# Sampling Colloids and Colloid-Associated Contaminants in Ground Water

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## Abstract

It has recently been recognized that mobile colloids may affect the transport of contaminants in ground water. To determine the significance of this process, knowledge of both the total mobile load (dissolved + colloid-associated) and the dissolved concentration of a ground-water contaminant must be obtained. Additional information regarding mobile colloid characteristics and concentrations are required to predict accurately the fate and effects of contaminants at sites where significant quantities of colloids are found. To obtain this information, a sampling scheme has been designed and refined to collect mobile colloids while avoiding the inclusion of normally immobile subsurface and well-derived solids. The effectiveness of this sampling protocol was evaluated at a number of contaminated and pristine sites.

The sampling results indicated that slow, prolonged pumping of ground water is much more effective at obtaining ground-water samples that represent in situ colloid populations than bailing. Bailed samples from a coal tar-contaminated site contained 10-100 times greater colloid concentrations and up to 750 times greater polycyclic aromatic hydrocarbon concentrations as were detected in slowly pumped samples. The sampling results also indicated that ground-water colloid concentrations should be monitored in the field to determine the adequacy of purging if colloid and colloid-associated contaminants are of interest. To avoid changes in the natural ground-water colloid population through precipitation or coagulation, in situ ground-water chemistry conditions must be preserved during sampling and storage. Samples collected for determination of the total mobile load of colloids and low-solubility contaminants must not be filtered because some mobile colloids are removed by this process. Finally, suggestions that mobile colloids are present in ground water at any particular site should be corroborated with auxiliary data, such as colloid levels in "background" wells, colloid-size distributions, ground-water geochemistry, and colloid surface characteristics.

## Introduction

Contaminant fate and transport models are used to predict the temporal and spatial distributions of chemicals in ground water. Information obtained from these models is used to (1) develop exposure and risk assessments, (2) set site cleanup priorities based on these risks, (3) make decisions regarding the need for remedial action or containment at hazardous waste sites, and (4) evaluate alternative remediation strategies. Accurate model predictions will only be obtained if models are formulated to account for all important processes affecting contaminant transport in aquifers.

It has recently been recognized (McDowell-Boyer et al., 1986; McCarthy and Zachara, 1989) that mobile colloid phases, present in some aquifers and generally not accounted for in models, may significantly affect the transport and transformations of hydrophobic or particle-reactive contaminants [e.g., polycyclic aromatic hydrocarbons (PAHs); polychlorinated biphenyls (PCBs); radionuclides of Ru, Cs, U, Pu, Am, and metals such as Pb, Cr, Cu, and Ni]. In the past, when turbid water was obtained from a monitoring well, the suspended solids were presumed to be artifacts of ground-water collection and not present or mobile in the subsurface. Consequently, samples were filtered to remove suspended solids. It now seems possible that at least a portion of the suspended solids removed by filtration was actually mobile in the aquifer under natural ground-water flow conditions.

A means of distinguishing truly mobile suspended particles from artifactual suspended material is required to determine the importance of the mobile colloid phase in contaminant transport. In this paper, materials that are mobile in the subsurface under natural ground-water flow conditions are referred to as "mobile" or "in situ" colloids. For some ground-water flow conditions representative of the Massachusetts site, O'Melia (1990) calculated that suspended particles in the 0.1 to 1.0 $\mu$m size range experience the fewest collisions with the framework grains of the aquifer; thus, particles in this size range are the most likely to be mobile in ground water. "Artifactual" or "immobile" refer to particles which are found only in or near the well. The artifactual particles may have been introduced to the

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subsurface during well construction (drilling muds, benton-ite seals, backfill), produced by exposure of ground water to the atmosphere, or sheared from the aquifer material by pumping.

Mobile colloids are expected to affect the subsurface transport of contaminants if significant quantities of inher-ently hazardous colloids are present (asbestos, microorgan-isms) or significant quantities of toxic chemicals associate with mobile colloids. A wide variety of colloidal materials have been found in ground waters: humic substances and other macromolecules (Leenheer et al., 1974; West, 1984; Thurman, 1985; Enfield et al., 1989), micoorganisms (Keswick et al., 1982; McGinnis and DeWalle, 1983; Harvey et al., 1989), inorganic precipitates (Langmuir, 1969; Gschwend and Reynolds, 1987), and rock and mineral fragments (Nightingale and Bianchi, 1977; Degueldre et al., 1989; Ryan and Gschwend, 1990; Gschwend et al., 1990). Some field observations show that colloids can be transported up to hundreds of meters from their source (Reinhard, 1984; Robertson et al., 1984; Keswick et al., 1982; Buddemeier and Hunt, 1988; Short et al., 1988; Magaritz et al., 1990; Penrose et al., 1990). Additionally, numerous studies suggest that colloids are good sorbents for hydrophobic organic chemi-cals, metals, and radionuclides (McCarthy and Zachara, 1989; Puls, 1990). Hence, it is especially important to under-stand the role of colloids in contaminant transport at sites where low-solubility chemicals are present.

To assess the importance of the mobile colloidal phase at a particular site, information is required on both the total mobile load of contaminants and colloids as well as the distribution of that contaminant between the colloidal and dissolved phases. In addition, it is necessary to obtain information about mobile colloid characteristics such as elemental composition, sorptive character, solubility under relevant solution conditions, size, and surface charge. These properties determine the distribution of contaminants between the dissolved and colloidal phases and the mobility of the colloids in the aquifer.

To obtain this information, ground-water samples representative of mobile colloids must be collected. Sam-pling schemes have been designed and refined over the past decade to allow collection of ground-water samples repre-sentative of in situ concentrations (e.g., Barcelona et al., 1985). Initially, wells must be purged of water exposed to the atmosphere or otherwise affected by the presence of the well (Gibs and Imbrigiotta, 1990). Often, easily measured water chemistry parameters (e.g., specific conductance, pH) are monitored to determine required purging times. Losses of contaminants of interest due to sorption of dissolved species to well and sampling materials and volatilization must be minimized as samples are brought to the surface. Sample integrity must be preserved by avoiding exposure of samples to the atmosphere and contamination from well construc-tion and sampling materials.

Consideration of these factors is necessary for the col-lection of ground-water colloid samples as well; however, these solute sampling protocols may not be sufficient to ensure that colloids and colloid-associated species found in samples represent in situ conditions (Reynolds, 1985;

Backhus et al., 1986; Ryan, 1988; Puls and Barcelona, 1989; Puls, 1990). The well must be sufficiently purged of all artifactual particles prior to sampling; however, water chem-istry parameters typically monitored to judge the adequacy of purging may not be good indicators for ground waters containing colloidal material. Maintenance of in situ ground-water chemistry conditions during sampling and storage is particularly important in determination of mobile colloid concentrations and characteristics. Changes in ground-water chemistry can lead to precipitation of colloids not present in situ or induce changes in colloid characteris-tics due to coagulation. Aquifer materials which were immobile under natural ground-water flow conditions may be mobilized at pumping-induced ground-water velocities; thus, pumping rate may be an important consideration. Failure to address these issues can lead to inaccurate estima-tion of colloid and colloid-associated contaminant concen-trations, colloid characteristics, and the distribution of con-taminants between colloidal and dissolved phases.

In this paper, a sampling protocol designed to ensure that samples accurately reflect the in situ mobile colloid and associated contaminant concentrations is described. The results of numerous sampling experiences at various sites are summarized to justify the proposed sampling scheme and to indicate that colloids are found even in carefully collected ground waters. Recommendations are provided for sam-pling ground waters which may contain both dissolved and colloid-associated contaminants. The intent of the paper is to (1) describe a procedure to obtain samples which allows assessment of the importance of the colloidal phase, (2) suggest that more commonly used sampling schemes may provide misleading information regarding the importance of the mobile colloid phase and total mobile contaminant concentrations, and (3) call attention to the possibility that mobile colloidal material in the subsurface could affect the transport and transformations of low-solubility contam-inants.

