

Colloid Mobilization in Two Atlantic Coastal Plain Aquifers: Field Studies

JOSEPH N. RYAN AND PHILIP M. GSCHWEND

Ralph M. Parsons Laboratory, Department of Civil Engineering, Massachusetts Institute of Technology, Cambridge

The geochemical mechanisms leading to the mobilization of colloids in groundwater were investigated in the Pine Barrens of New Jersey and in rural central Delaware by sampling pairs of wells screened in oxic and anoxic groundwaters in the same geologic formations. Samples were carefully taken at very low flow rates ($\sim 100 \text{ mL min}^{-1}$) to avoid suspending immobilized particles. The colloidal matter was characterized by light-scattering photometry, scanning electron microscopy, energy-dispersive X ray analysis, microelectrophoresis, and Fe, Al, Si, and organic carbon analyses. The colloids, composed primarily of clays, were observed at high concentrations (up to 60 mg colloids/L) in the anoxic groundwaters, while the oxic groundwaters exhibited $\leq 1 \text{ mg colloids/L}$. Colloidal organic carbon was present in all groundwaters; but under anoxic conditions, one-third to one-half of the total organic carbon was associated with the inorganic colloids. The field evidence indicates that anoxic conditions cause the mobilization of soil colloids by dissolving the ferric oxyhydroxide coatings cementing the clay particles to the aquifer solids. The depletion of oxidized iron on the surfaces of immobile particles and the addition of organic carbon coatings on the soil particles and colloids apparently stabilizes the colloidal suspension in the anoxic groundwaters.

INTRODUCTION

Traditionally, the transport of pollutants in groundwater has been predicted by evaluating their distribution between two phases: (1) a dissolved, mobile phase and (2) a sorbed or precipitated, stationary phase associated with aquifer solids. Only recently has evidence accrued showing that significant concentrations of colloids exist in groundwater and that groundwater contaminants may be associated with this colloidal material [McDowell-Boyer *et al.*, 1986; Gschwend and Reynolds, 1987; Enfield and Bengtsson, 1988; Short *et al.*, 1988; Buddemeier and Hunt, 1988; Degueldre *et al.*, 1989]. Such colloids could include a variety of organic and inorganic particles suspended in the natural groundwater flow, spanning a size range from about 1 to 2 nm for organic macromolecules to a few micrometers for fragments of clays, oxides, and other solids. Generally, the same processes that control sorption of pollutants to aquifer solids also affect their association with colloidal material. Thus pollutants that bind most strongly to stationary aquifer solids, such as hydrophobic organic compounds and insoluble trace metal and radionuclide species, are also most likely to associate with colloidal matter. We should expect these substances to migrate faster than predicted by two-phase partitioning of the pollutants if colloids are present and mobile in the subsurface.

The association of contaminants with colloidal matter has important ramifications for groundwater sampling and analyses intended to quantify the mobile contaminant load (i.e., dissolved plus colloiddally associated species). Typically, filtration through $0.45\text{-}\mu\text{m}$ membrane filters has been performed to separate dissolved and particulate (and presumed immobile) phases of compounds of interest, although Kennedy *et al.* [1974], Danielsson [1982], Johnson and Wangersky [1985], and many others warn against the use of this arbitrary operational definition of dissolved constituents.

For compounds associated with colloidal matter, this separation overestimates the dissolved load because some of the colloidal material may be smaller than the filter pore diameter. On the other hand, the measurement of the mobile load of the compound is underestimated by analyzing filtered samples because colloids may be trapped on the filter surface by coagulation and attachment or simply because they are larger than the filter pore size.

Thus the characterization of the mobile load of a compound must not rely on separation by filtration; rather, the accurate determination of the mobile load requires the collection of samples representative of the colloid suspension in the aquifer. Groundwater sampling must minimize the disturbance of natural groundwater flow to avoid inclusion of immobile aquifer solids. To prevent the creation of colloids after sampling (e.g., precipitation of iron oxides), the *in situ* groundwater chemistry must be maintained by avoiding exposure to atmospheric gases, light, and elevated temperature, especially for anoxic samples.

The potential influence of colloidal matter in the migration of hazardous pollutants led us to investigate the factors controlling the presence of colloids in groundwater. We examined two phreatic Atlantic Coastal Plain aquifers in the Pine Barrens of southern New Jersey and rural-agricultural central Delaware. These aquifers represent vast potential reservoirs of easily obtainable, potable water available to major population centers. Unfortunately, they are particularly vulnerable to encroachments of burgeoning cities because the aquifer solids provide little capacity to abate the spread of contaminants. In preliminary surveys, we found that these groundwaters displayed wide variations in dissolved oxygen, iron, and organic carbon (D. G. Lord, U.S. Geological Survey, and A. S. Andres, Delaware Geological Survey, personal communications, 1987) and that the sandy aquifers were substantially cemented by iron oxide minerals [Crerar *et al.*, 1979; Denver, 1986]. Since iron oxides cement soil particles and colloids together in many sandy soils and sediments [Schwertmann, 1985; Pettijohn *et al.*, 1987], we anticipated that groundwater characteristics affecting iron

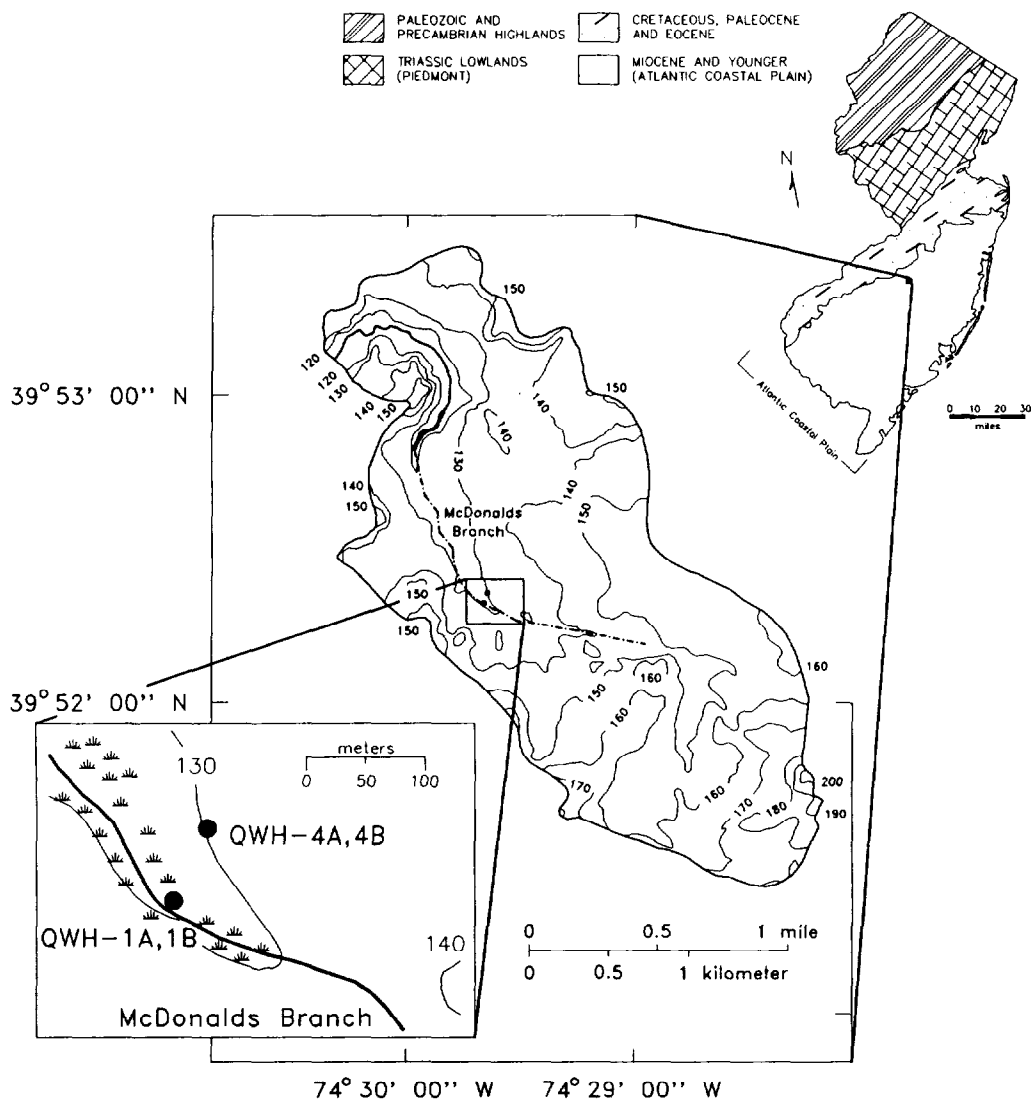


Fig. 1. Contour map (center) showing location of wells sampled in McDonalds Branch watershed, enlargement of sampling site (lower left), and geological provinces of New Jersey (upper right).

redox chemistry could be important in controlling the mobilization of soil colloids. Additionally, components of the dissolved organic carbon fraction, especially humic substances, could act as dispersants, coating clays and oxide mineral surfaces [Hunter and Liss, 1979; Tipping, 1981; Davis, 1982; Newton and Liss, 1987], thereby stabilizing colloids in suspension [Tipping and Higgins, 1982; Gibbs, 1983]. To examine the factors controlling colloid mobilization in these aquifers, we sampled groundwaters exhibiting contrasting redox chemistry collected from pairs of nearby wells screened in the same geologic formation. By application of careful sampling procedures, we sought to recover only colloids suspended in situ and to infer from the field data the geochemical processes governing their mobilization.

METHODS AND MATERIALS

Site Descriptions

The first site, the McDonalds Branch watershed, Lebanon State Forest, southern New Jersey, is located in a region of

low-relief, pine-dominated terrain known as the Pine Barrens, which covers most of the Atlantic Coastal Plain in New Jersey (Figure 1). Two distinct ecosystems can be identified in the Pine Barrens: the uplands, characterized by excessively well-drained soils and pine-oak vegetation; and the lowlands, distinguished by cedar and hardwood swamps, *Sphagnum*, and soils made up of muck and peat [Little, 1979]. The effects of acid deposition on the geochemistry of the McDonalds Branch watershed have been intensively studied by Johnson [1979], Swanson and Johnson [1980], Morgan [1984], Turner et al. [1985], Johnson and Lord [1987], and Lord et al. [1989]. The unconfined aquifer at the site is the Cohansey Sand, a regressive barrier beach deposit [Carter, 1978] typically composed of greater than 90% quartz [Rhodehamel, 1979a]. In the McDonalds Branch basin, kaolinite is the major clay mineral in the soil and sediment, while minor amounts of chlorite, illite, vermiculite, and mixed layer clays were also detected. Iron is abundant in the Cohansey Sand as ferric oxyhydroxide coatings on sand grains and as pyrite, siderite, glauconite, and vivianite in bogs near streams [Crerar et al., 1979]. The unconfined

