

Representative groundwater sampling using low-flow methods

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ENVIRONMENTAL GROUNDWATER monitoring is a relatively new science, and it continues to evolve. The earliest work borrowed materials and methods from the water supply well industry. However, the goals for a water supply well are much different from those of a monitoring well. With time, it became apparent that water well practices did not always satisfy the special requirements of environmental monitoring. One of the greatest disparities is in the water-bearing units. Water supply wells will tap the best available aquifer. Environmental monitoring wells must produce from the critically impacted geologic unit, usually irrespective of its actual ability to produce water.

One of the issues of sampling these formations is the role of colloids with respect to contaminant transport. Low-flow sampling was developed for collecting samples that are as undisturbed and representative as possible without filtration, thereby giving true and accurate information regarding water quality, including the colloidal content. This paper describes low-flow sampling methods and a site-specific application at Potlatch's industrial landfill in Cloquet, MN. The results of the complete investigation have been reported to the Minnesota Pollution Control Agency (1). After background is provided on traditional and low-flow monitoring methods and the Potlatch case study, the remainder of this paper presents the site-specific application of low-

flow monitoring at Potlatch's industrial waste landfill.

Sampling background

The goal of groundwater sampling is to collect samples that are as representative of the groundwater as possible. The contribution to sample turbidity made by conventional well-purging and -sampling techniques has generated much interest (2-4). Vigorous removal of groundwater in a typical monitoring well will likely mobilize otherwise stationary particulates and may also create artificial colloids formed by changes in dissolved gases or the breakup of larger colloids. Traditional bailer sampling or pumping may increase the concentrations of colloid-adsorbed metals and hydrophobic organic compounds in groundwater samples. Alternative approaches to sampling (5-7) suggest a procedure to minimize the introduction of otherwise immobile colloids into wells by slow, prolonged pumping.

Colloidal transport

Numerous studies have demonstrated that the presence of colloidal material in groundwater may facilitate the transport of organic and inorganic contaminants (8-14). Colloidal material with diameters in the range of 10^{-3} to $10\ \mu\text{m}$ may originate from macromolecular components of dissolved organic carbon, such as humic substances, biologic materials, and microemulsions of nonaqueous-phase liquids, or from inorganic mineral precipitates and weathering materials (13). The effect that colloidal material may have on contaminants in the saturated zone depends

GROUNDWATER SAMPLING

ABSTRACT

Regulatory agencies are increasingly requiring analysis of unfiltered groundwater samples from waste sites. Potlatch faced this requirement for analysis of metals and dioxins in groundwater during a remedial investigation/feasibility study (RI/FS) of its industrial solid waste landfill in Cloquet, MN. Initial groundwater samples were collected using traditional bailing methods, which yielded very turbid samples and correspondingly high contaminant concentrations.

To obtain samples that were more representative of the groundwater, Potlatch decided to use low-flow rate sampling methods, also called micro-purge. Although pump selection, field methods development, and increased sampling costs were a challenge, the results indicate that dioxins are not migrating in the groundwater and that metals are a concern in only a limited area. Typically, the samples collected by the low-flow rate method had contaminant concentrations two to four orders of magnitude lower than those collected by the traditional bailed method.

This methodology was controversial when proposed, and extra research was necessary to demonstrate its validity. The low-flow method is gaining acceptance; it continues to be used and refined at the Potlatch facility.

Application:

Low-flow rate groundwater sampling methods are gaining acceptance over traditional bailing methods.

on the nature of the relative attractions (e.g., van der Waals attractions, hydrogen bonding, dipole-dipole interactions, hydrophobicity, etc.) between the contaminants, the colloids, the groundwater, and the soil matrix. Metals will tend to attach to

negatively charged colloids. Dioxin, which is extremely hydrophobic (literally “hates” water—it has a very low solubility and is nonionic), tends to sorb to nonionic colloids.

Conventional groundwater sampling procedures (discussed in the next section) stress speed in purging and sampling and rely on filtering to compensate for turbidity. The representativeness of the resulting samples are questionable (4). Vigorous bailing of groundwater samples to develop and sample wells may increase oxygen concentrations and redox potentials as well as physically disturb particles and colloids in the well's zone of influence. This agitation of a monitoring well during bailing (in conjunction with other physical/chemical effects) may generate additional colloids or particulates with adsorbed organic and inorganic chemicals of concern.

