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# ROLE OF MOBILE COLLOIDS IN THE TRANSPORT OF CHEMICAL POLLUTANTS IN GROUNDWATERS

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## ABSTRACT

Mobile colloids in groundwater enhance the transport of chemicals which sorb to particle surfaces. This study addressed the potential for colloid-mediated transport in Wisconsin aquifers by developing fundamental data on colloid concentrations and properties in representative systems. The aquifers examined included those classified as fractured dolomite, sorted sand, and calcareous till, all highly oxic and relatively unperturbed. A broad range of characterization methods were applied to whole groundwater and colloid concentrates prepared by ultracentrifugation and ultrafiltration. Colloid sorption characteristics were probed with a  $^{14}\text{C}$ -labeled PCB congener. Colloid concentrations ranged from 200 to 700  $\mu\text{g liter}^{-1}$ , and seasonal variations were noted in at least two systems. Mass-size distributions were typically broad, with shallow maxima in the 30 to 50 and 400 to 1000 nm size intervals. Scanning electron microscopy/energy dispersive x-ray analysis (SEM/EDX) and elemental analysis revealed that larger colloids are dominated by clay and silica particles. Smaller particles, however, were more difficult to categorize. The organic matter component of colloid isolates was high, whereas concentrations of colloidal iron were generally low. Electrophoretic mobilities of colloidal particles were consistent with a model of colloid particles with a sorbed surface coating of organic matter. Three-phase partitioning experiments with 2,2',4,4'-tetrachlorobiphenyl (2,2',4,4'-TCBP) revealed that association with colloids can be significant, with up to 23% colloidally bound at natural colloid mass levels. Calculated partition coefficients for colloidal particles ranged from  $1.1 \times 10^5$  to  $4.4 \times 10^5$ . Using a retardation factor approach it was estimated that the presence of mobile colloids in the aquifers, on average, increases the mobility of 2,2',4,4'-TCBP by 10%.



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## ACRONYMS

SEM/EDX - Scanning electron microscopy/energy dispersive x-ray analysis

2,2',4,4'-TCBP - 2,2',4,4'-tetrachlorobiphenyl

DO - Dissolved oxygen

WDATCP - Wisconsin Department of Agriculture, Trade and Consumer Protection

LPE - Linear polyethylene

ICP/OES - Inductively coupled plasma/optical emission spectrometry

DOC - Dissolved organic carbon

NDIR - Non-dispersive infrared

NMWCO - Nominal molecular weight cutoff

GFAA - Graphite furnace atomic absorption spectrophotometry

QELS-PCS - Quasi-elastic light scattering - photon correlation spectroscopy

$K_{ow}$  - Octanol-water partition coefficient



## INTRODUCTION

The presence of synthetic organic contaminants in groundwater systems is a major problem currently facing regulatory and scientific communities. To develop management plans for groundwater protection, an understanding of the factors controlling contaminant transport is needed. The fate/transport models developed to date have difficulty in accurately predicting the movement and residence time of contaminants in aquifers and containment structures. Lack of fundamental data on the chemical and physical form of the contaminant within the aquifer and use of partitioning models which do not accurately reflect mechanisms of sorption and desorption are major factors in poor predictive ability.

Contaminant concentrations and transport in groundwater are usually considered to be regulated by partitioning between the immobile aquifer solid phase and the mobile groundwater solution phase (i.e., a two-phase model). However, recent evidence (McCarthy, 1990; Bouchard et al., 1989) shows that groundwater contains colloidal particles (a third phase) which move with the mobile phase. Association of contaminants (pesticides, metabolites, metals) with colloidal particles ( $< 1 \mu\text{m}$ ) might greatly enhance contaminant transport and have a major influence on contaminant fate and degradation. Direct information on the amounts and nature of mobile colloids is limited and only recently have researchers begun to address factors which may be involved in colloid formation and fate (McCarthy and Zachara, 1989). A need exists for information that allows the role of colloid-mediated transport in subsurface environments and Wisconsin groundwaters in particular, to be assessed.

In view of the current lack of information, an exploratory study was undertaken focusing on three questions: 1. the concentrations of mobile colloids in groundwater, 2. their chemical and physical properties, and 3. their capacity for enhancing transport of chemical contaminants. The approach involved sampling groundwater from four representative aquifers in Wisconsin, isolation of colloids by ultracentrifugation and ultrafiltration techniques, measurement of selected physical and chemical properties of isolated or concentrated particles, and analysis of their contaminant binding characteristics.





## MATERIALS AND METHODS

Field work was carried out in two stages. Stage one goals were to evaluate four diverse Wisconsin aquifers for: 1. colloid concentration, 2. colloid mass-size distribution, 3. phase partitioning (using a  $^{14}\text{C}$ -labeled PCB congener probe), 4. solution geochemistry, and 5. general suitability for more detailed colloid characterization in stage two. An important additional aspect of the first stage was development and evaluation of appropriate sample collection and processing techniques. Work in stage two focused on three wells, culled from the eight surveyed in stage one, and each representative of a major aquifer system. Large volume samples were collected at these sites, colloidal particles were concentrated and/or isolated, and selected chemical and physical properties of colloidal particles were determined. Partitioning experiments on colloid concentrates also were performed in stage two.

The four aquifers under evaluation are described in Table 1. Two wells from each site were sampled. For stage one sampling a bladder pump (stainless steel body) was used at all sites except well 1 where a peristaltic pump was used and at well 2 where a bailer was used. Withdrawal rates ranged from 0.3 to 0.6 liter  $\text{min}^{-1}$  with the bladder pump; the peristaltic pump flow rate averaged 0.12 liter  $\text{min}^{-1}$ . Measurements of pH (Orion Model 701), dissolved oxygen (DO), and temperature (YSI Model 58) were made in a flow-through cell and *in situ*. Water table heights were monitored with a resistance type water level meter. At least five well volumes were purged prior to sample collection, except at the Door County site where only one well volume was removed. The sampling point, 40 ft above well bottom, and short water residence time in the well minimizes sampling artifacts at the Door County site. After purging, 4 liters of groundwater was collected in vessels compatible with the various analytes. Subsamples were taken for immediate filtration (pre-weighed 0.4  $\mu\text{m}$  Nuclepore filters) into an acid-spiked LPE container. Filters were freeze-dried and reweighed to provide an estimate of large particle mass. The acidified filtrates were analyzed for major metals by ICP, and major anions determined on a separate unacidified subsample. Filtration for DOC were performed in the laboratory, typically within 6 hours of collection. DOC samples were collected and processed in ashed darkened glassware. Parallel filtrations through 1.0  $\mu\text{m}$  Nuclepore and 0.02  $\mu\text{m}$  Anotec filters were performed in an attempt to measure "dissolved" and colloidal carbon pools. Carbon determinations were by persulfate oxidation/NDIR detection (OI Model 700). Low particle concentrations and precision of filtration and oxidation steps, however, did not allow colloidal carbon to be estimated by difference.

A 2-liter subsample collected in glass containers was used for measurement of mass-size distributions. Nuclepore filters of 5.0, 1.0, 0.4, 0.1, 0.05, and 0.03  $\mu\text{m}$  pore size were kept in serial and parallel filtration designs. Pressure differentials and filter loadings (20 to 40  $\mu\text{g}/47$  mm diameter filter), were low to help control filter pore clogging. Concentration polarization (Leppard et al., 1989) was minimized by slow filtration rates. Particle masses were determined on a Perkin Elmer (Model AD-2) microbalance. Extensive use of control filters minimized the influence of atmospheric moisture variations on mass measurements.

