GUIDELINES AND TECHNIQUES FOR OBTAINING WATER SAMPLES THAT ACCURATELY REPRESENT THE WATER CHEMISTRY OF AN AQUIFER

U.S. GEOLOGICAL SURVEY

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By Hans C. Claassen

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METRIC TO INCH-POUND

Multiply SI units	by	To obtain inch-pound units
	Length	
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
	Volume	
liter (L)	33.82	ounce, fluid (oz)
liter (L)	1.057	quart (qt)
liter (L)	0.2642	gallon (gal)
cubic meter (m^3)	35.31	cubic foot (ft^3)
cubic meter (m^3)	264.2	gallon (gal)
cubic meter (m^3)	0.0008107	acre-foot (acre-ft)
	Flow	
liter per second (L/s)	15.85	gallon per minute (gal/min)
cubic meter per day (m^3/d)	264.2	gallon per day (gal/d)
	Temperature	
degree Celsius (°C)	F = 9/5°C + 32	degree Fahrenheit (°F)
	Specific conductance	
microsiemen per centimeter at 25° Celsius (µS/cm at 25°C)	1.000	micromho per centimeter at 25° Celsius (µmho/cm at 25°C)
	Transmissivity	
square meter per day (m^2/d)	10.76	square foot per day (ft^2/d)
	Pressure	
kilopascal (kPa)	0.1450	pound per square inch ($lb/in.^2$)

may be made at large cost and with considerable uncertainty. Ground-water hydrologists need to be aware of the limitations placed on them by the nature of the system they attempt to understand, and they need to consequently appreciate the care that needs to be used in making observations. This paper is dedicated to guidance for making these observations.

Another aspect of ground-water sampling is determination of what constitutes a useful definition of a water sample. The distinction between matter in true solution and matter in suspension is not entirely arbitrary. Ordinarily, the most difficulty in distinguishing solid from liquid is in the particle-size range commonly called colloidal: 0.001 to 1 μm (micrometer). Particles near the upper end of this range can be seen by ordinary optical equipment, whereas particles at the lower end behave like simple ions or molecules in solution. If a water is filtered through a membrane with a mean pore diameter of 0.45 μm, as is the recommended practice in the U.S. Geological Survey, almost the entire colloidal range is included in the filtrate. The increase of the filter cake during filtration decreases the mean pore diameter of the resulting filtration. We are thus faced not only with a decision regarding the maximum particle size that will be considered "in solution," but also a potential change in this value as the sample collection proceeds. The 0.45 μm-filtered sample is a measure of what may be present in suspension with the ground water and, therefore, becomes a working definition of "in solution." Nevertheless the potential problem exists (for example, when chemical precipitation of a solid phase is occurring) of being unable to make a clear distinction between solid and liquid phases.

Purpose and Scope; Source of Data

This report will provide guidance to determine which locations and methods will provide ground-water samples to fulfill stated requirements. Some of the guidelines (unreferenced) are based only upon conjecture; no controlled experimentation validates them. Validation and modification of the methods is by the informal procedure outlined below. The author's experience and the experience of those whom he has consulted generally is the source of the advice given; however, it is believed that much of it would withstand the rigors of experimentation. One needs to assume a cautious and inquisitive attitude when planning and conducting a ground-water sampling program. The successful investigator constantly questions his methods and results.

For an example of the informal validation and modification process, where logical conjecture is reviewed when new observations are made, consider the following:

Problem statement: What is the effect on the chemistry of ground water when mild steel is used in a particular application as casing or pump column?
Initial conjectural statement: Water, containing minimal dissolved-iron concentrations will dissolve small quantities of steel (causing corrosion) resulting in greater dissolved-iron values than naturally exist in formation water.

GUIDELINES AND TECHNIQUES FOR OBTAINING WATER SAMPLES THAT ACCURATELY REPRESENT THE WATER CHEMISTRY OF AN AQUIFER

By Hans C. Claassen

ABSTRACT

Obtaining ground-water samples that accurately represent the water chemistry of an aquifer is a complex task. Before a ground-water sampling program can be started, an understanding of the kind of chemical data needed and the potential changes in water chemistry resulting from various drilling, well-completion, and sampling techniques is needed. This report provides a basis for such an evaluation and permits a choice of techniques that will result in obtaining the best possible data for the time and money allocated.

INTRODUCTION

Fundamental Considerations and Definitions

To most ground-water hydrologists, the "sampling" of ground water denotes the removal of water and its dissolved and suspended constituents from beneath the land surface and subjecting it to analysis in order to characterize some of its physical, chemical, and biological properties. But sampling has a more precise meaning to a statistician; it indicates that a sample is a part (subset) of a population (set) presumed to have the characteristics of that population. Ground-water hydrologists imply this same meaning when they obtain a ground-water sample; that is, they assume that the sample is representative of the aquifer from which it came and will, therefore, tell them something about the chemical or biologic activity that was not sampled but is present in the aquifer at the time of sampling. Thus the water in the aquifer (or region of aquifer) of interest becomes the population and the sample becomes the subset.

Scientists commonly assess the degree of population representation of a sample in one parameter by qualitatively determining the representation of that sample in one or more other parameters. This technique is frequently successful in instances where the population is reasonably homogeneous and can be clearly defined, such as in chemical evaluation of a well-mixed lake or stream that does not change with time. Here the extent of the system (population) usually can be determined easily and observations readily made. However, in ground-water studies, identification of the population is considerably more difficult; individual observations are more costly and time-consuming and have greater uncertainty than observations made on surface-water systems. Ground-water hydrologists concerned with evaluating water chemistry or biology are faced with a major task. They must make observations on a system whose extent can only be approximated, within which each observation

Observation: A radioactive tracer, injected in a well, yields unexpectedly high dilutions of tracer when removed by pumping.

Revised conjectural statement: Water in contact with a corroded casing and pump column may lose trace elements, such as the injected tracer, by sorption on the oxide coating present.

The following presentation is given in the sequence used by most ground-water hydrologists, beginning with project planning and continuing through all phases of study. Certain aspects are appropriate to more than one activity or phase during the project. The techniques are intended to provide the best data collection possible for the time and money expended.

SELECTION OF GROUND-WATER SAMPLING SITES

Sampling locations and analytical determinations made on samples collected will be determined by the project objectives. For example, a person whose project was funded to monitor the tritium concentration in public water supplies in a three-county metropolitan area would have an easier task choosing where to sample and what to measure than would a person whose project objectives were to define the ground-water geochemistry of a complex system of aquifers and predict the effect of large-scale irrigation development on ground-water quality.

For the latter type of study, data requirements generally are demanding in terms of materials and manpower, which commonly results in a decision to compromise quality for quantity. It is usually wise to resist the temptation to obtain large numbers of improperly-collected samples but instead expend project funds in a manner that results in fewer, but better, samples. The categories of study type that follow are discussed in order of increasing complexity in network-sampling design.

Monitoring of Water Supplies

Monitoring is the periodic measurement of certain specified chemical constituents or physical properties, usually those related to public health; see for example: U.S. Environmental Protection Agency, 1975, 1976a, 1976b, and 1977.

Because it is the water actually consumed that is of interest, samples need to be obtained at point of use. Changes in ground-water quality brought about by passage through the delivery system or by water-conditioning facilities (such as chlorination, filtration, or softening) are included in the sample obtained.

Hydrologic Survey

The hydrologic ground-water survey generally is called the well and spring inventory; its purpose is to characterize natural spatial variability in ground-water quality in a specified area, or to document conditions prior to the occurrence of an anticipated change in the area. The sites selected depend on the total funding available, number of potential sites, and the physical properties and chemical or biological constituents chosen for study. Usually studies are done in two phases: first, a few properties and constituents are selected to define major chemical or biologic divisions of the hydrologic system. Sites for more detailed study are then chosen on the basis of their representation of the major divisions of the hydrologic system. For example, phase one may consist of obtaining specific-conductance values for each potential sampling site in the area to be studied. These data may form the basis for selecting samples for more complete chemical analyses. As the number of analytical properties and constituents increases, requirements for geohydrologic, well-completion, well-use, and well-history data become more critical. For example, large quantities of analytical data from a site are of little value if the source of the water cannot be identified with reasonable certainty. Determining concentrations of redox-sensitive elements in samples obtained from stagnant supplies also would be questionable.

Monitoring of Contamination

Studies designed to monitor the migration of contaminants in an aquifer system require very precise hydrologic information to select sampling sites. In order to intercept the contaminant and document its movement in the ground-water system, reasonable estimates of the horizontal and vertical movement of ground water and the hydraulic properties of the system need to be obtained so the sampling locations will be in the path of the migrating contaminant(s) and be a reasonable distance from the source.

Sample-collection methods need to minimize changes in composition brought about by entry into or residence in the well; yet, only a minimum volume of water can be removed so the ground-water flow patterns in the vicinity of the well are not disturbed. Trace-element concentrations generally are of interest in contamination studies; precautions need to be taken to insure that well completion and sampling methods are compatible with the chemical reactions of these trace elements. For example, samples obtained for analysis of dissolved gases or redox-sensitive elements need to be processed in completely closed systems prior to separation or preservation. Some problems may be minimized by onsite analysis, because it takes time for many sample-composition changes to occur. However, this procedure has limitations, because onsite analysis is more difficult and generally less precise than laboratory analysis. The magnitude of changes in sample composition that may occur through processing and preservation techniques needs to be compared with the precision and accuracy of the onsite method. Length of time and cost involved in obtaining valid data need not be the only considerations in planning a sampling program at a particular site. Cost limitations exist for all projects; therefore, constraints on the number of sites sampled or the number and type of analyses performed on a particular sample will exist. However, quality is more valuable than quantity, because the results could be inaccurate or misleading if sample quality is compromised.

Geochemical Studies or Regional Hydrologic Studies

Geochemical studies or regional hydrologic studies vary in scope and complexity. In its simplest form, the regional hydrologic study is equivalent to the hydrologic survey. A geochemical study may not in some instances differ from water-quality aspects of a general hydrologic study, but increased sophistication in data-collection and data-manipulation techniques usually are implied. For example, a regional hydrologic study may use only total salinity (dissolved solids or total major ions) in describing the ground-water system. In contrast, a geochemical study would always use additional physical and chemical data to assess the state of the aqueous system with respect to the geologic framework of mineral components (that is, the mineral species) with which it is in contact. These additional data might include core samples for determining hydrologic and mineralogic properties, and very-precisely-determined water-chemistry properties and constituents for thermodynamic calculations. The range in complexity of these studies will result in a corresponding range of constraints on the choice of sampling locations. However, one requirement common to all these studies is: the sample needs to be representative of a definable part of the aquifer. This usually unstated assumption is the basis for most interpretations of water-chemistry and biologic data; it indicates that the hydrologic system is known and an understanding of the chemical and biological processes will be obtained by analysis of the ground-water samples. In other studies, the converse assumption may be true; that is, an understanding of the hydrologic system may be indicated from a knowledge of the chemical and biological processes. In every study, the assumption is made that the water samples are representative of a definable source. The importance of aquifer representation, methods of evaluation of degree of representation, and enhancement of aquifer representation of a specific sampling site will be stressed throughout this report.

THE AQUIFER-REPRESENTATION CRITERION

To understand the term aquifer representation as it pertains to the chemistry of ground water, consider a generalized example (fig. 1). On a microscopic scale, each grain of material in the alluvial aquifer is surrounded by a film of water whose composition is related to the mineralogic composition of that grain, the grain-size distribution (total effective surface), and the saturated effective porosity that is the volume of liquid free to move in contact with the grains. If the four grains shown in figure 1A are mineralogically different, the water composition in contact with any one of them may be different from that in contact with any other. This is an example of microscopic inhomogeneity. If the different types of grains are randomly distributed throughout the aquifer, macroscopic water samples will be of similar compositions. If, however, the grain types are not randomly distributed throughout the aquifer (as in the alluvial aquifer of fig. 1A, to the right of the well), but concentrated in certain regions, the water chemistry may vary from one sample to another depending on where in the aquifer it was obtained. This is an example of macroscopic inhomogeneity. Some water-chemistry differences may be present at the interface

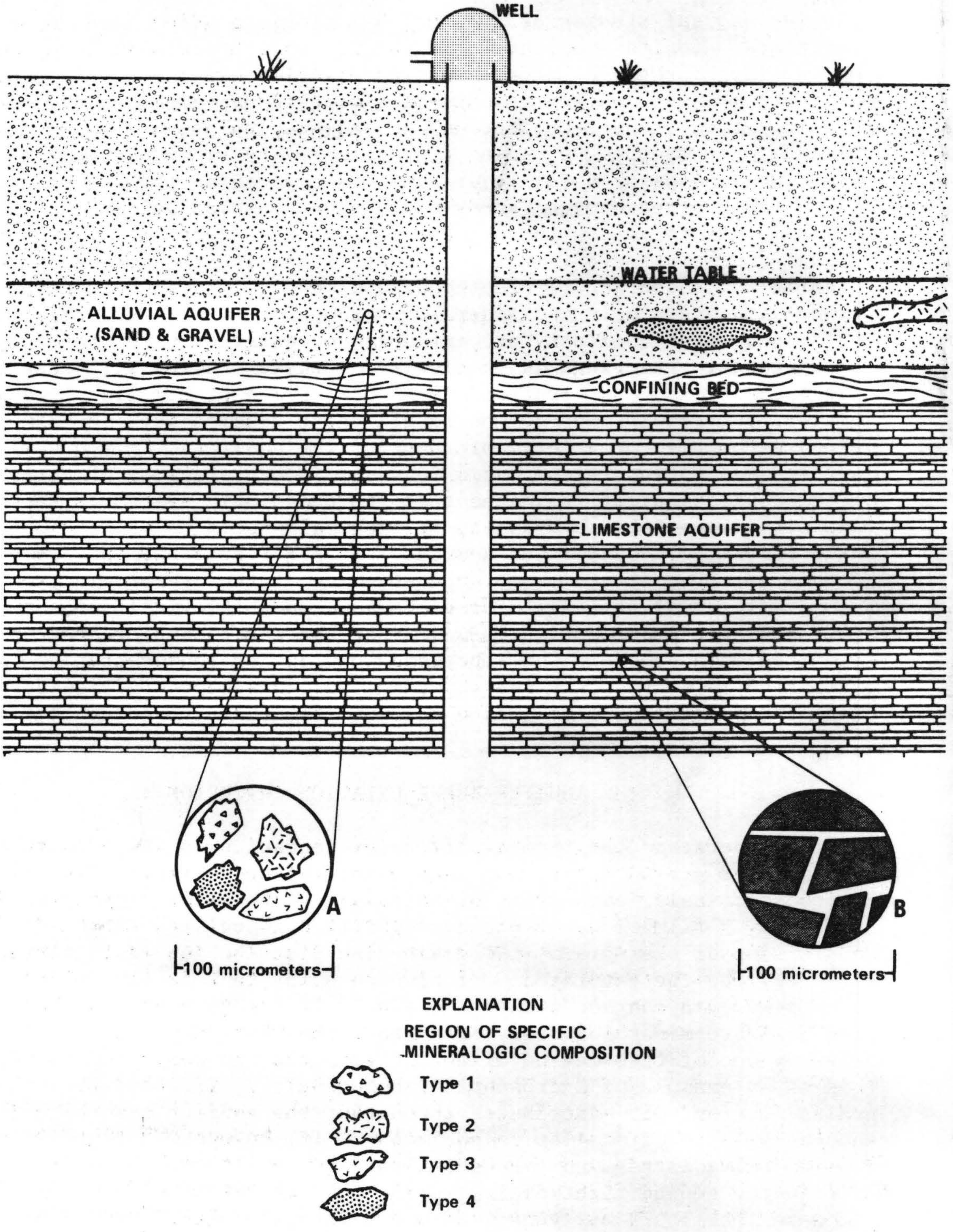


Figure 1.--Aquifer macro- and micro-inhomogeneity.

between the saturated and unsaturated zones associated with water-table aquifers. At this interface, gaseous diffusion into or out of the water may affect the carbon dioxide-bicarbonate-carbonate balance or change the distribution of sensitive species.