## Methods
### Sampling Sites

Ground-water samples were obtained over the last five years from the sites listed in Table 1. The sites sampled represented a wide range of geologic conditions and included both pristine and contaminated sites. At each site, samples were collected from both "contaminated" wells (wells screened within a plume of ground water whose chemistry has been changed in some way from that of the surrounding aquifer, most commonly by input of leachate or wastes) and "background" wells (wells screened outside the altered sub-surface region). Samples were obtained through 5 cm (2 in.) monitoring wells at all sites. Most of the wells were drilled by hollow stem auger.

### Sampling Procedures

The sampling protocol (Table 2) and setup (Figure 1), designed to ensure that samples accurately reflect the in situ mobile colloid and associated contaminant concentrations, includes prolonged slow pumping and maintenance of in

## Table 1. Characteristics of Sites Studied for Sampling of Colloids

| Site/well | Site description | Well depth (m)/ construction | Screen interval (m)/ slot size (mm) | Water table (m) | Colloids found | Ref. |
|---|---|---|---|---|---|---|
| *Massachusetts: Glacial outwash aquifer, stratified sand and gravel contaminated by infiltration of secondarily treated sewage* | | | | | | |
| FSW343-57 Fig. 2, "Contaminated" | Within plume | 17.4 /PVC | 16.8-17.4/0.25 | 6.5 | < 7 mg/l ferrous phosphate | 1, 2 |
| | | | | | ~1 mg/l org. colloids | 3 |
| FSW350-77 | Within plume | 23.5 /PVC | 22.9-23.5/0.25 | 1.2 | ~1 mg/l organic colloids | 3 |
| FSW242-77 Fig. 2, "Background" | Outside plume | 23.4 /PVC | 22.5-23.4/0.25 | 6.8 | < 0.1 mg/l organic colloids | 3 |
| FSW239-64 | Within plume | 19.5 /PVC | 18.6-19.5/0.25 | 1.6 | < 1 mg/l ferrous phosphate | 1, 2 |
| *NJ Pine Barrens: Atlantic Coastal Plain aquifer, Cohansey Sand, pristine upland and swamp areas* | | | | | | |
| Swamp Deep QWH-1B Fig. 2, "Contaminated" | Anoxic | 9.2 /PVC | 8.3-9.2/0.25 | At surface | ~60 mg/l kaolinite | 4 |
| Upland Deep QWH-4B Fig. 2, "Background" | Oxic | 10.9 /PVC | 10-10.9/0.64 | 1.96 | ≤ 1 mg/l | 4 |
| *Delaware: Delaware coastal plain, fluvial quartz sand, agricultural* | | | | | | |
| Lc42-01 Fig. 2, "Contaminated" | Anoxic | 16.8 /PVC* | 15.3-16.8 | 2.1 | ~6 mg/l kaolinite and muscovite | 4 |
| Md22-01 Fig. 2, "Background" | Oxic | 5.5 /PVC* | 4.0-5.5 | 3.5 | ≤ 1 mg/l | 4 |
| *Nevada: Sand and gravel alluvium, primarily quartz with several percent carbonate, coal-fired power plant, recharge through buried coal ash* | | | | | | |
| A | Near buried ash | 32.0 /PVC* | 22.9-32.0 | 24.6 | 10-100 mg/l silicates | 5 |
| B | Downgradient | 35.0 /PVC* | 16.8-35.0 | 17.8 | ≤ 1 mg/l | 5 |
| C | Upgradient | 79.0 /PVC* | 36.6-79.0 | 32. | ≤ 1 mg/l | 5 |
| D | Downgradient | 33.5 /PVC* | 21.3-33.5 | 22.9 | 10-100 mg/l silicates | 5 |
| *Connecticut: Alluvial sand, gravel and boulders, coal tar contaminated* | | | | | | |
| A | Source area | 13.11/SS* | 7.01-13.11/0.51 | 4.97 | ~mg/l clay-like | 6, 7 |
| B Fig. 2, "Contaminated" | Downgradient | 7.31/SS | 4.26-7.31/0.51 | 4.84 | ~mg/l clay-like | 6, 7 |
| C | Downgradient | 7.01/SS | 3.96-7.01/0.51 | 4.72 | ~mg/l clay-like | 6, 7 |
| D Fig. 3 | Source area | 5.49/SS* | 4.88-5.49/0.51 | 4.97 | ~mg/l clay-like | 6, 7 |
| *New York: Medium to coarse grained sand, coal tar contaminated* | | | | | | |
| A Fig. 2, "Contaminated" | Source area | 4.88/SS | 3.35-4.88 | ~2.7 | ~mg/l | 8, 9 |
| B | Downgradient | 5.64/PVC | 4.11-5.64 | 2.9 | 2 mg/l | 8, 9 |
| C Fig. 2, "Background" | Background | 6.4 /PVC | 4.88-6.4 | 2.9 | ≤ 1 mg/l | 8, 9 |

*Bentonite seal.

References: (1) Reynolds, 1985; (2) Gschwend and Reynolds, 1987; (3) Backhus and Gschwend, 1990; (4) Ryan and Gschwend, 1990; (5) Gschwend et al., 1990; (6) Gschwend et al., 1988; (7) Backhus, 1990; (8) Groher et al., 1990; (9) Groher, 1990.

situ ground-water chemistry conditions throughout sampling and storage.

For most of the analyses described below, ground-water samples were pumped to the surface with a small, submersible, gear-driven, positive-displacement pump that fits inside a 5 cm (2 in.) diameter well (model SP-202, Fultz, Inc., Lewistown, PA). The surface area over which the ground water contacts the pump is constructed of stainless steel and Teflon and is very small in comparison with other pumps. The pumping rate was controlled by a variable voltage AC-DC converter powered by a generator, allowing minimum steady pumping rates of about 100 ml/min (0.03 gal/min) to be maintained at most wells. Ground water was pumped to the surface through a continuous piece of polypropylene [0.64 cm (¼ in.) id] or aluminum [0.48 cm (3/16 in.) id] tubing.

To minimize required well purging times, the ground-water sampling zone was isolated by an inflatable packer

**Table 2. Recommended Protocol for Ground-Water Sampling of Colloids and Colloid-Associated Constituents**

1. Measure depth to water and calculate standing water volume.

2. (Optional) Make "dipstick" observation of any layering in the well (e.g., floating NAPL).

3. Slowly lower inlet/pump to sampling depth.

4. Inflate packer(s) to reduce well volume and isolate inlet from settled particles at well bottom or floating NAPL at surface.

5. Initiate pumping at a slow flow rate ("slow" is still somewhat arbitrary; pumping rates near 100 ml/min were most commonly used in our work). Avoid surging. Observe air bubbles displaced from sample tube to assess progress of steady pumping until water arrives at the surface.

6. Measure volumetric flow rate and adjust pumping rate as necessary.

7. Use a flow-through cell to monitor temperature, specific conductivity, pH, Eh, and dissolved oxygen. Repeatedly collect water and assess turbidity.

8. (Optional) Initiate slow pumping at another well(s) on-site. In addition to sampling wells within the "contaminated" zone of the aquifer, "background" wells should be sampled. The background well should be located outside the contaminated zone, but constructed and developed in the same manner and screened in the same aquifer as the "contaminated" well.

9. After turbidity has stabilized, collect water samples for mobile contaminant analysis in suitable flow-through vessels (e.g., glassware for organic chemicals). Minimize contact with air. DO NOT FILTER for ground-water analyses. Preserve as appropriate (e.g., store in cold and dark for organic chemicals).

10. (Optional) Collect colloid samples on membrane filters (e.g., 0.015 or 0.030 $\mu$m) or by ultrafiltration (e.g., Penrose et al., 1990) in the field and store for SEM/EDX and XRD analysis.

constructed of polyvinyl chloride and viton (QED Environmental Systems, Inc., Ann Arbor, MI) and placed 20 to 70 cm (8-28 in.) above the pump inlet. In a few instances, to determine whether purging times could be further reduced, packers were placed both above and directly below the pump.