Table 1. Description of the four aquifers evaluated

Site	Description
<p>Waunakee (Wells 1 and 2)</p>	<p>Aquifer in calcareous till Gently sloping ground moraine Atrazine study site Two wells from field of 25 sampled Well 1 - 6.4 m (21 ft) well, multi-level piezometer, 5.1 cm (2-inch) PVC, peristaltic pump used, tubing in place Well 2 - 19.8 m (65 ft) well, 5.1 cm (2-inch) PVC, bailed Both wells, sand and gravel grouted</p>
<p>Mount Horeb (Wells 3 and 4)</p>	<p>Aquifer in Ordovician dolomite Driftless area, relatively steep valley Atrazine study site Two wells from field of six sampled Well 3 - 21.0 m (69 ft) well, 5.1 cm (2-inch) PVC, bladder pump used Well 4 - 52.2 m (171 ft) well, 5.1 cm (2-inch) PVC, bladder pump used Both wells sand and gravel grouted</p>
<p>Door County-Sevastopool (Wells 5 and 6)</p>	<p>Aquifer in fractured Silurian dolomite Gently sloping, thin ground moraine Two wells from field of seven sampled Well 5 - 73.2 m (240 ft) well, 15.2 cm (6-inch) uncased borehole, bladder pump used Well 6 - 18.3 m (60 ft) well, 15.2 cm (6-inch) uncased borehole, bladder pump used</p>
<p>Lower Wisconsin River - Arena Area (Wells 7 and 8)</p>	<p>Aquifer in sorted sand Nearly flat, outwash flood plain, driftless region One well, of three, at atrazine study site (experimental farm) Well 7 - 7.6 m (25 ft) well, 5.1 cm (2-inch) PVC, indigenous grouting One well, of three, that DATCP maintains Well 8 - 7.6 m (25 ft) well, 5.1 cm (2-inch) PVC, indigenous grouting Bladder pump used at both sites</p>

A tracer partitioning technique was used on unaltered samples and concentrates to estimate contaminant phase distribution. A  $^{14}\text{C}$ -labeled tetrachlorobiphenyl (2,2',4,4'-TCBP) was spiked into a groundwater sample and allowed to equilibrate for 1 to 2 days. The sample was subsequently filtered at 1.0 and 0.02  $\mu\text{m}$  (Anotec) to recover particulate and colloidal phases, respectively. Tracer in the 0.02  $\mu\text{m}$  filtrate was further partitioned into truly dissolved and DOC associated by a C-18 column sorption technique (Landrum et al., 1984). A Waters Sep-Pak C-18 reverse phase column was used in these experiments. Sorption of dissolved PCB to Anotec filter represented <2% of particulate activity. The significance of DOC sorption to the C-18 column was evaluated with a series of humic acid solutions. Over 98.5% of humic material was recovered, indicating that DOC sorption is small. The problem of trapping larger colloids/particles in the column matrix was avoided by passage of only the 0.02  $\mu\text{m}$  filtrate through the column. Desorption of PCB from colloids onto the C-18 column during passage of groundwater was evaluated experimentally and found to be insignificant. Dissolved tracer activity was calculated as:

$$\text{Total} - (\text{Colloid} > 0.02 \mu\text{m} + \text{Colloid} < 0.02 \mu\text{m})$$

$^{14}\text{C}$ -activity was quantified by liquid scintillation counting (Packard Instruments Tri-Carb 1900 CA).

Three wells were selected for more extensive colloid characterization in stage two. Well 5 in Door County (fractured dolomite), well 8 in Arena (sorted sand), and well 1 in Waunakee (calcareous till) were selected for stage two sampling based on data from the first round sampling. At each site a 150 to 250 liter sample was obtained and colloidal particles were concentrated by continuous-flow ultracentrifugation and/or ultrafiltration. Measurements of mass and dissolved chemistries, as described under stage one sampling, were repeated in stage two.

A high capacity electric submersible pump was used to obtain 250 liters of groundwater from the Door County site in November 1990 after removal of five well volumes. The sample was collected in 50-liter LPE carboys and returned to the laboratory for ultracentrifuge processing. A peristaltic pump operating at 1.1 to 1.2 liter  $\text{min}^{-1}$  was employed at the Arena site to collect large volume samples on two dates. In March 1991 a 230-liter sample was obtained and concentrated in the laboratory by ultracentrifugation. In April 1991, a 170-liter sample was concentrated in the field with the ultrafiltration system. The Waunakee site was sampled in June 1991 with a peristaltic pump using a flow rate of 0.085 liter  $\text{min}^{-1}$ . A 160-liter sample was obtained, and processed in the laboratory with the ultrafiltration system.

The ultracentrifuge system incorporates an ultracentrifuge (Beckman Model L8-80M), a continuous-flow zonal rotor (Model CF-32 Ti), and a peristaltic pumping system. Groundwater was pumped through the rotor at a flow rate of 30 ml  $\text{min}^{-1}$ . The rotor was operated at 31,500 rpm, in a 1 micron vacuum and was maintained at near *in situ* temperatures (8 to 10° C). In this manner groundwater colloids in 140 to 200 liter sub-samples were concentrated to 0.5 liter. Collection efficiencies for particles with sedimentation coefficients (S) of 50 to 100 are predicted to approach 100%. Concentrated colloids were characterized directly in suspension (ultracentrifuge concentrate) or after removal of solution by filtration.

This technique has several significant attributes which make it exemplary for colloid collection and concentration: 1. no contaminating filters are used -- the sample contacts only titanium -- sorption losses are minimal; 2. the sample is concentrated in a natural groundwater matrix -- no ionic strength or major ion changes occur; 3. concentrate is readily recovered; 4. large volumes can be processed; and 5. sample can be processed without exposure to air. Drawbacks of the technique include relatively long processing time and poor retention efficiencies for low density particles resulting from the dependence on particle sedimentation coefficient. The latter two factors were addressed by the application of a high capacity ultrafiltration cell.

The ultrafiltration system is comprised of a high capacity tangential flow ultrafiltration cell (Millipore Pellicon Model XX42PSY60), recirculation and feed pumps, and a 15 liter detention vessel. The apparatus is mounted on a 1.5 x 0.61 m (5 x 2 ft) stable platform for transport to field sites. Processing rates (permeate) through the five membrane cassette (10,000 nominal molecular weight cutoff [NMWCO], regenerated cellulose) are in the range of 500 ml min<sup>-1</sup> at a transmembrane pressure of 25 psig and sample tangential flow (retentate) of 6 liter min<sup>-1</sup>. In approximately 5 hours colloidal material in a 150-liter groundwater sample is concentrated by a factor of 75 to 100 (final concentrate volume 1.5 to 2.0 liters).

Major element analysis of colloidal material was performed on weighed subsamples of solids after removal of solution phase by filtration (0.03 and 0.05  $\mu\text{m}$  Nuclepore filters). Particles were completely solubilized in a teflon bomb acid digestion technique (Eggimann and Betzer, 1976). Concentrations of Al, Ca, Fe, and Mn were determined by zeeman corrected graphite furnace atomic absorption (GFAA) (Perkin Elmer 5100Z). Colorimetric techniques were employed for Si and P.

Colloidal organic carbon was estimated from differences in carbon content between suspension concentrates and centrifugates/ultrafiltrates, after correction for inorganic carbon (removed by acidification). Carbon content was determined by a persulfate oxidation/NDIR detection method (OI Model 700), and a high temperature combustion technique (Shimadzu Model 5000). The protein content of colloidal concentrates was determined by Coomassie assay.

The electrophoretic mobility spectra of colloidal particle concentrates was measured on a Pen-Kem System 3000. Modal particle size information was obtained by light scattering (QELS-PCS; Brookhaven BI-200 M).

Subsamples of concentrates, processed through 0.03, 0.05, and 0.4  $\mu\text{m}$  Nuclepore filters, were examined by SEM/EDX (50  $\text{\AA}$  Au coated) to determine the morphology, size, and elemental composition of colloids.

## RESULTS AND DISCUSSION

### Sampling Protocol and Field Data

Collection of a "representative" groundwater sample is critical to the evaluation of colloid concentration and colloid-mediated transport. Improper well installation and/or inappropriate sample collection and processing can compromise sample integrity (Ryan and Gschwend, 1990; Perret et al., 1990). Large particle contamination can occur from several sources including 1. sediment accumulation in well bottom, 2. improperly grouted well, 3. shearing from high pumping rates, 4. improperly flushed well, and 5. dirty sampling apparatus. Colloid concentrations may also be altered by sorption to sampler surfaces, scavenging by large particles, and filtration by incompatible grouting. Though difficult to predict precisely, particles larger than several microns in size would not move through most aquifers and if found in significant quantities would indicate an unrepresentative sample.

