



ENVIRONMENTAL RESEARCH BRIEF

Colloidal-Facilitated Transport of Inorganic Contaminants in Ground Water: Part I. Sampling Considerations

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Abstract

Investigations at Pinal Creek, Arizona, evaluated routine sampling procedures for determination of aqueous inorganic geochemistry and assessment of contaminant transport by colloidal mobility. Sampling variables included pump type and flow rate, collection under air or nitrogen, and filter pore diameter. During well purging and sample collection, suspended particle size and number as well as dissolved oxygen, temperature, specific conductance, pH, and redox potential were monitored. Laboratory analyses of both unfiltered samples and the filtrates were performed by inductively coupled argon plasma, atomic absorption with graphite furnace, and ion chromatography. Scanning electron microscopy with Energy Dispersive X-ray was also used for analysis of the filtered particulates.

Suspended particle counts consistently required approximately twice as long as the other field-monitored indicators to stabilize. High-flow-rate pumps entrained normally nonmobile particles. Differences in elemental concentrations using different filter-pore sizes were generally not large with only two wells having differences greater than 10 percent in most elemental concentrations, although trends showed increasing concentrations with increasing filter pore sizes in most wells. Similar differences (> 10%) were observed for some wells when samples were collected under nitrogen rather than in air. Fe^{2+}/Fe^{3+} ratios for air-collected samples were smaller than for samples

collected under a nitrogen atmosphere, reflecting sampling-induced oxidation.

Introduction

Ground-water samples that are representative of actual ground-water quality are, at best, difficult to obtain (Claassen, 1982). Disturbance of the subsurface environment is unavoidable during well construction activities. Additional disturbance during sample collection may drastically alter ground-water chemistry due to oxidation, sorption, mixing, and turbulent flow resulting in inaccurate estimations of contaminant loading and transport predictions. A common study objective is to determine what constituents are mobile in an aquifer. Many ground-water samples are filtered to exclude particles dislodged from the local well environment, because those particles are not mobile at ordinary ground-water velocities. Because geochemical models are based on the thermodynamics of dissolved constituents, small pore-diameter filters have been preferred as the best way to separate dissolved from particulate constituents.

In practice, 0.45- μ m filters are commonly used to balance between the objectives of isolating dissolved constituents and permitting reasonable use in the field. Unfortunately, particle sizes do not have an express lower bound so that the right filter can perfectly separate particles from solutes. Particles with diameters from 0.003 to 10 μ m, referred to as colloids, may form in certain environments and be mobile at ground-water velocities. Use of 0.45- μ m filtration may exclude an important component of the contaminant load at some waste sites, particularly where highly toxic metals are involved (Puls and Barcelona, 1989).

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Many studies have demonstrated contaminant transport by colloidal mobility (Gschwend and Reynolds, 1987; Eichholz et al. 1982; Enfield and Bengtsson, 1988; Robertson, 1984). There is increasing concern that current methods of ground-water sample collection may exclude this component of the contaminant loading in a given system. If the purpose of sampling is to estimate contaminant transport, substantial underestimations of mobility may result, because of colloidal associations. Numerous studies attest to the strong sorptive capabilities of secondary clay minerals; hydrous Fe, Al, and Mn oxides; and humic material of colloidal dimensions. Takayanagi and Wong (1984) determined that more than 70 percent of the total Se in river waters adjacent to the Chesapeake Bay was associated with organic and inorganic colloidal particles. Buddemeier and Rego (1986) found that virtually all the activity of Mn, Co, Sb, Cs, Ce, and Eu was associated with colloidal particles in ground-water samples from underground nuclear-test cavities at the Nevada Test Site. Colloidal particles generated in batch experiments by Sheppard et al. (1979) and Puls et al. (1989) were shown to retain substantial proportions of radionuclides. Further work by Sheppard et al. (1980) concluded that the transport of radionuclides by colloidal clay particles should be considered in contaminant-transport models.

Filtration is part of this concern; but other factors, such as sample exposure to atmospheres different from aquifer environments and pump-induced disturbance of the sampling zone, are also important. Oxidation-induced precipitation and sorption processes, many of which are kinetically rapid (seconds to minutes), may cause previously dissolved species to be removed during filtration, resulting in lower metal concentrations than are actually present in the aquifer. Filter loading and clogging with fine particles may also occur, reducing the nominal pore size of the filter and introducing errors due to changing effective pore size (Danielsson, 1982).

Background

A workshop was convened at the Robert S. Kerr Environmental Research Laboratory (RSKERL) of the U.S. Environmental Protection Agency in 1988 to examine these issues and provide technical guidance based on currently available scientific information. A Superfund Ground Water Issue Paper resulting from the workshop emphasized the importance of well construction and sampling methodology in obtaining representative water chemistry data (Puls and Barcelona, 1989). Workshop recommendations in the area of ground-water sampling are briefly summarized below:

Purging

Water that remains in the well casing between sampling periods is unrepresentative of water in the formation opposite the screened interval. It must be removed by purging or isolated from the collected sample by a packer arrangement prior to the collection of representative water samples. It is important to purge the stagnant water at flow rates below those used in development to avoid further development, well damage or the disturbance of accumulated corrosion or reaction products in the well.

