. The iron and aluminum hydrous oxide colloids found in the Swamp Shallow groundwater are the products of intense chemical weathering of clays. The hydrous oxides have intrinsic positive surface charges at the low pH of the groundwater, but they are probably heavily coated by organic carbon. With the organic coating, the hydrous oxides are colloidally stable by steric stabilization as
suggested by Tipping and Higgins (1982) and inhibited from further dissolution.

In this evaluation of the contrast in colloid mobility and geochemistry between three McDonalds Branch groundwaters, we have started with clean sediments composed primarily of quartz surfaces and introduced dissolved iron and populations of clay and hydrous oxide colloids. The low ionic strength, acidic, oxic Upland Deep removed the colloids from suspension by coagulation and settling, by adsorption to goethite-coated quartz grains, and perhaps most importantly, by blocking clay illuviation in a zone of reduced permeability. In the low ionic strength, acidic, and anoxic Swamp Deep groundwater, the colloid population is detached from the aquifer substrate by the dissolution and reduction of the ferric oxyhydroxide coatings and stabilized in suspension by a uniform negatively-charged organic coating. The Swamp Shallow particles are also affected by organic coatings: the hydrous oxides may be stabilized by heavy organic coatings and steric stabilization.
CHAPTER 4. COLLOIDS IN DELAWARE GROUNDWATER

4.1 Site Description: Geology, Hydrology, and Geochemistry

Many municipalities in Delaware tap the unconfined aquifers of the Coastal Plain for water supplies. Often they have encountered groundwaters containing concentrations of iron and nitrate high enough to restrict the use of the groundwater. Also, organic carbon concentrations in these groundwaters are often in excess of the median dissolved organic carbon content of groundwaters reported by Leenheer et al. (1974). In April, 1987, we sampled three groundwaters containing high iron and organic carbon levels to evaluate the nature and distribution of colloids in Delaware Coastal Plain aquifers. The three wells were spread throughout the state in three different geologic units. The April reconnaissance survey revealed substantial colloid abundance in well Lc42–01 near the Kent County town of Harrington. For the October, 1987, sampling, the investigation was focused to 2 wells near Harrington, Lc42–01 and Md22–01. The second well was selected to illustrate the local contrast in groundwater chemistry and its effect on colloid abundance. The well locations are shown in Figure 4.1.

4.1.1. Regional Setting

Most of the Coastal Plain in Delaware is covered by a sheet of sand known as the Columbia deposits (Pleistocene). The Columbia deposits potentially constitute the most productive aquifer in Delaware (Jordan, 1964). Several geologic units have been designated in the Columbia deposits (some of which are currently disputed). Near Harrington, the Staytonville Unit and the Columbia Formation comprise the
Figure 4.1. Location of Wells in Delaware.
unconfined aquifer.

The surficial layers of sediment present at the wells located near Harrington probably represent the Staytonville Unit. The Staytonville Unit consists mainly of medium-grained sands with some fine and coarse sands and silt. The bedding of the unit is irregular with abrupt lateral and vertical color changes and the thickness varies from zero to 13 meters in central Delaware. In many exposures, the sediment is mottled in texture and color, indicating reworking by bottom-dwelling organisms during deposition. Based on analysis of pollen found in the Staytonville Unit sediments, the environment of deposition is thought to be a fresh-water swamp (Jordan and Talley, 1976). For a number of wells near Harrington, Talley (1975) identified the mottled silty sands in the upper six meters of well logs as those of the Staytonville Unit.

The Columbia Formation is a fluvial and shoreline sequence of sediments that initially filled channels cut into the underlying Miocene Chesapeake Group and later spread laterally to form a coalescing sheet of sand ranging in thickness from 14 to 30 meters. The sediments were deposited in a variety of environments reflecting the advance and retreat of the sea during the Pleistocene, including barrier beach, dune, salt marsh, estuarine, bay, and fresh water swamp. Sediments of the Columbia Formation are primarily medium- to coarse-grained sands and gravels, but thin, discontinuous lenses of clay and silt are also present (Jordan, 1964). The average composition of the subarkosic sands is about 83 percent quartz, 12 percent orthoclase feldspar, 3 percent plagioclase feldspar, 1 percent mica (muscovite and biotite), and trace quantities of a large number of metamorphic heavy minerals (zircon, epidote, amphibole, sillimanite, tourmaline, and rutile). The sands are typically unconsolidated, although the presence of interstitial clays and iron oxides can cause considerable induration (Jordan and Talley, 1976). In the Harrington area, sand grains are frequently stained with limonite. The base of the Columbia
Formation is usually identified by a thin layer of limonitic crust.

The underlying Chesapeake Group is a marine and marginal–marine sequence of sediments consisting mainly of grey and bluish-grey silt, interbeds of fine–to medium–grained sands, and some shell beds (Jordan, 1962). In some locations, the sandy interbeds, designated the Manokin Unit, act as part of the unconfined aquifer.

The average depth to the groundwater table is about 1.5 to 3 meters near Harrington, so the hydrologic properties and composition of the soil layer have an important effect on the infiltration rate and chemistry of precipitation (Denver, 1986). Soils at the study sites consist mainly of sand, with varying amounts of silt and clay. The permeability of the soil decreases with increasing silt and clay content (U.S. Dept. Agriculture, 1971).

Annual precipitation in the area is about 109 cm, of which 67 percent is evaporated (Johnston, 1973). The remaining 33 percent of the precipitation enters the unconfined aquifer as recharge, because the very flat topography reduces surface runoff to streams to a negligible amount. Groundwater generally follows the topography towards small streams and drainage ditches in shallow low–gradient recharge and discharge paths through the high–permeability unconfined aquifer (average K = 3.2·10^{-2} cm/sec, Johnston (1977)). The hydraulic gradients in the surficial aquifer range from about 0.56 to 1.9 m/km (Sundstrom and Pickett, 1970), so groundwater velocities of about 4.5·10^{-5} to 1.5·10^{-4} cm/sec are expected for the surficial aquifer, assuming a porosity of 0.4. These groundwater velocities are comparable to the groundwater velocity calculated for the typical Pine Barrens groundwater. Groundwater discharge into streams contributes about 75 percent of the flow of most streams. The larger stream systems, the Nanticoke and Marshyhope Rivers, receive groundwater discharge from longer, deeper flow paths that extend from groundwater divides to the base of the rivers.
The groundwater chemistry of the unconfined aquifer near Harrington is the product of the geology of the formations, the hydrology of the soils and the aquifer, and the workings of several geochemical processes: infiltrating precipitation, weathering of minerals, redox reactions, cation exchange reactions, and anthropogenic inputs. Two types of "typical" groundwaters have been identified in the study area (Denver, 1986): 1) a near-neutral pH, anoxic, groundwater with high dissolved iron; and 2) an acidic, oxic groundwater containing trace levels of dissolved iron. The major dissolved constituents of the typical groundwaters, compiled from a number of groundwater samples taken from wells near Harrington and analyzed by the Delaware Geological Survey (DGS), are shown in Table 4.1.

The infiltrating precipitation is the major contributor of dissolved ions to the groundwater. The average precipitation pH is 4.34 and the major ionic constituents of the precipitation are H⁺, Na⁺, NH₄⁺, Cl⁻, SO₄²⁻, and NO₃⁻ (as measured at Lewes, Delaware, only two kilometers inland from Delaware Bay). The precipitation at the site is probably lower in Cl⁻ concentrations and slightly higher in Ca²⁺ and Mg²⁺ because Harrington, Delaware is about 20 km inland. Most of the ions in the groundwater are derived from precipitation. Table 4.1 compares the precipitation chemistry with the typical groundwater chemistries. The concentrations of the constituents of the infiltrating water are actually about 3 times as concentrated as the precipitation due to evapotranspiration of the water at the surface (Cushing et al., 1973).

The chemical weathering of the major minerals in the Columbia Formation has a major effect on the groundwater chemistry. The incongruent dissolution of the feldspars (orthoclase and plagioclase) and micas (muscovite and biotite) releases cations and increases the alkalinity, forms silicic acid, and produces an aluminum–rich solid residue, kaolinite:
Table 4.1. Mean chemical composition of precipitation and groundwater near Harrington, Delaware (after Denver, 1986).

<table>
<thead>
<tr>
<th></th>
<th>Precipitation</th>
<th>Anoxic Groundwater&lt;sup&gt;1&lt;/sup&gt;</th>
<th>Oxic Groundwater&lt;sup&gt;2&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp °C</td>
<td>n.a.</td>
<td>14.5 (11.5–16.0)</td>
<td>15.0 (12.0–18.0)</td>
</tr>
<tr>
<td>pH</td>
<td>4.34</td>
<td>6.3 (5.8–6.8)</td>
<td>5.3 (4.6–5.9)</td>
</tr>
<tr>
<td>DO mg/L</td>
<td>n.a.</td>
<td>0.2 (0.0–0.8)</td>
<td>6.1 (4.2–7.3)</td>
</tr>
<tr>
<td>Spec. Cond.</td>
<td>n.a.</td>
<td>116 (52–209)</td>
<td>147 (93–259)</td>
</tr>
<tr>
<td>Alk. mg/L</td>
<td>n.a.</td>
<td>43.4 (2.0–78.7)</td>
<td>7.9 (1.6–18.4)</td>
</tr>
<tr>
<td>Na&lt;sup&gt;+&lt;/sup&gt; μM</td>
<td>53</td>
<td>363 (270–522)</td>
<td>417 (252–522)</td>
</tr>
<tr>
<td>K&lt;sup&gt;+&lt;/sup&gt; μM</td>
<td>2.3</td>
<td>27 (23–31)</td>
<td>40 (23–69)</td>
</tr>
<tr>
<td>Ca&lt;sup&gt;2+&lt;/sup&gt; μM</td>
<td>3.0</td>
<td>208 (158–300)</td>
<td>123 (90–168)</td>
</tr>
<tr>
<td>Mg&lt;sup&gt;2+&lt;/sup&gt; μM</td>
<td>5.1</td>
<td>73 (62–86)</td>
<td>57 (35–78)</td>
</tr>
<tr>
<td>NH&lt;sub&gt;4&lt;/sub&gt; μM</td>
<td>13</td>
<td>11 (7.0–17)</td>
<td>0.7 (0.6–1.2)</td>
</tr>
<tr>
<td>Cl&lt;sup&gt;–&lt;/sup&gt; μM</td>
<td>54</td>
<td>270 (163–451)</td>
<td>332 (228–535)</td>
</tr>
<tr>
<td>SO&lt;sub&gt;4&lt;/sub&gt;2&lt;sup&gt;–&lt;/sup&gt; μM</td>
<td>22</td>
<td>221 (59–448)</td>
<td>17 (7.3–24)</td>
</tr>
<tr>
<td>NO&lt;sub&gt;3&lt;/sub&gt; μM</td>
<td>20</td>
<td>1.6 (&lt;1.6–3.0)</td>
<td>126 (55–226)</td>
</tr>
<tr>
<td>PO&lt;sub&gt;4&lt;/sub&gt;3&lt;sup&gt;–&lt;/sup&gt; μM</td>
<td>n.a.</td>
<td>6.0 (0.6–10.5)</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>DOC* mg C/L</td>
<td>n.a.</td>
<td>2.2 (1.5–3.2)</td>
<td>5.4 (2.1–11)</td>
</tr>
<tr>
<td>Fe Diss. μM</td>
<td>n.a.</td>
<td>290 (100–510)</td>
<td>0.1 (&lt;0.1–0.2)</td>
</tr>
<tr>
<td>Al Diss. μM</td>
<td>n.a.</td>
<td>&lt;0.3</td>
<td>0.8 (&lt;0.3–1.5)</td>
</tr>
<tr>
<td>SiO&lt;sub&gt;2&lt;/sub&gt; Diss. μM</td>
<td>n.a.</td>
<td>533 (383–617)</td>
<td>354 (163–483)</td>
</tr>
</tbody>
</table>

<sup>1</sup> Data from wells Lc42–01, Lc42–02, Lc55–01, Mc53–01, and Mc31–03 (see Talley and Andres (1987) for explanation of Delaware well numbering code).