These concerns were addressed in our methodology. Well selection criteria included drilling method, type of grouting, and casing/screening materials and dimensions. The wells chosen were uncased boreholes in fractured rock or 2-inch PVC-cased monitoring wells carefully grouted with sand or indigenous material. Sample withdrawal rates were kept below those which would cause a measurable drawdown of water level in the well. At least five well volumes were removed prior to sampling. If a significant fraction of total particle mass was found in particles  $> 5 \mu\text{m}$ , the sample was considered compromised. All samples, including large 200-liter samples, were maintained at near *in situ* temperatures during collection and held at 5 °C if not immediately processed.

Tables 2 and 3 summarize stage one and stage two field data. Groundwater geochemistries are summarized in Tables 4 and 5. The data indicate that all wells were well oxygenated (at least  $7 \text{ mg liter}^{-1}$ ) with low levels of filtrable iron and manganese. Given our processing protocol and these conditions, sampling induced precipitation of iron oxides would be minimal. This finding was supported by a time series experiment where changes in iron concentrate and particle mass were followed; the changes were found to be insignificant. Some depression of oxygen levels is noted in Door County wells. Groundwater temperatures declined significantly at all sites between the fall initial survey and winter/spring large volume collections. These aquifers are relatively shallow and recharge can be rapid. pH values varied within a narrow range for all wells (6.5 to 7.3) and only slight changes were noted between fall and spring sampling.

### Groundwater Geochemistry

The major ion chemistry of sites 1 to 6 are typical of calcareous till and dolomite aquifers throughout the state. Well 2, located near a farm house, shows severe impact from salt and nitrate and is excluded from further analysis. Calcium levels are lower by a factor of 5 to 6, and magnesium levels are lower by four to five times in sandy wells (7 and 8) than at sites 1 to

Table 2. Field data: Stage one sampling.

Well	Sampling date	Well depth		Sample depth		pH	DO, mg liter <sup>-1</sup>	Temperature, °C
		m	ft	m	ft			
1†	9/12/90	6.3	21	5.5	18	7.3	7.4	14.6
2	9/12/90	19.8	65	15.2	50	6.7	7.5	11.3
3	9/18/90	21.0	69	20.1	66	7.1	11.2	10.8
4	9/18/90	52.2	171	51.2	168	6.9	10.6	10.8
5†	9/25/90	73.2	240	59.5	195	7.3	6.8	10.0
6	9/25/90	18.3	60	15.2	50	7.2	7.6	8.6
7	9/27/90	7.6	25	6.3	21	5.8	10.7	11.3
8†	9/27/90	7.6	25	6.3	21	6.5	11.5	11.9

†Stage two sampling sites.

Table 3. Field data: Stage two sampling.

Site	Sampling date	pH	Temperature, °C	DO, mg liter <sup>-1</sup>	Pumping rate, liter min <sup>-1</sup>	Concentration method†
Door County	11/20/90	7.17	7.9	8.25	70	UC
Arena	02/06/91	6.85	9.5	9.77	1.1	UC
Arena	04/11/91	6.73	8.4	10.7	1.2	UF
Waunakee	06/05/91	7.24	8.2	10.2	0.085	UF

†UC is ultracentrifugation; UF is ultrafiltration.

Table 4. Aquifer geochemistry: Cations, mg liter<sup>-1</sup>.

Well	Ca	Mg	Na	K	Fe	Mn
1†	93.8	52.6	6.49	<0.6	<0.01	<0.003
2	165	78.6	78.2	<0.6	<0.01	0.199
3	74.3	39.9	<0.6	<0.6	<0.01	<0.003
4	74.3	39.7	<0.6	<0.6	<0.01	<0.003
5†	68.8	35.3	<0.6	2.65	<0.01	<0.003
6	74.8	38.2	0.86	4.52	<0.01	<0.003
7	12.7	12.1	1.92	<0.6	<0.01	<0.003
8†	25.7	9.3	0.86	<0.6	<0.01	<0.003

†Stage two sampling sites.

Table 5. Aquifer geochemistry: Anions and others, mg liter<sup>-1</sup>.

Well	DOC	Si	Cl	S	NO <sub>3</sub> -N	PO <sub>4</sub> -P
1†	1.39	12.4	39.0	11.7	2.0	0.0323
2	3.44	12.4	211	17.6	29.5	0.0117
3	0.62	4.83	7.5	5.6	4.5	0.0077
4	0.76	5.26	7.5	5.7	7.5	0.0105
5†	3.00	2.35	14.5	7.4	9.0	0.0131
6	3.68	2.31	11.5	6.7	8.0	0.0176
7	0.65	3.19	6.50	4.3	14.5	0.0049
8†	0.52	5.20	26.5	3.5	8.5	0.0159

†Stage two sampling sites.



6. Well 8 appears to contain excess calcium chloride relative to the other sandy aquifer Well 7. DOC levels ranged from 0.52 to 0.64 mg liter<sup>-1</sup> in sandy aquifers, to 1.39 mg liter<sup>-1</sup> in Waunakee till, to >3 mg liter<sup>-1</sup> at the fractured dolomite site. Silicon also exhibited about a six fold range in concentration between sites, ranging from a low of 2.3 mg liter<sup>-1</sup> in Door County to 12.4 mg liter<sup>-1</sup> at Waunakee. Wells within a given general aquifer matrix exhibited similar solution geochemistries. As mentioned previously, wells 1, 5, and 8 were chosen for repeat, large volume sampling. These sites cover the full range of DOC, Si, and Ca concentrations and allow us to test relationships between solution and particle geochemistry. Little variance from fall values in major ion chemistries of wells 1, 5, and 8 were noted on repeat sampling. We attempted to select wells that represent common Wisconsin aquifer matrices, minimally impacted by point pollution sources or generalized areas of reducing conditions. By observing these criteria the task of colloidal characterization was more difficult.

### Colloid Mass Concentration and Mass-Size Structure

Total colloid mass concentrations, determined from Nuclepore filtrations of unaltered groundwater, are given in Table 6 along with total particle mass concentrations. Colloid concentrations in the first round of sampling ranged from a low of 201  $\mu\text{g liter}^{-1}$  at a Mt. Horeb well to 709  $\mu\text{g liter}^{-1}$  at the Waunakee site; with a modal value of 325  $\mu\text{g liter}^{-1}$ . As a percentage of total mass, colloid masses ranged from 33% (Mt. Horeb) to 60 to 70% (Door County and Waunakee sites). Colloidal is defined here as < 1.0  $\mu\text{m}$ . If the mass data from the two wells in each aquifer system are pooled, there is no significant difference in colloid concentrations between systems. The exception is the Waunakee site (well 1), exhibiting roughly double the modal value. Colloid and total mass levels measured in the second phase of sampling differed in several respects from those of the first round. While the Door County data reveal remarkable consistency (colloid mass 339 versus 335  $\mu\text{g liter}^{-1}$ ; total mass 389 to 455 versus 512  $\mu\text{g liter}^{-1}$ ), the other two systems show marked reductions in colloid mass and total mass in spring collections. Colloid concentrations declined a barely significant 30% at the Arena site, while total mass fell by >60%. At the Waunakee site, colloid and total mass declined approximately 65%. The percentage of total mass represented by colloids was exceptionally consistent in the second round of sampling, averaging 76%. It is tempting to attribute the observed changes to seasonally variable physical and geochemical processes, however, until more detailed sampling is accomplished it is reported as an interesting trend. Pumping and processing methods were, however, consistent between rounds. The high flow, relatively deep, extremely permeable, fractured dolomite system (Door County) may be relatively insensitive to seasonally variable stresses, while the shallow, relatively low flow Waunakee system, in particular, may respond to environmental stresses such as temperature changes, oxygen demand, and water table fluctuations.

