Colloid Mobilization in Two Atlantic Coastal Plain Aquifers: Field Studies

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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 (~100 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 ≥1 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-Boyse et al., 1986; Gschwend and Reynolds, 1987; Enfield and Bengtsson, 1988; Short et al., 1988; Buddebohm and Hunt, 1988; Dequeudre 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 colloidally associated species). Typically, filtration through 0.45-μm 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 [Cerco 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
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
The 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 Cohasney 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, oxide 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 shoreface sequence of sands containing about 83% quartz, 15% feldspars, 1% micas, 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, oxide 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 groundwater, 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 colloidal load. Another well, Ml22-01, located about 5 km southeast of well Lc42-01, was also sampled in October 1987 and found to contain acidic, oxide groundwater. Thus these two wells represent the two groundwater types identified by Denver [1986]. Well Lc42-01 was installed in September 1982, and well Ml22-01 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.
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 Bakhtus 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 (~100 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, E₅, 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 EM1 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,
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 (\(R^2 = 0.9955\)): \(I = 355 \times C - 395.5\), 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 \(N\) HNO\(_3\) 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\(^\circ\)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-\(\mu\)m 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 3400 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-\(\mu\)m 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\(_{\alpha}\) X-ray generator was used to analyze the samples, and the diffractogram was interpreted using a computer-based peak identification routine.

The laboratory were used to handle the groundwater samples was cleaned by soaking in 2 \(N\) HNO\(_3\) 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-\(\mu\)m Nuclepore filters. The total and filtered samples were acidified to pH 1.0 by addition of concentrated HNO\(_3\) 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 ±4%. For determination of total and dissolved organic carbon, the total and filtered samples were separated by 0.030 μm Nucleopore 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 CO₂ 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 ±10%.

The volume of groundwater forced through each filter was less than 1 mL cm⁻², 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 0.30-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 (ζV) of the particles using the rationalized form of the Henry equation for ζ < 25 mV and 0.1 ≤ κa ≤ 200, where κ is the reciprocal Debye-Hückel double-layer thickness and a is the radius of curvature of the particle [Smith, 1973]:

\[
\zeta = \frac{3}{2} \frac{U \mu}{\varepsilon_0} [1 + f(\kappa a)]^{-1}
\]

where \( U \) is the mean electrophoretic mobility of the particle (m² s⁻¹ V⁻¹), \( \mu \) is the dynamic viscosity of the fluid (kg m⁻¹ s⁻¹), \( \varepsilon_0 \) is the dielectric constant of water (78.54 for water at 25°C), \( 10^{12} \) C² J⁻¹ 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 \( \kappa a \) values. At \( \kappa a > 200 \), the Henry equation converges to the Smoluchowski equation (\( \zeta = U \mu / \varepsilon_0 \)). 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 \( \kappa a \) for the natural and acidified samples assuming that the radius of curvature of the average particle observed was 1 μm. Values of \( \kappa a \) for the groundwater ranged from about 50 to 500. The error associated with the measurements of mobility is about ±10%, but as the particle mobility approaches zero, the error increases to about ±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 Ml22-01 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 [Lanomait, 1971a]; however, the effect of disequilibrium between irreversible and biologically mediated redox reactions (such as \( H_2S-SO_4^- \)) 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 (<50 < 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 polydisperse nature of the groundwater particle distributions and the presence of large (>1 μm) 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 [Gischwind 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 Ml22-01 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]