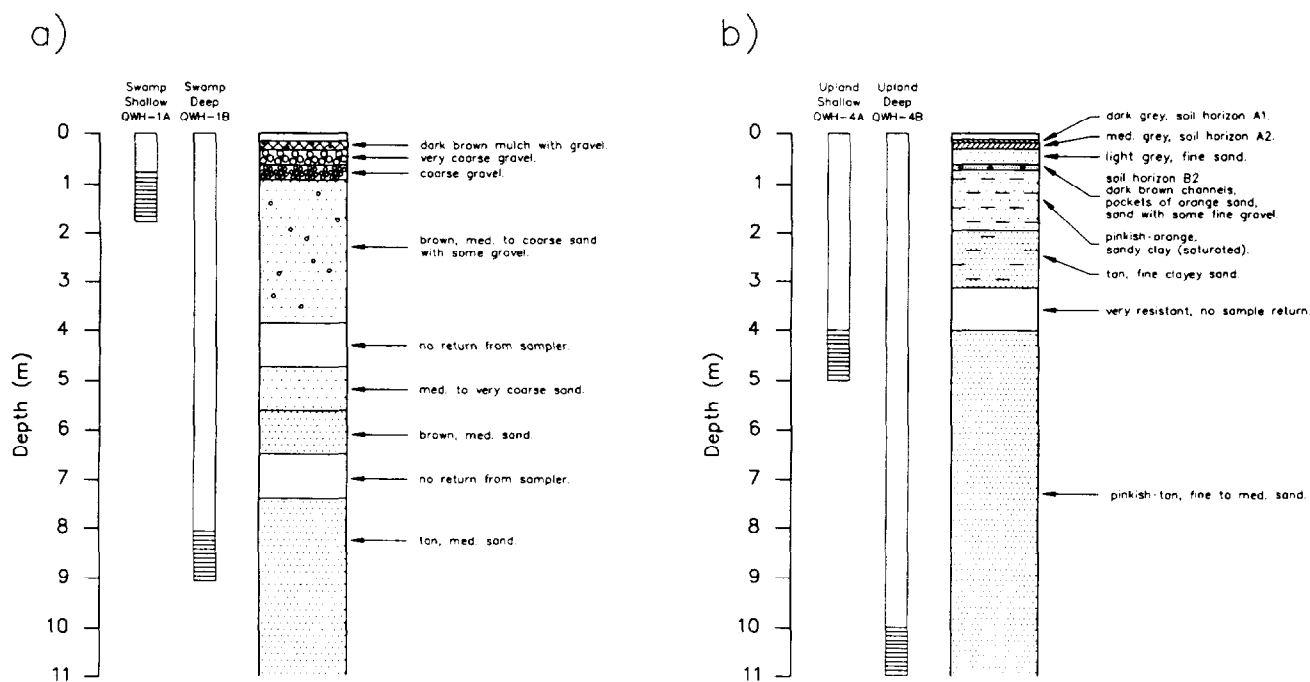


Fig. 2. Geologic log at McDonalds Branch watershed, New Jersey Pine Barrens, (a) upland site and (b) swamp site.

aquifer is about 20 m thick at the site, and the groundwater flow velocity averages about 0.1 m/d [Rhodehamel, 1979b].

The chemistry of the McDonalds Branch groundwater, and the Pine Barrens groundwater in general, is remarkably similar to the chemistry of the infiltrating precipitation due to the relatively inert nature of the Cohansey Sand [Yuretich *et al.*, 1981; Johnsson and Lord, 1987; Morgan and Good, 1988; Lord *et al.*, 1989]. Sodium, potassium, and chloride pass through the aquifer conservatively, while the other major ions are enriched or retained only moderately. Organic carbon, iron, aluminum, magnesium, and silicic acid are added to the groundwater through the decay of plant matter and the weathering of minerals.

The two pairs of wells sampled in April 1987 are located about 60 m apart near the headwaters of the McDonalds Branch. The first pair of wells, QWH-1A ("Swamp Shallow") and QWH-1B ("Swamp Deep"), were installed side-by-side in a hardwood swamp adjacent to the intermittent McDonalds Branch and screened at different depths below the peat layer of the swamp. These wells sample acidic, anoxic groundwater high in dissolved iron and organic carbon. The second pair of wells, QWH-4A ("Upland Shallow") and QWH-4B ("Upland Deep") were screened at different depths in acidic, oxic groundwater low in dissolved iron and organic carbon. The wells were installed without drilling fluids by the hollow-stem auger drilling method in August 1984. The wells are constructed of 5-cm-diameter PVC tubing and PVC screens of slot widths 0.25 and 0.64 mm. The auger holes were backfilled with native quartz sand, and the wells were developed by pumping and surging at a flow rate of about 4 L min⁻¹. Other well construction details and the lithology of the sediments are shown in Figure 2. In October 1987 the Upland Shallow groundwater was not resampled because it was determined to be similar in chemistry and colloid load to the Upland Deep groundwater.

The second site, located on low-relief rural-agricultural

terrain around the central Delaware town of Harrington (Figure 3), is part of the Delaware Coastal Plain. The unconfined aquifer at the site is primarily part of the Columbia Formation, a fluvial and shoreline sequence of sands containing about 83% quartz, 15% feldspar, 1% mica, and trace quantities of a large number of metamorphic minerals [Jordan, 1964]. Sand grains are frequently stained with ferric oxyhydroxides, and the base of the formation is marked by a thin layer of iron oxide cementation. The unconfined aquifer is about 20 m thick at the site, and the average groundwater velocity ranges from about 0.05 to 0.1 m/d [Johnston, 1977]. Denver [1986] identified two groundwater types in the unconfined aquifers of central Delaware: (1) a near-neutral pH, anoxic groundwater containing high iron concentrations, and (2) in acidic, oxic groundwater containing low iron concentrations. The differences in groundwater chemistry were attributed to the drainage characteristics of the surficial soil layer: oxidation of organic carbon in poorly drained soils produced anoxic groundwaters, while well-drained soils promoted infiltration of aerated rainwater.

Three wells screened in the unconfined aquifer of the Delaware Coastal Plain were sampled in April 1987: well Db24-17, near Newark, Delaware; well Lc42-01, near Harrington; and well Qe44-01, near Laurel, Delaware (Figure 3). The investigation was focused to well Lc42-01, which samples near-neutral pH, anoxic groundwater, because it contained the highest natural colloid load. Another well, Md22-01, located about 5 km southeast of well Lc42-01, was also sampled in October 1987 and found to contain acidic, oxic groundwater. Thus these two wells represent the two groundwater types identified by Denver [1986]. Well Lc42-01 was installed in September 1982, and well Md22-01 in October 1987 by hollow-stem auger without drilling fluids. The wells are constructed of 5-cm-diameter PVC tubing and screens, surrounded by quartz sand pack, sealed by bentonite grout above the well screen, and developed by pumping

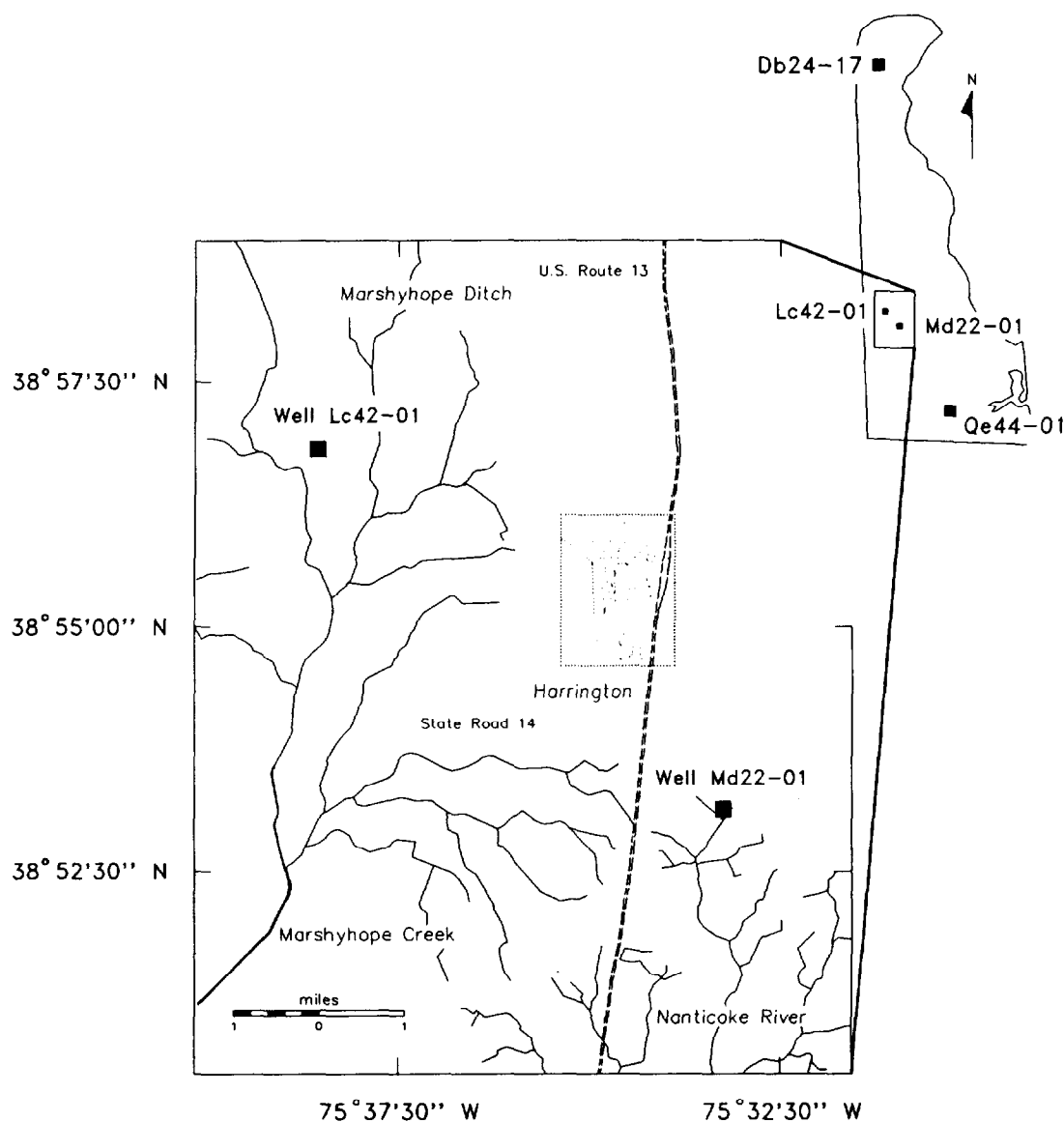


Fig. 3. Location of wells sampled near Harrington, Delaware, with inset showing location of wells sampled throughout Delaware.

and surging. Further well construction details and the lithology of the sites are shown in Figure 4.

Groundwater Sample Collection

The sampling procedure used in this investigation, developed by Reynolds [1985] and Backhus *et al.* [1986], and refined by Ryan [1988], minimized the introduction of artificially suspended particles into the samples by withdrawing water at very slow pumping rates ($\sim 100 \text{ mL min}^{-1}$). The sampling procedure also maintained the *in situ* groundwater chemistry by avoiding exposure to the atmosphere, light, and temperature above that of the groundwater. When separation of the dissolved constituents of the groundwater from the total sample was necessary, the samples were pressure filtered through Nuclepore membrane filters.

