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Metals in Ground Water: Sampling Artifacts and Reproducibility

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ABSTRACT

Field studies evaluated sampling procedures for determination of aqueous inorganic geochemistry and assessment of contaminant transport by colloidal mobility. Research at three different metal-contaminated sites has shown that 0.45 μm filtration has not removed potentially mobile colloids, when samples have been collected using low pumping flow rates (~ 0.2 - 0.3 L/min). However, when pumping velocities greatly exceed formation groundwater flow velocities, large differences between filtered and unfiltered samples are observed, and neither are representative of values obtained with the low flow-rate pumped samples. There was a strong inverse correlation between turbidity and representativeness of samples. Several different sampling devices were evaluated in wells (PVC) ranging in depths from 10 to 160 ft. Those devices which caused the least disturbance (i.e. turbidity) also produced the most reproducible samples irrespective of filtration. The following water quality indicators were monitored during well purging: dissolved O_2 , pH, Eh, temperature, specific conductance, and turbidity. Sampling was not initiated until all indicators had reached steady-state (usually ~ 2 to 3 casing volumes). In all cases turbidity was slowest to reach steady-state values, followed by dissolved oxygen and redox potential. Temperature, specific conductance, and pH results were generally insensitive to well purging variations.

INTRODUCTION

A primary ground-water sampling objective is the acquisition of representative elemental and molecular concentrations for the purpose of risk assessment at hazardous waste sites. These samples should include contaminants sorbed to naturally suspended inorganic and organic colloids, in addition to dissolved species. Particles with diameters less than 10 μm , referred to as colloids, may form in certain subsurface environments and be mobile at ground-water velocities.

Several studies have demonstrated contaminant transport by colloidal mobility (1,2,3,4). 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 total contaminant transport, substantial underestimations of contaminant mobility may result, due to its colloidal association. Numerous studies attest to the strong sorptive capabilities of secondary clay minerals; hydrous Fe, Al, and Mn oxides; and humic material of colloidal dimensions (5,6,7,8,9). If colloids as large as 0.45 - 3 μm are mobile, and capable of transporting contaminants large distances, then sampling protocols must make allowances for this component of transport. Likewise, transport models must incorporate this mechanism to provide better contaminant migration predictions.

If a secondary objective is accurate 'dissolved' inorganic concentrations, then samples should be filtered through 0.1 μm pore size filters or smaller in the field using in-line devices, and acidified immediately to $\text{pH} < 2$ with concentrated HNO_3 . Historically, 0.45 μm pore size filters have been used to differentiate between dissolved and particulate phases in water samples (10). If the intent of such

sediments, underlain by a sloping fractured bedrock surface. Sediment thickness ranges from 0 to 17 m. Glacial deposits consist of basal and ablation tills and glaciomarine sediments. The basal tills consist of gray, silty, fine to medium sands with gravel, coarse sand, cobbles, and boulders. Ablation till is less dense and consists of brown, fine to medium sand with silt, and layers of coarse sand and gravel. Glaciomarine deposits consist of gray to olive clayey silts with thin lenses of sand. The bedrock consists of interbedded phyllites with quartz stringers and secondary pyrite mineralization. Analysis of ground-water flow is complicated by both the fractured nature of the bedrock and an apparent ground-water divide in the overburden. Upward gradients have been determined at some locations associated with ground-water discharge to surface drainages. Depth to water table ranges from 1 to 2 m below ground surface.

The third site is near Elizabeth City, North Carolina, about 100 km south of Norfolk, Virginia and 60 km inland from the Outer Banks of North Carolina. A chrome plating shop, in use for more than 30 years, has discharged acidic chromium wastes into the soils and aquifer immediately below the shop. The site geology consists of typical Atlantic coastal plain sediments characterized by complex and variable sequences of surficial sands, silts and clays. In the vicinity of the plating shop, the uppermost soils are fine sand to sandy loam, overlying a thin sandy clay layer at about 2 m, overlying sand and silty fine sands, with pockets of silt and clay. In some locations, a dense gray clay layer substitutes for the sandy clay at 2 m. Fine to medium sands dominate from 4 to 20 m. A dense gray clay unit persists at a depth of 20 m. This depth is slightly variable and dips gently from north to south. Ground-water flow is generally to the northeast, however in the immediate vicinity of the plating shop, flow appears to be directly toward the Pasquotank River about 60 m north of the shop. Ground-water flow is somewhat complicated due to wind tides. Depth to ground water is about 2 m. An estimated hydraulic conductivity value of 15 m/d was based on aquifer test data. An average ground-water flow velocity for the site has been estimated as low as 0.004 m/d (28).