<table>
<thead>
<tr>
<th>Component</th>
<th>Swamp Shallow</th>
<th>Swamp Deep</th>
<th>Upland Deep</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Lord et al.*</td>
<td>This Work†</td>
<td>Lord et al.*</td>
</tr>
<tr>
<td>Light-scattering intensity, c s⁻¹</td>
<td>500</td>
<td>20,000</td>
<td>300</td>
</tr>
<tr>
<td>Colloids, mg L⁻¹</td>
<td>~2</td>
<td>~60</td>
<td>~60</td>
</tr>
<tr>
<td>Temperature, °C</td>
<td>9.4</td>
<td>12</td>
<td>11</td>
</tr>
<tr>
<td>pH</td>
<td>3.9</td>
<td>3.7</td>
<td>4.9</td>
</tr>
<tr>
<td>Eμ, V</td>
<td>~0.028</td>
<td>~0.29</td>
<td>~0.19</td>
</tr>
<tr>
<td>DOC, μM</td>
<td>16</td>
<td>95</td>
<td>34</td>
</tr>
<tr>
<td>Conductivity, μS cm⁻¹</td>
<td>110</td>
<td>93</td>
<td>27</td>
</tr>
<tr>
<td>Alkalinity, μeq L⁻¹</td>
<td>~210</td>
<td>7.5</td>
<td>~</td>
</tr>
<tr>
<td>Ionic strength, μM</td>
<td>~1000</td>
<td>~260</td>
<td>~1000</td>
</tr>
<tr>
<td>Na⁺, μM</td>
<td>100</td>
<td>~78</td>
<td>~65</td>
</tr>
<tr>
<td>K⁺, μM</td>
<td>4.9</td>
<td>4.6</td>
<td>~7</td>
</tr>
<tr>
<td>Ca²⁺, μM</td>
<td>18</td>
<td>10</td>
<td>~40</td>
</tr>
<tr>
<td>Mg²⁺, μM</td>
<td>22</td>
<td>12</td>
<td>~41</td>
</tr>
<tr>
<td>NH₄⁺, μM</td>
<td>3.1</td>
<td>0.7</td>
<td>~0.3</td>
</tr>
<tr>
<td>Cl⁻, μM</td>
<td>160</td>
<td>95</td>
<td>~81</td>
</tr>
<tr>
<td>SO₄²⁻, μM</td>
<td>160</td>
<td>31</td>
<td>~68</td>
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<tr>
<td>NO₃⁻, μM</td>
<td>~1</td>
<td>~1</td>
<td>~4.0</td>
</tr>
<tr>
<td>Si, μM</td>
<td>~</td>
<td>~</td>
<td>~67.8</td>
</tr>
<tr>
<td>Total, Dissolved</td>
<td>91</td>
<td>105</td>
<td>82</td>
</tr>
<tr>
<td>Fe, μM</td>
<td>~</td>
<td>~</td>
<td>~</td>
</tr>
<tr>
<td>Total, Dissolved</td>
<td>51</td>
<td>36.6</td>
<td>37</td>
</tr>
<tr>
<td>Al, μM</td>
<td>~</td>
<td>~</td>
<td>~</td>
</tr>
<tr>
<td>Total, Dissolved</td>
<td>61</td>
<td>43.8</td>
<td>4.0</td>
</tr>
<tr>
<td>TOC, mg C L⁻¹</td>
<td>~</td>
<td>~</td>
<td>~</td>
</tr>
<tr>
<td>DOC</td>
<td>19</td>
<td>46</td>
<td>1.2</td>
</tr>
</tbody>
</table>

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 (±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 Mudrock 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 Cohasey Sand [Rhodehamel, 1979a; Cerrara 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

<table>
<thead>
<tr>
<th></th>
<th>Anoxic GW*</th>
<th>Lc42-01 (This Work)†</th>
<th>Oxic GW*</th>
<th>Md22-01 (This Work)†</th>
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<tbody>
<tr>
<td>Light-scattering intensity, c s⁻¹</td>
<td>2,100</td>
<td>260</td>
<td></td>
<td></td>
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<td>Colloids, mg L⁻¹</td>
<td>—6</td>
<td>—1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature, °C</td>
<td>14.5</td>
<td>14.0</td>
<td>15.0</td>
<td>18.0</td>
</tr>
<tr>
<td>pH</td>
<td>6.3</td>
<td>6.2</td>
<td>5.3</td>
<td>4.3</td>
</tr>
<tr>
<td>Eₜ, V</td>
<td>—</td>
<td>+0.10</td>
<td>—</td>
<td>+0.38</td>
</tr>
<tr>
<td>DO, μM</td>
<td>&lt;10</td>
<td>19</td>
<td>200</td>
<td>180</td>
</tr>
<tr>
<td>Conductivity, μS cm⁻¹</td>
<td>120</td>
<td>175</td>
<td>150</td>
<td>320</td>
</tr>
<tr>
<td>Alkalinity, mg L⁻¹</td>
<td>43</td>
<td>—</td>
<td>7.9</td>
<td>—</td>
</tr>
<tr>
<td>Ionic strength, mM</td>
<td>2.1</td>
<td>—</td>
<td>1.0</td>
<td>—</td>
</tr>
<tr>
<td>Na⁺, μM</td>
<td>300</td>
<td>—</td>
<td>420</td>
<td>—</td>
</tr>
<tr>
<td>K⁺, μM</td>
<td>27</td>
<td>—</td>
<td>40</td>
<td>—</td>
</tr>
<tr>
<td>Ca²⁺, μM</td>
<td>210</td>
<td>—</td>
<td>120</td>
<td>—</td>
</tr>
<tr>
<td>Mg²⁺, μM</td>
<td>73</td>
<td>—</td>
<td>57</td>
<td>—</td>
</tr>
<tr>
<td>NH₄⁺, μM</td>
<td>11</td>
<td>—</td>
<td>0.7</td>
<td>—</td>
</tr>
<tr>
<td>Cl⁻, μM</td>
<td>270</td>
<td>—</td>
<td>340</td>
<td>—</td>
</tr>
<tr>
<td>SO₄²⁻, μM</td>
<td>220</td>
<td>—</td>
<td>17</td>
<td>—</td>
</tr>
<tr>
<td>NO₃⁻, μM</td>
<td>1.6</td>
<td>—</td>
<td>130</td>
<td>—</td>
</tr>
<tr>
<td>Si, μM</td>
<td>Total</td>
<td>426</td>
<td>—</td>
<td>280</td>
</tr>
<tr>
<td>Dissolved</td>
<td>530</td>
<td>406</td>
<td>350</td>
<td>251</td>
</tr>
<tr>
<td>Fe, μM</td>
<td>Total</td>
<td>144</td>
<td>—</td>
<td>0.8</td>
</tr>
<tr>
<td>Dissolved</td>
<td>290</td>
<td>70.7</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>Al, μM</td>
<td>Total</td>
<td>6.4</td>
<td>—</td>
<td>21.5</td>
</tr>
<tr>
<td>Dissolved</td>
<td>&lt;0.1</td>
<td>0.4</td>
<td>0.1</td>
<td>71.5</td>
</tr>
<tr>
<td>TOC, mg C L⁻¹</td>
<td>3.3</td>
<td>—</td>
<td>1.1</td>
<td>—</td>
</tr>
<tr>
<td>DOC</td>
<td>2.2</td>
<td>2.1</td>
<td>5.4</td>
<td>1.0</td>
</tr>
</tbody>
</table>