Isolation of Sampling Zone

Isolation of the sampling zone is necessary to minimize the purge volume as well as to minimize air contact. This is

especially important since Eh/pH conditions of the formation waters are often sensitive to dissolved-gas content. Inflatable packers can be used to achieve isolation of the sampling zone.

Pumping for Sample Collection

It is recommended that a positive displacement pump be used. Other types of sample collection (e.g. bailing) may cause displacement of non-mobile particles or substantially alter ground-water chemistry leading to colloid formation (e.g. vacuum pumps). Surging must be avoided, and a flow rate close to the actual ground-water flow rate should be employed. While an initial approximation, flow rates around 100 to 500 ml/min have been used to successfully sample ground waters in a quiescent mode.

Assessment of Water Constituents During Purging and Sampling

Monitoring for dissolved oxygen, temperature, specific conductance, pH and turbidity during purging and sampling is recommended to determine baseline ground-water quality conditions prior to sampling.

Filtration

For estimates of contaminant mobility, filtration with coarse filters ($\geq 2 \mu\text{m}$) using the same procedures as above or collection of unfiltered samples is recommended. Filtration for accurate estimations of geochemistry should be performed in the field with in-line pressure filtration using a large (e.g. 142 mm) polycarbonate-type (thin with sharp pore-size cutoff) 0.1 μm filter. Air contact should be minimized and entirely excluded for some samples. Acidification of samples to $< \text{pH } 2$ should be performed immediately. The filter holder should be non-metallic. Holders made of steel are subject to corrosion and may introduce non-formation metals into samples. Prewashing of filters should be routinely performed.

In an effort to test the efficacy of these recommendations, a joint study by the U.S. Environmental Protection Agency and the U.S. Geological Survey was begun in the spring of 1988. Collection of representative unfiltered samples is quite challenging in many systems because of the difficulty of excluding nonsuspended or artifact particulates. Because no sampling technique is totally passive, all contaminant-mobility estimates based on unfiltered samples are biased toward overestimation. An attempt was made to minimize this bias by carefully following the workshop recommendations.

Purpose and Objectives

The specific objectives of the study were to evaluate perturbations to the ground-water geochemistry during sample collection and, in particular, to identify those factors that caused significant differences in elemental concentrations or concentrations and size distributions of suspended particles in samples collected for analysis. Samples for both dissolved and suspended contaminants were collected. Filters smaller than 0.45 μm were used to sample for dissolved constituents and for comparison with the unfiltered or coarsely filtered samples. This document summarizes the results of the study and addresses the efficacy of the 1988 RSKERL filtration workshop recommendations on ground-water sampling for metals analyses.

Study Site

The study site is located at Pinal Creek, near Globe, Arizona, about 130 km east of Phoenix and about 170 km north of Tucson. Copper has been mined since 1903 from granite porphyry adjacent to an aquifer at the site. A band of unconsolidated alluvium 300 to 800 m wide, as much as 50 m thick, and about 20 km long forms the upper, central part of the aquifer in a valley along Miami Wash and Pinal Creek (Figures 1 and 2). Most of the sediment in the alluvium ranges in size from fine sand to coarse gravel, but clay and boulder lenses also are present. Alluvial basin fill more than 100 m thick forms the remainder of the aquifer beneath and adjacent to the unconsolidated alluvium. Peterson (1962) described the geology of the area.

During 1940-86, acidic mining waste solutions were discarded in an unlined lake formed behind waste and tailings piles. In 1986, pH at the lake surface was about 2.7 and the lake volume was about $5.5 \times 10^6 \text{ m}^3$. By May 1988, virtually all the lake water had been spread on inactive tailings piles to evaporate. Contamination of ground and surface waters in the area has been described by Eychaner (1989). The distribution of pH in the aquifer was used as a guide in selecting wells to sample for this study (Figure 1).

Water levels and chemical quality have been monitored since 1984 in several groups of observation wells (Figure 1). Each group consists of separate wells individually completed with 10-cm-diameter polyvinylchloride casing and a single well screen. Most of the well screens are 0.9 m long; the longest screen in a

well sampled for this study is 6.1 m. Most of the wells were drilled by the hydraulic rotary method using bentonite-based drilling mud; five wells were drilled by the hollow-stem auger method. The annulus in the screened interval was packed with washed pea gravel from a nearby uncontaminated area. The gravel pack was capped with a 1-m layer of bentonite pellets. Each well was developed by jetting high-pressure air through the screen to dislodge and remove fine-grained material. Comprehensive data from the study area are available (Eychaner et al, 1989).

In the alluvium, hydraulic conductivity is on the order of 200 m/d on the basis of cross-sectional area, hydraulic gradient, and measured outflow (C.C. Neaville, hydrologist, U.S. Geological Survey, written commun., 1990). For thick sections of basin fill, hydraulic conductivity was estimated from aquifer tests of two wells to range from 0.1 to 0.2 m/d (Neaville, written commun., 1990).

Near the sampled wells, hydraulic conductivity was estimated on the basis of measured water-level declines and pumping rates during sampling periods using the solution of the unsteady ground-water flow equation (Lohman, 1979, eq. 44). The estimates are within an order of magnitude at best, but are useful for comparisons among the wells because of the similarities in construction. The estimates range from 10 to 150 m/d for wells in the alluvium or uppermost basin fill. Estimated hydraulic conductivity for well 105, deeper in the basin fill, was 0.5 m/d. On the basis of hydraulic gradients that range from 0.005 to 0.008 and assumed porosity of 0.2 or 0.3, average ground-water flow velocities near the wells range from 0.02 to 3 m/d.