INSTRUMENTATION AND METHODS

Ground water was collected from more than 30 wells at the three sites studied, which covered a range of pH, solute concentration, redox and hydraulic conductivity (Table 1).

TABLE 1. Ground-water quality parameters for the three sites.

Site:	Arizona	Maine	North Carolina
pH (units)	3.5-6.1	6.0-7.8	5.7-6.9
Sp. Cond. ($\mu\text{S}/\text{cm}$)	3020-7070	80-1600	170-800
Temp. ($^{\circ}\text{C}$)	18.0-19.0	14.0-18.0	18.0-20.0
Oxygen (mg/L)	0.01-0.39	0.20-1.60	0.03-2.1
Redox Pot. (v)	0.25-0.44	0.08-0.19	0.22-0.38
Hydr. Conduct. (m/d)	0.5-200	~ 12	~ 0.5
Colloids (mg/L)	0.1-20	0.5-22	0.1-2.0

The sampling set-up used at the Saco and Elizabeth City sites is depicted in Figure 1. This was similar to the arrangement used in Globe, where a laser light scattering instrument was used for tracking particle concentrations instead of a turbidimeter and a bladder or submersible pump was used instead of a peristaltic pump (25). For comparison, a bailer was used in addition to the peristaltic pump at Saco and at Elizabeth City (Table 2). A multiparameter instrument with flow-through cell was employed in all cases to monitor pH, temperature, specific conductance, redox, and dissolved oxygen during purging and sample collection. Sample collection was initiated when all parameters, including turbidity, reached steady-state. An inflatable packer was used with the bladder and low-rate submersible pumps to reduce necessary purge volumes at the Globe site.

Figure 2 for well MW101 at Saco is typical of the trends for parameter equilibration during purging. Specific conductance, pH and temperature (not shown) were the least sensitive parameters, attaining steady-state values rather rapidly. In addition to the more sensitive parameters, contaminant concentrations are also plotted in Figure 3 for well MW1 at Elizabeth City. Chromate concentrations were shown to follow trends similar to turbidity, redox, and dissolved oxygen, the most equilibration-sensitive parameters.

Filtration Apparatus

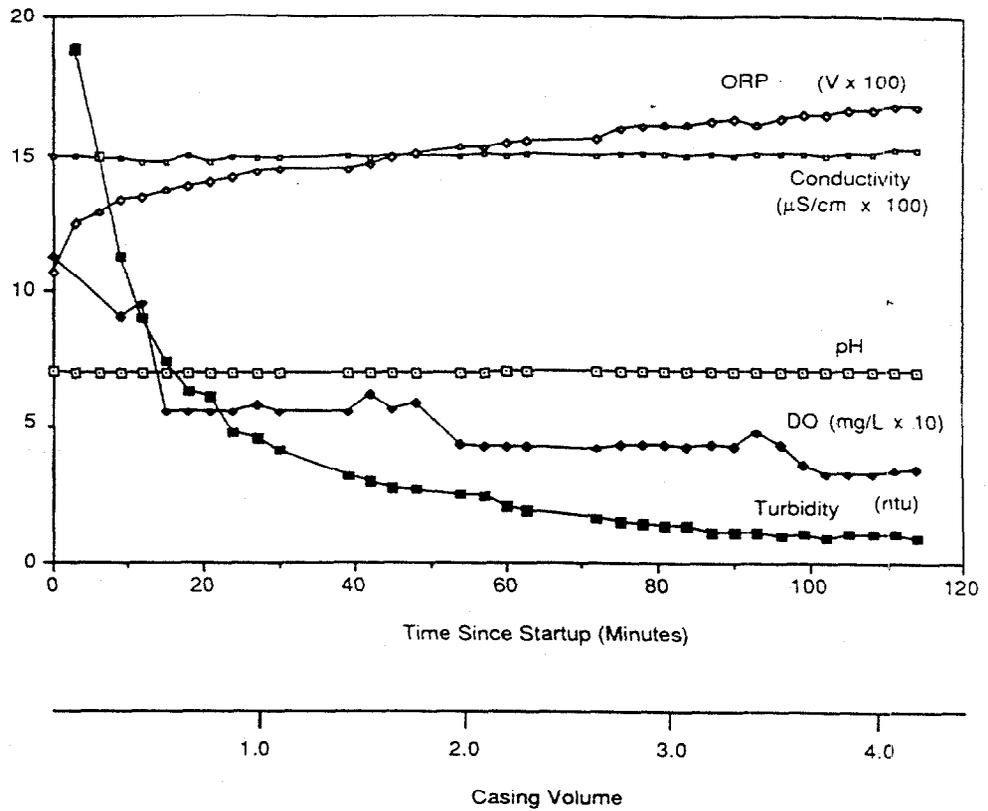


FIGURE 2. Equilibration of ground-water quality parameters during well purging (well MW101, Saco, ME, peristaltic pump at 0.2 L/min).