<sup>2</sup> Data from wells Lc11–01, Lc23–03, Lc51–01, Mc13–01, Mc22–01, Mc51–01, and Md31–04.

* DOC = Dissolved Organic Carbon, dissolved = 0.45 μm–filtered.
† Dissolved = 0.45 μm–filtered.
n.a. = not analyzed.
Orthoclase is more abundant than plagioclase in the sediments because it is more resistant to weathering; therefore Na$^+$ and Ca$^{2+}$ weathered from plagioclase feldspar are more abundant than K$^+$ weathered from orthoclase feldspar (Denver, 1986; Garrels and Christ, 1965). Similarly, for the micas, muscovite is more resistant to weathering than biotite; thus, it is more abundant in the sediments (Phillips and Griffen, 1981). Most of the biotite originally deposited in the sediment has dissolved and released Fe$^{2+}$, Mg$^{2+}$, and K$^+$ to the groundwater. Chemical weathering is most intense in the soil zone, where plant respiration and degradation increases the CO$_2$ content by 10 to 100 times the concentration of infiltrating precipitation (Drever, 1982). In areas of intense chemical weathering, further dissolution of kaolinite occurs and insoluble aluminum hydroxides, such as gibbsite, are produced:

\[
\text{kaolinite} \rightarrow \text{gibbsite}
\]

\[
\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 5 \text{H}_2\text{O} \rightleftharpoons 2 \text{Al(OH)}_3 + 2 \text{H}_4\text{SiO}_4
\]  

Iron oxyhydroxides, such as goethite and limonite, are typically associated with the deposition of aluminum oxides as products of intense weathering of iron-containing minerals (Leeder, 1982). Dissolved silicate concentrations in the groundwater exceed the solubility of quartz (about 100 $\mu$M), indicating that clay and feldspar weathering control the H$_4$SiO$_4$ concentration. The groundwater is substantially undersaturated with respect to amorphous silica.

Oxidation–reduction reactions in the groundwater affect the redox states of iron, nitrogen, and sulfur in the unconfined aquifer. High iron and nitrogen...
concentrations are the two primary water quality concerns throughout Delaware (Denver, 1986). In the oxic soil zone, the plant respiration and degradation can be described as oxidation of organic carbon. The oxidation of organic carbon produces CO$_2$, nitrate, and sulfate and consumes dissolved oxygen. The production of CO$_2$ enhances the weathering of alumino–silicate minerals, thereby increasing the alkalinity of the groundwater. After the exhaustion of available dissolved oxygen, organic carbon oxidation may proceed to the reduction of nitrate, Fe(III), and sulfate by this progression of reactions:

\[
\begin{align*}
O_2 \cdot g + CH_2O & \rightleftharpoons CO_2 \cdot g + H_2O & (4.5) \\
4 NO_3^- + 5 CH_2O + 4 H^+ & \rightleftharpoons 5 CO_2 \cdot g + 2 N_2 \cdot g + 7 H_2O & (4.6) \\
4 Fe(OH)_3 \cdot s + CH_2O + 8 H^+ & \rightleftharpoons CO_2 \cdot g + 4 Fe^{2+} + 11 H_2O & (4.7) \\
SO_4^{2-} + 2 CH_2O + H^+ & \rightleftharpoons CO_2 \cdot g + HS^- + 2 H_2O & (4.8)
\end{align*}
\]

The rate and degree of dissolved oxygen consumption and nitrate, ferric iron, and sulfate reduction depend on the frequency of infiltration of oxic precipitation, the nature and depth distribution of organic matter, and the porosity and permeability of the soil. Reducing conditions are known to occur near the land surface in poorly drained soils with high organic content. Oxygen, nitrate, Fe(III), and sulfate not reduced in the soil zone move into the underlying aquifer, where they may be transformed during the oxidation of remaining organic matter.

Clay minerals in the aquifer formation modify water chemistry by cation exchange reactions. Pickett (1970) reported that kaolinite, illite, and vermiculite are the prominent clays in the soils near Harrington. The micas, muscovite and biotite, are also important cation exchange surfaces. Vermiculite, and to a lesser extent, micas, are capable of adsorbing and holding Ca$^{2+}$ and Mg$^{2+}$ in groundwater at neutral pH, while Na$^+$ and K$^+$ are released into the groundwater and carried away. Illite has essentially the same structure as mica, but fewer Si atoms are substituted in the tetrahedra and fewer interlayer cations are present to balance the
negative charge. Kaolinite, with its fixed lattice, has much lower capacity to adsorb cations. Table 4.2 shows the cation exchange capacities of the common clay minerals present in the Columbia deposits.

Finally, anthropogenic inputs have had some impact on the groundwater chemistry, even though relatively pristine sites were sought for this investigation. The main anthropogenic inputs come from agricultural land use—application of inorganic fertilizer, manure, and lime. The low dissolved solids concentration and nearness of the water table to the land surface make the groundwater chemistry especially vulnerable to agricultural land use. Nitrogen, the major anthropogenic input, is a component of inorganic fertilizer and manure and is added mainly in the form of ammonium and organic nitrogen compounds. In oxic soil zones, the ammonium and organic nitrogen undergo nitrification, i.e., they are oxidized to nitrite, then rapidly to nitrate, in the presence of nitrifying bacteria. Nitrification decreases the pH of the soil water. In anoxic soil zones, nitrification does not occur and nitrogen remains in the form of ammonium and organic nitrogen. Ammonium is adsorbed strongly onto vermiculite and illite (Denver, 1986).

The application of inorganic fertilizers adds potassium, chlorine, phosphorus, and sulfur to the groundwater in the forms of KCl, P₂O₅, and gypsum, respectively. Potassium content in soils is high, but 90 percent of it remains in unweathered minerals or it is bound on interlayer exchange sites in clays (Brady, 1974). Chloride concentrations in excess of the 160 µM present in the infiltrating precipitation suggests that anthropogenic inputs (fertilizer or sewage) may be significant. Phosphate in the groundwater is mainly the product of fertilizer, but septic tank sewage and animal wastes also contribute significant fractions. Only trace amounts of phosphate–bearing minerals have been found in Delaware (Jordan, 1964).

The application of lime to the farm land in the form of crushed dolomite buffers the acidity caused by the nitrification of ammonium and organic nitrogen.
Table 4.2. Cation Exchange Capacities (CEC) of clay minerals (after Drever, 1982; Greenland and Mott, 1978).

<table>
<thead>
<tr>
<th>Clay</th>
<th>CEC (meq/100 g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vermiculite</td>
<td>120 to 200</td>
</tr>
<tr>
<td>Micas</td>
<td>30 to 80</td>
</tr>
<tr>
<td>Illite</td>
<td>10 to 40</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>2 to 5</td>
</tr>
</tbody>
</table>
It also enhances the availability and uptake of calcium, magnesium, molybdenum, and phosphorus to plants and reduces the solubility of iron, aluminum, and manganese, which can be toxic to plants (Denver, 1986).

4.1.2. Site-specific Description

The two wells sampled in October, 1987 represent the two distinct groundwater types encountered in the unconfined aquifer near Harrington, Delaware. Sampling at the first well, Lc42–01, revealed a substantial colloid population in near-neutral, anoxic groundwater, although the representativeness of the April samples is questionable. The October sampling of Lc42–01 was intended to check the original results using better pumping techniques and field monitoring of colloid concentration. Well Lc42–01 is located in a mixed farmland/woods area covered by poorly-drained soils of the Pocomoke or Fallsington series (U.S. Dept. Agriculture, 1971). The well location is shown in Figure 4.1. Topographically, the area is flat and drainage is toward nearby ditches leading into the slow-flowing Marshyhope Creek. The well is drilled to a depth of 16.8 meters and screened over an interval of 1.5 meters in the Columbia Formation (well construction details appear in Table 4.3 and a representation of the drilling log is shown in Figure 4.2). The groundwater in the formation is near-neutral pH, anoxic, and very high in iron.

Another well, Lc42–02, at the same site was drilled to a depth of 7.6 meters, but could not be sampled using the techniques developed for this investigation because the casing diameter was only 3.2 cm. The shallow groundwater is higher in Na⁺ and Cl⁻, possibly influenced by nearby residential septic systems and fertilizer application (about 20 to 30 meters distant to the east), or salting of the roads just a few meters away. Concentrations of iron and alkalinity were higher and sulfate was lower in the shallow groundwater, according to DGS analyses (Denver, 1986),
Table 4.3. Well construction details of the Delaware monitoring wells (after field data supplied by A.S. Andres, DGS).

<table>
<thead>
<tr>
<th></th>
<th>Lc42–01</th>
<th>Md22–01</th>
<th>Db24–17</th>
<th>Qe44–01</th>
</tr>
</thead>
<tbody>
<tr>
<td>Land Elevation (m)</td>
<td>17.7</td>
<td>18.3</td>
<td>23.5</td>
<td>14.9</td>
</tr>
<tr>
<td>Hydraulic Head (m)</td>
<td>15.6</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Well Depth (m)</td>
<td>16.8</td>
<td>5.5</td>
<td>8.0</td>
<td>8.2</td>
</tr>
<tr>
<td>Screened Interval (m)</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.2</td>
</tr>
<tr>
<td>Well Diameter (cm)</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Date Installed</td>
<td>9/82</td>
<td>10/87</td>
<td>6/86</td>
<td>8/81</td>
</tr>
</tbody>
</table>

<sup>1</sup> referenced to National Geodetic vertical datum of 1929.
Figure 4.2. Well Construction and Lithology at Well Lc42-01

- Brown, top soil.
- Light brown, silty fine sand.
- Grey, sandy clay with iron-oxide streaks.
- Tan, fine to medium sand (coarsens with depth) with traces of gravel.
- Grey, very fine sand with traces of clay.
- Tan, medium to coarse sand with traces of clay and 15 cm layers of gravel.
- Tan, silty fine sand.
- Tan, fine to medium sand with traces of gravel.
- Orange, iron oxide cementation (base of Columbia Fm. and unconfined aquifer).
- Grey, clay (Chesapeake Group).