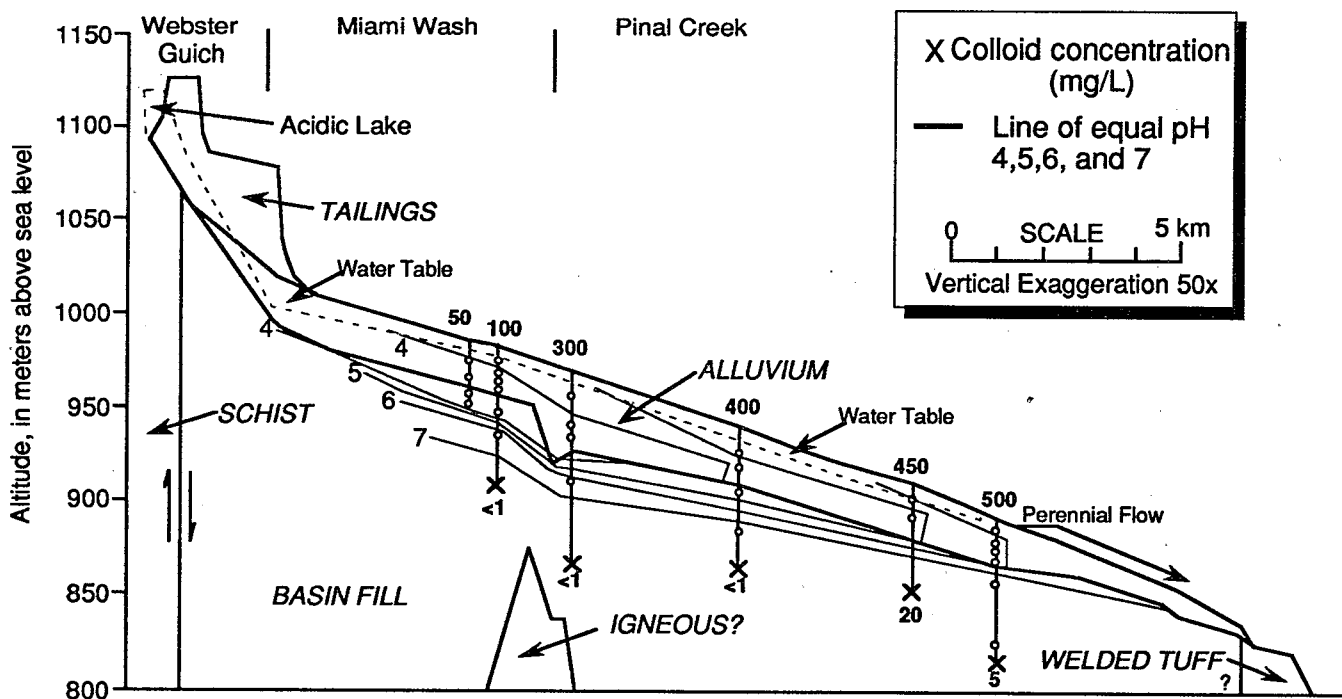


Figure 1. Hydrogeologic Section of the Aquifer

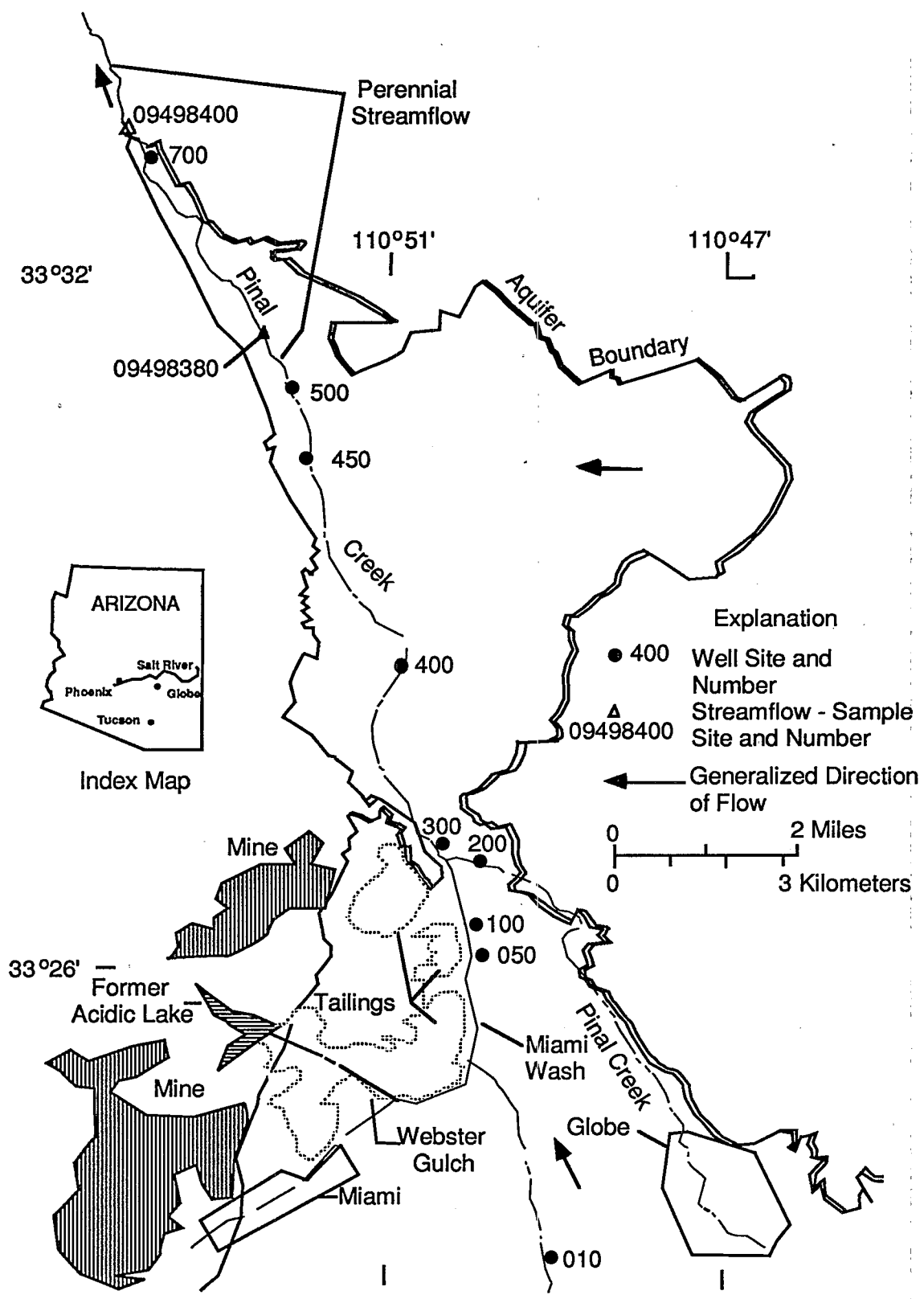


Figure 2. Plan-View of Study Site

Instrumentation and Methods

Ground water was collected during two field seasons from twelve wells selected to represent the range of pH, solute concentration, and hydraulic conductivity along Pinal Creek (Figures 1 and 2). Three different pumps were used (Table 1). At the lowest discharge, velocities induced at the borehole face were estimated to range from 1 to 5 times the average ground-water velocity close to each well in the alluvium. In the basin fill underlying the alluvium, even the lowest discharge resulted in velocities more than 400 times that of the ground water.

Water that remained in the well between sampling sessions was purged, as it was judged to be unrepresentative of formation water. An inflatable packer was used with the bladder and low-rate submersible pumps to reduce necessary purge volumes. During purging, a Hydrolab Surveyor II¹ with a flow-through cell was used to monitor temperature, specific conductance, pH, dissolved oxygen, and oxidation-reduction potential (Pt electrode). Samples were collected only after each indicator reached an acceptably stable value, generally a value that changed by less than its measurement uncertainty during one purge volume. From 3 to 24 volumes were purged before sampling, and the high flow rate submersible pump generally purged the larger volumes.

During the second field season, a Malvern Autosizer IIc was used to measure suspended particles in the diameter range from 0.003 to 3 μm . The instrument determines the size distribution of suspended particles in this size range using laser light scattering techniques together with photon correlation spectroscopy. Particle-concentration estimates were based on calibration curves constructed using linear correlation ($r^2 = 0.999$) between photon counts by the instrument and known concentrations of kaolinite, a secondary clay mineral. The kaolinite used was a reference standard obtained from the Clay Minerals Repository at the University of Missouri. Kaolinite was identified by Scanning Electron Microscopy with Energy Dispersive X-Ray (SEM-EDX) on many of the filters from the sampled wells. Other particles captured on filters and identified by SEM-EDX included iron oxides, smectite, jarosite, silica, and gypsum. Although the assumption that minerals in the reference

