



Guidelines for sampling ground water

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Fundamental to proper sampling of well water to assess groundwater contamination is an understanding that the composition of water collected from a well is frequently a function of the extent to which the well was pumped (or bailed) prior to sampling, the length of time since water was last withdrawn from the well, and—in some instances—the method of sampling. This is a result of several factors. The ground water of an area frequently occurs in multiple strata or aquifers that con-

Investigators should never assume that commonly used sampling and analytical methods are applicable to all situations.

tribute ground water to a well at different rates depending on the head, the permeability of the aquifer material, and other variables. Further, it is rare that the chemical composition of each aquifer-layer is the same; therefore, the composition of the water in a well that penetrates several aquifer-layers will almost certainly change, sometimes drastically, as a function of the length of time since the last pumping or sampling, or as a function of the length of time the well is pumped.

Ground water in areas near waste disposal sites is frequently anoxic and hence tends to contain high concentrations of soluble iron. This condition can result in variable concentration as a function of pumping. In standing water in a well open to the atmosphere, the dissolved iron will be oxidized to ferric hydroxide, which will precipitate and slowly settle in the well. Ferric hydroxide is an efficient scavenger of a wide variety of contaminants and would tend to cause the well water to have lower concentrations of many contaminants of concern than those actually present in the aquifer(s). It is very important in sampling ground waters to be certain that the water collected has the same oxidation-reduction and other chemical characteristics as the aquifers from which the water was derived.

Also potentially affecting the chemical characteristics of well water is the material used in constructing the well. Metal pipes can corrode and add metal to the water. Iron-containing pipe tends to leach iron, which could form ferric hydroxide and remove other contam-

inants from the water, as described above. Sometimes, relatively inert plastic pipe is used but with metallic, such as brass, well screens. These screens, especially in more acidic waters, tend to corrode, contributing copper, zinc, and other trace metals to the water. Although plastic is the most desirable construction material in most cases, plastic pipe can sometimes leach metals (such as zinc, used as plasticizers), as well as a variety of trace organics derived directly from the pipe, or various cement or bonding materials used to join sections of pipe. This situation further points to the necessity of pumping a well vigorously before sampling to ensure that the water collected does not contain foreign materials not representative of the aquifers being sampled.

It is important to realize that contaminants derived from waste disposal sites often do not mix rapidly with the water in an aquifer, but rather tend to move as a relatively thin layer on the surface of the aquifer, or—because of a higher density created by high salt content—near the bottom of the aquifer. This situation further contributes to changes in composition of water collected from wells as a function of the degree of pumping.

WATER SAMPLING PROCEDURE

When a new well is developed for groundwater sampling purposes, it should be pumped vigorously until the water appears free of suspended solids (SS). The well should be allowed to stand several days and then pumped again to flush it. If the water is clear (essentially free of turbidity), then the well sampling program can be initiated.

The proper approach for initial sampling of ground waters from a well is to collect a series of samples as a function of pumping time to define how long the well must be pumped (number of well volumes) prior to collecting a sample, to be certain that water collected is representative of the ground water. The sampling frequency to be used for this evaluation should be determined for each particular well. As a general guideline, a well should be sampled at 1, 2, 4, 6, and—if possible—10 well volumes during pumping. The well volume is estimated by the diameter of the well and depth of the

water in the well at the time of initiation of pumping. If the well is a low-yield well, it may become necessary to forego the higher well volume samples. If this is done, then it must be realized that the composition of the water in the final sample may still not be representative of the ground water in the region.

Each of these samples should be analyzed for the constituents of concern, as well as certain bulk chemical properties, such as specific conductance, temperature, and dissolved oxygen (DO). The specific conductance value provides valuable information on the relative contributions of waters from various aquifers in a particular well. If it is found that the specific conductance changes with duration of pumping, then it is almost certain that the concentrations of trace contaminants of interest will also be changing. The DO data are useful to indicate the redox state of the ground water. If the DO concentration of the water in the aquifers is less than about 1 mg/l, then the potential exists for ferric hydroxide to be precipitating and scavenging contaminants of interest when the aquifer water sample is exposed to the atmosphere in the well, in the sample container, or during sample handling. If the sample contains dissolved iron concentrations of 0.01 mg/l or greater, then all sample collection and manipulation in the field and laboratory must be done so as to avoid exposing the sample to air. This precaution may be particularly important during the sample filtration step. It may be necessary to filter the samples in a glove bag under a nitrogen atmosphere.

Examination of the groundwater composition data as a function of well volumes pumped should show a leveling off to a plateau value with increasing well volumes pumped. At the well volume at which composition data values plateau, composition is independent of well sampling technique. If a plateau is not obtained, then great caution must be exercised in interpreting the groundwater characteristics data. Rather than being representative of the ground water in aquifers penetrated by the well that have not been sealed off, the measured groundwater composition is indicative of sampling, or sample holding techniques, or both, that make the data essentially worthless for water quality evaluation purposes.