A third situation is shown in figure 1B. This aquifer is lithologically homogeneous and its water chemistry is dependent only on the fracture surface area and the volume of liquid in those fractures. This situation results in the water composition varying somewhat from place to place on a microscopic scale, but remaining macroscopically homogeneous.

The foregoing discussion assumed that the water being sampled was confined to a particular geohydrologic unit. A hypothetical situation wherein a single geohydrologic unit assumed homogeneous, containing two distinct water types, is shown in figure 2; one water type is derived from interaction with limestone and alluvium, and the second type is representative of contact with the alluvium alone. A short period of pumping at each well (A, B, and C) will produce three different water chemistries, although each well is completed in the same material, to the same depth. Clearly, the first step in obtaining an aquifer-representative sample is aquifer definition. Most aquifers are microscopically heterogeneous; some are homogeneous on a larger scale; all are probably heterogeneous on a regional scale. Therefore, the problem of determining aquifer representation is one of deciding how large a volume of aquifer we wish to represent. This determination usually is qualitative: a volume large enough to avoid local heterogeneities, but smaller than one that would include regional variability usually is desired. Data using these criteria usually allow for changes in water chemistry along the flow path to be evaluated, as well as determine the effects of other water sources on the aquifer under investigation.

Evaluating Aquifer Representation

Monitoring changes in water-quality properties and constituents, as water production proceeds, is used to obtain representative ground-water samples from wells, when available data insure that the well is likely to penetrate a single geohydrologic unit. The properties generally chosen are specific conductance (a measure of total ion composition) and pH (a single component generally very sensitive to changes in water composition). The monitoring procedure is necessitated to integrate local inhomogeneities; as water production (usually by pumping) progresses, the cone of depression becomes larger, integrating the discharge over an increasingly larger part of the aquifer. Because this method only indicates when a steady-state water quality has been reached, it is not the sole criterion of aquifer representation. Wells completed in more than one aquifer or not fully penetrating a single aquifer present special situations, where a time-invariant water chemistry does not equate to aquifer representation. To recognize these situations, a complete description of the geologic and hydrologic regimes penetrated by the well and completion and history need to be known. These

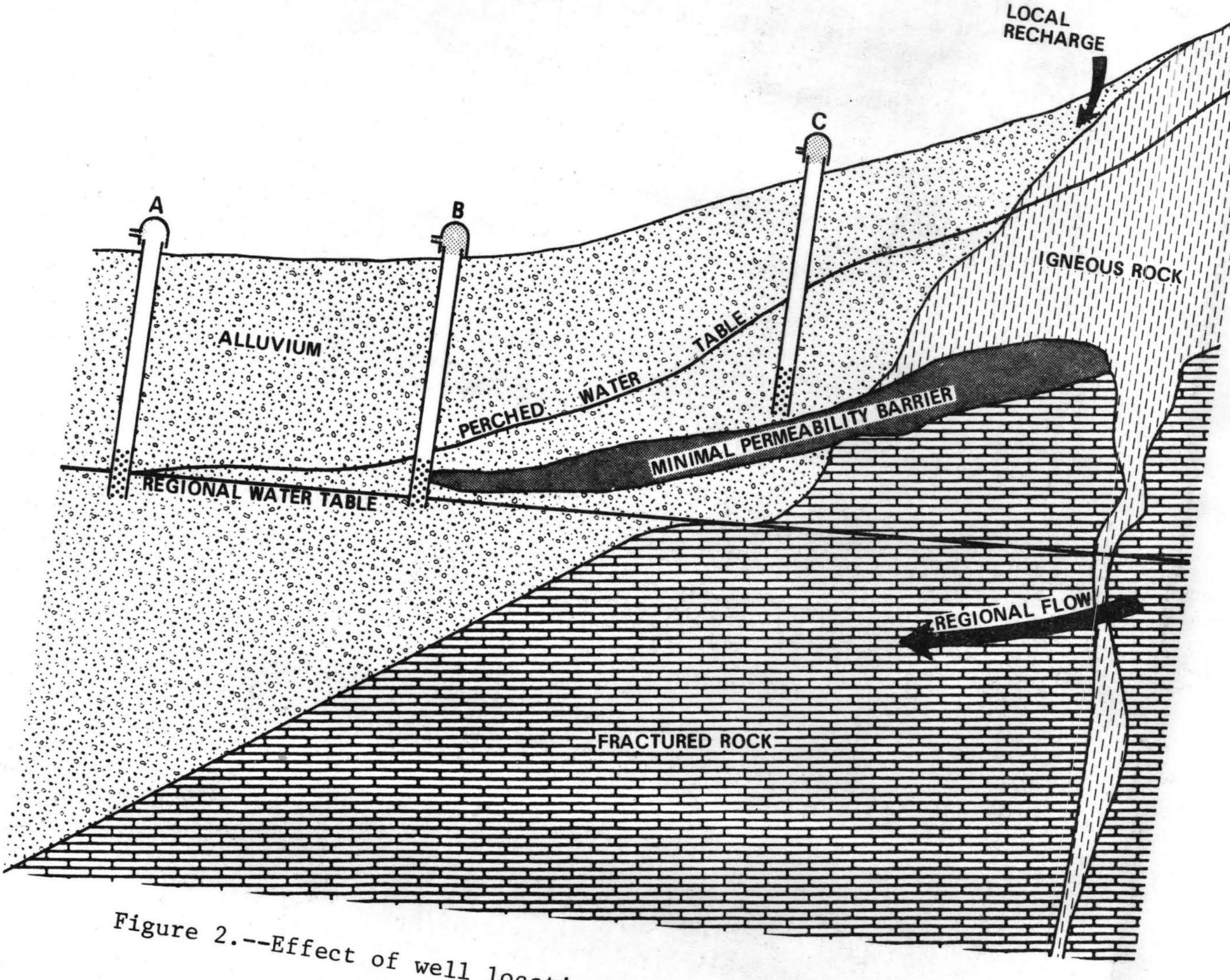


Figure 2.--Effect of well location on aquifer(s) penetrated.

well data will result in defining the source of the water being produced by the well, the first (and most important) step in obtaining an aquifer-representative sample. The following example illustrates some techniques that may be used to define the water source and to evaluate the aquifer representation of water samples obtained therefrom.

Consider a study to determine the water-chemistry variations both areally and with depth in a large irrigated valley. A published hydrologic atlas shows that the valley fill comprises two aquifers, one a water-table aquifer and the other an artesian system. The hydrologic atlas also contains a simplified, not-to-scale, cross section indicating the approximate location of the confining bed separating the two aquifers. The location of this boundary needs to be known within a few tens of feet; however, a literature search has identified only a few geologic quadrangle maps, each with a north-south and east-west cross section, fortunately at a usable scale. The hydrologic atlas has provided a plan view of the area and allowed choice of sampling locations that would provide adequate areal coverage, but insufficient data were provided to determine which of the aquifers is the source of the water.

To evaluate the tentative sampling locations for source definition and aquifer representation, a search of the State Engineer's records or those of the State Department of Water Resources is made to obtain well drilling and completion information. No records are found for a few of the locations; the ground-water hydrologist decides not to search for new locations as replacements at this time. The remaining drillers' reports are used to construct scale drawings relating lithologic descriptions, well-completion data, and hydraulic data. Although there are drillers' reports available for most of the chosen locations, the information they contain may be incomplete. Most reports contain lithologic logs, subject to large variability in description technique; however, many do not contain hydraulic data, such as static water level, production rate, and drawdown. Well-completion data such as cemented intervals, type (or extent) of gravel pack, and screened or perforated intervals generally are also not reported. The missing data can sometimes be obtained from the owner by visiting the site. Because the objective of this data accumulation is to define the source of the water being pumped and to relate the source to the hydrologic system, it is important that all lithologic, completion, and construction data be available for the well to be included in the sampling program. A checklist of data requirements desirable for source definition is given in table 1. Each topic and its effect on source definition and aquifer representation will be discussed in detail.

Well Information Relating to Water-Source Definition and Aquifer Representation of Sample

Drilling History

It is obvious that well depth is an important factor in determining which water-yielding formations are penetrated, but the drilling method and type of circulating fluid used may have an equally important effect on both

Table 1.--*Checklist of data requirements for water-source definition and aquifer representation of ground-water samples*

A. Drilling history

  1. Well depth and diameter
  2. Drill-bit type and circulating fluid
  3. Lithologic data from cores or cuttings
  4. Well-development before casing
  5. Geophysical logs obtained

B. Well-completion data

  1. Casing sizes and depths
  2. Casing material(s)
  3. Cemented intervals
  4. Plugs, stabilizers, and so forth, left in hole
  5. Gravel packing: volume, sizes, and type of material
  6. Screened, perforated, or milled casing or other intervals which allow water to enter the borehole
  7. Pump type, setting, intake location, construction materials, and pump-column type and diameter

C. Well pumping history

  1. Rate
  2. Frequency

D. Estimation of effect of contaminants introduced into aquifer during well drilling and completion on native water quality

E. Effect of in-place water-production system on the composition of ground-water sample

  1. Addition of contaminants
  2. Removal of constituents

    a. Sorption
    b. Precipitation
    c. Degassing

water source and its aquifer representation. While most common drilling methods produce fine material that coats the borehole wall (called the skin effect), some drilling methods may be more deleterious to aquifer representation than others. Augering of shallow holes probably produces the least skin effect; drilling with cable tool produces some fine rock chips that fill some native pore spaces; rotary drilling produces a similar effect, but also contributes additional plugging material in the form of additives to the circulating fluid. The most common of these is "mud," a mixture of water, bentonite clay, and other additives. These muds effectively perform the functions required by the drilling process; they prevent caving in the borehole, seal the borehole wall to prevent loss of circulating medium, cool and lubricate the bit, and remove the cuttings. Mechanical requirements for efficiently producing a hole to be used for collecting hydrologic data are counterproductive to obtaining the data. The degree to which drilling fluids penetrate a given formation will depend on the viscosity of the fluids and the applied pressure. Minimal-viscosity fluids may penetrate the formation further but may be removed easily during the well-development phase, whereas high-viscosity materials may be nearly impossible to remove by circulating water although they do not significantly penetrate the formation. If a significant part of the drilled hole is plugged by drilling fluids, well development will be difficult or inadequate, and producing zones may be chosen that exclude the plugged intervals. This may result in a water sample that does not represent the entire thickness of aquifer, and also results in incorrect hydrologic data being obtained from the aquifer. It may be argued that permeable intervals will be under sufficient hydraulic head to remove mud caked on the borehole wall when the hole is jetted, but this is not a foregone conclusion.

A significant range in drilling-fluid compositions exists, resulting in a consequently significant range in water-chemistry effects. There is some evidence both from onsite experience and laboratory experimentation (W. A. Beetem, R. L. Emerson, and L. J. Schroder, U.S. Geological Survey, written commun., 1971) that significant changes in water quality are effected by the presence of drilling mud in a well. Most of the changes can only be qualitatively inferred from estimates of mud composition; however, very significant affects on both major- and minor-constituent concentrations are caused by mud contamination. These effects require that an assessment be made as to when the contaminants have been removed. Such assessments may be made at the well site, using the following criteria:

1. Turbidity. Water needs to be removed from the well until it is visually clear. Turbidimeters can be used in a qualitative way to provide more precise estimates of change than visual observations.

2. Specific conductance and pH. Measurements of both properties need to be made periodically until three successive samples register identical values. Measurements need to be made only on visually clear samples.

In addition to the drilling-fluid effects on formation-water quality discussed above, the drilling history may provide information regarding locations of water-producing zones, or hydrologic history of the aquifer. Changes in rate of drilling-fluid loss or in rate of bit penetration may indicate fractured, cavernous, or other very permeable zones. The driller's log also generally indicates when water was first encountered. Deepening of a well needs to be correlated to water-use requirements or lowering of a regional water table.

Method to Estimate Effects of Contaminants Introduced During Drilling on Well-Cleanout Time and on Aquifer Representation

Under many drilling conditions (for example, drill-stem testing) the constraint exists that sufficient time may not be available for the above criteria to be met, because of the expense associated with the additional drilling-rig time involved. The effect of time spent cleaning out the hole on the relative deviation from true aquifer-water concentration of a particular constituent, B, is shown in figure 3. The ordinate, Y,

$$Y = \frac{\text{true concentration of B - measured concentration of B}}{\text{true concentration of B + contaminant concentration B}}$$

is a measure of relative approach to zero concentration of the contaminant in the sample, collected after a given pumping or other cleanout-procedure time shown on the abscissa, X. Curve 1 represents the limiting case, where the contaminating solution contains none of the constituent being measured. The earliest samples, though mostly contaminant solution, contain virtually zero concentration of constituent B. In this case, the contaminating fluid acts to dilute true aquifer water with respect to constituent B. The value of the ordinate for this earliest sample is:

$$Y = \frac{\text{true concentration of B-0}}{\text{true concentration of B+0}} = 1.$$

As pumping continues, a greater proportion of the water removed represents the aquifer water, true concentrations of constituent B are approached, and the value of the ordinate approaches

$$Y = \frac{\text{true concentration of B-true concentration of B}}{\text{true concentration of B+0}} = 0.$$