Water chemistry parameters were monitored during purging and after sampling by pumping the ground water directly into a flow-through cell equipped with pH, Eh, dissolved oxygen (DO), temperature, and specific conductance electrodes. The pH, Eh, and specific conductance electrodes were calibrated at the initial temperature of the pumped ground water in the calibration chamber of the flow-through cell. The DO meter was calibrated to an oxygen-saturated solution at ambient air temperature.

Turbidity was monitored with two different instruments. Samples for the first instrument, a Coulter N4 submicron particle analyzer fitted with a 3 mW He-Ne laser and a low dark-counts photomultiplier tube, were collected by overfilling 1 cm path length spectrophotometric cells. The cells were then tightly capped and equilibrated for 1 minute in a temperature-controlled sample chamber. The mean and standard deviation of the light scattering intensity (counts/

sec) were determined by averaging at least 30 intensity measurements recorded over a 3 minute period. Samples for the second instrument, a Hach Ratio X/R turbidity meter, were collected by overfilling and capping 35 ml glass vials. The vials were equilibrated for 1 minute in the instrument and the steady turbidity (NTU) was recorded. For both instruments, the sample cells were rinsed repeatedly with deionized water between samples, and background measurements were obtained periodically in the field using deionized water. In some cases, the light scattering intensities measured by the Coulter N4 often had large fluctuations owing to infrequent, but extremely high, intensities measured as large particles settled through the narrow sample volume defined by the laser beam.

To collect ground-water colloids, the sampling tube was disconnected from the flow-through cell, and ground water was taken up in 5 ml disposable plastic syringes by joining the end of the sampling tube to the syringe tip and allowing the plunger to be displaced backwards. The syringe was rinsed several times with ground water, bubbles were displaced, and the syringe was connected to a Millipore Swinnex filter holder containing a 15 or 30 nm pore size
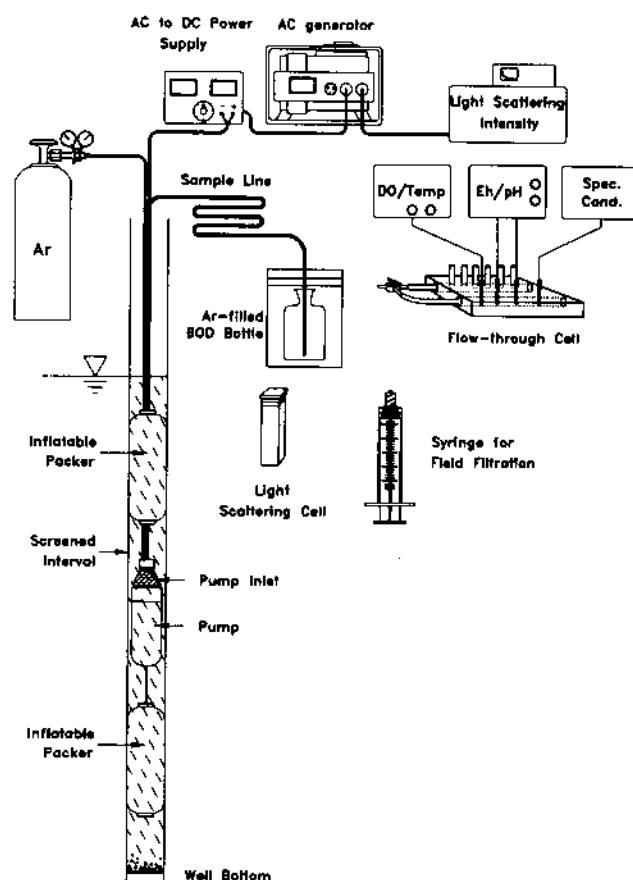


Fig. 1. Sampling setup for collection of ground water from monitoring wells when colloids or colloid-associated chemicals may be of importance. A positive displacement pump, controlled by a variable power supply, withdraws water from a volume between two packers and delivers it to a flow-through cell or cuvette for assessment of chemical parameters or turbidity or to syringe for colloid collection by filtration or to a DO bottle for laboratory analysis.

Nuclepore polycarbonate membrane filter. The sample was forced through the filter by pressure from weights (0.8 kg/cm$^2$). The filter was rinsed with 5 ml of distilled, deionized water, and placed in a covered petri plate in a desiccator to dry.

Unfiltered ground-water samples for laboratory analysis of colloids and solution properties were collected in glass bottles used for dissolved oxygen (DO) analysis. These bottles have specially designed stoppers which allow closure without inclusion of head space; therefore, they minimize the exchange of gases between the sample and the atmosphere during storage. Prior to sampling, the DO bottles were filled with argon. Samples were collected by inserting the sampling tube to the bottom of the bottle and overfilling the bottle (by at least half of its volume). The water samples were stored in a cooler in the field, then refrigerated at ground-water temperature in the dark until analysis.

Ground-water samples for PAH analyses were collected in 40 ml screw-cap glass centrifuge tubes. To minimize sorptive losses of PAHs to the teflon cap liners of the tubes, solvent-rinsed aluminum foil was used to line the caps. Using a balance in the field, tubes were filled directly with a known mass of ground water. A 2 ml aliquot of methylene chloride was added to each tube, and the tube was capped and shaken to begin the extraction of PAHs from the sample for subsequent laboratory analysis.

In addition to the sampling setup described above, two alternative means of sampling collection were used: (1) a bailer and (2) a peristaltic pump. For comparative purposes, a bottom-loading stainless steel bailer was used to collect samples at some wells. After three well volumes were purged by bailer, samples were collected. Subsequently, an additional five well volumes were withdrawn and more samples were collected.

A peristaltic pump was used to very slowly withdraw samples from one well in the coal tar source area. This pump was capable of reliably pumping at a slower flow rate than the gear-driven pump; furthermore, sample collection with the peristaltic pump minimized the disturbance of a tar layer known to exist at the bottom of the well because only the sampling tube entered the well. The peristaltic pump system drew water from the well through stainless steel tubing at a flow rate of 20 ml/min (0.005 gal/min). At the ground surface, the metal tubing was connected to a glass stopcock. Glass tubing, connected to the stopcock outlet, entered a DO bottle through a silicone rubber stopper, and water pulled from the well filled the DO bottle from the bottom up. Another piece of glass tubing, positioned to prevent the water from contacting the stopper, exited the top of the DO bottle through the rubber stopper. This tubing was connected to another glass stopcock, which was connected to the peristaltic pump. In this manner, the sample could be collected without contacting the flexible tubing in the peristaltic pump head. Surging of the well was avoided when sample bottles were exchanged by closing both stopcocks, exchanging an empty bottle for the filled bottle, opening the stopcock between the bottle and the pump to evacuate the empty bottle, and, after a brief interval, opening the second stopcock to permit resumption of ground-water withdrawal.

## Laboratory Analysis
### Colloids

Field-filtered ground-water particles were analyzed by scanning electron microscopy/energy-dispersive x-ray spectroscopy (SEM/EDX) to examine directly colloid-size distributions and determine elemental composition of colloids. Desiccated filters were attached to stubs with double-sided adhesive tape, and coated with gold. Both morphology and elemental composition of individual particles were used to identify some minerals. X-ray powder diffraction (XRD) was also used to confirm the identity of some minerals. Details for samples from the different sites can be found in Gschwend and Reynolds (1987), Ryan and Gschwend (1990), Gschwend et al. (1990), Groher (1990), and Backhus (1990).

Estimates of ground-water colloid concentrations were obtained by light scattering photometry using the Coulter N4 and Hach Ratio X/R in the field and laboratory to detect changes in colloid abundance during storage. Colloid concentrations were estimated by comparing the light scattering intensity or turbidity of the ground water with those of suspensions of known concentrations of colloidal materials of similar size and optical properties. For example, SEM/EDX and XRD analysis of colloids collected on filters revealed that kaolinite plates were the predominant colloids in many of the ground-water samples. Therefore, pure kaolinite standards of known particle-size range (separated by settling) were used to estimate colloid concentrations in these ground-water samples.

Attempts were made to determine colloid-size distributions by photon correlation spectroscopy. In most cases, scattering material was not present in sufficient quantities or in sufficiently simple size distributions to allow sizing by this method. Some samples were filtered using a 1 $\mu$m pore diameter membrane filter and reanalyzed by light scattering to assess whether any portion of the colloids were susceptible to removal by sample filtration.