Traditional methods

It is generally accepted that the water in the well casing may not be representative of the formation water, so it needs to be purged prior to collecting the analytical samples. Traditional materials and methods stress speed and maintaining the status quo. Traditional sampling methods rely on purging and sampling using bailers or high-speed pumps to remove 3–5 well casing volumes. This can lead to excessive drawdown, accelerated groundwater flow, aeration of water in the well, stirring up of sediments in the well, and abrasion of the well casing. Following this purge, there is a cursory evaluation of water quality stability—usually pH, temperature, and specific conductivity—which have been shown to be poor indicators of the actual variation between “stagnant” well water and “fresh” formation water (7).

Finally, the analytical samples are collected; these samples need to be filtered to compensate for the excess turbidity. Usually, only samples for

analysis of metals are filtered. Filtering is done using a default pore filter size (typically 0.45 μm) that is the middle of the size range for colloids. This default method does not take into account site-specific factors, which might include contaminant transport by colloids larger than 0.45 μm or the presence of organic contaminants on colloids (7, 14).

Low-flow sampling

Low-flow sampling was developed to allow for collection of samples while causing as little disturbance in the well and the surrounding formation as possible, and to base the collection of the analytical samples on continuous observations of stability parameters during purging. In this manner, representative unfiltered samples can be collected.

Low-flow is somewhat of a misnomer, because the important factor is the velocity with which water enters the pump intake and that is imparted to the formation (7). It does not necessarily relate to the rate with which water is discharged from the pump. Water level drawdown in the well during purging and sampling provides the best indication of the stress imparted by the sampling process, and so the change in water level is a stabilization parameter (7).

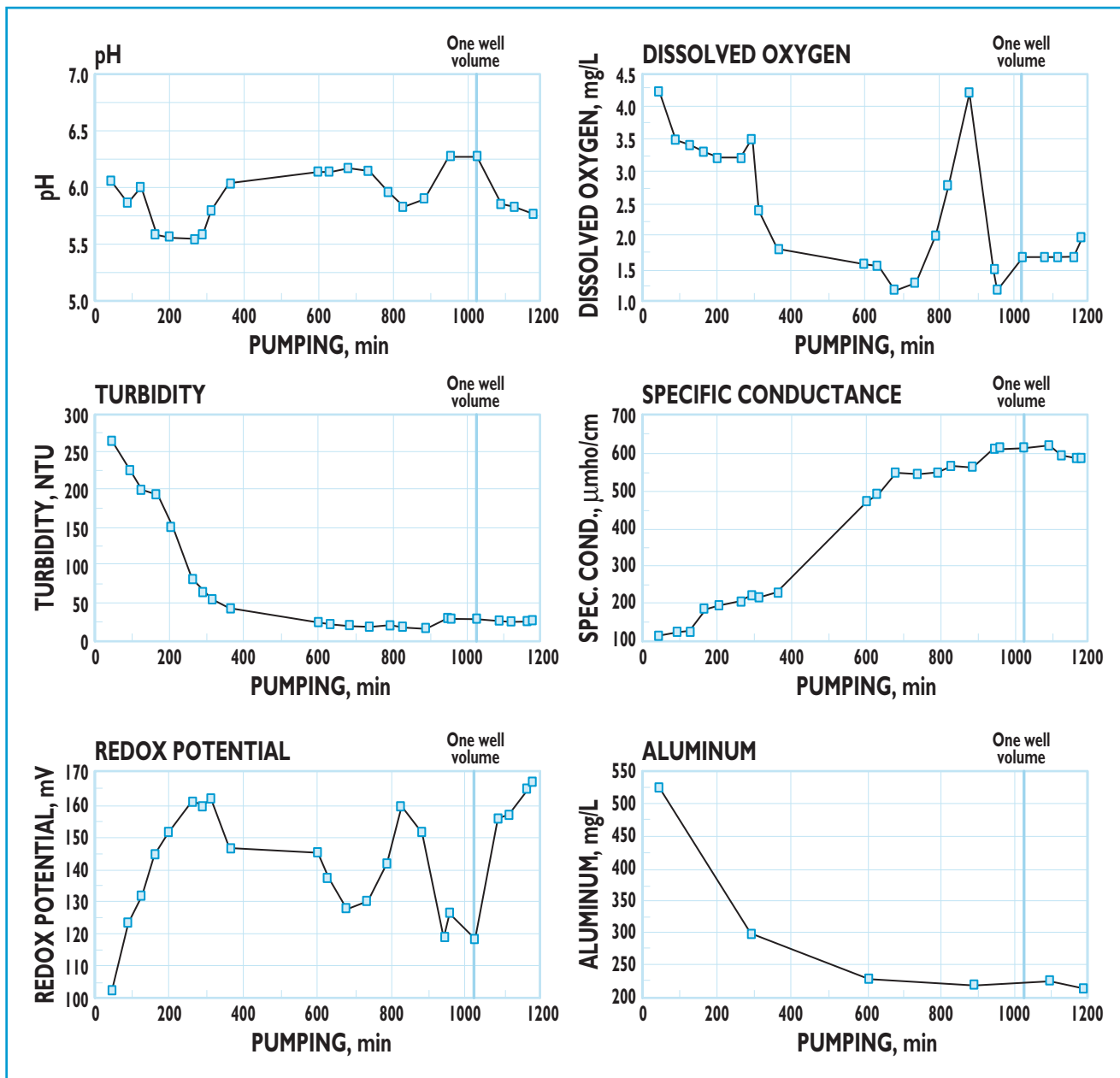
The pumping rate should be stable and specific to the well being sampled. The pump discharge should be set at a rate that minimizes drawdown. Typically, flow rates are 0.1–0.5 mL/min, but coarser formations may allow higher flow rates as long as little or no drawdown is created. Low-flow purging should be done with the pump intake located in the middle or slightly above the middle of the screened interval (7). These methods often bring about groundwater stabilization with the removal of 1–3 well volumes (15, 16). In high-hydraulic-conductivity formations with dedicated equipment, wells may stabilize as soon as

