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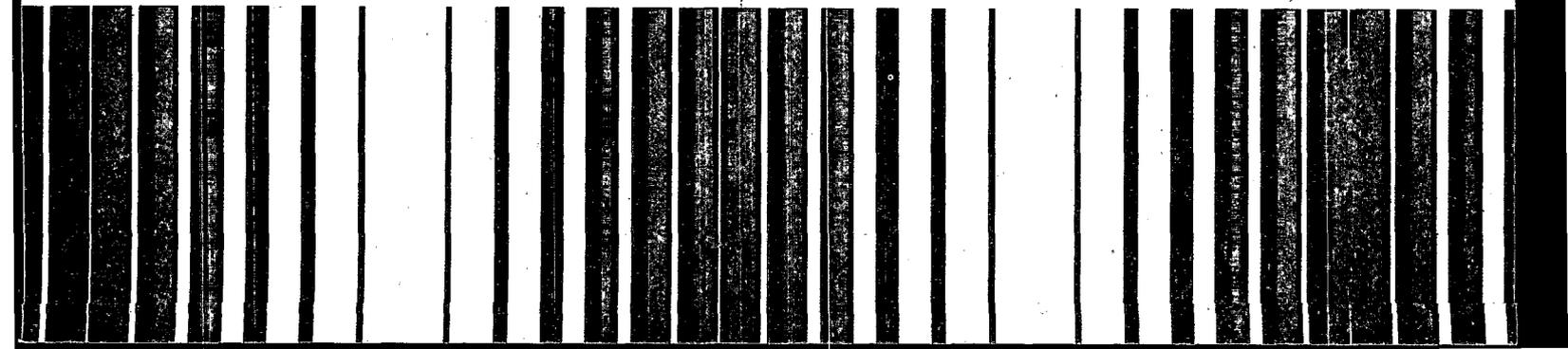
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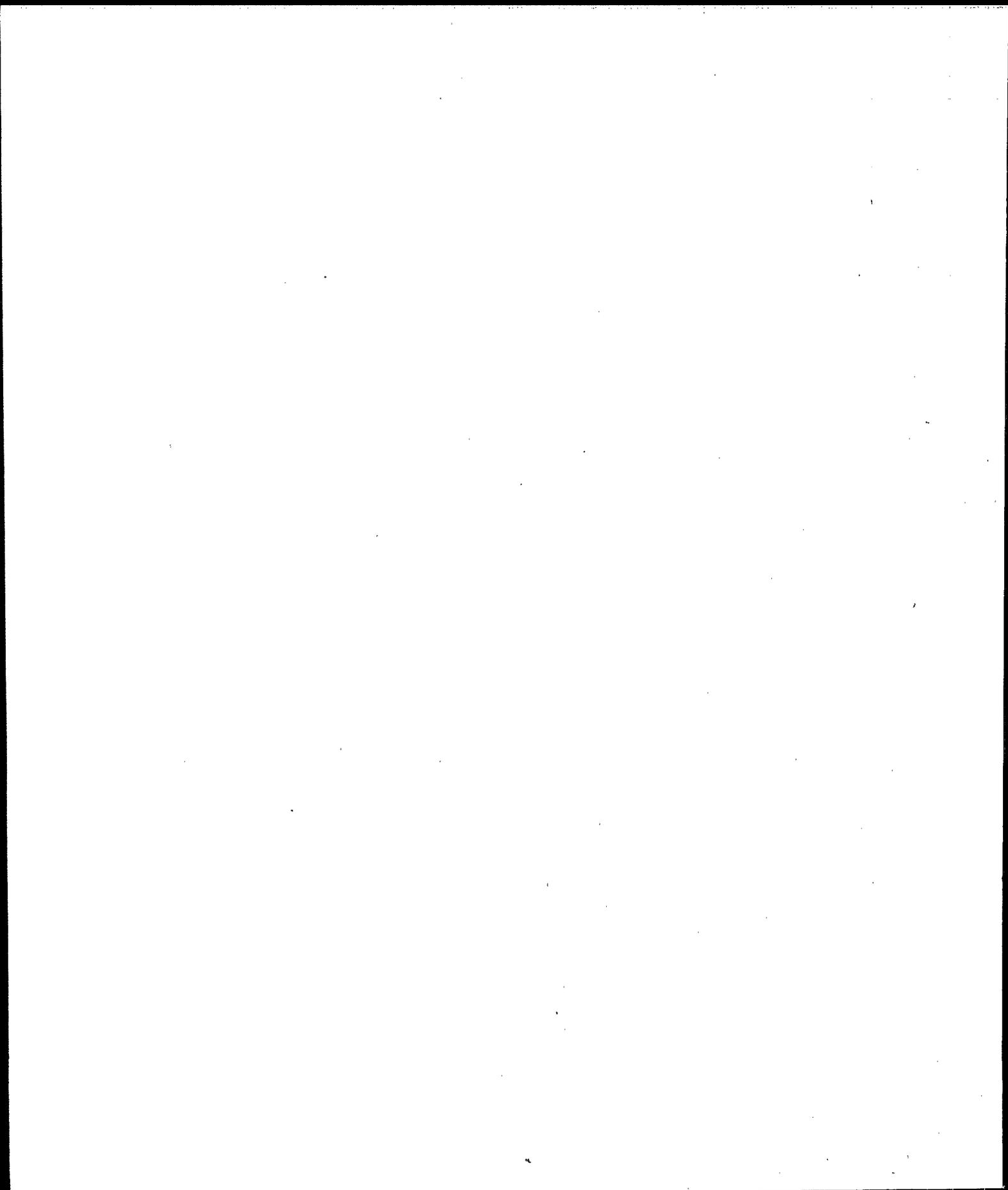


Handbook

Ground Water

Volume II: Methodology





EPA/625/6-90/016b
July 1991

Handbook

Ground Water Volume II: Methodology

U.S. Environmental Protection Agency
Office of Research and Development

Center for Environmental Research Information
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NOTICE

This document has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

This document is not intended to be a guidance or support document for a specific regulatory program. Guidance documents are available from EPA and must be consulted to address specific regulatory issues.

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Volume I, Ground Water and Contamination, was published in September 1990 (EPA/625/6-90/016a). Volume II, Methodology describes various investigative approaches and techniques. Although extensively revised, part of Volume II was obtained from previous publications, "Handbook: Ground Water" (EPA/625/6-87/016) and "Protection of Public Water Supplies from Ground-Water Contamination" (EPA/625/4-85/016).

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Preface

The subsurface environment of ground water is characterized by a complex interplay of physical, geochemical and biological forces that govern the release, transport and fate of a variety of chemical substances. There are literally as many varied hydrogeologic settings as there are types and numbers of contaminant sources. In situations where ground-water investigations are most necessary, there are frequently many variables of land and ground-water use and contaminant source characteristics which cannot be fully characterized.

The impact of natural ground-water recharge and discharge processes on distributions of chemical constituents is understood for only a few types of chemical species. Also, these processes may be modified by both natural phenomena and man's activities so as to further complicate apparent spatial or temporal trends in water quality. Since so many climatic, demographic and hydrogeologic factors may vary from place to place, or even small areas within specific sites, there can be no single "standard" approach for assessing and protecting the quality of ground water that will be applicable in all cases.

Despite these uncertainties, investigations are under way and they are used as a basis for making decisions about the need for, and usefulness of, alternative corrective and preventive actions. Decision makers, therefore, need some assurance that elements of uncertainty are minimized and that hydrogeologic investigations provide reliable results.

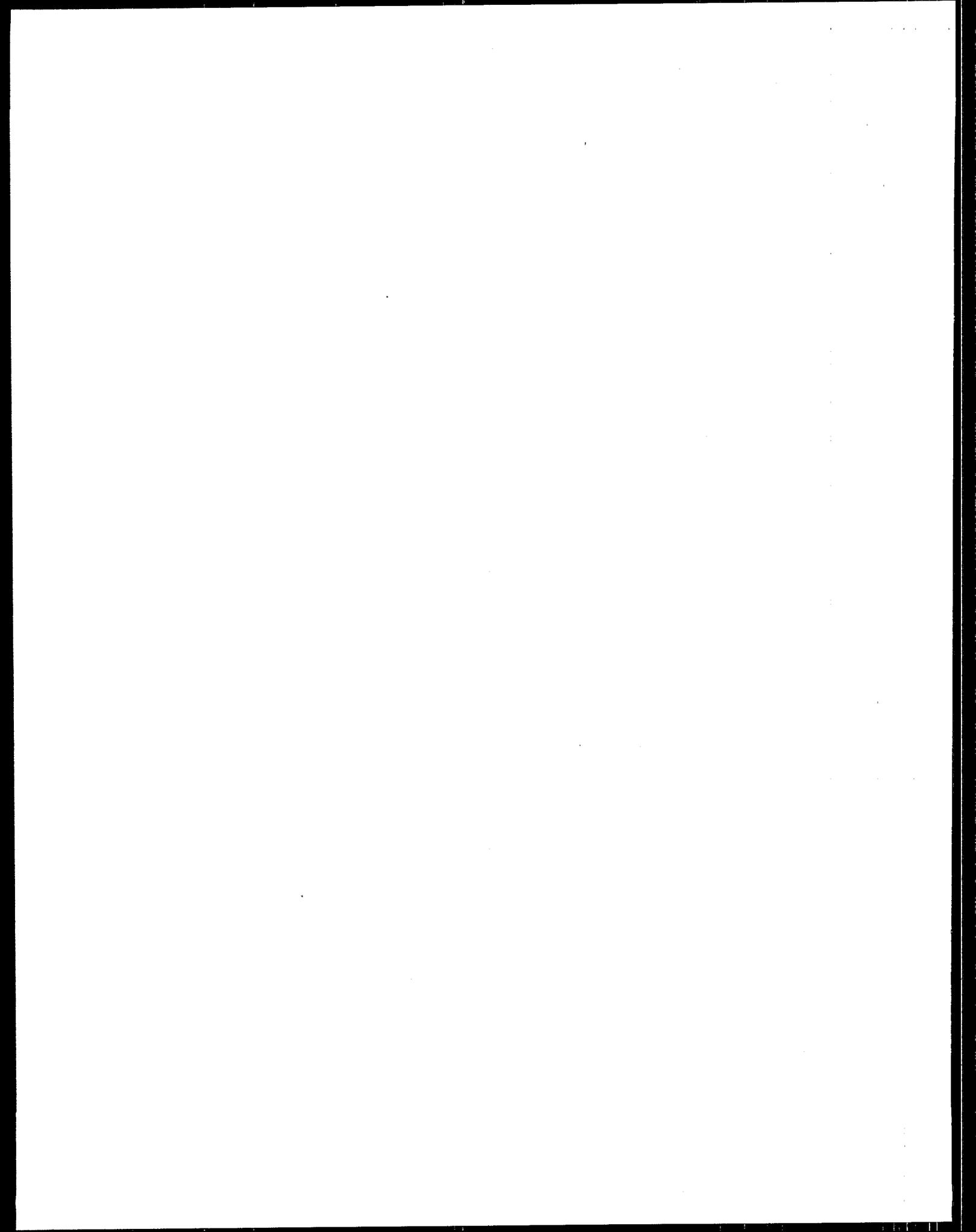
A purpose of this document is to discuss measures that can be taken to ensure that uncertainties do not undermine our ability to make reliable predictions about the response of contamination to various corrective or preventive measures.

EPA conducts considerable research in ground water to support its regulatory needs. In recent years, scientific knowledge about ground-water systems has been increasing rapidly. Researchers in the Office of Research and Development have made improvements in technology for assessing the subsurface, in adapting techniques from other disciplines to successfully identify specific contaminants in ground water, in assessing the behavior of certain chemicals in some geologic materials and in advancing the state-of-the-art of remedial technologies.

An important part of EPA's ground-water research program is to transmit research information to decision makers, field managers and the scientific community. This publication has been developed to assist that effort and, additionally, to help satisfy an immediate Agency need to promote the transfer of technology that is applicable to ground-water contamination control and prevention.

The need exists for a resource document that brings together available technical information in a form convenient for ground-water personnel within EPA and state and local governments on whom EPA ultimately depends for proper ground-water management. The information contained in this handbook is intended to meet that need. It is applicable to many programs that deal with the ground-water resource. However, it is not intended as a guidance or support document for a specific regulatory program.

GUIDANCE DOCUMENTS ARE AVAILABLE FROM EPA AND MUST BE CONSULTED TO ADDRESS SPECIFIC REGULATORY ISSUES.



MONITORING WELL DESIGN AND CONSTRUCTION

The principal objective of constructing monitoring wells is to provide access to an otherwise inaccessible environment. Monitoring wells are used to evaluate topics within various disciplines, including geology, hydrology, chemistry, and biology. In ground-water quality monitoring, wells are used for collecting ground-water samples, which upon analysis may allow description of a contaminant plume, or the movement of a particular chemical (or biological) constituent, or ensure that potential contaminants are not moving past a particular point.

Ground-Water Monitoring Program Goals

Each purpose for ground-water monitoring—ambient monitoring, source monitoring, case preparation monitoring, and research monitoring—must satisfy somewhat different requirements, and may necessitate different strategies for well design and construction (Barcelona and others, 1984). At the outset, the goals of the intended monitoring program must be clearly understood and thought should be given to the potential future use of the wells in other, possibly different, monitoring programs.

Regional investigations of ground-water quality involve ambient monitoring. Such investigations seek to establish an overall picture of the quality of water within all or parts of an aquifer. Generally, sample collection is conducted routinely over a period of many years to determine changes in quality over time. Often, changes in quality are related to long-term changes in land use (e.g., the effects of urbanization). Monitoring conducted for Safe Drinking Water Act compliance generally falls in this category.

Samples commonly are collected from a variety of public and private water supply wells for ambient quality investigations. Because of the diversity of sources, the data obtained through some ambient monitoring programs may not meet the strict well design and construction requirements imposed by the three other

types of monitoring. However, such programs are important for detecting significant changes in aquifer water quality over time and space and protecting public health.

Regulatory monitoring at potential contaminant sources is considered source monitoring. Under this type of program, monitoring wells are located and designed to detect the movement of specific pollutants outside of the boundaries of a particular facility (e.g., treatment, storage, or disposal). Ground-water sampling to define contaminant plume extent and geometry would fall into this monitoring classification. Monitoring well design and construction are tailored to the site geology and contaminant chemistry. With source monitoring, quantitative aspects of analytical results become most important because the level of contaminant concentration may require specific regulatory action.

Monitoring for case preparation, such as legal proceedings in environmental enforcement, requires a level of detail similar to source monitoring. Source monitoring, in fact, often becomes a part of legal proceedings to establish whether or not environmental damage has occurred and to identify the responsible party. This is a prime example of one type of monitoring program evolving into another. The appropriateness and integrity of monitoring well design and construction methods will come under close scrutiny in legal proceedings. In such cases, the course of action taken during the monitoring investigation, the decisions made concerning well design and construction, and the reasons for those decisions must be clearly established and documented.

Monitoring for research generally requires a level of sophistication beyond that required of any other type of monitoring (this, of course, depends upon the types and concentrations of constituents being sought and the overall objectives of the research). Detailed information is often needed to support the basic concepts and expand understanding of the complex mechanisms of

ground-water movement and solute/contaminant transport.

The goals of any proposed ground-water monitoring program should be clearly stated and understood before making any decisions on the types and numbers of wells needed, their locations, depth, constituents of interest, and methods of collection, storage, transportation, and analysis.

As each of these decisions is made, consideration must be given to the costs involved in each step of the monitoring program and how compromises in one step may affect the integrity and outcome of the other steps. For example, cost savings in well construction materials may so severely limit the usefulness of a well that another well may need to be constructed at the same location for the reliable addition of a single chemical parameter.

Monitoring Well Design Components

Monitoring well design and construction methods follow production well design and construction techniques; a monitoring well, however, is built specifically to give access to the ground water so that a "representative" sample of water can be withdrawn and analyzed. While well efficiency and yield is important, the ability to produce large amounts of water for supply purposes is not the primary objective.

Emphasis is placed instead on constructing a well that will provide easily obtainable ground-water samples that will give reliable, meaningful information. Therefore, materials and techniques used for constructing a monitoring well must not materially alter the quality of the water being sampled. An understanding of the chemistry of suspected pollutants and the geologic setting in which the monitoring well is to be constructed play a major role in the drilling technique and well construction materials used.

Several components need to be considered in monitoring well design: location and number of wells, diameter, casing and screen material, screen length and depth of placement, sealing material, well development, and well security. Often, discussion of one component will impinge upon other components.

Location and Number

Locating monitoring wells spatially and vertically to ensure that the ground-water flow regime of concern is being monitored is obviously one of the most important components in ground-water quality monitoring design. Monitoring well locations (sites) and the number of wells

in the monitoring program are closely linked. The number of wells and their location are principally determined by the purpose of the monitoring program. In most monitoring situations, the goal is to determine the effect that some surface or near-surface activity has had on nearby ground-water quality. Most dissolved constituents will descend vertically through the unsaturated zone beneath the area of activity and then, upon reaching the saturated zone, move horizontally in the direction of ground-water flow. Therefore, monitoring wells are normally completed downgradient in the first permeable water-bearing unit encountered. Consideration should be given to natural (seasonal) fluctuations, which can amount to several feet throughout the year and from one year to the next, and artificial fluctuations brought about largely by pumping, which can amount to several tens of feet in only a few hours. Artificial fluctuations also are caused by lagoon operation, which can cause a rise or "mound" in the water table.

Preliminary boreholes and monitoring wells can be constructed to collect and analyze geologic material samples, to measure ground-water levels, and to collect water-quality samples, all of which provide a guide to the future placement of additional wells. Accurate water-level information must be obtained to determine if local ground-water flow paths and gradients differ significantly from the regional appraisal.

The analysis of water-quality samples from the preliminary wells can direct the placement of additional wells. Such data are helpful in the vertical arrangement of sampling points, especially for a contaminant that is denser than water. Without some preliminary chemical data, it is usually very difficult to determine the location of the most contaminated zone.

Site geology, site hydrology, source characteristics, contaminant characteristics, and the size of the area under investigation all help determine where and how many wells should be constructed. Certainly, the more complicated the geology and hydrology, the more complex the contaminant and source, and the larger the area being investigated, the greater the number of monitoring wells that will be required.

Diameter

In the past, the diameter of a monitoring well was based primarily on the size of the device (bailer, pump, etc.) used to withdraw the water samples. This practice was similar to that followed for water supply well design. For example, a domestic water well is commonly 4 to 6 inches in diameter, which is of sufficient size to accommodate a submersible pump capable of delivering from 5 to 20 gallons per minute. Municipal, industrial,

and irrigation wells have greater diameters to handle larger pumps, and to increase the available screen open area so the well can produce water efficiently.

This practice worked well in very permeable formations, where an aquifer capable of furnishing large volumes of water was present. However, unlike most water-supply wells, monitoring wells are quite often completed in very marginal water-producing zones. Pumping one or more well volumes of water (the amount of water stored in the well casing under nonpumping conditions) from a well built in low-yielding materials (Gibb and others, 1981) may present a serious problem if the well has a large diameter.

Figure 1-1 illustrates the amount of water in storage per foot of casing for different well casing diameters. Well casings with diameters of 2 and 6 inches will contain 0.16 and 1.47 gallons of water per foot of casing, respectively. Purging four well volumes from a well containing 10 feet of water would require removal of 6.4 gallons of water from a 2-inch well and 58.8 gallons of water from a 6-inch well. Under low-yielding conditions, it can take considerable time to recover enough water from the well to collect a sample (see Figure 1-2).