(from well log data supplied by A.S. Andres, Del. Geol. Survey)
indicating a greater degree of reduction. Nitrate was below detection limit in both wells. Dissolved iron concentrations, as reported by homeowners in the area, vary widely over short distances. The soil drainage characteristics are quite different over short distances near Lc42–01. The boring at Lc42–01 and another boring approximately 30 meters to the south reveal about 1 meter of mottled sand overlying a dense, grey clay layer stained by iron oxides (boundary between oxidizing and reducing groundwaters), but Denver (1986) reports that a boring less than 30 meters to the northwest revealed only ferric oxide–indurated sands were present near the surface.

The second well sampled in this investigation, Md22–01, was sampled in October, 1987, to provide a chemical contrast to the Lc42–01 groundwater. The DGS installed the well in early October, 1987, as a replacement for a destroyed piezometer; no past chemical analyses were available. It is expected that the groundwater chemistry of the well is similar to the other acidic, oxic groundwaters sampled in the area and compiled in Table 4.1. Well Md22–01 is located adjacent to a cultivated field and a drainage ditch alongside a light road (Figure 4.1). The surface soils, designated as the Evesboro series (U.S. Dept. Agriculture, 1971) are excessively well–drained soils. The area is very flat and the topography slopes very gradually toward the headwaters of the Nanticoke River to the south. The well is drilled to a depth of 5.5 meters and screened over 1.5 meters. The Staytonville Unit is present at the site, but its thickness at this location is difficult to determine. Based on an interpretation of the well log, shown in Figure 4.3, the boundary between the Staytonville Unit and the Columbia Formation is between 4 and 4.5 meters below the land surface, where the tan silty sands grade into white sands. The well screen is located at this boundary. Well construction details are given in Table 4.3.
Figure 4.3. Well Construction and Lithology at Well Md22-01

(from well log data supplied by A.S. Andres, Del. Geol. Survey)
Two additional wells were sampled in Delaware during the reconnaissance survey in April, 1987, but not in October, 1987. The northernmost well, Db24-17, is located southeast of Newark, Delaware in a residential area known as Frogtown. The newly-installed well was poorly developed and produced groundwater heavily laden with sand and silt. The southernmost well, Qe44-01, was located a few kilometers west of Trap Rock State Park near Laurel, Delaware in a residential/agricultural area. The well was screened in Columbia deposits, which, in southern Delaware, are primarily coarse-grained sands resulting from beach deposits (Jordan, 1964). The locations of wells Db24-17 and Qe44-01 are shown in Figure 4.1 and the well construction details are listed in Table 4.3.
4.2. **Laboratory Methods and Materials**

The laboratory methods, materials and instruments used in the analysis of the Delaware groundwaters are the same as those described previously for the analysis of the Pine Barrens groundwaters in Section 3.2. Total and dissolved Fe, Al, and Si were measured on a graphite furnace AAS. Total and dissolved organic carbon were measured by wet oxidation of organic carbon to CO$_2$ and IR analysis. Light scattering intensities were measured for filtered and unfiltered samples. Groundwater filters were examined by SEM/EDX to determine particle size, morphology, and composition.

X-ray diffraction analysis was attempted on the particles settled from the Lc42–61 groundwater collected in April, 1987. The resulting diffraction patterns were not characteristic of any common minerals expected in the aquifer, including those identified by SEM/EDX and those reported to be present in the soils and aquifer sediments by Pickett (1970) and Jordan (1964).
4.3 Results

4.3.1. April 1987 Sampling

The results of the April, 1987 sampling are summarized in Table 4.4. These samples are not considered to be representative of the natural colloid load because of sampling difficulties and the inability to monitor colloid concentration in the field, as explained in Chapter 2. The results were useful for refining the sampling procedure and planning future sampling strategy. The groundwater sampled from well Db24-17, near Newark, Delaware, was full of orange silt and clay which quickly settled to the bottom of the sample containers and clogged the filter pores. The heavy sediment load was attributed to poor well development; thus, the samples taken did not reflect the natural colloid population. Well Qe44-01, near Trap Rock State Park in southern Delaware, produced groundwater that scattered as much light as well Lc42-01, but the filter examined by SEM was not as densely covered with particles. The groundwater from well Lc42-01, near Harrington, Delaware, scattered significant amounts of light and it is situated in an area that was the subject of a detailed hydrogeochemical study by Denver (1986).

In October, 1987, well Lc42-01 and a nearby well, Md22-01, were sampled using the refined sampling procedures described in Chapter 2 to examine the effect of local variability in groundwater chemistry on colloid abundance in the Columbia Formation aquifer.

For the April sampling, the field-measured chemical parameters reported are the stabilized values measured during the purging and sampling of the wells (Table 4.4). The data collected at well Lc42-01 is similar to data compiled by Denver (1986) for five groundwater samples collected during the period December, 1982 to September, 1983. We measured a pH of 6.2 in the field, which is in close agreement
Table 4.4. Summary of results for Delaware groundwater collected in April, 1987.

<table>
<thead>
<tr>
<th>Field Parameters</th>
<th>Lc42–01</th>
<th>Db24–17</th>
<th>Qc44–01</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature, °C</td>
<td>12.5</td>
<td>11.0</td>
<td>12.0</td>
</tr>
<tr>
<td>pH</td>
<td>6.2</td>
<td>5.4</td>
<td>5.3</td>
</tr>
<tr>
<td>Eh, V</td>
<td>0.110</td>
<td>0.230</td>
<td>0.240</td>
</tr>
<tr>
<td>Dissolved O₂, μM</td>
<td>19</td>
<td>200</td>
<td>30</td>
</tr>
<tr>
<td>Specific Conductivity, μS</td>
<td>162</td>
<td>155</td>
<td>282</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Laboratory Parameters</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Average Light Scattering Intensity (± σ) counts/sec</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>unfiltered</td>
<td>3120</td>
<td>220000</td>
<td>3500</td>
</tr>
<tr>
<td></td>
<td>(±2100)</td>
<td>(±62000)</td>
<td>(±1770)</td>
</tr>
<tr>
<td>3 μm–filtered</td>
<td>3360</td>
<td>227</td>
<td>1820</td>
</tr>
<tr>
<td></td>
<td>(±1590)</td>
<td>(±223)</td>
<td>(±183)</td>
</tr>
<tr>
<td>ultrafiltered¹</td>
<td>59.0</td>
<td>n.a.</td>
<td>48.0</td>
</tr>
<tr>
<td></td>
<td>(±23.0)</td>
<td></td>
<td>(±8.3)</td>
</tr>
</tbody>
</table>

¹ ultrafiltered = 500 molecular weight cutoff filters.

n.a. = not analyzed.
with the average pH for anoxic wells in the region, listed in Table 4.1; however, the average pH measured in the field by the Delaware Geological Survey (DGS) was 6.7, and in their lab, the average pH was 6.0. Generally, field measurement of pH reduces the problem of CO₂ degassing, which would cause an increase in pH; in this case, however, the pH decreased during storage. The decline in pH may be due to oxygenation of the sample, which could lead to further oxidation of organic matter and production of CO₂. The dissolved oxygen concentration measured for this investigation was about 19 μM, which is considered anoxic given the accuracy of the DO meter in the ≤ 30 μM range. The DGS consistently measured 0.00 μM dissolved oxygen in well Lc42-01. The specific conductivity was measured at 162 μS, which is significantly higher than the mean value measured by the DGS, 124 μS. Each of the values measured by the DGS was consistent over the measurement period, not varying by more than ± 5 percent for the field measurements.

For the April samples, the light scattering data, collected in laboratory measurements, illustrates the effect of differential filtration on the groundwaters; however, the colloid concentrations are not expected to represent actual groundwater colloid loads. After 3 μm—filtering, the groundwater from Lc42-01 retained all of its light scattering intensity, suggesting that the particles are predominantly less than 3 μm in diameter. The groundwater from well Db24-17 produced the highest light scattering intensity recorded in this investigation, 2.20·10⁵ counts/sec; however, particles settled to the bottom of the sample cell during the five minutes necessary to measure the scattering intensity. Upon filtering with 3 μm filters, the scattering intensity was drastically reduced to a level only 4 times greater than the background (ddH₂O in quartz cells: about 25 to 40 counts/sec). The light scattering intensity measured in the groundwater from well Qe44-01 slightly exceeded that of the Lc42-01 groundwater and about half of the scattering particles were removed by 3 μm—filtering. Ultrafiltration (500 m.w.,
cutoff) of the Qe44–01 groundwater reduced the light scattering to the background level.

The size distribution and nature of the particles trapped on 100 nm filters collected in April were examined by SEM/EDX analysis. These particles may provide some insight to the minerals present in the aquifer, but they do not reflect the true groundwater colloid load. In the Lc42–01 groundwater, a huge diversity of particles covered the filter with a density similar to that of the Pine Barrens Swamp Shallow and Upland Shallow groundwaters, confirming the scattering intensity measurements. The majority of the particles were less than 3 μm in diameter as suggested by the scattering intensity of the 3 μm–filtered sample. The most abundant particles were subrounded plates ranging in diameter from <100 nm to as large as 10 μm. The plates were composed of about 50 percent Si, 40 percent Al, and 10 percent K, with an occasional trace of iron. The larger particles tended to be higher in K and gathered into booklets or random clumps of plates; the smaller particles were lower in K (some were pure Si and Al in a 1:1 ratio) and were mainly present as individual plates. Other particles detected on the filter were present only in isolated or scattered occurrences: 1) rounded, euhedral grains about 1 μm²; 2) 100 nm to 1 μm long lath–like particles, often emanating from a central base; 3) clumps of rounded tentacles about 300 nm long radiating from a central base; 4) 100 nm to 300 nm spheres associated with rounded, anhedral particles with coral–like surfaces; and 5) well–preserved Q–shaped outlines of organic material about 2 μm in diameter with 2 μm–long "tails," and their broken remains. Only the predominant clays were analyzed by EDX due to the small size and dispersed nature of the uncommon particles. Examples of the particles observed in the Lc42–01 groundwater are shown in Figure 4.4.

The filter containing particles from the Db24–17 groundwater, pumped from the undeveloped well, was so heavily covered with large (up to 50 μm) particles that
Figure 4.4. Scanning electron micrographs of Lc42–01 groundwater particles collected on 100 nm filters in April, 1987.

SEM photographs on following page.

Figure 4.4a. Photo No. 17, top of page.
Typical assortment of Lc42–01 particles—primarily clay plates, some organic particles.
Scale bar 1 μm, magnification 12,000 times.

Figure 4.4b. Photo No. 13, bottom of page.
"Booklet" of clay plates and individual plates in background.
Scale bar 1 μm, magnification 24,000 times.
Figure 4.4. Scanning electron micrographs of Lc42–01 groundwater particles collected on 100 nm filters in April, 1987.

SEM photographs on following page.

Figure 4.4c. Photo No. 15, top of page.
Cluster of amorphous ferric hydroxide, clay particles and organic matter in background.
Scale bar 1 µm, magnification 25,000 times.