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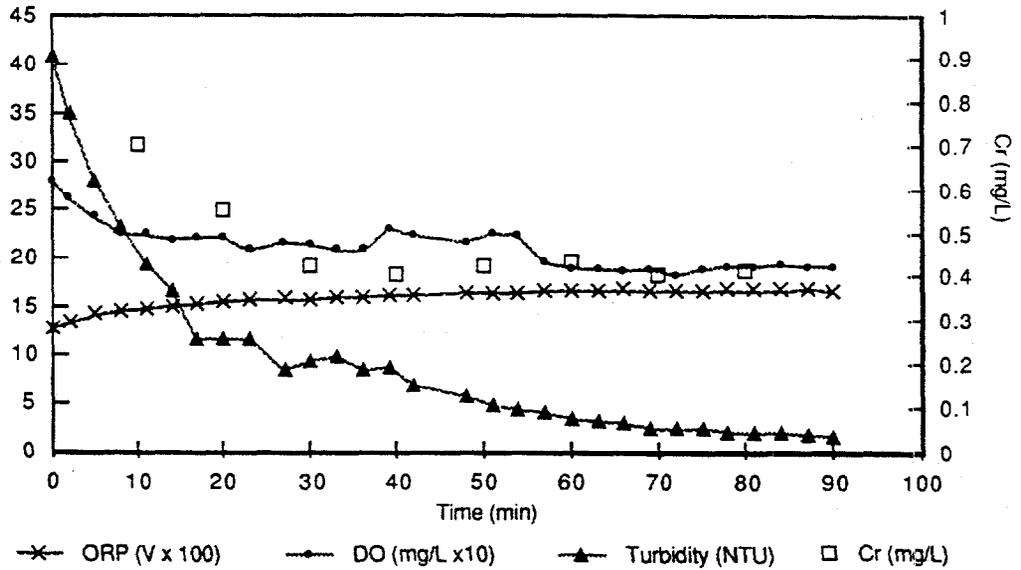


FIGURE 3. Equilibration of most sensitive ground-water quality parameters and chromate concentration during well purging (well 1, Elizabeth City, NC, peristaltic pump at 0.2 L/min).