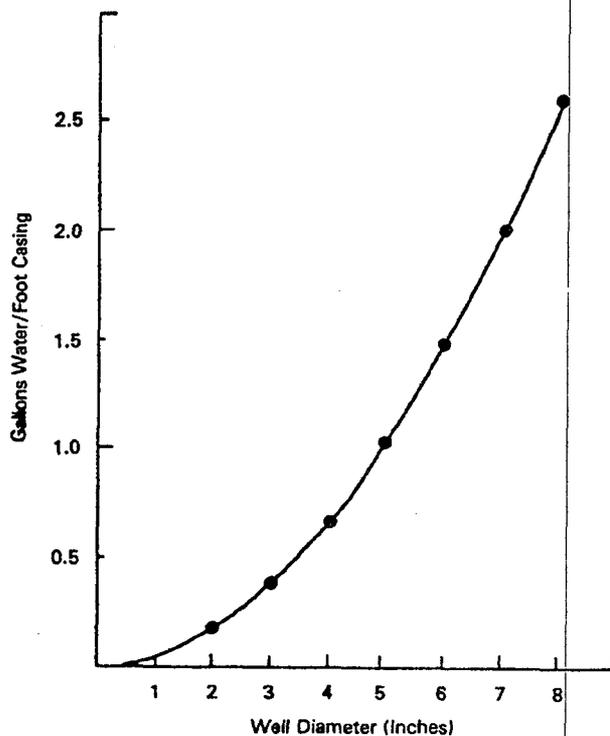
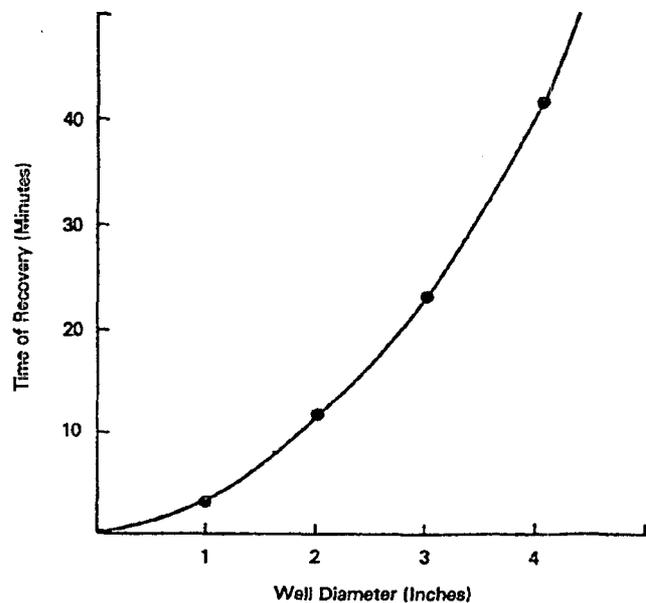


Figure 1-1. Volume of Water Stored Per Foot of Well Casing for Different Diameter Casings (from Rinaldo-Lee, 1983)



Assumptions: $K = 1 \times 10^{-6}$ cm/sec, well screen = 10', 10' of water above screen, 6' of water instantaneously removed

Figure 1-2. Time Required for Recovery After Slug of Water Removed (from Rinaldo-Lee, 1983)

In addition, when hazardous constituents are present in the ground water, the purged water must be properly disposed. Therefore, the quantity of water pumped from the well should be minimized for reasons of safety, as well as disposal cost. Cost of well construction also is a consideration. Wells less than 4 inches in diameter are much less expensive than large diameter wells in terms of both cost of materials and cost of drilling.

For these reasons and with the advent of a variety of commercially available small-diameter pumps (less than 2 inches OD) capable of lifting water over 100 feet, 2-inch ID wells have become the standard in monitoring well technology.

Large diameter wells can be useful in situations where monitoring may be followed by remedial actions involving reclamation and treatment of the contaminated ground water. In some instances, the "monitoring" well may become a "supply" well to remove contaminated water for treatment. Larger diameter wells also merit consideration when monitoring is required at depths of hundreds of feet and in situations where the additional strength of large diameter casing is needed. For sampling at several depths beneath one location, several monitoring wells have been nested in a single borehole (Johnson, 1983). This type of technique will require drilling a larger diameter hole to accommodate the multiple well casings. Again, the use of smaller diameter

casing provides advantages by allowing more wells to be nested in the borehole, thus easing construction and reducing drilling expenses.

Casing and Screen Material

The type of material used for a monitoring well can have a distinct effect on the quality of the water sample to be collected (Barcelona and others, 1985; Gillham and others, 1983; and Miller, 1982). The materials of choice should retain their structural integrity for the duration of the monitoring program under actual subsurface conditions. They should neither adsorb nor leach chemical constituents that would bias the representativeness of the samples collected.

Galvanized steel casing can impart iron, manganese, zinc, and cadmium to many waters, and steel casing may contribute iron and manganese to a sample. PVC pipe has been shown to release and adsorb trace amounts of various organic constituents to water after prolonged exposure (Miller, 1982). PVC solvent cements used to attach sections of PVC pipe also have been shown to release significant quantities of organic compounds.

Teflon^R and glass are among the most inert materials considered for monitoring well construction. Glass, however, is difficult and expensive to use under most field conditions. Teflon^R also is very expensive; with technological advances, Teflon^R-coated casings and screens may become available. Stainless steel also offers desirable properties for monitoring, but it too is expensive.

A reasoned strategy for ground-water monitoring must consider the effects of contaminated water on well construction materials as well. Unfortunately, there is limited published information on the performance of specific materials in varied hydrogeologic settings (Pettyjohn and others, 1981). The following is a preliminary ranking of commonly used materials exposed to different solutions representing the principal soluble species present in hazardous waste site investigations (Barcelona and others, 1984). They are listed in order of best to worst in terms of chemical resistance:

- Teflon^R
- Stainless Steel 316
- Stainless Steel 304
- PVC Type 1
- Lo-Carbon Steel
- Galvanized Steel
- Carbon Steel

Polyvinyl chloride (PVC Type I) is very chemically resistant except to low molecular weight ketones,

aldehydes, and chlorinated solvents. Generally, as the organic content of a solution increases, direct attack on the polymer matrix or solvent absorption, adsorption, or leaching may occur. This reaction, however, has not been observed with Teflon^R. Provided that sound construction practices are followed, Teflon^R can be expected to outperform all other casing and sampling materials (Barcelona and others, 1984).

Stainless steels are the most chemically resistant of the ferrous materials. Stainless steel, however, may be sensitive to the chloride ion, which can cause pitting corrosion, especially over long-term exposures under acidic conditions. Given the similarity in price, workability, and performance, the remaining ferrous materials (lo-carbon, galvanized steel, and carbon) provide little advantage over one another for casing/screen construction.

Significant levels of organic components found in PVC primers and adhesives (such as tetrahydrofuran, methylethylketone, cyclohexanone, and methylisobutylketone) were detected in well water several months after well installation (Sosebee and others, 1982). The presence of compounds such as these can mask the presence of other similar volatile compounds (Miller, 1982). Therefore, when using PVC and other similar materials, such as ABS, polypropylene, or polyethylene, for well construction, threaded joints are the preferred means for connecting sections together.

In many situations, it may be possible to compromise accuracy or precision for initial cost, depending on the objectives of the monitoring program. For example, if the contaminants of interest are already defined and they do not include substances that might bleed or sorb, it may be reasonable to use wells cased with a less expensive material.

Wells constructed of less than optimum materials might be used for sampling if identically fabricated wells are constructed in uncontaminated parts of the monitored aquifer to provide ground-water samples for use as "blanks" (Pettyjohn and others, 1981). Such blanks, however, may not adequately address problems of adsorption on, or leaching from, the casing material induced by contaminants in the ground water. It may be feasible to use two or more kinds of casing materials in the saturated zone and above the seasonal high water table, such as Teflon^R or stainless steel, and use a more appropriate material, such as PVC or galvanized steel casing, above static water level.

Trying to save money by compromising on material quality or suitability, however, may eventually increase program cost by creating the need for reanalysis, or

worse, monitoring well reconstruction. Each case requires careful consideration and the analytical laboratory should be fully aware of the construction materials used.

Care also must be taken in preparing the casing and well screen materials prior to installation. At a minimum, materials should be washed with detergent and rinsed thoroughly with clean water. Steam-cleaning and high pressure, hot water cleaners provide excellent cleaning of cutting oils and lubricants left on casings and screens after their manufacture (particularly for metal casing and screen materials). To ensure that these and other sampling materials are protected from contamination prior to placement down-hole, materials should be covered (with plastic sheeting or other material), and kept off the ground.

All wells should allow free entry of water. The water produced should be as clear and silt-free as possible. For drinking water supplies, sediment in the raw water can create additional pumping and treatment costs and lead to the general unpalatability of the water. With monitoring wells, sediment-laden water can greatly lengthen filtering time and create chemical interference in sample analyses.

Commercially manufactured well screens are preferred for monitoring wells so long as the screen slot size is appropriate. Sawed or torch-cut casing may be satisfactory in deposits where medium to coarse sand or gravel predominate. In formations where fine sand, silt, and clay predominate, sawed or torch-cut slots will be too large to retain the aquifer materials, and the well may clog or fill with sediment. The practice of sawing slots in PVC pipe should be avoided in monitoring situations where organic chemicals are of concern, because this procedure exposes fresh surfaces of PVC, increasing the possibility of releasing compound ingredients or reaction products.

It may be helpful to have several slot-sized well screens on site so that the proper manufactured screen and slots can be placed in the hole after the aquifer materials have been inspected. Gravel pack of a size compatible with the selected screen slot size will further help retain the finer fractions of material and allow free entry of water into the well by creating a zone of higher permeability around the well screen.

For natural-packed wells, where relatively homogeneous, coarse materials predominate, a slot size should be selected based on the effective size and uniformity coefficient of the formation materials. The effective size is equivalent to the sieve size that will retain 90 percent (or passes 10 percent) of the formation

material; the uniformity coefficient is the ratio of the sieve size that will retain 40 percent (or pass 60 percent) of the formation material to the effective size (Aller and others 1989). If an artificial pack is used, a uniform gravel-pack size that is from three to five times the 50 percent retained size of the formation and a screen size that will retain at least 90 percent of the pack material should be selected (Walker, 1974). The gravel-pack should be composed of clean, uniform quartz sand.

The gravel-pack should be placed carefully to avoid bridging in the hole and to allow uniform settling around the screen. A tremie pipe can be used to guide the sand to the bottom of the hole and around the screen. The pipe should be lifted slowly as the annulus between the screen and borehole as the borehole fills. If the depth of water standing in the annulus is not great, the sand can be simply poured from the surface. The volume of sand required to fill the annulus to the desired depth (usually about 1 foot above the top of the screen) should be calculated. Field measurements should be taken to confirm that the pack has reached this level before backfilling or sealing procedures start.

Screen Length and Depth of Placement

The length of screen and the depth at which it is placed depend, to a large degree, on the behavior of the contaminant as it moves through the unsaturated and saturated zones, and on the goal of the monitoring program. When monitoring an aquifer used as a water supply, the entire thickness of the water-bearing formation could be screened (just as a production well might be). In regional aquifer studies, production wells commonly are used for sampling. Such samples would provide water integrated over the entire thickness of the water-bearing zone(s), and would be similar in quality to what would be found in a drinking-water supply.

When specific depth intervals must be sampled at one location, vertical nesting of wells is common. This technique is often necessary when the saturated zone is too thick to adequately monitor with one long-screened section (which would dilute the collected sample). Since contaminants tend to stratify within the saturated zone, collecting a sample integrated over a thick zone will provide little or no information on the depth and concentration that a contaminant may have reached. Furthermore, nested wells provide information on the water level or potential that exists at each well screen. These data are essential to an understanding of the vertical component of flow.

Screen lengths of 1 to 2 feet are common in detailed plume geometry investigations. Thick aquifers would require that several wells be completed at different depth intervals. In such situations (and depending on

the magnitude of the aquifers saturated thickness), screen lengths of no more than 5 to 10 feet should be used. Monitoring wells can be constructed in separate holes placed closely together or in one larger diameter hole, as shown in Figure 1-3. Vertical movement of contaminants in the well bore before and after well completion may be difficult to prevent since it is difficult to seal several wells in one hole. Thus, multiple holes may need to be drilled to ensure well integrity. Specially constructed installations have been developed to sample a large number of points vertically over short intervals (Morrison and Brewer, 1981; Pickens, 1981; and Torstensson, 1984; Figures 1-4 and 1-5).

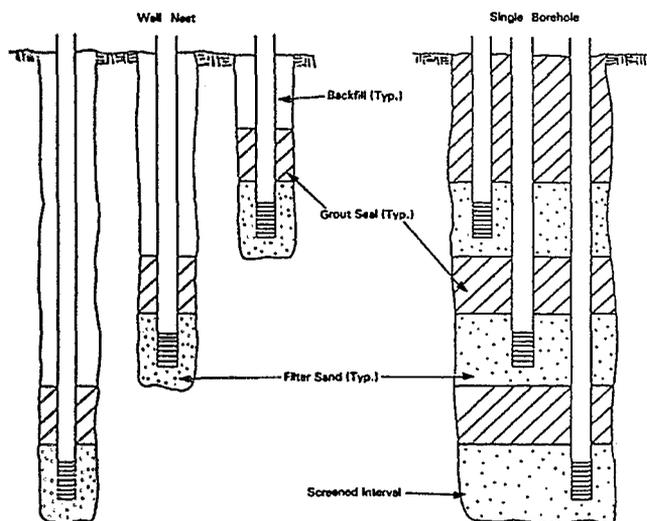


Figure 1-3. Typical Multiwell Installations (from Johnson, 1983)

In other situations, only the first water-bearing zone encountered will require monitoring (for example, when monitoring near a potential contaminant source in a relatively impermeable glacial till). The "aquifer" or zone of interest in such an instance may be only several inches to a few feet thick. Screen length should be limited to 1 to 2 feet in these cases to minimize siltation problems from surrounding fine-grained materials and possible dilution effects from water contributed by uncontaminated zones.

Because of the chemical reactions that occur when ground water contacts the atmosphere, particularly when dealing with volatile compounds, the screened section should not be aerated. Generally, well depth should assure that the screened section is always fully submerged. The design should consider fluctuations in the elevation of the top of the saturated zone caused by seasonal variations or human-induced changes.

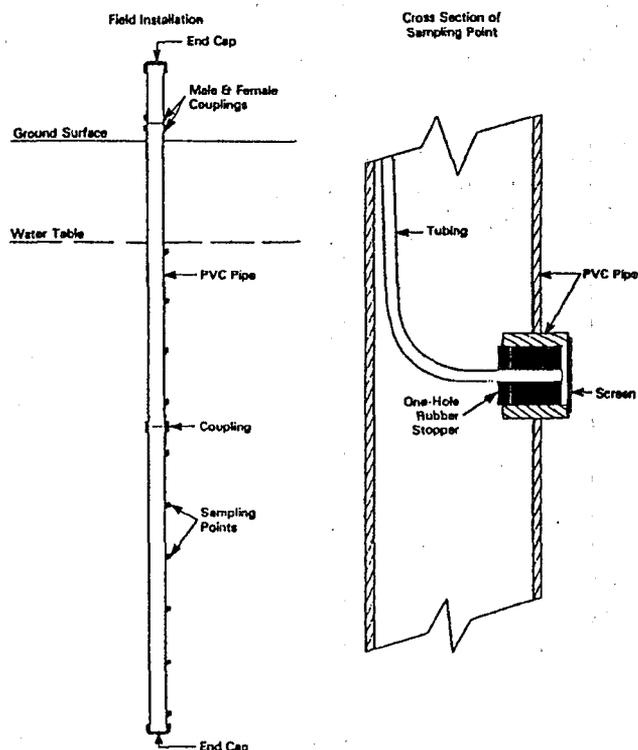


Figure 1-4. Schematic Diagram of a Multilevel Sampling Device (from Pickens and others, 1981)

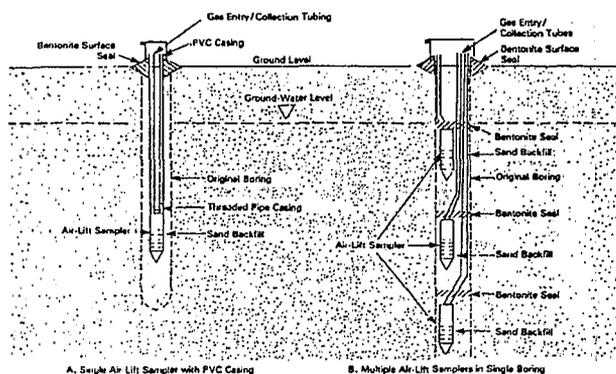


Figure 1-5. Single (a) and Multiple (b) Installation Configurations for an Air-Lift Sampler (from Morrison and Brewer, 1981)

Monitoring for contaminants with densities different than water demands special attention. In particular, low density organic compounds, such as gasoline, will float on the ground-water surface (Gillham and others, 1983). Monitoring wells constructed to detect floating contaminants should contain screens that extend above the zone of saturation so that these lighter substances can enter the well. The screen length and position must

accommodate the magnitude and depth of variations in water-table elevation. However, the thickness of floating products in the well does not necessarily indicate the thickness of the product in the aquifer.

Sealing Materials and Procedures

It is critical that the screened part of each monitoring well access ground water from a specific depth interval. Vertical movement of ground water in the vicinity of the well can greatly influence sample quality (Keith and others, 1982). Rainwater can infiltrate backfill, potentially diluting or contaminating samples; vertical seepage of leachate along the well casing will also produce unrepresentative samples (particularly important in multilevel installations such as in Figures 1-3, 1-4, and 1-5). Even more importantly, the creation of a conduit in the annulus of the monitoring well that could contribute to or hasten the spread of contamination is to be strictly avoided. Several methods have been employed successfully to isolate contaminated zones during the drilling process (Burkland and Raber, 1983; Perry and Hart, 1985).

Monitoring wells are usually sealed with neat cement grout, dry bentonite (powdered, granulated, or pelletized), or bentonite slurry. Well seals usually are installed at two places within the annulus: one just above the screened interval and the other at the ground surface to inhibit downward leakage of surface contaminants.

Bentonite traditionally has been considered to provide a much better seal than cement. However, recent investigations on the use of clay liners for hazardous waste disposal have shown that some organic compounds migrate through bentonite with little or no attenuation (Brown, and others, 1983). Therefore, cement may offer some benefits over bentonite.

Bentonite most often is used as a down-hole seal to prevent vertical migration within the well annulus. When bentonite must be placed below the water table (or where water has risen in the borehole), it is recommended that a bentonite slurry be tremied down the annulus to fill the hole from the bottom upward. In collapsible material conditions, where the borehole has collapsed to a point just above the water table, dry bentonite (granulated or pelletized works best) can be poured down the hole.

Bentonite clay has appreciable ion-exchange capacity, which may interfere with the chemistry of collected samples when the seal is adjacent to the screen or well intake. When improperly placed, cement grout has been known to seriously affect the pH of sampled water. Therefore, special attention and care should be exercised

during placement of a down-hole seal. Approximately 1 foot (at a minimum) of gravel-pack or naturally collapsed material should extend above the top of the well screen to ensure that the sealing materials do not migrate downward into the well screen. If the sealing material is too watery before being placed down the hole, sealing materials may settle or migrate into the gravel-pack or screened area, and the fine materials in the seal may penetrate the natural or artificial pack.

While a neat cement (sand and cement, no gravel) grout is often recommended, especially for surface sealing, shrinkage and cracking of the cement upon curing and weathering can create an improper seal. Shrink-resistant cement (such as Type K Expansive Cement) and mixtures of small amounts of bentonite with neat cement have been used successfully to help prevent cracking.

Development

Development is a facet of monitoring well installation that often is overlooked. During the drilling process, fine-grained materials smear on the sides of the borehole, forming a mud "cake" that reduces the hydraulic conductivity of the materials opposite the screened part of the well. To facilitate entry of water into the monitoring well (a particularly important factor for low-yielding geologic materials), this mud cake must be broken down and the fine-grained materials removed from the well or well bore. Development also removes fluids, primarily water, which are introduced to the water-bearing formations during the drilling process.

Additionally, monitoring wells must be developed to provide water free of suspended solids for sampling. When sampling for metal ions and other inorganic constituents, water samples must be filtered and preserved at the well site at the time of sample collection. Improperly developed monitoring wells will produce samples containing suspended sediments that will both bias the chemical analysis of the collected samples and frequently cause clogging of the field filtering mechanisms.

The time and money spent for this important procedure will expedite sample filtration and result in samples more representative of water contained in the formation being monitored. The time saved in field filtration alone will more than offset the cost of development.

Successful development methods include bailing, surging, and flushing with air or water. The basic principle behind each method is to create reversals of flow in and out of the well (and/or borehole), which tend to break down the mud cake and draw the finer materials into the hole for removal. This process also aids in removing the finer fraction of materials in proximity to the borehole,

leaving behind a "natural" pack of coarser-grained materials.

Years ago, small-diameter well development most commonly was achieved through use of a bailer. The bailer was about the only "instrument" that had been developed for use in such wells. Rapidly dropping and retrieving the bailer in and out of the water caused a back-and-forth action of water in the well, moving some of the more loosely bound fine-grained materials into the well where they could be removed.

Depending on the depth of water in the well, the length of the well screen, and the volume of water the bailer could displace, this method was not always very efficient. "Surge blocks," which could fit inside 2-inch diameter wells, provided some improvement over bailing techniques. Such devices are simply plungers that, when moved vigorously up and down, transfer that energy to an in-and-out action on the water near the well screen. Surge blocks have the potential to move larger quantities of water with higher velocities, but they pose some risk to the well casing and screen if the surge block fits too tightly or if the up-and-down action becomes too vigorous. Improved surge block design has been the subject of some recent investigation (Schalla and Landick, 1985).

In more productive aquifers, "overpumping" has been a popular method for well development. With this method, a pump is alternately turned on (usually at a slightly higher rate than the well can sustain) and off to simulate a surging action in the well. A problem with this method is that overpumping does not create as pronounced an outward movement of water as does surging. Overpumping may tend to bridge the fine and coarse materials, limiting the movement of the fine materials into the well and thereby limiting the effectiveness of the method.