Figure 4.4d. Photo No. 7, bottom of page.
"Q"-shaped organism, possibly pollen, lath-shaped crystalline particles in upper left probably goethite.
Scale bar 1 µm, magnification 25,000 times.
the filter itself was not visible through all the debris. Such large particles are not expected to be suspended in natural groundwater flows. The particles appeared to be primarily booklets of plates of clay (the composition was not determined by EDX because the particles do not represent the natural colloid population). The groundwater collected from well Qe44–01 did not cover the filter as heavily as the Lc42–01 groundwater, belying the light scattering result which indicates that the groundwaters have similar amounts of light scattering particles. The measured light scattering results may be a statistical aberration caused by a few large particles drifting through the light scattering sampling volume scattering a disproportionate amount of light. The particles trapped on the 100 nm filter appear to be primarily individual weathered clay plates ranging in diameter from less than 100 nm to 3 \( \mu \)m. Given the paucity of particles larger than 3 \( \mu \)m on the filter, the decrease in scattering intensity after 3 \( \mu \)m–filtering is not expected; therefore, the unfiltered scattering intensity may indeed be too high.

4.3.2. October 1987 Sampling

The results from the laboratory analysis of samples collected during October, 1987 sampling of wells Lc42–01 and Md22–01 near Harrington, Delaware are summarized in Table 4.5.

The field–measured chemical parameters measured during the purging and sampling of well Lc42–01 are similar to those measured in April, 1987, with the exception of a slight increase in specific conductivity. The differences between the chemical parameters measured for this investigation and the existing data for the well, compiled in Denver (1986), are discussed above in April, 1987 sampling section.
<table>
<thead>
<tr>
<th>Field Parameters</th>
<th></th>
<th>Lc42–01</th>
<th>Md22–01</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature °C</td>
<td>14.0</td>
<td>18.0</td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>6.2</td>
<td>4.3</td>
<td></td>
</tr>
<tr>
<td>Eh V</td>
<td>0.100</td>
<td>0.380</td>
<td></td>
</tr>
<tr>
<td>Dissolved O₂ μM</td>
<td>16</td>
<td>180</td>
<td></td>
</tr>
<tr>
<td>Specific Conductivity μS</td>
<td>175</td>
<td>320</td>
<td></td>
</tr>
<tr>
<td>Scattering Intensity counts/sec</td>
<td>2050 (±1120)</td>
<td>263 (±195)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Laboratory Parameters</th>
<th>Lc42–01</th>
<th>Md22–01</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOC¹ mg C/L</td>
<td>3.3</td>
<td>1.1</td>
</tr>
<tr>
<td>DOC²</td>
<td>2.1</td>
<td>n.a.</td>
</tr>
<tr>
<td>Total Fe μM</td>
<td>144 (±7.0)*</td>
<td>0.8 (±0.1)</td>
</tr>
<tr>
<td>Diss. Fe μM</td>
<td>70.7 (±12.5)</td>
<td>0.2 (±0.1)</td>
</tr>
<tr>
<td>Total Al μM</td>
<td>6.4 (±1.7)</td>
<td>21.5 (±0.9)</td>
</tr>
<tr>
<td>Diss. Al μM</td>
<td>0.4 (±0.2)</td>
<td>21.5 (±0.5)</td>
</tr>
<tr>
<td>Total Si μM</td>
<td>426 (±46)</td>
<td>280 (±11)</td>
</tr>
<tr>
<td>Diss. Si μM</td>
<td>406 (±22)</td>
<td>251 (±14)</td>
</tr>
</tbody>
</table>

n.a. = not analyzed.

¹ TOC = Total Organic Carbon.
² DOC = Dissolved Organic Carbon, dissolved = 30 nm–filtered.
³ Diss. = Dissolved, 15 nm–filtered.
* Standard deviation of the mean.
The chemistry of the groundwater in well Md22–01 can be compared with the average chemical composition of oxic groundwaters in nearby wells listed in Table 4.1. The pH measured in the Md22–01 groundwater is significantly lower than the pH of nearby oxic groundwaters. Dissolved oxygen measured in well Md22–01 is nearly the same as the mean dissolved oxygen concentration. The specific conductivity measured in Md22–01 groundwater is significantly higher than the range of oxic groundwaters. The characteristics can be attributed to the shallow screened depth of well Md22–01 beneath well–drained soil and its location between a roadside drainage ditch and a cultivated field. Precipitation and agricultural inputs may add a large amount of H+ and other ions to the groundwater, leading to the anomalously low pH and high specific conductivity in Md22–01.

The light scattering results obtained in the field are also reported in Table 4.5. The Lc42–01 groundwater samples measured in the field scattered about two–thirds as much light as the samples taken in April, 1987 and measured in the lab. If the decrease in scattering intensity is actually significant, it may be due to improvements in sampling technique and "in–the–field" light scattering analysis, which allowed the effectiveness of purging to be monitored. In April, the groundwater may have been sampled before the colloid concentration decreased to a stable level. The scattering intensity of the Md22–01 groundwater stabilized at a level about 2\(\frac{1}{2}\) times greater than the field background.

The concentrations of total and dissolved iron, aluminum, and silicon in the Lc42–01 and Md22–01 groundwaters are shown in Figure 4.5. The Lc42–01 groundwater is lower in total Fe and total Si than the mean dissolved (0.45 \(\mu\)m–filtered) levels for Fe (260 \(\pm\) 27 \(\mu\)M) and Si (600 \(\pm\) 36 \(\mu\)M) reported by the DGS. For Al, the DGS reports < 0.3 \(\mu\)M, the detection limit of their method; for this investigation, the dissolved (15 nm–filtered) Al concentration is similar, but the total Al concentration is considerably higher. The Md22–01 groundwater contains
Figure 4.5. Fe, Si, and Al in Harrington Groundwaters

Well Lc42-01

Well Md22-01

Concentration (μM)

Total
Filtered (15 nm)
concentrations of Fe and Si similar to those measured in the other oxic
groundwaters in the region, but the total and dissolved Al concentrations are
substantially higher than the range reported by the DGS. The increased dissolution
of clays and aluminum hydrous oxides and the greater solubility of the Al\(^{3+}\) and
Al(OH)_2\(^{2+}\) ions at pH 4.3 may be responsible for the high Al concentrations.

The differences between the total and dissolved concentrations of Fe, Al, and
Si measured for this investigation is shown in Figure 4.6. The differences are
interpreted as the colloidal load excluded from the 15 nm-filtered dissolved samples.
Colloidal Fe, Al, and Si are derived from Fe and Al oxyhydroxides and the partial
dissolution of clays at the reduced pH used for AAS analysis. The Lc42-01
groundwater contains a large concentration of Fe in its colloidal load, but relatively
little Al or Si. The colloidal concentration of Si is uncertain given the large
variability associated with the total Si measurement (shown in Figure 4.5).

The colloidal concentration of Fe in the groundwater from well Md22-01 is
very small, but significant, and the colloidal concentration of Si is large. Aluminum
is totally dissolved in the Md22-01 groundwater and it is most likely present as Al\(^{3+}\)
at the low pH, but Al\(^{3+}\)-humic substance complexes may also be important. The
origin of the high colloidal Si concentration is unknown. It may be derived from the
dissolution of small amorphous SiO\(_2\) particles in the samples acidified for analysis;
however, light scattering and SEM/EDX results do not reveal such particles and the
H\(_4\)SiO\(_4\) concentration is substantially less than saturation with respect to
amorphous silica.

The total and dissolved organic carbon analyses for Lc42-01 groundwater
show relatively high levels of organic carbon. The difference between the total and
dissolved fraction indicates that about 1.2 mg C/L is associated with particles > 30
nm in diameter. Only the total organic carbon concentration was determined for
the Md22-01 groundwater because the light scattering and SEM/EDX results
Figure 4.6. Suspended Fe, Si, and Al in Harrington Groundwater

Well Lc42-01

Well Md22-01
indicated that there were very few particles that would be retained on a 30 nm filter. The organic carbon content of the Md22–01 groundwater is near the median groundwater organic carbon concentration measured by Leenheer et al. (1974).

The SEM/EDX results are summarized in Table A.2 in the Appendix. In Chapter 2, it was noted that the particle abundance is well–correlated to the light scattering intensities for the groundwaters from both wells. The Lc42–01 groundwater colloids are primarily platy alumino–silicates with varying amounts of cations, particularly K and Ca, ranging in size from < 100 nm to about 2 μm, but particles as large as 20 μm also appeared in the final filter sample. These particles may remain suspended because their extreme oblateness decreases their settling velocity. Two types of alumino–silicate plate particles were distinguished: 1) high–K clay, usually present in larger, more angular plates composed of about 53.4 percent Si, 36.8 percent Al, 3.1 percent Fe, 5.8 percent K, and a trace of Ti, on average; and 2) low–K clay, usually more weathered and smaller in size, composed of 53.0 percent Si, 43.2 percent Al, 1.5 percent Fe, 0.8 percent K, and 1.1 percent Ca. Less abundant particles included some large (up to 5 μm) subhedral particles composed of 82.9 percent Fe, 12.3 percent Si, and 4.4 percent Al; some small (up to 300 nm diameter) spheres consisting of 92.2 percent Ti and 7.8 percent Si; and a few large (1 μm to 5 μm) euhedral subangular grains composed of 36.4 percent Si, 33.0 percent Ca, 12.4 percent Fe, and lesser amounts of Cl, Al, S, and K. These last particles have features in common with particles found on the field blanks. Also present on the Lc42–01 filter were some particles with no discernible peaks in the EDX analysis, assumed to be primarily organic in nature. These particles included long, thin curled bars reminiscent of the degraded Q–shaped structures found on the April, 1987 filter and a few jumbles of organic debris up to 2 μm in diameter. The Ti–rich spheres were associated with a clump of organic material, including two lath–like bars. Examples of the particles observed in the Lc42–01 groundwater are
shown in SEM photographs in Figures 4.7 and 2.11.

The high-K clays in the Lc42–01 groundwater are identified as muscovite, a basic Al–K mica, by the method of Mudroch et al. (1977). The K/Si ratio is lower than the mean ratio measured in standards probably due to the removal of K by weathering and cation exchange. The trace of titanium detected in the muscovite is probably present as isomorphic substitutions of silicon in the tetrahedral layer (Dolcater et al., 1970). Muscovite and biotite are the most common micas; however, muscovite is more abundant because it is more resistant to weathering than biotite. Muscovite is characteristic of nearly all grades of metamorphic rocks, including the schists and gneisses common in the Appalachian range. Muscovite also occurs abundantly in argillaceous sedimentary rocks, often interlayered with other clays (Phillips and Griffen, 1981).

The low-K clays in the Lc42–01 groundwater are identified as kaolinite by their average composition and morphology. Kaolinite is the product of intense weathering of Ca–poor granites and metamorphic rocks. It is formed in humid, acidic environments and is commonly associated with quartz, micas, and iron hydrous oxides (Phillips and Griffen, 1981).