Published values of colloid concentrations in groundwaters of similar origin are few. In studies of groundwater colloids, either direct mass measurements were not attempted (Short et al., 1988; Degueldre et al., 1989; Waber et al., 1990) or the system was perturbed (Gschwend and Reynolds, 1987) or anoxic (Ryan and Gschwend, 1990), resulting in exceptionally high colloid concentrations. Ryan and Gschwend (1990) report a colloid concentration of  $\leq 1 \text{ mg liter}^{-1}$  for oxic groundwaters in a graded sand aquifer in New Jersey. Their mass values were based on a calibration of light scattering data with synthetic suspensions of kaolinite. Degueldre et al. (1989) report colloid mass concentrations of 100 to 200  $\mu\text{g liter}^{-1}$  for a fractured granite

aquifer. Their estimates were based on SEM counting of filter collected particles and assumptions of particle density. Groundwater colloid concentrations of approximately 200  $\mu\text{g liter}^{-1}$  were reported by Waber et al. (1990), who based their estimates on elemental analysis of ultrafiltration concentrates and postulates of particle phases.

Table 6. Colloid mass summary: Stage 1 and stage 2 sampling.

	Colloid mass (1.0 - 0.03 $\mu\text{m}$ ), $\mu\text{g liter}^{-1}$	Total mass ( $> 0.03 \mu\text{m}$ ) $\mu\text{g liter}^{-1}$	Colloid mass, % of total mass
<u>Stage 1 Sampling</u>			
<u>Well</u>			
1	709	1,006	70
2	2,850	52,720†	5†
3	201	606	33
4	415	1,254	33
5	335	512	65
6	400	700	57
7	301	1,920	16
8	293	629	47
<u>Stage 2 Sampling</u>			
<u>Site</u>			
Door County, Well 5	339	389-455	75
Arena (UC)‡, Well 8	---	280	---
Arena (UF)‡, Well 8	195	247	79
Waunakee, Well 1	266	220-355	75

†Silt contaminated.

‡UC is ultracentrifugation; UF is ultrafiltration.

Examples of colloid mass-size distribution are given in Figure 1. Mass data are tabulated in Tables 7 and 8. When presented as log-log plots, most distributions are fairly uniform, though several groundwater samples show minima in colloid concentrations in the 100 to 400 nm size ranges. Maxima in the 30 to 50 and 400 to 1,000 nm size intervals are common. Very high colloid concentrations were evident in the 30 to 50 nm fraction at the Waunakee site in

Table 7. Particle mass-size distribution: Stage 1 sampling,  $\mu\text{g liter}^{-1}$ .

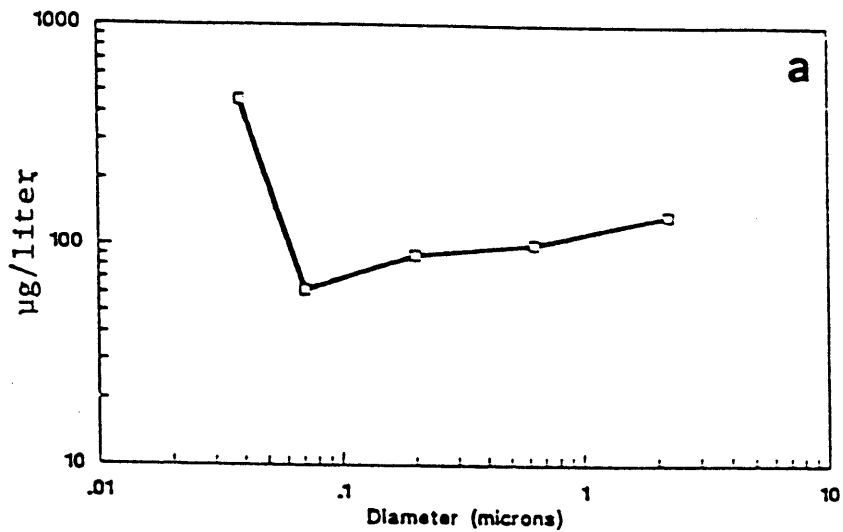
Size range $\mu\text{m}$	Well number							
	1	2†	3	4	5	6	7	8
> 5.0	160	36,930	260	640	130	220	1,280	247
5.0-1.0	137	1,390	145	199	47	80	335	89
1.0-0.4	100	1,000	44	54	122	53	121	53
0.4-0.1	89	450	30	68	19	39	13	39
0.1- 0.05	62	500	22	47	51	81	30	132
0.05- 0.03	458	905	105	246	143	228	137	70

†Silt contaminated.

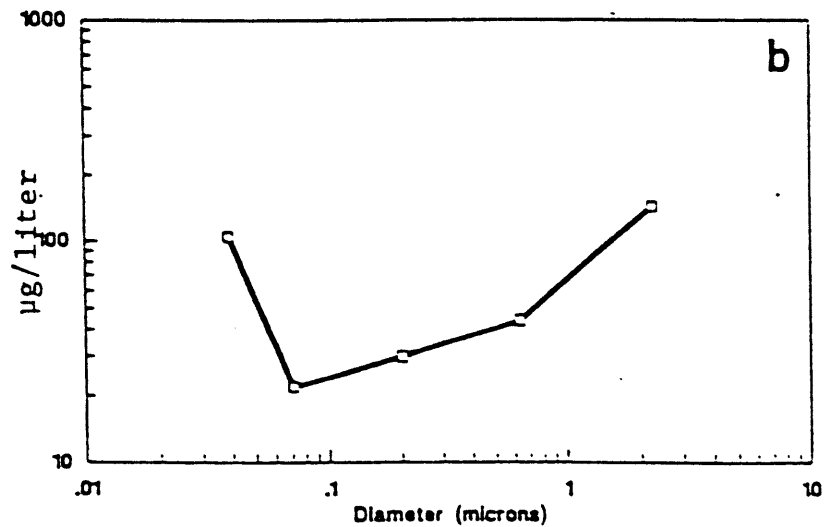
Table 8. Particle mass-size distribution: Stage 2 sampling,  $\mu\text{g liter}^{-1}$ .

Size Range, $\mu\text{m}$	Site	
	Door County (Well 5)	Waunakee (Well 1)
> 5.0	49	22
5.0 - 1.0	67	67
1.0 - 0.4	101	58
0.4 - 0.1	109	68
0.1 - 0.05	28	80
0.05 - 0.03	101	60