Groundwater was removed from the wells by a submersible, gear-driven, positive displacement pump (model SP-202, Fultz, Inc., Lewistown, Pennsylvania) that we modified

to withdraw groundwater at rates as low as 100 mL min^{-1} . The screened interval of the well was isolated from the overlying standing water by an inflatable packer, thus reducing the volume of water that had to be purged. Water chemistry properties (pH , E_H , specific conductivity, dissolved oxygen (DO), and temperature) were monitored in a sealed flow-through cell during well purging following calibration at the groundwater temperature. Light-scattering intensity measurements of the colloid abundance in samples collected in April 1987 were made upon returning to the laboratory using a laser light-scattering photometer (model N4, Coulter Electronics, Inc., Hialeah, Florida) fitted with a low dark counts, high gain photomultiplier (model 9893, Thorn EMI Gencom, Fairfield, New Jersey). The laboratory scattering measurements showed that the colloid abundance in the samples collected during purging gradually declined but never reached a consistent scattering intensity. Thus the water chemistry properties, which had reached stable levels,

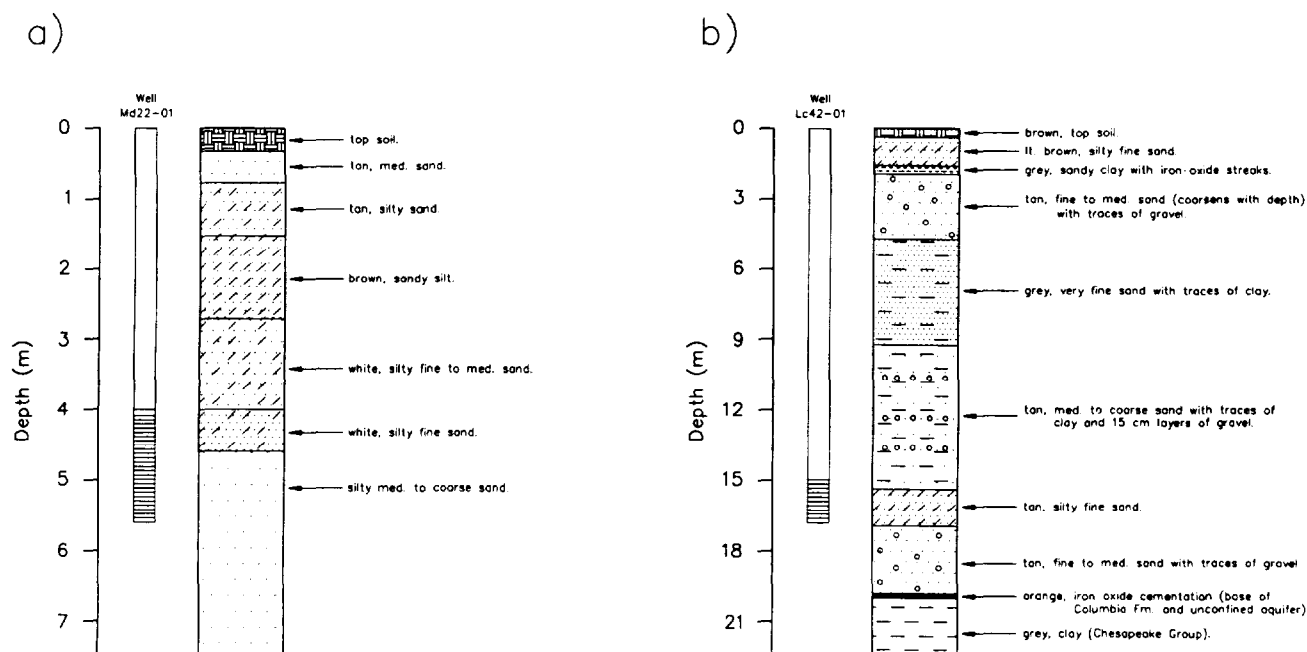


Fig. 4. Geologic log at site of (a) well Md22-01 and (b) well Lc42-01 near Harrington, Delaware.

did not accurately reflect the adequacy of purging standing water from the well for collecting colloid samples. Based on this observation, we infer that the zones of disturbed water chemistry and colloid load caused by the installation and presence of a monitoring well extend into the aquifer to different extents.

To assure that our samples were representative of the in situ colloid load, we monitored the groundwater particle concentration in the field in October 1987 during well purging. Stabilization of the light-scattering intensity of the groundwater samples was used as the primary criterion for determining the time (>3–6 hours) required to purge the standing water from the wells [Ryan, 1988].

To convert the light-scattering intensity measurements of the groundwater samples to colloid concentrations, we measured the scattering caused by suspensions of known colloids at 1–100 mg L⁻¹ concentrations. Scanning electron microscopy and energy-dispersive X ray analysis (SEM/EDX) of the groundwater particles collected on filters revealed that clay plates were the predominant groundwater particles. Thus we used colloidal kaolinite (E.M. Science, Cherry Hill, New Jersey), observed by SEM to be similar in size distribution and shape to the groundwater particles, to make the standard suspensions. These suspensions produced a linear calibration curve ($R^2 = 0.9955$): $I = 355.6C - 395.5$, where I is the scattering intensity (counts per second) and C is the kaolinite concentration (milligrams per liter).

All bottles, syringes, filters, and filter holders used in the field were cleaned by soaking in 2 N HNO₃ and rinsed with distilled deionized water at least three times. The groundwater samples were collected in argon-filled ground glass-stoppered DO bottles filled to overflowing and sealed in argon-filled plastic zipper-lock bags. The samples were stored in a cooler at about 4°C until they were transferred to a refrigerator held a few degrees below the groundwater temperature. Colloids for SEM/EDX examination were obtained in the field by filtering 5 mL of groundwater collected

in polyethylene syringes through 0.015-μm Nuclepore polycarbonate membrane filters (25-mm diameter) and rinsing the filters with 5 mL of distilled deionized water to remove ions that might precipitate during drying in a desiccator.

Laboratory Analyses

The groundwater filter samples were examined by SEM/EDX to determine the morphology, size, and elemental composition of the particles trapped on the filters. The filters were gold plated and analyzed on a Cambridge Stereoscan MkIII SEM equipped with a Tracor-Northern model 5400 fully quantitative EDX. The filters were systematically scanned, and EDX analyses were performed on representative particles. The mean elemental compositions of common particles, such as the clay plates, were estimated by averaging the compositions of at least 10 similar particles.

X ray diffraction (XRD) analysis was also attempted on random powder mounts of particles collected from 250 mL of groundwater suction-filtered through 0.45-μm Nuclepore silver membrane filters, but only the Swamp Deep sample yielded a sufficient amount of suspended sediment to obtain identifiable diffraction peaks. A Rigaku RU300 X ray diffractometer equipped with a Cu-K_α X ray generator was used to analyze the samples, and the diffractogram was interpreted using a computer-based peak identification routine.

The laboratory was used to handle the groundwater samples was cleaned by soaking in 2 N HNO₃ and rinsing at least three times in distilled deionized water. All transfers of the samples were performed in an argon-filled glove bag to minimize exposure of the samples to the atmosphere. The groundwater samples were analyzed for total and "dissolved" concentrations of Fe, Al, Si, and organic carbon. For Fe, Al, and Si, the dissolved fractions were separated by filtering through 0.015-μm Nuclepore filters. The total and filtered samples were acidified to pH 1.0 by addition of concentrated HNO₃ Ultrex one day prior to analysis on a

Perkin-Elmer model 372 atomic absorption spectrophotometer equipped with a model HGA 400 graphite furnace atomizer. The precision associated with this method was approximately $\pm 4\%$. For determination of total and dissolved organic carbon, the total and filtered samples were separated by 0.030- μm Nuclepore filtration, and then acidified, purged of inorganic carbon, and persulfate oxidized at 121°C for 30 min in sealed ampoules following the method of Menzel and Vaccaro [1964]. The CO_2 evolved from the oxidation of the organic carbon was measured by an infrared detector on an Oceanography International model 524 total carbon system. The precision associated with this method was about $\pm 10\%$.

The volume of groundwater forced through each filter was less than 1 mL/cm², and the mass loadings on the filters did not exceed 0.5 mg, suggesting that we were well below the threshold of pore clogging observed by Danielsson [1982]. The larger 0.030- μm pore diameter filters were used for the organic carbon analyses to reduce filtration time for the larger sample volumes needed for replicates. Since we focused our study on the clay and oxide colloids and any associated organic coatings, the difference between the 0.015- and 0.030- μm pore diameters of the membrane filters was considered to be negligible. Since we did not use ultrafiltration techniques, it should be noted that neither membrane filter would have retained very small colloids such as organic macromolecules.

Finally, the electrophoretic mobilities and zeta potentials of the particles in the Swamp Deep and Lc42-01 groundwater samples were determined by measuring the particle velocities under the influence of an electric field in a Rank Brothers (Cambridge, England) model MkII microelectrophoresis apparatus. The mean mobilities of at least 20 particles were used to calculate the zeta potential $\zeta(\text{V})$ of the particles using the rationalized form of the Henry equation for $\zeta < 25$ mV and $0.1 \leq \kappa a \leq 200$, where κ is the reciprocal Debye-Huckel double-layer thickness and a is the radius of curvature of the particle [Smith, 1973]:

$$\zeta = \frac{3}{2} \frac{U\mu}{\epsilon\epsilon_0} [1 + f(\kappa a)]^{-1}$$

where U is the mean electrophoretic mobility of the particle ($\text{m}^2 \text{s}^{-1} \text{V}^{-1}$), μ is the dynamic viscosity of the fluid ($\text{kg m}^{-1} \text{s}^{-1}$), ϵ is the dielectric constant of water (78.54 for water at 25°C), ϵ_0 is the permittivity of free space ($8.854 \times 10^{-12} \text{ C}^2 \text{J}^{-1} \text{m}^{-1}$), and $[1 + f(\kappa a)]$ is a correction factor accounting for the retardation caused by the movement of counter ions in the opposite direction for a range of κa values. At $\kappa a > 200$, the Henry equation converges to the Smoluchowski equation ($\zeta = U\mu/\epsilon\epsilon_0$). The change in particle mobility as a function of decreasing pH was also measured by adding 0.1 N HCl to the suspension to determine the point of zero charge (PZC) of the particle surfaces. Values of the Henry equation correction factor were determined by calculating κa for the natural and acidified samples assuming that the radius of curvature of the average particle observed was 1 μm . Values of κa for the groundwater ranged from about 50 to 500. The error associated with the measurements of mobility is about $\pm 10\%$, but as the particle mobility approaches zero, the error increases to about $\pm 20\%$.

RESULTS

The chemistry of groundwaters sampled from neighboring wells in the McDonalds Branch watershed (Table 1) and near Harrington, Delaware (Table 2) varied widely, revealing two distinct groundwaters at these sites. Most notably, the Swamp Deep groundwater was nearly anoxic, while the Upland Deep groundwater, only 60 m away, contained a relatively high concentration of dissolved oxygen. Similarly, the Lc42-01 groundwater was virtually anoxic, while the Md22-01 groundwater was well aerated. We consider dissolved oxygen concentrations of about 30 μM or less to reflect anoxic conditions in the aquifer because the long residence time of the groundwater in our sample tubing allows some oxygen to diffuse into the groundwater [Holm et al., 1988].

The field-measured groundwater chemical properties agreed well with past analyses of the groundwaters at these sites, also listed in Tables 1 and 2. The E_H measurements were stable and reproducible during 5-min readings after the purging of a few well volumes of water. In the groundwaters with high iron concentrations, the E_H measurements may represent the redox state of the system dominated by some Fe(II)-Fe(III) redox couple [Langmuir, 1971a]; however, the effect of disequilibrium between irreversible and biologically mediated redox reactions (such as $\text{H}_2\text{S}-\text{SO}_4^{2-}$) on the system redox potential cannot be determined [Morris and Stumm, 1967; Lindberg and Runnells, 1984].

The anoxic groundwater from the Swamp Deep and Lc42-01 wells scattered much more light than the groundwaters from nearby wells and distilled water blanks ($\sim 50 \text{ c s}^{-1}$) (Tables 1 and 2). These field measurements were observed after the removal of 10–20 well volumes and remained constant for more than an hour of continued pumping (an additional 3–4 well volumes). The approximate colloid concentrations, estimated by using the light-scattering results of the standard kaolinite suspensions, were about 60 mg colloids L^{-1} in the Swamp Deep groundwater and about 6 mg colloids L^{-1} in the Lc42-01 groundwater. It is uncertain whether the ≤ 1 -mg colloids L^{-1} levels seen in the samples of the neighboring groundwaters reflect sampling and sample-handling artifacts or truly suspended particles. The poly-disperse nature of the groundwater particle distributions and the presence of large ($> 1 \mu\text{m}$) suspended particles in these samples precluded reproducible size distribution analysis using photon correlation spectroscopy (PCS), the autocorrelation of time-varying light-scattering data. In our experience, the sizing of natural, heterogeneous colloid suspensions by PCS has proven difficult; only our studies of ferrous phosphate colloids yielded reproducible results to this sizing approach [Gschwend and Reynolds, 1987].