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, 1988]. 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 Fe(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 composed 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 Si⁴⁺ atoms with an Al³⁺ atom in the tetrahedral layers [Greenland and Moir, 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
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 colloiddally 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.
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; Kuo 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 $E_d$ 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 titration 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 Fe$^{3+}$, which is oxidized to Fe$^{4+}$ 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 Cohanset 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 [Dikeman et al., 1967; Walker et al., 1978; Bodd, 1986; Matlock 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
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.

### TABLE 4. Electrophoretic Mobilities and $\zeta$ Potentials of Groundwater Particles Under Natural and Acidified Conditions

<table>
<thead>
<tr>
<th>Groundwater</th>
<th>pH</th>
<th>Mobility, ($m^2 \cdot s^{-1}$)</th>
<th>$\zeta$ Potential, mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Swamp Deep</td>
<td>4.6</td>
<td>$-0.81 \times 10^8$</td>
<td>$-11$</td>
</tr>
<tr>
<td></td>
<td>3.3</td>
<td>$-0.45 \times 10^8$</td>
<td>$-6.0$</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>$+0.72 \times 10^8$</td>
<td>$+9.5$</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>$+0.74 \times 10^8$</td>
<td>$+9.6$</td>
</tr>
<tr>
<td>Lc42-01</td>
<td>6.4</td>
<td>$-1.91 \times 10^8$</td>
<td>$-25$</td>
</tr>
<tr>
<td></td>
<td>3.6</td>
<td>$-1.40 \times 10^8$</td>
<td>$-18$</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>$-0.90 \times 10^8$</td>
<td>$-12$</td>
</tr>
<tr>
<td></td>
<td>2.3</td>
<td>$-0.45 \times 10^8$</td>
<td>$-5.9$</td>
</tr>
<tr>
<td></td>
<td>1.7</td>
<td>$0 \times 10^8$</td>
<td>$0$</td>
</tr>
</tbody>
</table>
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 large 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 [Swartz-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 colloidally 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 [Cerar 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 suspensions 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 colloidally 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 unsaturated 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 Whitemore, 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 $10^{-40}$ to $10^{-43}$) 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 exist with Fe(II) 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...
Fe(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 downgradient 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 cementation 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 (~100 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-$\mu$m filtra-
tion clearly causes overestimates of the actual dissolved load by
including colloids of diameter <0.45 μm in the dissolved
fraction, and underestimates of the actual mobile load by
excluding mobilized colloids >0.45μm diameter. To mea-
sure 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 respon-
sive 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 nm. The oxic, acidic Upland Deep ground-
water, sampled only 60 m away from the Swamp Deep well and
in the same geologic formation, was nearly devoid of sus-
pended particles.

The chemistry of the groundwaters of central Delaware
depends on the permeability of the overlying soil layer
[Denver, 1986]. The anoxic Lac-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 nm. The oxic, acidic Md-22-01 groundwater
contained very low colloid concentrations (<1 mg L⁻¹).

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

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