Once it is established how long (that is, how many well volumes) a particular well needs to be pumped before a representative sample is collected, then—for future sampling—the well can be pumped for that number of volumes before sampling. An evaluation of the concentration-pumping duration (well volume) relationship should be made at least twice each year for 3 years for each sampling well (that is, once each spring-summer and again each fall-winter). This reevaluation is especially important for wells that are located in areas with widely fluctuating water tables where more frequent sampling program evaluation should be made in order to determine the extent of water table variations and their influence on the water composition-duration of

pumping relationships. Depending on the year-to-year variability in concentration-pumping relationships during the first 3 years, it should be possible to decrease the frequency of reevaluation to every 3 to 4 years. The reevaluation can readily be done by collecting samples before and after the previously selected well volume flushing period.

The type of pump used in sample collection must also be evaluated to ensure that it does not alter the composition of the water. Gas lift systems can readily change the pH of the water being sampled by changing the CO₂ partial pressure within the water. Further, gas lift pumping systems that have DO in the pumping gas, such as air or impure nitrogen, could result in the oxidation of ferrous iron to ferric iron, which—as discussed elsewhere in this section—has a marked impact on the forms and amounts of chemical contaminants in the water. The oxidation of iron can also affect the pH of the water through iron hydrolysis reactions, which can have an impact on the thermodynamics and kinetics of a wide variety of other reactions that can occur within the system. In general, gas lift pumping systems should be avoided because of these problems. If used, they must be carefully evaluated relative to mechanical and bailing methods. It should be noted that mechanical pumps and bailers should be made of plastic material or coated with plastic, and should be lubricant-free so as to avoid contamination of the water by the pump or bailer. Every pumping or bailing system considered for use should be evaluated for its potential to contaminate the water being sampled.

For certain types of pumps or bailers, it may be possible to use metallic apparatus when the rate of transfer of metals and other contaminants is sufficiently slow compared to the rate-volume of water being sampled, to avoid a significant degree of contamination. It should be noted that new pumps, tubing, and so on are particularly prone to releasing contaminants to water with which they come into contact. New apparatus should be soaked in water for at least a day, then thoroughly rinsed prior to use. One of the most notorious of such problems is caused by the zinc derived from plastics and rubber. Normally, the high release rate of zinc observed initially in these cases is rapidly decreased upon soaking.

Gibb *et al.* (1) of the Illinois State Water Survey have a contract with the U. S. Environmental Protection Agency (EPA) to investigate monitoring with sampling and preservation techniques. Although at the time of preparation of their paper (1980) their work had only just begun, it is expected, based on the direction that the Gibb *et al.* study is taking, that these authors will soon be obtaining data that will demonstrate the various kinds of problems that are discussed in this section and that are generally known by those familiar with appropriate methods for groundwater sampling.

Information on procedures for collection and field

analysis of groundwater samples for unstable components is provided by Wood(2). Also, the reader is referred to the *Groundwater Monitoring Review* (Lehr(3)) for additional information on overall approaches that should be used in sampling and sample handling for groundwater quality monitoring.

SAMPLING FREQUENCY AND LOCATION

The groundwater monitoring wells should be positioned to monitor overall water quality characteristics of the ground water in the region, and both up- and down-groundwater hydraulic gradient from suspected specific sources of contaminants such as a waste disposal area, the sludge dewatering lagoons, contaminant storage areas, any sumps created to collect surface runoff, and so on. One or more up-hydraulic gradient monitoring wells should be drilled at the site. Several groundwater sampling wells should also be positioned along the property line of the site to properly define the character of the ground water entering and leaving the site. The wells should be drilled to a depth of approximately 3 m below the expected minimum annual water table for the region at that specific location. If the aquifer is more than 5 m thick, then it is recommended that a nest of three wells be constructed—to sample waters at about 1 m below the upper elevation of the aquifer, at mid-aquifer elevation, and near the bottom of the aquifer. The uppermost wells should be positioned so that their sampling points are always within the aquifer. For widely fluctuating water tables, this may require several aquifer surface wells. Some geological strata have high permeability layers of sand, sandy clays, and so on. Many of these layers are relatively thin. Any water-bearing layers of this type located near waste disposal facilities should have monitoring wells constructed to sample the water within the lenses.

Of particular concern at most sites are the nearby wells used for domestic and agricultural water supply. Such wells should be monitored as part of the overall monitoring program. The monitoring of the water of these wells and of the monitoring wells should be conducted at monthly intervals for 1 year to establish the variability of the composition. If the wells have reasonably constant compositions (that is, the concentrations in the well can be predicted with a reasonable reliability based on previously conducted studies), then the frequency of sampling during the second year can be reduced to quarterly. If the variability remains about the same during the second year, then the frequency of sampling can be reduced to twice a year in subsequent years. It may, with several years' records, be possible to reduce the frequency of sampling of monitoring wells of this type to once a year.