Assessment of Fe, Al, Si, and organic C in total and filtered groundwater samples indicated the importance of each of these elements in the colloidal phase in the Swamp Deep and Lc42-01 groundwaters (Tables 1 and 2). In contrast, results for the Upland Deep and Md22-01 groundwaters showed lower total amounts of these elements and little or no difference between total and filtered samples. In the groundwaters containing substantial particle concentrations (Swamp Deep in the Pine Barrens and Lc42-01 in central Delaware), the significant difference between the total and filtered organic carbon measurements indicates that about one-third to one-half of the organic carbon was associated

TABLE 1. Summary of Results for McDonalds Branch Groundwater Collected in October 1987 Compared With Chemistry of McDonalds Branch Groundwater for January 1985 to February 1986 From Lord *et al.* [1989]

	Swamp Shallow		Swamp Deep		Upland Deep	
	Lord et al.*	This Work†	Lord et al.*	This Work†	Lord et al.*	This Work†
Light-scattering intensity, c s^{-1}		560		20,000		330
Colloids, mg L^{-1}		~2		~60		≤1
Temperature, °C	9.4	12	11	10	12	13
pH	3.9	3.7	4.9	4.5	5.1	4.8
E_H , V	—	+0.28	—	+0.29	—	+0.34
DO, μM	16	25	34	30	180	190
Conductivity, $\mu\text{S cm}^{-1}$	110	93	27	37	32	39
Alkalinity, $\mu\text{eq L}^{-1}$	-210	—	7.5	—	—	—
Ionic strength, μM	—	1000	—	260	—	410
Na^+ , μM	100	—	78	—	65	—
K^+ , μM	4.9	—	4.6	—	7.7	—
Ca^{2+} , μM	18	—	10	—	40	—
Mg^{2+} , μM	22	—	12	—	41	—
NH_4^+ , μM	3.1	—	0.7	—	0.3	—
Cl^- , μM	160	—	95	—	81	—
SO_4^{2-} , μM	160	—	31	—	68	—
NO_3^- , μM	<1	—	<1	—	4.0	—
Si, μM						
Total	—	133	—	138	—	67.8
Dissolved	91	105	82	61.7	52	56.3
Fe, μM						
Total	—	44.3	—	22.3	—	0.55
Dissolved	51	36.6	37	7.70	0.1	0.19
Al, μM						
Total	—	53.5	—	58.3	—	1.95
Dissolved	61	43.8	4.0	4.37	1.1	1.56
TOC, mg C L^{-1}	—	52	—	1.4	—	0.8
DOC	19	46	1.2	0.7	1.3	0.8

The wells are described in text. Dash means not analyzed.

*Dissolved constituents defined by 0.45- μm filtration.

†Dissolved constituents defined by 0.015- or 0.030- μm filtration.

with particles not passing through a 0.030- μm filter. The Swamp Shallow groundwater had very high levels of total organic C, total Fe, and total Al; but unlike the Swamp Deep groundwater, these total element measures were not so dramatically different from the corresponding filtered sample results. The difference between the total and filtered organic carbon in the Swamp Shallow groundwater may not be significant given the precision of the method ($\pm 10\%$). The 0.015- and 0.030- μm membrane filters used to separate the total and "dissolved" fractions of the groundwater constituents provide more accurate separation than the 0.45- μm filters used in past analyses; however, organic macromolecules and the smallest inorganic soil colloids still pass through the pores of these filters. The dissolved Fe, Al, and Si concentrations we report are similar to those measured using 0.45- μm filters in previous investigations (Tables 1 and 2). The total organic carbon results generally agree with past measurements, even though those dissolved organic carbon (DOC) concentrations were determined by 0.45- μm filtration.

The SEM/EDX analyses of colloids collected on 0.015- μm filters revealed their abundance, size, and composition. SEM observations of filters collected during the well purging showed a decrease in particle abundance as a function of pumping time, confirming the results of the light-scattering photometry. For the Swamp Deep groundwater obtained after 7 hours of pumping, three types of particles were observed: (1) low-Fe aluminosilicate plates, (2) high-Fe

aluminosilicate plates, and (3) Fe-rich lath-shaped and botryoidal crystalline fragments (SEM micrographs in Figure 5, mean compositions of colloids in Table 3). Using the clay mineral classification method of *Mudroch et al.* [1977], the low-Fe plates were identified as kaolinite and the high-Fe plates were identified as chamosite, an Fe(II)-chlorite. The presence of the kaolinite and chamosite minerals in the Swamp Deep groundwater was confirmed by XRD. Based on the morphology and high Fe content of the lath-shaped and botryoidal crystals, they were identified as goethite, a common product of intense weathering in acidic soils of temperate climates [Langmuir, 1971b; Schwertmann, 1985]. Kaolinite, chlorite, and goethite are all known to be important components of the Cohansey Sand [Rhodehamel, 1979a; Crerar *et al.*, 1979]. The possibility that the ferric oxyhydroxide minerals observed on the filters arose from oxidation and precipitation of dissolved Fe(II) after sampling is unlikely, since the low pH of the Pine Barrens groundwater results in very slow kinetics of Fe(II) oxidation [Stumm and Lee, 1961] and because the particles exhibited well-developed crystalline structures.

The sparsely covered Upland Deep groundwater filters contained particles identified as kaolinite. The Swamp Shallow groundwater filters were lightly covered by quartz fragments and Al- and Fe-rich particles. The particles appeared amorphous and may be gibbsite and ferric hydroxide minerals, products of the chemical weathering occurring in

TABLE 2. Summary of Results for Harrington Groundwater Collected in October 1987 Compared With Chemistry of Typical Groundwaters at Nearby Sites

	Anoxic GW*	Lc42-01 (This Work)†	Oxic GW*	Md22-01 (This Work)†
Light-scattering intensity, c s^{-1}		2,100		260
Colloids, mg L^{-1}		~6		≤1
Temperature, °C	14.5	14.0	15.0	18.0
pH	6.3	6.2	5.3	4.3
E_H , V	—	+0.10	—	+0.38
DO, μM	<10	19	200	180
Conductivity, $\mu\text{S cm}^{-1}$	120	175	150	320
Alkalinity, mg L^{-1}	43	—	7.9	—
Ionic strength, mM		2.1		1.0
Na^+ , μM	360	—	420	—
K^+ , μM	27	—	40	—
Ca^{2+} , μM	210	—	120	—
Mg^{2+} , μM	73	—	57	—
NH_4^+ , μM	11	—	0.7	—
Cl^- , μM	270	—	330	—
SO_4^{2-} , μM	220	—	17	—
NO_3^- , μM	1.6	—	130	—
Si, μM				
Total	—	426	—	280
Dissolved	530	406	350	251
Fe, μM				
Total	—	144	—	0.8
Dissolved	290	70.7	0.1	0.2
Al, μM				
Total	—	6.4	—	21.5
Dissolved	<0.3	0.4	0.8	21.5
TOC, mg C L^{-1}	—	3.3	—	1.1
DOC	2.2	2.1	5.4	1.0

Anoxic groundwater (GW) data from wells Lc42-01, Lc42-02, Lc55-01, Mc53-01, Mc31-03, oxic groundwater data from wells Lc11-01, Lc23-03, Lc51-01, Mc13-01, Mc22-01, Mc51-01, Md31-04 [Denver, 1986]. Dash means not analyzed.

*Dissolved constituents defined by 0.45- μm filtration.

†Dissolved constituents defined by 0.015- or 0.030- μm filtration.

the very acidic Swamp Shallow groundwater. The mean compositions of these particles are listed in Table 3.

The Lc42-01 groundwater filters were covered predominantly by two types of particles: (1) low-K aluminosilicate plates and (2) high-K aluminosilicate plates. The low-K plates were identified as kaolinite, and the high-K plates were identified as muscovite by classification of their mean compositions (Table 3). Muscovite is known to be a minor component (1%) of the Columbia Formation sediments [Jordan, 1964]. Traces of Ti were detected in the clay plates and are probably present as isomorphic substitutions of silicon [Dolcater *et al.*, 1970]. Other particles observed on the Lc42-01 filter include Fe-rich spherical particles, probably amorphous $\text{Fe}(\text{OH})_3$; small Ti-rich spheres, possibly diagenetic alteration products of rutile; and aggregations of primarily organic material, possibly microbial in origin. Ferric hydroxides and oxyhydroxides are common in the soil layers in central Delaware [Denver, 1986], and rutile is a common trace heavy mineral in the Columbia Formation [Jordan, 1964]. The colloid sizes are apparent in SEM micrographs of these particles shown in Figure 6. The Md22-01 groundwater filters were sparsely covered with high-K aluminosilicate plates identified as muscovite fragments (Table 3).

Electrophoretic mobility observations demonstrated that the Swamp Deep and Lc42-01 groundwater colloids were negatively charged at the natural pH of the groundwaters (Table 4), as expected for these particles, which are com-

posed predominantly of clays. Calculated ζ potentials are quite modest, only -11 mV for the Swamp Deep colloids and -25 mV for the Lc42-01 colloids. The point of zero charge (PZC) of the particles, determined by interpolating the mobility-pH data, occurred at approximately pH 3.0 for the Swamp Deep colloids, slightly lower than the range of overall PZCs compiled for kaolinite (3.3–4.6 [Parks, 1967]). The PZC of the Lc42-01 groundwater particles, composed primarily of muscovite and kaolinite, occurred at approximately pH 1.7. The "permanent" negative charge of the muscovite surfaces, caused by the isomorphic substitution of one in every four Si^{4+} atoms with an Al^{3+} atom in the tetrahedral layers [Greenland and Mott, 1978], lowers the PZC of the mixture. The calculated ζ potentials of these particles are significantly lower than those measured for purified samples of kaolinite [Williams and Williams, 1978] and mica [Pashley, 1985] at comparable pH and ionic strengths.