Pumping with air also has been used effectively (Figure 1-6). Better development has been accomplished by attaching differently shaped devices to the end of an airline to force the air out into the formation. Figure 1-7 shows an example. Such a device causes a much more vigorous action on the movement of material in proximity to the well screen while also pushing water to the ground surface.

Air development techniques may expose field crews to hazardous constituents when highly contaminated groundwater is present. The technique also may cause chemical reactions with species present in the groundwater, especially volatile organic compounds. Care also must be taken to filter the injected air to prevent contamination of the well environment with oil and other lubricants present in the compressor and airlines.

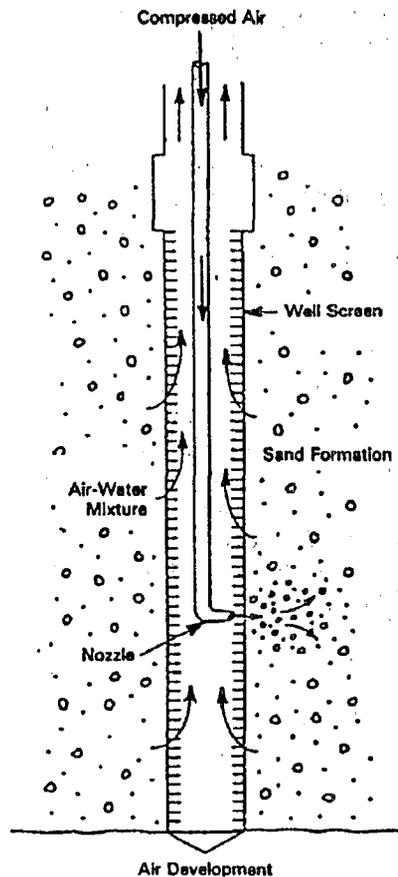


Figure 1-6. Well Developments with Compressed Air

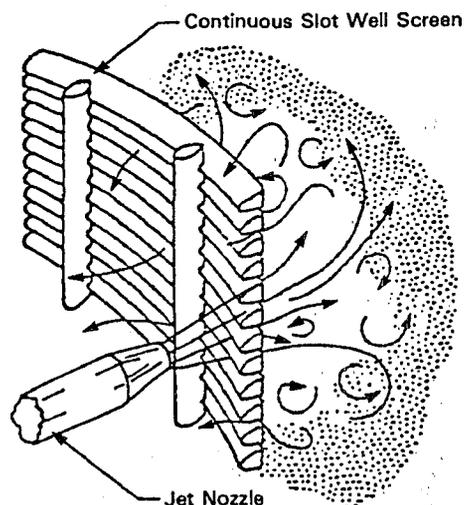


Figure 1-7. The Effects of High-Velocity Jetting Used for Well Development through Openings in a Continuous-Slot Well Screen

Development procedures for monitoring wells in relatively unproductive geologic materials are somewhat limited. Due to the low hydraulic conductivity of the materials, surging of water in and out of the well casing is extremely difficult. Also, when the well is pumped, the entry rate of the water is inadequate to effectively remove fines from the well bore and the gravel-pack material outside the well screen.

Where an open borehole can be sustained in this type of geologic setting, clean water can be circulated down the well casing, out through the screen, and back up the borehole (Figure 1-8). Relatively high water velocities can be maintained and the mud cake from the borehole wall can be broken down effectively and removed. Because of the low hydraulic conductivity of the geologic materials outside the well, only a small amount of water will penetrate the formation being monitored. This development procedure can be done before and after placement of a gravel-pack but must be conducted before a well has been sealed. After the gravel-pack has been installed, water should not be circulated too quickly or the gravel-pack will be lifted out of the borehole. Immediately following development, the well should be sealed, backfilled, and pumped for a short period to stabilize the formation around the outside of the screen and to ensure that the well will produce fairly clear water.

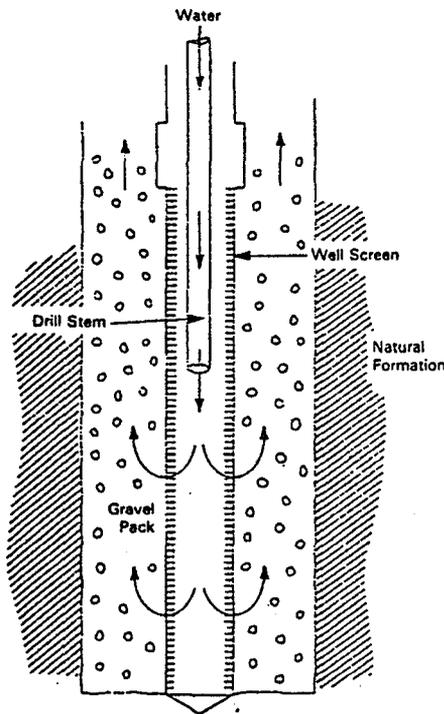


Figure 1-8. Well Development by Back-Flushing with Water

Security

For most monitoring well installations, some precautions must be exercised to protect the surface portions of the well from damage. In many instances, inadvertent vehicular accidents do occur; also, monitoring well installations seem particularly vulnerable to grass mowers. Vandalism is often a major concern, from spontaneous "hunters" looking for a likely target to premeditated destruction of property associated with an unpopular operation. Several simple solutions can be employed to help minimize the damage due to accidental collisions. However, outwitting the determined vandal may be an impossible undertaking and certainly an expensive one.

The basic problem in maintaining the physical condition of any monitoring well is anticipating the hazards that might befall that particular installation. Some situations may call for making the well highly visible whereas others may require keeping the well inconspicuous.

Where the most likely problem is one of vehicular contact, be it mowers, construction traffic, or other types of two-, three-, or four-wheeled traffic, the first thing that can be done is to make the top of the well easy to see. It should extend far enough above ground to be visible above grass, weeds, or small shrubs. If that is not practical, use a "flag" that extends above the well casing. A flag is also helpful for periods when leaves or snow have buried low-lying objects.

The well casing should also be painted a bright color (orange and yellow are the most visible). This not only makes the well more visible but also protects metal casing material from rusting. Care should be taken to prevent paint from getting inside the well casing or in threaded fittings that may contact sampling equipment.

The owners/operators of the site being monitored should also know the location of each installation. They should receive maps clearly and exactly indicating the position of the wells, and their employees should be informed of the importance of those installations, the cost associated with them, and the difficulty involved in replacement.

The segment of the well that extends above the ground also can be reinforced, particularly if the well is constructed of PVC or Teflon[®]. The well could be constructed such that only the portion of the well above the water table is metal. In this manner, the integrity of the sample is maintained as ground water contacts only inert material, and the physical condition of the well is maintained as the upper metal portion is better able to withstand impact.

There are two arguments to consider when constructing

a well in this manner. The arguments focus on the weak point in the well construction: at or near the juncture of the metal and nonmetal casings. One argument suggests that a longer section of metal casing is superior because its additional length in the ground provides more strength. Thus, a break is less likely to occur (although the casing is likely to be bent). The other argument suggests that should a break in the casing occur, a shorter length of metal casing is superior because a break nearer to ground surface is easier to repair. Each argument has its merits; only experience with site conditions is likely to produce the best solution.

The use of "well protectors" is another popular solution that involves the use of a larger diameter steel casing placed around the monitoring well at the ground surface and extending several feet below ground (Figure 1-9). The protectors are usually seated in the cement surface seal to a depth below the frost line.

Commonly, well protectors are equipped with a locking cap, which ensures against tampering with the inside of the well. Dropping objects down the well may clog the well screen or prohibit the sampling device from reaching water, and the quality of the ground water may be altered, particularly where small quantities (perhaps drops) of an organic liquid may be sufficient to completely contaminate the well.

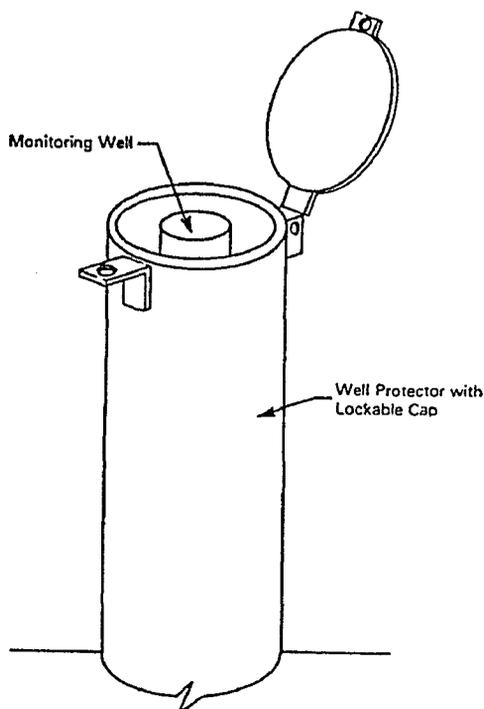


Figure 1-9. Typical Well Protector Installation

Problems associated with vandalism run from simple curiosity to outright wanton destruction. Obviously, sites within secured, fenced areas are less likely to be vandalized. However, there is probably no sure way to deter the determined vandal, short of posting a 24-hour guard. In such situations, well protectors are a must. The wells should be kept as inconspicuous as possible. However, the benefits of "hiding" monitoring wells must be weighed against the costs of delays in finding them for sampling and the potential costs for repairs or maintenance on untried security designs.

In some situations, it might be a good policy to notify the public of the need for the monitoring wells. Properly asserting that each well serves an environmental monitoring purpose and that the wells have been constructed to ensure public well-being may create a civic conscience that would help to minimize vandalism.

As with all the previously mentioned monitoring well components, no single solution will best meet every monitoring situation. Knowledge of the social, political, and economic conditions of the geographic area and circumstances surrounding the need for ground-water monitoring will dictate, to a large degree, the type of well protection needed.

Monitoring Well Drilling Methods

As might be expected, different drilling techniques can influence the quality of a ground-water sample. This applies to the drilling method employed (e.g., augered, driven, or rotary), as well as the driller. There is no substitute for a conscientious driller willing to take the extra time and care necessary to complete a good monitoring well installation.

Among the criteria used to select an appropriate drilling method are the following factors, listed in order of importance:

1. Hydrologic information
 - a. type of formation
 - b. depth of drilling
 - c. depth of desired screen setting below the top of the zone of saturation
2. Types of pollutants expected
3. Location of drilling site, i.e., accessibility
4. Design of monitoring well
5. Availability of drilling equipment

Table 1-1 summarizes several different drilling methods, and their advantages and disadvantages when used for monitoring well construction. Several excellent publications are referenced for detailed discussions (Campbell and Lehr, 1973; Fenn and others, 1977;

Method	Drilling Principle	Advantages	Disadvantages
Drive Point	1.25 to 2 inch ID casing with pointed screen mechanically driven to depth.	<p>Inexpensive.</p> <p>Easy to install, by hand if necessary.</p> <p>Water samples can be collected as drilling proceeds.</p> <p>Depending on overburden, a good seal between casing and formation can be achieved.</p>	<p>Difficult to sample from smaller diameter drive points if water level is below suction lift. Bailing possible.</p> <p>No formation samples can be collected.</p> <p>Limited to fairly soft materials. Hard to penetrate compact, gravelly materials.</p> <p>Hard to develop. Screen may become clogged if thick clays are penetrated.</p> <p>PVC and Teflon casing and screen are not strong enough to be driven. Must use metal construction materials which may influence some water quality determinations.</p>
Auger, Hollow- and Solid-stem	Successive 5-foot flights of spiral-shaped drill stem are rotated into the ground to create a hole. Cuttings are brought to the surface by the turning action of the auger.	<p>Inexpensive.</p> <p>Fairly simple operation. Small rigs can get to difficult-to-reach areas. Quick set-up time.</p> <p>Can quickly construct shallow wells in firm, noncavey materials.</p> <p>No drilling fluid required.</p> <p>Use of hollow-stem augers greatly facilitates collection of split-spoon samples.</p> <p>Small-diameter wells can be built inside hollow-stem flights when geologic material are cavey.</p>	<p>Depth of penetration limited, especially in cavey materials. Maximum depths 150 feet.</p> <p>Cannot be used in rock or well-cemented formations. Difficult to drill in cobbles/boulders.</p> <p>Log of well is difficult to interpret without collection of split spoons due to the lag time for cuttings to reach ground surface.</p> <p>Vertical leakage of water through borehole during drilling is likely to occur.</p> <p>Solid-stem limited to fine grained, unconsolidated materials that will not collapse when unsupported.</p> <p>With hollow-stem flights, heaving materials can present a problem. May need to add water down auger to control heaving or wash materials from auger before completing well.</p>
Jetting	Washing action of water forced out of the bottom of the drill rod clears hole to allow penetration. Cuttings brought to surface by water flowing up the outside of the drill rod.	<p>Inexpensive. Driller often not needed for shallow holes.</p> <p>In firm, noncavey deposits where hole will stand open, well construction fairly simple.</p>	<p>Somewhat slow, especially with increasing depth.</p> <p>Extremely difficult to use in very coarse materials, i.e., cobbles/boulders.</p> <p>A water supply is needed that is under enough pressure to penetrate the geologic materials present.</p> <p>Difficult to interpret sequence of geologic material from cuttings.</p> <p>Maximum depth 150 feet, depending on geology and water pressure capabilities.</p>
Cable-tool (Percussion)	Hole created by dropping a heavy "string" of drill tools into well bore, crushing materials at bottom. Cuttings are removed occasionally by bailer. Generally, casing is driven just ahead of the the bottom of the hole; a hole greater than 6 inches in diameter is usually made.	<p>Can be used in rock formations as well as unconsolidated formations.</p> <p>Fairly accurate logs can be prepared from cuttings if collected often enough.</p> <p>Driving a casing ahead of hole minimizes cross-contamination by vertical leakage of formation waters.</p> <p>Core samples can be obtained easily.</p>	<p>Requires an experienced driller.</p> <p>Heavy steel drive pipe used to keep hole open and drilling "tools" can limit accessibility.</p> <p>Cannot run some geophysical logs due to presence of drive pipe.</p> <p>Relatively slow drilling method.</p>

Table 1-1. Advantages and Disadvantages of Selected Drilling Methods for Monitoring Well Construction

Method	Drilling Principle	Advantages	Disadvantages
Hydraulic Rotary	Rotating bit breaks formation; cuttings are brought to the surface by a circulating fluid (mud). Mud is forced down the bit, and up the annulus between the drill stem and hole wall. Cuttings are removed by settling in a "mud pit" at the ground surface and the mud is circulated back down the drill stem.	Drilling is fairly quick in all types of geologic materials. Borehole will stay open from formation of a mud wall on sides of borehole by the circulating drilling mud. Eases geophysical logging and well construction. Geologic cores can be collected. Virtually unlimited depths possible.	Expensive, requires experienced driller and fair amount of peripheral equipment. Completed well may be difficult to develop, especially small-diameter wells, because of mud wall on borehole. Geologic logging by visual inspection of cuttings is fair due to presence of drilling mud. Thin beds of sand, gravel, or clay may be missed. Presence of drilling mud can contaminate water samples, especially the organic, biodegradable muds. Circulation of drilling fluid through a contaminated zone can create a hazard at the ground surface with the mud pit and cross-contaminate clean zones during circulation.
Reverse Rotary	Similar to Hydraulic Rotary method except the drilling fluid is circulated down the borehole outside the drill stem and is pumped up the inside, just the reverse of the normal rotary method. Water is used as the drilling fluid, rather than a mud, and the hole is kept open by the hydrostatic pressure of the water standing in the borehole.	Creates a very "clean" hole, not dirtied with drilling mud. Can be used in all geologic formations. Very deep penetrations possible. Split-spoon sampling possible.	A large water supply is needed to maintain hydrostatic pressure in deep holes and when highly conductive formations are encountered. Expensive-experienced driller and much peripheral equipment required. Hole diameters are usually large, commonly 18 inches or greater. Cross-contamination from circulating water likely. Geologic samples brought to surface are generally poor, circulating water will "wash" finer materials from sample.
Air Rotary	Very similar to Hydraulic Rotary, the main difference being that air is used as the primary drilling fluid as opposed to mud or water.	Can be used in all geologic formations; most successful in highly fractured environments. Useful at any depth. Fairly quick. Drilling mud or water not required.	Relatively expensive. Cross-contamination from vertical communication possible. Air will be mixed with water in the hole and that which is blown from the hole, potentially creating unwanted reactions with contaminants; may affect "representative" samples. Cuttings and water blown from the hole can pose a hazard to crew and surrounding environment if toxic compounds encountered. Organic foam additives to aid cuttings removal may contaminate samples.
Air-Percussion Rotary or Downhole-Hammer	Air Rotary with a reciprocating hammer connected to the bit to fracture rock.	Very fast penetrations. Useful in all geologic formations. Only small amounts of water needed for dust and bit temperature control. Cross contamination potential can be reduced by driving casing.	Relatively expensive. As with most hydraulic rotary methods, the rig is fairly heavy, limiting accessibility. Vertical mixing of water and air creates cross-contamination potential. Hazard posed to surface environment if toxic compounds encountered. Organic foam additives for cuttings' removal may contaminate samples.

Table 1-1. Continued

Johnson, Inc., 1972; and Scalf and others, 1981). The table also gives a concept of the advantages and disadvantages that need to be considered when choosing a drilling technique for different site and monitoring situations (see, also, Lewis, 1982; Luhdorff and Scalmanini, 1982; Minning, 1982; and Voytek, 1983).

Hollow-stem augering is one of the most desirable drilling methods for constructing monitoring wells. No drilling fluids are used and disturbance of the geologic materials penetrated is minimal. Depths are usually limited to no more than 150 feet. Typically, auger rigs are not used when consolidated rock must be penetrated.

In formations where the borehole will not stand open, the monitoring well can be constructed inside the hollow-stem auger prior to its removal from the hole. Generally, this limits the diameter of the well that can be built to 4 inches. The hollow-stem has an added advantage in offering the ability to collect continuous in situ geologic samples without removal of the auger sections.

The solid-stem auger is most useful in fine-grained, unconsolidated materials that will not collapse when unsupported. The method is similar to the hollow-stem except that the auger flights must be removed from the hole to allow the insertion of the well casing and screen. Cores cannot be collected when using a solid-stem. Therefore, geologic sampling must rely on cuttings that come to the surface, which is an unreliable method because the depth from which the cuttings are derived is not precisely known.

Cable-tool drilling is one of the oldest methods used in the water well industry. Even though the rate of penetration is rather slow, this method offers many advantages for monitoring well construction. With the cable-tool, excellent formation samples can be collected and the presence of thin permeable zones can be detected. As drilling progresses, a casing is normally driven and this provides an ideal temporary casing within which to construct the monitoring well.

In air-rotary drilling, air is forced down the drill stem and back up the borehole to remove the cuttings. This technique has been found to be particularly well suited to drilling in fractured rock. If the monitoring is intended for organic compounds, the air must be filtered to ensure that oil from the air compressor is not introduced into the formation to be monitored. Air-rotary should not be used in highly contaminated environments because the water and cuttings blown out of the hole are difficult to control and can pose a hazard to the drill crew and observers. Where volatile compounds are of interest, air-rotary can volatilize them and cause water samples

to be unrepresentative of in situ conditions. The use of foam additives to aid cuttings' removal presents the opportunity for organic contamination of the monitoring well.

Air-rotary with percussion hammer increases the effectiveness of air-rotary for materials likely to cave and highly creviced formations. Addition of the percussion hammer gives air-rotary the ability to drive casing, which reduces the loss of air circulation in fractured rock and aids in maintaining an open hole in soft formations. The capability to construct monitoring wells inside the driven casing, prior to its being pulled, adds to the appeal of air-percussion. However, the problems with contamination and crew safety must be considered.

Reverse circulation rotary drilling has limited application for monitoring well construction. Reverse circulation rotary requires that large quantities of water be circulated down the borehole and up the drill stem to remove cuttings. If permeable formations are encountered, significant quantities of water can move into the formation to be monitored, thus altering the quality of the water to be sampled.

Hydraulic or "mud" rotary is probably the most popular method used in the water well industry. Hydraulic rotary, however, presents some disadvantages for monitoring well construction. In hydraulic rotary technique, a drilling mud (usually bentonite) is circulated down the drill stem and up the borehole to remove cuttings. The mud creates a wall on the side of the borehole that must be removed from the screened area by development procedures. With small diameter wells, the drilling mud is not always completely removed. The ion-exchange potential of most drilling muds is high and may effectively reduce the concentration of trace metals in water entering the well. In addition, the use of biodegradable, organic drilling muds, rather than bentonite, can introduce organic components to water sampled from the well.

Most ground-water monitoring wells will be completed in glacial or unconsolidated materials, and generally will be less than 75 feet in depth. In these applications, hollow-stem augering usually will be the method of choice. Solid-stem auger, cable-tool, and air-percussion also offer advantages depending on the geology and contaminant of interest.