the water in the pump is purged, because natural groundwater flow is constantly purging the water in the well and the low-flow method creates little or no mixing with the water above the screen.

Water quality stabilization is determined by observing the trends of a number of parameters that are measured and evaluated in the field during purging. Water quality stabilization is achieved when the parameters “flat line” (Fig. 1). It is not necessary to have or even consider “purging” and “stabilization” as separate steps. Measurements of the field parameters can begin as soon as the pumping rate is stabilized. Stabilization parameters include pH, specific conductance, redox potential, dissolved oxygen, temperature, and turbidity. Of these, pH and temperature have the lowest degree of indicativeness, and turbidity has the highest. Turbidity is typically the last parameter to stabilize. Excessive purge times are invariably the result of establishing turbidity stabilization requirements that are too stringent (7). Many regulators use 10 nephelometric turbidity units (NTUs) as a criteria, even though natural turbidity in groundwater at a site may be higher (7).

Low-flow sampling can be performed using either dedicated or portable equipment. The advantages of dedicated equipment include less disturbance in the well (which is an overall goal of the method), less purge water, less decontamination, and less setup time. However, dedicated equipment requires a higher initial investment.

Low-flow sampling data may be comparable to historical data collected by traditional methods from a site. Although the sample collection method should be linked to the data, the data from the two methods can probably be correlated, and the necessity for using low-flow method should be re-examined. However, if



1. Field stabilization data from well W121, summer 1994

the data collected by low-flow methods are different from historical data collected by traditional methods, then the two types of data cannot be correlated, and the old data should be noted as questionable.

Potlatch case study

Potlatch Corp. applied low-flow sampling at its industrial solid waste landfill in Cloquet, MN. The landfill, which began as a slurry basin in the 1950s, has a 40-acre footprint. At its closest, it is within 100 ft of the St. Louis River. This river is the largest

tributary to Lake Superior, and the community took an active interest in the site investigations.

Initial groundwater samples were collected from 1990 through 1992 using traditional methods. Some of the unfiltered samples contained metals and dioxins at concentrations that exceeded the water quality standards in the landfill permit, which was issued in July 1992. Early investigation methods included filtering of samples, both for metals and dioxins. However, the staff at the Minnesota

Pollution Control Agency (MPCA) were concerned about the dioxins sorbing to the filter materials. A review of research on this topic was not sufficient to allay their concerns. Unfiltered groundwater samples testing for both dioxins and metals became a requirement in the permit, as did a general site remedial investigation, which included investigation of dioxins and metals in the groundwater. The close proximity to the river was a major concern, especially with respect to dioxins.