Curve 4 represents a similar situation, but the effects of contaminant and aquifer are reversed; that is, constituent B is not present in true aquifer-water samples, but is present only in the contaminating solution. In the first sample,

$$Y = \frac{\text{0-concentration of B in contaminant}}{\text{0-concentration of B in contaminant}} = -1,$$

and in the sample collected after a long pumping time

$$Y = \frac{\text{0-0}}{\text{0+concentration of B in contaminant}} = 0.$$

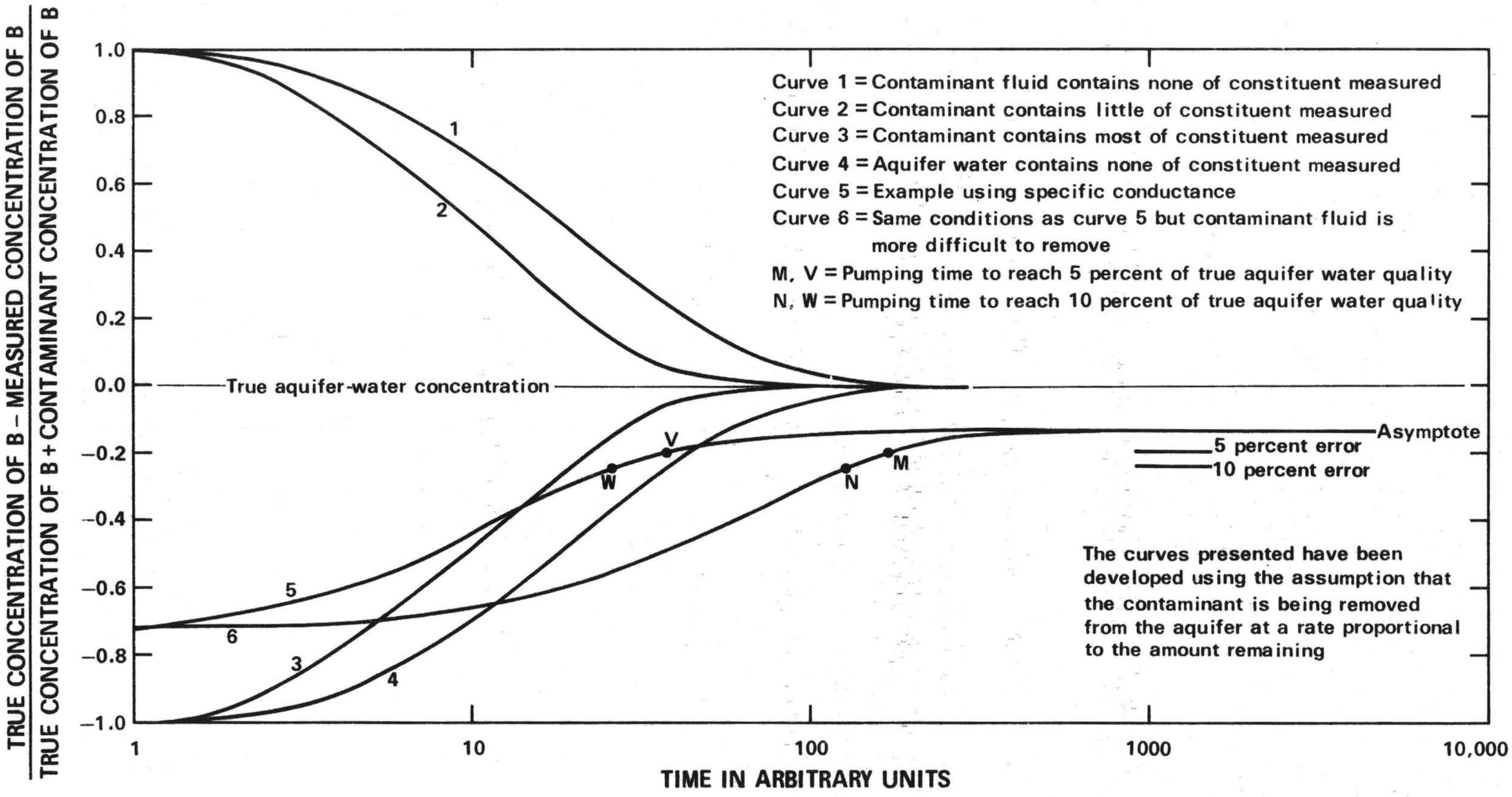


Figure 3.--Effect of pumping time, permeability, and error limit on quality of water sample obtained for a specified constituent.

For intermediate situations where constituent B is present in both aquifer water and contaminant, true aquifer-water concentrations will be approached more quickly, and the curves would be shifted to the left and lie between curves 1 and 4. If the contaminant were less difficult to remove than under the conditions represented by curves 1 and 4, curves 2 and 3 might result. Remember that a construct such as figure 3 would be different for each constituent present in the water; some contaminants would be more difficult to remove than others. Therefore, there is no guarantee that monitoring of a particular constituent until it no longer changes with time will indicate that true aquifer-water composition is represented for all constituents. Note further (fig. 3) that doubling of the pumping time may not result in significant improvement in aquifer representation; for example, curve 4 shows that by time 50, constituent B is within 16 percent of true aquifer-water concentration, but by time 100, it is only improved to being within 5 percent.

Assuming a cost and time constraint on obtaining representative aquifer samples, how may a ground-water hydrologist decide how long to pump, or when a sample collected after a given pumping time is sufficiently representative? The following steps may be used as a general rule.

1. Assign an arbitrary value for the true aquifer-water value or concentration of the property or constituent being monitored at the well site;

2. Make periodic measurements of this property or constituent as pumping continues. These measurements need to be made with a frequency similar to those made during a pumping test (see, for example, Lohman, 1972);

3. Plot the data in the manner illustrated in figure 3.

Example: Property to be measured is specific conductance; arbitrarily assigned aquifer concentration of this property is 500 μmho (micromhos per centimeter at 25° Celsius). Assume that the first sample represents pure contaminant. Data obtained:

Time (units)	Meaured value (micromhos per centimeter at 25° Celsius)	Y
1	3070	-0.72
2	2940	-.68
5	2570	-.58
10	2110	-.45
25	1390	-.25
75	1120	-.17

Note that very little change is occurring in successive measurements, and the plot (curve 5) indicates an asymptote at about -0.14. The fact that the asymptote is not at zero indicates that an incorrect choice was made of "true-aquifer value" for specific conductance. An estimate of the correct value may be made by using the asymptote obtained by plotting:

$$\frac{500 - \text{measured value}}{3{,}570} = -0.14;$$

therefore, the measured value = 1,000, a value reached after pumping for about 200 time units. Alternatively, the data could be plotted against time and extrapolated to long times. The conclusion is that, if the extrapolation to an asymptote does not allow sufficient accuracy to be attained in the allotted pumping time, no effort should be expended in obtaining a sample from that well or zone. If in the above example (fig. 3, curve 5), a 5-percent error in sample composition (indicated by specific conductance) could be tolerated, a pumping time of 47 units is required, as represented by point V, the intersection of the 5-percent error line with the data curve. If 40 units of time had been allotted for cleaning the hole, the decision could be made to continue 7 units beyond the allotted time to reach the 5-percent error line or, alternatively, pumping could be halted at 27 units, thereby accepting a 10-percent error. The time savings of 13 units could be applied to another well or zone. Curve 6 (fig. 3) represents similar contaminant and aquifer-water qualities as in the above example, but the contaminant is much more difficult to remove. It takes 130 units of pumping time to reach 10 percent of the true water quality (N) and 170 units to reach 5 percent (M). If the programmed time for water sampling were 40 units (as in the previous case), a 33 percent error would have to be accepted. Data with this error would, in most instances, be unacceptable. These estimates are for the measured property or constituent only, and the approach to true value or concentration for other properties or constituents may be different. Generally, however, other properties and major dissolved constituents will be affected in a manner similar to specific conductance.

Lithologic log of drilled hole

Although well drillers generally are required by State or local agencies to prepare a log of formations penetrated during drilling, description techniques among drillers varies and a correlation of formations may be difficult to produce. An accurate mineralogic composition may be valuable for correlating aquifer material and water quality, but may be obtained only from a petrographic study of the aquifer material.

Geophysical-logging data

Geophysical techniques are divided into two major categories: surface techniques and borehole techniques. The borehole techniques are the most varied and potentially the most useful for defining the hydrologic system penetrated by the borehole. An excellent discussion on the use of geophysical techniques may be found in Keys and MacCary, 1971. Use of a single logging technique seldom yields unequivocal results; several techniques need to be used and interpretation of the results is demanding. Experienced personnel need to be consulted in planning a geophysical logging program and in interpretation of the results.

Well completion and development

The term "completion" refers to all activities subsequent to drilling operation. Well development refers to the changes brought about by the removal of material that retards flow of water to the pump. This material normally is fine particulates, either present in the aquifer or introduced during drilling, or chemical and biological encrustation on the well screen or perforated casing. Well-development procedures range from simply pumping or bailing, to surging, and introduction of solutions to remove chemical or biological encrustation. Because material may be introduced into the well during development, a sufficient period of pumping is needed after drilling to remove these materials. A complete well history from the owner, other sources, or both will indicate the processes used. Although some cleanout and development may occur prior to installation of casing, instability of the hole generally dictates that casing is set as the hole is drilled, or as soon as total depth is reached. Because the hole usually is drilled significantly larger than the outside diameter of the casing to be installed (exception: casing driven as hole is deepened), the casing may be hung from a cemented-surface interval. This results in an open annulus between casing and borehole wall that may act as a conduit for water, allowing zones above screened or perforated intervals to contribute to the water produced by the well. A lead packing shoe may be placed above the screened interval and cement circulated to the surface in shallow wells. This procedure eliminates the aforementioned problem. It can never be assumed that, because a well is cased in a specified interval, no water is being produced from that interval. The seriousness of the water-quality effect of the leakage depends primarily on the ratio of the transmissivity of the major producing interval to all other intervals in the well. Two different transmissivity situations are shown in figure 4A and B. In figure 4A, transmissivity of the upper zone is minimal compared to that of the screened interval, and the effect of leakage will be small. However, in figure 4B, transmissivities are not significantly different and contributions from the upper zone may affect the water chemistry produced from the lower zone. The effect of a thick zone with minimal hydraulic conductivity will be similar to that of a thinner zone of greater hydraulic conductivity. Cementing the lower part of the upper zone will decrease the leakage significantly, if the formation has minimal vertical hydraulic conductivity and the cement bond to the formation is good.

The cement will affect the water quality, especially during the curing process. Cement mixtures contain additives to compensate for the natural shrinkage that occurs with neat (pure) cement. These additives, combined with the natural curing process, cause an increase in pH, dissolved solids, and temperature of water in contact with the cement. In test holes (not water wells) completed in "aquifers" with minimal hydraulic conductivity, the water in contact with cement may represent a large proportion of the total water produced. At first, the increased pH causes precipitation of the calcium and bicarbonate ions from the native water; as the pH decreases with pumping, soluble salts present in the cement (and perhaps the cement itself) may be leached, increasing the calcium- and bicarbonate-ion concentrations to concentrations greater than the natural water. Because of the lack of an

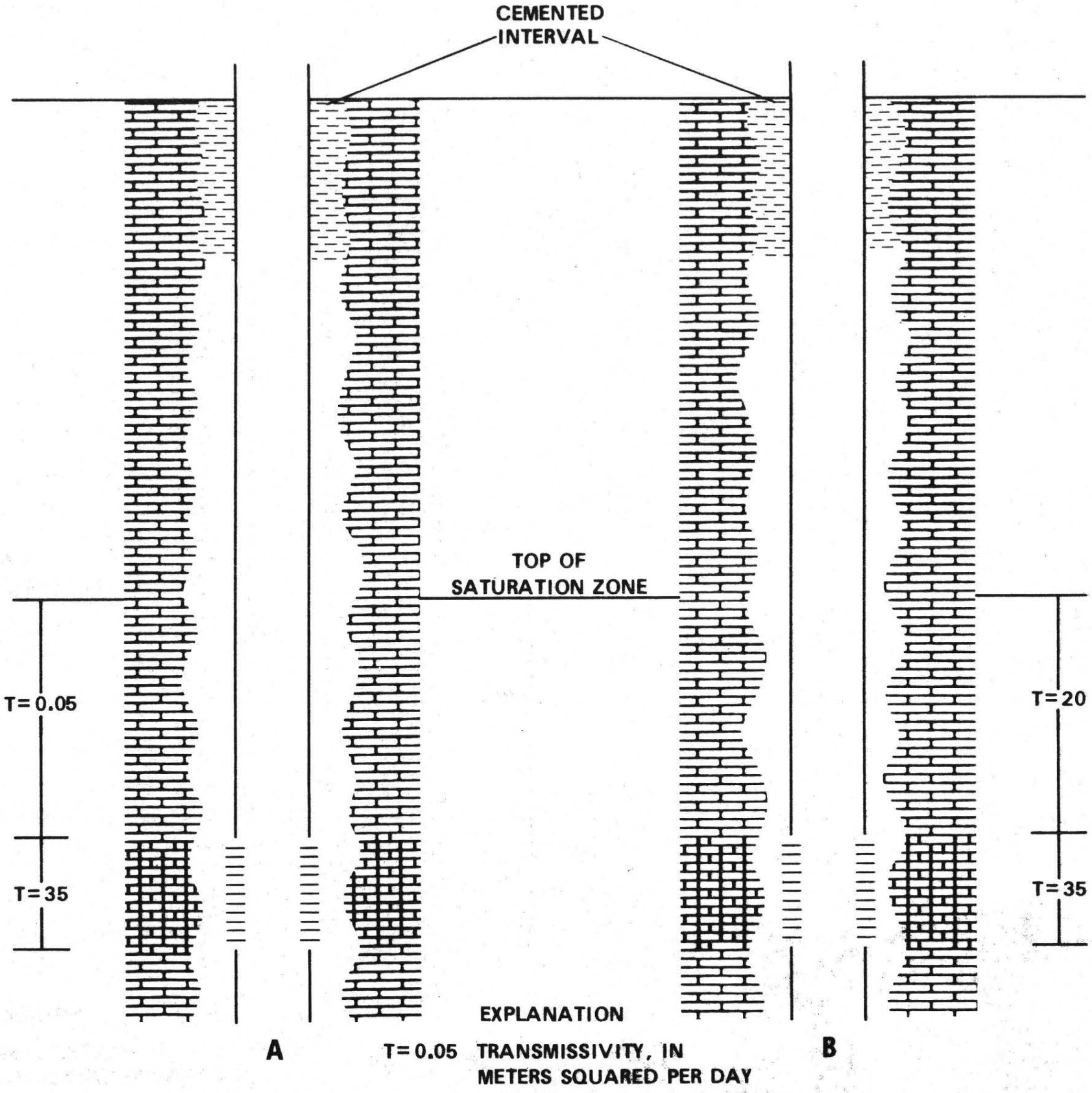


Figure 4.--Relative transmissivity of two producing zones in a well; produced water quality is affected in a way that is proportional to the ratio of the transmissivities.

identifiable zone of dominant transmissivity, test holes in materials with minimal hydraulic conductivity rarely yield water samples representative of the aquifer. Considerable effort to clean the contaminated water from these holes needs to be made to obtain valid results. Drilling programs designed for the collection of potentiometric data rarely allow for such a degree of effort, and useful water-quality data are rarely obtained.

Although casing and cementing may have a significant effect on the location from which water is obtained, the manner of water entry to the completed hole also may have an impact on the quantity and quality. For a given degree of development, a well-designed screen admits most water, vertically-slotted casing admits the second largest quantity, and gun perforations admit the least quantity. Effects of degree of well development cannot be separated from effects of choice of "screen." Gun perforations are plugged easily with formation material; such plugging hinders natural development of a well. An improperly-developed well does not necessarily result in an unrepresentative water-chemistry sample; however, only limited hydrologic data may be obtained from the well.

Wells generally are drilled larger than the projected screen to be used (under-reamed) and the annulus between screen and borehole wall filled with gravel. This gravel packing can help the natural process of well development; however, the kind of gravel used needs to be known, so its effect on water quality can be assessed. In most cases, contact time between the water and the gravel pack is sufficiently short that no changes in water composition would be expected.

If a thick aquifer is present and is not vertically homogeneous, the depth of penetration of a well will affect the chemistry of the water produced. This effect generally can be observed in areas where the water is used both for irrigation and domestic supplies. If the aquifer hydraulic properties are the same throughout the area, domestic wells generally are completed shallower than irrigation wells, which may result in different water quality. Contaminants from land surface may seep easily into the shallow wells and, in addition to depth inhomogeneity, an areal inhomogeneity may need to be considered.