Geologic Samples

Permit applications for disposal of waste materials often require that geologic samples be collected at the disposal site. Investigations of ground-water movement and contaminant transport also should include the collection of geologic samples for physical inspection and testing.

Stratigraphic samples are best collected during monitoring well drilling.

Samples can be collected continuously, at each change in stratigraphic unit, or, in homogeneous materials, at regular intervals. These samples may later be classified, tested, and analyzed for physical properties, such as particle-size distribution, textural classification, and hydraulic conductivity, and for chemical analyses, such as ion-exchange capacity, chemical composition, and specific parameter leachability.

Probably the most common method of material sampling is a "split-spoon" sampler. This device consists of a hollow cylinder, 2 inches in diameter, that is 12 or 18 inches long, and split in half lengthwise. The halves are held together with threaded couplings at each end; the top end attaches to the drill rod, and the bottom end is a drive shoe (Figure 1-10a). The sampler is lowered to the bottom of the hole and driven ahead of the hole with a weighted "hammer" striking an anvil at the upper end of the drill rod. The sample is forced up the inside of the hollow tube and is held in place with a basket trap or flap valve. The trap or valve allows the sample to enter the tube but not exit, although retention of noncohesive, sandy material in the tube is often difficult. After the sampler is withdrawn from the hole, the sample is removed by unscrewing the couplings and separating the collection tube.

Another common sampler is the thin wall tube or "Shelby" tube. These tubes are usually 2 to 5-1/2 inches in diameter and about 24 inches long. The cutting edge of the tube is sharpened and the upper end is attached to a coupling head by means of cap screws or a retaining pin (Figure 1-10b). A Shelby tube has a minimum ratio of wall area to sample area and creates the least disturbance to the sample of any drive-type sampler in current use (for hydraulic conductivity tests, minimal disturbance is critical). After retraction, the tube is disconnected from the head and the sample is forced from the tube with a jack or press. If sample preservation is a major concern, the tube can be sealed and shipped to the laboratory.

Apart from permit requirements, material samples are very helpful for deciding at what depth to complete a monitoring well. Unexpected changes encountered during drilling can alter preconceived ideas concerning the local ground-water flow regime. In many instances, the driller will be able to detect a variation in the formation by a change in penetration rate, sound, or "feel" of the drilling rig. However, due to the lag time for cuttings to come to the surface and the amount of mixing the cuttings may undergo as they come up the

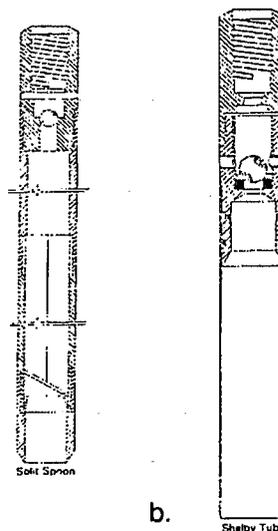


Figure 1-10. Cross-Sectional Views of (a) Split Spoon and (b) Shelby Tube Samplers (from Mobile Drilling Co., 1972)

borehole, the only way to exactly determine the character of the subsurface is to stop drilling and collect a sample.

Case History

Several different types of monitoring wells were constructed during the investigation of a volatile organic contaminant plume in northern Illinois (Wehrmann, 1984). A brief summary of the types of wells employed and the reasons for their use helps illustrate how an actual ground-water quality monitoring problem was approached.

During the final weeks of a 1-year study of nitrate in ground water in north-central Illinois, the presence of several organic compounds was detected in the drinking water of all five homes sampled within a large rural residential subdivision. The principal compound, trichloroethylene (TCE), was present in concentrations ranging from 50 to 1,000 micrograms per liter ($\mu\text{g}/\text{L}$). All the homes in the subdivision used private wells, 65 to 75 feet deep, that tapped a surficial sand and gravel deposit. Figure 1-11 shows a geologic cross section of the study area.

Two immediate concerns needed to be addressed. First, how many other water wells were affected and, second, what was the contaminant source? Early thoughts connected the TCE to the contamination potential of the large number of septic systems in the subdivision. Earlier work (Wehrmann, 1983) had established a south-southwest direction of ground-

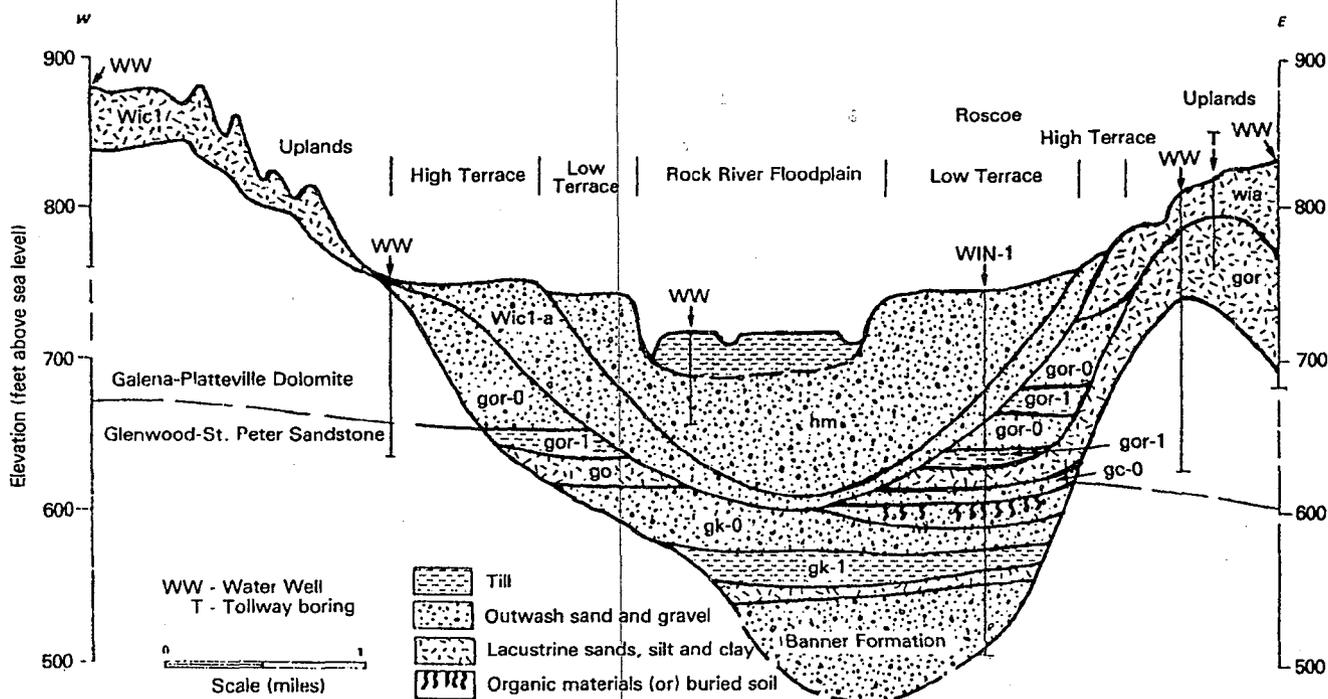


Figure 1-11. East-West Cross Section Across Rock River Valley at Roscoe (from Berg and others, 1981)

water flow beneath the subdivision. Because the area upgradient of the subdivision was primarily farmland, several monitoring wells were placed in that area to help confirm or deny the possibility that the septic systems were the source of the TCE.

Five "temporary" monitoring wells were constructed upgradient of the affected subdivision. Original plans called for driving a 2-inch diameter sandpoint to depths from 40 to 70 feet. Water samples would be collected at 10-foot intervals as the point was driven. Once 70 feet was reached, the sandpoint would be pulled, the hole properly abandoned, and the point driven at a new sampling location. The first hole was to be placed north (upgradient) of a domestic well found to be highly contaminated, and additional holes were to be placed successively in an upgradient direction across the field. In this manner, ground-water samples could be collected quickly at many depths and locations, the well materials recovered, and the field left relatively undisturbed.

Once drilling commenced, however, it became clear that driving sandpoints into the coarse sand and gravel

was not possible. Consequently, an air-percussion rig was brought on site and a new approach was established. A 4-inch diameter screen, 2 feet long and with a drive shoe, was welded to a 4-inch diameter steel casing. This assembly was driven by air hammer to the desired sampling depth. The bottom of the drive shoe, being open, forced the penetrated geologic materials into the casing and screen. These materials were then removed by air rotary once the desired depth was reached. All well construction materials were steam-cleaned prior to use to avoid cross-contamination. Figure 1-12 shows the locations of the temporary well sites and the analytical results for TCE from samples bailed at depths of 40 and 50 feet.

The temporary sampling program revealed that the contaminant source was outside of the subdivision. Due to the construction and sampling methods employed for these wells, emphasis was not placed on the quantitative aspects of the sampling results; however, important qualitative conclusions were made. The temporary wells confirmed the presence of VOCs directly upgradient of the subdivision and provided information for the

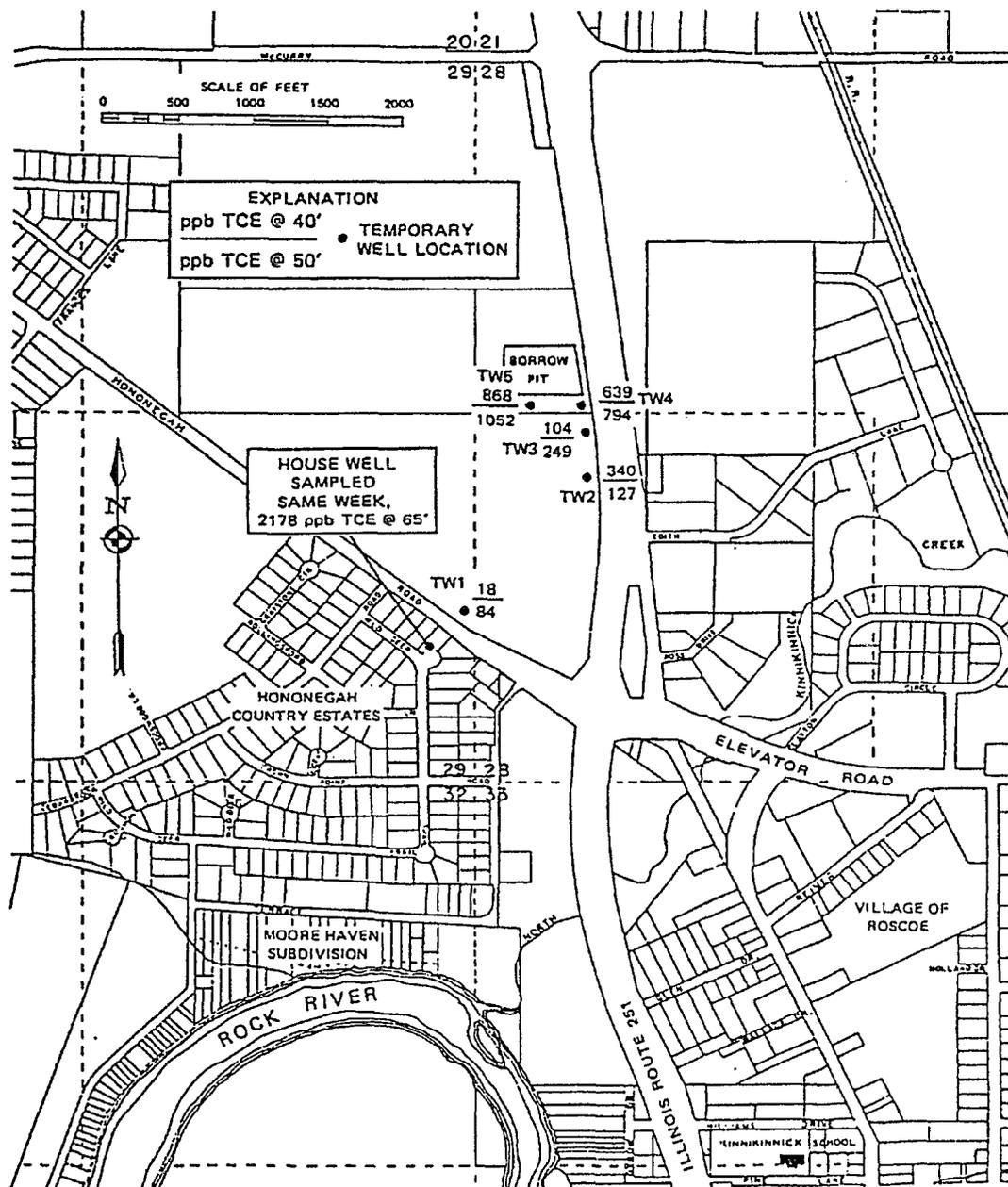


Figure 1-12. Locations and TCE Concentrations for Temporary Monitoring Wells at Roscoe, Illinois (from Wehrmann, 1984)

subsequent location and depth of nine permanent monitoring wells.

Due to the problems associated with organic compound leachability and adsorption from PVC casing and screen, flush-threaded stainless steel casing and screen, 2 inches in diameter, were used for the permanent monitoring wells. The screens were 2 feet long with 0.01-inch wire-wound slot openings. All materials

associated with the monitoring well construction, including the drill rig, were steam-cleaned prior to the commencement of drilling to avoid organic contamination from cutting oils and grease. Prior to use, the casing and screen materials were kept off site in a covered, protected area. To ensure that the sandy materials would not collapse after drilling, casing lengths and the screen were joined aboveground and placed inside of the augers before the auger flights were pulled out of the

hole. The sand and gravel below the water table collapsed around the screen and casing as the augers were removed. To prevent vertical movement of water down along the casing, about 3 feet of a wet bentonite/cement mixture was placed in the annulus just above the water table. Cuttings (principally clean, fine to medium sand) were backfilled above the bentonite/cement seal to within 4 feet of land surface. Another bentonite/cement mixture was placed to form a seal at ground surface, further preventing movement of water

down along the well casing. A 4-inch diameter steel protective cover with locking cap was placed over the casing and into the surface seal to protect against vandalism.

The nine wells were drilled at four locations with paired wells at three sites and a nest of three wells at one site (Figure 1-13). The locations were based on the analytical results of the samples taken from the temporary wells and basic knowledge of the ground-water flow direction.

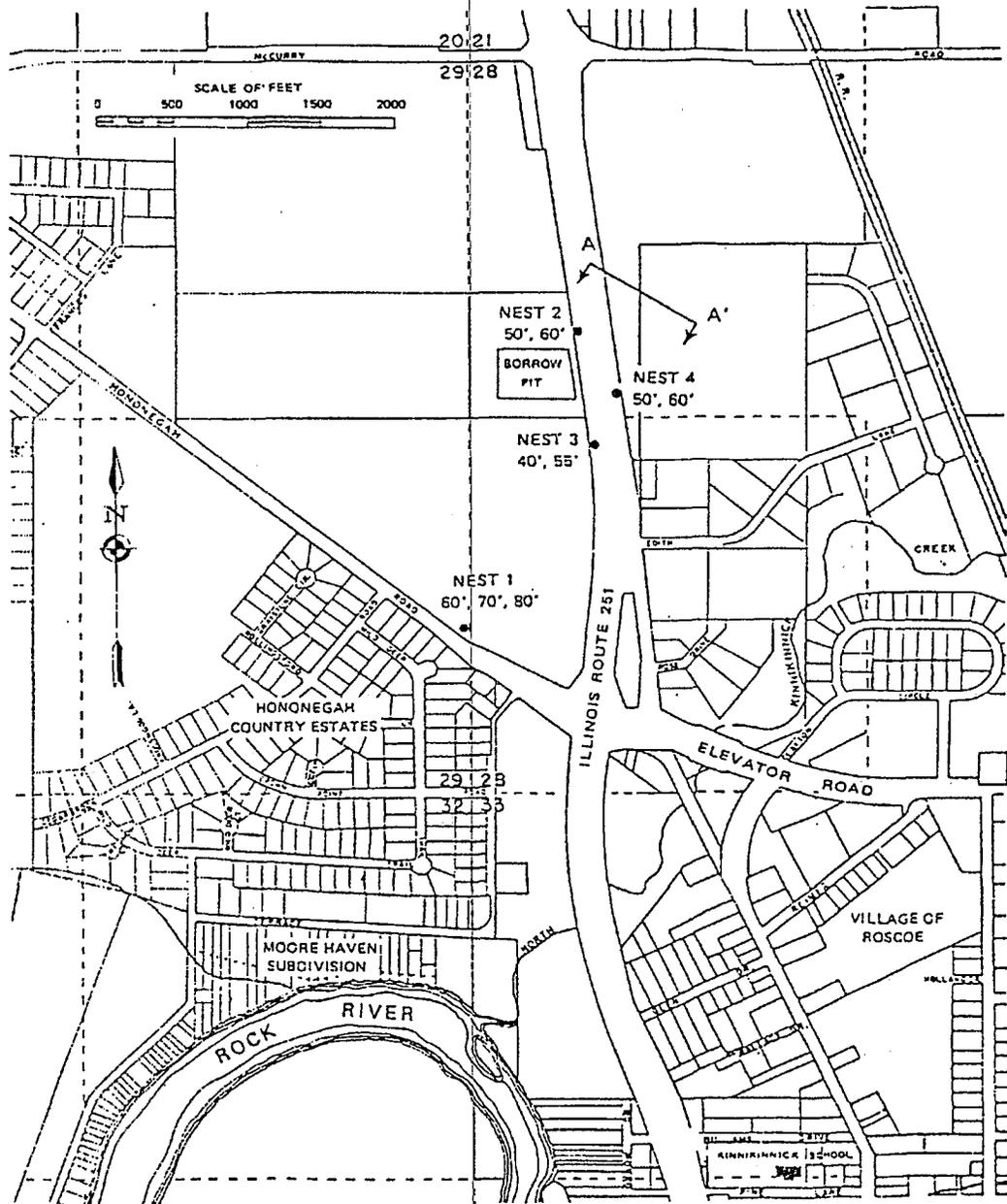


Figure 1-13. Location of Monitoring Well Nests and Cross Section A-A' at Roscoe, Illinois (from Wehrmann, 1984)

Locations were numbered as nests 1 through 4 in order of their construction. Nest 1, located immediately north of the affected subdivision, consists of three wells completed at depths of approximately 60, 70, and 80 feet below ground surface. Nest 2 consists of two wells, one 50 feet deep, and the other 60 feet deep. Nest 3 consists of two wells 40 and 55 feet deep, while nest 4 consists of two wells 50 and 60 feet deep.

Prior to completing the monitoring wells, it was felt an additional well, 100 feet deep and adjacent to nest 1, was needed to further define the vertical extent of the contaminant plume. Because the hollow-stem auger rig was no longer available, arrangements were made to use a cable-tool rig. The well was constructed over a period of 2 days, which was somewhat slower than any of the other methods previously used (but typical of cable-tool speeds). A 6-inch casing was driven several feet, a bit was used to break up the materials inside the casing, and then the materials were removed from the casing with a dart-valve bailer. This procedure was repeated until 100 feet was reached; then the well casing and screen were screwed together and lowered down the hole. The 6-inch casing was then pulled back, which allowed the hole to collapse about the well, which was constructed of stainless steel exactly like the other nine monitoring wells. All drilling equipment and well construction materials were steam-cleaned prior to use.

Appraisal of the sampling results of the monitoring wells and the domestic wells in the area produced the pictorial representations shown in Figures 1-14 and 1-15. Figure

1-14 conceptually illustrates a downgradient cross section of the TCE plume in the vicinity of monitoring nests 2, 3, and 4. Figure 1-15 shows the likely extent of the VOC contaminant plume. This map includes a limited amount of data from privately owned monitoring wells located on industrial property just upgradient of monitoring nests 2 and 4. The dashed lines indicate the probable extent of the contaminant plume based on the dimensions of the plume where it passes beneath the developed area along the Rock River.

This monitoring situation clearly indicates the role different drilling and construction techniques can play in a ground-water sampling strategy. In each instance, much consideration was given to the effect the methods used for construction and sampling would have on the resultant chemical data. Where quantitative results for a fairly "quick" preliminary investigation were not necessary and driving sandpoints was too difficult, air-percussion rotary methods were deemed acceptable. For the placement of the permanent monitoring wells, wells that may become crucial for contaminant source identification and possibly for litigation, the hollow-stem auger was the technique of choice. Finally, when the hollow-stem auger was not available, a cable-tool rig was chosen. Since only one hole was to be drilled, the relative slowness of the method became less important. Also, the depth of completion (100 feet) in the covey sand and gravel made the cable-tool preferable over the hollow-stem. In addition, each method chosen was capable of maintaining an open hole without the use of drilling mud, which could have affected the results of the chemical analyses of the ground water.