The large iron-rich particles in the Lc42–01 groundwater are relatively amorphous. They are probably ferric hydroxide particles, but siderite is also possible in the high alkalinity groundwater. The small Ti–rich spheres are most likely rutile, a titanium oxide identified in the heavy mineral fraction of the Columbia deposit sediments (Jordan, 1964). Rutile is a common alteration product of Ti–rich minerals and usually occurs in sedimentary deposits as detrital grains (Phillips and Griffen, 1981).

The Md22–01 groundwater contained exclusively alumino–silicate plates ranging in size from < 100 nm to as large as 40 μm for one particle on the filter; however, the common large particle size was about 3 to 4 μm in diameter. They are
Figure 4.7. Scanning electron micrographs of Lc42–01 groundwater particles collected on 15 nm filters in October, 1987.

SEM photographs on following page.

Figure 4.7a. Photo No. 20, top of page.
Clump of clay in left half of photo dominated by muscovite (Si 53%, Al 36%, K 6%, Fe 3%).
Darker clay plate to right and below center is kaolinite (Si 52%, Al 47%, Fe 0.5%).
Scale bar 4 μm, magnification ~5,000 times.

Figure 4.7b. Photo No. 25, bottom of page.
Small, spherical particles to lower right are Ti-rich (Ti 92%, Si 8%).
Kaolinite particles in background, rods are possibly biogenic.
Scale bar 1 μm, magnification ~15,000 times.
composed of about 52.7 percent Si, 36.4 percent Al, 8 percent K, 1.5 percent Fe, and traces of Ca and Ti. A trend of decreasing particle size, decreasing angularity, and decreasing K content was observed. Typical particles from the Md22–01 groundwater are shown in Figure 2.13. The filter membranes show some unexplained signs of degradation. The degradation, evident as a widening of the filter pores, apparently occurred after the filtering because particles smaller than the enlarged pores are present on the filter.

The K–rich clay particles in the Md22–01 groundwater are identified as muscovite by the method of Mudroch et al. (1977). The correlation of lower K content and decreasing particle size and angularity suggest that physical and chemical weathering influence colloid size and nature. The large Si–rich particles found in both groundwaters are most likely quartz fragments.
4.4. Discussion and Interpretation of Results

Many of the same geochemical processes that influence colloid stability in the Pine Barrens groundwater are evident in the Harrington groundwaters, although the geologic and hydrologic factors which affect the groundwater geochemistry are not so obvious at the surface, as they are in the Pine Barrens. The two sites near Harrington appear quite similar on the surface—both wells are located in low—relief, rural areas near cultivated fields and light roads. The geology and hydrology that influence groundwater chemistry and colloid stability are hidden beneath the surface, in the composition of the soil and upper layers of sediment. The results of this investigation, supplemented by the conclusions of Denver (1986), will be discussed and applied to explain the unique aspects of colloid stability in the Harrington groundwaters.

4.4.1. Effects of Geology and Hydrology on Groundwater Chemistry

The drainage characteristics of the soils can be correlated with various aspects of the groundwater chemistry in the Harrington area, particularly the iron and nitrate concentrations and the specific conductivity of the underlying groundwater (Denver, 1986). In the vicinity of well Lc42–01, poorly—drained soils with high clay, silt, and organic matter contents predominate at the surface. Near well Md22–01, excessively well—drained soils composed primarily of sand have developed.

The difference in soil composition between Lc42–01 and Md22–01 is evident in the well logs. The surface sediments in the Lc42–01 boring (Figure 4.2) are composed of a thin layer of topsoil and silty fine sand underlain by a layer of iron—stained clay. The Md22–01 boring (Figure 4.3) revealed slightly thicker
topsoil underlain by medium–grained sands. The relative permeabilities of the soils were evident during field sampling—the soil at Lc42–01 was moist and the water pumped from the well pooled at the surface, while the dry and cracked soil around Md22–01 quickly soaked up the pumped water.

The low–permeability shallow sediments at Lc42–01 accumulate organic matter because the infiltration of oxygenated rain water is retarded; therefore the oxidation of organic carbon is slow. At Lc42–01, the available dissolved oxygen is consumed by in the surface sediments by oxidation of organic carbon. Oxidation of dissolved ferrous iron released by the weathering of ferruginous biotite also consumes dissolved oxygen in the soil zone. The iron–stained shallow clay layer marks the boundary between the oxic and anoxic zones of the aquifer (Denver, 1986), where dissolved Fe(II) is oxidized and hydrolyzed to less-soluble Fe(III) species. The sands below the clay layer, in the anoxic zone, are tan and grey in color and show no signs of ferric oxyhydroxide coating, except at the very bottom of the Columbia Formation aquifer. The contact with the underlying sediments of the Chesapeake Group may mark another oxic–anoxic boundary. The incomplete oxidation of organic carbon in the shallow sediments leads to high total organic carbon concentrations in the Lc42–01 groundwater. About one-third of the organic carbon is associated with the > 30 nm fraction, suggesting it is primarily present as coatings of the positively–charged surfaces of inorganic colloids.

The shallow and deep groundwaters at Lc42–01 are hydraulically connected (Denver, 1986), but the less–reducing conditions of the deep groundwater (Lc42–01) suggest that the groundwater reaching the deep well is not solely from vertical infiltration. Apparently, there is a source of oxygenated groundwater assisting in the oxidation of organic carbon and diminishing the reduction of SO₄²⁻ to H₂S in the deep groundwater. The oxygenated groundwater may be flowing to Lc42–01 along horizontal flow paths along the base of the Columbia Formation aquifer. The low
permeability clay of the underlying Chesapeake Group encourages the horizontal
movement of groundwater along the base of the surficial aquifer. Oxic
groundwaters occur below high permeability sediments, as seen at Md22–01, and
may be transported horizontally to zones of anoxic groundwater, such as those at
Lc42–01. The lateral extent of the clay lens detected at Lc42–01 is uncertain, but
based on the two nearby borings (each about 30 meters distant from Lc42–01), the
clay lens is probably a small-scale feature. Jordan (1964) noted that clay layers are
present as irregular, discontinuous lenses, consistent with the varied environments
of deposition. The extreme variability in groundwater quality in Kent County is
attributed to differences in soil drainage characteristics by Denver (1986), but the
presence of discontinuous shallow clay lenses may be the underlying cause of the
differences in soil permeability as well as colloid abundance and iron content in the
anoxic groundwater.

The preferential dissolution of biotite in the aquifer is indicated by the
predominance of muscovite in the sediments, even though biotite is usually more
abundant in source rocks (Leeder, 1982). The incongruent dissolution of biotite
adds large amounts of K⁺, Mg²⁺, and Fe²⁺ to the groundwater as shown in the
reaction (4.3). The dissolved Fe²⁺ is oxidized and hydrolyzed to form ferric
hydroxide coatings in the clay layer above the anoxic zone.

The iron-stained clay lens detected below the soil zone at Lc42–01 may be
formed by the illuviation processes described by Folks and Riecken (1956),
Dijkerman et al. (1967), and Bond (1986). The clay lens is a continuing source of
clay colloids to the underlying Lc42–01 groundwater, similar to the clay layer
detected in the Pine Barrens Upland boring (Section 3.4.1). The dispersion of clay
colloids from the clay lens must also include dispersion of the ferric hydroxide
coatings. The control of clay colloid size and abundance by lattice tension (van
Olphen, 1977) may partially account for the relatively low colloid concentration in
the Lc42–01 groundwater compared to the Swamp Deep groundwater of the Pine Barrens, as muscovite, a three-layer clay, is less prone to disperse than kaolinite, a two-layer clay. The actual abundance of clays in the sediment may have more influence over the colloid abundance—the Columbia Formation contains only about 1 percent clay, while the Cohanseyn sand contains about 11 percent clay.

The geochemistry of iron is dominated by the Fe(II)–Fe(III) redox reaction and the pH of the Lc42–01 groundwater. Under the near-neutral pH, anoxic conditions, Fe$^{2+}$ is expected to be the predominant dissolved iron species and Fe(OH)$_2^+$ would be the major dissolved Fe(III) species; however, humic substances may complex a substantial portion of the Fe(III) in the groundwater. The redox reaction between the Fe(II) and Fe(III) species is considered to be at equilibrium because the oxidation of Fe(II) is relatively rapid at the groundwater pH of 6.2. The concentrations and redox state of dissolved iron may be controlled by the solubility of a number of iron minerals, including ferric hydroxide, goethite, siderite, and pyrite, and ferruginous clays. The ferric oxyhydroxide coatings were detected in the Lc42–01 boring in the shallow clay layer and at the base of the surficial aquifer. Pyrite formation is known to occur in anoxic sediments associated with salt marsh deposition in Delaware (Lord and Church, 1983). The Lc42–01 groundwater is saturated with respect to siderite precipitation. Dissolved iron may also react with silicate, chloride, and phosphate, but the groundwater was not sufficiently saturated with respect to any solid phases of iron with these ligands according to the geochemical modeling of Denver (1986).

The $p$e–$p$H diagram in Figure 4.8 shows the equilibrium stability fields of these dissolved iron species and iron-bearing minerals at standard temperature and pressure. The use of redox potential measurements assumes that a reversible Fe(II)–Fe(III) redox couple is dominating the redox potential of the groundwater and that the Pt electrode is measuring that potential. For the Lc42–01
Figure 4.8. pe–pH Diagram for the Fe–O–S–CO$_2$–H$_2$O system

Lc42-01 groundwater

Fe$_T$ = 71 µM  S$_T$ = 450 µM  CO$_2T$ = 550 µM

pH = 6.2  pe = 1.7

T = 25°C  P = 1 atm
groundwater, these assumptions are reasonable because iron is abundant and the near-neutral pH permits relatively rapid oxidation of Fe(II) species (Langmuir, 1971a; Whitfield, 1974). The high concentration of sulfate in the groundwater suggests that the sulfate-sulfide redox couple could also affect the redox potential of the system; however, at the low temperatures of the groundwater, the reduction of \( \text{SO}_4^{2-} \) to \( \text{H}_2\text{S} \) is quite sluggish without the aid of biological mediation (Hem, 1970; Ohmoto and Lasaga, 1982). The iron concentration is set equal to the measured concentration of dissolved iron. Total sulfur is set equal to the average concentration of dissolved \( \text{SO}_4^{2-} \) measured in the Lc42–01 groundwater by the DGS. The upper limit of pyrite stability is calculated with the \( \text{SO}_4^{2-} \) concentration equal to the measured \( \text{SO}_4^{2-} \) because the precipitation of iron sulfide would occur at very low sulfide concentration (Drever, 1982). Total CO\(_2\) is set equal to the average alkalinity measured by the DGS. Bicarbonate is expected to be the major form of the total CO\(_2\) at the pH of siderite stability. The thermodynamic data used to construct this diagram were taken from Wagman et al. (1968), Wagman et al. (1969), and Robie et al. (1978). The use of activity coefficients in the calculations does not significantly affect the interpretation of the pe–pH diagram.