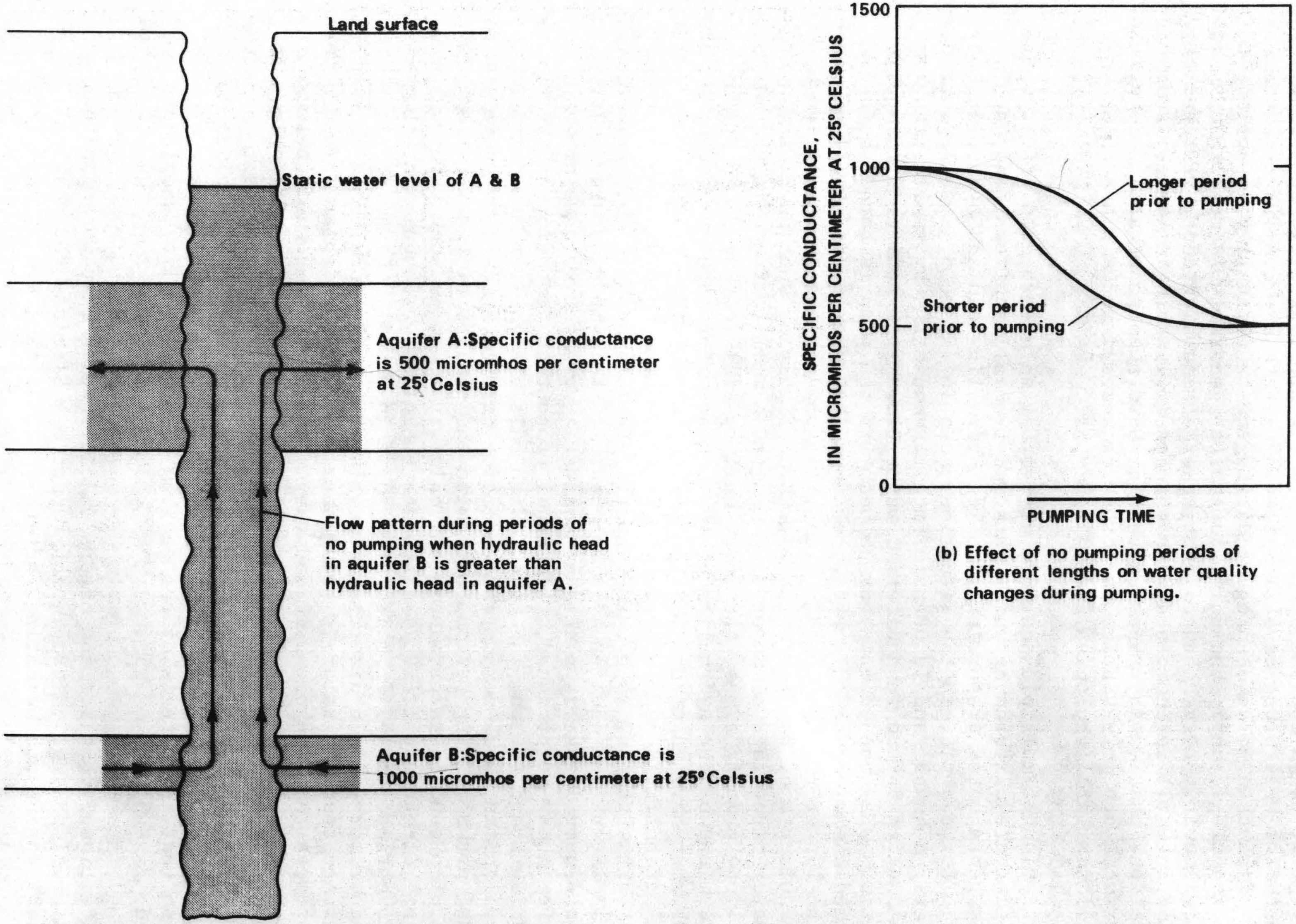
Drilling and well-development processes may cause significant changes in hydrologic and water-chemistry data obtained from a well source; there also are other activities that produce similar effects and that require action to minimize these effects. One of these is a hydraulic-testing technique that uses injection of water into an aquifer rather than withdrawal, to determine the hydraulic properties. This introduces water into the system that needs to be removed before obtaining a representative sample. Fortunately, constituents in the injected water ordinarily do not interact significantly with the constituents in the native water, and the injected water generally can be removed by pumping. The problem can be minimized by using water previously withdrawn from the well as the injected water. Careful records of the volume of foreign water injected need to be compared with the water volume removed and with the changes in indicator-constituent concentrations, as explained earlier.

Well completed in more than one aquifer

Although it is an extension of the aquifer heterogeneity concept, the multiple-aquifer well presents a situation somewhat more complex than those previously discussed. The meaning of heterogeneity ordinarily is applied to a single hydrogeologic unit; the multiple aquifer generally is more than a single hydrogeologic unit. Large changes in hydraulic head with depth measured or observed during drilling combined with changes in lithologic facies, commonly are indications that new hydrogeologic units have been penetrated. Sometimes the differences are more subtle, as for a fractured interval in a thick sequence of similar lithologies.

Penetration of multiple aquifers may go beyond an expected effect where water samples are mixtures of water obtained from all aquifers, and each aquifer is represented proportional to its hydraulic head and hydraulic conductivity. For example, in the situation shown in figure 5, a well penetrates two aquifers, A and B, and is open to both. Because the hydraulic head is higher in aquifer B than in aquifer A, water flows from aquifer B to aquifer A during periods when the well is not pumped. If the pump is turned on and a sample immediately taken, only the water from the lower aquifer will be represented; the longer the no-pumping period, the greater the contamination of water in aquifer A by water from aquifer B. As pumping continues, an increasingly greater percentage of water from aquifer A will be found in the mixture until, at long pumping times, the water quality will represent the steady-state determined by the hydraulics of the system. Note that placement of the pump intake may have an effect on resultant water quality: if the pump intake is placed at aquifer B and the ability of that zone to yield water is not surpassed by the pumping rate used (that is, the drawdown is not very large), very little water from aquifer A will appear in the pump discharge. If, however, the pump intake is placed at aquifer A, greater volumes of water from aquifer A may be produced, the actual proportion depending on hydraulics of the aquifers and the pumping rate. With multiple-aquifer penetration, aquifer hydraulics, well completion, location of pump intake, and duration of no-pumping versus pumping periods determine the quality of the water sample. Isolation of producing intervals is the only way to avoid such complex situations. Blankennagel (1967) discusses techniques and equipment that can be used to obtain samples from isolated zones in a well. Cased holes, perforated or screened in discrete intervals, cannot be sampled in this manner with assurance that the water is being obtained from the isolated zone. The annulus between the borehole wall and the casing may be a conduit between the aquifers, and the water produced in a given interval may have its origin in a different interval. Cementing of the annulus between zones may not guarantee that the bypass has been stopped. Great importance needs to be given to determining if the annulus has been cemented properly in a stable region of the hole so that the effects of the seal on the water-quality sample can be determined.

An additional complication occurs in older wells that were finished with thin-wall steel casing. A completion report may disclose the sealing of aquifer A by casing and cementing, but that casing may have a break from



(a) Flow patterns during periods of no pumping

(b) Effect of no pumping periods of different lengths on water quality changes during pumping.

Figure 5.--A. Flow patterns during periods of no pumping; and
B. Effect of no-pumping periods of different lengths on water-chemistry changes during pumping.

corrosion or earth movement and may admit water to the well. Reports of sudden improvement in well yield may bear further investigation, especially if no additional well-development activities have been conducted.

Geophysical-logging techniques may provide a powerful method to investigate flow patterns, casing integrity, quality of cement bond, and other factors that determine the source and aquifer representation of a sample obtained from a well. These techniques commonly provide the only means to convert a "mystery sample" to one from which valid conclusions can be drawn. Use of these techniques need to be increased, and each operating unit involved in sample collection needs to have expertise in geophysical logging and interpretation available.

Miscellaneous Aspects of Well-Completion Affecting Water Chemistry

Wells subject to corrosion commonly are considered to contaminate samples with corrosion products, especially if ground water does not have reduced forms of ions found in the well-construction materials. This is true, but a potentially greater problem in obtaining representative samples is removal of trace constituents by corrosion products. These products, usually hydroxides or oxides of iron or manganese, have large surface areas and a great propensity for sorption of dissolved and colloidal constituents.

A well in regular use will reach steady state between the casing surface and the water in contact with it, minimizing the rate at which changes in water quality occur as the water passes through casing and discharge line. Observation wells may not meet these conditions; neither may wells used in tracer tests or in studies of pollutants, since insufficient time or water volume may pass for "equilibrium" to be established prior to sampling.

Encrustation (chemical precipitation), on the other hand, always results in solute-concentration changes. The encrustation may be caused by the large pressure decrease that the water undergoes as it passes through the well screen or perforations. Mineral precipitation also may be triggered by temperature fluctuations as the water moves from the aquifer to the point of discharge. These changes in conditions may be sufficient to cause nucleation (that is, start precipitation) of constituents that are present in excess of the equilibrium concentration; however, the changes may merely produce a shift in equilibrium concentrations. In either case, there is no guarantee that precipitation will occur. Sufficient evidence of encrustation and plugging of screens exists to make the phenomenon a matter for consideration.

Some of the aforementioned problems are obviated by the use of plastic or fiberglass casing, but the plastic or fiberglass present other problems. Inorganic ions are sorbed very little by plastic and, consequently, quickly establish steady-state; however, some organic compounds have a significant affinity for plastics. Furthermore, both organic compounds and trace elements are released by some plastics, especially shortly after the plastics are first placed in service. Encrustation may be unaffected by use of plastic pipe or casing.

Changes from ambient aquifer conditions caused when samples are removed for collection and analysis may be quite significant, changes in water chemistry need to be anticipated and attempts made to minimize them, as follows:

1. Pumping the well at the fastest rate consistent with minimal well loss minimizes pressure decreases at well screens, minimizes contact time between water and discharge line, and also minimizes temperature changes.

2. When systems that are not regularly pumped and that do not have a virtually time-invariant water quality are sampled, interpretations of analytical results need to be cautious. For example, early data obtained from a tracer test may be affected by passage of the water through well components that could add or subtract dissolved species.

3. In sampling for trace elements, the components of screen, casing, pump impellers and diffusers, and discharge tubing might affect the water chemistry. After anomalies appear in analytical results, questions are asked. This will continue to occur; however, the search for explanations commonly can be averted by an analysis of potential problems prior to sampling. For example, in sampling to determine dissolved iron, one might wish to avoid sampling an acidic water being produced through a steel casing with a brass well screen. A well containing both galvanized and ungalvanized steel components in contact with an acidic ground water needs to be avoided in sampling for zinc, because corrosion of the components would be expected to yield dissolved zinc readily.

Source Definition and Collection of Representative Samples from Springs

Springs generally can be considered completely analogous to wells: if undeveloped, their flow rate is proportional to the volume of aquifer environment sampled; if developed, the type of development needs to be known and its effect on water quality evaluated, as discussed in the section on obtaining samples from wells.

Most springs have slower discharge rates compared to producing wells in the same formation, and will tend to represent smaller parts of a hydrologic system. The water chemistry of minute flows (seeps) may be affected significantly by excessive evaporation, plant transpiration, and root respiration; thus, the water chemistry would be expected to change significantly as water moves through the soil zone prior to being discharged. Larger flows may be subject to the same processes, but the contact time with the zone producing the changes may be sufficiently short that the volume transpired or evaporated would constitute only a small fraction of total flow. This would result in little change in water chemistry.

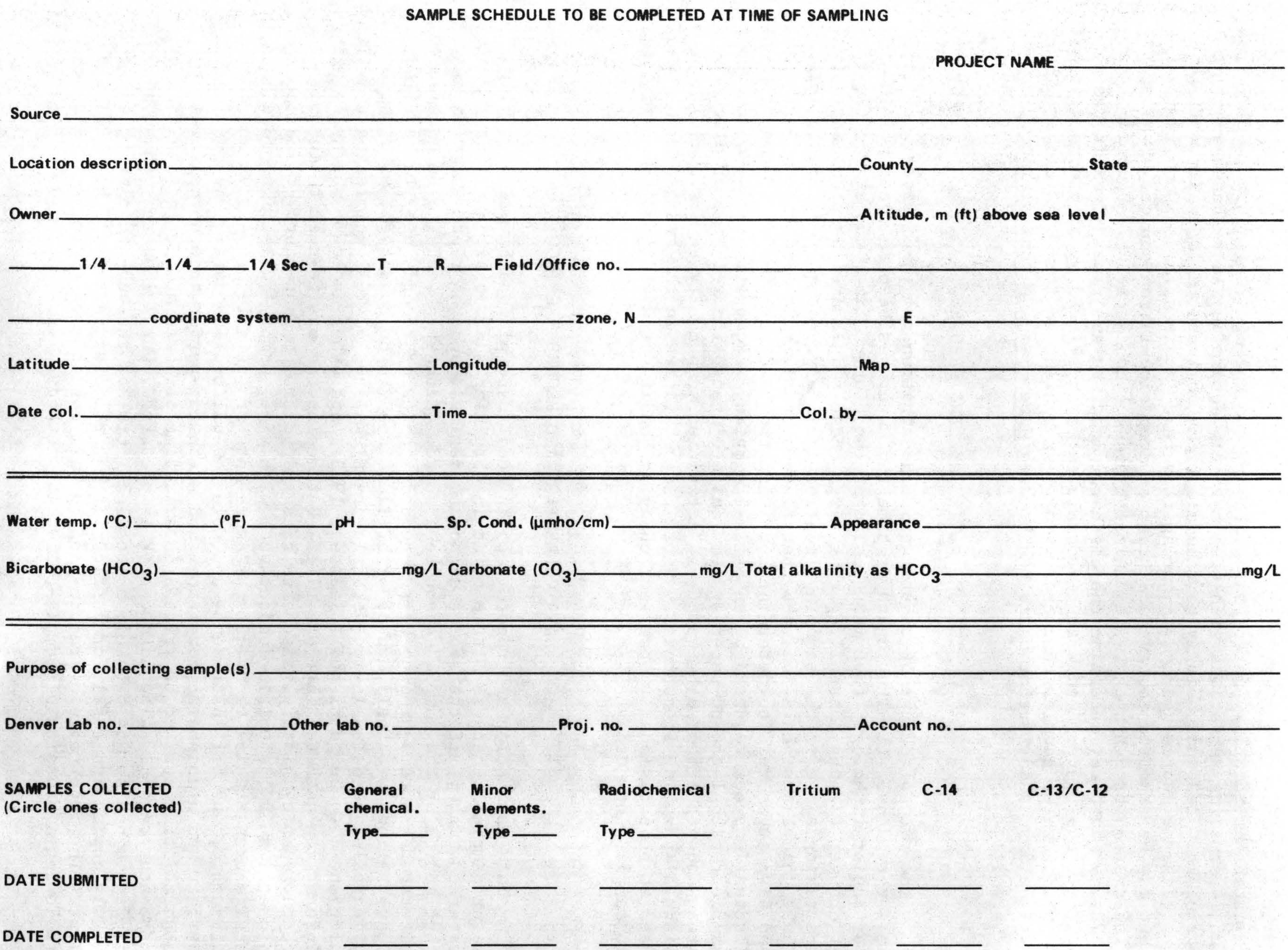
A spring source is more difficult to evaluate than a well, because only surficial lithology generally is known. Geologic mapping is incomplete in many areas and hydrologists may have to do their own geologic reconnaissance to determine the flow system represented by the spring. Gaging the spring flow and determining variations with time may help determine the recharge area. A spring that responds quickly to rainfall from local storms generally will have its recharge source nearby. A spring flow that is virtually seasonally invariant can be expected to have a distant or deep circulation source, or have a flow system through rocks with minimal hydraulic conductivity. Faulting, topography, or both may determine the discharge location and rate. Even if the water source can be determined with reasonable certainty, it is usually more difficult to obtain water samples that truly represent ambient aquifer conditions. This will be discussed further under the heading Water Samples from Springs.