standard adequately represent the sum total of all the colloids in the aquifer is not entirely true, photon counts provide at least a relative measure of suspended particle concentrations.

Colloid concentrations took longer to stabilize than other field indicators, about 50 percent longer than dissolved oxygen or redox potential, and about twice as long as specific conductance, pH, or temperature. Well 107 was representative of the variation of the indicators during purging at most of the wells (Figure 3). Stable values of the indicators at selected wells are listed in Table 2.

Samples were collected both in air and under nitrogen using a field glove box. Unfiltered and filtered samples were collected, the latter using 142-mm-diameter Millipore and Nucleopore membrane filters ranging in pore size from 0.03 to 10.0 μm . Samples were acidified in the field immediately after filtering with double distilled concentrated nitric acid to pH < 2. Working in the glove box was difficult, and handling thin membrane filters with latex gloves was particularly cumbersome.

Elemental analyses were performed with inductively coupled plasma (ICP) for most elements; atomic absorption with graphite furnace (AAGF) for Cd, Pb, and As; and ion chromatography (IC) for chloride and sulfate. Analytical precision on the ICP and AAGF were $\leq \pm 10$ percent, and on the IC $\leq \pm 5$ percent. Scanning Electron Microscopy with Energy Dispersive X-Ray (SEM-EDX) was used to identify colloidal material captured on the membrane filters.

Effects of Sampling Variables

Pumping Rates

Differences in pumping rates were expected to cause differences in the concentrations and size distributions of colloidal particles in suspensions and differences in elemental concentrations after filtration. Ten wells were purged and sampled with as many as three different types of pumps in June 1988 and March 1989. Pumping rates ranged from 0.6 to 92 L/min, corresponding to velocities of 25 to 3900 m/d at the well screens. Samples were filtered in air through 0.4- μm filters, filtrates were analyzed for

Table 1. Pumps used in ground water sampling.

