



# Project Summary

## Evaluation of Sampling and Field-Filtration Methods for the Analysis of Trace Metals in Ground Water

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Selected ground water sampling and field-filtration methods were evaluated to determine their effects on field parameters and trace metal concentrations in samples collected under several types of field conditions. The study focused on conditions where traditional approaches may produce turbid samples, which often leads to filtration of suspended particles from the sample before laboratory chemical analysis. However, filtration may also remove colloidal particles that may be important to the transport of hydrophobic organic contaminants and trace metals. The specific sampling and filtration variables investigated in this study were (1) filtration with 0.45- $\mu\text{m}$  or 5.0- $\mu\text{m}$  pore size filters versus no filtration; (2) sampling device, specifically, bladder pump, submersible-centrifugal pump, and bailer; and (3) sampling pump discharge rate during purging and sample collection using a "low" rate of 300 mL/min and a "moderate" rate of 1000 mL/min. Three field sites were visited: an active municipal solid waste landfill in Wisconsin, a closed solid waste landfill in Washington, and a site contaminated by industrial waste in Nevada. The evaluation included three wells each at the Wisconsin and Washington sites and two wells at the Nevada site. Filtration with 5.0- $\mu\text{m}$  filters was conducted only at one well at each site.

The effects of field filtration were most evident for the bailer, which often produced trace metal concentrations in unfiltered samples that were orders-of-magnitude higher than in 0.45- $\mu\text{m}$ -fil-

tered samples. The largest differences occurred at the most turbid wells and in samples containing the highest particle concentrations. Similar effects were observed in some samples collected by pumps from the most turbid wells, particularly the low yield well. For most pump sampling, however, differences in concentrations between 0.45- $\mu\text{m}$ -filtered and unfiltered samples were not significant and particle concentrations were significantly lower than those produced by the bailer. Bailers caused more disturbance of the sampling zone than the three pumping methods as evidenced by measurements of field parameters and concentrations of particles, major ions, and trace metals. Little variation was observed in the analytical determinations between the pumped samples but some variation existed in the field indicator parameters—primarily, temperature, dissolved oxygen, and turbidity. Trace metal concentrations in 0.45- $\mu\text{m}$ -filtered samples were generally independent of sampling method, suggesting that these constituents were present as dissolved species and not associated with particles, or associated with particles smaller than 0.4  $\mu\text{m}$ . At wells where 5.0- $\mu\text{m}$  filtration was conducted, physical and hydrochemical conditions resulted in minimal differences between trace metal concentrations in the 5.0- $\mu\text{m}$ -filtered, 0.45- $\mu\text{m}$ -filtered, and unfiltered samples.

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*project that is fully documented in a separate report of the same title (see Project Report ordering information at back).*

## Introduction

Historically, ground water contaminants were considered to be partitioned between two phases, a mobile phase composed of dissolved (aqueous) solutes in water transported by natural ground water flow and a normally immobile solid phase composed of the matrix materials of the water-bearing zone. The action of purging and sampling a monitoring well installed in unconsolidated materials may provide sufficient energy to suspend matrix materials that have accumulated in the sampling zone and well bore and incorporate them in ground-water samples. Inclusion of metals associated with these normally immobile matrix particles may bias analytical determinations, leading to elevated and improbable concentrations of mobile contaminants if suspended particle concentrations are very high. As a result, ground water samples are commonly filtered in the field to remove these suspended particles. Filtration has been considered particularly necessary under turbid conditions where high particle (sediment) loadings might lead to significant analytical bias through inclusion of large quantities of matrix metals in the analysis. Alternatively, the presence of particles in samples might also bias analytical determinations through removal of metal ions from solution during shipment and storage as a result of interactions with particle surfaces.

Unfortunately, indiscriminant use of field filtration ignores the presence of particles, known as colloids, in ground water that may exist between the extremes of solutes and sediments. Potential association of metals with colloids has important implications for the practice of field filtration because the boundary between the particulate and dissolved has been operationally defined at 0.45 $\mu$ m. This boundary presumes that the component retained on a 0.45  $\mu$ m filter represents suspended solids, while the component that passed through the filter represents dissolved metals.