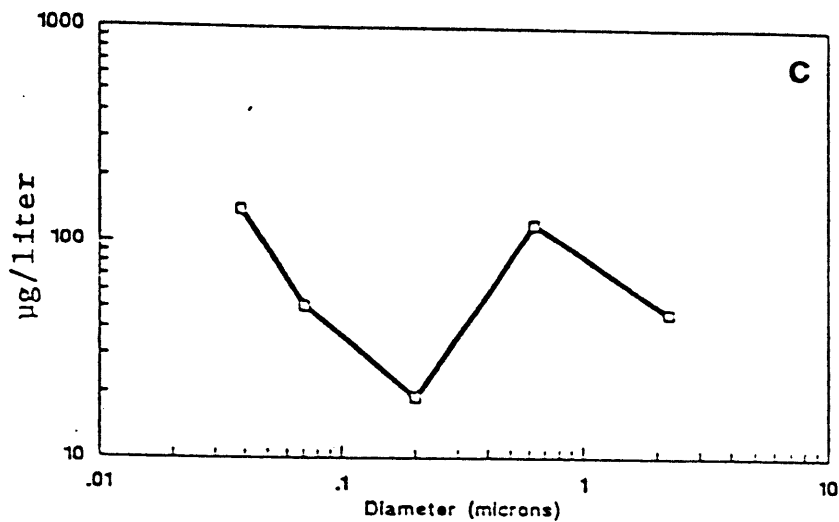
Waunakee Site : Well 1



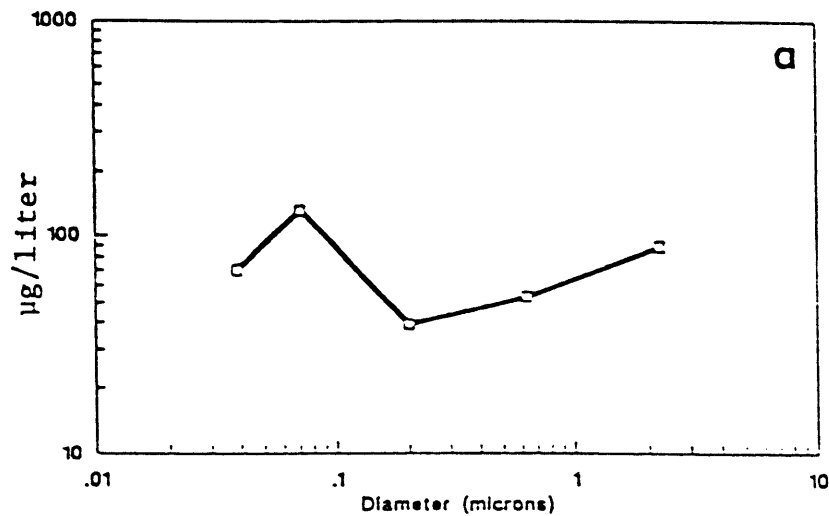
Mt Horeb Site : Well 3



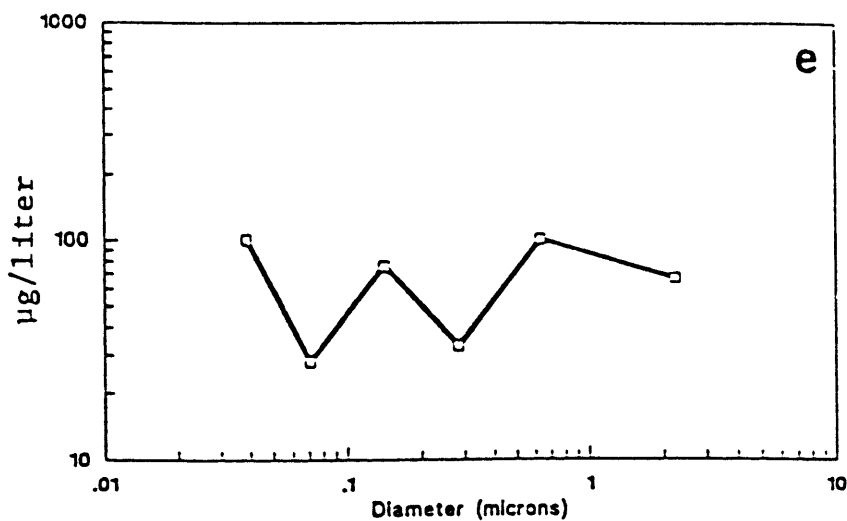
Door County Site : Well 5



Arena Site : Well 8



Door County: 2nd Stage Sampling



Arena: 2nd Stage Sampling

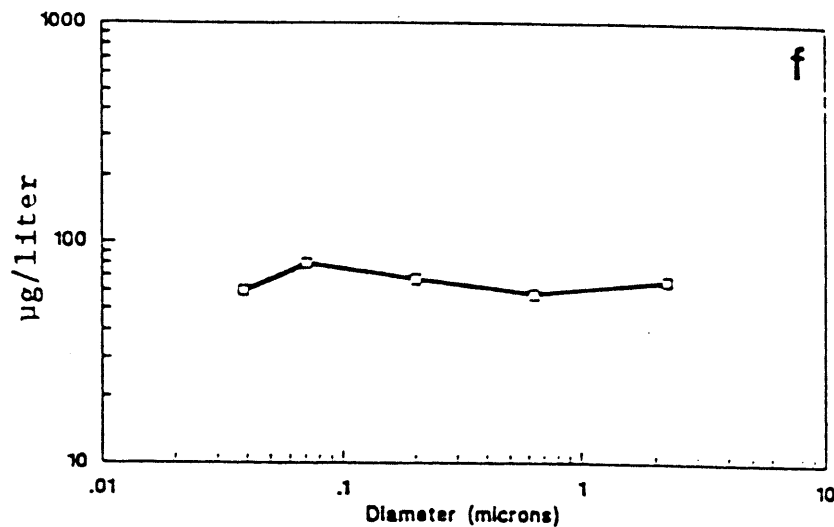


Figure 1. Colloid mass-size distribution.

### Door County Colloid Concentrate

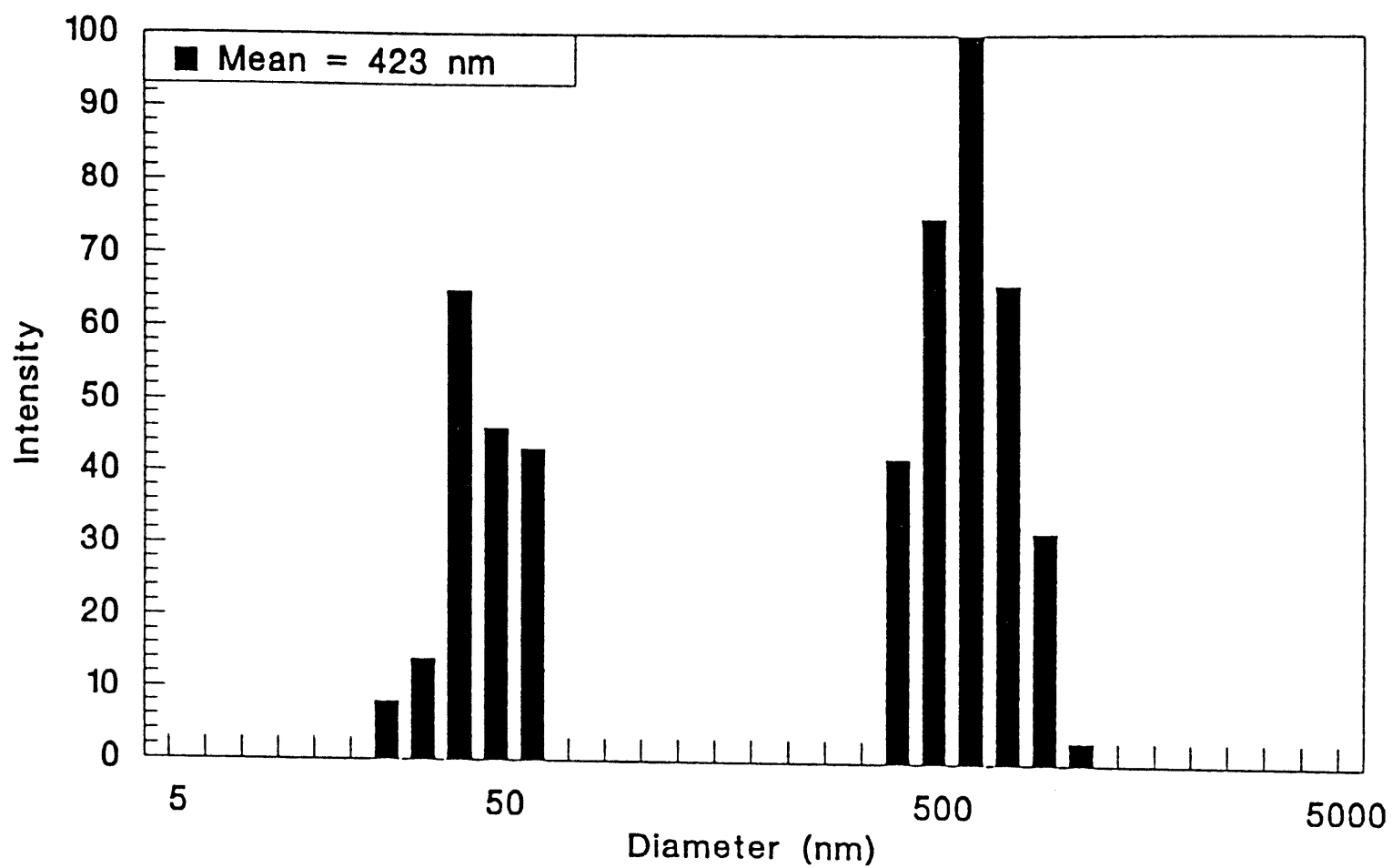


Figure 2. QELS/PCS particle sizing.