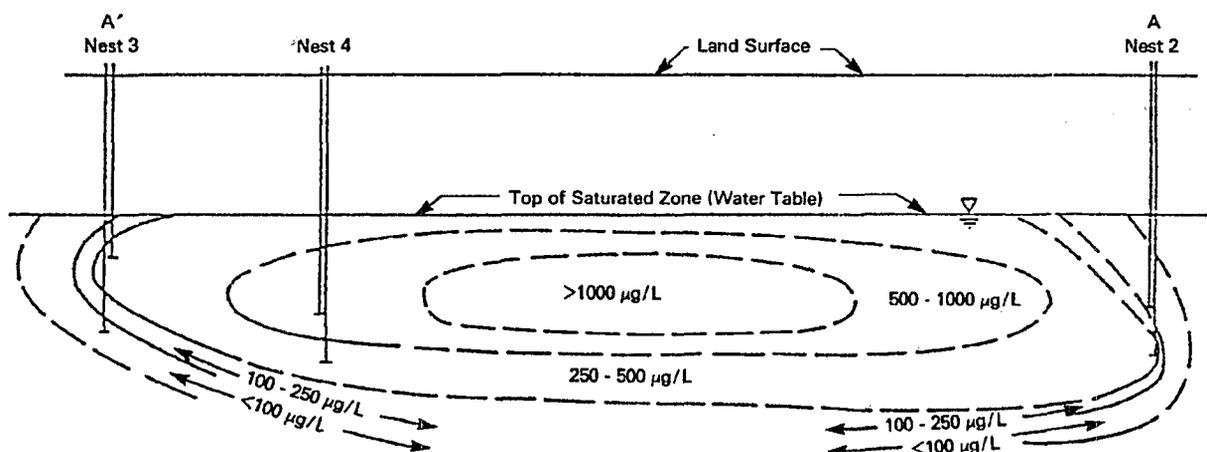


Figure 1-14. Cross Section A-A' through Monitoring nests 2, 3, and 4, Looking in the Direction of Ground-Water Flow (from Wehrmann, 1984)

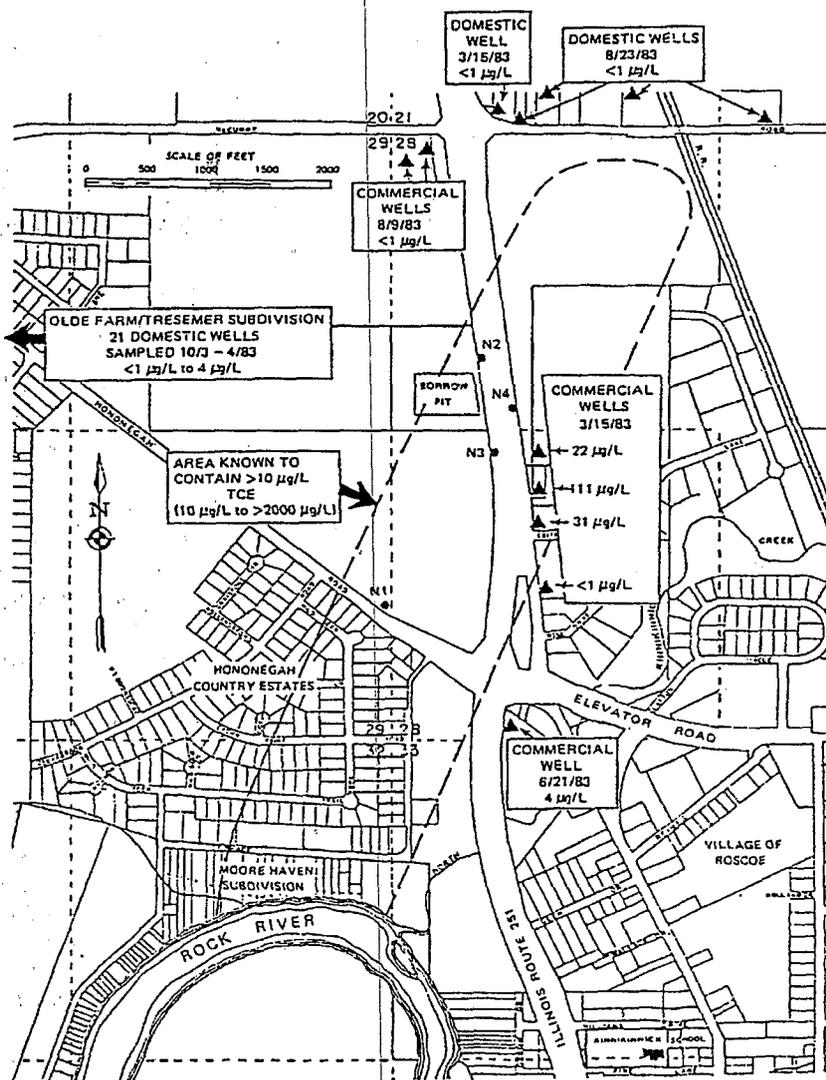


Figure 1-15. General Area of Known TCE Contamination (from Wehrmann, 1984)

Summary

Critical considerations for the design of ground-water quality monitoring networks include alternatives for well design and drilling techniques. With a knowledge of the principal chemical constituents of interest and the local hydrogeology, and appreciation of subsurface geochemistry, appropriate materials for well design and drilling techniques can be selected. Whenever possible, physical disturbance and the amount of foreign material introduced into the subsurface should be minimized.

The choices of drilling methods and well construction materials are very important in every type of ground-

water monitoring program. Details of network construction can introduce significant bias into monitoring data, which frequently may be corrected only by repeating the process of well siting, installation, completion, and development. This can be quite costly in time, effort, money, and loss of information. Undue expense is avoidable if planning decisions are made cautiously with an eye to the future.

The expanding scientific literature on effective ground-water monitoring techniques should be read and evaluated on a continuing basis. This information will help supplement guidelines, such as this, for applications to specific monitoring efforts.

References

Aller, and others, 1989, Handbook of Suggested Practices for the design and installation of ground-water monitoring wells: National Water Well Association, Dublin, OH EPA 600/4-89/034.

Barcelona, M.J., J.P. Gibb, J.A. Helfrich, and E.E. Garske, 1985, Practical guide for ground-water sampling: Illinois State Water Survey, U.S. Environmental Protection Agency, Robert S. Kerr Environmental Research Laboratory, Ada, OK, and Environmental Monitoring and Support Laboratory, Las Vegas, NV.

Barcelona, M.J., 1984, TOC determinations in ground water: *Ground Water*, v.22, no.1, pp.18-24.

Barcelona, M.J., J.A. Helfrich, E.E. Garske, and J.P. Gibb, 1984, A laboratory evaluation of ground water sampling mechanisms: *Ground Water Monitoring Review*, v.4, no. 2, pp. 32-41.

Barcelona, J.J., J.P. Gibb, and R.A. Miller, 1984. A guide to the selection of materials for monitoring well construction and ground-water sampling. Illinois State Water Survey Contract Report 327. Illinois State Water Survey, Champaign, IL.

Berg, R.C., J.P. Kempton, and A.N. Stecyk. 1981, Geology for planning in Boone and Winnebago Counties, Illinois: Illinois State Geological Survey Circular 531, Illinois State Geological Survey, Urbana,

Brown, K.W., J. Green, and J.C. Thomas, 1983, The influence of selected organic liquids on the permeability of clay liners: Proc. of the Ninth Annual Research Symposium: Land Disposal, Incineration, and Treatment of Hazardous Wastes. U.S. Environmental Protection Agency SHWRD/EPCS, May 2-4, 1983, Ft. Mitchell, KY.

Burkland, P.W., and E. Raber, 1983, Method to avoid ground-water mixing between two aquifers during drilling and well completion procedures: *Ground Water Monitoring Review*, v. 3, no. 4, pp. 48-55.

Campbell, M.D. and J.H. Lehr, 1973, Water well technology: McGraw-Hill Book Company, New York, NY.

Fenn, D., E. Coccozza, J. Isbister, O. Braids, B. Yare, and P. Roux, 1977, Procedures manual for ground water monitoring at solid waste disposal facilities (SW-611). U.S. Environmental Protection Agency, Cincinnati, OH.

Gibb, J.P., R.M. Schuller, and R.A. Griffin, 1981, Procedures for the collection of representative water

quality data from monitoring wells: Cooperative Groundwater Report. Illinois State Water and Geological Surveys, Champaign, IL.

Gillham, R.W., M.J.L. Robin, J.F. Barker, and J.A. Cherry, 1983, Groundwater monitoring and sample bias: American Petroleum Institute Publication 4367, Environmental Affairs Department.

Illinois State Water Survey and Illinois State Geological Survey, 1984, Proceedings of the 1984 ISWS/ISGS Groundwater Monitoring Workshop. February 27-28, Champaign, IL.

Illinois State Water Survey and Illinois State Geological Survey, 1982, Proceedings of the 1982 ISWS/ISGS Groundwater Monitoring Workshop. Illinois Section of American Water Works Association. February 22-23, 1982, Champaign, IL.

Johnson, T.L., 1983, A comparison of well nests vs. single-well completions: *Ground Water Monitoring Review*, v. 3, no. 1, pp. 76-78.

Johnson, E.E., Inc., 1972, Ground water and wells. Johnson Division, Universal Oil Products Co., St. Paul, MN.

Keith, S.J., L.G. Wilson, H.R. Fitch, and D.M. Esposito, 1982, Sources of spatial-temporal variability in Ground-Water Quality Data and Methods of Control: Case Study of the Cortaro Monitoring Program, Arizona: Proc. of the Second National Symposium on Aquifer Restoration and Ground Water Monitoring. National Water Well Association, May 26-28, Columbus, OH.

Lewis, R.W., 1982, Custom designing of monitoring wells for specific pollutants and hydrogeologic conditions: Proc. of the Second National Symposium on Aquifer Restoration and Ground Water Monitoring. National Water Well Association, May 26-28, Columbus, OH.

Luhdorff, E.E., Jr., and J.C. Scalmanini, 1982, Selection of drilling method, well design and sampling equipment for wells for monitoring organic contamination: Proc. of the Second National Symposium on Aquifer Restoration and Ground Water Monitoring, National Water Well Association, May 26-28, Columbus, OH.

Mackay, D.M., P.V. Roberts, and J.A. Cherry, 1985, Transport of organic contaminants in groundwater: *Environmental Science & Technology*, v. 19, no. 5, pp. 384-392.

Miller, G.D., 1982, Uptake and release of lead, chromium and trace level volatile organics exposed to synthetic well casings: Proc. of Second National Symposium on

Aquifer Restoration and Ground Water Monitoring. National Water Well Association, May 26-28, Columbus, OH.

Minning, R.C., 1982, Monitoring well design and installation: Proc. of Second National Symposium on Aquifer Restoration and Ground Water Monitoring. National Water Well Association, May 26-28, Columbus, OH.

Mobile Drilling Company, 1972, Soil sampling equipment-accessories: Catalog 650. Mobile Drilling Company, Indianapolis, IN.

Morrison, R.D. and P.E. Brewer, 1981, Air-lift samplers for zone of saturation monitoring: Ground Water Monitoring Review, v. 1, no. 1, pp. 52-55.

Naymik, T.G. and M.E. Sievers, 1983, Groundwater tracer experiment (II) at Sand Ridge State Forest, Illinois: Illinois State Water Survey Contract Report 334, Illinois State Water Survey, Champaign, IL.

Naymik, T.G. and J.J. Barcelona, 1981, Characterization of a contaminant plume in groundwater, Meredosia, Illinois: Ground Water, v. 16, no. 3, pp. 149-157.

O'Hearn, M., 1982, Groundwater monitoring at the Havana Power Station's ash disposal ponds and treatment lagoon: Confidential Contract Report, Illinois State Water Survey, Champaign, IL.

Perry, C.A. and R.J. Hart, 1985, Installation of observation wells on hazardous waste sites in Kansas using a hollow-stem auger: Ground Monitoring Review, v. 5, no. 4, pp. 70-73.

Pettyjohn, W.A. and A.W. Hounslow, 1982, Organic compounds and ground-water pollution: Proc. of Second National Symposium on Aquifer Restoration and Ground Water Monitoring. National Water Well Association, May 26-28, Columbus, OH.

Pettyjohn, W.A., W.J. Dunlap, R. Cosby, and J.W. Keeley, 1981, Sampling ground water for organic contaminants: Ground Water v. 19, no. 2, pp. 180-189.

Pfannkuch, H.O., 1981, Problems of monitoring network design to detect unanticipated contamination: Proc. of First National Ground Water Quality Monitoring Symposium and Exposition, National Water Well Association, May 29-30, Columbus, OH.

Pickens, J.F., J.A. Cherry, R.M. Coupland, G.E. Grisak, W.F. Merritt, and B.A. Risto, 1981, A multi-level device

for ground-water sampling: Ground Water Monitoring Review, v. 1, no. 1, pp. 48-51.

Rinaldo-Lee, M. B., 1983, Small- vs. large-diameter monitoring wells: Ground Water Monitoring Review, v. 3, no. 1, pp. 72-75.

Scalf, M.R., J.F. McNabb, W.J. Dunlap, R.L. Cosby, and J. Fryberger, 1981, Manual of ground-water sampling procedures: NWWA/EPA Series, National Water Well Association, Worthington, OH. EPA-600/2-81-160.

Schalla, R., and R.W. Landick, 1985, A new valved and air-vented surge plunger for developing small-diameter monitor wells: Proc. of Third National Symposium and Exposition on Ground-Water Instrumentation, National Water Well Association, October 2-4, San Diego, CA.

Sosebee, J.B., Jr. and others 1982. Contamination of groundwater samples with PVC adhesives and PVC primer from monitor wells: Environmental Science and Engineering, Inc., Gainesville, FL.

Torstensson, B.A., 1984, A new system for ground water monitoring: Ground Water Monitoring Review, v. 4, no. 4, pp. 131-138.

Voytek, J.E., Jr., 1983, Considerations in the design and installation of monitoring wells: Ground Water Monitoring Review, v. 3, no. 1, pp. 70-71.

Walker, W.H., 1974, Tube wells, open wells, and optimum ground-water resource development: Ground Water, v. 12, no. 1, pp. 10-15.

Wehrmann, H.A., 1984, An investigation of a volatile organic chemical plume in northern Winnebago County, Illinois: Illinois State Water Survey Contract Report 346, Illinois State Water Survey, Champaign,

Wehrmann, H.A., 1983, Monitoring well design and construction: Ground Water Age, v. 17, no. 8, pp. 35-38.

Wehrmann, H.A., 1983, Potential nitrate contamination of groundwater in the Roscoe Area, Winnebago County, Illinois: Illinois State Water Survey Contract Report 325, Illinois State Water Survey, Champaign, IL.

Wehrmann, H.A., 1982, Groundwater monitoring for fly ash leachate, Baldwin Power Station, Illinois Power Company. Confidential Contract Report, Illinois State Water Survey, Champaign, IL.

Chapter 2

GROUND-WATER SAMPLING

Introduction

Background

Ground-water sampling is conducted to provide information on the condition of subsurface water resources. Whether the goal of the monitoring effort is detection or assessment of contamination, the information gathered during sampling efforts must be of known quality and be well documented. The most efficient way to accomplish these goals is by developing a sampling protocol, which is tailored to the information needs of the program and the hydrogeology of the site or region under investigation. This sampling protocol incorporates detailed descriptions of sampling procedures and other techniques that, of themselves, are not sufficient to document data quality or reliability. Sampling protocols are central parts of networks or investigatory strategies.

The need for reliable ground-water sampling procedures has been recognized for years by a variety of professional, regulatory, public, and private groups. The technical basis for the use of selected sampling procedures for environmental chemistry studies has been developed for surface-water applications over the last four decades. Ground-water quality monitoring programs, however, have unique needs and goals that are fundamentally different from previous investigative activities. The reliable detection and assessment of subsurface contamination require minimal disturbance of geochemical and hydrogeologic conditions during sampling.

At this time, proven well construction, sampling, and analytical protocols for ground-water sampling have been developed for many of the more problematic chemical constituents of interest. However, the acceptance of these procedures and protocols must await more careful documentation and firm regulatory guidelines for monitoring program execution. The time and expense of characterizing actual subsurface

conditions place severe restraints on the methods that can be employed. Since the technical basis for documented, reliable drilling, sample collection, and handling procedures is in the early stages of development, conscientious efforts to document method performance under real conditions should be a part of any ground-water investigation (Barcelona and others, 1985; Scalf and others, 1981).

Information Sources

Much of the literature on routine ground-water monitoring methodology has been published in the last 10 years. The bulk of this work has emphasized ambient resource or contaminant resource monitoring (detection and assessment), rather than case preparation or enforcement efforts. General references that are useful to the design and execution of sampling efforts are the U.S. Geological Survey (1977), Wood (1976), the U.S. Environmental Protection Agency (Brass and others, 1977; Dunlap and others, 1977; Fenn and others, 1977; Sisk, 1981) and others (National Council of the Paper Industry, 1982; Tinlin, 1976). In large part, these works treat sampling in the context of overall monitoring programs, providing descriptions of available sampling mechanisms, sample collection techniques, and sample handling procedures. The impact of specific methodologies on the usefulness or reliability of the resulting data has received little discussion (Gibb and others, 1981).

High-quality chemical data collection is essential in ground-water monitoring programs. The technical difficulties involved in "representative" samplings have been recognized only recently (Gibb and others, 1981; Grisak and others, 1978). The long-term collection of high-quality ground-water chemistry data is more involved than merely selecting a sampling mechanism and agreeing on sample handling procedures. Efforts to detect and assess contamination can be unrewarding without accurate (i.e., unbiased) and precise (i.e., comparable and complete) concentration data on

ground-water chemical constituents. Also, the expense of data collection and management argue for documentation of data quality.

Gillham and others (1983) published a very useful reference on the principal sources of bias and imprecision in ground-water monitoring results. Their treatment is extensive and stresses the minimization of random error, which can enter into well construction, sample collection, and sample handling operations. They further stress the importance of collecting precise data over time to maximize the effectiveness of trend analysis, particularly for regulatory purposes. Accuracy also is very important, since the ultimate reliability of statistical comparisons of results from different wells (e.g., upgradient versus downgradient samples) may depend on differences between mean values for selected constituents from relatively small replicate sample sets. Therefore, systematic error must be controlled by selecting proven methods for establishing sampling points and sample collection to ensure known levels of accuracy.

The Subsurface Environment

The subsurface environment may be categorized broadly into two zones, the unsaturated or vadose zone and the saturated zone. The use of the term "vadose" is more accurate because isolated saturated areas may exist in the unsaturated zone above the water table of unconfined aquifers.

Investigators have discovered recently that the subsurface is neither devoid of oxygen (Winograd and Robertson, 1982) nor sterile (Wilson and McNabb, 1983; Wilson and others, 1983). These facts may significantly influence the mobility and persistence of chemical species, as well as the transformations of the original components of contaminant mixtures (Schwarzenbach and others, 1985) that have been released to the subsurface.

The subsurface environment also is quite different from surface water systems in that vertical gradients in pressure and dissolved gas content have been observed within the usual depth ranges of monitoring interest (i.e., 1 to 150 m [3 to 500 ft]). In some cases, these gradients can be linked to well-defined hydrologic or geochemical processes. However, reports of apparently anomalous geochemical processes have increased in recent years, particularly at contaminated sites (Barcelona and Garske, 1983; Heaton and Vogel, 1981; Schwarzenbach and others, 1985; Winograd and Robertson, 1982; Wood and Petraitis, 1984).

The subsurface environment is not as readily accessible as surface water systems, and some disturbance is

necessary to collect samples of earth materials or ground water. Therefore, "representative" (i.e., artifact or error free) sampling is really a function of the degree of detail needed to characterize subsurface hydrologic and geochemical conditions and the care taken to minimize disturbance of these conditions in the process (Claasen, 1982). Each well or boring represents a potential conduit for short-circuited contaminant migration or ground-water flow, which must be considered a potential liability to investigative activities.

The subsurface environment is dynamic over extended time frames and the processes of recharge and ground-water flow are very important to a thorough understanding of the system. Detailed descriptions of contaminant distribution, transport, and transformation necessarily rely on the understanding of basic flow and fluid transport processes. Short-term investigations may only provide a snapshot of contaminant levels or distributions. Since water-quality monitoring data are normally collected on discrete dates, it is very important that reliable collection methods are used to assure high data quality over the course of the investigation. The reliability of the methods should be investigated thoroughly during the preliminary phase of monitoring network implementation.

Although the scope of this discussion is on sampling ground water for chemical analysis, the same data quality requirements apply to water-level measurements and to hydraulic conductivity testing. These hydrologic determinations form the basis for interpreting chemical constituent data and may well limit the validity of fluid or solute transport model applications. Hydrologic measurements must be included in the development of the quality assurance/quality control (QA/QC) program for ground-water quality monitoring networks.