### Ground Water

Measurements of the chemical composition of both whole and filtered ground-water samples were obtained by atomic absorption and emission spectroscopy, ion chromatography, organic carbon analysis, and colorimetric techniques. Specific details of these analyses for samples from various sites can be found in Gschwend and Reynolds (1987), Ryan and Gschwend (1990), Gschwend et al. (1990), and Backhus and Gschwend (1990).

PAH concentrations in ground water from the coal tar-contaminated sites were determined by selected ion monitoring-gas chromatography mass spectrometry (SIM-GCMS) of the methylene chloride extracts of the 40 ml samples collected in the field. The extraction, started in the field, was continued on a shaker in the laboratory after the samples were spiked with a series of deuterated PAH internal standards (d10 phenanthrene, d10 pyrene, d12 chrysene, and d12 perylene). The tubes were wrapped in foil to minimize photodegradation. The methylene chloride extracts were stored at $-14°$C in the dark until they were analyzed by SIM-GCMS using a Hewlett Packard 5995B gas

chromatograph-mass spectrometer equipped with a DB5, 30 m, 0.25 μm film thickness capillary column, programmed from 40°C to 300°C at 10°C/min. Individual PAH concentrations were determined using peak heights of the corresponding PAH in external standards. PAH concentrations were corrected for any losses during sample concentration steps using the observed recovery of the nearest eluting internal standard.

## Results and Discussion
### Well Purging

A well is considered adequately purged when the water chemistry parameters monitored during purging level off at stable values (Barcelona et al., 1985). In our work, water chemistry parameters, turbidity, and, at one site, contaminant concentrations were monitored during purging to determine whether the various parameters monitored in the field provided guidelines for evaluating the adequacy of well purging for obtaining samples representative of in situ ground-water colloid and contaminant concentration.

### Variation of Turbidity During Purging

The variation of turbidity during purging was qualitatively quite similar at all wells sampled (Figure 2). In most of the wells, turbidity was initially high and gradually decreased to a constant level after the removal of 10 to 20 l (2.6 to 5.3 gal). At the constant turbidity level, the variation in turbidity was less than ± 15% of the mean turbidity value. Even in samples that did not initially appear turbid to the eye, light scattering measurements diminished over time to a constant level. At the Massachusetts site, ground water was sampled several times over the course of a year and the turbidity declined in a similar manner on each occasion (see "contaminated" Massachusetts well in Figure 2). We believe that the low light scattering intensities observed in ground water initially removed from the "contaminated" Massachusetts well resulted from the removal of distilled water that remained in the sampling tube after cleaning.

For all "background" wells, turbidity leveled off at values approaching that observed for distilled water (50-100 counts/sec for light scattering photometry or about 0.05 NTU for turbidity measurements, as indicated by the dotted lines in Figure 2). In ground water removed from the "contaminated" wells, the constant turbidity levels were substantially higher than the turbidity of the distilled water blank, indicating that detectable quantities of colloids were suspended in the ground water, presumably mobilized by the alteration of ground-water chemistry in the "contaminated" plume. The light scattering data suggest colloid concentrations in the "contaminated" wells ranged from 1 to 100 mg/l (Table 1).

### Variation of Water Chemistry Parameters During Purging

Variations in the water chemistry parameters (pH, Eh, DO, and specific conductance) measured during the purging of the "contaminated" well at the Connecticut coal tar site (well D, in the coal tar source area) did not follow the variation of turbidity (Figure 3). Similar results were

observed in all other wells sampled (Ryan, 1988; Backhus, 1990; and Groher, 1990), but only data obtained at the "contaminated" Connecticut well are presented because they can be compared with the variations in PAH concentrations in the same well.

Observed pH values fluctuated about a constant value between 7.0 and 7.2 after removal of 5 l (1.3 gal) at a flow rate of ~ 150 ml/min (0.04 gal/min). Similarly, DO and Eh values varied about 0.4 ± 0.2 mg/l and 0.13 ± 0.03 volts, respectively, after removal of 5 l from the well. In contrast, turbidity values decreased steadily during the removal of 26 l (6.9 gal). Turbidity decreased by a factor of 24 between samples taken after purging 7 l and 26 l, but pH, DO, and Eh values remained stable over the same time frame.

The increase in turbidity observed after 30 l were removed may have resulted from an inadvertent increase in the pumping rate during the sampling period. Increasing turbidity with increasing flow rate has been observed at other sites when the flow rate was intentionally increased (Figure 2, NY, NJ, DE). Alternatively, this increase could reflect heterogeneity in colloid concentrations within the aquifer. The continued decrease in TOC values over the entire pumping period may reflect variations within the aquifer.

The water temperature mimicked the changes in ambient air temperature because the lines were not sufficiently insulated to maintain the ground-water temperature as the water slowly traveled through excess tubing at the surface. This change in temperature over the pumping period may have affected water chemistry parameter measurements (particularly specific conductance) because the meters were calibrated only at the initial ground-water temperature.

The results from this well suggest that the amount of well purging required may vary depending on which parameters are monitored. It is often not possible to monitor contaminant concentrations in real time in the field. Therefore, a parameter which closely mimics the variations of the contaminants of interest should be monitored in the field to determine the appropriate volume which must be purged to obtain samples representative of in situ ground-water contaminant loads.

### Colloid-Associated Contaminants

Turbidity may be a useful parameter for determining appropriate purging times for low-solubility, particle-reactive contaminants like PAHs. Variations in the concentrations of the PAHs, with the exception of naphthalene, follow the variations in turbidity during pumping (Figure 3). A continuous decrease in the concentrations of phenanthrene, pyrene, and chrysene/benz(a)anthracene was observed throughout the first 26 l (6.9 gal) of pumping, as was observed with turbidity. After 26 l, an increase in the concentrations of these contaminants was observed with a concurrent increase in turbidity.