September. Sizing of the Door County concentrate (November sample) by dynamic light scattering (QELS/PCS) indicated two major particle populations, one with a modal size near 50 nm and another at 600 nm (Figure 2), which is consistent with Nuclepore size fractionation experiments.

Particle concentrations in Arena and Waunakee concentrates were below the level required for accurate light scattering measurements. If the groundwater colloids in these samples were monodisperse, it would have been possible to analyze at these concentrations. However, the particle size distribution in both samples appeared to be broad. Ryan and Gshwend (1990) have also commented on the problems in applying QELS to polydisperse groundwater colloids.

### Colloid Mobility

Figure 3 presents electrophoretic mobility distributions for concentrated Door County and Waunakee groundwater colloids at ambient pHs. The relatively narrow, unimodal distributions indicate a uniformity in the surface potential-determining structure of the particles. The mean mobilities,  $-0.748$  and  $-1.021 \text{ m}^2 \text{ sec}^{-1} \text{ v}^{-1} \times 10^8$ , are similar in sign and magnitude to the few published data on mobilities of particles in groundwater (Ryan and Gschwend, 1990) and natural waters (Bryant and Williams, 1987; Gerritsen and Bradley, 1987). Estimates of zeta potential ( $\zeta$ ), along with a summary of mobility data, are presented in Table 9. The data are consistent with a model of colloid particles with a sorbed surface coating of organic carbon (e.g., humic substances sorbed to clay or metal oxide particle surfaces). Natural organic matter and uncoated clays at groundwater pHs exhibit a negative charge. It has been shown (Ryan and Gschwend 1990), however, that in most environments clays strongly sorb organic matter. It is probable that the uniform negative charge promotes colloid stability in the groundwater environment.

Table 9. Electrophoretic mobility and zeta potential of groundwater colloids.

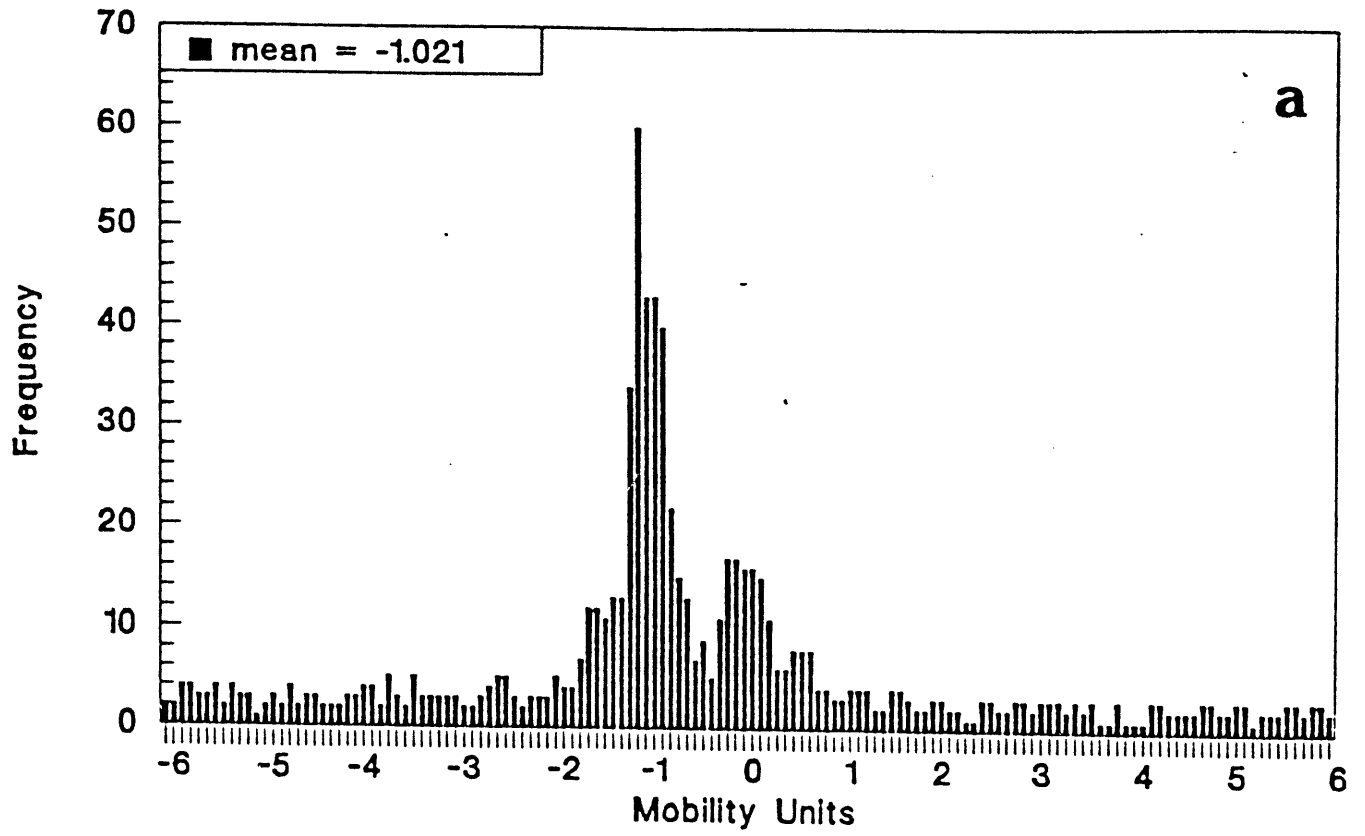
Site	pH	Mobility $\text{m}^2 \text{ sec}^{-1} \text{ v}^{-1} \times 10^8$	Zeta potential† mV
Door County	7.4	-0.748	-10
Waunakee	7.3	-1.021	-15

†Zeta potential ( $\zeta$ ) was calculated using the Smoluchowski equation.  $\kappa a$  is assumed to be  $> 200$ .

### Colloid Geochemistry

The elemental analysis of groundwater colloids is summarized in Table 10. Work is still in progress on several elements, including Ca, Mg, K and carbon by high temperature combustion, however, Si, Al, Fe, C, P, and N analyses have been completed. Nitrogen was estimated from the protein assay using a protein:N ratio of 6.25.