The Sampling Problem and Parameter Selection

Cost-effective water-quality sampling is difficult in ground-water systems because proven field procedures have not been extensively documented. Regulations that call for "representative sampling" alone are not sufficient to ensure high-quality data collection. The most appropriate monitoring and sampling procedures for a ground-water quality network will depend on the specific purpose of the program. Resource evaluation, contaminant detection, remedial action assessments, and litigation studies are purposes for which effective networks can be designed once the information needs have been identified. Due to the time, personnel needs, and cost of most water-quality monitoring programs, the optimal network design should be phased so as to make the most of the available information as it is collected. This approach allows for the gradual refinement of program goals as the network is implemented.

Two fundamental considerations are common to most ground-water quality monitoring programs: establishing individual sampling points (i.e., in space and time) and determining the elements of the water sampling protocol that will be sufficient to meet the information needs of the overall program. The placement and number of sampling points can be phased to gradually increase the scale of the monitoring program. Similarly, the chemical constituents of initial interest should provide background ground-water quality data from which a list of likely contaminants may be prepared as the program progresses. Table 2-1 shows candidate chemical and hydrologic parameters for both detective and assessment monitoring activities. Special care should be taken to account for possible subsurface transformation of the principal pollutant species. Ground-water transport of contaminants can produce chemical distributions that vary substantially over time and space. In particular, transformation of organic compounds can change substantially the identity of the original contaminant mixture (Mackay and others, 1985; Schwarzenbach and others, 1985).

Detective Monitoring	
Chemical Parameters*	
pH, Ω^{-1} , TOC, TOX, Alkalinity, TDS, Eh, Cl ⁻ , NO ₃ ⁻ , SO ₄ ⁻² , PO ₄ ⁼ , SiO ₂ , Na ⁺ , K ⁺ , Ca ⁺⁺ , Mg ⁺⁺ , NH ₄ ⁺ , Fe, Mn	
Hydrologic Parameters	
Water Level, Hydraulic Conductivity	
Assessment Monitoring	
Chemical Parameters*	
pH, Ω^{-1} , TOC, TOX, Alkalinity, TDS, Eh, Cl ⁻ , NO ₃ ⁻ , SO ₄ ⁻² , PO ₄ ⁼ , SiO ₂ , B, Na ⁺ , K ⁺ , Ca ⁺⁺ , Mg ⁺⁺ , NH ₄ ⁺ , Fe, Mn, Zn, Cd, Cu, Pb, Cr, Ni, Ag, Hg, As, Sb, Se, Be	
Hydrologic Parameters	
Water Level, Hydraulic Conductivity	

* Ω^{-1} = specific conductance, a measure of the charged species in solution.

Table 2-1. Suggested Measurements for Ground-Water Monitoring Programs

Contaminant detection is generally the most important aspect of a water-quality program, and must be assured in network design. False negative contaminant readings due to the loss of chemical constituents or the introduction of interfering substances that mask the presence of the contaminants in water samples can be very serious. Such errors may delay needed remedial action and expose either the public or the environment to an unreasonably high risk. False positive observations of contaminants may call for costly remedial actions or more intensive study, which are not warranted by the actual situation. Thus, reliable sample collection and data interpretation procedures are central to an optimized network design.

In this respect, monitoring in the vadose zone is attractive because it should provide an element of "early" detection capability. The methodologies available for this type of monitoring have been under development for some time. There are distinct limitations, however, to many of the available monitoring devices (Everett and McMillion, 1985; Everett and others, 1982; Wilson, 1981; Wilson, 1983), and it is frequently difficult to relate observed vadose zone concentrations quantitatively to actual contaminant distributions in ground water (Everett and others, 1984; Lindau and Spalding, 1984). Soil gas sampling techniques and underground storage tank monitors have been commercially developed that can be extremely useful for source scouting. Given the complexity of vadose zone monitoring procedures and the need for additional investigation (Robbins and Gemmell, 1985), implementing these techniques in routine ground-water monitoring networks may be difficult.

This chapter addresses water-quality sampling in the saturated zone, reflecting the advanced state of monitoring technology appropriate for this compartment of the subsurface. There are a number of useful reference materials for the development of effective ground-water sampling protocols, which include information on the types of drilling methods, well construction materials, sampling mechanisms, and sample handling methods currently available (Barcelona and others, 1985; Barcelona and others, 1983; Gillham and others, 1983; Scalf and others, 1981; Todd and others, 1976). To collect sensitive, high-quality contaminant concentration data, investigators must identify the type and magnitude of errors that may arise in ground-water sampling. Figure 2-1 presents a generalized diagram of the steps involved in sampling and the principal sources of error.

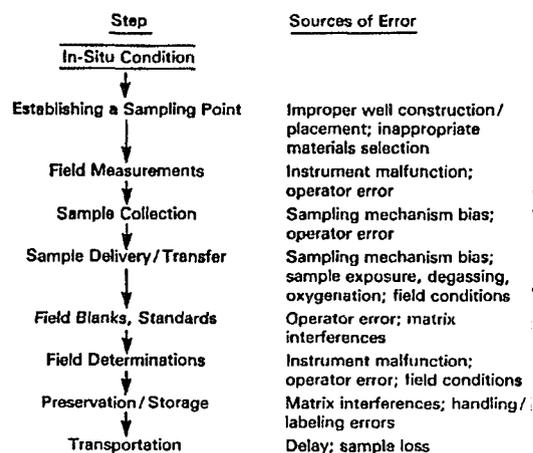


Figure 2-1. Steps and Sources of Error in Ground-Water Sampling

Strict error control at each step is necessary for the collection of high-quality data representative of in situ conditions.

There are two major obstacles to controlling ground-water sampling errors. First, field blanks, standards, and split samples used in data quality assurance programs cannot account for changes that may occur in the integrity of samples prior to sample delivery to the land surface. Second, most of the sources of error that may affect sample integrity prior to delivery are not well documented in the literature for many of the contaminants of current interest. Among these sources of error are the contamination of the subsurface by drilling fluids, grouts, or sealing materials; the sorptive or leaching effects on water samples due to well casing; pump or sampling tubing materials' exposures; and the effects on the solution chemistry due to oxygenation, depressurization, or gas exchange caused by the sampling mechanism. These sources of error have been investigated to some extent for volatile organic contaminants under laboratory conditions. However, to achieve confidence in field monitoring and sampling instrumentation for routine applications, common sense and a "research" approach to regulatory monitoring may be needed. Two of the most critical elements of a monitoring program are establishing both reliable sampling points and simple, efficient sampling protocols that will yield data of known quality.

Establishing a Sampling Point

Taking adequate care in selecting drilling methods, well construction materials, and well development techniques should allow the approximation of representative ground-water sampling from a monitoring well. The representative nature of the water samples can be maintained consistently with a trained sampling staff and good field-laboratory communication. Also, important hydrologic measurements, such as water level and hydraulic conductivity, can be made from the same sampling point. A representative water sample may then be defined as a minimally disturbed sample taken after proper well purging, which will allow the determination of the chemical constituents of interest at predetermined levels of accuracy and precision. Sophisticated monitoring technology and sampling instrumentation are poor substitutes for an experienced sampling team that can follow a proven sampling protocol.

This section details some of the considerations in establishing a reliable sampling point. There are a number of alternative approaches for selecting a sampling point in monitoring network design, including

deploying arrays of either nested monitoring wells or multilevel devices (Barvenik and Cadwgan, 1983; Pickens and others, 1978) at various sites within the area of interest. Different approaches have their individual merits, based on the ease of verifying sampling point isolation, durability, cost, ease of installation, and site-specific factors.

The most effective option for specific programs should be chosen with representative sampling criteria in mind. The sampling points must be durable, inert towards the chemical constituents of interest, allow for purging of stagnant water, provide sufficient water for analytical work with minimum disturbance, and permit the evaluation of the hydrologic characteristics of the formation of interest. Monitoring wells can be constructed to meet these criteria because a variety of drilling methods, materials, sampling mechanisms, and pumping regimes for sampling and hydrologic measurements can be selected to meet the current needs of most monitoring programs.

The placement and number of wells will depend on the complexity of the hydrologic setting and the degree of spatial and temporal detail needed to meet the goals of the program. Both the directions and approximate rates of ground-water movement must be known in order to satisfactorily interpret the chemical data. With this knowledge, it also may be possible to estimate the nature and location of pollutant sources (Gorelick and others, 1983). Subsurface geophysical techniques can be very helpful in determining the optimum placement of monitoring wells under appropriate conditions and when sufficient hydrogeologic information is available (Evans and Schweitzer, 1984). Well placement should be viewed as an evolutionary activity that may expand or contract as the needs of the program dictate.

Well Design and Construction

Effective monitoring well design and construction require considerable care and at least some understanding of the hydrogeology and subsurface geochemistry of the site. Preliminary borings, well drilling experience, and the details of the operational history of a site can be very helpful. Monitoring well design criteria include depth, screen size, gravel-pack specifications, and yield potential. These considerations differ substantially from those applied to production wells. The simplest, small diameter well completions that will permit development, accommodate the sampling gear, and minimize the need to purge large volumes of potentially contaminated water are preferred for effective routine monitoring activities. Helpful references include Barcelona and others (1983), Scalf and others (1981), and Wehrmann (1983).

Well Drilling

The selection of a particular drilling technique should depend on the geology of the site, the expected depths of the wells, and the suitability of drilling equipment for the contaminants of interest (see Chapter 1). Regardless of the technique used, every effort should be made to minimize subsurface disturbance. For critical applications, the drilling rig and tools should be steam-cleaned to minimize the potential for cross-contamination between formations or successive borings. The use of drilling muds can be a liability for trace chemical constituent investigations because foreign organic matter will be introduced into the penetrated formations. Even "clay" muds without polymeric additives contain some organic matter, which is added to stabilize the clay suspension and may interfere with some analytical determinations. Table 2-2 contains information on the total and soluble organic carbon contents of some common drilling and grouting materials (Wood, 1976). The effects of drilling muds on ground-water solution chemistry have not been investigated in detail.

However, existing reports indicate that the organic carbon introduced during drilling can cause false water-quality observations for long periods of time (Barcelona, 1984; Brobst, 1984). The fact that these interferences are observable for gross indicators of levels of organic carbon compounds (i.e., TOC) and reduced substances (i.e., COD) strongly suggests that drilling aids are a potential source of serious error. Special situations may call for innovative drilling techniques (Yare, 1975).

Well Development, Hydraulic Performance, and Purging Strategy

Once a well is completed, it is necessary to prepare the sampling point for water sampling and begin to evaluate the hydraulic characteristics of the producing zone.

These steps provide a basis for maintaining reliable sampling points over the duration of a ground-water monitoring program.

Well Development. The proper development of monitoring wells is essential to the collection of "representative" water samples. During the drilling process, fine particles are forced through the sides of the borehole into the formation, forming a mud cake that reduces the hydraulic conductivity of the materials in the immediate area of the well bore. To allow water from the formation being monitored to freely enter the monitoring well, this mud cake must be broken down opposite the well screen and the fine material removed from the well. This process also enhances the yield potential of the well, which is a critical factor when constructing monitoring wells in low-yielding geologic materials.

More importantly, monitoring wells must be developed to provide water free of suspended solids. When sampling for metal ions and other dissolved inorganic constituents, water samples must be filtered and preserved at the well site at the time of sample collection. Improperly developed monitoring wells will produce samples containing suspended sediments that may both bias the chemical analysis of the collected samples and cause frequent clogging of field filtering mechanisms. The additional time and money spent for well development will expedite sample filtration and result in samples that are more representative of water chemistry in the formation being monitored.

Development procedures used for monitoring wells are similar to those used for production wells. The first step in development involves the movement of water at alternately high and low velocity into and out of the well

	Ash (% by wt)	Organic Content (% by wt)	Soluble Carbon (% by wt)	Soluble Carbon in Total Organic Content (% by wt)
"Bentonite" muds/grouts				
Volclay* (~90% montmorillonite)	98.2	1.8	<0.001	94.4
Benseal [†]	88.5	11.5	<0.001	3.7
"Organic" muds/drilling aids				
Ez-Mud [‡] (acrylamide-sodium acrylate copolymer dispersed in food-grade oil [normally used in 0.25% dilution])	11.5	21.5	17.9	2.1
Revert [§] (guar bean starch-based mixture)	1.6	98.4	33.8	85.6

*All percentages determined on a moisture-free basis.

[†]Trademark of American Colloid Co.

[‡]Trademark of NL Baroid/NL Industries Inc.

[§]Trademark of Johnson Division, UOP Inc.

Source: Wood, 1976.

Table 2-2. Composition of Selected Sealing and Drilling Muds

screen and gravel-pack to break down the mud cake on the well bore and loosen fine particles in the borehole. This step is followed by pumping to remove these materials from the well and the immediate area outside the well screen. This procedure should be continued until the water pumped from the well is visually free of suspended materials or sediments.

Hydraulic Performance of Monitoring Wells. The importance of understanding the hydraulics of the geologic materials at a site cannot be overemphasized. Collection of accurate water-level data from properly located and constructed wells provides information on the direction of ground-water flow. The success of a monitoring program also depends on knowledge of the rates of travel of both the ground water and solutes. The response of a monitoring well to pumping also must be known to determine the proper rate and length of time of pumping prior to collecting a water sample.

Hydraulic conductivity measurements provide a basis for judging the hydraulic connection of the monitoring well and adjacent screened formation to the hydrogeologic setting. These measurements also allow an experienced hydrologist to estimate an optimal sampling frequency for the monitoring program (Barcelona and others, 1985).

Traditionally, hydraulic conductivity testing has been achieved by collecting drill samples, which were then taken to the laboratory for testing. Several techniques involving laboratory permeameters are routinely used. Falling head or constant head permeameter tests on recompacted samples in fixed wall or triaxial test cells are among the most common. The relative applicability of these techniques depends on both operator skill and methodology since calibration standards are not available. The major problem with laboratory test procedures is that the determined values are based on recompacted geologic samples rather than undisturbed geologic materials. Only limited work has been done to date on performing laboratory tests on "undisturbed" samples to improve the field applicability of laboratory hydraulic conductivity results. Melby (1989) reported that laboratory-determined values of hydraulic conductivity for cores of unconsolidated, fine-grained material from Oklahoma were three to six orders of magnitude smaller than values determined by aquifer testing. Considerable care must be exercised when evaluating laboratory-derived hydraulic conductivity coefficients.

Hydraulic conductivity is most effectively determined under field conditions by aquifer testing methods, such as pumping or slug testing (see Chapter 4). The water-level drawdown can be measured during pumping.

Alternatively, water levels can be measured after the static water level is depressed by application of gas pressure or elevated by the introduction of a slug of water. These procedures are rather straightforward for wells that have been properly developed.

Well Purging Strategies. The number of well volumes to be removed from a monitoring well prior to collecting a water sample must be tailored to the hydraulic properties of the geologic materials being monitored, the well construction parameters, the desired pumping rate, and the sampling methodology to be employed. No single number of well volumes to be pumped fits all situations. The goal in establishing a well purging strategy is to obtain water from the geologic materials being monitored while minimizing the disturbance of the regional flow system and the collected sample. To accomplish this goal, a basic understanding of well hydraulics and the effects of pumping on the quality of water samples is essential. Water that has remained in the well casing more than about 2 hours has had the opportunity to exchange gases with the atmosphere and to interact with the well casing material. Therefore, the chemistry of water stored in the well casing is not representative of that in the aquifer and should not be collected for analysis. Purge volumes and pumping rates should be evaluated on a case-by-case basis.

Gibb (1981) has shown how the measurements of hydraulic conductivity can be used to estimate the well-purging requirement. Figures 2-2a and 2-2b show an example of this procedure. In practice, it may be necessary to test the hydraulic conductivity of several wells within a network. The calculated purging requirement should then be verified by measurements of pH and specific conductance during pumping to signal equilibration of the water being collected.

The selection of purging rates and volumes of water to be pumped prior to sample collection also can be influenced by the anticipated water quality. In hazardous environments where purged water must be contained and disposed of in a permitted facility, it is desirable to minimize this amount. This can be accomplished by pumping the wells at very low pumping rates (100 mL/min) to minimize the drawdown in the well and maximize the percentage of aquifer water delivered to the surface in the shortest period of time. Pumping at low rates, in effect, isolates the column of stagnant water in the well bore and negates the need for its removal. This approach is only valid in cases where the pump intake is placed at the top of, or in, the well screen.

In summary, well purging strategies should be established by (1) determining the hydraulic performance of the well; (2) calculating reasonable purging

requirements, pumping rates, and volumes based on hydraulic conductivity data, well construction data, site hydrologic conditions, and anticipated water quality; (3) measuring the well purging parameters to verify chemical "equilibrated" conditions; and (4) documenting the entire effort (actual pumping rate, volumes pumped, and purging parameter measurements before and after sample collection).

Given:

48-foot deep, 2-inch diameter well
 2-foot long screen
 3-foot thick aquifer
 static water level about 15 feet below land surface
 hydraulic conductivity = 10^{-2} cm/sec

Assumptions:

A desired purge rate of 500 mL/min and sampling rate of 100 mL/min will be used.

Calculations:

One well volume = (48 ft - 15 ft) x 613 mL/ft (2-inch diameter well)
 = 20.2 liters

Aquifer Transmissivity = hydraulic conductivity x aquifer thickness
 = 10^{-4} m/sec x 1 meter
 = 10^{-4} m²/sec or 8.64 m²/day

From Figure 2-2b:

At 5 minutes: 95% aquifer water and
 (5 min x 0.5 L/min)/20.2 L
 = 0.12 well volumes

At 10 minutes: 100% aquifer water and
 (10 min x 0.5 L/min)/20.2 L
 = 0.24 well volumes

It appears that a high percentage of aquifer water can be obtained within a relatively short time of pumping at 500 mL·min⁻¹. This pumping rate is below that used during well development to prevent well damage or further development.

Figure 2-2a. Example of Well Purging Requirement Estimating Procedure (Barcelona and others, 1985)

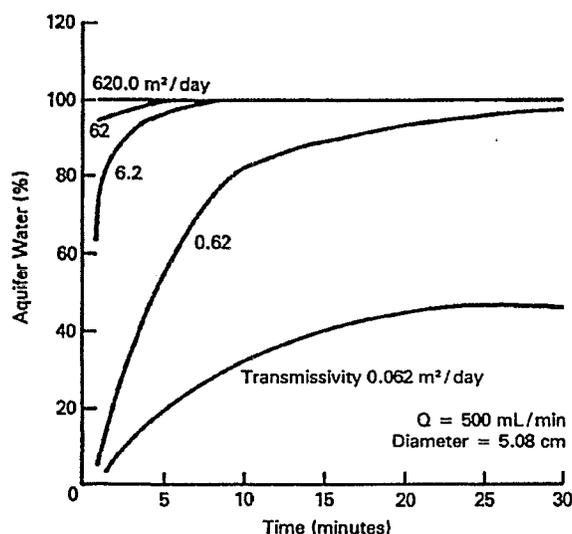


Figure 2-2b. Percentage of Aquifer Water Versus Time for Different Transmissivities

Sampling Materials and Mechanisms. In many monitoring situations, it is not possible to predict the requirements that either materials for well casings, pumps, and tubing, or pumping mechanisms must meet in order to provide error-free samples of ground water. Ideally, these components of the system should be durable and inert relative to the chemical properties of samples or the subsurface so as to neither contaminate nor remove chemical constituents from the water samples. Due to the long duration of regulatory program requirements, well casing materials, in particular, must be sufficiently durable and nonreactive to last several decades. It is generally much easier to substitute more appropriate sampling pumps or pump/tubing materials as knowledge of subsurface conditions improves than to drill additional wells to replace inadequate well casing or screen materials. Also, there is no simple way to account for errors that occur prior to handling a sample at the land surface. Therefore, it is good practice to carefully choose the components of the sampling system that make up the rigid materials in well casing/screens or pumps, and the flexible materials used in sample delivery tubing.

Rigid Materials. An experienced hydrologist can base well construction details mainly on hydrogeologic criteria, even in challenging situations where a separate contaminant phase may be present (Villaume, 1985). However, the best material for a specific monitoring application must be selected by considering subsurface geochemistry and the likely contaminants of interest. Therefore, strength, durability, and inertness should be balanced with cost considerations in the choice of rigid materials for well casing, screens, pumps, etc. (see Chapter 1).

Common well casing materials include TFE (Teflon[®]), PVC (polyvinyl chloride), stainless steel, and other ferrous materials. The strength, durability, and potential for sorptive or leaching interferences with chemical constituents have been reviewed in detail for these materials (Barcelona and others, 1985; Barcelona and others, 1983). Unfortunately, there is very little documentation of the severity or magnitude of well casing interferences from actual field investigations. This is the point at which optimized monitoring network design takes on an element of "research," as the components of the monitoring installation will need to be systematically evaluated.