Low-solubility compounds are expected to be predominantly associated with the colloids suspended in the ground water; thus the concentrations of low-solubility PAHs might be expected to vary similarly to colloid abundance. Contam-
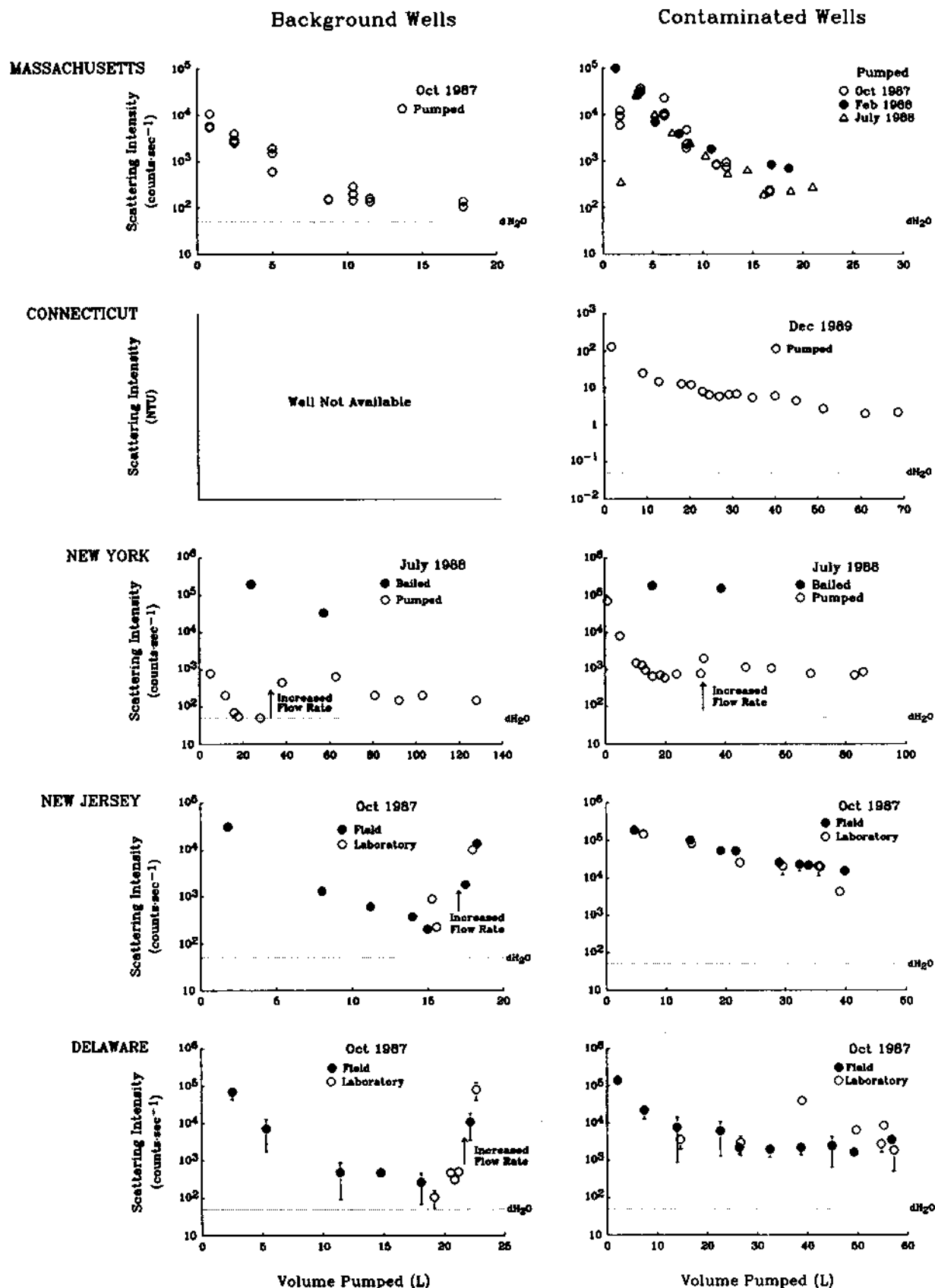
Fig. 2. Variations of ground-water turbidity for samples during slow pumping from "background" wells that exhibit regional ground-water geochemistry and from "contaminated" wells that are screened where water chemistry has been altered so that it deviates from the corresponding background condition. The horizontal dotted lines indicate the turbidity exhibited by distilled water. Four wells showed increased turbidity when pumping rate is increased. Results from the Massachusetts site indicate the reproducibility of such time courses; the New York site results contrast turbidities in samples obtained by bailing. The New Jersey and Delaware site results show that light scattering intensity measured in laboratory samples were sometimes quite different from those measured in the field.
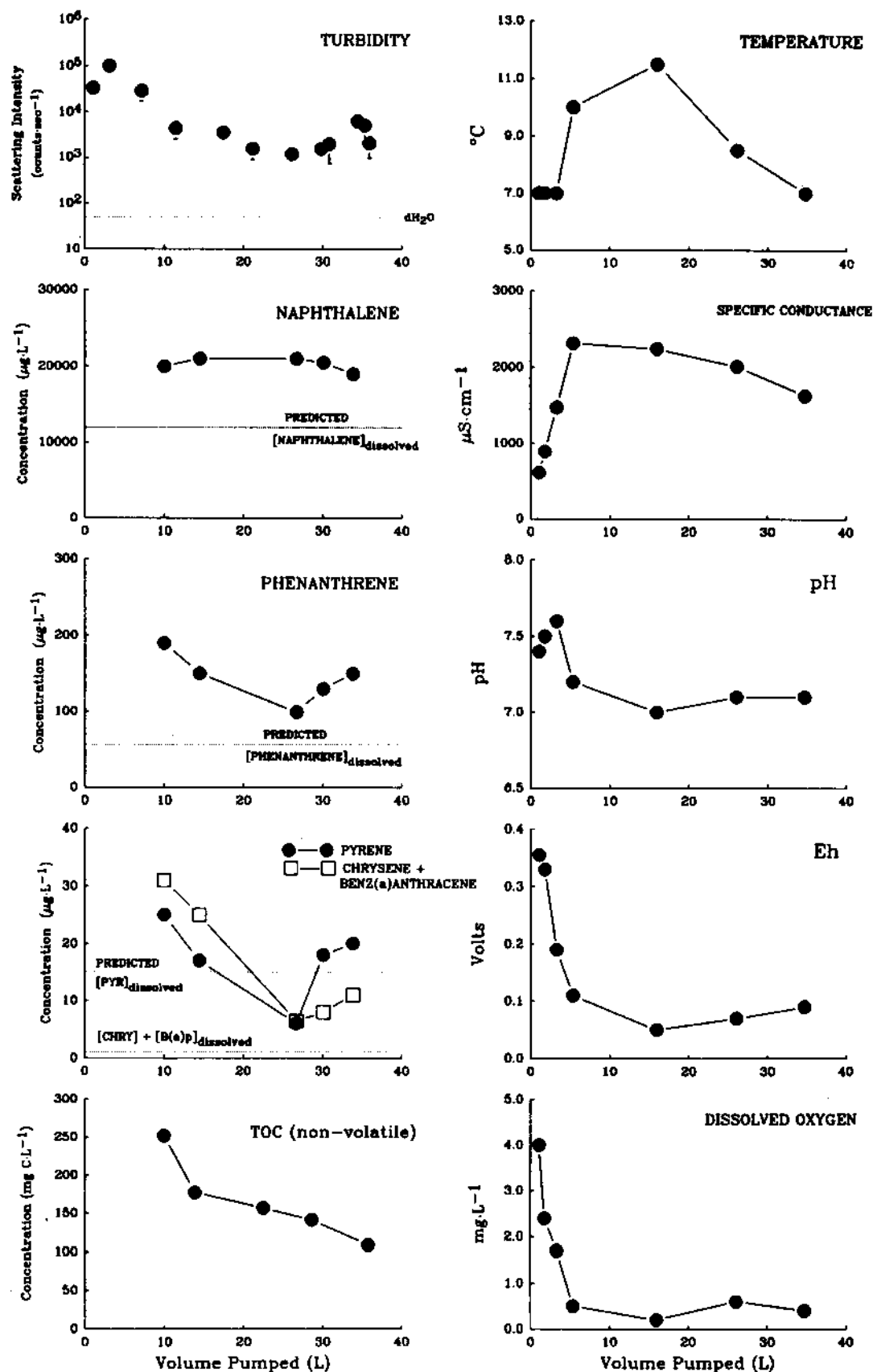
Fig. 3. Variations of water chemistry parameters observed at the Connecticut site (well D). Turbidity decreased until about 20 l had been removed, while other commonly monitored parameters (conductivity, pH, Eh, DO) stabilized much sooner, at about 6 l removed. The relatively water-soluble naphthalene did not covary with turbidity, but the less soluble PAHs appeared to do so.

inants with higher aqueous solubilities or concentrations far in excess of the observed colloid concentrations are not expected to covary with turbidity. Naphthalene, the highest solubility contaminant analyzed, does not covary with turbidity.

It is difficult to accurately determine the amount of contaminant associated with the colloidal phase due to phase separation problems and losses by sorption to filters; however, the possibility that colloid-associated contaminants are present in samples (e.g., from well D at the CT site) can be assessed by comparing the expected dissolved concentrations of PAHs in equilibrium with the coal tar present at the bottom of "contaminated" well D to the measured PAH concentrations in ground water from this well. Observed PAH concentrations in excess of expected dissolved phase concentrations could indicate colloid association. The predicted dissolved concentration of a compound i can be calculated from its mole fraction aqueous solubility (or its hypothetical subcooled liquid solubility for compounds that are solids at the temperature of interest) ($sol'y_i^{water}$), the mole fraction of the compound in the coal tar ($X_i^{tar}$), and the activity coefficient of the compound in the tar ($\gamma_i^{tar}$) as follows:

$$[\text{dissolved } i]_{predicted} = (sol'y_i^{water}) \cdot (\gamma_i^{tar}) \cdot (X_i^{tar}).$$

The predicted dissolved concentrations, indicated by dotted lines in Figure 3, were calculated assuming that (1) the measured weight fraction of these constituents, obtained by gas chromatographic analysis of the tar, provided good estimates of the mole fraction of these compounds in the tar, and (2) the activity coefficient of the compounds in the tar is equal to 1. These approximations should provide a prediction within a factor of three of the true dissolved concentration that would be observed in water equilibrated with this tar (Groher, 1990).