The former slurry basin underlying the landfill consists of the perimeter dike (made up of various fill materials) and slurried wastes (wastewater treatment plant sludge, lime mud, etc.). Above the slurry basin, the landfill contains primarily wood ash and dregs. The landfill overlies bedrock, which has moderate to very low hydraulic conductivity. There is no known aquifer beneath the site, so all the groundwater discharges to the St. Louis River.

Potlatch believed that the unfiltered, bailed samples were not representative of actual groundwater quality. A groundwater sampling technique was needed that would yield unfiltered samples that were representative of groundwater quality.

LOW-FLOW METHODS AT POTLATCH

Potlatch reviewed the existing and emerging sampling methods available, and determined that low-flow sampling was the most suitable for addressing its site concerns. Since low-flow methods were outside of the accepted methodologies in Minnesota at the time, the MPCA required a detailed sampling plan and supplementary investigations in support of the new methodology.

Selection of equipment

An all-stainless-steel, positive-displacement, gas-drive, double-valve pump was chosen for low-flow sampling due to the tendency of dioxins and furans to sorb onto other material like plastic or Teflon, and because it was capable of very low pumping rates. Both dedicated and portable pumps were used. Stainless steel riser tube was used at those wells with dedicated pumps where dioxins were of concern. Polypropylene tubing was used in the portable pumps.

The Potlatch investigation relied mainly on existing wells at the site, which included (a) 2-in.-ID stainless steel wells with 0.010-in. slotted screens and a sand pack installed

using a hollow-stem auger and (b) an open hole in fractured bedrock using only water with no additives as drilling fluid. Four new 2-in. stainless steel wells were also added. The wells are 10–60 ft deep.

Field testing and development of methods

All wells were test pumped and stabilized prior to the first monitoring event. This allowed for practice with the low-flow sampling method and equipment, and for establishing the initial well-specific pumping rates. The low-flow sampling method was refined after each of the events, although care was taken not to change anything so drastically as to bring into question the comparability of one event's results to the next. A target of 0.5 ft or less of drawdown was chosen based on the low production rates of the well, and the high background gradient and pumping rates were modified based on observed drawdown. Flow rates were measured with graduated cylinders, and purged water volumes were recorded. Pump flow rates were regulated from a control unit, allowing adjustment of pressure/vent cycles of the pump chamber. The wells were purged, and the samples were collected at very low pumping rates—10 to 100 mL/min—due to the low productivity of the formations. Drawdown was monitored continuously with a data logger during purging and sampling.

The six stabilization parameters monitored in the field included redox potential, pH, temperature, specific conductivity, dissolved oxygen, and turbidity. Stabilization parameters were measured on-site at a frequency of approximately six per well volume. Samples for measuring field stabilization parameters were collected in laboratory-grade glassware. Stabilization measurements were performed and recorded after a sufficient volume of groundwater (approximately 300 mL) was col-

lected from the pump. The preferred method of measuring the field parameters is in a flow-through cell. However, at the time, there was no commercially available cell that permitted measuring all the parameters selected for this work. In addition, most available cells were designed for much higher flow rates. At Potlatch, pump discharge was collected in a beaker that could accommodate all the probes.

Sampling implementation

The investigation included 16 wells. Seven wells in the areas of potential dioxin contamination had dedicated pumps. Portable pumps were used in nine other wells across the remainder of the site.

The remedial investigation included three monitoring events, one each in the fall of 1993 and the spring and summer of 1994. Routine monitoring has continued since the investigation was completed, with use of the low-flow monitoring continuing whenever unfiltered samples are required, and dioxin analysis according to the site permit.

The analytical parameters were chosen based on the results of monitoring that was conducted prior to the fall of 1993 and included the parameters that historically exceeded permit standards as well as those necessary for reviewing overall water quality and data QA/QC. The parameters included three major groups: dioxins and furans, metals, and nonmetal, inorganic compounds.