Waunakee Colloid Concentrate



Door County Colloid Concentrate

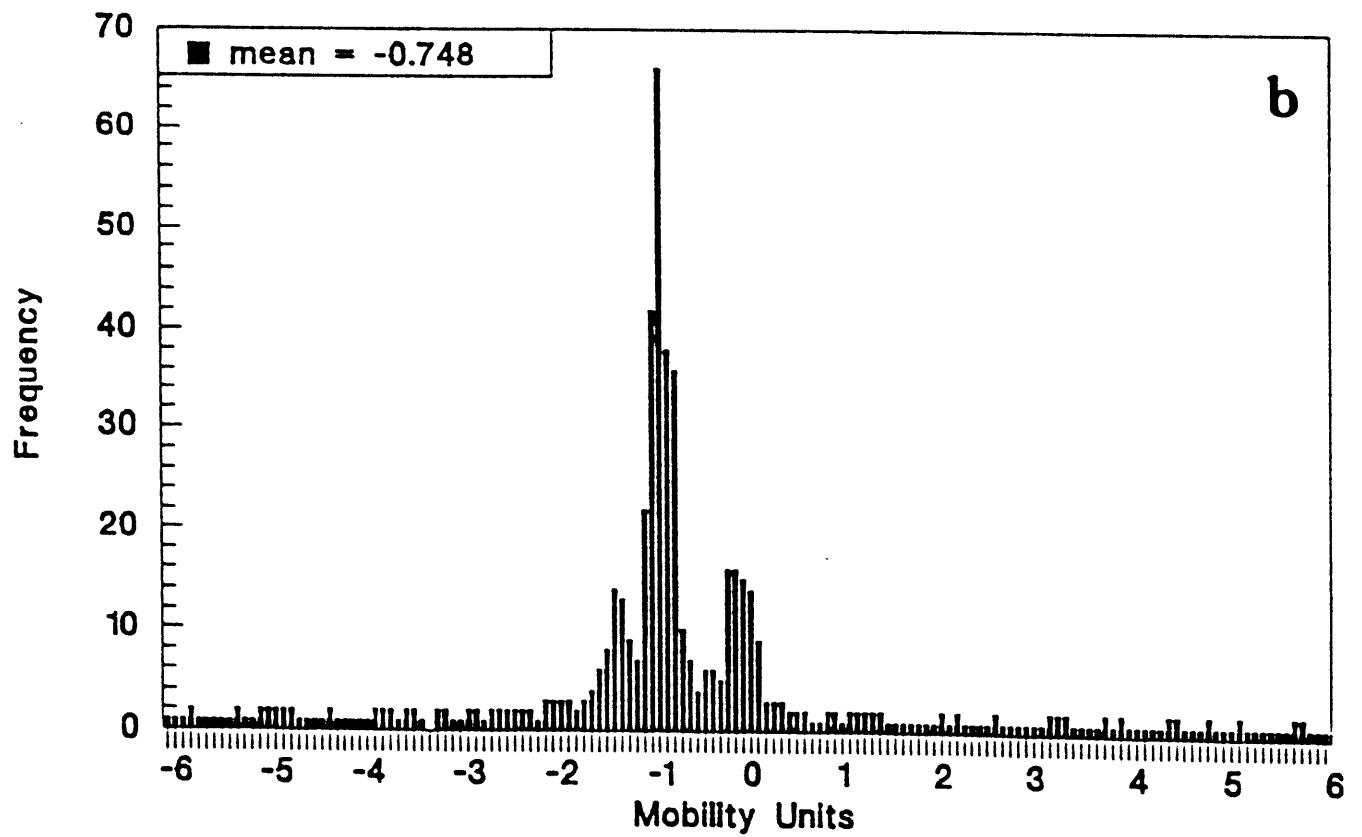


Figure 3. Electrophoretic mobility.

Table 10. Colloid elemental composition, mg g<sup>-1</sup>.

Site	Si	Al	Fe	Ca	C	P	N
Door County >0.05 μm	46.8	7.11	4.19	4.36	57	12.6	12
Door County >0.4 μm	43.0	4.06	2.83	7.68	---	7.83	---
Arena (UC)†	40.2	3.25	2.44		123	12.1	9.2
Arena (UF)†	117‡	24.8‡	24.6‡		99‡	8.13	3‡
Waunakee	97.2	5.85	1.98		<60	1.17	<9

†UC is ultracentrifuge processed; UF is ultrafiltration processed.

‡Lower level of confidence.

Silicon concentrations range from 40 to 47 mg g<sup>-1</sup> at the Door County and Arena sites to nearly 100 mg g<sup>-1</sup> in Waunakee. The relatively high Si content of Waunakee colloids correlates with the highest dissolved Si levels of the four systems studied. SEM micrographs of Waunakee colloidal particles revealed the presence of numerous oval-spherical, 0.5-μm diameter particles, which EDX analysis shows to be comprised primarily of Si and O. These findings suggest that nucleated precipitation of a silicon-based polymer/mineral may be occurring.

Aluminum concentrations (7.1 mg g<sup>-1</sup>) and iron levels (4.2 mg g<sup>-1</sup>) in Door County colloids are roughly double those present in Arena and Waunakee colloids. Much of this enrichment is in the 0.4 to 0.05 μm size fraction, as indicated by the difference between >0.05 and >0.4 μm digestions (Table 10). Carbon levels range from 57 to 123 mg g<sup>-1</sup>, with no obvious relationship to dissolved organic carbon. It is likely that the carbon values reported here are low as a result of poor analytical recovery by persulfate digestion. Nitrogen data and organic carbon - K<sub>d</sub> regressions imply that carbon levels could be as much as 2 to 3 times higher than measured. We are in the process of confirming the carbon data with a high temperature combustion technique. Phosphorus levels in colloidal particles at the Arena and Door County sites are quite high, indicating an association with clay or oxide particles.

These data represent some of the first direct measurements of colloid elemental composition in oxic, "unperturbed" aquifers. Short et al. (1988) have reported Fe and Si content of colloids in a chlorite schist aquifer and Ryan and Gschwend (1990) give major metal composition of colloids in a sandy aquifer, based on EDX single particle analysis. Degueldre et al. (1989) also used electron microscope based methods in reporting elemental composition of colloids from a fractured granitic aquifer. Waber et al. (1990) estimated the phase composition of groundwater colloids based on measurements of TOC, Fe, and Al in ultrafiltration concentrate solutions. Organic matter was the dominant colloidal phase in the aquifer studied (heterogeneous glaciofluvial deposits).



It is difficult to perform a mass accounting without detailed knowledge of the mineralogy of the colloids, however, by making a few reasonable assumptions (Shafer, 1988), an exploratory description is possible. Aluminum and silicon are major constituents of clays and other aluminosilicates, whereas iron can be present in clays and oxides. We assume a molar Si:Al ratio of aluminosilicates of 3, and a molar Fe:Al ratio in aluminosilicates of 4. Any Si not accounted for in aluminosilicates is assumed to be present as SiO<sub>2</sub>. Any excess Fe is assumed to exist as oxyhydroxides (FeOOH). Ca in these systems is assumed to be a component of dolomite. Finally, a factor of 11 is used to convert Al to aluminosilicate mass and a factor of 2 is used to convert organic carbon to organic matter (Table 11).

Table 11. Mass/phase accounting of groundwater colloids.

Site	Phase, mg g <sup>-1</sup>				
	Al-silicate	SiO <sub>2</sub>	FeOOH	Org-Matter	Dolomite
Door County	80	55	0.9	115 (200-300)	20
Arena	30	70	1.3	250 (500-750)	
Waunakee	65	175	<0.2	100 (200-300)	

In all systems, organic matter appears to be the major colloid model phase, although SiO<sub>2</sub> co-dominates at the Waunakee site. Aluminosilicates -- probably clays -- are important components, unlike iron (as FeOOH) which constitutes only a small fraction.

As mentioned previously, SEM/EDX examination of Waunakee colloids revealed that the larger colloids were dominated by spherical- to oval-shaped, relatively smooth surfaced particles, which EDX analysis indicated comprised of silicon and oxygen. Also present were numerous particles shaped like stacked rectangular plates containing potassium which we identified as clays. Much less common were long thread-like particles, 100 to 150 nm in diameter, which we have not identified, but probably are organic in nature. These larger forms exist among a "background" of <100 nm particles which certainly dominate in terms of particle numbers. Larger colloids in the Arena samples were dominated by clays and, as in Waunakee collections, numerous <100 nm particles were present. These small particles appeared to have a crinkled, angular surface. Also found were 200 to 500 nm particles which had the appearance of aggregates of the small angular particles. Small colloids were less numerous in the Door County sample. Many intermediate sized (100 to 300 nm) angular fragments were present, as were aggregates of the type found in the Arena samples.

### Polychlorinated Biphenyl Probe Partitioning

A three-phase partitioning technique was employed to directly assess the influence of colloidal particles on partitioning of a model contaminant. The model tracer chosen, 2,2',4,4'-

TCBP, is representative of moderately hydrophobic ( $\log K_{ow} = 5.9$ ) organic contaminants. Partitioning studies were carried out in whole groundwater (Stage 1 and 2 sampling) and in colloid concentrates (Stage 2). Procedural details and experiments designed to establish the validity of the technique were discussed in the methods section. Partitioning experiments were typically done in triplicate, and data are presented in Tables 12-14.