The results of these calculations show that the measured concentrations of the highest solubility PAH, naphthalene in ground water from well D, are similar to the predicted dissolved phase concentration within the error of the estimate. On the other hand, the measured concentrations of the lowest solubility PAHs, chrysene/benz(a)anthracene, are six to 10 times greater than the predicted values; thus, the measured chrysene/benz(a)anthracene concentrations are significantly greater than the predicted values. The significant excess of measured chrysene/benz(a)anthracene may suggest that some of this low-solubility contaminant is associated with the colloidal material observed in the ground water.

Alternatively, entrainment of immiscible droplets of coal tar could account for measured PAH concentrations in excess of expected dissolved concentrations. Entrainment of only 1-3 $\mu$l coal tar/l is necessary to account for the excess calculated for the lowest concentrations of phenanthrene and chrysene measured; less than 10 $\mu$l coal tar/l is required to explain the excess for the highest levels of phenanthrene, pyrene, and chrysene measured. These observations suggest that extreme care must be taken in sampling wells within a source area to avoid entrainment of source material which

may not be mobile. The use of two packers which straddle the pump may be helpful in this regard.

## Turbidity as a Well-Purging Criterion

Turbidity measurements may be a useful surrogate for determining the amount of well purging required to obtain samples representative of mobile hydrophobic contaminant concentrations. Clearly, more comparisons of turbidity and contaminant time courses at other contaminated sites are required to determine whether turbidity is likely to be a good surrogate at many sites. The importance of choosing the appropriate parameter to monitor the extent of purging can be illustrated by comparing observed PAH concentrations in samples collected after various purging volumes. If pH, Eh, or DO had been utilized to determine the extent of purging required at the Connecticut site, purging would have been deemed adequate after a smaller number of well volumes had been removed and significantly higher levels of low-solubility PAHs would have been reported. For example, if sampling was begun after the removal of three to five well volumes, the samples obtained would have contained concentrations of chrysene + benz(a)anthracene six times higher than that which we believe were mobile. Likewise, if sampling had been performed after removing 18 l (4.8 gal), when pH, Eh, and DO measurements had clearly stabilized, the concentrations of chrysene + benz(a)anthracene still would have been more than four times greater than those obtained after 26 l were removed.

Our observations from the other sites examined also support the conclusion that parameters commonly monitored in the field are not good indicators of the completeness of well purging for colloids and, consequently, colloid-associated contaminants. In only two out of 15 wells was the variation of turbidity during purging similar to that of other parameters measured in the field. Usually, pH, Eh, specific conductance, and DO stabilized well before turbidity observations. Therefore, monitoring of ground-water turbidity in the field and sampling only after turbidity has reached a stable level is recommended (Table 2, steps 7 and 9) if accurate estimates of mobile loads of contaminants and colloids are required.

## Sources of Artifactual Turbidity

The initially high, but steadily decreasing, turbidity levels observed during well purging may be caused by (1) removal of well construction-related particles, (2) purging of particles formed or collected within the well casing, or (3) shearing of particles attached to aquifer material near the well. If the initial artifactual turbidity was caused by well construction (e.g., sealing material like bentonite, fine particles from materials used to backfill the well, aquifer material from drilling), the initially high-turbidity level should diminish with each sampling. However, at the Massachusetts wells sampled several times over a nine-month period, similar initial turbidity levels were observed each time these wells were sampled (Figure 2). Also, SEM/EDX observations of the solids in the ground-water samples did not reveal evidence of well construction materials in any of the wells

sampled. These observations suggest that the high initial turbidity observed in the early phases of well purging cannot be attributed solely to artifacts of well construction.

The hypothesis that artifactual turbidity is derived from the purging of particles formed or collected within the well casing is substantiated by "dipstick" observations in several wells (the dipstick is a glass tube lowered into the well and carefully withdrawn with suction applied at the top). For example, flocculent orange particles were visible in the water column sample obtained from contaminated well B at the Connecticut site [settled in the bottom 30 cm (12 in.) of the well and suspended in the top 5 cm (2 in.) at the water table]. This material was probably iron oxide colloids precipitated by oxygenation of the anoxic ground water in the well casing. Also, coal tar was found in the bottom 15-20 cm (6-8 in.) of well D at the Connecticut site. In the source area at the New York site, an oily film was observed floating at the water table and about 17 cm (7 in.) of coal tar was found at the bottom of well A. The suspension of such solid or tarry materials as the sampling gear is lowered down the well probably contributes greatly to the observed initial high turbidities and PAH levels. Thus, cautious insertion of sampling gear into wells and avoidance of contact with the well bottom is recommended (Table 2, step 3). In addition, the use of a "dipstick" is recommended (Table 2, step 2) to identify the presence of nonaqueous phase liquids within the well so that precautions can be taken to minimize contamination of the sampling gear and consequently samples.

To the extent that suspension of bottom material is responsible for turbidity observations, preventing this material from entering the sampling zone could reduce required purging times. The use of a second packer below the pump to reduce the amount of settled material reaching the pump was tested in a Massachusetts well. The pump, straddled by two packers, was carefully lowered down the well, packers were inflated, and ground water was pumped to the surface at a flow rate near 100 ml/min (0.026 gal/min). The initial turbidity of this water was roughly 200 counts/sec. The turbidity remained constant during the purging of 12 l (3 gal); then the flow rate was increased to 1100 ml/min (0.29 gal/min). The turbidity remained nearly the same as that observed at the lower flow rate during the removal of the next 30 l (8 gal). The pump was then pulled to the surface, the bottom packer was removed, and the pump with only one packer was carefully placed down the well and set at the same sampling depth. The initial samples when pumping commenced at a flow rate of 175 ml/min (0.046 gal/min) were nearly 7000 counts/sec. After the removal of about 3 l (0.8 gal), the turbidity was back to 200 counts/sec; after 7 l (1.8 gal) were removed, the turbidity was indistinguishable from distilled water samples (50 counts/sec). When the flow rate was increased to 1300 ml/min (0.34 gal/min) with this one-packer configuration, the first turbidity reading obtained was at 300 counts/sec; after 6.5 l (1.7 gal) were removed, turbidity had declined back to the level of distilled water. This suggests that resuspension of bottom material, which is more accessible to the pump head when only a top packer was used, was contributing to initial high-turbidity observations at this well. The use of two packers may be useful to reduce purging times and initial turbidity (Table 2, step 4).

The third possible source of artifactual turbidity is the suspension of solids, immobile in the natural ground-water flow, by shearing. Shear may be induced by pumping and perhaps even by surging from lowering the sampling gear into the well. Pumping and surging result in ground-water flow at velocities greater than natural velocities or in directions different from natural directions near the well. The amount of shear induced in the aquifer is expected to be proportional to the square of the ground-water pore velocity, so higher pumping rates are expected to induce greater shear in the aquifer. For the aquifer at the New Jersey site, Ryan (1988) calculated that pumping rates greater than 100 ml/min could induce shear rates capable of mobilizing particles outside the aquifer zone disturbed by well construction. Additionally, shearable fine particles may persist in the disturbed zone around the well even though well development is intended to remove fine particles generated by well installation. The well, a conduit to the atmosphere, produces local disturbances to the natural ground-water chemistry that may result in deposition of suspendable particles near the well. Thus, it is expected that lower pumping rates would minimize collection of artifactual colloids and aid in identification of in situ colloids.

### Pumping Rate

The turbidity variations during purging discussed above were observed at pumping rates of less than 200 ml/min. Tests to determine the effect of higher pumping rates on the time courses and final turbidity levels were performed at several wells in New York, Delaware, and New Jersey [note arrows in Figure 2 indicating the pumping rate increase from about 100 to 1000 ml/min (0.026 to 0.26 gal/min)]. In all cases, the turbidity increased sharply in response to the pumping rate increase after a turbidity plateau had been established at the lower pumping rate. We interpret this increase in turbidity to reflect greater inclusion of artifactual solids due to increased shear.