Groundwater samples for chemical analysis were obtained by filling containers directly from the pump discharge. Unfiltered sample bottles were filled directly from the pump discharge into the laboratory-supplied sample container. Filtered samples were collected in a separate sample container and then filtered on-site into the laboratory-supplied sample container. Samples were handled following standard chain-of-custody procedures and analyzed fol-

lowing standard laboratory procedures with detection limits appropriate to the site water quality criteria.

Supporting investigations

Five subtasks, discussed as follows, were completed to demonstrate the validity of the low-flow method. Some of these subtasks were based on published studies of low-flow pumping, and some were original to this study (5).

Surrogate aluminum samples.

Water quality stabilization was verified by the periodic collection of unfiltered samples; the samples were collected during stabilization and later analyzed for aluminum. The aluminum concentrations of these unfiltered samples are considered to be a surrogate of overall water quality and an additional baseline to which field parameters were compared. That is, if the aluminum concentration stabilized at or before the time that we determined water quality stabilization based on the field parameters, then our field assessment of stabilization was correct.

Progressively filtered samples.

In an attempt to determine the distribution of metals and dioxins on colloids, samples from selected wells were progressively filtered through a number of pore sizes. Samples from three wells taken during the fall 1993 sampling event were sequentially filtered through membrane filters of 0.8, 0.45, and 0.1- μm pore sizes. The 0.45- μm size is the most commonly used filter in traditional groundwater sampling methods; the other sizes bracket 0.45 μm . Filtrates from all three pore sizes were preserved and submitted to the laboratory for metals analysis. In addition, the 0.45- μm filtrates were analyzed for dioxins and furans. Samples from two wells were sequentially filtered through membrane filters of 0.45, 0.1, and 0.02- μm pore sizes during the summer 1994 sampling event, based on the results of the first round. Filtrates were preserved and analyzed for metals.

SEM/EDX investigation of colloids. Membrane filters (see previous section) were examined by scanning electron microscopy (SEM) to investigate the nature of the colloids. Colloid compositions were determined semiquantitatively by energy-dispersive X-ray analysis (EDX). All SEM observations were made in the backscatter imaging mode.

Sampling method comparison.

To assure that any observed changes in water quality were brought about by the use of low-flow sampling, one well was resampled using traditional methods immediately after it had been sampled by low-flow methods.

Extended field data collection.

Field parameters were typically monitored only as long as it took to demonstrate relative stability over three successive measurements. This procedure was demonstrated to be valid by taking extended field data measurements in two different ways. First, one well was purged for an extended period after initial stabilization to see if the parameter values drifted significantly. Second, an additional set of field parameter measurements was taken immediately following the collection of the analytical samples in a number of wells, again to see if the values had drifted during sample collection.

RESULTS

The use of low-flow sampling at Potlatch was successful in that the validity of the method was demonstrated and representative samples of the groundwater were obtained. The methodology was used as presented in the technical journals, and the field results were consistent with those reported by others.

Well purging and stabilization

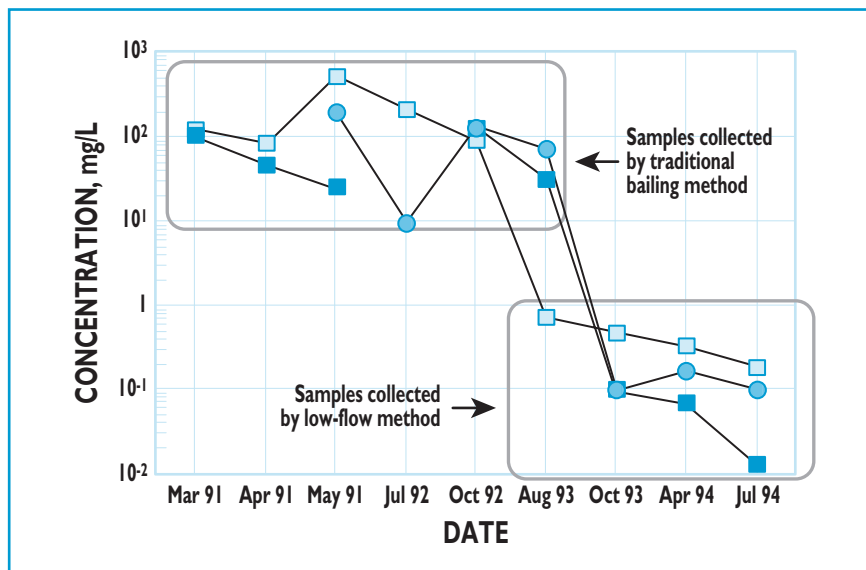
The time required for setup, stabilization, and sampling varied from 5 hours to over 80 hours per well depending on the formation characteristics and the volume of water standing in the well. This far exceeds

the time of traditional sampling methods, illustrating a primary drawback of low-flow sampling.