DISCUSSION

Groundwater Sampling for Colloids

The sampling results indicate that the groundwater collection techniques employed in this study succeed in sampling colloids suspended in situ and in avoiding the inclusion of immobile soil colloids and formation of colloids during sample storage. We risked resuspension of the same types

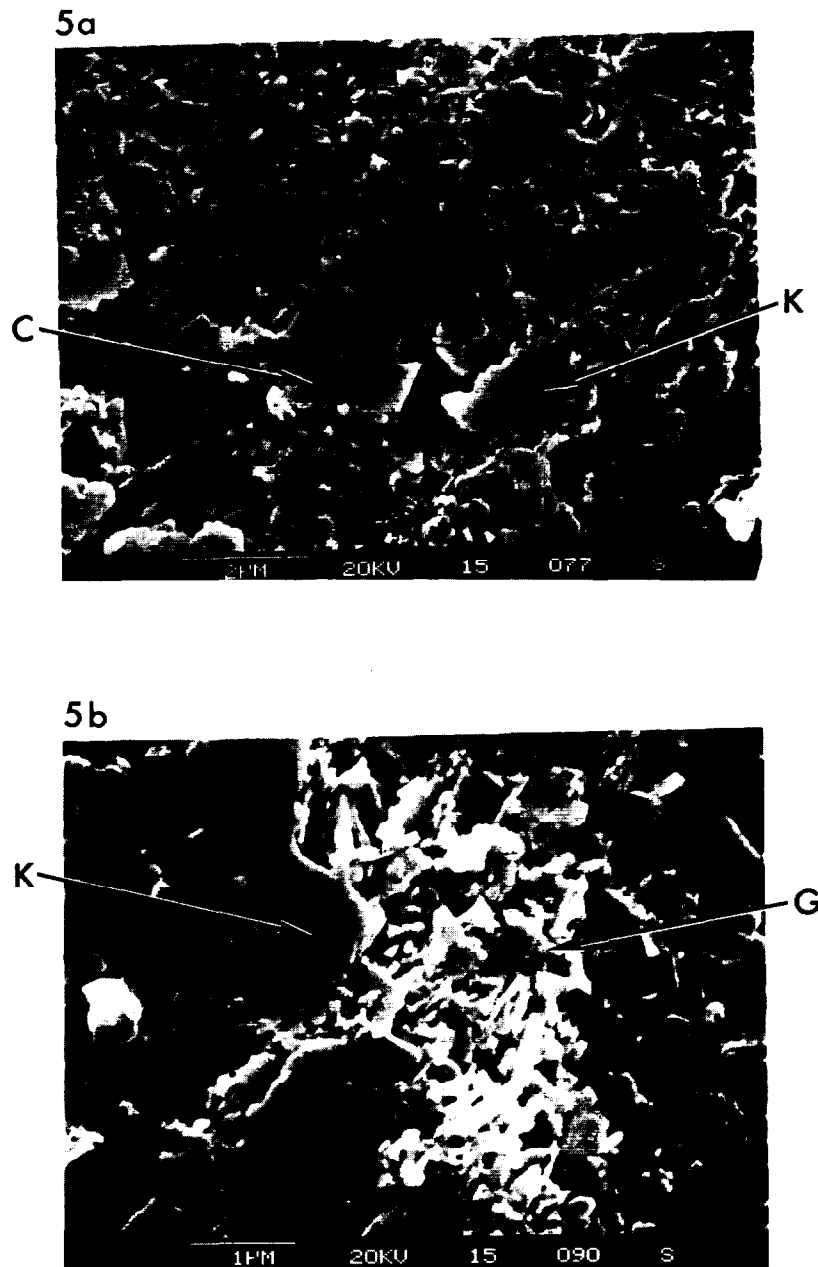


Fig. 5. SEM micrographs of Swamp Deep groundwater particles, scale bars at bottom. (a) Typical distribution of clay colloids observed in Swamp Deep groundwater: C, chamosite; K, kaolinite, as identified by EDX and XRD. (b) Cluster of lath-shaped or botryoidal colloidal Fe-rich crystals identified as goethite (G) and large kaolinite platelet (K).

and quantities of soil colloids by pumping groundwater from two pairs of wells screened in the same geologic formations, yet the samples varied widely in colloid load. The extremely low light-scattering intensities measured in the oxic groundwaters (only 5–7 times greater than that of distilled water) indicate that well installation procedures, resuspension of particles from the bottom of the well, and shearing of immobilized soil colloids did not introduce significant amounts of submicron particles to our samples after 10–20 well volumes were purged. Colloid abundance declined to a steady plateau after exhaustive flushing in the anoxic groundwaters, indicating that we were collecting groundwater representative of the formation and not the standing

water near the well (where pumping-induced shear stresses and groundwater chemistry changes due to the presence of the well would be most likely to alter the aquifer conditions). For all groundwaters sampled, the steady colloid load was very much lower than that seen in groundwater initially recovered from the well, or even in groundwater collected after flushing the standard three well volumes. Finally, the particle suspensions (i.e., predominantly clays) are colloidally stable during sampling and storage when groundwater conditions are preserved; thus we conclude that the colloids detected in the water after our long slow pumping were actually suspended in situ and moving through the subsurface regions sampled by these wells.

TABLE 3. Summary of EDX Results for Groundwater Colloids Collected on 0.015- μ m Filters: Average Elemental Compositions of Particles ($N \geq 10$ particles), Listed by Relative Abundance of Particles in Each Sample

Groundwater	Particle Composition, mol%						Identified as
	Al	Si	Fe	K	Ca	Ti	
Swamp Deep	43.2	52.4	3.5	—	—	—	kaolinite
	40.6	46.4	11.1	—	—	—	chamosite (Fe-chlorite)
	22.5	22.7	53.8	—	—	—	goethite
Upland Deep	46.8	50.7	2.0	—	—	—	kaolinite
Swamp Shallow	2.8	96.4	—	—	—	—	quartz
	98.0	2.0	—	—	—	—	gibbsite (?)
	4.2	8.2	87.6	—	—	—	Fe(OH) ₃ (?)
Lc42-01	43.2	53.0	1.5	0.8	1.0	1.0	kaolinite
	36.8	53.4	3.1	5.8	—	0.9	muscovite
	4.4	12.3	82.9	—	—	—	Fe(OH) ₃ (?)
Md22-01	—	7.8	—	—	—	92.2	rutile, TiO ₂ (?)
	36.4	52.7	1.5	8.0	1.0	0.7	muscovite

Factors Controlling Colloid Mobilization

The sharp contrasts in chemistry between groundwaters with high colloid concentrations (Swamp Deep and Lc42-01) versus those with very low colloid concentrations (Upland Deep and Md22-01) indicate that the effects of anoxic conditions are responsible for mobilizing the colloids in these subsurface environments. While changes in the ionic strength of groundwater have been implicated in clay mobilization previously [Nightingale and Bianchi, 1977; Kia *et al.*, 1987], our field data do not indicate that ionic strength was controlling colloid mobilization in these groundwaters. Instead, suspended colloids were observed only in the groundwaters with measured E_H below +0.3 V at both sites. These anoxic waters were also enriched in dissolved iron, presumably as ferrous iron. From this contrast, we hypothesize that the presence or absence of the clay colloids in these groundwaters is controlled by the ability of oxidized forms of iron to remove the colloids from suspension by binding them to aquifer solids. The stability of ferric iron species is in turn primarily controlled by the redox potential and pH of the groundwater.

In the oxic groundwaters, the field data indicate that the clay colloids are immobilized by attachment to iron oxides coating the quartz grains that make up the framework of the aquifer. Under certain conditions, clay colloids may self-coagulate or become attached to aquifer solids by attraction between their positively charged edges and negatively charged surfaces (clay faces, uncoated quartz grains); but their filtration and coagulation would be greatly facilitated by a positively charged intermediary, such as ferric iron. The weathering of Fe-bearing minerals in the sediment generates Fe²⁺, which is oxidized to Fe³⁺ and hydrolyzed to various Fe(III) species. The adsorption of dissolved Fe(III) species on the quartz grains can lead to a reversal of charge on the quartz grain surface and buildup of ferric oxyhydroxide coatings (as observed by James and Healy [1972] for other multivalent cations). At the groundwater pH, ferric oxyhydroxide coatings formed on the quartz surfaces of the Cohansey Sand are positively charged; therefore we expect that these coatings are responsible for binding the clay colloids to immobile aquifer solids. Suspended clay particles could also be coagulated by dissolved Fe(III) species, Fe(III) polymers, and Fe(III) oxides [Packham, 1965; Oades, 1984;

Goldberg and Glaubig, 1987], and these aggregates could become attached to the ferric oxyhydroxide coatings.

The Fe(III) cementation hypothesis is supported by interpretation of the geologic logs for these sites. The oxic Upland Deep groundwater is essentially colloid free despite the presence of a clay layer just below the soil zone (as shown in Figure 2a). The clay layer and the underlying sandy sediments are stained a pinkish orange tinge, suggesting that clay is attached to the iron-oxide-cemented quartz grains of the aquifer. The infiltration of clay particles into soils and sediments has been observed in a number of field and laboratory settings [Dijkerman *et al.*, 1967; Walker *et al.*, 1978; Bond, 1986; Matlack *et al.*, 1989]. Iron oxides are often associated with such illuvial bands [Folks and Riecken, 1956].

At the Md22-01 site, the geologic log (Figure 4a) shows no evidence of distinct clay layers or staining by iron oxide coatings in the sediment. The low colloid concentration may be attributed to the lack of a source of clay colloids in the sediments or to coagulation and filtration of colloids by other means.

In contrast, the geologic log for the Swamp Deep site (Figure 2b) shows that the sandy sediments beneath the swamp do not exhibit the characteristic colors of attached clay particles and ferric oxyhydroxide coatings apparent in the Upland Deep geologic log. The decaying plant matter in the swamp generates large quantities of organic carbon, evident from the extremely high concentrations of organic carbon in the Swamp Shallow groundwater just below the peat layer of the swamp. Based on hydraulic head data [Lord *et al.*, 1989] this groundwater infiltrates downward to the depth of the Swamp Deep well. When the organic carbon-rich groundwater flows through sediments coated by ferric oxyhydroxides, we postulate that the Fe(III) coatings on the quartz grains are reduced and dissolved and attached clay colloids are mobilized.

Experimental work has identified a range of measured redox potentials that mark the initiation of ferric oxide reduction and dissolution. Carroll [1958] observed bacterial reduction of iron oxide coatings on kaolinite at pH 5.5 and redox potential of +0.18 V. Patrick and Henderson [1981a, b] and Miller *et al.* [1985] have identified redox potentials between +0.2 and +0.3 V as the threshold for reduction and

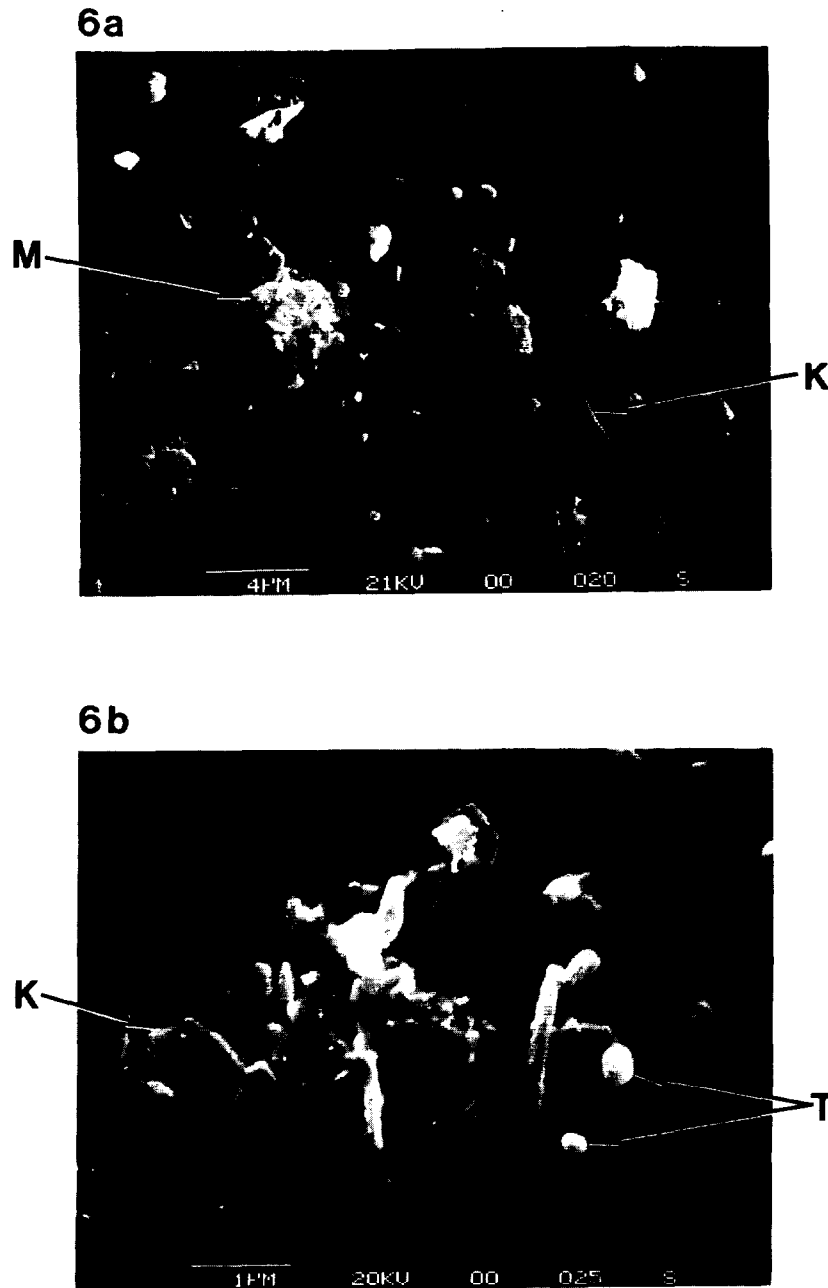


Fig. 6. SEM micrographs of Lc42-01 groundwater particles, scale bars at bottom. (a) cluster of poorly crystalline muscovite plates (M) and kaolinite (K), as identified by EDX. (b) Enlarged view of plate of kaolinite (K), rod-shaped particles biogenic in origin (no EDX signal above background), small Ti-rich spheres (T).

dissolution of iron oxides in soils; therefore we expect that ferric iron species will begin to be reduced at the redox potential of the Swamp Deep site (+0.29 V).