The Lc42–01 groundwater, with pe of 1.7 and pH of 6.2, falls just within the stability field of dissolved Fe\(^{2+}\), very close to the stability of amorphous ferric hydroxide. Thus, the Fe\(^{2+}\)–Fe(OH)\(_3\)\(\cdot\)\(s\) redox couple probably exerts a dominant control on the dissolved iron geochemistry, in contrast with the Swamp Deep groundwater of the Pine Barrens, where the Fe\(^{2+}\)–Fe(OH)\(_s\) redox couple apparently controls the redox state and concentration of dissolved iron. Back and Barnes (1965) and Langmuir (1969) studied similar groundwaters and also found that the Fe\(^{2+}\)–Fe(III) oxyhydroxide redox couple controlled the measured redox potential of the groundwater and the dissolved iron concentration. The variable limit of stability of goethite is also shown in Figure 4.8 by the shaded zone, which
represents the difference in stability between pure goethite and disordered goethite, as discussed in Section 3.4.1. The Lc42–01 groundwater is stable with respect to goethite. The colloidal goethite crystals may be the products of aging and dehydration of ferric hydroxide in the soil zone; however, the presence of organic carbon inhibits the crystallization of ferric oxyhydroxides (Schwertmann, 1966; Kodama and Schnitzer, 1977). The colloidal goethite may be transported to Lc42–01 groundwater by water dispersing particles from the overlying clay lens or by horizontal flow from nearby oxic groundwater.

At Md22–01, the oxygenated rain water rapidly infiltrates through the high–permeability surface sediments. The organic carbon is efficiently oxidized and the dissolved oxygen concentration remains high at the depth of the groundwater sampling point (about 4 to 5.5 meters). In the oxic groundwater, the accumulation of ferric oxyhydroxide coatings might be expected, similar to the oxic Upland Deep groundwater in the Pine Barrens; however, the aquifer sediments are primarily white and tan sands. The lack of ferric oxyhydroxide coatings on the aquifer sediment and the very low concentration of dissolved iron in the groundwater suggest that sources of dissolved iron are much less abundant in the sediments at Md22–01. In contrast with the Lc42–01 boring, no distinct clay layers or clayey sediments were detected in the Md22–01 boring. In addition to the low dissolved iron, low dissolved silicate and alkalinity levels indicate that weatherable minerals (particularly clay minerals) are far less abundant at Md22–01 than at Lc42–01.

Dissolved aluminum concentrations are substantially higher in the low pH Md22–01 groundwater. The primary dissolved aluminum species would be Al³⁺ and AlOH²⁺. Dissolved iron is expected to be present primarily as Fe²⁺, despite the oxic conditions in the groundwater because the oxidation of Fe(II) to Fe(III) is very slow at pH < 6. The major dissolved Fe(III) species would be FeOH₂⁺, which would tend to be strongly adsorbed to quartz surfaces in the aquifer.
The paucity of clay minerals in the aquifer sediments is also reflected in the very low colloidal concentration of the Md22–01 groundwater. The clay colloids that were detected by SEM/EDX were identified as muscovite, which is a trace mineral component of the aquifer sediments. Muscovite is expected to be part of the colloidal load regardless of the presence of distinct clay layers, which are most likely composed of a significant fraction of kaolinite, illite, and other more stable clays.

The contrast in chemistry in the Harrington groundwaters is definitely related to the hydrologic properties of the soils, as Denver (1986) concludes; however, the laterally discontinuous clay lens present at Lc42–01 is the major influence on the groundwater chemistry and colloid formation. The shallow clay lens presents a low permeability barrier to infiltrating oxygen–saturated water, creating the anoxic zone in the underlying aquifer. The weathering of the clay minerals, fueled by the generation of CO₂ in the soil zone, releases cations, boosts the alkalinity of the groundwater, and increases its buffering capacity. The anoxic, reducing conditions inhibit the formation of ferric oxyhydroxide coatings on the aquifer substrate. At Md22–01, dissolved oxygen is plentiful and organic carbon is less abundant in the groundwater because the surface sediments are highly permeable. The lack of clay minerals is apparent in the low alkalinity and low pH of similar oxic groundwaters and in the low dissolved iron and clay colloid concentration in the Md22–01 groundwater.

4.4.2. Colloid Formation and Stability in the Harrington Groundwaters

The contrast in colloid abundance observed between the anoxic Lc42–01 groundwater and the oxic Md22–01 groundwater superficially appears to be quite similar to the contrast in colloid abundance observed between the Swamp Deep and
Upland Deep groundwaters of the Pine Barrens. Indeed, the colloidal stability of the wide variety of particles in the Lc42–01 groundwater appears to be principally affected by the iron geochemistry and the control of surface properties by organic carbon coatings. In the Md22–01 groundwater, however, the low colloid concentration is most likely due to the apparent paucity of clay minerals in the aquifer sediments.

The colloidal particles in the Lc42–01 groundwater include clays (muscovite and kaolinite), goethite and other amorphous iron–rich minerals, and the titanium–rich spheres. The surface properties of kaolinite and ferric oxyhydroxide particles were reviewed in Section 3.4.2. Muscovite is a dioctahedral three–layer clay. The surface properties of the muscovite colloids are similar to those of kaolinite, except muscovite has two siloxane surfaces exposed on its basal plates instead of the siloxane and gibbsite basal plates exposed on kaolinite. In common micas, isomorphic substitution of every fourth silicon by an aluminum ion results in a "permanent" charge deficiency that is balanced by potassium ions in the interlayer positions (Greenland and Mott, 1978). On the external surfaces, the K⁺ ions are readily exchanged for other cations.

The edges of muscovites are dominated by hydrous oxide surfaces, similar to kaolinite. The surface charge of the edges will be determined by the combined PZC of the silanol and aluminol groups exposed on the edges. The edges contain 2 silanol groups for every 1 aluminol group, so the "theoretical" PZC of the edge of a three layer clay is probably lower than the PZC of 7.2 determined for the kaolinite edge by Williams and Williams (1978).

In the Lc42–01 groundwater, the faces of kaolinite particles will be negatively–charged and the edges will be positively–charged. The muscovite faces will have a similar "permanent" negatively–charged face. The negative charge density of muscovite will be much greater than that of kaolinite due to increased
isomorphic substitution; therefore, cation exchange will be a much more important process for the muscovite colloids. At pH 6.2, the muscovite edges would probably be close to their point of zero charge.

The rutile spheres are expected to behave similarly to the hydrous oxides discussed in Section 3.4.2. The PZC of natural rutile is 4.7; for hydrated rutile, the PZC is 6.0 (Parks, 1965). In the Lc42–01 groundwater, the unhydrated rutile colloid will be negatively–charged, but the hydrated rutile will be very close to its PZC. The ferric oxyhydroxide colloids will be positively–charged at the groundwater pH.

Iron redox reactions and their effect on colloid stability are relatively straightforward in the Lc42–01 groundwater compared to the iron geochemistry in the groundwaters of the Pine Barrens. At the reducing conditions that exist in the Lc42–01 groundwater, dissolved Fe$^{2+}$ is the major form of iron. Ferric oxyhydroxide formation on the quartz grains was not detected in the anoxic zone of the aquifer. The laboratory experiments of Gotoh and Patrick (1974) roughly duplicated the Lc42–01 Eh–pH conditions in a controlled test chamber. In a water–logged iron–rich soil held at a slightly lower Eh of 0.100 V and approximately the same pH, nearly all the iron was dissolved, while very little iron remained in the form of insoluble ferric oxyhydroxides. The reducing conditions apparently limit the concentration of dissolved Fe(III) to such low levels that the negatively–charged quartz surfaces in the anoxic zone of the aquifer remain free of ferric oxyhydroxide coatings. Complexation by humic substances may also limit the availability of Fe(III) for adsorption to the silica surfaces (Senisi et al., 1977; Crerar et al., 1981).

As groundwater infiltrates downward at Lc42–01, clay colloids are weathered and illuviated from the shallow, iron–stained clay lens and directly from the the aquifer sediments, which contain about 1 percent mica. The ferric oxyhydroxide colloids are probably formed in the oxic zone as a result of incongruent weathering.
of iron–bearing clay minerals, especially ferruginous biotite. Dissolved Fe(III) species oxidized from Fe$^{2+}$ are hydrolyzed at the groundwater pH and probably are attached to quartz or clay surfaces. Initially, ferric hydroxide precipitation occurs in the oxic zones, as in the shallow clay layer, and the ferric hydroxide gradually ages to less–hydrated forms of ferric oxyhydroxides—limonite and goethite. The fragmentation of iron–stained clay colloids creates ferric oxyhydroxide colloids of varying degrees of crystallinity. The rutile colloids may be the products of weathering and breakup of larger rutile grains; however, the smooth, spherical shape and the silicon impurity (about 8 percent) suggest that the rutile colloids are precipitated from a solution saturated with Ti. If the rutile colloids are precipitated in solution, they are probably quite hydrated, so they may be very close to their PZC at the groundwater pH.

The difference between the total organic carbon and dissolved organic carbon measured in the Lc42–01 groundwater (1.2 mg C/L) indicates that organic matter coatings on the various inorganic particles found in the Lc42–01 groundwater play a crucial role in the colloid stability. In the absence of organic coatings, the clay colloids found in the Lc42–01 groundwater would quickly destabilize. The coagulation of clays by Fe$^{3+}$ and Al$^{3+}$ hydrolysis products and oxides would effectively remove colloids from suspension (Packham, 1965; Oades, 1984; Goldberg and Glaubig, 1987). The self–coagulation of clays is less important in the Lc42–01 groundwater because the pH is relatively close to the PZC of the clay edges, especially for muscovite. Diffusion and attachment to aquifer surfaces would remove the smallest clay colloids (< 100 nm diameter) by electrostatic attraction of the positively–charged edges to negatively–charged quartz surfaces.

The positively–charged ferric oxyhydroxide colloids would be removed from suspension by attachment to negatively–charged surfaces, primarily the quartz grains. Ferric oxyhydroxide colloids may also be attached to the
negatively-charged faces of clay colloids (Jones and Uehara, 1973; Greenland, 1975; Cavallaro and McBride, 1984). The unhydrated rutile colloids would form a relatively stable negatively-charged suspension at the groundwater pH, but the hydrated rutile colloids would probably coagulate rapidly because their PZC is close to the groundwater pH.

The presence of organic coatings is indicated by the persistence of colloid stability in the face of these otherwise efficient removal processes. The discussion of the effects of organic coatings on colloid stability for the Swamp Deep groundwater also applies to the Lc42–01 groundwater. The organic matter is strongly adsorbed to positively-charged hydrous oxide surfaces, including the edges of clays and possibly the gibbsite basal plate of kaolinite (Tipping, 1982; Davis, 1982), leaving the colloid population with a uniform negative charge. The rate of coagulation of clays and hydrous oxides is greatly reduced by organic coatings (Gibbs, 1983; Tipping and Higgins, 1982). The increased coagulation of organically-coated clays and oxides by high concentrations of bivalent cations, such as those encountered in estuarine mixing (Tipping and Cooke, 1982), does not occur in the groundwater due to relatively low Ca$^{2+}$ and Mg$^{2+}$ concentrations.