At the New York site, we continued to monitor the turbidity after the pumping rate increase. In the background well, turbidity leveled off at 41 ± 6 counts/sec (essentially the level of the deionized water blank) after removing 20 l (5.3 gal) at a pumping rate of 120 ml/min (0.032 gal/min). After pumping an additional 50 to 60 l (13 to 16 gal) at 950 ml/min (0.25 gal/min), turbidity leveled off at 230 ± 30 counts/sec. In this case, turbidity reached a stable level in less time at the higher pumping rate, but the stable level was significantly higher than that observed at the lower pumping rate. The same test was performed at a contaminated well at the New York site, and a similar variation in turbidity was observed, but turbidity at the higher pumping rate eventually approached the same stable level observed at the lower pumping rate. Thus, the results regarding the effect of high pumping rates are inconclusive and the "slow" pumping rate recommended in our protocol (Table 2, step 5) remains somewhat arbitrary. Similar tests need to be performed at more wells to determine whether higher pumping rates can be used to reduce purging times without adding artifactual
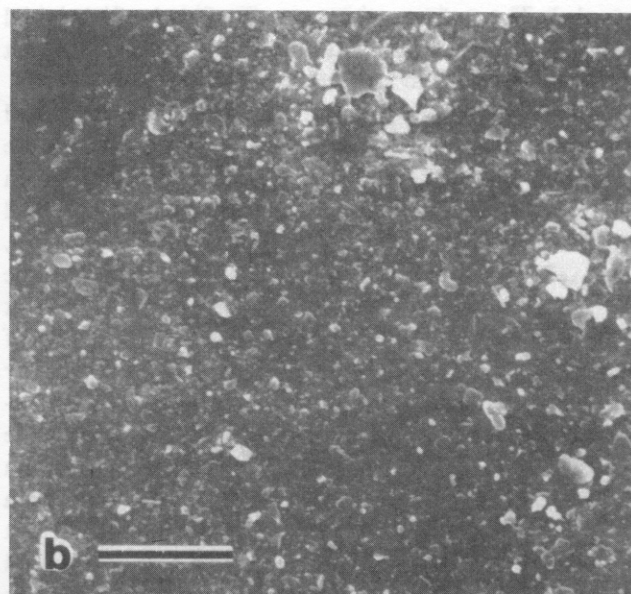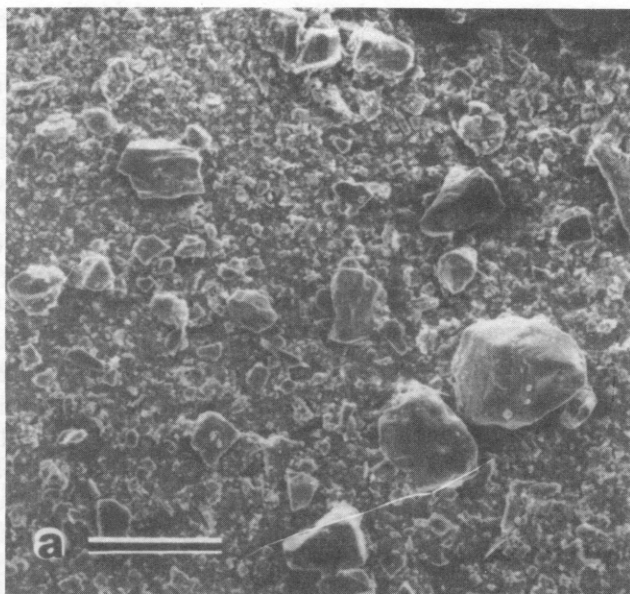
**Fig. 4.** Scanning electron micrographs of particles collected on 30 nm Nuclepore filters showed the dramatic difference in size of particles from bailed versus pumped ground-water samples from the same well: (a) collected by bailing after removing three well volumes; scale bar indicates 100 $\mu$m, and (b) obtained at the same well on the following day by slow pumping; scale bar indicates 10 $\mu$m.

solids. Additionally, tests need to be performed to confirm that still lower colloid levels are not found when pumping rates less than 100 ml/min (0.026 gal/min) or when "passive" ground-water sampling systems (Magaritz et al., 1990) are used.

### Pumping vs. Bailing

Samples collected by bailing were compared to samples collected by slow pumping [less than 200 ml/min (0.053 gal/min)] from the same wells at the New York site. Bailed samples were obtained after the removal of three and eight well volumes and pumped samples were obtained on the following day. The turbidity of the bailed samples was orders of magnitude higher than that of the pumped samples (Figure 2). Not only was the observed turbidity higher in bailed samples, but SEM micrographs of the particles retained on 15 nm Nuclepore filters showed there was an enormous difference in the size of particles in these samples (Figure 4). The bailed sample contained particles in the range of 1-100 $\mu$m, whereas the pumped sample contained mainly particles less than 5 $\mu$m in diameter. SEM/EDX analysis of the filter samples indicated that the large particles in the bailed samples were composed mainly of silicon (presumably quartz grains); the smaller plates present in both samples contained both aluminum and silicon (clay). It is possible that the smaller plates in both samples were mobile in situ; however, it is very unlikely that the 100 $\mu$m particles were mobile in porous media at ground-water flow rates. These results suggest that bailing may collect particles and particle-associated contaminants which are not representative of in situ mobile loads. Thus the sampling protocol described in Table 2 specifies pumping rather than bailing for purging and sampling of monitoring wells.

The implications of these observed differences in bailed versus pumped samples is clearly illustrated by comparison of the PAH concentrations found in bailed and pumped samples from the coal tar source region monitoring well at the New York site (Groher et al., 1990). Bailed ground water, sampled after purging three well volumes, contained 750 times as much benzo(a)pyrene, 380 times as much chrysene + benz(a)anthracene, 92 times as much pyrene, and 26 times as much phenanthrene as found in samples pumped from the same well at 20 ml/min (0.0053 gal/min, via peristaltic pump) on the following day. The pumped sample concentrations corresponded closely to values predicted for dissolution of these PAHs from this particular tar into the water (calculated as the product of each compound's hypothetical liquid solubility and its weight fraction in the tar). It is possible the bailed samples contain either PAHs associated with immobile particles or with entrained coal tar (known to exist at the bottom of this well from the "dipstick" observations). Use of the data obtained by bailing samples using standard purging protocol (US EPA) at this site would lead to substantial overestimation of the contaminant concentrations in ground water and exposure risk. Comparison of contaminant concentrations in bailed samples and slowly pumped samples at other sites are necessary to determine whether the discrepancy observed at this site is common.

### Filtration of Ground-Water Samples

The strategy proposed in this paper for differentiating between artifactual colloids and colloids which are mobile within the aquifer is to minimize creation and collection of the artifactual colloids using the protocol described above. An alternative strategy would be to attempt to separate artifactual and mobile colloids collected by filtering the sample. Although this strategy would reduce the possibility of overestimation of mobile colloid and contaminant loads, filtration could lead to underestimation of true mobile loads of contaminants by removing colloids which were actually

mobile in situ. Traditionally, filters with nominal pore size of 0.45 μm have been used to filter ground water. Results from several sites suggest that this practice eliminates a major portion of the colloids collected after prolonged slow pumping. When samples from the Nevada site were filtered through a 1 μm filter, the light scattering intensity of the sample was reduced by almost two orders of magnitude (Gschwend et al., 1990). At the New Jersey site, such filtration diminished the light scattering by a factor of six (Ryan, 1988). Hence, collection of samples by the recommended protocol (Table 2, step 9) is suggested instead of sample filtration if total mobile loads of colloids and colloid-associated contaminants are to be determined.