Brand ¹	Type	Power Supply	Diameter (mm)	Discharge (L/min)
GeoTech	bladder	compressed air	44	0.6 - 1.1
Keck	submersible	12 V dc	44	2.8 - 3.8
Grundfos	submersible	240 V ac	95	12 - 92

¹ Use of brand names is for identification purposes only and does not imply endorsement by any agency of the United States Government.

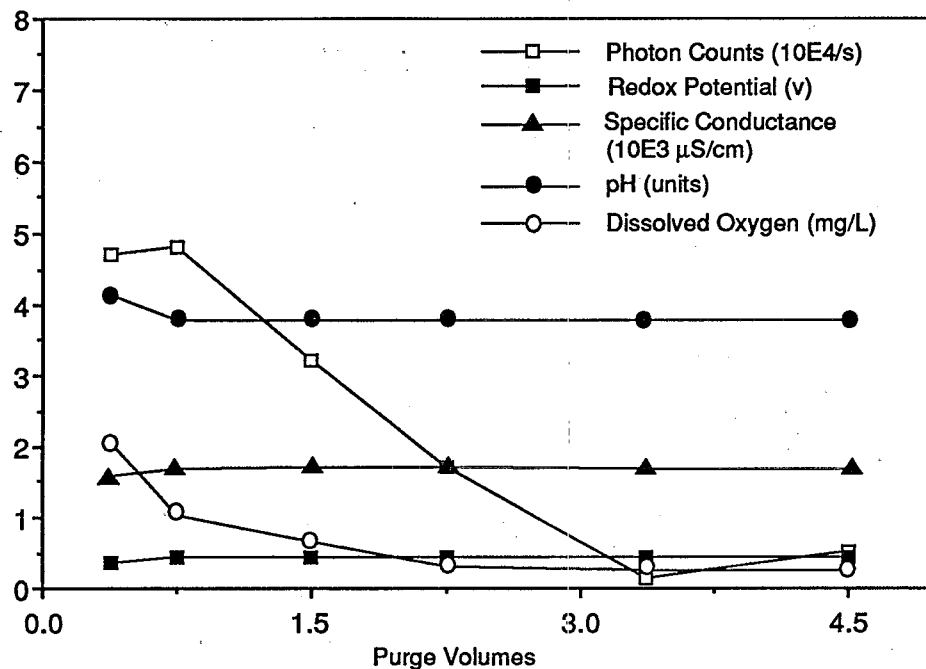


Figure 3. Changes in Water Quality Indicators During Purging of Well 107 (Keck Pump, 3/89)

Table 2. Ground-water quality indicators for selected wells.

Well:	104	105	107	303	403	451	503
pH (units)	3.92	6.08	3.48	4.27	5.05	4.73	5.74
Sp.Cond.(μS/cm)	3020	4300	7070	3210	3200	4060	3620
Temp.(°C)	18.0	19.0	18.4	19.0	18.8	18.9	18.9
Oxygen(mg/L)	0.39	—	0.14	0.01	0.07	0.24	0.22
Redox Pot.(v)	0.44	0.28	0.44	0.37	0.38	0.25	0.32
Colloids (mg/L)	—	0.4	0.3	—	—	20	0.1

cations using ICP, and the filters were examined using SEM-EDX. Particle concentrations and size distributions were monitored in 1989 for five wells on unfiltered samples.

Cation concentrations differed by less than 10 percent between pumping rates for seven of the ten wells. These seven wells generally had low particle counts, and low filter loading was observed using SEM-EDX. Well 503, in the alluvium, was representative of the seven wells. Figure 4 illustrates changes in water-quality indicators in well 503, where the bladder pump was used to purge and sample, followed by use of the low-rate and high-rate submersible pumps. The well therefore was purged with the bladder pump prior to placement of the latter two pumps. Colloid concentration stabilized at 0.1 mg/L during pumping at 1.1 L/min and increased to 0.7 mg/L when discharge increased to 3.8 L/min before stabilizing again at 0.1 mg/L. When discharge increased to 30 L/min, however, colloid concentration initially increased to 4.4 mg/L before finally stabilizing at 0.2 mg/L. Particle-size distributions for the final sample with each pump are also shown in Figure 4. The low-discharge pumps produced monomodal distributions of the same size particles. The highest discharge produced larger and slightly more particles in a bimodal distribution because of increased turbulence. The predominant mineral identified on the filters from well 503 was gypsum, which was accompanied by some iron oxide, kaolinite, and other particles that contained Fe+Al+S. Analytical concentrations of metals did not differ significantly but did reflect the observed mineralogy.

For samples from the three wells where observed cation differences exceeded 10 percent, measured particle counts and filter loading were also significantly higher than for the other

seven wells. Particle counts differed by factors of 5 to 130 between pumping rates. Cation concentrations differed by as much as 50 percent for both major and trace elements. Cation concentrations were generally highest in samples with the lowest counts (least turbid), but some anomalous behavior was observed for some elements (Table 3). Pump-induced entrainment of colloidal particles could decrease dissolved cation concentrations by sorption on freshly exposed surfaces of particles which had been retained on filters.