Collection of ground water samples for analysis of metals concentrations is required under several U.S. environmental regulations, including CERCLA (Superfund), RCRA Subtitle C (Hazardous Waste), and RCRA Subtitle D (Solid Waste). As a result, the debate regarding ground water metals samples impacts a wide range of sampling programs and a large number of sites, suggesting the need for further research. This study was un-

dertaken to investigate how concentrations of trace metals were affected by selected methods of sample collection and field-filtration. The objectives of the study were to provide a survey of the impacts of the following aspects of ground-water sampling:

- 1) Impacts of sample collection method on determinations of field parameters.
- 2) Impacts of filtration with 0.45- $\mu$ m or 5.0  $\mu$ m pore size filters versus no filtration on trace metal concentrations.
- 3) Impacts of sampling device—specifically, bailer, bladder pump, submersible-centrifugal pump (at a “low” discharge rate of 300 mL/min), and submersible-centrifugal pump (at a “moderate” discharge rate of 1000 mL/min), on trace metal concentrations.
- 4) Impacts of sampling device on particle size distribution and total concentration.

The study focused on sampling in conventional standpipe monitoring wells under conditions where traditional approaches to sampling may produce turbid samples.

## Procedure

The monitoring wells sampled were constructed of polyvinyl chloride, and were 5.08 cm in diameter, with the exception of one 10.2 cm diameter well. The top of the well screens ranged from 2 to 19 m below ground surface, with well screen lengths of 0.6 to 6.0 m. The static water level ranged from 1 to 14 m below ground surface. Volumes of water within the well screens ranged from 1.2 to 50 L. Although certainly not representative of geologic and hydrogeochemical conditions at all solid waste landfills and hazardous waste sites, these sites provided typical field conditions where traditional approaches to ground-water sampling produce turbid samples.

Four methods of collecting samples from conventional standpipe monitoring wells were evaluated using three types of sampling devices and pump discharge rates. These methods were utilized at eight of the nine wells. The first method used a dual-check valve bailer with a volume of approximately 0.4 L. Samples were transferred from the bailer directly to the sample bottles for unfiltered samples or to a filtration vessel for filtered samples. Compressed nitrogen gas was used to drive the samples through either membrane filters or disposable cartridge filters. The second sampling method was a sub-

mersible-centrifugal pump (CP1) operated at a flow rate of approximately 300 mL/min. Filtration was conducted in-line with disposable cartridge filters. The third method was a bladder pump (BP) operated at a flow rate of approximately 500 mL/min at the Wisconsin site or 1000 mL/min at the other sites. The fourth method was a submersible-centrifugal pump (CP2) operated at a flow rate of approximately 1000 mL/min. Discharge rates were measured at ground surface and were controlled by the pump speed rather than by flow restrictors or valves. These discharge rates were used for both purging and sampling. Filtration for methods three and four was conducted in the same manner as for method two. The pumps and bailer were positioned to collect samples from about 0.6 m below the top of the well screen.

Measurements of turbidity, dissolved oxygen (DO), temperature, electrical conductivity (EC), and pH of the pump discharge were made in-line, while measurements of these parameters for the bailer discharge were made off-line. Stabilization of these parameters provided an indication of equilibrium between incoming ground water, the action of the sampler, and stagnant water in the well; thereby suggesting that purging was complete. The relative values of these parameters also provided a means for comparing the sampling methods with respect to their ability to minimize disturbance in the sampling zone. Estimates of particle size distribution were determined gravimetrically by serial ultrafiltration using microfilters of 5.0  $\mu$ m, 0.4  $\mu$ m, 0.1  $\mu$ m, and 0.03  $\mu$ m pore size.

## Results and Discussion

The results of the study demonstrate three important factors that influence the accuracy of field parameters measurements during sampling from conventional standpipe monitoring wells: measurement techniques, sampling method, and hydraulics of the well. Impacts related to measurement techniques were considered minor because a single individual conducted all the field measurements and all procedures followed established protocol. In contrast, sampling method and well hydraulics had impacts on values of field parameters in some of the sampling events that masked all other factors. The relative disturbance in the sampling zone caused by a sampling method was most evident in the field measurements of turbidity and DO, particularly under low-yield conditions. When the discharge rate exceeded the well yield, the increasing hydraulic gradient between the formation and the well mobilized large quantities of particles,

thereby elevating turbidity values. Continued removal of water from the well dewatered the filter pack, leading to gravity drainage of pore water and sediments and continually increasing turbidity values. Bailer turbidity values were further elevated by the surging action of the bailer. Elevated DO values of the bailer and BP at 1 L/min in low-yield wells reflect the formation of a large air-water interface which increased the potential for oxygenation of incoming ground water as the filter pack was dewatered. The bailer caused additional aeration of the samples as a result of the increased exposure to the atmosphere during sample collection and transfer. The lower discharge rate of 0.3 L/min, which was generally closer to the well yield, resulted in less variability and more representative values of turbidity and DO, as well as lower purged volumes.