Polymeric materials have the potential to absorb dissolved chemical constituents and leach either previously sorbed substances or components of the polymer formulations. Similarly, ferrous materials may adsorb dissolved chemical constituents and leach metal

ions or corrosion products, which may introduce errors into the results of chemical analysis. This potential in both cases is real, yet not completely understood. The recommendations in the references noted above can be summarized as follows:

Teflon^R is the well casing material least likely to cause significant error in ground-water monitoring programs focused on either organic or inorganic chemical constituents. It has sufficient strength for most applications at shallow depth (i.e., < 100 m) and is among the most inert materials ever made. For deeper installations, it can be linked to another material above the highest seasonal water level.

Stainless steel (either 316 or 304 type) well casing, under noncorrosive conditions, is the second least likely material to cause significant error for organic chemical constituent monitoring investigations. Fe, Mn, or Cr may be released, under corrosive conditions. Organic constituent sorption effects also may provide significant sources of error after corrosion processes have altered the virgin surface.

Rigid PVC well casing material that has National Sanitation Foundation approval should be used in monitoring well applications when noncemented or threaded joints are used, and organic chemical constituents are not expected to be of either present or future interest. Significant losses of strength, durability and inertness (i.e., sorption or leaching) may be expected under conditions where organic contaminants are

present in high concentration. PVC should, however, perform adequately in inorganic chemical constituent studies when concentrations of organic constituents are not high and tin or antimony species are not being targeted.

Monitoring wells made of appropriate materials and screened over discrete sections of the saturated thickness of geologic formations can yield a wealth of chemical and hydrologic information. Whether or not this level of performance is achieved frequently may depend on the care taken in evaluating the hydraulic performance of the sampling point.

Flexible Materials. Pump components and sample delivery tubing may contact a water sample more intimately than other components of a sampling system, including storage vessels and well casing. Similar considerations of inertness and noncontaminating properties apply to tubing, bladder, gasket and seal materials. Experimental evidence (Barcelona and others, 1985) has supported earlier recommendations drawn from manufacturers' specifications (Barcelona and others, 1983). A summary is provided in Table 2-3. Again, the care taken in materials' selection for the specific needs of the sampling program can pay real dividends and provides greater assurance of error-free sampling.

Sample Mechanisms. It is important to remember that sampling mechanisms themselves are not protocols. The sampling protocol for a particular monitoring network

Materials	Recommendations
Polytetrafluoroethylene (Teflon [*])	Recommended for most monitoring work, particularly for detailed organic analytical schemes. The material least likely to introduce significant sampling bias or imprecision. The easiest material to clean in order to prevent cross-contamination.
Polypropylene Polyethylene (linear)	Strongly recommended for corrosive high dissolved solids solutions. Less likely to introduce significant bias into analytical results than polymer formulations (PVC) or other flexible materials with the exception of Teflon [*] .
PVC (flexible)	Not recommended for detailed organic analytical schemes. Plasticizers and stabilizers make up a sizable percentage of the material by weight as long as it remains flexible. Documented interferences are likely with several priority pollutant classes.
Viton [*] Silicone (medical grade only) Neoprene	Flexible elastomeric materials for gaskets, O-rings, bladder, and tubing applications. Performance expected to be a function of exposure type and the order of chemical resistance as shown. Recommended only when a more suitable material is not available for the specific use. Actual controlled exposure trials may be useful in assessing the potential for analytical bias.

*Trademark of DuPont, Inc.

Table 2-3. Recommendations for Flexible Materials in Sampling Applications

is basically a step-by-step written description of the procedures used for well purging, delivering samples to the surface, and handling samples in the field. Once the protocol has been developed and used in a particular investigation, it provides a basis for modifying the program, if the extent or type of contamination requires more intensive work. An appropriate sampling mechanism is, however, an important part of any protocol. Ideally, the pumping mechanism should be capable of purging the well of stagnant water at rates of liters or gallons per minute and also of delivering ground water to the surface so that sample bottles may be filled at low flow rates (i.e., about 100 mL/min⁻¹) to minimize turbulence and degassing of the sample. In this way the criteria for representative sampling can be met while keeping the purging and sample collection steps simple. Nielsen and Yeates (1985) reviewed the types of sample collection mechanisms commercially available (Anonymous, 1985). This review supports the results, of research studies of their performance (Barcelona and others, 1984; Stoltzenburg and Nichols, 1985). Figure 2-3 shows examples of types of pumps or other samplers, which are fully described in a number of references (Barcelona and others, 1985; Gillham and others, 1983; Scaf and others, 1981). Given all of the varied hydrogeologic settings and potential chemical constituents of interest, several types of pumps or sampling mechanisms may be suitable for specific applications. Figure 2-4 contains some recommendations for reliable sampling mechanisms relative to the sensitivity of the sample to error. The main criteria for sampling pumps are the capabilities to purge stagnant water from the well and to deliver the water samples to the surface with minimal loss of sample integrity. Clearly, a mechanism that is shown to provide accurate and precise samples for volatile organic compound determinations should be suitable for most chemical constituents of interest.

After establishing a sampling point and the means to collect a sample, the next step is the development of the detailed sampling protocol.

Elements of the Sampling Protocol

There are few aspects of this subject that generate more controversy than the sampling steps, which make up the sampling protocol. Efforts to develop reliable protocols and optimize sampling procedures require particular attention to sampling mechanism effects on the integrity of ground-water samples (Barcelona and others, 1984; Stoltzenburg and Nichols, 1985), as well as to the potential errors involved in well purging, delivery tubing exposures (Barcelona and others, 1985; Ho, 1983), sample handling, and the impact of sampling

frequency on both the sensitivity and reliability of chemical constituent monitoring results. Quality assurance measures, including field blanks, standards, and split control samples, cannot account for errors in these steps of the sampling protocol. Actually, the sampling protocol is the focus of the overall study network design (Nacht, 1983), and it should be prepared flexibly so that it can be refined as information on site improves.

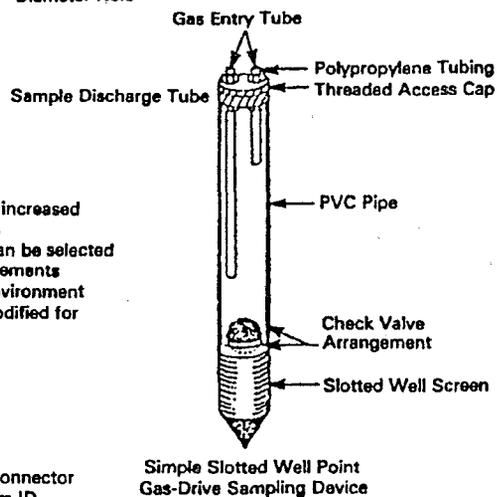
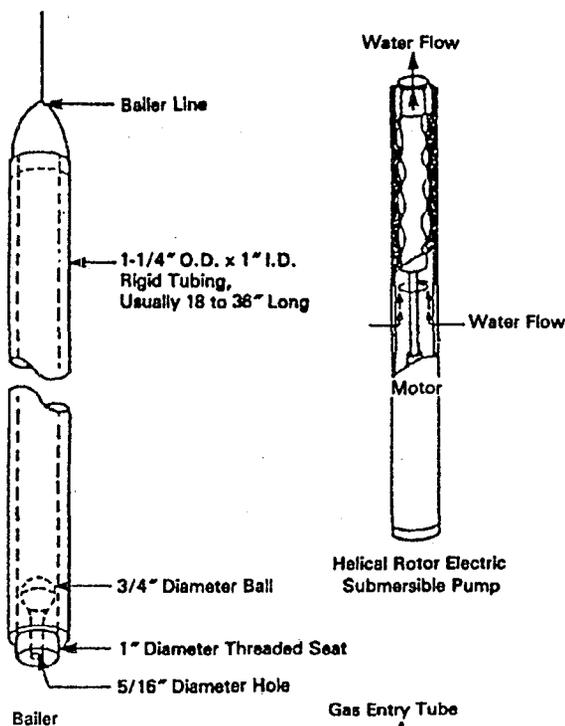
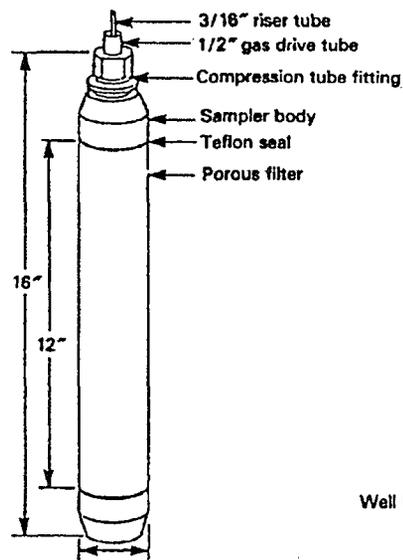
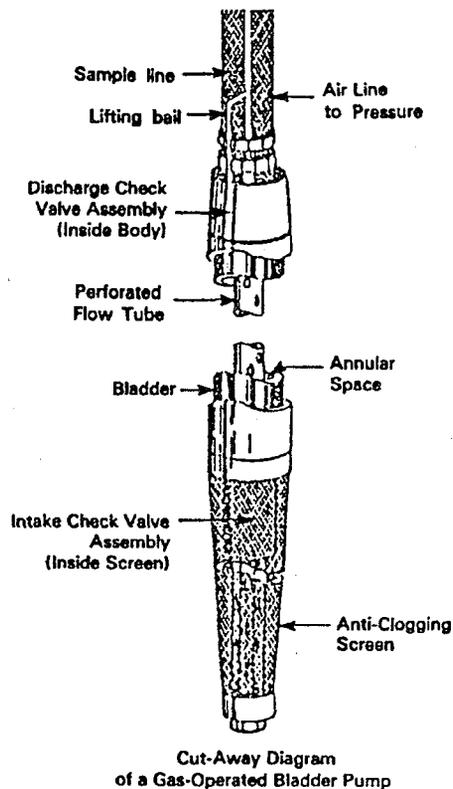
Each step within the protocol has a bearing on the quality and completeness of the information being collected. This is perhaps best shown by the progression of steps depicted in Figure 2-5. Corresponding to each step is a goal and recommendation for achieving that goal. The principal utility of this description is that it provides an outlined agenda for high-quality chemical and water-quality data.

To ensure maximum utility of the sampling effort and resulting data, it is essential to document the sampling protocol as performed in the field. In addition to noting the obvious information (i.e., persons conducting the sampling, equipment used, weather conditions, adherence to the protocol, and unusual observations), three basic elements of the sampling protocol should be recorded: (1) water-level measurements made prior to sampling, (2) the volume and rate at which water is removed from the well prior to sample collection (well purging), and (3) the actual sample collection, including measurement of well-purging parameters, sample preservation, sample handling, and chain of custody.

Water-Level Measurement

Prior to well purging or sample collection, it is extremely important to measure and record the water level in the well. These measurements are needed to estimate the amount of water to be purged prior to sample collection. Likewise, this information can be useful when interpreting monitoring results. Low water levels may reflect the influence of the cone of depression surrounding a nearby production well. High water levels, compared to measurements made at other times of the year, may be indicative of recent recharge events. In relatively shallow settings, high water levels from recent natural recharge events may result in the increase of certain constituents leached from the unsaturated zone or in the dilution of the dissolved solids content in the collected sample.

Documenting the nonpumping water levels for all wells at a site will provide historical information on the hydraulic conditions at the site. Analysis of this information may reveal changes in flow paths and serve as a check on the effectiveness of the wells to monitor changing hydrologic conditions. It is very useful to develop an



Notes:

1. Sampler length can be increased for special applications
2. Fabrication materials can be selected to meet analysis requirements and in situ chemical environment
3. Tubing sizes can be modified for special applications

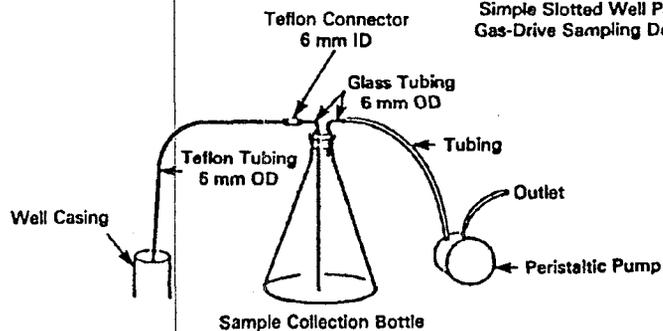


Figure 2-3. Schematic Diagrams of Common Ground-Water Sampling Devices (Neilsen and Yeates, 1985)

Type of constituent	Example of constituent	Positive displacement bladder pumps	Thief, in situ or dual check valve bailers	Mechanical positive displacement pumps	Gas-drive devices	Suction mechanisms
INCREASING RELIABILITY OF SAMPLING MECHANISMS ←						
Volatile Organic Compounds Organometallics Dissolved Gases Well-purging Parameters Trace Inorganic Metal Species Reduced Species Major Cations & Anions	Chloroform TOX CH ₃ Hg O ₂ , CO ₂ pH, Ω ⁻¹ Eh Fe, Cu NO ₂ ⁻ , S ⁻ Na ⁺ , K ⁺ , Ca ⁺⁺ Mg ⁺⁺ Cl ⁻ , SO ₄ ⁻	Superior performance for most applications Superior performance for most applications Superior performance for most applications Superior performance for most applications	May be adequate if well purging is assured May be adequate if well purging is assured May be adequate if well purging is assured Adequate May be adequate if well purging is assured	May be adequate if design and operation are controlled May be adequate if design and operation are controlled Adequate Adequate	Not recommended Not recommended May be adequate Adequate	Not recommended Not recommended May be adequate if materials are appropriate Adequate

Figure 2-4. Matrix of Sensitive Chemical Constituents and Various Sampling Mechanisms

Step	Goal	Recommendations
Hydrologic Measurements	Establish nonpumping water level.	Measure the water level to ±0.3 cm (±0.01 ft).
Well Purging	Remove or isolate stagnant H ₂ O which would otherwise bias representative sample.	Pump water until well purging parameters (e.g., pH, T, Ω ⁻¹ , Eh) stabilize to ±10% over at least two successive well volumes pumped.
Sample Collection	Collect samples at land surface or in well-bore with minimal disturbance of sample chemistry.	Pumping rates should be limited to ~100 mL/min for volatile organics and gas-sensitive parameters.
Filtration/Preservation	Filtration permits determination of soluble constituents and is a form of preservation. It should be done in the field as soon as possible after collection.	Filter: Trace metals, inorganic anions/cations, alkalinity. Do not filter: TOC, TOX, volatile organic compound samples; other organic compound samples only when required.
Field Determinations	Field analyses of samples will effectively avoid bias in determining parameters/constituents which do not store well; e.g., gases, alkalinity, pH.	Samples for determining gases, alkalinity and pH should be analyzed in the field if at all possible.
Field Blanks/Standards	These blanks and standards will permit the correction of analytical results for changes which may occur after sample collection: preservation, storage, and transport.	At least one blank and one standard for each sensitive parameter should be made up in the field on each day of sampling. Spiked samples are also recommended for good QA/QC.
Sample Storage/Transport	Refrigerate and protect samples to minimize their chemical alteration prior to analysis.	Observe maximum sample holding or storage periods recommended by the Agency. Documentation of actual holding periods should be carefully performed.

Figure 2-5. Generalized Ground-Water Sampling Protocol

understanding of the seasonal changes in water levels and associated chemical concentration variability at the monitored site.

Purging

The volume of stagnant water that should be removed from the monitoring well should be calculated from the analysis of field hydraulic conductivity measurements.

Rule-of-thumb guidelines for the volume of water to be purged can cause time delays and unnecessary pumping of excess contaminated water. These rules (i.e., 3-, 5- or 10-well volumes) largely ignore the hydraulic characteristics of individual wells and geologic settings. One advantage of using the same pump to both purge stagnant water and collect samples is the ability to measure pH and specific conductance in an in-line flow

cell. These parameters aid in verifying the purging efficiency and also provide a consistent basis for comparing samples from a single well or wells at a particular site. Since pH is a standard variable for aqueous solutions that is affected by degassing and depressurization (i.e., loss of CO₂), in-line measurements provide more accurate and precise determinations than discrete samples collected by grab sampling mechanisms.

The following example illustrates some of the other advantages of verifying the purge requirement for monitoring wells.

Documentation of the actual well purging process employed should be a part of a standard field sampling protocol. The calculated well purging requirement (e.g., >90 percent aquifer water) calls for the removal of five well volumes prior to sample collection. Field measurements of the well purging parameters have historically confirmed this recommended procedure. During a subsequent sampling effort, 12 well volumes were pumped before stabilized well purging parameter readings were obtained. Several possible causes could be explored: (1) a limited plume of contaminants may have been present at the well at the beginning of sampling and inadvertently discarded while pumping in an attempt to obtain stabilized indicator parameter readings; (2) the hydraulic properties of the well may have changed due to silting or encrustation of the screen, indicating the need for well rehabilitation or maintenance; (3) the flow-through device used for measuring the indicator parameters may have been malfunctioning; or (4) the well may have been tampered with by the introduction of a contaminant or relatively clean water in an attempt to bias the sample results.

Sample Collection and Handling

Water samples should be collected when the solution chemistry of the ground water being pumped has stabilized as indicated by pH, Eh, specific conductance, and temperature readings.

In practice, stable sample chemistry is indicated when the purging parameter measurements have stabilized over two successive well volumes. First, samples for volatile constituents, TOC, TOX, and those constituents that require field filtration or field determination should be collected. Then large-volume samples for extractable organic compounds, total metals, or nutrient anion determinations should be collected.

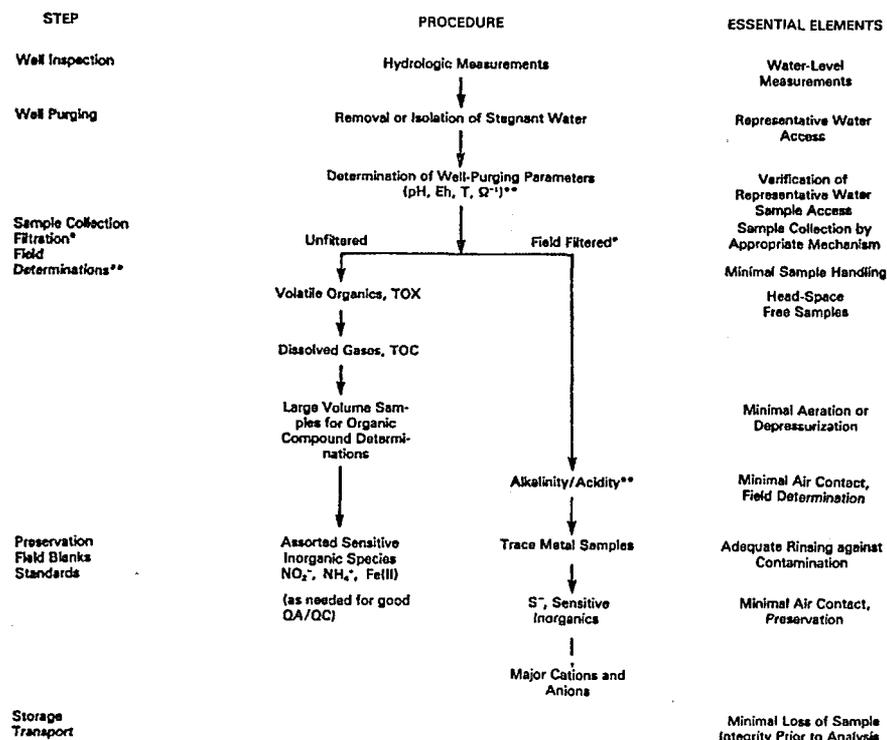
All samples should be collected as close as possible to the well head. A "tee" fitting placed ahead of the in-line device for measuring the well purging parameters makes

this more convenient. Regardless of the sample mechanism in use or the components of the sampling train, wells that are located upgradient of a site, and therefore are expected to be representative of background quality, should be sampled first to minimize the potential for cross-contamination. Laboratory detergent solutions and distilled water should be used to clean the sampling train between samples. An acid rinse (0.1 N HCl) or solvent rinse (i.e., hexane or methanol) may be used to supplement these cleaning steps, if necessary. Cleaning procedures should be followed by distilled water rinses, which may be saved to check cleaning efficiency.

The order in which samples are taken for specific types of chemical analyses should be decided by the sensitivity of the samples to handling (i.e., most sensitive first) and the need for specific information. For example, the flowchart shown in Figure 2-6 depicts a priority order for a generalized sample collection effort. The samples for organic chemical constituent determinations are taken in decreasing order of sensitivity to handling errors, while the inorganic chemical constituents, which may require filtration, are taken afterwards.

Instances arise, even with properly developed monitoring wells, that call for the filtration of water samples. It should be evident, however, that adequate well development procedures, which require 2 to 3 hours of bailing, swabbing, pumping, or air purging at each well, may save many hours in sample filtration. Well development may have to be repeated at periodic intervals to minimize the collection of turbid samples. In this respect, it is important to minimize the disturbance of fines that accumulate in the well bore. This can be achieved by careful placement of the sampling pump intake at the top of the screened interval, low pumping rates, and avoiding the use of bailing techniques that disturb sediment accumulations.