Water quality typically stabilized (determined when the trend for each parameter approximated a flat line) after removing less than one-half of the volume of water in the well, although in some instances, removal of up to three well volumes was required. While water quality stabilization was successful, the detailed stabilization behavior did not appear to be repeatable from one sampling event to the next on a well-by-well basis. Three wells that are affected by river fluctuations took the longest to stabilize.

The water quality in the well screened in waste never achieved the degree of stabilization of the other wells. Some parameters, especially pH, did not change throughout the purge/stabilization process, so these parameters provided no indication of stability. Although in some wells, turbidity was a better indicator, in others, redox potential was the better indicator. Ninety percent of the time, the wells stabilized with a turbidity of less than 5 NTUs, and the remaining times, turbidity stabilized at 10–20 NTUs. Specific conductivity ranked third in its tendency to indicate stability. Temperature results were deemed invalid due to ambient air temperature effects on the field samples collected at such low discharge rates.

The target of 0.5 ft or less of drawdown was exceeded about 30% of the time because of the extremely low hydraulic conductivity of the formation. Upon review of all the data, drawdowns of up to 2 ft in some wells did not seem to increase metals concentrations. However, this may be specific to this site, based on results from other studies. The process of connecting a new compressed gas tank often altered the pumping rate sufficiently to temporarily affect the water quality stability.



2. Total dioxin and furan concentrations in groundwater samples.

A number of criteria were evaluated to determine when water quality at a well was stabilized. Some of these criteria are as follows:

- Setting absolute goals for each parameter (i.e., less than 10 NTUs for turbidity)
- Using a statistical measure of variance
- Setting individual goals for each parameter at each well based on past performance
- Setting a percent variation.

The method that finally worked the best was to set up a control chart, which was simply a graph of the data. Water quality stability, equated to pumping representative formation water, was assumed when the trend of each parameter approximated a flat line. Figure 1 illustrates an example of the water quality stabilization plots that were generated each time a well was sampled. Some parameters may continue to exhibit some variability, but we interpreted a parameter as being stable when it appeared to vary about a mean value and not around an increasing or decreasing trend. Overall water quality is not achieved until all field parameters have stabilized. In the example shown on Fig. 1, analytical sample collection began after the last field

data point measurement (1200 min).

Supporting investigations

The results from each of the supporting investigations tended to confirm the validity of the low-flow sampling method and were consistent with the results reported in previous studies of the method.

Surrogate aluminum samples.

The aluminum concentrations tended to be significantly higher than historic baseline values in the early purge samples; these concentrations then declined and stabilized at historic levels within the removal of one well volume of pumping (Fig. 1). The change in aluminum concentration over time during stabilization was most closely matched by the change in turbidity (Fig. 1). This indicates that turbidity is the best field indicator of water quality stability, especially for metals monitoring, confirming numerous other studies (7).

Progressively filtered samples.

Results from the progressively filtered samples were the same for all the wells. Metals concentrations varied little between each of the three filtrates and the unfiltered sample from each well. The only exception was iron, which may reflect the presence of iron oxides that have aggregated into various-sized particles. Similar results were obtained from fall 1993 samples analyzed for diox-

ins/furans, with no significant difference in the results of unfiltered and 0.45- μ m filtered samples. Colloids at the site may be smaller than 0.02 μ m (the smallest filter size used), but filtering these sizes is difficult.

SEM/EDX investigation of colloids. SEM/EDX inspection of the surface of the filter membranes revealed no distinguishable organic colloids or unusual inorganic colloids. Most inorganic particulate matter was identified as common minerals (quartz, feldspars, micas, and occasional hornblendes or other mafic materials), small fragments of steel (likely from the well installation process), and barium sulfate crystals (origin unknown).

Sampling method comparison.