Thus, the colloid population in the Lc42–01 groundwater is stabilized by a uniform negative charge imposed on the surfaces by coatings of organic matter. The organic coatings also inhibit further weathering of the clay colloids and reduction of the Fe(III) in the ferric oxyhydroxides (Theis and Singer, 1974). This scenario of colloid stability is supported by the study of the successive control of surface properties of clays by ferric hydroxide coatings and organic matter coatings in an acid mine drainage stream (Newton and Liss, 1987) discussed in Section 3.4.3.

In Lc42–01, muscovite, kaolinite, and ferric oxyhydroxide colloids made up the major portion of the colloid load, but in the Md22–01 groundwater, only a few muscovite colloids were detected. The lack of a distinct clay layer at Md22–01
represents the lack of a source of clay colloids produced by intense weathering of the minerals in the soil zone, such as kaolinite. In the Md22–01 groundwater, the dissolved iron concentration is very low, and it would be reasonable to expect that the dissolved iron is strongly adsorbed by the silica surfaces in the aquifer, as we postulated for the oxic Upland Deep groundwater in the Pine Barrens. The Md22–01 boring revealed otherwise; the quartz surfaces in the aquifer are relatively free of ferric oxyhydroxide coatings. Thus, the lack of a distinct clay layer also represents the lack of a source of abundant dissolved iron from readily weathered ferruginous clays, such as biotite. The Md22–01 groundwater apparently is relatively free of colloids because the primary source of colloids in the Lc42–01 groundwater, the shallow clay lens, is not present at Md22–01.
CHAPTER 5. CONCLUSION

5.1. **Summary**

This investigation has characterized the nature and distribution of colloids in two Atlantic Coastal Plain aquifers and identified common factors influencing the stability of the colloids. In soils and sediments containing clay and iron, reducing conditions can facilitate the release of inorganic colloidal matter from aquifer surfaces into suspension. Ferric iron apparently operates as the "glue" holding the soil constituents together. Anoxic, reducing conditions, caused by the oxidation of heavy loads of organic matter, dissolve Fe(III) hydrous oxides and reduce Fe(III) species to Fe(II). The incomplete oxidation of organic matter results in relatively high concentrations of colloidal organic carbon in the groundwater. The colloidal organic carbon, recognized as an important component of the colloid load on its own, also contributes to the stability of inorganic colloids by forming a surface coating that changes the surface properties.

The nature and distribution of groundwater colloids is not well known for two main reasons: 1) the significance of colloids in groundwater has not been recognized in the past; and 2) the inability to obtain groundwater samples representative of the natural colloid load. We have discussed the significance of colloids in enhancing the transport of pollutants; this is the prime motivation for this investigation. In other disciplines, many aspects of colloid behavior in groundwater have been studied, including clay dispersion in oil field formations, agricultural soils, and recharge basins. Furthermore, the organic compound sorption and metal binding properties of humic substances in natural waters, are also well known. Despite this, in the field of contaminant hydrogeology, groundwater turbidity was mainly considered an impediment to proper analysis for dissolved...
constituents; it was generally thought that colloidal matter would settle out at low groundwater flow rates or adhere to aquifer solids.

The current practice in groundwater sampling does not produce samples representative of the natural colloid load. Well design and installation often preclude obtaining accurate samples, although in some geologic formations, the use of highly disruptive drilling techniques cannot be avoided. The removal of standing water from the well to sample the formation water (purging) is normally performed at high pumping rates (1 to 4 L/min) that cause suspension of particles settled and adhered to the aquifer surfaces. The criteria used to determine the duration of purging, usually the stabilization of some chemical parameters and the removal of a specified number of well volumes, are not adequate when the colloid content of the groundwater is of interest. Finally, the common practice of filtering samples through 0.45 μm membrane filters to define the "dissolved" load leads to overestimates of the true dissolved concentrations of elements that make up colloids. In short, the distribution and nature of natural colloidal matter is indiscernible using standard sampling techniques.

Sampling procedures for assuring the collection of groundwater samples containing the natural colloid load were developed by Reynolds (1985) and Backhus et al. (1986). In this investigation, we refined these procedures by monitoring the colloid concentration during the purging of the wells. Colloid concentration was determined in the field by measuring the light scattering intensity of the particles suspended in the groundwater. The stabilization of the colloid concentration was used as the main criterion for judging the effectiveness of purging. Usually, the chemical parameters had stabilized and the "3 to 5" well volumes had been removed long before the colloid concentration leveled off during purging. The importance of the low pumping rate (100 mL/min) used to purge and sample the groundwater was illustrated by estimates of the shear stress incident on the particles attached to the
aquifer surfaces. Comparisons of the shear rates produced by a range of pumping rates to the shear rates necessary to detach particles from surfaces (Shiga et al., 1985) and disaggregate clays in suspension (Hunt, 1982) showed that the 100 mL/min pumping rate would not disturb settled and adhered particles. More tangible evidence was found in the examination of the groundwater particles collected on filters. The high pumping rate (1 L/min) suspended large quartz grains (> 10 μm) that were never suspended by the 100 mL/min pumping rate.

In the sandy, unconfined aquifer of the Pine Barrens in New Jersey, colloids were found in the acidic, nearly anoxic Swamp Deep groundwater underlymg the swampy banks of McDonalds Branch, a small stream in Lebanon State Forest. The colloids analyzed by SEM/EDX were composed of dispersed clay particles and ferric oxyhydroxide particles in the size range of less than 100 nm to 3 μm. The colloid concentration was estimated at about 60 mg/L by light scattering intensity. The total organic carbon concentration was about two times as high as the dissolved (30 nm-filtered) organic carbon concentration (1.4 mg C/L and 0.7 mg C/L). Samples from the nearby acidic, oxic Upland Deep groundwater were nearly free of colloidal matter. The total organic carbon concentration was 0.8 mg C/L and the dissolved concentration was assumed to be the same, based on the paucity of particles larger than 30 nm.

An examination of the geology and hydrology of the McDonalds Branch watershed indicated that the distribution of distinct clay layers in the sediments and the generation of organic carbon in the swamp bordering the stream are the major influences on the groundwater chemistry and colloid formation and stability. Fragmentation and dispersion of the clay minerals by infiltrating rain water produce the bulk of the colloidal matter in the Swamp Deep groundwater. Weathering and dissolution of the clay layer provides dissolved iron to the groundwater. In the oxic Upland Deep groundwater, the dissolved Fe(III) species are strongly adsorbed to
quartz surfaces, possibly to such an extent that the negatively-charged quartz surfaces are converted to positively-charged ferric oxyhydroxide (goethite) surfaces. The pinkish-orange color of the sands in the Upland Deep sediment support this inference. Clay colloids in the groundwater beneath the uplands are probably coagulated in the dilute groundwater either by self-coagulation or by adsorption of Fe(III) and Al(III), or electrostatically drawn to aquifer surfaces and adhered. In the Swamp Deep groundwater, the oxidation of organic carbon has produced nearly anoxic, reducing conditions and slightly lower pH. Under the reducing conditions, the ferric oxyhydroxides and the Fe(III) adsorbed to the coagulated clays are marginally unstable; therefore, the clay colloids are not attached to the quartz surfaces. The white and tan color of the sands beneath the swamp attest to the lack of ferric oxyhydroxide coating. The half of the total organic carbon excluded by the 30 nm filtration is probably present as surface coatings on the inorganic colloids. The stability of the colloidal particles is greatly enhanced by the organic coatings. In the Swamp Shallow groundwater, about 1 meter beneath the muck layer of the swamp, the very high organic carbon concentrations indicate that humic substances probably have a dominating effect on the acidity and trace metal complexation of the shallow groundwater.

In the sandy, unconfined aquifer of central Delaware, near the town of Harrington, colloids were found in the near-neutral, anoxic Lc42-01 groundwater. The majority of the colloids varied in size from less than 100 nm to about 2 μm and they were composed principally of clays and hydrous oxides corresponding to the mineral content of the formation. The Fe and Ti hydrous oxide colloids appeared to have been formed in situ in the groundwater. The colloids were present at about 6 mg/L concentration. In the nearby acidic, oxic Md22-01 groundwater underlying very similar, low relief, cultivated land, colloidal matter was essentially absent. The difference in colloidal abundance between the two groundwaters (and also the
difference between their chemistry) was primarily attributed to the presence of a low-permeability clay lens in the sediments above the Lc42-01 groundwater. The infiltration of dilute rain water disperses and fragments clay minerals and weathering of the clay provides an abundance of iron and other cations. The clay lens inhibits the infiltration of oxygenated water; hence the oxidation of organic carbon has consumed the dissolved oxygen and reduced the nitrate and ferric iron in the shallow sediments. The sediments are grey to tan in color below the clay lens, indicating the lack of any ferric hydroxide coating in the anoxic zone. About one-third of the total organic carbon (TOC = 3.3 mg C/L) is associated with the >30 nm fraction, probably present as coatings of particles. At Md22-01, no distinct clay layer was detected in the subsurface. Apparently, there was no significant source of colloidal material besides the clay minerals present as trace components in the formation. The abundance of colloids in suspension was probably reduced to very low levels by coagulation.

The occurrence of the majority of the colloids in the groundwaters observed in this investigation is thus linked to the dispersion of clay from the soils and sediments and the maintainance of their stability by organic coatings. Colloids of hydrous metal oxides (Fe, Al, and Ti) were also noted in the groundwaters—their formation may be by dispersion or in situ precipitation at near-neutral pH. Anoxic, reducing conditions, often associated with high organic carbon concentrations, also promote colloid stability in sandy aquifers by reducing Fe(III). The reduction of Fe(III) to Fe(II) prevents the formation of ferric hydroxide coatings on quartz surfaces and inhibits the coagulation of clays by Fe(III) adsorption.
5.2. Implications of the Results

The motivation for characterizing the nature and distribution of colloids in groundwater was established by reviewing the importance of colloidal transport of sorbed pollutants. It is clear from this investigation that colloidal matter can be quite abundant in sandy, unconfined aquifers. Furthermore, the study of Langmuir (1969) suggests that deeper aquifers can also contain significant quantities of natural colloidal matter. In deeper groundwaters, the concentration of organic carbon generally decreases due to increased oxidation. In fractured aquifers, the potential for inorganic colloid formation and stability must be considered. The rapid groundwater flow in fractures is capable of suspending larger particles. Easily fragmented material, such as clay minerals and other alteration products, typically fill the fractures and they may be easily dispersed in the fracture flow.

The focus of this investigation was on colloidal matter that could be easily "seen" by light scattering and SEM/EDX analysis, although the abundance of colloidal organic carbon is more important to the transport of pollutants. The major component of colloidal organic carbon, humic substances, more effectively mobilize hydrophobic organic compounds because the partitioning depends on the organic carbon fraction of the sorbent. For example, the sorbing capacity of 100 mg/L of inorganic colloids coated by organic carbon with the $f_{oc}$ estimated at 1 percent is matched by only 1 mg C/L humic substances. Similarly, the binding constants for metal–humic substance complexation generally favors the formation of the metal–humic substance complex over complexes with inorganic ligands, adsorption, or ion exchange.