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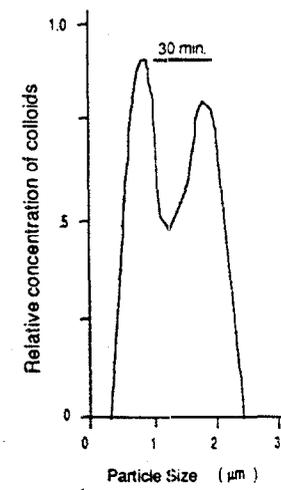
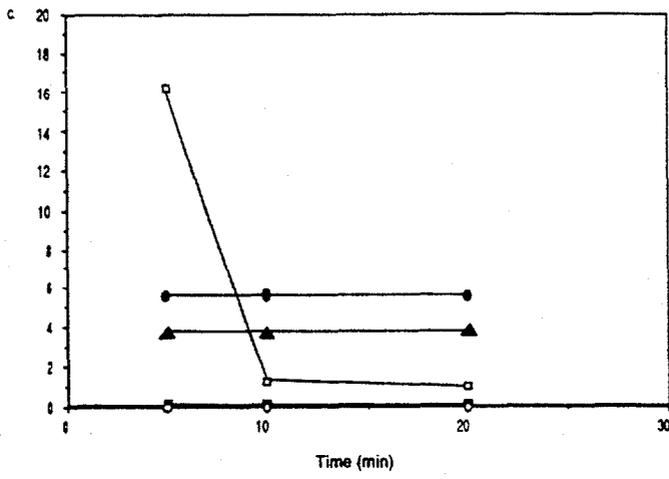
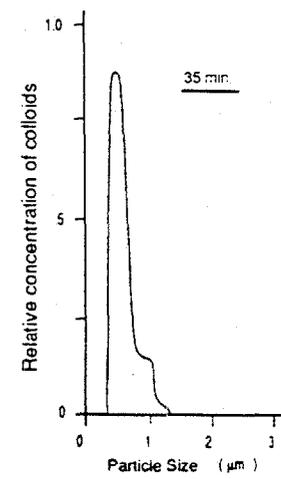
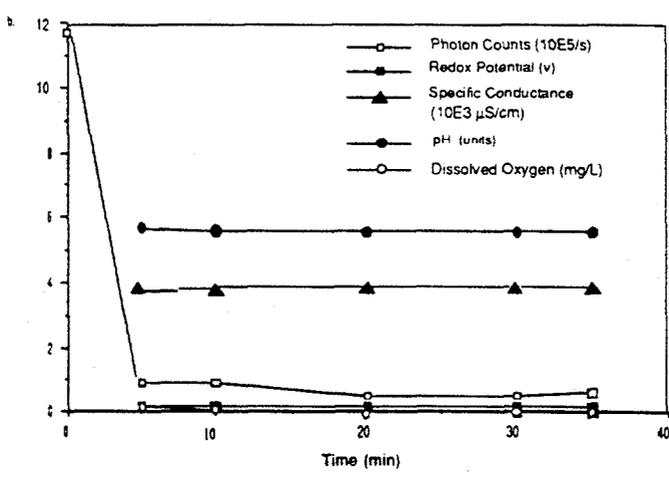
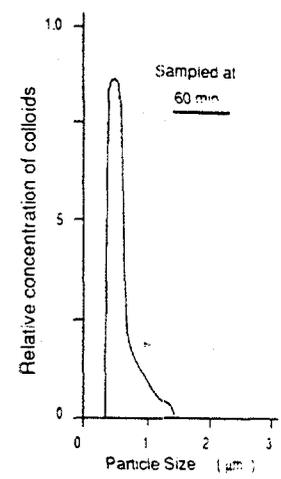
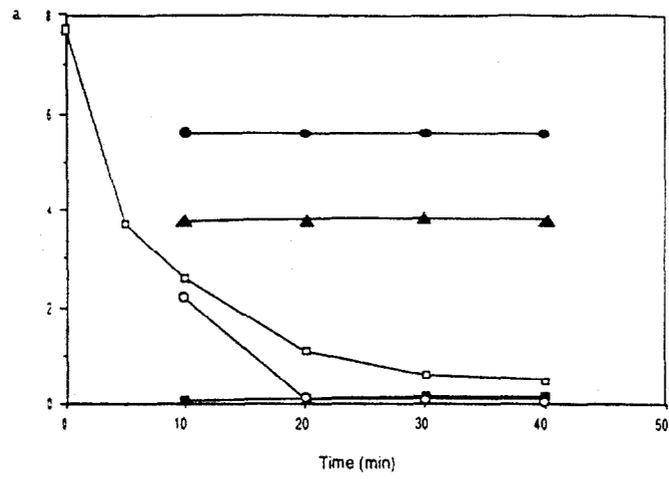


FIGURE 4 a-c. Changes in ground-water quality parameters and suspended particle size during well purging (well 503, Globe, AZ: [a] bladder pump; [b] low speed submersible pump; [c] high speed submersible pump).

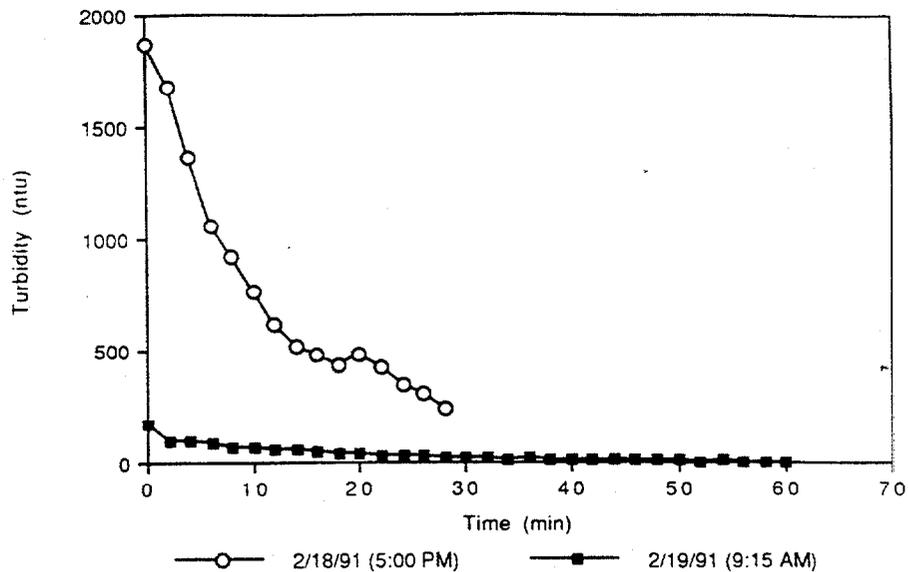


FIGURE 6. Comparison of turbidity equilibrations for well 8 (Elizabeth City, NC) using the peristaltic pump at 0.2 L/min immediately upon insertion of pump tubing (2/18/91) and following overnight (passive) equilibration (2/19/91).