GROUND-WATER SAMPLING FREQUENCY

The rate of change of constituent concentration in ground water with time is governed by: (1) The length of time the water has been in contact with a particular lithology; that is, the longer the contact time, the slower the rate of change; (2) the possibility that large changes in constituent concentration are taking place if the sampling location is in a recharge or discharge area. These guidelines would indicate that frequent sampling be undertaken in recharge and discharge areas to determine both magnitude and periodicity of compositional fluctuations before deciding on a final sampling frequency. Locations chosen to sample regional ground-water systems quite distant from recharge or discharge areas and not affected by water-use activities, can easily be assigned annual or biennial sampling frequencies. Water-use activities in the area of such a well need to be occasionally observed; changing conditions would prompt an increase in sampling frequency.

DATA COLLECTION AND RECORD KEEPING

Data collection and record keeping need to be planned before obtaining a water sample. There is little point in obtaining additional data (for example, water chemistry) if the source cannot be defined, and the representation of that source by the sample cannot be assured. Each step needs to be documented. Literature sources need to be referenced; copies of records need to be filed; conversations with well owners or drillers need to be condensed, with names of principals and dates included; scale-drawn sketches of well completion and lithology need to be completed (Claassen, 1973); and other geologic and hydrologic information gathered into one file. Data collected onsite need to include: recent pumping history, discharge rate and volume, measurements of indicator properties (pH, specific conductance) with time, sample-collection procedures, onsite preservation techniques, measurements of unstable properties and constituents, and all instrument- and solution-calibration data. Observations of surface and atmospheric conditions and equipment-performance normalities or abnormalities need to be written down at time of observation, in some form of permanent record. A bound notebook is preferred, but a looseleaf sheet such as figure 6 also may be used; a looseleaf form has the advantage of being easily copied and easily crossfiled; it has the disadvantage of being easily lost. The importance of record-keeping will continue to be emphasized in the following discussion of sample-collection methods.



SAMPLE SCHEDULE TO BE COMPLETED AT TIME OF SAMPLING

PROJECT NAME ____________

Source ____________

Location description ____________ County ____________ State ____________

Owner ____________ Altitude, m (ft) above sea level ____________

____ 1/4 ____ 1/4 ____ 1/4 Sec ____ T ____ R ____ Field/Office no. ____________

____________ coordinate system ____________ zone, N ____________ E ____________

Latitude ____________ Longitude ____________ Map ____________

Date col. ____________ Time ____________ Col. by ____________

Water temp. (°C) ____ (°F) ____ pH ____ Sp. Cond. (μmho/cm) ____________ Appearance ____________

Bicarbonate (HCO_3) ____________ mg/L Carbonate (CO_3) ____________ mg/L Total alkalinity as HCO_3 ____________ mg/L

Purpose of collecting sample(s) ____________

Denver Lab no. ____________ Other lab no. ____________ Proj. no. ____________ Account no. ____________

SAMPLES COLLECTED (Circle ones collected)	General chemical. Type ____	Minor elements. Type ____	Radiochemical Type ____	Tritium	C-14	C-13/C-12
DATE SUBMITTED	____	____	____	____	____	____
DATE COMPLETED	____	____	____	____	____	____

Figure 6.--Example of looseleaf record of onsite observations and measurements.

WELL

Type ____________ Use ____________ Waterbearing formation ____________

Depth, m (ft) ____________ (meas/reptd); Cased to, m (ft) ____________ (meas/reptd); Diameter, cm (in) ____________

Date drilled ____________ How completed ____________

Static water level, m (ft) ____________ Date measured ____________ Interval sampled, m (ft) ____________

Yield, m^3/d (gal/min) ____________ Date measured ____________ Drawdown ____________ Time pumped ____________

Time pumped before sampling ____________ Quantity pumped before sampling ____________

____

SPRING

Type ____________ Use ____________ Discharge, m^3/d (gal/min) ____________

Waterbearing formation ____________

____

STREAM

U.S. Geological Survey Gaging Sta. no. ____________ Gage height, m (ft) ____________ Discharge, m^3/d (ft^3/s) ____________

____

LAKE OR RESERVOIR

Type ____________ Use ____________ Capacity, m^3 (acre-ft) ____________

____

Additional notes ____________

____

____

To differentiate between metric and inch-pound units, place parenthesis around inch-pound units.

Figure 6.--Example of looseleaf record of onsite observations and measurements--Continued.

WATER SAMPLES OBTAINED FROM THE WATER SOURCE

Drilling and development of a well may cause substantial changes in aquifer water quality that can only be remedied by removal of contaminants. In addition, the process by which water is transported from the aquifer to the point at which samples are taken and measurements made, may produce some change in water quality.

The water in the aquifer, under natural conditions, is in contact with a particular lithology, under a given pressure (usually different from atmospheric) and has a given temperature. It may or may not be in equilibrium with its surroundings; there is much evidence to indicate that equilibrium is the exception rather than the rule. Now suppose that a water-removal device is inserted into the aquifer, without introduction of foreign material and without perturbing the state of the system. Water is then removed at a rate consistent with the hydraulic properties of the aquifer. As the water moves toward the pump impellers, its velocity increases significantly, and the pressure associated with it decreases correspondingly. Water under pressure of thousands of kilopascals may be subject to forces causing its pressure to be decreased to perhaps 100 kPa (kilopascals). These drastic changes may result in precipitation of certain minerals resulting from shifts in chemical equilibrium (Moore, 1962) or from nucleation of supersaturated species. Temperature changes may produce the same effect, although relative temperature changes usually will be smaller than pressure changes. Both temperature and pressure changes will affect concentrations of dissolved gases, which in turn may affect other dissolved species.

In addition to pressure and temperature changes that water must undergo in its movement to land surface, consider that the water also has been removed from its lithologic surroundings and placed in a foreign environment of metal, plastic, or both. This new material, however, presents a smaller surface area per unit volume of water, and the water is in contact with it only a relatively short time, under conditions of active pumping. In contrast, under non-pumping conditions, the contact time may be quite long, and significant changes in water chemistry may occur.

Water flows through the discharge line at a rate and pressure determined by the hydraulic characteristics of the aquifer, the pump design and rating, and the total lift. A sample may be collected from the point where the water reaches land surface, or it may be collected after the water has flowed through additional discharge line or water-treatment facilities. The farther it flows, the greater is the potential for change. Samples need to be collected at the point closest to the source. Furthermore, a sample removed from the discharge line, subjected to atmospheric pressure (open-system conditions), and then processed onsite, may undergo changes in chemistry. A system that allows onsite processing to take place under discharge-line pressure and temperature (closed-system conditions) is preferred (Wood, 1976), but seldom used. The most commonly used procedure involves transfer of the sample from discharge line to a container that is directly or indirectly attached to processing or measuring equipment. Water passing through a processing unit generally is allowed to run into another container that may contain a preservative, which serves as temporary storage prior to analysis.

The entire transfer process from aquifer to analysis is one that subjects the water sample to possible change each step of the way. Because the quality and quantity of change is unknown, processes and materials that may cause change need to be avoided; this is the principle of positive avoidance.

Techniques of water transfer from aquifer to sample container and the possible effects on water quality will be discussed next. The principle of positive avoidance will be emphasized.

Obtaining Samples from Wells Equipped with a Pump

Although there are many ways to classify pumps by design or application, the factors that cause water-quality changes produced by a particular pumping system will form the basis of the following discussion. A comprehensive discussion of pump types, function, and application can be found in a manual produced by Johnson Division, Universal Oil Products (1972).

As discussed earlier in the section on miscellaneous aspects of well completion affecting water quality, pumps may affect water quality in two ways: (1) By their method of operation; and (2) by the construction materials interacting with the particular water being produced. The goal in sampling is to use a water-removal system that results in the smallest possible change in conditions to which the water will be subject as it is transported to land surface. Water from the aquifer needs to be moved at a rate sufficient to sample a large part of the aquifer environment, at a pressure similar to that in the aquifer. This is best accomplished by a pump that pushes the water from the aquifer to the surface (fig. 7A and 7B). The pump impellers are located close to the producing zone; water flows from the aquifer into the pump column where it is pushed upward under pressure. If a check valve at the discharge point is set to open at a pressure greater than exists in the aquifer, the water is transported to the surface at a pressure similar to that which exists in the aquifer. Pressure changes occurring at well screen and pump intake have not been included in the above discussion; they may be minimized by choosing a pumping rate suited to the aquifer being sampled. If aquifer pressure is significant, the choice of pump needs to be made with care to avoid damage to the pump.

Figure 7B illustrates use of the same equipment, but the pump impellers are set a little below the normal pumping level in the well. This type of submersible installation is used more often than the one illustrated in figure 7A, because it is more economical; less money is spent for pump column and electrical cable. Water produced by this well travels uphole under conditions of gradually-decreasing pressure, until entering the pump intake to be repressured, as in the first example. If dissolved gases are present in the aquifer, some may be lost when the pressure is decreased. Little can be done to alleviate this problem, unless there is sufficient room between the casing and pump column (and any associated stabilizers) for a sampler that is equipped to obtained pressurized samples to be placed at the level of the aquifer. To insure aquifer representation, the pump needs to be operating at the time the samples are taken using this procedure.

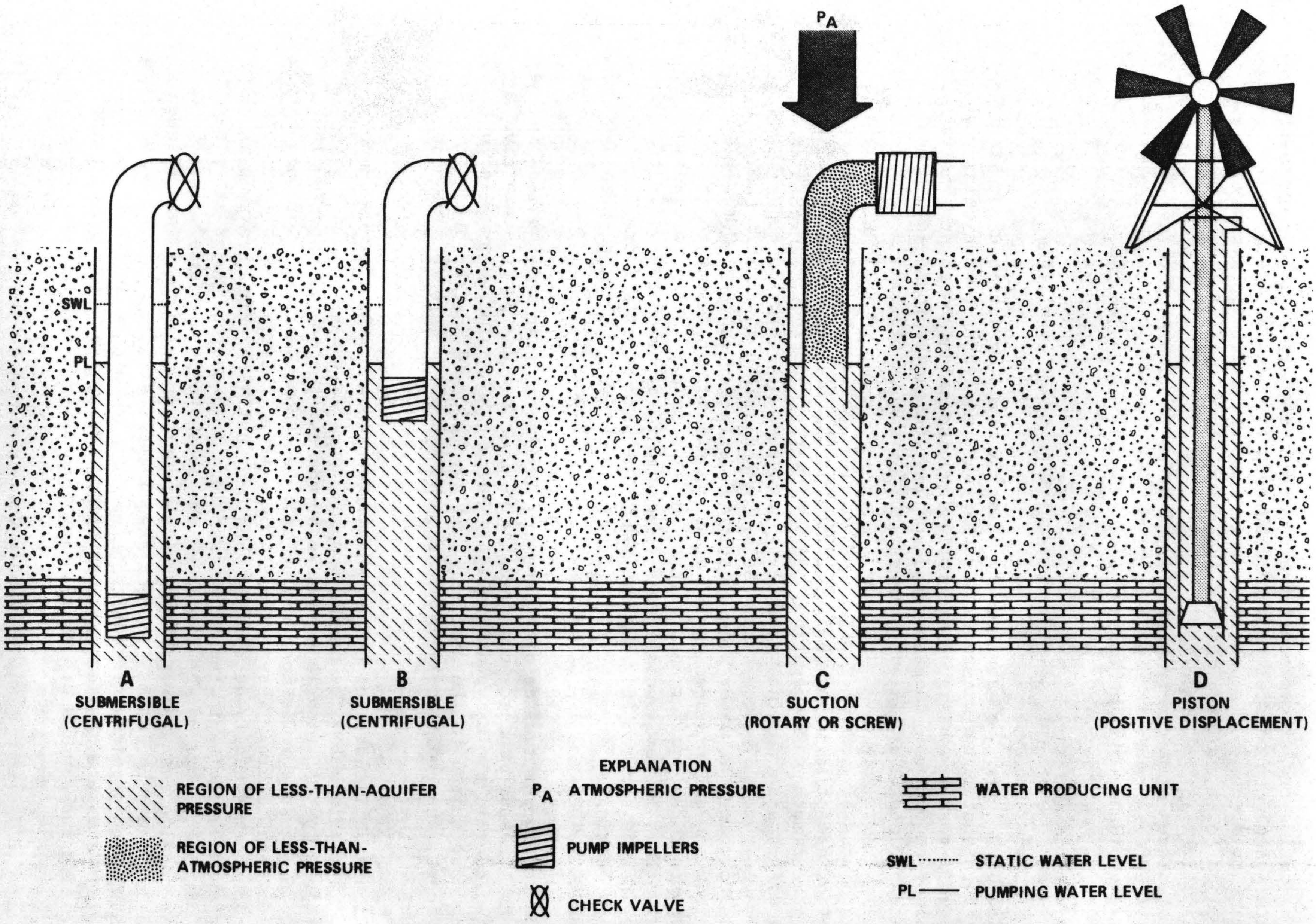


Figure 7.--Pump installations commonly found in ground-water sampling.

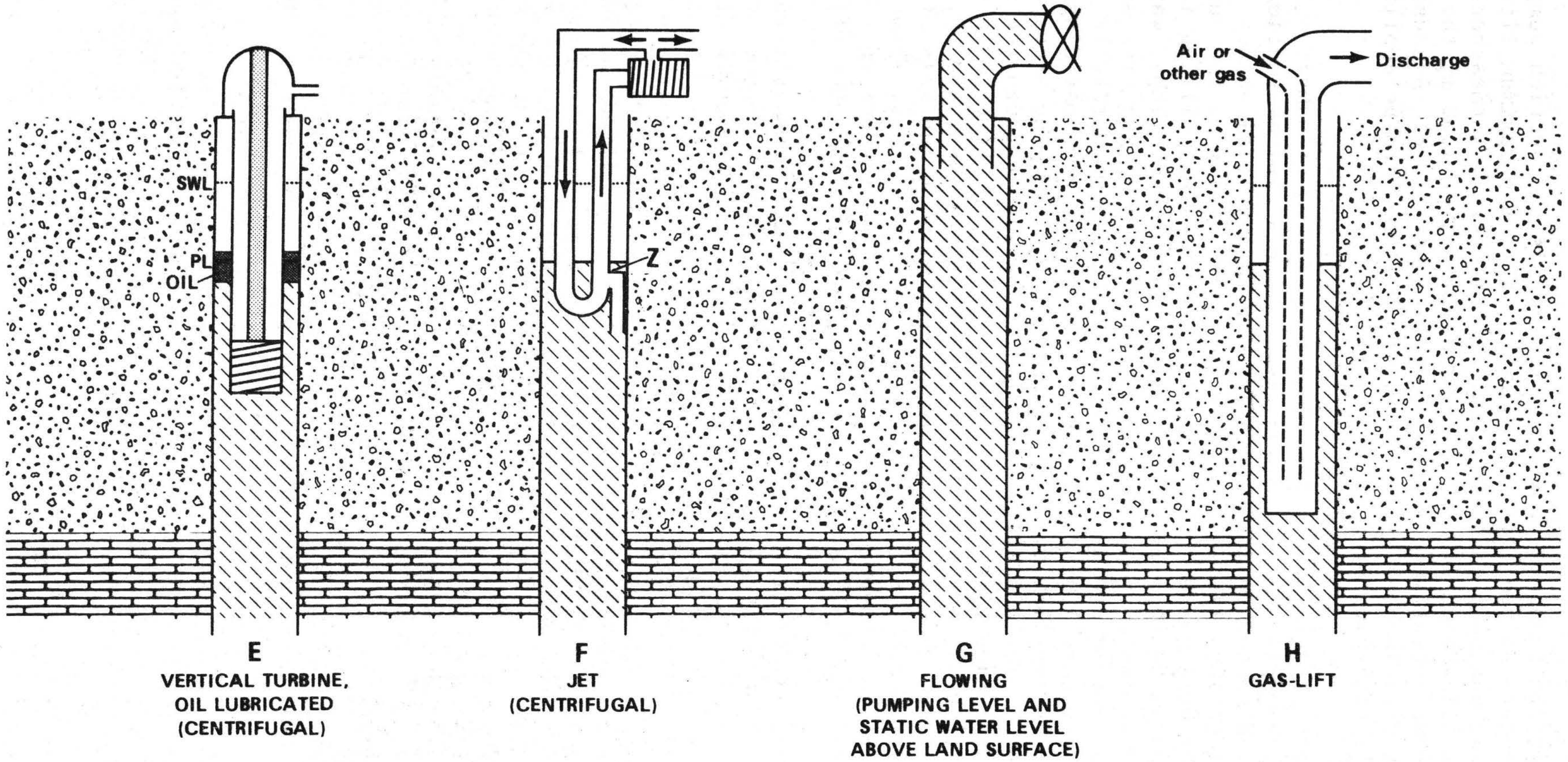


Figure 7.--Pump installations commonly found in ground-water sampling--Continued.