In addition to the overall monitoring wells of the region that are positioned along the upper and lower hydraulic gradient property lines for the site, plus existing wells in use near the site that could potentially be contaminated by the site's operation, it is desirable to locate several series of wells within relatively short distances of potential sources of contaminants (for example, the solid waste disposal area, sludge lagoons, and sumps for surface runoff collection). These wells should be set up to monitor ground waters passing through the potential site of contamination—both upstream and downstream of this site. The wells should be located a few meters from the area to detect groundwater contamination before it becomes a generalized problem of the area. These wells should also be sampled at monthly intervals and then at quarterly intervals after concentration-time patterns are established. It is recommended that the frequency of sampling at these wells not be reduced below quarterly so as to ensure that any problems of groundwater contamination are detected as early as possible. The monitoring wells for the specific contaminant source monitoring should be drilled 1 to 3 m below the area's annual low-water table position. The groundwater hydrology may necessitate the construction of nests of three wells of the type described above for peripheral site monitoring.

MONITORING PARAMETERS

In general, the following parameters should be measured on all well samples:

pH	arsenic
temperature	barium
specific conductance	beryllium
turbidity	boron
chloride	cadmium
sodium	chromium
dissolved oxygen	copper
calcium	fluoride
magnesium	hydrogen sulfide
alkalinity	lead
total organic carbon	mercury
dissolved organic carbon	nickel
soluble orthophosphate	potassium
ammonia	selenium
nitrate	phenolic compounds

A gas chromatograph (GC) scan should be made for chlorinated hydrocarbons, both low molecular weight solvent-like materials and higher molecular weight pesticides and PCBs; any herbicides, pesticides, and so on, used as part of maintenance of the property; plus any specific contaminants present in waste or contaminant sources that are identified by the current on-going studies of EPA and others on the characteristics of solid waste leachate. Further, for areas that are associated with

a specific source site, such as sludge lagoons and runoff water from storage areas, the list of contaminants should include any potentially hazardous materials known to have been introduced into these areas.

ANALYTICAL METHODS

In general, the analytical methods should be those procedures prescribed by EPA (4), "Standard Methods"(5), or equivalent. Care must be taken to ensure that the analytical methods used and the technician can measure each component of concern with the desired precision and accuracy. For most contaminants of concern the lower detection limit should be severalfold less than, but preferably an order of magnitude below, the critical level or standard for each particular contaminant. EPA's "Red Book" for water quality criteria (6) provides useful guides to concentrations of contaminants that may be of concern in aquatic systems.

The November 1980 *Federal Register* (7) presents the revised EPA water quality criteria. The critical concentrations for some contaminants demonstrate the need for significantly decreasing the detection limits of the EPA's approved analytical methods for monitoring groundwater quality. The November 1980 *Federal Register* lists concentrations of contaminants that are suspected to cause cancer in man when the water containing them is consumed over extended periods of time. For example, a concentration of beryllium at 3.7×10^3 $\mu\text{g}/\text{l}$ would be expected to cause one additional cancer in a million people consuming water so contaminated, but the beryllium detection limit of the EPA procedure is 5 $\mu\text{g}/\text{l}$. This means that a municipal well located near a hazardous waste disposal site that has accepted beryllium-containing wastes could contain concentrations of beryllium in the water that are listed as nondetectable based on EPA-recommended and -approved procedures; but such water could cause an additional 1250 cancer cases in a population of a million people. The situation for beryllium is not atypical of what occurs for a number of contaminants when one compares the detection limits of the analytical methods recommended by EPA for monitoring hazardous waste disposal sites with the concentrations that EPA has determined to be potentially harmful to man through consumption of groundwaters containing the contaminants. For further discussion of the role of groundwater monitoring in siting hazardous waste disposal sites, consult Lee and Jones(8). This situation reveals the importance of being certain that hazardous waste disposal takes place in areas where the waste components are completely immobilized or detoxified and the natural geological strata do not possess any high permeability layers or lenses that would allow rapid transport of contaminants from the disposal site pits to the wells of the region.

Associated with a water quality monitoring program should be an evaluation of the reliability of the proposed sampling, handling, and analytical techniques. The investigator should never fall into the trap of the "Standard Methods syndrome" (Lee and Jones(9)) of assuming that a particular method, even one commonly used by others in similar types of studies, is applicable to a particular situation. The investigative approach must be used to evaluate the sampling, handling, and analytical methods on a site-specific basis. A small amount of time spent in evaluating methods can make the difference between generating considerable amounts of worthless data and developing a data base that can be used to assess the present composition of the waters being sampled as well as the changes in composition with time. Lee and Jones (9, 10) present discussions of problems frequently encountered in obtaining good quality analytical data. These papers, as well as the EPA quality control handbook (11), should be consulted for specific guidance on the numbers of replicate analyses, spiked samples, standard additions, and blanks that should be processed with each analytical run.

It is important that laboratory turnaround time between sample collection and data work-up be less than 2 weeks. A water quality data handling system should be established in which, as each set of data is received, it is automatically reviewed shortly after receipt to ensure that:

- It is consistent with previously collected data;
- There are no concentrations of contaminants above critical concentrations that could impair beneficial uses of the water; and
- Changes can be made in the study program, if and when needed.

Further, each year someone knowledgeable in surface and groundwater quality should prepare a report discussing what has been found from the year's data and its potential implications for groundwater and surface water contamination.

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