The dependence of colloid stability on organic coatings and reducing conditions has important implications for waste disposal. The studies of Kimmel and Braid (1980), Nicholson et al. (1983), Gschwend and Reynolds (1987), and
many others in the literature report that contaminant plumes emanating from landfills, sewage beds, and other waste disposal sites produce leachates with high organic carbon concentrations. Due to the oxidation of the abundant organic carbon, leachate plumes are generally anoxic, reducing zones of groundwater. Based on the results of this investigation, we would expect the enhancement of pollutant transport by colloidal matter in aquifers similar to those of the New Jersey and Delaware Coastal Plain. The hydrous oxide minerals would be dissolved and reduced, clay particles are released into suspension, and organic carbon coatings would stabilize the colloids. The colloidal organic carbon would be expected to play the major role in mobilizing the pollutants, but inorganic colloids coated by organic carbon could be equally important in mobilizing metals and significant in mobilizing organic compounds.

The dissolution of iron and manganese hydrous oxides by the advance of reducing conditions along the flow path would also liberate the trace metals co-precipitated with oxides (Baedecker and Back, 1979). If the dissolved Fe and Mn reprecipitate in situ in a colloidal form, as we postulated for some of the Fe- and Ti-rich particles observed in this investigation, a substantial amount of of trace metals (and radionuclides) may co-precipitate with the colloidal oxides. The amount of trace metals co-precipitated would be much greater than the amount that could be adsorbed to the surface of such colloids. Thus, in a pollutant plume, the co-precipitation of trace metals and radionuclides with colloidal oxides could significantly increase the transport of the metals. Organic carbon coatings would be expected to adsorb to their positively-charged surfaces, further enhancing their stability.

Reducing conditions may also cause the mobilization of organic carbon bound to oxide coatings on quartz surfaces in the aquifer. Upon dissolution of the positively-charged oxide coatings, the quartz surfaces revert to negative charge and
organic carbon is no longer attracted to aquifer surfaces by electrostatic attraction. The amount of organic carbon released in a sandy aquifer (composed of 90 percent quartz grains of mean diameter 0.25 mm, $\rho = 2.65$ g/cm$^3$, porosity of 0.4, and $f_{OC} = 0.001$) could amount to an additional 4 mg C/L.

The dispersion and stabilization of clays in reducing, anoxic zones of groundwater may have important implications for the use of clay liners as containment layers in hazardous waste landfills. Clay liners may be substantially disintegrated and illuviated over long periods of time, the diminishing the sorption and cation exchange capacity and increasing the permeability of the barrier. Clays dispersed from the liner may also enhance the transport of strongly sorbed pollutants. Furthermore, illuviation of the clays to other zones of the aquifer may form new low-permeability layers that could channel groundwater flow into restricted areas, thus increasing the groundwater velocity and the migration of the pollutants.

Many other hazardous waste sites involve spills and plumes that impose reducing conditions on the groundwater and contribute large amounts of colloidal organic matter to the groundwater. For example, coal tar sites are frequently characterized by a light fraction of pollutants that "float" on top of the groundwater at the water table. The immiscible layer inhibits the infiltration of oxygenated groundwater and an anoxic zone of groundwater would develop below the pollutants. Transport of some of the very insoluble organic compounds commonly associated with coal tar sites (PAHs) may be enhanced by colloidal matter.

The importance of colloidal organic carbon in the enhancement of radionuclide transport is already well-documented (Champ et al., 1984; Means et al., 1978). The effect of inorganic colloids on their transport will have to be considered for the high-level nuclear waste repository being designed in Nevada. The repository is to be located a few hundred meters down in volcanic tuff, above
the water table. The effect of the sparse amounts of infiltrating rain water will have to be considered on the illuviation of the secondary clay minerals that have formed in the sediments, as well as the transport of organic carbon.

In considering the analysis of the transport of pollutants, we must keep in mind that the retardation coefficient describes the relative velocity of the pollutant's migration in a homogeneous porous medium. The increased mobilization of only a small fraction of the pollutant may pose a significant environmental hazard. The basic assumptions upon which the partition coefficient is determined—linear, reversible adsorption at equilibrium over a given concentration range—are often neglected in applying partition coefficients (Reardon, 1981). In a pollutant plume, only a finite amount of sorptive capacity is available and when it is utilized, retardation no longer occurs and pollutant migration is increased. Groundwater flow may carry pollutants past sorption sites to quickly for reactions to come to equilibrium. This is not common in homogeneous porous media, but in formations containing fractures and heterogeneities, sorption is reduced because the surface area of the formation exposed to the pollutant is reduced. Therefore, the assumptions involved in Darcian flow through porous media may be said to apply for the proper application of the retardation estimate.

This investigation thus provides a step toward the characterization of the nature and distribution of colloids in groundwater. The processes of colloid formation and stability must be further understood before we can properly evaluate their effect on the migration of pollutants.
APPENDIX
Table A.1. Summary of SEM/EDX results on McDonalds Branch groundwater colloids collected on 15 nm filters in October, 1987.

<table>
<thead>
<tr>
<th>Well</th>
<th>Filter No.</th>
<th>EDX No.</th>
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<th>Al</th>
<th>Fe</th>
<th>Na</th>
<th>K</th>
<th>Ca</th>
<th>Cl</th>
<th>Size, Roundness, Form</th>
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<td>42.5</td>
<td>9.0</td>
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<td></td>
<td>2 μm-3 μm angular plates</td>
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<td>258 min</td>
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<td></td>
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<tr>
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<td>2 min</td>
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<td>44.4</td>
<td>3.3</td>
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<td></td>
<td></td>
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<td>3 μm² subrounded plate</td>
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<tr>
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<td>43.3</td>
<td>4.1</td>
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<td>2 μm-6 μm very angular plate</td>
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</tr>
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<td>54.3</td>
<td>42.7</td>
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<td>4 μm-6 μm angular plate</td>
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<td>3.6</td>
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<td>(?) in &lt;0.5 μm² plates</td>
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<td></td>
<td></td>
<td>0.1 μm² to 0.3 μm² subrounded plates</td>
<td></td>
</tr>
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<td></td>
<td></td>
<td>15b</td>
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<td>20.3</td>
<td>54.4</td>
<td>0.4</td>
<td>1.7</td>
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<td>0.2 μm-1 μm subhedral rounded lath</td>
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Table A.1. Continued

<table>
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<th>Al</th>
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<th>Na</th>
<th>K</th>
<th>Ca</th>
<th>Cl</th>
<th>S</th>
<th>Atomic Number Percent</th>
<th>Size, Roundness* Form</th>
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<tbody>
<tr>
<td>Upland</td>
<td>150 min</td>
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<td>50.7</td>
<td>46.1</td>
<td>0.7</td>
<td>1.1</td>
<td>1.4</td>
<td>1.9</td>
<td></td>
<td></td>
<td></td>
<td>1 μm-1 μm subrounded plate</td>
</tr>
<tr>
<td>Deep</td>
<td>4</td>
<td>3</td>
<td>47.7</td>
<td>21.5</td>
<td>29.5</td>
<td></td>
<td>1.3</td>
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<td>1.5 μm-1.2 μm subrounded plate</td>
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<td>2.2</td>
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<td></td>
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<td>6 μm-10 μm subrounded grain</td>
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<td>2 μm-3 μm subrounded grain</td>
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</tr>
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<td>97.3</td>
<td>1.7</td>
<td>1.0</td>
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<td></td>
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<td></td>
<td>4 μm-10 μm very angular grain</td>
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</tr>
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<td>93.3</td>
<td>5.3</td>
<td>1.4</td>
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<td>2 μm-5 μm angular grain</td>
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</tr>
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<td>29.8</td>
<td>55.3</td>
<td>14.9</td>
<td></td>
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<td></td>
<td></td>
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<td>0.5 μm-1 μm subhedral hexagonal plate (?)</td>
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</tr>
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<td>48.9</td>
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<td></td>
<td></td>
<td></td>
<td>15 μm-30 μm subangular plate</td>
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<td>4.5</td>
<td>14.8</td>
<td>37.9</td>
<td>42.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10 μm-15 μm very angular grain</td>
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Table A.2. Summary of SEM/EDX results on Harrington, Delaware groundwater colloids collected on 15 nm filters in October, 1987.

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<th>Atomic Number Percent</th>
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<td>Lc42–01</td>
<td>105 min</td>
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<td>Si 97.7 Al 1.8 Fe 0.1 Ti 0.2 K 0.2 Ca Cl S</td>
<td>3 μm-8 μm very angular grain</td>
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<tr>
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<td>57.6</td>
<td>3.1 4.4</td>
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</tr>
<tr>
<td></td>
<td>205 min</td>
<td>5</td>
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<td>4 μm-6 μm rounded plate</td>
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<tr>
<td></td>
<td>3</td>
<td>52.0</td>
<td>44.0 2.2</td>
<td>clump of small (&lt;0.5 μm) plates</td>
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<tr>
<td></td>
<td>6</td>
<td>49.1</td>
<td>40.0 2.2</td>
<td>1 μm² rounded plates</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>57.9</td>
<td>39.4 2.7</td>
<td>1.5 μm-2 μm booklet of plates</td>
</tr>
<tr>
<td></td>
<td>295 min</td>
<td>8</td>
<td>Si 52.5 Al 46.4 Fe 0.5 Ti 0.5 K 1.5 Ca Cl S</td>
<td>0.5 μm-1 μm subrounded plates</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>12.3</td>
<td>4.4 82.9</td>
<td>1 μm² subrounded plate</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>7.8</td>
<td>92.2</td>
<td>2 μm-5 μm subhedral subangular grain</td>
</tr>
<tr>
<td></td>
<td>360 min</td>
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<td>Si 50.4 Al 38.4 Fe 1.1 Ti 9.8 K 1.5 Ca Cl S</td>
<td>0.2 μm to 0.3 μm diameter spheres</td>
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<td>15</td>
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<td>37.4 2.5</td>
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<td>1 μm² subangular plate</td>
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<td>52.4</td>
<td>46.6 0.5</td>
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<tr>
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<tr>
<td>High Flow</td>
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<td>16</td>
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Table A.2. Continued.

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<tr>
<th>Well</th>
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<th>Fe</th>
<th>Ti</th>
<th>K</th>
<th>Ca</th>
<th>Cl</th>
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<td>1.9</td>
<td>0.3</td>
<td>7.4</td>
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<td></td>
<td>0.2</td>
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<td>37.9</td>
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</table>

<table>
<thead>
<tr>
<th>Size, Roundness*, Form</th>
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<td>30 μm-40 μm very angular plate</td>
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</tr>
<tr>
<td>1.5 μm² subangular plate</td>
</tr>
<tr>
<td>6 μm-8 μm very angular grain</td>
</tr>
<tr>
<td>3 μm-4 μm angular booklet of plates</td>
</tr>
<tr>
<td>clump of small angular plates</td>
</tr>
<tr>
<td>15 μm-30 μm subangular plate</td>
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<tr>
<td>10 μm-15 μm very angular grain</td>
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