The geology and chemistry at Lc42-01 indicate that the same processes influencing colloid mobilization in the Swamp Deep groundwater are operating at the Lc42-01 groundwater as well. The geologic log at Lc42-01 shows no iron staining below the shallow clay lens or above the iron oxide-cemented base of the Columbia Formation (Figure 4b). The soil at Lc42-01 is classified as poorly drained, i.e., relatively impermeable [U.S. Department of Agriculture, 1971]; therefore the infiltration of aerated rain water is quite slow. The poorly drained soils are generally organic-rich due to the slow decomposition of plant matter in the soil de-

TABLE 4. Electrophoretic Mobilities and ζ Potentials of Groundwater Particles Under Natural and Acidified Conditions

Groundwater	pH	Mobility, ($\text{m}^2 \text{s}^{-1} \text{V}^{-1}) \times 10^8$	ζ Potential, mV
Swamp Deep	4.6	-0.81	-11.
	3.3	-0.45	-6.0
	2.5	+0.72	+9.5
	1.5	+0.74	+9.6
Lc42-01	6.4	-1.91	-25.
	3.6	-1.40	-18.
	3.0	-0.90	-12.
	2.3	-0.45	-5.9
	1.7	~0	~0

prived of aerated water. Oxidation of the abundant organic carbon produces anoxic, reducing conditions at depth, similar to the effect of the hardwood swamp adjacent to McDonalds Branch in the Pine Barrens. The dissolved iron concentration is high, indicating that Fe(II) species are the predominant form of iron in the groundwater. The low redox potential of the Lc42-01 groundwater (+0.10 V) indicates that ferric iron species would be reduced and dissolved.

Factors Controlling Colloid Stabilization in Suspension

The field evidence indicates that depletion of iron oxide coatings promotes the initial mobilization of colloids in the anoxic groundwaters, but additional factors must allow them to remain suspended. The colloidal stability of the primarily kaolinite suspension in the Swamp Deep and Lc42-01 groundwater depends on the groundwater chemistry and the surface properties of the clay colloids. In the absence of effective collector surfaces, we would still expect the clay suspensions to coagulate rapidly for a number of reasons: (1) the small amounts of iron associated with the kaolinite clays are likely present on the surfaces [Carroll, 1958; Sumner, 1963; Greenland, 1975], thus diminishing electrostatic repulsion; (2) the ionic strengths and bivalent cation concentrations observed in the groundwaters exceed the critical coagulation concentrations of clays [Swartzen-Allen and Matijevic, 1976], especially in the higher ionic strength Lc42-01 groundwater; and (3) the clay colloids are susceptible to self-coagulation and filtration by attraction of their positively charged edges to negatively charged surfaces [van Olphen, 1977]. However, the clay suspensions remained colloiddally stable in our sealed sample containers over a number of months.

We postulate that organic matter coatings contribute to the persistence of the clay colloid suspensions. The association of roughly half of the total organic carbon in the Swamp Deep groundwater and about one-third of the total organic carbon in the Lc42-01 groundwater with >30-nm particles implies that organic carbon coatings were certainly present. The organic carbon load in Pine Barrens groundwater is probably composed primarily of low molecular weight humic substances [Crerar *et al.*, 1981], and agricultural soil leachates recharging groundwater at Lc42-01 should also have substantial humic material [Leenheer and Stuber, 1981]. Humic substances are strongly adsorbed to positively charged oxide surfaces, including clay edges [Davis, 1982]. The adsorption of organic carbon is known to produce uniformly, negatively charged surfaces on particles suspended in coastal waters, estuaries, and freshwater lakes [Hunter and Liss, 1979; Tipping, 1981; Davis, 1982; Newton and Liss, 1987]. These organic coatings increase the colloidal stability of the particles by steric and electrostatic stabilization [Tipping and Higgins, 1982; Gibbs, 1983].

The electrophoretic mobilities measured for our groundwater particles are uniformly negative, as would be expected for both organically coated and uncoated clays at the groundwater pH. The adsorption of organic matter would result in the neutralization of some of their positively charged edge sites, thus producing the anomalously low PZCs measured for these clays. The less abundant iron oxide particles and iron sorbed on clay surfaces would also be expected to strongly adsorb humic substances, resulting in

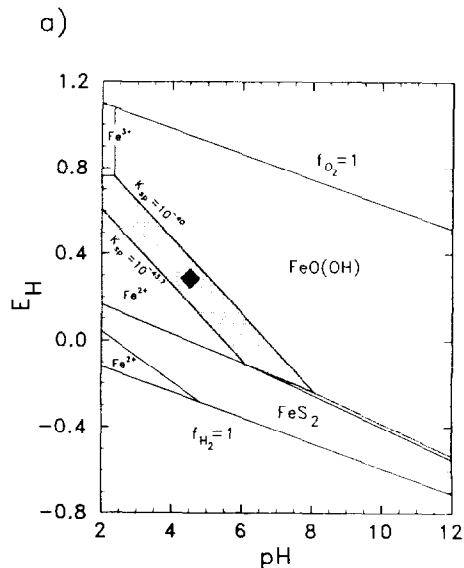


Fig. 7a. E_H -pH diagram for Swamp Deep groundwater, $T = 25^\circ\text{C}$, $P = 1$ atm, Fe-O-S-H₂O system with $\text{Fe}_T = 7.7 \mu\text{M}$, $S_T = 31 \mu\text{M}$. The shaded area represents the solubility range of goethite from $K_{sp} = 10^{-40.0}$ to $K_{sp} = 10^{-43.7}$, for variation in particle size from about 0.01 to 1 μm , respectively. The thermodynamic data are taken from Wagman *et al.* [1969] and Robie *et al.* [1978]. Diamond indicates the E_H and pH of Swamp Deep groundwater.

colloiddally stable, negatively charged particles [Tipping and Cooke, 1982; Tipping and Higgins, 1982]. Thus attachment of macromolecular polyelectrolytes is a feasible explanation for the colloidal stability of these groundwater suspensions.

Additionally, the weathering of cations from the clays may contribute to their colloidal stabilization. The unsatisfied surface negative charge in the clay would increase, and hence the electrostatic repulsion between clay fragments would also increase.

Thermodynamic Stability of Iron Oxide Colloids

The presence of iron oxide colloids in our suspensions from both Swamp Deep and Lc42-01, where the groundwater is reducing, may at first appear inconsistent with the anoxic conditions. However, the E_H -pH diagram prepared for the conditions of the Swamp Deep groundwater (Figure 7a) shows that colloidal goethite is thermodynamically stable. The solubility of goethite colloids of less than about 1- μm dimension depends on the size of particles [Langmuir, 1971b; Langmuir and Whittemore, 1971]. Smaller particles are more soluble than larger crystals because the surface energy contribution rises in proportion to the increase in surface area:volume ratio. The E_H -pH diagram (Figure 7a) indicates that goethite crystals in the range of about 0.01 to 1 μm (corresponding to a K_{sp} range of 10^{-40} – $10^{-43.7}$) could exist in equilibrium with the observed dissolved Fe(II) concentration. Our observation of goethite in this size range in the Swamp Deep groundwater confirms that these iron oxide colloids can coexist with Fe^{2+} under these E_H -pH conditions. Similarly, the E_H -pH diagram constructed for the Lc42-01 groundwater (Figure 7b) indicates that the groundwater is saturated with respect to amorphous

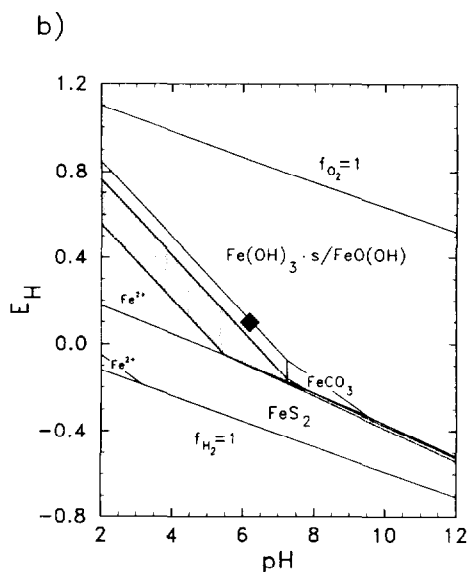


Fig. 7b. E_H -pH diagram for Lc42-01 groundwater, $T = 25^\circ\text{C}$, $P = 1$ atm, $\text{Fe-O-S-CO}_2\text{-H}_2\text{O}$ system, $\text{Fe}_T = 71 \mu\text{M}$, $S_T = 450 \mu\text{M}$, $\text{CO}_{2T} = 550 \mu\text{M}$. The shaded area represents the stability range of goethite over range of particle sizes as in Figure 7a. The solid line between the regions of $\text{Fe}^{+2}(\text{aq})$ and $\text{Fe}(\text{OH})_3(\text{s})$ represents the solubility of amorphous ferric hydroxide. The thermodynamic data are taken from Wagman *et al.* [1968, 1969] and Robie *et al.* [1978]. Diamond indicates the E_H and pH of Lc42-01 groundwater.

$\text{Fe}(\text{OH})_3$, so the observation of spherical, noncrystalline, iron-rich particles in the Lc42-01 groundwater is supported.

Implications for Contaminant Transport

The dependence of colloid mobilization in sandy, iron-oxide-coated sediments on the onset of reducing conditions has important ramifications for waste disposal. The studies of Kimmel and Braids [1980], Nicholson *et al.* [1983], and many others find that contaminant plumes emanating from landfills, sewage infiltration beds, and other disposal sites typically produce reducing, organic carbon-rich leachates. In these plumes, iron and manganese oxides are reduced and dissolved and, as a result, we expect that preexisting soil colloids may be released into suspension. The dissolution of iron and manganese oxides by the advance of reducing conditions along the flow path of a contaminant plume would also liberate trace metals coprecipitated with the oxides [Baedecker and Back, 1979]. If the dissolved iron and manganese were to reprecipitate in a colloidal form upon entering an oxic zone, trace metals may coprecipitate with these colloidal oxides instead of on a stationary phase; thus the transport of these trace metals may be significantly increased. Interestingly, supersaturation of groundwaters in response to changing aquifer conditions (E_H , pH) along the flow path has previously been found to cause the precipitation of iron oxide colloids in natural groundwaters. Langmuir [1969] reported on the stability of ferric oxyhydroxide colloids formed by *in situ* precipitation in a New Jersey Coastal Plain aquifer. The colloids were produced by the natural evolution of recharging groundwater from aerated, dilute, low pH (5–6) infiltrating water to anoxic, high pH (7–8) groundwater further down dip into the formation. Postma and Brockenhuus-Schack [1987] also reported the

observation of iron-rich suspended particles in a glacial outwash aquifer in Denmark.