Somewhat less variable results were observed between sampling methods in wells where purging and sampling rate did not exceed the well yield. Under these conditions, hydraulic gradients into the well were minimal, the filter pack was not dewatered, and turbidity was generally lower. The two pumping methods produced similar values of most field measurements, while the surging action of the bailer produced turbidity values that were approximately two orders-of-magnitude higher than those produced by the pumps. Likewise, DO values in bailed samples were elevated with respect to the pump values, an artifact of the bailing process. The pumps produced equilibrium DO and turbidity conditions with relatively low purged volumes, while the bailer produced high values of these parameters and did not reach equilibrium after greater purged volumes. Results of the study indicate that DO is sensitive to the purging process and further suggest that DO may be an important indicator of the volume required to remove stagnant water from the sampling system.

As with DO, turbidity exhibited a strong dependence on sampling method. The highest turbidity values were obtained with the bailers, while the lowest turbidities were obtained with the pumps. Equilibration of turbidity, like DO and oxidation-reduction conditions (Eh), is often related to sample collection method.

Values of pH showed little variation between pump methods with most values falling within the range of  $\pm 0.2$  pH units for a given well. Bailed pH values were also within this range but were usually higher than the pumped values, possibly reflecting degassing of  $\text{CO}_2$  from the samples during collection and pH measurement. In addition, pH reached equilib-

rium at lower purged volumes than all the other parameters, independent of sampling method. Although pH is an important indicator of the speciation of trace metals in ground water, the relatively uniform values across devices at individual wells do not alone suggest that similar metals species might be present.

In almost every case, samples collected by bailer contained higher particle concentrations than those collected by the pumps, with the greatest differences occurring at the most turbid wells. Furthermore, the size distribution of particles in most bailed samples was highly skewed toward larger particles, with over 96% larger than  $0.45 \mu\text{m}$ , and generally over 93% larger than  $5.0 \mu\text{m}$ . The quantities and sizes of these particles suggest that they were not mobile in ground water under natural flow conditions but were primarily the artifacts of well construction, development, and purging and were mobilized by agitation in the sampling zone caused by bailing. The particle size distribution in samples pumped from the most turbid (low-yield) wells were also skewed toward larger particles, but total particle concentrations were much lower than in the bailed samples. In the less turbid (high-yield) wells, total particle concentrations in pumped samples were orders-of-magnitude lower than in bailed samples, reflecting the lower degree of agitation caused by the pumping methods. Also, particle sizes in the pumped samples were generally more uniformly distributed; approximately 50% of the particles were larger than  $0.45 \mu\text{m}$ .

Differences in metal concentrations between filtered and unfiltered samples were most evident in low-yield and highly-turbid wells, particularly when the samples were collected by bailer. In fact, several metals present in unfiltered bailed samples were below detection levels in the corresponding filtered samples. The large differences in concentration between filtered and unfiltered bailed samples reflect the association of metals with the high concentrations of artifactual particles entrained during bailing. For example, iron in the sampling zone likely existed as iron hydroxide particles, particles containing elemental iron, and ferrous iron sorbed to particle surfaces. Removal of the majority of particles during filtration therefore greatly reduced iron concentrations in the filtered samples. Other metals likely existed as aqueous species sorbed to particle surfaces, or as elemental components of particles originating as aquifer solids, and their concentrations were similarly reduced by filtration. Additionally, ferrous iron may have oxidized and precipitated during bailing,

transfer, and filtering of the samples, and then removed during filtration. Finally, the formation of a thick filter cake during filtration of bailed samples likely reduced the effective pore size of the filter membrane, thereby blocking passage of some particles smaller than  $0.45 \mu\text{m}$ ; this would further reduce the concentrations of associated metals in the sample.

Trace metal concentrations in unfiltered samples pumped from low-yield and highly turbid wells were generally lower than in unfiltered samples bailed from the same wells. This reflects the lower degree of agitation associated with pumping and, as a result, the lower artifactual particle concentrations. Removal of the larger particles in the pumped samples did, however, cause filtered samples to contain lower metal concentrations than unfiltered samples, though the differences in concentration were much lower than in bailed samples. Unfiltered metal concentrations in samples pumped at 1 L/min were often slightly higher than in samples pumped at 0.3 L/min, but the concentrations in the filtered samples from both pumps were essentially the same. Furthermore, metals concentrations in filtered pumped samples did not differ significantly from those in filtered bailed samples.