Differences in cation concentrations were especially noticeable at well 105. In March 1989, pumping at 2.8 L/min mobilized 13 times more particles and decreased Ca, Mg, Mn, and Sr concentrations by 10 to 25 percent, compared to pumping at 0.9 L/min (Table 3). For equal volumes of filtrate, SEM photographs showed that the proportion of the area of a 0.1 µm filter covered with particles was about 1 percent for the lower pumping rate and about 30 percent for the higher rate. In June 1988, pumping at 12 L/min decreased concentrations of Ca, Mg, Mn, Co, Ni, and Sr by 20 to 50 percent compared to pumping at 1 L/min. Well 105 is screened in the basin fill, which has the lowest ground-water flow velocity in this study. Even at the lowest pumping rate, the velocity induced at the borehole face was more than 400 times the normal ground-water velocity. Water pumped from well 105 was visibly murky at times.

Pumping well 451 at 0.8 L/min produced seven times more particles than pumping at 3.4 L/min and decreased concentrations of six cations by 10 to 50 percent. Again, the less turbid water generally had the larger concentrations, but the higher pumping rate unexpectedly produced the less turbid water. This well had the highest colloid concentrations of any well (Table 4). The

Table 3. Cation and colloid concentrations, mg/L, after purging at different rates (March 1989, 0.4 µm filter, sampled in air).

Well	105	105	451	451	503	503	503
Discharge (L/min)	0.9	2.8	0.8	3.4	1.1	3.8	30
Colloids	0.3	4.0	20	3.0	0.1	0.1	0.2
Ca	579	478	586	623	703	704	704
Mg	149	117	150	162	148	146	147
K	40	37	16	13	12	11	11
Fe	<.4	<.4	156	151	<.4	<.4	<.4
Mn	6.6	5.0	108	113	76	76	73
Al	<.4	<.4	6.5	10.0	<.4	<.4	<.4
Cu	<.4	<.4	6.4	12.4	<.4	<.4	<.4
Co	<.4	<.4	1.5	1.8	<.4	<.4	<.4
Ni	<.4	<.4	0.3	0.4	0.6	0.6	0.6
Sr	1.6	1.4	1.9	2.1	2.3	2.3	2.3
Zn	0.7	0.9	3.0	3.9	0.06	0.04	0.04

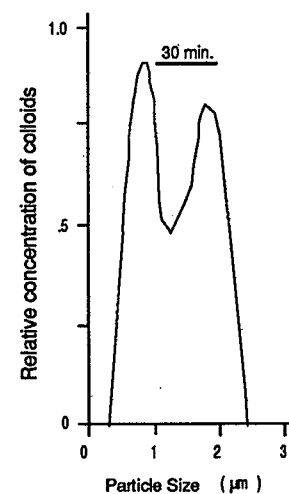
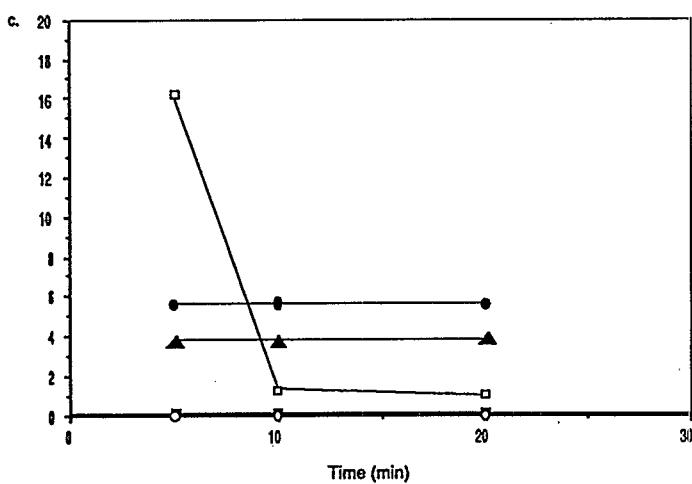
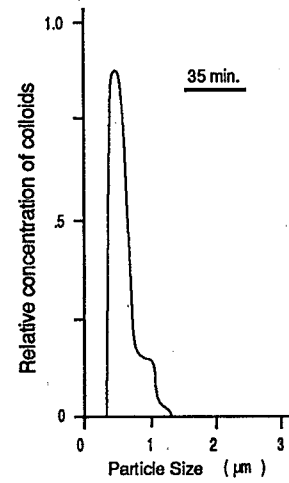
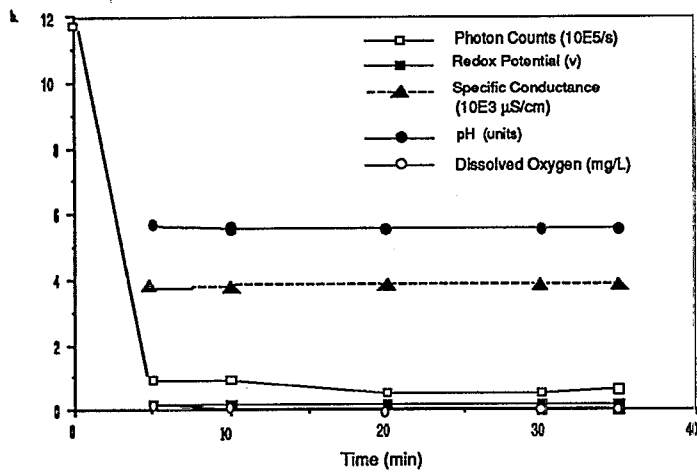
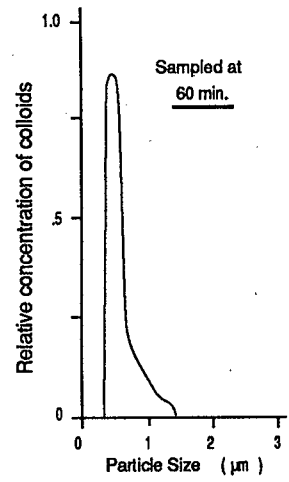
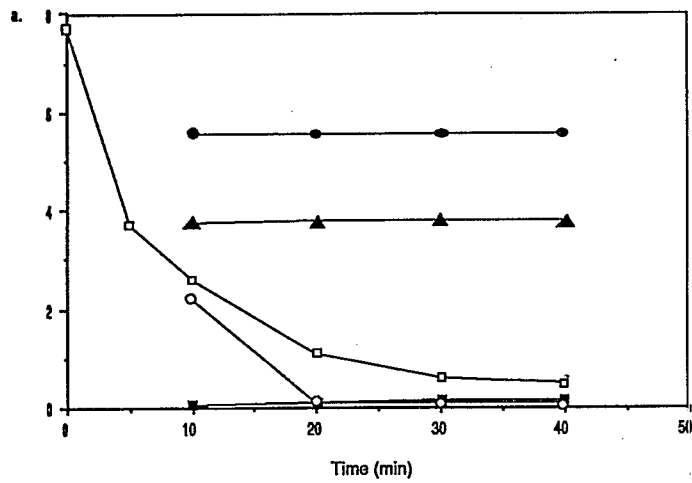