The reduction and dissolution of hydrous oxides in anoxic plumes may also cause the release of clays and macromolecular organic carbon adsorbed to the positively charged hydrous oxide surfaces. This would have two effects: (1) the retardation of transport of organic compounds and metals due to their binding to these colloidal phases on immobile solids would be decreased, and (2) the colloidal load moving with the groundwater would be significantly increased. Mobilized clays and macromolecular organic carbon could carry many types of hazardous pollutants, including trace metals, radionuclides [Means *et al.*, 1978], and hydrophobic organic compounds [Enfield and Bengtsson, 1988].

The ubiquity of iron oxides acting as cementation in soils and sediments suggests that the findings of this investigation may be important in predicting the behavior of colloids in aquifers of similar geology. We anticipate that colloid mobilization and enhanced migration of colloid-associated pollutants must be considered whenever subsurface geochemical conditions are altered such that iron oxide cementation is dissolved. In an analogous situation, geologic formations cemented by calcite also appear to be susceptible to decementation and colloid mobilization [Gschwend *et al.*, 1988]. Thus we may be able to predict the behavior of colloids in an aquifer in response to changes in groundwater geochemistry if we know what soil colloids are present and what secondary mineral phase(s) serves to bind the system.

CONCLUSIONS

In the past, the nature and distribution of groundwater colloids have been poorly characterized primarily because of the difficulty encountered in obtaining samples representative of the actual suspended colloid load. The sampling techniques used in this investigation yield samples containing colloids only where geochemical conditions provide a feasible explanation for the mobilization and stabilization of colloidal suspensions in the groundwater. Thus we believe that the colloids observed in these groundwaters are actually suspended and mobile *in situ*. To acquire samples representative of the mobile load, we emphasize three tactics designed to ensure the collection of accurate groundwater samples: (1) low pumping rate ($\sim 100 \text{ mL min}^{-1}$) purging and sampling, to minimize the disturbance of natural groundwater velocities and the suspension of attached and settled particles; (2) anoxic sample collection and storage techniques, to avoid exposure of the samples to the atmosphere, and (3) monitoring of the groundwater colloid concentration in the field by light-scattering measurements, to evaluate the effectiveness of purging the standing water from the well.

Standard sampling procedures typically specify the purging of 3–5 well volumes and the stabilization of groundwater chemical properties measured in the field (dissolved oxygen, pH, E_H , specific conductivity, and temperature) as prerequisites to obtaining samples representative of the water in the formation. This investigation showed that these standards would produce samples with colloid concentrations substantially higher than the stabilized colloid concentrations monitored in the field by light-scattering intensity measurements during the purging of 10–20 well volumes.

The standard practice of separating the dissolved and particulate loads of a groundwater sample by $0.45\text{-}\mu\text{m}$ filtra-

tion clearly causes overestimates of the actual dissolved load by including colloids of diameter $<0.45 \mu\text{m}$ in the dissolved fraction, and underestimates of the actual mobile load by excluding mobilized colloids $>0.45\text{-}\mu\text{m}$ diameter. To measure the mobile load of a constituent in the groundwater, we must allow the porous medium itself to act as the filter. Distinctions between the dissolved and particulate load of a sample should be made only by using the smallest pore size membrane filters available or analytical techniques responsive only to dissolved species.

In the McDonalds Branch watershed in the Pine Barrens of southern New Jersey, the acidic, anoxic Swamp Deep groundwater contained about 60 mg L^{-1} suspended particles identified as kaolinite and chamosite plate fragments and some goethite crystals. About one-half of the total organic carbon (0.7 mg C L^{-1}) was associated with particles of diameter $>30 \text{ nm}$. The oxic, acidic Upland Deep groundwater, sampled only 60 m away from the Swamp Deep well and in the same geologic formation, was nearly devoid of suspended particles.

The chemistry of the groundwaters of central Delaware depends on the permeability of the overlying soil layer [Denver, 1986]. The anoxic Lc42-01 groundwater, overlain by poorly drained soils that inhibit the infiltration of aerated rainwater, contained about 6 mg L^{-1} inorganic colloids identified mainly as muscovite and kaolinite fragments and amorphous Fe hydrous oxides. About one-third of the total organic carbon (1.2 mg C L^{-1}) was associated with particles of diameter $>30 \text{ nm}$. The oxic, acidic Md22-01 groundwater contained very low colloid concentrations ($<1 \text{ mg L}^{-1}$).

Based on our field evidence, we infer that reducing conditions, brought about by the oxidation of organic carbon, induce decementation of the iron oxides and the release of colloids in sandy sediments. The lack of effective collector surfaces (ferric oxyhydroxide coatings on the quartz grains) and the adsorption of organic carbon components, especially humic substances, to positively charged colloid surfaces apparently stabilizes the colloidal suspension in the groundwater.

Acknowledgments. We gratefully acknowledge the assistance of Debbie Lord and Pat Johnsson of the U.S. Geological Survey, Water Resources Division, West Trenton, New Jersey, and Scott Andres of the Delaware Geological Survey, Newark, Delaware, in arranging access to sampling sites and providing background information. We are indebted to Deb Backhus and John MacFarlane for assistance during sample collection trips. John MacFarlane also prepared a number of the graphics accompanying this report. Also, we are grateful to Liyuan Liang for helping with the microelectrophoresis measurements at the California Institute of Technology. Finally, we acknowledge Frank Wobber of the Office of Health and Environmental Research, Ecological Research Division, U.S. Department of Energy for financially supporting this investigation under contract DE-FG02-86ER60413. The manuscript benefited from the comments of Francois Morel.

REFERENCES

- Backhus, D., P. M. Gschwend, and M. D. Reynolds, Sampling colloids in groundwater (abstract), *Eos Trans. AGU*, 67, 954, 1986.
- Baedecker, M. J., and W. Back, Modern marine sediments as a natural analog to the chemically stressed environment of a landfill, *J. Hydrol.*, 43, 393–414, 1979.
- Bond, W. J., Illuvial band formation in a laboratory column of sand, *Soil Sci. Soc. Am. J.*, 50, 265–267, 1986.
- Buddemeier, R. W., and J. R. Hunt, Transport of colloidal contaminants in groundwater: Radionuclide migration at the Nevada Test Site, *Appl. Geochem.*, 3, 535–548, 1988.
- Carroll, D., Role of clay minerals in the transportation of iron, *Geochim. Cosmochim. Acta*, 14, 1–27, 1958.
- Carter, C. H., A regressive barrier and barrier-protected deposit: Depositional environments and geographic setting of the Late Tertiary Cohansey Sand, *J. Sediment. Petrol.*, 48, 933–950, 1978.
- Crerar, D. A., G. W. Knox, and J. L. Means, Biogeochemistry of bog iron in the New Jersey Pine Barrens, *Chem. Geol.*, 24, 111–136, 1979.
- Crerar, D. A., J. L. Means, R. F. Yuretich, M. P. Borcsik, J. L. Amster, D. W. Hastings, G. W. Knox, K. E. Lyon, and R. F. Quiett, Hydrogeochemistry of the New Jersey Coastal Plain, 2, Transport and deposition of iron, aluminum, dissolved organic matter, and selected trace elements in stream, ground-, and estuary water, *Chem. Geol.*, 33, 23–44, 1981.
- Danielsson, L. G., On the use of filters for distinguishing between dissolved and particulate fractions in natural waters, *Water Res.*, 16, 179–182, 1982.
- Davis, J. A., Adsorption of natural dissolved organic matter at the oxide/water interface, *Geochim. Cosmochim. Acta*, 46, 2381–2393, 1982.
- Degeldre, C., B. Baeyens, W. Goerlich, J. Riga, J. Verbist, and P. Stadelmann, Colloids in water from a subsurface fracture in granitic rock, Grimsel Test Site, Switzerland, *Geochim. Cosmochim. Acta*, 53, 603–610, 1989.
- Denver, J. M., Hydrogeology and geochemistry of the unconfined aquifer, west-central and southwestern Delaware, *Rep. Invest. 41*, 100 pp., Del. Geol. Surv., Newark, 1986.
- Dijkerman, J. C., M. G. Cline, and G. W. Olson, Properties and genesis of textural subsoil lamellae, *Soil Sci.*, 104, 7–16, 1967.
- Dolcater, D. L., J. K. Syers, and M. L. Jackson, Titanium as free oxide and substituted forms in kaolinites and other soil minerals, *Clays Clay Miner.*, 18, 71–79, 1970.
- Enfield, C. G., and G. Bengtsson, Macromolecular transport of hydrophobic contaminants in aqueous environments, *Ground Water*, 26, 64–70, 1988.
- Folks, H. C., and F. F. Riecken, Physical and chemical properties of some Iowa soil profiles with clay-iron bands, *Soil Sci. Soc. Am. Proc.*, 20, 575–580, 1956.
- Gibbs, R. J., Effect of natural organic coatings on the coagulation of particles, *Environ. Sci. Technol.*, 17, 237–240, 1983.
- Goldberg, S., and R. A. Glaubig, Effect of saturating cation, pH, and aluminum and iron oxide on the flocculation of kaolinite and montmorillonite, *Clays Clay Miner.*, 35, 220–227, 1987.
- Greenland, D. J., Charge characteristics of some kaolinite-iron hydroxide complexes, *Clay Miner.*, 10, 407–416, 1975.
- Greenland, D. J., and C. J. B. Mott, Surfaces of soil particles, in *The Chemistry of Soil Constituents*, edited by D. J. Greenland and M. H. B. Hayes, pp. 321–353, John Wiley, New York, 1978.
- Gschwend, P. M., and M. D. Reynolds, Monodisperse ferrous phosphate colloids in an anoxic groundwater plume, *J. Contam. Hydrol.*, 1, 309–327, 1987.
- Gschwend, P. M., D. Backhus, and J. K. MacFarlane, Mobilization of colloids in groundwater due to infiltration of water near an electric generating station, *Rep. MIT-EL 88-004*, Mass. Inst. Technol. Energy Lab., 28 pp., Cambridge, 1988.
- Holm, T. R., G. K. George, and M. J. Barcelona, Oxygen transfer through flexible tubing and its effects on ground water sampling results, *Ground Water Monit. Rev.*, 8, 83–89, 1988.
- Hunter, K. A., and P. S. Liss, The surface charge of suspended particles in estuarine and coastal waters, *Nature*, 282, 823–825, 1979.
- James, R. O., and T. W. Healy, Adsorption of hydrolyzable metal ions at the oxide-water interface, II, Charge reversal of SiO_2 and TiO_2 colloids by adsorbed Co(II) , La(III) , and Th(IV) as model systems, *J. Colloid Interface Sci.*, 40, 53–64, 1972.
- Johnson, A. H., Acidification of headwater streams in the New Jersey Pine Barrens, *J. Environ. Qual.*, 14, 314–323, 1979.
- Johnson, B. D., and P. L. Wangersky, Seawater filtration: Particle flow and impaction considerations, *Limnol. Oceanogr.*, 30, 966–971, 1985.
- Johnsson, P. A., and D. G. Lord, Water budget and chemical input/output budgets for McDonalds Branch basin, New Jersey Pinelands (abstract), *Eos Trans. AGU*, 68, 271, 1987.
- Johnston, R. H., Digital model of the unconfined aquifer in central