An installation found in many shallow wells is the suction pump. Because atmospheric pressure at sea level is about 100 kPa, the maximum lift for a 100-percent-efficient pump would be about 10 m (meters). Atmospheric pressure decreases about 1.1 kPa per 100-m rise in elevation; at 1500 m, the maximum lift for a 100-percent-efficient pump would be about 8.3 m. Because pumps are not 100-percent efficient, a factor of 0.5 to 0.7 needs to be applied to the theoretical lift to arrive at a practical value.

Suction pumps generally are less desirable for water sampling than the submersibles previously discussed (see fig. 7C for a typical suction pump installation). When the (primed) pump is started a partial vacuum is created in the intake (suction) line; atmospheric pressure acting on the surface of the water in the well pushes water into the suction line, filling it and allowing it to be pushed by the impellers to the point of use. Thus, water flows from the aquifer to the pump intake at a pressure decreasing from aquifer pressure to atmospheric pressure, and then from the pump intake to the impellers at a pressure less than atmospheric. Water may lose dissolved gases as it moves to the impellers, but it may gain gases from the atmosphere (for example, carbon dioxide and oxygen) during its passage through the suction line, if all connections are not absolutely airtight. These gases may change not only the carbon dioxide and bicarbonate concentrations, and pH, but also concentrations of oxidizable ions, such as iron (II) or manganese (II). Radioactive species present in air, such as tritiated water vapor, also may be introduced. Airtight connections on the suction line are not only needed to minimize chemical changes, but also are needed to maximize pump efficiency.

The windmill illustrated in figure 7D is a common pump in rural areas. It is virtually a deep-well adaptation of the pitcher pump found at many farmsteads, where a shallow water table exists. A mechanical source of power is transmitted from land surface to the pump piston by means of a solid rod (sucker rod). The piston has two check valves that allow water to be drawn into the cylinder below the piston on the upstroke, and be discharged above the piston on the downstroke. The same water is then lifted the length of the piston's stroke on the following upstroke. The pumping rate is governed by the size of the cylinder and the length and frequency of the strokes. As in the case of the submersible pump previously discussed, the intake of the piston is seldom placed any deeper than required for complete submergence. If a check valve were placed in the discharge line, the same situation would exist as illustrated in figure 7A. However, the line generally is open to atmospheric pressure, and the water is subjected to a pressure change from the value at the producing zone to atmospheric pressure as it travels up the well and through the discharge line. Well losses (inefficiency in producing capacity and resulting from well construction) from windmills are minimal, because the pumping rate is usually no more than a few tenths of one liter per second.

A vertical turbine pump commonly used in irrigation wells is shown in figure 7E. Ordinarily, irrigation is only used if a productive aquifer is present that has a static water level close to land surface. This pump generally is used in situations where the pumping level is below one that could be handled by a suction pump. The effect of the turbine, as far as water-quality changes are concerned, is similar to the submersible pump (fig. 7B), with one possible exception. Because the power unit is at land surface, a rigid shaft connects the motor to the impellers. This shaft rests on bearing surfaces located at intervals along its length, and these bearings require lubrication. Newer units are water lubricated, but older units were lubricated by oil, which accumulated on the water surface. Because the water sample could be contaminated with oil, caution needs to be used when sampling water from these installations for organic constituents or trace elements.

The jet pump, illustrated in figure 7F, commonly is found in domestic-use, shallow-well applications, where its inefficiency is not a serious drawback. The advantage of the jet pump is that all its moving parts are placed outside the well. After the pump is primed, water is pumped down the tubing past a constricting nozzle at point Z (fig. 7F), which causes a low-pressure region to form in the suction line. Additional water is thus drawn into the tubing, makes its way to the impellers, and then is discharged. The low-pressure region between the producing zone and nozzle is less than aquifer pressure, as is the recirculating part of the system if the discharge pressure chosen is less than aquifer pressure. The only additional drawback to this type of installation, compared to a submersible or turbine pump, is the added danger of changes in water quality resulting from increased contact time of the water with the pump materials. This is caused by recirculation and repeated pressure cycling and could change water quality. It is more likely that changes might occur in water that is supersaturated with respect to a solid phase, than in water that is undersaturated.

Figure 7G illustrates a well that has its static water level and pumping level above land surface. Under shut-in conditions, pressure at land surface may be almost that of the aquifer; normally, however, there will be some decrease from the producing zone to the wellhead. Samples collected under closed-system conditions ordinarily should be subject to no more change than water obtained from systems fitted with submersible or turbine pumps.

However, although a flowing well presents a nearly ideal water-quality sampling condition, significant changes might occur in waters that are saturated or supersaturated with certain gases. For example, consider a water saturated with carbon dioxide at aquifer temperature and pressure. The well is allowed to flow, and the water is subjected to a decrease in pressure but no decrease in temperature. Gas is exsolved and bubbles form; that is, a single-phase system becomes a two-phase system. Because carbon dioxide is lost from solution, the pH increases. Mineral species whose solubility is dependent upon hydrogen-ion concentration (iron hydroxides, alkaline-earth carbonates) may precipitate. The kinetics of these reactions generally operate in the sampler's favor and, although the potential for change does exist, it generally does not become an accomplished fact until the sample has been collected. However, do not assume that this will always be the case.

One installation that is uncommon in producing water wells is the gas-lift (air-lift) pump (fig. 7H). If a sufficient volume of gas at a sufficiently high pressure is discharged inside submerged tubing, water will be lifted and will flow at the surface. All of the potential problems causing water-chemistry changes that have been previously discussed are present with this type of pump, especially if air is used. Use of nitrogen gas minimizes the effect, but degassing of constituents may still occur.

Effect of Distribution Lines and Water-Treatment Facilities on Water Quality

The most aquifer representative water-quality samples are those collected at the wellhead. This can almost always be done, although some modification to existing plumbing may have to be made. Quite commonly, the wellhead consists of a tee with a pipe plug in one arm. This can be removed and a reducer nipple and valve installed for sampling. Pipe-to-hose couplings can be attached if plastic tubing is used as a distribution line to sampling and measurement equipment in a mobile unit. A typical wellhead modification is shown in figure 8. To minimize contamination from added plumbing parts, they may be thoroughly cleaned, sprayed with teflon aerosol, and leached of water-soluble components prior to use. Permission to modify the wellhead always needs to be obtained from the owner.

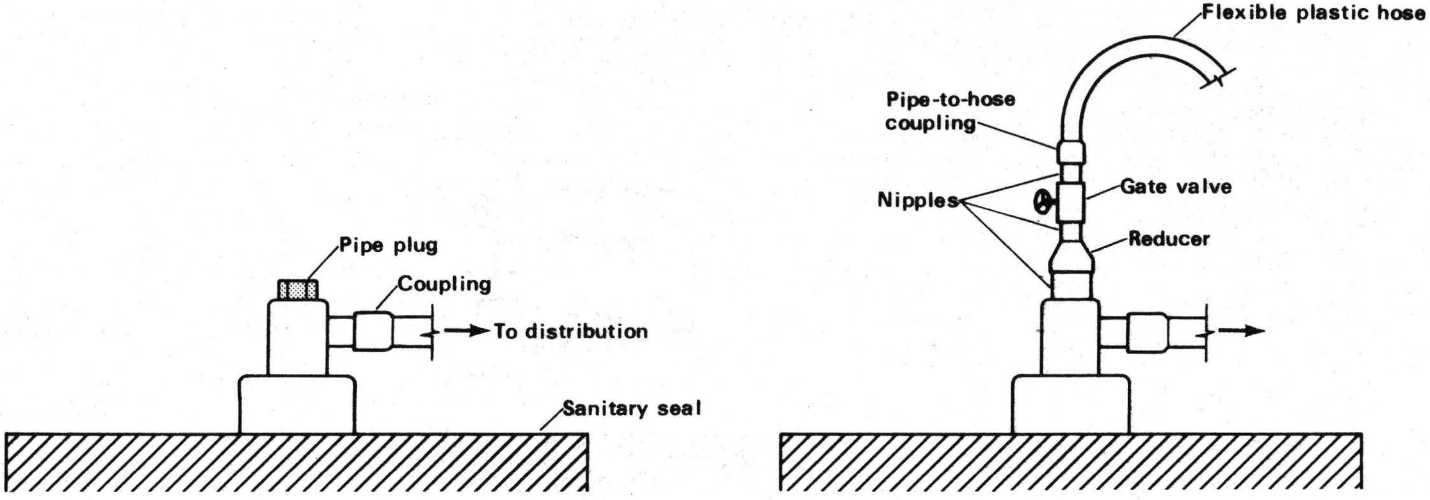
Distribution Lines

If samples cannot be collected at the wellhead, the effect of the distribution system needs to be estimated. Potential effects of both steel and plastic conduit already have been discussed. Temperature variation is one effect that generally is not present to any great extent in the well, but may be significant above ground. Some water-distribution systems lie entirely or partly above ground and are subject to large temperature fluctuations, depending on season and solar insolation (that is, whether days are sunny or cloudy). Length of travel from wellhead to sampling location is important in estimating the extent of temperature change the sample will undergo. Temperature, as well as pressure change, affects chemical equilibrium. Sudden temperature change may cause a supersaturated condition to be terminated, resulting in large changes in water chemistry. Because it is very difficult to predict what will happen, we consider what may happen, and try to design our sampling efforts to avert the possibility.

The distribution system presents other obstacles to aquifer-representative samples. The following water-quality modification devices commonly are found in public and private systems.

Filtration Units

A filtration unit may be as simple as a sand filter to remove silt, or as complex as a bed of activated charcoal to remove color and odor. The charcoal bed will remove organic compounds and trace elements as well as some of the major constituents. Under some conditions, the filters may add compounds to the water in exchange for those in solution.



BEFORE
(Native state)

AFTER
(Modified)

Figure 8.--Typical wellhead modification for ground-water sampling.

Cartridges containing cellulose filters also are used. These may circumvent the effective dissolved-versus-suspended constituent separation that results from the filtration process at time of sample collection.

Storage and Pressure Tanks

There are principally three types of storage tanks: (1) Open or closed tanks designed for gravity flow; (2) closed tanks with high-pressure air cushions, and (3) closed pressure tanks with flexible-diaphragm (bladder). The first of these is subject to degassing, evaporation, and temperature change and the water-chemistry changes that may result (as previously discussed). The second presents the potential for injection of carbon dioxide and oxygen into the water, because the pressures generally are three or more times atmospheric. The last type is a recent solution to an age-old problem associated with domestic water distribution systems: the "waterlogged" pressure tank. The waterlogging is a result of water-solubility of the air used as a cushion. This new design separates the air and the water from each other by using a flexible diaphragm. Although the diaphragm is not truly airtight, it slows down the solution of the gases significantly and considerably lengthens the life of the pressure system. It is important that the diaphragm be made of inert material or have been installed for a sufficiently long time, so that it no longer affects the quality of water in contact with it.

Water Softeners

Water softeners commonly are found as part of a water-distribution system. Their purpose is to remove most of the divalent cations causing "permanent hardness" (usually calcium and magnesium ions) in the water supply by exchange for sodium. It is obvious that samples obtained after passage through a softener would not represent true ground-water quality.

Disinfecting Procedures

Both continuous disinfection devices (usually using chlorine gas) and batch techniques (usually using calcium hypochlorite) are found in water-distribution systems. Changes in major ions, pH, and minor elements are produced by the disinfection process. CAUTION: Some well owners perform batch disinfection on their wells or cisterns; inquiry regarding individual practice needs to be made prior to any sampling to determine if a representative sample can be obtained.

Obtaining Samples from Wells not Equipped with a Pump

Although most sampling is done from regularly-used water systems, occasionally the need arises to sample abandoned sites or to obtain samples from wells drilled as part of an exploration program.

Installation of Pump

Any of the pumping systems previously discussed can be used in a well, but the submersible pump is easy to use and enables collection of samples that provide relevant data. The size of pump chosen will depend on the aquifer yield, the total hydraulic head (lift plus discharge pressure), and the discharge rate desired. Pump manufacturers offer assistance in choosing the correct pump. Support cable will be needed that is strong enough to allow the pump to be pulled if it becomes wedged or experiences friction from the rough walls of an uncased or crooked well. Portable electric power to match the pump requirements probably will have to be supplied, because abandoned or new wellsites may not have appropriate power available. Some experience in providing watertight electrical connections is needed in attaching the pump, electrical cable, and discharge line to the support cable to guarantee that it will not slip. Slippage produces loops in the cables and discharge line that become jammed in the well, making pump removal difficult, if not impossible. Uncased holes, especially those that are not perfectly vertical, present a hazard to the electrical cable; rubbing of the cable against the sides of the hole removes the insulation and causes electrical shorting. Armored cable, though expensive, minimizes this problem. When an abandoned well has been chosen for pump installation, a mandrel the same size and shape as the pump needs to be run in and out of the well several times to guarantee that the pump can be set at the desired level and removed. Much expensive equipment may be lost and the well rendered useless if the pump cannot be recovered. A drilling rig may have to be used to remove the pump and associated material.

Another pump commonly used in wells that require only small lift is the suction pump. The meaning of suction pump as used here, is a pump that allows the entire pumping unit to remain at land surface, and only the suction (intake) line to be lowered into the well. Whether the pumping unit uses a centrifugal or positive-displacement principle generally is unimportant. Usually only slow pumping rates (0.3-1.3 L/s) can be sustained by such units. Very productive wells with static water levels near land surface may be pumped at faster rates.

The two methods discussed above generally represent the most practical solution to obtaining water samples from wells without permanent pumping installations. As indicated previously, any water removal method can be used provided appropriate caution is observed and the method is consistent with preservation of the water-quality properties and constituents of interest.