Figure 4a-c. Changes In Water Quality Indicators During Purging of Well 503: (a) Bladder Pump; (b) Low Speed Submersible Pump; (c) High Speed Submersible Pump

Table 4. Pumping rate data for selected wells and pumps.

Well	Date Sampled	Pump Discharge (L/min)	Intake Velocity (m/d)	Formation Velocity (m/d)	Relative Velocity ²	Colloid Concentration (mg/L)
105	6-14-88	1.0	42	0.012	460	
		12	510		5500	
303	3-7-89	0.9	38	1.33	410	0.3
		2.8	120		1300	4.0
		0.7	30		2.9	
403	6-15-88	24	1000	2.93	99	
		0.8	34		1.5	
451	3-9-89	27	1100	0.25	51	
		0.8	26		5.3	20
452	3-9-89	3.4	110	0.75	22	3.0
		0.8	28		1.8	0.2
503	6-16-88	28	980	1.63	61	10
		1.0	42		3.4	
	45	1900	150			
	3-8-89	1.1	47	3.7	0.1	
		3.8	160	13	0.1	
		30	1300	100	0.2	

² Ratio of induced velocity at the borehole face to average ground-water velocity in the adjacent formation.

samples collected in March 1989 were noticeably turbid, even after 2 hours of purging with the bladder pump. In fact, lower particle counts by the slightly higher rate pump may have resulted from the additional purge time, as the latter was inserted following purging and sampling with the bladder pump. Two factors may contribute to the high colloid concentrations at well 451:

- it is in relatively fine grained sediment in the alluvium, and
- it is in a part of the aquifer where pH is changing rapidly and iron oxide coatings on colloidal clay are dissolving.

For this data set, particle concentrations were not predictable from pumping rate, purge volume, flow velocity at the screen, or the ratio of velocity induced at the borehole face to local ground-water flow velocity. Measured particle concentrations appear to depend on interactions of these factors as well as geology, well construction, and water chemistry.

Filtration Differences

Concentration differences among samples filtered through pore sizes ranging from 0.1 to 10 µm were generally less than 10 percent. Only wells 303 (Table 5) and well 503 had differences of greater than 10 percent in most elemental concentrations. The larger differences commonly were associated with use of the high-rate submersible pump, and concentrations generally increased with increasing filter-pore size.

Differences less than 10 percent generally were observed for waters that have pH less than 4, which does not favor colloid formation. The largest observed differences for well 403, for

Table 5. Cation concentrations, in mg/L, for well 303 using different filters (June 1988, 24 L/min, sampled in air).

Element	0.1 µm	0.4 µm	10 µm
Ca	391	424	492
Mg	91	100	20
K	4.73	5.49	9.76
Fe	171	87	211
Mn	37.7	40.8	45.5
Al	6.74	7.61	9.93
Co	0.68	0.75	0.86
Cu	15.0	16.7	19.2
Ni	0.68	0.75	0.88
Zn	2.75	3.27	4.13

example, were for Al, Cu, Fe, and Mg, but no consistent trend of concentration with filter pore size is apparent (Table 6).

Filtration differences of greater than 10 percent were also generally associated with use of the high-rate submersible pump because of the increased entrainment of particulates as observed above.

Table 6. Cation concentrations, in mg/L, for well 403 using different filters (June 1988, 0.8 L/min, sampled in air).