Averaged for all Stage 1 wells, the percent of TCBP associated with particles  $> 0.02 \mu\text{m}$  was 17%. Percentages ranged from a low of 10.9% at well 3 in Mt. Horeb to 23.4% in well 1 at Waunakee. The fraction of particle-associated PCB was related to suspended mass, however, particle sorption characteristics differ as shown by the significant variation in partition coefficient. Association of TCBP with colloidal particles  $< 0.02 \mu\text{m}$  is essentially insignificant, probably indicating that high molecular weight organic molecules (DOC) in this size class do not have the proper structure for dissolution (partitioning) of a molecule the size of a chlorinated biphenyl.

The fraction of particle associated TCBP found in Stage 2 sampling was generally less than in Stage 1, primarily reflecting the lower mass levels present in spring samples. A comparison of partition coefficients between fall and spring collections reveals that in the Waunakee and Arena (April) sites no significant difference existed. However, Door County spring  $K_d$ 's were statistically lower than in fall, indicating a change in colloid composition. Changing particle populations ( $K_d$  influence) and concentrations indicate a potential for seasonally variable transportation.

The significance of colloid facilitated transport to overall contaminant mobility can be predicted by a retardation factor approach. In the absence of colloids (a two-phase model) the retardation factor, R, is given by:

$$R = 1 + [(\rho_b K_d^{\text{soil}}) \div (\eta)] \quad (\text{Eq. 1})$$

If a colloid term is included, the relationship becomes:

$$R^{\text{true}} = 1 + [(\rho_b K_d^{\text{soil}}) \div (\eta(1 + K_d^{\text{coll}} [\text{SCM}]))] \quad (\text{Eq. 2})$$

where:

- $\rho_b$  = soil bulk density;
- $\eta$  = soil porosity;
- [SCM] = colloid mass concentration; and
- $K_d$  = partition coefficient of contaminant between solid phase ( $C_{\text{particulate}}$  or  $C_{\text{coll}}$ ) and aqueous phase ( $C_w$ ).

Thus, colloids will decrease R for bound solutes and increase their mobility. Predicted mobility enhancements for 2,2',4,4'-TCBP based on measured partition coefficients and colloid

Table 12. PCB probe phase partitioning: Stage 2 sampling.

Well	Distribution between phase†, %			Partition coefficient, $k_d$ , liter $\text{kg}^{-1}$
	> 0.02 $\mu\text{m}$	< 0.02 $\mu\text{m}$ Colloidal	Truly Dissolved	
1	23.4	0.27	76.4	$3.03 \times 10^5$
3	10.9	0.46	88.6	$2.03 \times 10^5$
4	15.6	0.15	84.3	$1.47 \times 10^5$
5	17.0	0.88	82.1	$4.05 \times 10^5$
6	20.8	0.32	78.9	$3.77 \times 10^5$
7	17.2	0.11	82.7	$1.08 \times 10^5$
8	14.9	0.15	85.0	$2.78 \times 10^5$

†TCBP spiked into whole groundwater samples. Average total TCBP spike concentration =  $20.6 \mu\text{g liter}^{-1}$ ; PCB water solubility  $\approx 50 \mu\text{g liter}^{-1}$ .

Table 13. PCB probe phase partitioning: Stage 2; whole water samples.

Site	% Distribution between phase†, %			Partition coefficient, $k_d$ , liter $\text{kg}^{-1}$
	> 0.02 $\mu\text{m}$	< 0.02 $\mu\text{m}$ colloidal	Truly dissolved	
Door County	8.3	0.3	91.4	$1.65 \times 10^5$
Arena (February)	10.1	0.1	89.8	$4.02 \times 10^5$
Arena (April)	7.8	0.2	92.0	$3.45 \times 10^5$
Waunakee	6.4	0.3	93.3	$2.49 \times 10^5$

†Total TCBP concentration averaged  $10.8 \mu\text{g liter}^{-1}$ .

Table 14. PCB probe phase partitioning: Stage 2; concentrate samples.

Site	Particle mass concentration of concentrate, mg liter <sup>-1</sup>	Partition coefficient, K <sub>d</sub> , liter kg <sup>-1</sup>
Door County	9.99	2.29 ± 0.35 x 10 <sup>5</sup>
Arena (February)	8.20	1.67 ± 0.42 x 10 <sup>5</sup>
Arena (April)	0.48	4.38 ± 1.18 x 10 <sup>5</sup>
Waunakee	2.58	3.21 ± 0.65 x 10 <sup>5</sup>

Table 15. Predicted mobility enhancement.

Site	K <sub>d</sub> (Colloid), liter kg <sup>-1</sup>	Colloid mass, mg liter <sup>-1</sup>	Increase in mobility, %
Door County	2.29 x 10 <sup>5</sup>	0.422	9.7
Arena (February)	1.67 x 10 <sup>5</sup>	0.280	4.7
Arena (April)	4.38 x 10 <sup>5</sup>	0.247	10.8
Waunakee	3.21 x 10 <sup>5</sup>	0.273	8.8

concentrations are shown in Table 15. Mobility enhancements on the order of 10% are predicted. Eq. 2 illustrates the dependence of colloid facilitated transport on  $K_d^{\text{coll}}$  and colloid concentration. The significance of this mechanism will increase in proportion to the hydrophobicity of the contaminant. For compounds with  $K_d$ 's  $< 10^5$ , only small increases in mobility are predicted at colloid concentrations of  $< 0.5 \text{ mg liter}^{-1}$ .

## CONCLUSIONS

This study was undertaken to provide fundamental information on the concentrations and chemical and physical properties of mobile colloids in four representative, relatively unperturbed aquifers in Wisconsin. In addition, experiments were performed to evaluate the capacity of colloidal particles for enhancing transport of chemical contaminants.

Measured colloid ( $< 1.0 \mu\text{g}$ ) mass concentrations ranged from 200 to 700  $\mu \text{ liter}^{-1}$ , with a modal value of 325  $\mu\text{g liter}^{-1}$ . As a percentage of total mass, colloid masses typically ranged from 70 to 80%, although values in the 30 to 50% range were also measured. Marked reduction in colloid and total mass abundance were seen at two sites in spring collections as compared with fall sampling, which may reflect susceptibility to seasonally variable temperature and water table levels. The measured colloid abundances fall within the range of the few other published estimates of natural colloid levels in groundwater.

Mass-size distributions were typically broad with shallow maxima in the 30 to 50 and 400 to 1,000 nm size intervals. SEM/EDX analysis of colloids confirmed the heterogeneous nature of the particle populations: larger sizes dominated by clay and silica particles; smaller particles more difficult to categorize, but probably high in organic matter.

The relatively narrow unimodal mobility distributions indicate a uniformity in surface potential-determining structure of particles, this despite the obvious heterogeneous particle matrices. The data are consistent with a model of colloid particles with a sorbed surface coating of organic carbon and it is probable that the uniform negative charge promotes colloid stability in the groundwater system.

In all systems organic matter was the major colloid model phase representing 20 to 75% of particle mass. Al-silicate contributions ranged from 3% at Arena to 8% at Door County, whereas silica levels ranged from a low of 5.5% in Door County to nearly 18% at Waunakee. Iron oxide levels were typically low ( $< 1.0\%$ ).

Three-phase partitioning experiments with 2,2',4,4'-TCBP in both whole groundwater and colloid concentrates revealed that association with colloids can be significant with up to 23% colloidally bound at natural colloid mass levels. Calculated partition coefficients for colloidal particles ranged from  $1.1 \times 10^5$  to  $4.4 \times 10^5$ . Using a retardation factor approach it was estimated that the presence of mobile colloids in the aquifers, on average, increase the mobility of 2,2',4,4'-TCBP by 10%. Thus, colloid-mediated transport of contaminants may be significant, particularly for compounds with  $K_d$ 's  $> 10^5$ .

These data represent some of the first direct measurements of colloid abundance and chemical composition in oxic "unperturbed" aquifers and will enable us to address specific factors influencing colloid formation and fate in aquifers.



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