### Maintenance of In Situ Conditions

It is imperative that in situ chemical conditions be maintained in ground-water samples to investigate the nature and abundance of colloids. While it might not be possible to maintain the pressure of samples collected from deep aquifers, exchange of oxygen and carbon dioxide with the atmosphere can be minimized to avoid changes in solution chemistry (DO, Eh, redox states, pH, carbonate equilibria). Without prevention of gas exchange, changes in solution chemistry may result in formation of new colloids by precipitation of oxides and carbonates and loss of natural colloids through coagulation and settling. This type of post-sampling artifact is the suspected cause of the occasional discrepancies between turbidity measurements made in the field versus those repeated on returning to the laboratory (e.g., Figure 2 for New Jersey and Delaware sites). At the Massachusetts site, where ferrous phosphate colloids were found, intentional aeration of the ground-water samples over a period of 8 hrs caused the turbidity to increase by an order of magnitude, while ferrous iron concentrations decreased in accordance with reported kinetics of its oxidation (Reynolds, 1985). These observations lead to the conclusion that both the concentration and character of colloids found in a ground-water sample may be incorrectly evaluated if in situ conditions are not maintained during ground-water sampling, storage, and analysis.

### Confirmation of Mobile Colloid Concentrations and Characteristics

In the discussions above, we have relied on the decline of turbidity from initially high levels to a stable level during prolonged slow pumping as the criterion for qualifying the suspended solids collected as natural in situ colloids. We also rely on colloid characterization, ground-water chemistry analysis, and comparisons of results between "background" and "contaminated" wells to support conclusions that colloids collected in the samples are natural in situ colloids.

To confirm that the suspended solids observed in samples are not artifactual solids, we have used three approaches. First, the appearance and composition of colloids observed in the ground-water samples are compared with colloidal material associated with well construction. If SEM/EDX analysis revealed colloids of composition similar to bentonite in samples collected through bentonite-sealed wells or colloids that appeared to be iron oxides in a sample collected

through a steel well, then these colloids would be considered suspect due to similarities to well construction materials.

Second, colloid size can be used to evaluate the likelihood of in situ colloid suspension. Colloids larger than several micrometers in diameter are probably not mobile in aquifers under natural ground-water flow conditions due to gravitational settling (Yao et al., 1971). Hence, large colloids like those observed in the bailed samples collected from the New York site are certainly suspect.

Third, at each site, samples were obtained from "background" and "contaminated" zones of the aquifer through wells constructed and developed in the same manner (Table 2, step 8). Suspended solids observed in the "background" and "contaminated" samples and the geochemical conditions of the regional aquifer and the "contaminated" plume were compared. Based on alteration of the regional geochemical conditions by the "contaminated" plume and expected colloids solubilities and surface charges, explanations have been surmised for the presence of mobile colloids at several of the sites sampled. At the Massachusetts site, it is hypothesized that the changes in ground-water chemistry due to the influence of the plume of secondarily treated sewage led to precipitation of colloids (Gschwend and Reynolds, 1987). At the New Jersey, Delaware (Ryan and Gschwend, 1990), and Nevada sites (Gschwend et al., 1990), it is hypothesized that changes in ground-water chemistry led to dissolution of secondary mineral phases (iron oxyhydroxides or calcium carbonates) which had cemented colloidal material to the aquifer solids, and consequently colloidal material was mobilized.

### Practical Considerations

Some additional practical considerations become important when the pumping rate is lowered below 100 ml/min (0.026 gal/min). The first issue involves the availability of positive displacement pumps for sampling 5 cm (2 in.) diameter wells at pumping rates of ≤ 100 ml/min. The positive displacement gear-driven pump used in much of our work was chosen because the sample contact area was small and constructed of relatively inert materials. However, operation of the pump at pumping rates of < 100 ml/min was plagued by frequent stalling. Positive displacement bladder pumps can pump reliably at low pumping rates, but these pumps typically have high sample contact surface areas constructed of materials unsuitable for sampling hydrophobic organic compounds. Thus, in the instances where we have been interested in pumping slower than 100 ml/min, peristaltic pumps have been utilized. The drawback of using peristaltic pumps is the possibility of sample degassing caused by suction.

Another practical set of issues arising from the use of slow pumping rates involves longer residence time in the pump and tubing. This enhances the possibility of losses due to sorption, volatilization, and degassing. At the Connecticut site, increased residence time in the sample tubing led to changes in water temperature that mirrored changes in air temperature. At the Massachusetts site, we encountered a more insidious problem with increased residence time at the "contaminated" well. When the anoxic ground water was

pumped at near 100 ml/min, light scattering intensity leveled off at several hundred counts/sec on three different occasions ("contaminated" MA, Figure 2) and samples stored for months in DO bottles remained clear. But when ground water was pumped at 50 ml/min (0.013 gal/min), light scattering intensity leveled off at several thousand counts/sec and the ground water became visually turbid and orange-tinged soon after collection. The increase in residence time due to the decrease in pumping rate presumably allowed oxygen to permeate the polypropylene sample tubing and initiate ferrous iron oxidation. Holm et al. (1988) found that oxygen could contaminate samples via diffusion through some tubing materials. It is suggested that the use of even less permeable tubing (aluminum or stainless steel) may be necessary at some sites if it is found that very low pumping rates are required to obtain information about mobile colloid phases and accurate estimates of total mobile contaminant concentrations. With longer residence times, it is also crucial that the least sorptive materials be used (e.g., relatively flexible aluminum tubing for organic contaminants, polypropylene or teflon for metals).

Finally, some may argue that slow pumping of monitoring wells may result in protracted times for field personnel to remain on-site. Much of this problem can be mitigated by (1) initiating slow pumping of many wells simultaneously (Table 2, step 8) and (2) utilizing pumping equipment that can be left unattended. It must be recognized that all subsequent chemical analyses, fate and risk assessment, and remediation design will be of dubious value if the requisite steps are not taken to acquire ground-water samples which accurately reflect the in situ subsurface conditions. The extra time and cost of carefully collecting samples which provide accurate estimates of contaminant concentrations must be weighed against the cost of a bad decision based on inaccurate estimates. Perhaps a good strategy would be to periodically sample wells by both the commonly used strategy and the strategy proposed here. If there is no significant difference in the results obtained by both methods, then the more cost-effective method should be used.

## Conclusions and Recommendations

The sampling protocol outlined in Table 2 was designed to collect ground water for analysis of both dissolved and colloid-associated chemicals. This sampling scheme was tested and used at a variety of sites over the past five years. A number of conclusions and recommendations can be drawn from our sampling experiences.

1. Slow prolonged pumping is preferred over bailing. Bailed samples collected from a coal tar-contaminated site contained 10-100 times higher concentrations of suspended solids and much higher concentrations of PAHs than found in carefully pumped samples. The results of sampling experiments at pumping rates higher and lower than 100 ml/min are not yet conclusive. Further tests should be conducted to determine the effect of pumping rate on ground-water colloid observations.

2. Ground-water turbidity should be monitored in the field to determine when a well is adequately purged for studies pertaining to colloids or low-solubility contaminants. More commonly monitored parameters used for judging adequacy of purging often stabilized well before turbidity measurements. Use of these parameters or reliance on purging a specified number of well volumes to determine when a well has been sufficiently purged could lead to overestimation of mobile colloid and colloid-associated contaminant loads.

3. The sampling protocol should maintain in situ ground-water conditions during both sampling and storage. Sample contact with the atmosphere can alter natural colloid populations. To this end, the sampling system described includes a positive displacement pump, relatively nonsorptive and impermeable tubing with a minimum number of joints and valves, flow-through monitoring, and sampling by methods suited for DO determination.

4. Ground-water samples should not be filtered if estimates of total mobile loads of contaminants are required. Filters can remove mobile ground-water colloids from samples.

5. The suspected presence of colloids suspended in situ should be corroborated by auxiliary data (e.g., colloid levels in "background" wells, colloid-size distributions, ground-water geochemistry, and colloid surface charge).

Colloids have been found at a variety of sites using this sampling protocol (Table 1), suggesting that the presence of colloidal phases in ground water may be a common phenomenon. The significance of colloids in contaminant transport is yet to be determined. We believe that the sampling protocol outlined in Table 2 has provided accurate assessment of total mobile contaminant loads and suspended colloid characteristics and concentrations in various ground waters and will be of use in future studies to determine the significance of this transport process.

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