In less turbid and high-yield wells, unfiltered bailed samples usually contained the highest metal concentrations of all samples, but the differences between these concentrations and concentrations in filtered samples were much smaller than for low-yield and turbid wells. Several metals showed only slight differences between filtered and unfiltered results in bailed samples. These results reflect the lower proportion of artifactual particles removed during filtration as compared to the low-yield and turbid wells, but also are related to the metal speciation at each well. Differences between filtered and unfiltered pumped samples were minimal, and the concentrations were essentially the same as those in the filtered bailed samples, despite the variability in proportion of particles smaller than  $0.45 \mu\text{m}$ . This suggests that many metals existed primarily as dissolved species and/or were associated with particles smaller than  $0.45 \mu\text{m}$  in the less turbid and high-yield wells included in this study.

## Conclusions and Recommendations

Field determinations of unstable parameters DO and turbidity were the most sensitive to disturbance of the sampling zone, with values produced by bailing often orders-of-magnitude higher than those produced by the pumps. Variations in in-

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indicator parameters EC and pH were insignificant between the four sampling methods, suggesting they were less related to disturbance of the sampling zone than DO and turbidity. Temperature showed little variation between the bladder pump and bailer but was highly elevated by the operation of the submersible centrifugal pump at low discharge rates.

The relationship of turbidity to particle concentration and its sensitivity to the purging process, relative to other indicator parameters, suggests that turbidity may be a useful indicator of relative particle concentrations between wells and of stabilization of particle concentrations during monitoring well purging. If mobile particles are thought to be important to transport of contaminants in ground water, use of field parameters such as pH, temperature, or EC as criteria for determining adequate sampling conditions may result in underpurging.

The effects of field filtration on trace metal concentrations were most evident when a bailer was used to sample low-yield and/or turbid wells. Concentrations in unfiltered bailed samples were up to several orders-of-magnitude higher than in filtered bailed, filtered pumped, and unfiltered pumped samples. Elevated metal concentrations in unfiltered bailed samples reflected the entrainment of large quantities of normally immobile artificial particles and their associated matrix metals, and unknown quantities of contaminant metals. Pumping at low to moderate rates in low-yield and/or turbid wells resulted in

less agitation in the sampling zone, lower particle concentrations, and reduced effects of field filtration on metal concentrations.

The effects of field filtration were the least evident in high-yield wells and/or low-turbidity wells. Samples bailed from these wells exhibited much smaller differences between unfiltered and 0.45- $\mu\text{m}$ -filtered samples. However, bailing clearly mobilized artificial particles that caused elevated metal concentrations in most unfiltered bailed samples. Samples collected by the bailer and immediately filtered exhibited trace metal concentrations that were roughly equivalent to those produced by the pumps and in-line filtration. Samples pumped from these wells exhibited virtually no differences between unfiltered and filtered samples, reflecting the minimal entrainment of artificial particles larger than 0.45  $\mu\text{m}$  during sampling at low to moderate pumping rates. Concentrations in filtered samples bailed from high-yield wells and/or low-turbidity wells were generally equivalent to concentrations in pumped samples. This reflects the removal of larger, normally immobile artificial particles and associated metals from the bailed samples.

Although the three sample-collection methods generally produced similar results when samples from less turbid wells were filtered, the pumping methods produced the most consistent overall results. Most metals showed little variation between filtered and unfiltered pumped samples, reflecting the minimal agitation

in the sampling zone and sample during purging and sample collection. Use of submersible pumps at low speeds may reduce the uncertainty in results when collecting samples of inorganic ground-water constituents that have the potential to associate with particles in ground water.

Since this study included only a limited number of wells at three sites, it does not represent the wide variety of geologic and hydrogeochemical conditions likely to be present at all solid waste or hazardous waste landfills. As a result, more information is required from a variety of sites regarding the presence of colloidal particles and the importance of these particles in the transport of trace metals and other contaminants in ground water. A better understanding of colloidal transport processes in ground-water environments could be gained from research focused on describing hydrogeochemical conditions and colloid size distribution, composition, movement, and association with trace metals at a variety of solid waste and hazardous waste sites.

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The complete report, entitled "Evaluation of Sampling and Field-Filtration Methods for the Analysis of Trace Metals in Ground Water," (Order No. PB94-201993/AS; Cost: \$19.50, subject to change) will be available only from:

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