Both a traditional bailed sample and a low-flow pumped sample were collected from one well during the summer 1994 sampling event and analyzed for unfiltered metals. The bailed sample contained notably higher concentrations of metals, which are presumed to be related to particulate matter in the well or to be disturbed by the action of bailing the well, and not to actual groundwater quality. This indicated that the observed change in water quality after implementing low-flow sampling was due to sampling methodology and not to other factors, such as a dramatic shift in actual groundwater quality at the site.

Extended field data collection.

During the spring 1994 event, one well was purged of ten volumes prior to sampling. Water quality stabilized after the removal of four well volumes and remained stable thereafter. Additional water quality measurements were taken after the sampling had been completed at nine wells during the spring and summer events in 1994. The postsampling water quality generally compared very closely to the presampling water quality at the end of stabilization. These results indicate that field

monitoring of water quality stabilization, especially that of redox potential and turbidity, is a better method of determining when sampling should begin than counting the number of well volumes removed.

Compliance results

Based on the documentation of the field methods of the low-flow methodology and the supporting investigations, both Potlatch and the state regulators had confidence in the results. Following implementation of the low-flow methods, two metals continued to be detected at concentrations greater than the naturally occurring levels at the site and the permit water quality performance standards. Potlatch has since completed remedial actions for these metals.

The greatest concern at the onset of the investigation was chlorinated dioxins and furans, which had been detected in the unfiltered samples collected by traditional methods. The concentrations of total dioxins and furans in the unfiltered low-flow samples were approximately three orders of magnitude lower than those in the unfiltered samples collected by traditional methods (see Fig. 2). The concentration of 2,3,7,8-tetrachlorodibenzo-p-dioxin in the low-flow samples were and remain below detection limits, whereas this material had been detected in a number of samples collected by traditional methods. As a result, Potlatch was not required to take further action with respect to dioxins in groundwater.

CONCLUSIONS

The goal in low-flow sampling is to minimize disturbances in the well and aquifer by matching the water withdrawal rate to the well production rate. In this way, the groundwater flows that are in and near the well are close to the natural flow rates in the formation. The best practical

measure of this is drawdown in the well. Low-flow is relative to each well. A low-flow pumping rate in an 8-in. well screened in gravel would be higher than a low-flow pumping rate in a 2-in. well screened in silt. Low-flow sampling allows collection of samples that are technically superior to bailed samples because this method minimizes disturbance in the well and in the formation.

Potlatch successfully applied low-flow sampling to monitoring at its industrial solid waste landfill in Cloquet, MN. The most significant finding was that dioxins are not migrating at significant concentrations, and concerns regarding metals were greatly reduced. The use of low-flow sampling gave Potlatch, the regulators, and community members the confidence that the results were representative of real groundwater quality. Potlatch continues to use low-flow sampling when unfiltered groundwater samples are required for metals and dioxins.

The results from low-flow sampling may not appear significantly different than those from traditional filtered samples. This was the case with Potlatch's results. However, low-flow sampling may be necessary if the regulators do not allow filtering for the critical parameters.

Low-flow sampling is not simple, nor is it inexpensive. It is likely that sampling will take more field time, more equipment, and more documentation. To properly implement low-flow sampling, new wells and/or new pumps may be required. In Potlatch's case, the company considers the added cost of the low-sampling method to be easily justified by avoiding the costly implementation of remediation based on unrepresentative groundwater samples.

In the future, studies using low-flow samples should not include the supporting investigations used by Potlatch, although some may have

specific applications. Some regulators, including Minnesota, are writing guidance documents for versions of low-flow sampling. This could make the process of approving and implementing the use of low-flow sampling much simpler, although this process will still be more involved and generally more expensive than traditional sampling methods.

Low-flow sampling is invaluable in a number of applications. One of the more common applications would be for deep wells in high-permeability formations with a large column of water. Traditional methods of sampling these wells require removing hundreds of gallons of water during purging and stabilization. Low-flow sampling could allow the removal of only a fraction of one well volume, saving disposal costs of large volumes of water. In this application, low-flow sampling is sometimes referred to as micro-purge sampling, and in contrast to the Potlatch experience, this application should take less field time than traditional methods. Other useful applications are at those sites where contaminants of concern include those with very low water quality criteria, like dioxin. In this case, low-flow monitoring is technically appropriate. Finally, low-flow sampling may be required if there is a question about the validity of samples collected by traditional methods. **TJ**

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