Figure 7 shows chromium levels in samples from well 1 at Elizabeth City where samples were collected both with a peristaltic pump (0.2 L/min) and with a bailer.

The purge time for water quality parameter equilibration using the peristaltic was 1.3 hr or about two casing volumes. Bailed samples were collected after a standard three volumes had been purged. There were no significant differences in chromium concentrations between unfiltered, 5.0, 0.4 and 0.1 μm filtered samples, with the peristaltic pump. Not only were the bailed samples significantly different, but they were also 2 to 3 times higher than the peristaltic values. A similar response was observed in well 8 at the site. In all twelve wells, when the samples were collected with the peristaltic using a low pumping rate (~ 0.2 L/min) and the set-up depicted in Figure 1, there were no consistent differences observed in metal concentrations over the range from unfiltered to 0.1 μm -filtered.

Although the Saco site is a chrome tannery waste disposal site, the element of most interest in the ground water is arsenic. It is unclear at this time whether the elevated arsenic levels are naturally occurring or due to contamination. This is under further investigation since no historic data is available. Data from well 113 A (Figure 8) shows arsenic levels for samples collected using a peristaltic pump and a bailer. Similar results were observed in all wells with elevated arsenic at the site. Results are similar to those for chromium at Elizabeth City. Once again, there were consistently no differences observed in metal

TABLE 4. Cation concentrations, in mg/L, for well 51 using different filters (June 1988, 24 L/min, sampled in air).

Element	0.1 μm	0.4 μm	10 μm
Ca	383	385	417
Mg	313	317	343
K	7.0	7.5	10.3
Fe	2626	2662	2487
Mn	37.7	40.8	45.5
Al	214	222	251
Co	1.49	1.49	1.60
Ni	2.49	2.52	2.76
Zn	19.4	19.7	20.6

concentrations using different filter pore sizes, but large differences were observed for filtered and unfiltered bailed samples and these two sets of values were generally different from the peristaltic pump sampled values. The sampling set-up used with the peristaltic pump (Figure 1) consistently produced the most reproducible results and provides increased confidence that these samples are more representative than those collected with the bailer.

Bailers are commonly used for both purging and sampling in small diameter, shallow wells, because of their convenience and low cost. Most bailers draw in water immediately upon contact with water in the well casing. If the sampling zone or screened interval is any significant distance from this point, even more importance is placed upon adequate well purging prior to sample collection. However, this is almost impossible from the standpoint of obtaining representative turbidity and dissolved oxygen values. Repeated insertion and withdrawal of the bailer causes significant surging, mixing and aeration, even when operated carefully. In addition, any results obtained with the bailer are extremely operator-dependant and therefore quite variable. Equilibrated turbidity values at the Elizabeth City site with the peristaltic pump were generally less than 2 NTU's, while with the bailer they were greater than 200 NTU's. At the Saco site, peristaltic pump turbidity values were generally less than 5 NTU's, but with the bailers ranged from 5 to greater than 200 NTU's.

It was interesting to note that there seems to be no significant contribution to contaminant transport from suspended and mobile colloids greater than $0.1 \mu\text{m}$ at either the Elizabeth City or the Saco sites. However, this is not to say that colloidal facilitated transport by smaller particles may not occur at these sites.

Oxidation and Sampling

Oxidation of samples during sample collection, filtration, and preservation was assessed at the Pinal Creek, Arizona, site. Substantial differences were found for most wells between samples collected under nitrogen or in air. Work by Holm et al. (30) 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 oxygen concentrations were measured for well 303, where dissolved iron concentration was greater than 200 mg/L (Table 5). 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. The field-measured Eh value using a Pt electrode was 0.43 V. A calculated Eh value, assuming equilibrium between Fe^{3+} and $\text{Fe}(\text{OH})_3$, was 0.57 V (31). In March 1989, Fe^{2+} and Fe_{total} for well 51 were determined within one week of sample collection; Fe^{3+} was computed by difference, and Eh was calculated from the ratio of Fe^{3+} to Fe^{2+} . 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 (32) 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 (33). Values calculated from equilibrium constants rely on the assumption that $\text{Fe}(\text{OH})_3$ is the predominant solubility controlling phase. Samples collected under nitrogen may have received some exposure to oxygen during sample collection, processing, and analysis. The Fe^{3+} values for March 1989 were small differences between two large numbers and are uncertain. Irrespective of these and other limitations in estimating Eh,

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