Special techniques are needed when samples are desired from wells with substandard diameters (generally less than 10 cm). Commercial submersible equipment is not available for these installations, and only the suction pump or a specially-outfitted jet pump has been used in the past. The U.S. Geological Survey has developed three pumps that can be installed in small-diameter (greater than 5-cm) wells (Robert Middelburg, written commun., 1976; Mark Hillerich, written commun., 1977; Mark Ayers, written commun., 1977) and a fourth developed by Donald Signor, Lawrence, Kansas, has come to my attention. Care needs to be taken that the materials from which the pumps are constructed will not adversely affect the water quality.

Thief-Sampling Techniques

Although not ordinarily used as a technique for obtaining samples representative of the aquifer, so-called "thief-sampling," (obtaining a small-volume sample at a given point in the well) has been commonly used in ground-water sampling. Equipment is available for obtaining point samples in a well. Some of these devices have been illustrated in Rainwater and Thatcher (1960) and others. Perhaps the most versatile is the unit built by Well Reconnaissance Corp., Houston, Texas. This unit is in regular use by some government agencies, such as U.S. Geological Survey and U.S. Environmental Protection Agency. It is an electrically-operated unit that can be evacuated to prevent gas contamination; when lowered to any point in a well, a solenoid valve is opened to allow water to enter the collection chamber and the valve is then closed to prevent exchange of water as the unit is brought to the surface. Sample containers may hold any volume desired and can be designed to be removed from the sampling device under sealed conditions. Other thieving devices have been used: some rely on their impact with the bottom of the well to open a valve to admit water, while others require a "messenger," a weight that travels along the support cable to trip a valve after the sampler has reached the desired level in the well. The likelihood of obtaining an aquifer-representative sample by removing a small volume from within the casing or open hole is small. An example of a typical well is shown in figure 9; it indicates three possible sampling points: A, B, and C. Location C has the greatest probability of yielding an aquifer-representative sample. It is assumed in this example that horizontal ground-water flow is more important than any thermal, pressure, or diffusion gradients that would induce vertical movement of the water in the well. Locations B and A represent locations of increasing stagnancy, and therefore are less likely to be representative of aquifer-water composition; the degree of deviation in composition is dependent on the original water quality, the method of well completion, and the flow patterns in the well. Thief sampling needs to be done if samples are desired from wells not accessible to pumps, although it is expected that the development of the small-diameter pumps, referenced previously, virtually will replace thief sampling as a technique.

Sometimes a vertical sample profile of an aquifer is desired. If straddle packers are available or if samples can be obtained as the hole is deepened, useful samples may be obtained. Generally, a vertical sample profile in a completed well is meaningless, unless no vertical water movement takes place and the lateral flow is sufficiently important to minimize any thermal or diffusion effects; these conditions are seldom met.

Bailing and Swabbing

Bailing and swabbing are accomplished by using a cup- or bucket-shaped device on the end of a cable. The cup or bucket is equipped with a foot valve that allows water to pass through as the bucket is lowered into the well, but closes to allow the water to be lifted on the upstroke. Bailing is accomplished in the cased (or sometimes uncased) well, while swabbing is done through tubing. When straddle packers are used to isolate a particular zone in a well, swabbing

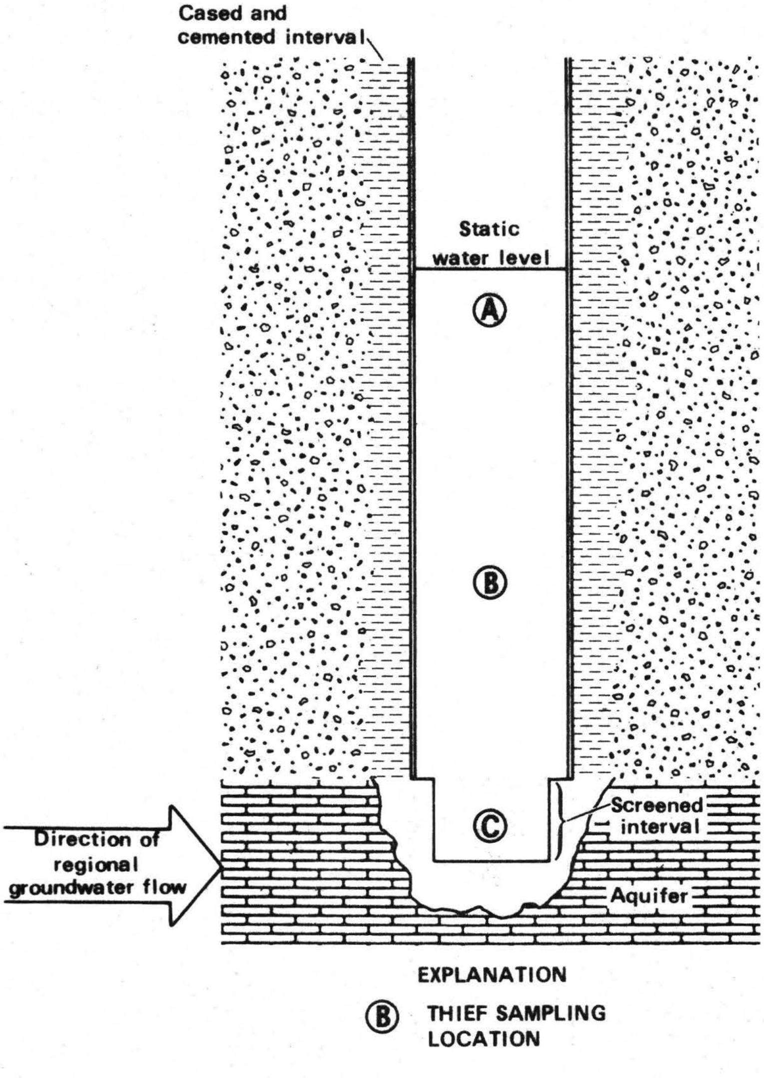


Figure 9.--Thief sampling of a typical well.

generally is used if the tubing is not large enough to admit a standard submersible pump. Currently, the use of a small-diameter pump in this application is unknown; however, the author sees no reason why such use could not replace swabbing.

Considerable bailing or swabbing generally is required to produce samples representative of the aquifer; the technique commonly is used in well development to remove sand and silt from the well. Some exchange of water occurs as the bail is brought up the well. Several hole-volumes of water need to be removed from a developed well before sampling is considered. If the well has not been previously developed, this needs to be accomplished prior to sampling; water quality needs to be monitored during the operation.

The fact that swabbing is done through tubing produces an additional source of contamination: tubing-joint compound. It is not known precisely what chemical effect this material has on water samples, but their visual appearance is altered.

One additional difficulty with the bailing methods is the requirement for a drilling rig or hoist and an experienced operator, to remove water at a reasonable rate. The cost generally is expensive, compared to installation of a submersible pump.

Samples from Uncased Wells

Uncased well probably is a misnomer, because wells, as generally defined, are cased to prevent collapse. Occasionally a test hole is drilled and abandoned, and later becomes a desirable sampling point. Once again, the submersible pump becomes the most appropriate method for obtaining water, unless the suction pump will provide useful samples and the hydraulics of the system make the suction pump a suitable choice. Bailing may not be possible if the hole is small-diameter or if it is crooked, and swabbing requires use of a drilling rig and tubing. Thief sampling presents the same shortcomings whether the hole is cased or uncased; it needs to be used only when no more appropriate method is available, understanding the probable interpretation limitations on resulting data.

Older uncased holes generally are not open to the water table and cannot be sampled without use of a workover drilling rig. If hydraulic heads decrease with depth, dewatering of upper zones takes place, and caving or bridging result. Reopening of these holes can be more difficult and costly than drilling a new hole; therefore, that alternative needs to be considered.

Obtaining Samples from Springs

Collection of samples from springs, as examples of ground water, presents some complications that are not different in kind to those presented by wells, but are different in magnitude. Recall the degassing and potential aeration problems associated with sampling deep aquifers by use of surface-based suction pumps for the basic principles. Two types of springs are illustrated in figure 10; not all springs will present all the problems associated with the seep; each sampling point needs to be studied for those complications present.

A Seep

A seep has a slow flow rate; ground water slowly undergoes the transition to surface water, allowing time for changes to occur. What changes might be expected? Seep areas usually are densely vegetated, and considerable volumes of carbon dioxide and oxygen are generated and consumed during certain times of the year. Often sufficient evaporation, transpiration, or composition change has taken place to cause visible precipitation of solids in seep areas. A decreased pH may result in rapid dissolution of rock and soil particles in the seep area, that may be of different origin than the bedrock aquifer represented by the recharge area. Slow passage of the water through the seep also may allow oxygen to dissolve in the water, changing what may have been a reducing water to an oxidizing water. Precipitation of iron and manganese hydroxides at or near the ground surface usually is an indication of this process.

Seeps may be developed to eliminate or lessen some of the above changes. Removal of the soil zone to allow increased flow generally results in samples that better represent ground water. An easier method to enhance ground-water representation is by the installation of the drive point (well point) into the soft earth associated with the seep. A description of materials and techniques for this approach can be found in a report by the U.S. Environmental Protection Agency (1974). A means for sampling the ground water, such as a suction pump, is then used if the water does not flow from the well point.

A Fissure Spring

The ideal fissure spring flows from bedrock, has little vegetation growing near the orifice, and flows at a sufficient rate to minimize the effects of surface contaminants. If the spring is located on a hillside, tubing generally can be inserted into the fissure to allow nearly closed-system sampling from the aquifer. If the spring is located in a level area, pools of water generally are present around the spring orifice and the orifice may be submerged. The best sample can then be obtained by using any suction pump or a miniature submersible pump. The important thing is to avoid sampling water that has been changed by surface or near-surface contaminants, those factors that change water quality and render it unrepresentative of ground water.

ONSITE PROCESSING OF WATER SAMPLES

The previous discussion has given some background concerning changes that may occur as water is transported from the aquifer to the wellhead. Many of the expected changes may not occur during this period because it is short;

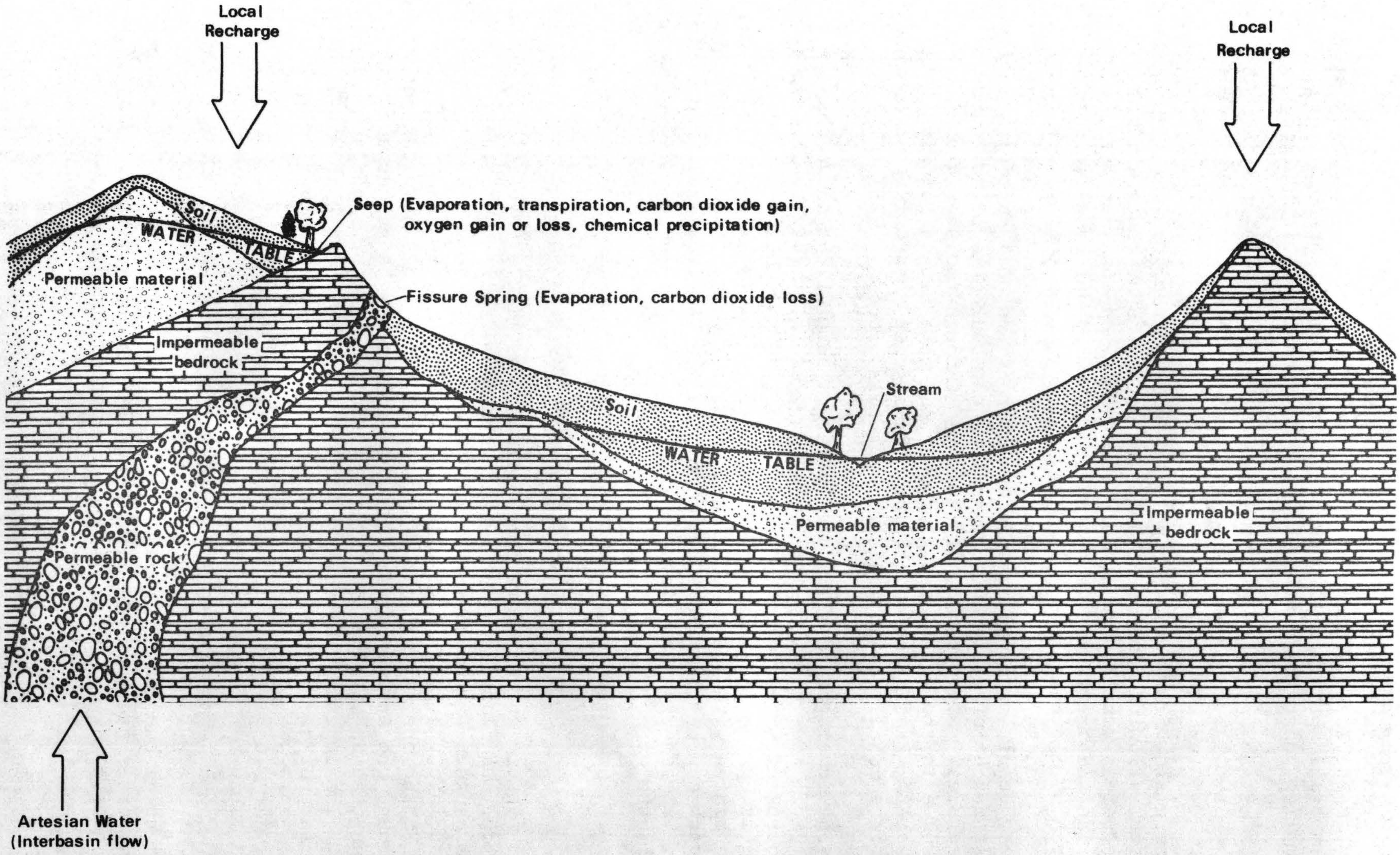


Figure 10.--How springs and seeps are indicators of ground-water quality.

that is, the rate of water-quality change is slow compared to the time of transport. However, the time from sample collection to laboratory analysis often is quite long, enough so that the rate at which the sample undergoes change becomes rapid compared to sample-to-laboratory transit time. It is for this reason that proper onsite preservation of samples is critical. The more rapid the processing, the less will be the chance for changes to occur. The timing of sample collection and preservation and onsite analytical determinations can be summed by the phrase: "The sooner the better, the later the riskier."

Onsite Processing Techniques: Inorganic Constituents

Early in the discussion of ground-water sampling, we established a definition of what constituted the dissolved fraction of a water sample and then went on to rationalize the choice of the 0.45-µm limit. Transport of the sample from aquifer to wellhead produces changes of varying severity and importance, depending on solute composition and constituents of interest; handling and storage of samples may produce much greater change. Temperature change and aeration are two of the most common perturbations when samples are collected by open-system techniques. As previously discussed, a closed system (such as described by Wood, 1976) in which the pumping pressure is used to filter the sample is the preferred technique, as it eliminates change that may be brought about by aeration or temperature change. If this cannot be used, several open-system handling techniques are available. The system chosen will depend on the size of sample required for the desired analytical schedule.

1. Barrel-type filter (nitrogen-pressure filtration). These filters can be subdivided into two types; one has the filter holder as an integral part of the reservoir and the other has a separate filter holder, with a valve between the reservoir and the filter holder. Both types have the disadvantage that a fixed volume of water is available per batch of sample. If volumes of water larger than the reservoir are required for analysis and samples are being obtained as a function of time, it will be impossible to refill the reservoir and guarantee that the "same" water is represented. The interchangeability of filters during filtration is a distinct advantage with hard-to-filter samples. The filtration unit needs to be equipped with a 200-kPa pressure-relief valve for safety.