Element	0.1 µm	0.4 µm	10 µm
Ca	533	533	554
Mg	133	113	116
K	5.58	5.47	5.65
Fe	0.45	6.63	1.22
Mn	34.6	34.9	34.7
Al	1.22	1.91	1.17
Co	0.36	0.36	0.37
Cu	1.62	2.14	1.57
Ni	0.41	0.42	0.44
Zn	0.90	0.95	1.60

Oxidation of Samples

Oxidation of samples during sample collection, filtration, and preservation generally resulted in substantial differences in most wells between samples collected under nitrogen or in air. Work by Holm et al. (1988) showed that diffusion of atmospheric gases through pump tubing can introduce measurable concentrations of oxygen into waters initially low in dissolved oxygen. This source of possible contamination for both sets of samples was minimized by collection of samples adjacent to the wellhead. Samples collected in air were directly exposed to atmospheric gases during filtration and acidification procedures. Significant differences (>10 percent) were observed in many of the wells. Variations in differences from well to well may have been caused by a number of different factors including:

- slightly different exposure times to air, depending on water-table depth and duration of filtration and preservation,
- dissolved-oxygen level,
- redox potential (Eh), and
- dissolved iron concentration.

Large differences in concentrations were measured for well 303, where dissolved iron concentration was greater than 200 mg/L (Table 7). Differences similar to those for well 303 were also observed in wells 51, 104, and 403. In contrast, the differences were small for well 503, where the dissolved iron concentration was less than 0.1 mg/L.

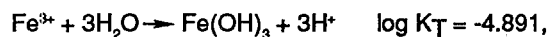
Another indication of the extent of oxidative effects on sample integrity was reflected in Eh values determined by various methods for well 51 (Figure 1). The field-measured Eh value using a Pt electrode was 0.43 V. A calculated Eh value, assuming equilibrium between Fe³⁺ and Fe(OH)₃, was 0.57 V (Stollenwerk and Eychaner, 1989). In March 1989, Fe²⁺ and Fe_{total} for well 51

Table 7. Cation concentrations, in mg/L, for samples collected in air and nitrogen under atmosphere (mg/L, 0.40-µm filter, < 1 L/min).

Element	Well 303		Well 503	
	air	nitrogen	air	nitrogen
Fe	177	215	0.04	0.09
Mn	37.4	44.7	68.3	68.7
Cd	0.02	0.02	0.01	0.01
Co	0.69	0.82	0.01	0.02
Cu	15.5	18.6	0.01	0.04
Ni	0.70	0.84	0.47	0.48
Zn	2.53	3.11	0.21	0.30

were determined within one week of sample collection; Fe³⁺ was computed by difference, and Eh was calculated from the ratio of Fe³⁺ to Fe²⁺. The calculated Eh was 0.51 V for the sample collected and analyzed in a nitrogen atmosphere and 0.76 V for the sample collected in air. Samples collected in the glove box were transported in nitrogen-pressurized containers, and the determinations were performed in laboratory glove boxes also pressurized with nitrogen.

Several possible errors are associated with all these Eh evaluation methods. Lindberg and Runnells (1984) showed that many field Eh measurements may not reflect true redox conditions in ground waters. However, in acidic waters such as these, field measurements using Pt electrodes may be valid (Nordstrom et al. 1979). Values calculated from equilibrium constants rely on the assumption that Fe(OH)₃ is the predominant solubility controlling phase. Stollenwerk and Eychaner (1989) used the equilibrium expression:



although other values have been reported for this reaction. Samples collected under nitrogen may have received some exposure to oxygen during sample collection, processing, and analysis. The Fe³⁺ values for March 1989 were small differences between two large numbers and are uncertain. Irrespective of these and other limitations in estimating Eh, the large difference observed between 0.76 V for the sample collected in air and the other Eh values for well 51 demonstrates the extent of oxidation that can occur if care is not taken to limit oxygen exposure during sample-collection activities in suboxic and anoxic environments.

Conclusions

Research at this site indicates that monitoring of water-quality indicators during well purging and sampling is important. In addition to the indicators most often monitored, turbidity also needs to be evaluated before collecting samples. In lieu of the use of a turbidimeter, purging for twice the time required for dissolved-oxygen equilibration may be a good rule of thumb.

The use of a low flow rate pump can minimize entrainment of nonmobile suspended particulates, oxygenation of formation water, and mixing of adjacent, possibly geochemically distinct, ground waters. Collection and processing of anoxic or suboxic ground water excluding atmospheric gases to the extent possible is desirable for representative and accurate water-chemistry data. The glove box used for collection of samples under nitrogen was cumbersome and difficult to use, especially in handling the thin membrane filters. If tubing of minimum length and maximum thickness were used, in-line filtration would probably mitigate the oxidation effects observed in the present study, making the use of a field glove box and accompanying nitrogen cylinders unnecessary. Although filtration differences generally were not significant at this site, trends indicate that care needs to be taken in selection of filter pore size and that samples need to be filtered in the field. Additional research is needed at sites with distinctly different hydrology, geology, and chemistry before final recommendations can be made concerning filtration. In the interim, collection of filtered and unfiltered samples for comparison purposes is suggested for at least a fraction of the samples collected. Filtered samples are needed for accurate aqueous geochemistry estimations, and unfiltered samples provide conservative estimates of contaminant mobility.

The sampling recommendations proposed by the RSKERL 1988 workshop participants were realistic and relatively easy to apply in the present study. Additional time was required for purging and sampling, but the additional care was warranted to obtain groundwater chemistry data which were as representative as possible.

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