- and southeastern Delaware, *Bull.* 15, 47 pp., Del. Geol. Surv., Newark, 1977.
- Jordan, R. R., Columbia (Pleistocene) sediments of Delaware, *Bull.* 12, 69 pp., Del. Geol. Surv., Newark, 1964.
- Kennedy, V. C., G. W. Zellweger, and B. F. Jones, Filter pore-size effects on the analysis of Al, Fe, Mn, and Ti in water, *Water Resour. Res.*, 10, 785-790, 1974.
- Kia, S. F., H. S. Fogler, and M. G. Reed, Effect of pH on colloiddally induced fines migration, *J. Colloid Interface Sci.* 118, 158-168, 1987.
- Kimmel, G. E., and O. C. Braids, Leachate plumes in ground water from Babylon and Islip landfills, Long Island, New York, *U.S. Geol. Surv. Prof. Pap.*, 1085, 38 pp., 1980.
- Langmuir, D., Geochemistry of iron in a coastal-plain groundwater of the Camden, New Jersey, area, *U.S. Geol. Surv. Prof. Pap.*, 650-C, C224-C235, 1969.
- Langmuir, D., Eh-pH determination, in *Procedures in Sedimentary Petrology*, edited by R. E. Carver, pp. 597-634, Wiley Interscience, 1971a.
- Langmuir, D., Particle size effect on the reaction goethite = hematite + water, *Am. J. Sci.*, 271, 147-156, 1971b.
- Langmuir, D., and D. O. Whittemore, Variations in the stability of precipitated ferric oxyhydroxides, in *Non-Equilibrium Systems in Natural Water Chemistry*, *Adv. Chem. Ser.*, vol. 106, edited by J. D. Hem, pp. 209-234, American Chemical Society, Washington, D. C., 1971.
- Leenheer, J. A., and H. A. Stuber, Migration through soil of organic solutes in an oil-shale process water, *Environ. Sci. Technol.*, 15, 1467-1475, 1981.
- Lindberg, R. D., and D. D. Runnells, Groundwater redox reactions: An analysis of equilibrium state applied to Eh measurements and geochemical modeling, *Science*, 225, 925-927, 1984.
- Little, S., Fire and plant succession in the New Jersey Pine Barrens, in *Pine Barrens: Ecosystem and Landscape*, edited by R. T. T. Forman, pp. 297-314, Academic, San Diego, Calif., 1979.
- Lord, D. G., J. L. Barringer, P. A. Johnsson, P. F. Schuster, R. L. Walker, J. E. Fairchild, B. N. Sroke, and E. Jacobsen, Hydrogeochemical data from an acidic deposition study at McDonalds Branch basin in the New Jersey Pinelands, 1983-1986, *U.S. Geol. Surv. Open File Rep.*, 88-500, in press, 1989.
- Matlack, K. S., D. W. Houseknecht, and K. R. Applin, Emplacement of clay into sand by infiltration, *J. Sediment. Petrol.*, 59, 77-87, 1989.
- McDowell-Boyer, L. M., J. R. Hunt, and N. Sitar, Particle transport through porous media, *Water Resour. Res.*, 22, 1901-1921, 1986.
- Means, J. L., D. A. Crerar, and J. O. Duguid, Migration of radioactive waste: Radionuclide mobilization by complexing agents, *Science*, 200, 1477-1481, 1978.
- Menzel, D. W., and R. F. Vaccaro, The measurement of dissolved organic and particulate carbon in seawater, *Limnol. Oceanogr.*, 9, 138-142, 1964.
- Miller, W. P., D. C. Martens, and L. W. Zelazny, Effects of manure amendment on soil chemical properties and hydrous oxides, *Soil Sci. Soc. Am. J.*, 49, 856-861, 1985.
- Morgan, M. D., Acidification of headwater streams in the New Jersey Pinelands: A re-evaluation, *Limnol. Oceanogr.*, 29, 1259-1266, 1984.
- Morgan, M. D., and R. E. Good, Stream chemistry in the New Jersey Pinelands: The influence of precipitation and watershed disturbance, *Water Resour. Res.*, 24, 1091-1100, 1988.
- Morris, J. C., and W. Stumm, Redox equilibria and measurements of potentials in the aquatic environment, in *Equilibrium Concepts in Natural Water Systems*, *Adv. Chem. Ser.*, vol. 67, edited by W. Stumm, pp. 270-285, American Chemical Society, Washington, D. C., 1967.
- Mudroch, A., A. J. Zeman, and R. Sandilands, Identification of mineral particles in fine grained lacustrine sediments with transmission electron microscope and X-ray energy dispersive spectroscopy, *J. Sediment. Petrol.*, 47, 244-250, 1977.
- Newton, P. P., and P. S. Liss, Positively charged suspended particles: Studies in an iron-rich river and its estuary, *Limnol. Oceanogr.*, 32, 1267-1276, 1987.
- Nicholson, R. V., J. A. Cherry, and E. J. Reardon, Migration of contaminants in groundwater at a landfill: A case study, 6, *Hydrogeochemistry*, *J. Hydrol.*, 63, 131-176, 1983.
- Nightingale, H. I., and W. C. Bianchi, Ground-water turbidity resulting from artificial recharge, *Ground Water*, 15, 146-152, 1977.
- Oades, J. M., Interactions of polycations of aluminum and iron with clays, *Clays Clay Miner.*, 32, 49-56, 1984.
- Packham, R. F., Some studies of the coagulation of dispersed clays with hydrolyzing salts, *J. Colloid Sci.*, 20, 81-92, 1965.
- Parks, G. A., Aqueous surface chemistry of oxides and complex oxide minerals, in *Equilibrium Concepts in Natural Water Systems*, *Adv. Chem. Ser.*, vol. 67, edited by W. Stumm, pp. 121-160, American Chemical Society, Washington, D. C., 1967.
- Pashley, R. M., Electromobility of mica particles dispersed in aqueous solutions, *Clays Clay Miner.*, 33, 193-199, 1985.
- Patrick, W. P., Jr., and R. E. Henderson, A method for controlling redox potential in packed soil cores, *Soil. Sci. Soc. Am. J.*, 45, 35-38, 1981a.
- Patrick, W. P., Jr., and R. E. Henderson, Reduction and reoxidation cycles of manganese and iron in flooded soil and in water solution, *Soil Sci. Soc. Am. J.*, 45, 855-859, 1981b.
- Pettijohn, F. J., R. E. Potter, and R. Siever, *Sand and Sandstone*, 2nd ed., 553 pp., Springer-Verlag, New York, 1987.
- Postma, D., and B. S. Brockenhuus-Schack, Diagenesis of iron in proglacial sand deposits of late- and post-Weichselian age, *J. Sediment. Petrol.*, 57, 1040-1053, 1987.
- Reynolds, M. D., Colloids in groundwater, M.S. thesis, 99 pp., Dep. of Civ. Eng., Mass. Inst. of Technol., Cambridge, 1985.
- Rhodehamel, E. C., Geology of the Pine Barrens of New Jersey, in *Pine Barrens: Ecosystem and Landscape*, edited by R. T. T. Forman, pp. 39-60, Academic, San Diego, Calif., 1979a.
- Rhodehamel, E. C., Hydrology of the New Jersey Pine Barrens, in *Pine Barrens: Ecosystem and Landscape*, edited by R. T. T. Forman, pp. 147-167, Academic, San Diego, Calif., 1979b.
- Robie, R. A., B. S. Hemingway, and J. R. Fisher, Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10^5 pascals) pressure and at higher temperatures, *U.S. Geol. Surv. Bull.* 1452, 456 pp., 1978.
- Ryan, J. N., Groundwater colloids in two Atlantic Coastal Plain aquifers: Colloid formation and stability, M.S. thesis, 250 pp., Dep. of Civ. Eng., Mass. Inst. of Technol., Cambridge, 1988.
- Schwertmann, U., The effect of pedogenic environments on iron oxide minerals, *Adv. Soil Sci.*, 1, 171-200, 1985.
- Short, S. A., R. T. Lowson, and J. Ellis, $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{234}\text{U}$ activity ratios in the colloidal phases of aquifers in lateritic weathered zones, *Geochim. Cosmochim. Acta*, 52, 2555-2563, 1988.
- Smith, A. L., Electrical phenomena associated with the solid-liquid interface, in *Dispersion of Powders in Liquids*, edited by G. D. Parfitt, pp. 86-131, John Wiley, New York, 1973.
- Stumm, W., and G. F. Lee, Oxygenation of ferrous iron, *Ind. Eng. Chem.*, 53, 143-146, 1961.
- Sumner, M. E., Effect of iron oxides on positive and negative charges in clays and soils, *Clay Miner. Bull.*, 5, 218-226, 1963.
- Swanson, K. A., and A. H. Johnson, Trace metal budgets for a forested watershed in the New Jersey Pine Barrens, *Water Resour. Res.*, 16, 373-376, 1980.
- Swartzen-Allen, S. L., and E. Matijevic, Colloid and surface properties of clay suspensions, III. Stability of montmorillonite and kaolinite, *J. Colloid Interface Sci.*, 56, 159-167, 1976.
- Tipping, E., The adsorption of aquatic humic substances by iron oxides, *Geochim. Cosmochim. Acta*, 45, 191-199, 1981.
- Tipping, E., and D. Cooke, The effects of adsorbed humic substances on the surface charge of goethite ($\alpha\text{-FeOOH}$) in freshwaters, *Geochim. Cosmochim. Acta*, 46, 75-80, 1982.
- Tipping, E., and D. C. Higgins, The effect of adsorbed humic substances on the colloid stability of haematite particles, *Colloids Surf.*, 5, 85-92, 1982.
- Turner, R. S., A. H. Johnson, and D. Wang, Biogeochemistry of aluminum in McDonalds Branch watershed, New Jersey Pine Barrens, *J. Environ. Qual.*, 14, 314-323, 1985.
- U.S. Department of Agriculture, Soil survey of Kent County, Delaware, 66 pp., Soil Conserv. Serv., Washington, D. C., 1971.
- van Olphen, H., *An Introduction to Clay Colloid Chemistry*, 2nd ed., 301 pp., Wiley Interscience, New York, 1977.
- Wagman, D. D., W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, Selected values of chemical thermodynamic properties, *NBS Tech. Note U.S.*, 270-3, 264 pp., 1968.
- Wagman, D. D., W. H. Evans, V. B. Parker, I. Halow, S. M.

- Bailey, and R. H. Schumm, Selected values of chemical thermodynamic properties, *NBS Tech. Note U.S.*, 270-4, 141 pp., 1969.
- Walker, T. R., B. Waugh, and A. J. Crone, Diagenesis in first-cycle desert alluvium of Cenozoic age, southwestern United States and northwestern Mexico, *Geol. Soc. Am. Bull.*, 89, 19-32, 1978.
- Williams, D. J. A., and K. P. Williams, Electrophoresis and zeta potential of kaolinite, *J. Colloid Interface Sci.*, 65, 79-87, 1978.
- Yuretich, R. F., D. A. Crerar, D. J. J. Kinsman, J. L. Means, and M. P. Borcsik, Hydrogeochemistry of the New Jersey Coastal Plain, 1, Major-element cycles in precipitation and river water, *Chem. Geol.*, 33, 1-21, 1981.
- P. M. Gschwend and J. N. Ryan, Ralph M. Parsons Laboratory, Department of Civil Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139.

(Received September 12, 1988;
revised September 14, 1989;
accepted September 18, 1989.)