2. Sandwich filter with remote reservoir (nitrogen-pressure filtration). This type has a reservoir (usually stainless steel) connected to a separate unit (commonly Plexiglas or stainless steel) containing the filter. The advantage of this system is that several reservoir sizes may be carried, depending on sample-size requirements, but only one filter holder. Filters can be changed any time during the filtration process. The disadvantage lies in the need for tubing to transfer the liquid from reservoir to filter. All connections can be fitted with quick-connects of the double-end-shutoff type, for ease in handling and in changing filters. The filtration system needs to be equipped with a 200-kPa pressure-relief valve for safety.

3. Suction filtration. A variety of units is commercially available, most of which were designed for laboratory operation using a water aspirator. Units can be connected to a vacuum pump or automobile intake manifold for the required suction. One or more traps need to be used to avoid contaminating the sample or the pump. A second filter placed between the filtration apparatus and the pump-suction fitting would be satisfactory in most cases.

Suction filtration is not satisfactory, as it intensifies the potential changes that are caused by open-system filtration techniques. Not only is the sample subjected to atmospheric pressure for a time, but it is under less than atmospheric pressure as it is filtered. This intensifies the potential for changes caused by degassing or aeration. Nitrogen-pressure filtration eliminates this problem.

Air-pressure filtration also has been used in onsite processing. This procedure presents potential for changes in oxidizable-ion concentrations as well as possible changes in some organic constituents. Compressed nitrogen needs to be used, rather than air.

Filters used in water filtration present an additional source of contamination. Some types yield significant quantities of dissolved ions to water samples, the significance becoming greater as the sample concentrations become smaller. It is important to allow a sufficient volume of sample to be wasted prior to actual sample collection; 100 mL (milliliters) has been found to be satisfactory. Washing with 0.1 N or 0.01 N spectrographic quality acid and deionized-water rinsing of filters also may be used to precondition some filter membranes. However, if sufficient water is available, it is desirable to simply allow 100 mL to flow to waste.

Theoretically, if a sample is collected in a sealed container whose walls do not interact with the water, and if no temperature or pressure changes occur, no change in the water chemistry should occur. That is only true if the sample has no potential for change; that is, if all components are in equilibrium. For example, a water containing no suspended material, but which is supersaturated with respect to certain solid mineral phases, could precipitate those mineral phases at any time. Another example, perhaps more commonly found, is one that involves a mixture of dissolved and suspended components of a water sample. These will continue to interact, regardless of whether they are in the natural environment or isolated from it in an inert container. Working with the natural environment, we compromise in collecting the perfect sample for one that is sufficiently representative, so that the purpose(s) for which the sample was collected are not negated. We are left with two choices: (1) Immediate separation of solid and liquid, and preservation of the separates; and (2) isolation of the whole sample so critical constituents are preserved. Some guidelines and cautions follow.

1. If the sample contains visible turbidity of any kind, immediate onsite separation and preservation are necessary. CAUTION: Visible turbidity could be caused by chemical precipitation resulting from sample transfer from aquifer to sampling point. Separation, in this case, would not result in the liquid separate being aquifer-representative; this is a sampling risk.

2. If the sample is visually clear, it is always best to perform onsite separation and preservation whenever possible. If this is not practical, the following technique may be used for some constituents. Sufficient sample for all analyses to be performed (as directed by the analytical laboratory) needs to be placed in a pyrex bottle with standard-taper, vacuum-grade pyrex stopper. The bottles are previously filled with 0.1 N hydrochloric or nitric acid, rinsed three times with deionized water, and then allowed to soak overnight in deionized water. The water is then discarded and the bottles refilled with deionized water until used; stoppers need to be processed similarly. The bottle should soak with sample water for 20 minutes, and the liquid then discarded. The bottle needs to be refilled to top of neck with a fresh water sample, and the stopper inserted and seated, forcing excess water out of the neck. Wire or tape is used to secure the stopper. This bottle needs to be preserved at original sample temperature during transit, by packing in a polyurethane foam container if a large pyrex bottle has been used. Smaller bottles can be placed in a stainless steel thermos that is pre-heated or pre-cooled with formation water, and filled with formation water after the sample bottle has been placed inside. These methods should keep samples near formation temperature, if it does not differ too much from ambient temperature. Very hot or very cold weather limits transit time, and special precautions may need to be taken, but experimentation will result in a method that will preserve the temperature long enough to bring the sample to a location suitable for further processing. The above procedure has been tested by the author for pH preservation and has been found satisfactory for a large number of water types. It is expected that the procedure would adapt to other constituents because pH is less stable than most constituents of interest to ground-water hydrologists.

The above processing techniques are applicable to the variety of inorganic constituents found in natural water; no processing technique is available that would be correct for all physical forms of all constituents. Once separation of liquid and solid is made, most samples for analysis of inorganic constituents are acidified with nitric acid, until the pH is decreased sufficiently to prevent sorption or precipitation of dissolved species. A pH of 2 has been the target for some samples (U.S. Geological Survey, written commun., 1982), and a pH of 1 for others (U.S. Geological Survey, written commun., 1977). These procedures will not work for all constituents, and analytical laboratory personnel will make recommendations regarding preservation procedures, containers (both size and type), and special shipping instructions that are appropriate for specific analyses and current analytical procedures. The laboratory performing the analytical work always needs to be consulted prior to any ground-water sampling, and the latest instructions obtained. Laboratory personnel are as interested in providing meaningful results as the ground-water hydrologist is in obtaining them.

As previously mentioned, unpublished results of the author indicate that the pyrex system discussed above may have long-term sample preservation potential for many constituents. Hydrogen-ion concentrations in some poorly buffered ground-water samples stored in the pyrex vacuum-stoppered bottles at constant temperature have remained virtually constant for more than 1 month. Because hydrogen ions have a significant potential for sorption, their stability in this system indicates that other species may be equally stable for similar periods of time. Because the effect of sample acidification on the preservation of dissolved species found in natural (and polluted) waters is not known with certainty, it may be that preservation without addition of acid is preferable; the constraints of this method need to be accepted.

If a sample is supersaturated with respect to certain solid-mineral phases, and, therefore, thermodynamically unstable, acidification will have preservation value for some constituents. For example, metal hydroxides and carbonates may be prevented from precipitating by increasing their solubility, however, some metal oxides are less soluble in acid solution and may precipitate. The metal oxides generally are present only in small concentration in natural waters. Each constituent for analysis needs to be considered for its best method of preservation; laboratory personnel can assist.

Onsite Processing Techniques: Organic Constituents, Microbiological Constituents

Many of the principles pertaining to the collection and preservation of samples for inorganic-constituent analysis apply to the collection and preservation of samples for organic-constituent analysis. The potential diversity of organic constituents present in natural water may be vastly greater than inorganic, when polluted waters are considered. Work by Leenheer and Huffman (1976); Leenheer, Malcolm, and White (1977); Wershaw and Goldberg (1972); Wershaw, Pinckney, and Booker (1977); and other investigators has resulted in identification and characterization of many of those organic constituents commonly found in water. Guidelines for collection and preservation of organic substances for analysis have been published by Goerlitz and Brown (1972) and updated by the U.S. Geological Survey (written commun., 1972). Laboratory personnel need to be consulted prior to collecting samples for organic-constituent analysis, to obtain the latest processing and preservation techniques.

As with collection and preservation of samples for other constituents, the techniques for onsite processing of samples for microbiological analysis are constantly being revised. A basic text has been written by Greeson and others (1977). Written communications by the U.S. Geological Survey regularly update the techniques reported in Greeson and others (1977) for use by Survey personnel.

ONSITE MEASUREMENTS AND SPECIAL-PRESERVATION TECHNIQUES

The justification for onsite measurement of certain commonly-measured unstable properties and constituents is identical to the previous discussion of the need for immediate processing of water samples for laboratory analysis, if accurate, reliable values are desired. Ground-water hydrologists are faced with a dichotomy: (1) Laboratory analysis generally is more precise than onsite analysis, but no adequate preservation technique may exist to guarantee that the analysis is representative of truly dissolved species under natural conditions; and (2) onsite analysis generally is more difficult and less precise, but results may be more representative of the actual water quality. Additional study of natural waters is necessary to define under what conditions and for which properties and constituents onsite measurements yield more meaningful data, compared to conditions under which satisfactory onsite-processing techniques coupled with laboratory analysis result in greater accuracy. An example of the resolution of such a dichotomy follows.

Reasonably precise analytical methods for aluminum have existed for some time, but concentrations determined in natural waters commonly were much larger than those predicted for "truly dissolved" aluminum complexes (Hem and others, 1973; Smith and Hem, 1972). It was discovered that some aluminum species could pass through the 0.45-μm filter membrane and be analyzed as dissolved aluminum by the laboratory (0.10-μm membrane filters have been used with greatly-improved results compared to the 0.45-μm membrane filters). Presser and Barnes (1974) developed a procedure that allowed complexation of dissolved aluminum under onsite conditions, extraction of the complex into an organic solvent resulting in separation from the raw-water sample and preservation for laboratory analysis. Aluminum data obtained in this manner have been consistent and interpretable. The method also can be used for manganese and iron. The onsite-extraction procedure is a preservation method, but the effort involved is similar to that of an onsite analysis.

An excellent detailed discussion of common constituents for which practical onsite procedures have been developed can be found in Wood (1976). Procedures included are for specific conductance, temperature, pH, carbonate plus bicarbonate (alkalinity), redox potential, and dissolved oxygen. Presser and Barnes (1974) discuss onsite determination of pH, alkalinity, ammonia, and sulfide.

Although onsite measurements of many different species may be made by use of ion-selective electrodes, practical considerations of reliability, sensitivity, and interferences make them advantageous only in special circumstances. The fluoride electrode is an exception and may be used with confidence at the activity levels found in natural waters.

Commercially-available kits designed to make onsite determinations of many common constituents have been used by soil scientists and agricultural engineers for many years. Precision of some of these kits is sometimes insufficient to meet project needs. Comparisons of onsite and laboratory values obtained from a variety of sources need to be made before completely relying on data obtained through the use of these kits.

A technique suggested by Presser and Barnes (1974) for the preservation of samples containing large dissolved-silica concentrations may have application to preservation of all samples that are thermodynamically unstable. The method involves simple dilution of the filtered sample with deionized water. Very pure water (type I) is needed if minute concentrations of certain species are to be measured, and careful record keeping is essential; the laboratory needs to be consulted before using this method.

CARE OF EQUIPMENT

Equipment used in water sampling comes into contact with a variety of environments, from waters of different compositions to dust and organic contaminants. In the laboratory, it is a simple task to keep equipment clean and in proper operating order, calibrated and ready for use. At the sampling site, however, it is a problem to keep the equipment in one piece, much less clean and calibrated. Care can be taken to insure that samples representative of the aquifer are obtained; however, that effort may be negated if the equipment used to obtain and process the sample and to make onsite determinations of unstable properties and constituents is not scrupulously clean and in documented operating condition.

Initial cleaning of equipment and instrument calibration always needs to be done before leaving the office. Office facilities usually are better and repairs can be completed more easily. A method for transporting cleaned and calibrated equipment needs to be devised; usually airtight and compartmented containers are needed to prevent dirt and moisture entry and to avoid breakage of glassware. Almost all processing equipment can be purchased which is manufactured from plastics to eliminate breakage; however, because of its lack of abrasion resistance, it is difficult to determine its state of cleanliness.

Glass- and Plastic-Ware

Ordinarily, a detergent wash, tapwater rinse, soaking in 0.1 N hydrochloric acid overnight, deionized-water soak, and air-drying is all that is required prior to leaving the office. If sufficient "glassware" is available, onsite cleaning can be eliminated entirely by avoiding reuse of any item. Special cleaning of equipment used for processing samples for organic-constituents analysis is needed. Goerlitz and Brown (1972) and laboratory personnel need to be consulted.

At the sampling site, cleaning of equipment generally can consist of simply rinsing with deionized water if nothing has been allowed to dry on the equipment. If water or sediment has dried on the equipment, it is much more difficult to remove, and detergent, acid wash, or both need to be used. Greater care against cross-contamination of samples needs to be taken if water qualities vary greatly from location to location. This is especially true when samples are obtained for analysis of radioisotopes or trace elements. If in doubt, either avoid reusing equipment or it may be rigorously cleaned prior to reuse. It helps to know as much as possible about what your samples may contain before collection, so adequate precautions can be taken.

Bottles used for processed-sample storage and shipment generally are obtained from the laboratory doing the analysis and have been properly cleaned. Use of the bottles only for samples originally intended will give the best results. If these bottles are not available, the laboratory personnel can provide instructions for appropriate bottle types and cleaning methods.

Instruments and Other Equipment

Cleaning of portable pumping equipment is more difficult than glass- and plastic-ware. Plastic tends to be easier to keep clean of inorganic contaminants than metal. Use of all-plastic pumps will avoid most contamination problems, but it is not possible to use these pumps in deep wells. If thorough cleaning of pumping equipment is desirable, acid-wash solution can be mixed in plastic-lined, 100 to 200-L barrels and pumped through the system, including discharge line. Deionized-water rinses may be accomplished similarly.

Instrument function always needs to be rigorously tested before leaving the office. This needs to include calibration checks, and measurements made on real or synthetic samples with compositions similar to those of the samples expected to be collected. For example, pH-electrode systems may operate properly in buffer solutions, but may have too long a response time for determining the pH of water containing minimal dissolved solids. This can be recognized and corrected before leaving the office, avoiding loss of onsite data. Lack of temperature compensation on certain scales of specific-conductance meters or incorrect cell constants for the intended application generally can be determined prior to departure.

Those parts of instruments (or equipment) subject to wear or breakage need to have replacements available for immediate use; examples include electrodes and batteries. Replacement parts always need to be checked for correct operation before leaving the office. Commonly, the spare parts turn out to be rejects from prior sample-collection activities or nonfunctional because of expired shelf life.

SUMMARY

Interpretation of ground-water chemical data implies that a representative sample of ground water is collected from a definable part of the subsurface environment. In contrast to surface-water sampling, the difficulty in achieving the aforementioned objective in ground-water sampling is considerably greater, due primarily to the fact that a large part of the required ground-water data is obtained by inference (geophysical logs, rock cuttings, and so forth), rather than by direct observation or measurement. Great care needs to be taken in obtaining ground-water samples and the associated data that will be used to define the source of those samples.

A variety of conditions exists that may affect the quality of ground-water samples as they are brought from the undisturbed aquifer to the points at which water-quality determinations are made. Conditions of drilling, hydraulic testing, and ground-water-withdrawal techniques may change the water quality from its native state. Generally it is not possible to assess the actual effect of these activities because of the time and money that would be involved. However, many of these problems may be avoided by judicious choice of techniques. If the problems cannot be avoided, evaluation of the validity of ground-water-quality data for specific purposes needs to be made on the basis of conditions under which the data were actually obtained; thus, the need for detailed documentation of the sampling process.

The steps to achieve the objective of valid ground-water quality samples are:

1. Determination of project objective;

2. Property and constituent selection to meet present and anticipated future objectives;

3. Selection of sampling location and definition of the hydrologic environment sampled;

4. Determination of well completion and drilling history, and its effect on water quality and hydraulic characteristics;

5. Determination of water-removal technique, and its effect on the water-quality properties and constituents of interest;

6. Selection of properties and constituents to be determined with onsite analysis;

7. Selection of sample preservation techniques for laboratory determined properties and constituents;

8. Recording, storage, and verification of data obtained.

If reliable data are obtained for each of the above steps, the validity and quality of ground-water data will be much improved over that which generally is obtained.

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