It is advisable to refrain from filtering TOC, TOX, or other organic compound samples because the increased handling required may result in the loss of chemical constituents of interest. Allowing any fine material to settle prior to analysis, followed by decanting the sample, is preferable to filtration in these instances. If filtration is necessary for the determination of extractable organic compounds, it should be performed in the laboratory using nitrogen pressure. When samples must be filtered, it may be necessary to run parallel sets of filtered and unfiltered samples with standards to establish the recovery of hydrophobic compounds. All of the materials' precautions used in the construction of the sampling train should be observed for filtration apparatus. Vacuum filtration of ground-water samples is not recommended.



* Denotes samples which should be filtered in order to determine dissolved constituents. Filtration should be accomplished preferably with in-line filters and pump pressure or by N₂ pressure methods. Samples for dissolved gases or volatile organics should not be filtered. In instances where well development procedures do not allow for turbidity-free samples and may bias analytical results, split samples should be spiked with standards before filtration. Both spiked samples and regular samples should be analyzed to determine recoveries from both types of handling.

** Denotes analytical determinations which should be made in the field.

Figure 2-6. Generalized Flow Diagram of Ground-Water Sampling Steps (Barcelona and others, 1985)

Water samples for dissolved inorganic chemical constituents (e.g., metals, alkalinity, and anionic species) should be filtered in the field. The preferred arrangement is an in-line filtration module, which utilizes sampling pump pressure for its operation. These modules have tubing connectors on the inlet and outlet parts and range in diameter from 2.5 to 15 cm. Large diameter filter holders, which can be rapidly disassembled for filter pad replacement, are the most convenient and efficient designs (Kennedy and others, 1976; Skougstad and Scarbo, 1968).

Representative sampling results from the execution of a carefully planned sampling protocol. An important consideration for maintaining sample integrity after collection is to minimize sample handling, which may bias subsequent determinations of chemical constituents. Since opportunities to collect high-quality data for the characterization of site conditions may be limited by time, it is prudent to conduct sample collection as carefully as possible from the beginning of the sampling period. It is preferable to risk error on the conservative side when doubt exists as to the sensitivity

of specific chemical constituents to sampling or handling errors. Repeat sampling or analysis cannot make up for lost data collection opportunities.

For samples collected for specific chemical constituents, recommended sample handling and analysis procedures may need to be modified. Samples that contain several chemicals and have undergone extended storage periods can cause significant problems. It is frequently more effective to perform a rapid field determination of specific inorganic constituents (e.g., alkalinity, pH, ferrous iron, sulfide, nitrite, or ammonium) than to attempt sample preservation followed by laboratory analysis of these samples.

Many samples can be held for the U.S. EPA recommended maximum holding times after proper preservation (Table 2-4).

Quality Assurance/Quality Control

Planning for valid water-quality data collection depends upon both the knowledge of the system and continued refinement of all sample handling/collection procedures.

Parameters (Type)	Volume Required (mL) 1 Sample*	Container (Material)	Preservation Method	Maximum Holding Period
Well Purging				
pH (grab)	50	T,S,P,G	None; field det.	<1 hr**
Ω^{-1} (grab)	100	T,S,P,G	None; field det.	<1 hr**
T (grab)	1000	T,S,P,G	None; field det.	None
Eh (grab)	1000	T,S,P,G	None; field det.	None
Contamination Indicators				
pH, Ω^{-1} (grab)	As above	As above	As above	As above
TOC	40	G,T	Dark, 4°C	24 hr
TOX	500	G,T	Dark, 4°C	5 days
Water Quality				
Dissolved gases (O ₂ , CH ₄ , CO ₂)	10 mL minimum	G,S	Dark, 4°C	<24 hr
Alkalinity/ Acidity	100	T,G,P	4°C/None	<6 hr**/ <24 hr
	Filtered under pressure with appropriate media			
(Fe, Mn, Na ⁺ , K ⁺ , Ca ⁺⁺ , Mg ⁺⁺)	All filtered 1000 mL	T,P	Field acidified to pH <2 with HNO ₃	6 months***
(PO ₄ ⁻ , Cl ⁻ , Silicate)	@50	(T,P,G glass only)	4°C	24 hr/ 7 days; 7 days
NO ₃ ⁻	100	T,P,G	4°C	24 hr
SO ₄ ⁻	50	T,P,G	4°C	7 days
NH ₄ ⁺	400	T,P,G	4°C/H ₂ SO ₄ to pH <2	24 hr/ 7 days
Phenols	500	T,G	4°C/H ₃ PO ₄ to pH <4	24 hr
Drinking Water Suitability As, Ba, Cd, Cr, Pb, Hg, Se, Ag	Same as above for water quality cations (Fe, Mn, etc.)	Same as above	Same as above	6 months
F ⁻	Same as chloride above	Same as above	Same as above	7 days
Remaining Organic Parameters	As for TOX/TOC, except where analytical method calls for acidification of sample			24 hr

*It is assumed that at each site, for each sampling date, replicates, a field blank and standards must be taken at equal volume to those of the samples.

**Temperature correction must be made for reliable reporting. Variations greater than $\pm 10\%$ may result from longer holding period.

***In the event that HNO₃ cannot be used because of shipping restrictions, the sample should be refrigerated to 4°C, shipped immediately, and acidified on receipt at the laboratory. Container should be rinsed with 1:1 HNO₃ and included with sample.

Note: T = Teflon; S = stainless steel; P = PVC, polypropylene, polyethylene; G = borosilicate glass.

From Scaif et al., 1981.

Table 2-4. Recommended Sample Handling and Preservation Procedures for a Detective Monitoring Program

As discussed earlier, the need to begin QA/QC planning with the installation of the sampling point cannot be overemphasized.

The use of field blanks, standards, and spiked samples for field QA/QC performance is analogous to the use of laboratory blanks, standards, and procedural or

validation standards. The fundamental goal of field QC is to ensure that the sample protocol is being executed faithfully and that situations that might lead to error are recognized before they seriously impact the data. The use of field blanks, standards, and spiked samples can account for changes in samples that occur during sample collection.

Field blanks and standards enable quantitative correction for bias (i.e., systematic errors), which arise due to handling, storage, transportation, and laboratory procedures. Spiked samples and blind controls provide the means to correct combined sampling and analytical accuracy or recoveries for the actual conditions to which the samples have been exposed.

All QC measures should be performed for at least the most sensitive chemical constituents for each sampling date. Examples of sensitive constituents would be benzene or trichloroethylene as volatile organic compounds and lead or iron as metals. It is difficult to use laboratory blanks alone for determining the limits of detection or quantitation. Laboratory distilled water may contain apparently higher levels of volatile organic compounds (e.g., methylene chloride) than would uncontaminated ground-water samples. The field blanks and spiked samples should be used for this purpose, conserving the results of lab blanks as checks on elevated laboratory background levels.

Whether or not the ground water is contaminated with interfering compounds, spiked samples provide a basis for both identifying the constituents of interest and correcting their recovery (or accuracy) based on the recovery of the spiked standard compounds. For example, if trichloroethylene in a spiked sample is recovered at a mean level of 80 percent (-20 percent bias), the concentrations of trichloroethylene determined

in the samples for this sampling date may be corrected by a factor of 1.2 for low recovery. Similarly, if 50 percent recovery (-50 percent bias) is reported for the spiked standard, it is likely that sample handling or analytical procedures are out of control and corrective measures should be taken at once. It is important to know if the laboratory has performed these corrections or taken corrective action when it reports the results of analyses. It should be further noted that many regulatory agencies require evidence of QC and analytical performance but do not generally accept data that have been corrected.

Field blanks, standards, and blind control samples provide independent checks on handling and storage, as well as the performance of the analytical laboratory. Ground-water analytical data are incomplete unless the analytical performance data (e.g., accuracy, precision, detection, and quantitation limits) are reported with each set of results. Discussions of whether ground-water quality has changed significantly must be tempered by the accuracy and precision performance for specific chemical constituents.

Table 2-5 is a useful guide to the preparation of field standards and spiking solutions for split samples. It is important that the field blanks and standards are made on the day of sampling and are subjected to all conditions to which the samples are exposed. Field spiked samples or blind controls should be prepared by spiking with concentrated stock standards in an appropriate

Stock Solution for Field Spike of Split Samples						
Sample Type	Volume	Composition	Field Standard (Concentration)	Solvent	Concentration of Components	Field Spike Volume
Alkalinity	50 mL	Na ⁺ , HCO ₃ ⁻	10.0; 25 (ppm)	H ₂ O	10,000; 25,000 (ppm)	(50 µL)
Anions	1 L	K ⁺ , Na ⁺ , Cl ⁻ , SO ₄ ⁻ , F ⁻ , NO ₃ ⁻ , PO ₄ ³⁻ , Si	25, 50 (ppm)	H ₂ O	25,000; 50,000 (ppm)	(1 mL)
Cations	1 L	Na ⁺ , K ⁺ , Ca ⁺⁺ , Mg ⁺⁺ , Cl ⁻ , NO ₃ ⁻	5.0; 10.0 (ppm)	H ₂ O, H ⁺ (acid)	5,000; 10,000 (ppm)	(1 mL)
Trace Metals	1 L	Cd ⁺⁺ , Cu ⁺⁺ , Pb ⁺⁺ , Cr ⁺⁺⁺ , Ni ⁺⁺ , Ag ⁺ , Fe ⁺⁺⁺ , Mn ⁺⁺	10.0; 25.0 (ppm)	H ₂ O, H ⁺ (acid)	10,000; 25,000 (ppm)	(1 mL)
TOC	40 mL	Acetone KHP	0.2; 0.5 (ppm-C) 1.8; 4.5 (ppm-C)	H ₂ O	200; 500 (ppm-C) 1,800; 4,500 (ppm-C)	(40 µL)
TOX	50 mL	Chloroform 2,4,6 Trichlorophenol	12.5; 25 (ppb) 12.5; 25 (ppb)	H ₂ O/poly* (ethylene glycol)	12,500; 25 (ppm) 12,500; 25 (ppm)	(500 µL)
Volatiles	40 mL	Dichlorobutane, Toluene Dibromopropane, Xylene	25; 50 (ppb)	H ₂ O/poly* (ethylene glycol)	25; 50 (ppm)	(40 µL)
Extractables A	1 L	Phenol Standards	25; 50 (ppb)	Methanol**	25; 50 (ppm)	(1 mL)
Extractables B	1 L	Polynuclear Aromatic Standards	25; 50 (ppb)	Methanol	25; 50 (ppm)	(1 mL)
Extractables C	1 L	Standards as Required	25; 50 (ppb)	Methanol	25; 50 (ppm)	(1 mL)

*75:25 water/polyethylene glycol (400 amu) mixture.

**Glass distilled methanol.

Table 2-5. Field Standard and Sample Spiking Solutions

background solution prior to the collection of any actual samples. Additional precautions should be taken against the depressurization of samples during air transport and the effects of undue exposure to light during sample handling and storage. All of the QC measures noted above will provide both a basis for high-quality data reporting and a known degree of confidence in data interpretation. Well-planned overall quality control programs also will minimize the uncertainty in long-term trends when different personnel have been involved in collection and analysis.

Sample Storage and Transport

The storage and transport of ground-water samples often are the most neglected elements of the sampling

protocol. Due care must be taken in sample collection, field determinations, and handling. Transport should be planned so as not to exceed sample holding time before laboratory analysis. Every effort should be made to inform the laboratory staff of the approximate time of arrival so that the most critical analytical determinations can be made within recommended storage periods. This may require that sampling schedules be adjusted so that the samples arrive at the laboratory during working hours.

The documentation of actual sample storage and treatment may be handled by chain of custody procedures. Figure 2-7 shows an example of a chain of custody form. Briefly, the chain of custody record should

CHAIN OF CUSTODY RECORD

Sampling Date _____ Site Name _____

Well or Sampling Points: _____

Sample Sets for Each: Inorganic, Organic, Both.

Inclusive Sample Numbers:

Company's Name _____ Telephone (____) _____

Address _____

number street city state zip

Collector's Name _____ Telephone (____) _____

Date Sampled _____ Time Started _____ Time Completed _____

Field Information (Precautions, Number of Samples, Number of Sample Boxes, Etc.):

1. _____

name organization location

2. _____

name organization location

Chain of Possession (After samples are transported off-site or to laboratory):

1. _____ (IN)

signature title

_____ (OUT)

name (printed) date/time of receipt

2. _____ (IN)

signature title

_____ (OUT)

name (printed) date/time of receipt

Analysis Information:

	Aliquot	Analysis Begun (date/time)	Initials	Analysis Completed (date/time)	Initials
1.					
2.					
3.					
4.					
5.					

Figure 2-7. Sample Chain of Custody Form

contain the dates and times of collection, receipt, and completion of all the analyses on a particular set of samples. Frequently, it is the only record that exists of the actual storage period prior to the reporting of analytical results. The sampling staff members who initiate the chain of custody should require that a copy of the form be returned to them with the analytical report. Otherwise, verification of sample storage and handling will be incomplete.

Shipping should be arranged to ensure that samples are neither lost nor damaged enroute to the laboratory. Several commercial suppliers of sampling kits permit refrigeration by freezer packs and include proper packing. It may be useful to include special labels or distinctive storage vessels for acid-preserved samples to accommodate shipping restrictions.

Summary

Ground-water sampling is conducted for a variety of reasons, ranging from detection or assessment of the extent of a contaminant release to evaluations of trends in regional water quality. Reliable sampling of the subsurface is inherently more difficult than either air or surface water sampling because of the inevitable disturbances that well drilling or pumping can cause and the inaccessibility of the sampling zone. Therefore, "representative" sampling generally requires minimal disturbance of the subsurface environment and the properties of a representative sample are scale dependent. For any particular case, the applicable criteria should be set at the beginning of the effort to judge representativeness.

Reliable sampling protocols are based on the hydrogeologic setting of the study site and the degree of analytical detail required by the monitoring program. Quality control begins with the evaluation of the hydraulic performance of the sampling point or well and the proper selection of mechanisms and materials for well purging and sample collection. All other elements of the program and variables that affect data validity may be accounted for by field blanks, standards, and control samples.

Although research is needed on a host of topics involved in ground-water sampling, defensible sampling protocols can be developed to ensure the collection of data of known quality for many types of programs. If properly planned and developed, long-term sampling efforts can benefit from the refinements that research progress will bring. Careful documentation will provide the key to this opportunity.

References

- Anonymous, 1985, Monitoring products, a buyers guide: *Ground Water Monitoring Review*, v. 5, no. 3, pp. 33-45.
- Barcelona, M.J., J.P. Gibb, J.A. Helfrich, and E.E. Garske, 1985, Practical guide for ground-water sampling: Illinois State Water Survey Contract Report 374, U.S. Environmental Protection Agency, Robert S. Kerr Environmental Research Laboratory, Ada, OK, and U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Las Vegas, NV.
- Barcelona, M.J., J.A. Helfrich, and E.E. Garske, 1985, Sampling tubing effects on ground water samples: *Analytical Chemistry*, v. 47, no. 2, pp. 460-464.
- Barcelona, M.J., J.A. Helfrich, E.E. Garske, and J.P. Gibb, 1984, A laboratory evaluation of ground-water sampling mechanisms: *Ground Water Monitoring Review*, v. 4, no. 2, pp. 32-41.
- Barcelona, M.J., 1984, TOC determinations in ground water: *Ground Water*, v. 22, no. 1, pp. 18-24.
- Barcelona, M.J., and E.E. Garske, 1983, Nitric oxide interference in the determination of dissolved oxygen by the azide-modified Winkler method: *Analytical Chemistry*, v. 55, pp. 965-967.
- Barcelona, M.J., J.P. Gibb, and R.A. Miller, 1983, A guide to the selection of materials for monitoring well construction and ground-water sampling: Illinois State Water Survey Contract Report, U.S. EPA-RSKERL, EPA-600/S2-84-024. 78 pp.
- Barcelona, M.J., 1983, Chemical problems in ground-water monitoring: Proc. of Third National Symposium on Aquifer Rehabilitation and Ground Water Monitoring, May 24-27, Columbus, OH.
- Barvenik, M.J. and R.M. Cadwgan, 1983, Multilevel gas-drive sampling of deep fractured rock aquifers in Virginia: *Ground Water Monitoring Review*, v. 3, no. 4, pp. 34-40.
- Brass, H.J., M.A. Feige, T. Halloran, J.W. Mellow, D. Munch, and R.F. Thomas, 1977, The national organic monitoring survey, samplings and analyses for purgeable organic compounds: in Pojasek, R.B., ed. *Drinking Water Quality Enhancement through Source Protection*, Ann Arbor, MI: Ann Arbor Science Publishers.
- Brobst, R.B., 1984, Effects of two selected drilling fluids on ground water sample chemistry: in *Monitoring Wells*,

Their Place in the Water Well Industry Educational Session, NWWA National Meeting and Exposition, Las Vegas, NV.

Claasen, H.C., 1982, Guidelines and techniques for obtaining water samples that accurately represent the water chemistry of an aquifer: U.S. Geological Survey Open File Report, Lakeland, CO.

Dunlap, W.J., J.F. McNabb, M.R. Scalf, and R.L. Cosby, 1977, Sampling for organic chemicals and microorganisms in the subsurface: U.S. Environmental Protection Agency, Robert S. Kerr Environmental Research Laboratory, Ada, OK. EPA-600/2-77-176.

Evans, R.B., and G.E. Schweitzer, 1984, Assessing hazardous waste problems: Environmental Science and Technology, v. 18, no. 11 pp. 330A-339A.

Everett, L.G. and L.G. McMillion, 1985, Operational ranges for suction lysimeters: Ground Water Monitoring Review, v. 5, no. 3, pp. 51-60.

Everett, L.G., L.G. Wilson, E.W. Haylman, and L.G. McMillion, 1984, Constraints and categories of vadose zone monitoring devices: Ground Water Monitoring Review, v. 4, no. 4.

Everett, L.G., L.G. Wilson, and L.G. McMillion, 1982, Vadose zone monitoring concepts for hazardous waste sites: Ground Water, v. 20, no. 3, pp. 312-324.

Fenn, D., E. Cocozza, J. Isbister, O. Braids, B. Yare, and P. Roux, 1977, Procedures manual for ground water monitoring at solid waste disposal facilities: U.S. Environmental Protection Agency, Cincinnati, OH: EPA-530/SW611.

Gibb, J.P., R.M. Schuller, and R.A. Griffin, 1981, Procedures for the collection of representative water quality data from monitoring wells: Illinois State Water Survey Cooperative Report 7, Champaign, IL: Illinois State Water Survey and Illinois State Geological Survey.

Gillham, R.W., M.J.L. Robin, J.F. Barker, and J.A. Cherry, 1983, Ground water monitoring and sample bias: API Pub. 4367 American Petroleum Institute.

Grisak, G.E., R.E. Jackson, and J.F. Pickens, 1978, Monitoring groundwater quality, the technical difficulties: Water Resources Bulletin, v. 6, pp. 210-232.

Gorelick, S.M., B. Evans, and I. Remsan, 1983, Identifying sources of ground water pollution, an optimization approach: Water Resources Research, v. 19, no. 3, pp. 779-790.

Heaton, T.H.E., and J.C. Vogel, 1981, "Excess air" in ground water: Journal Hydrology, v. 50, pp. 201-216.

Ho, J.S-Y., 1983, Effect of sampling variables on recovery of volatile organics in water: Journal American Water Works Association, v. 12, pp. 583-586.

Kennedy, V.C., E.A. Jenne, and J.M. Burchard, 1976, Backflushing filters for field processing of water samples prior to trace-element analysis: OpenFile Report 76-126, U.S. Geological Survey Water- Resources Investigations.

Lindau, C.W., and R. F. Spalding, 1984, Major procedural discrepancies in soil extracted nitrate levels and nitrogen isotopic values: Ground Water, v. 22, no. 3, pp. 273-278.

Mackay, D.M., P.V. Roberts, and J.A. Cherry, 1985, Transport of organic contaminants in ground water: Environmental Science and Technology, v. 19, no. 5, pp. 384-392.

Melby, J.T., 1989, A comparative study of hydraulic conductivity determinations for a fine-grained aquifer: unpubl. M.S. theses, School of Geology, Oklahoma State University, 171p.

Nacht, S.J., 1983, Monitoring sampling protocol considerations: Ground Water Monitoring Review Summer, pp. 23-29.

National Council of the Paper Industry for Air and Stream Improvement, 1982, A guide to groundwater sampling: Technical Bulletin 362, NCASI, New York, NY.

Nielsen, D.M., and G.L. Yeates, 1985, A comparison of sampling mechanisms available for small diameter ground water monitoring wells: Ground Water Monitoring Review, v. 5, no. 2, pp. 83-99.

Pickens, J.F., J.A. Cherry, G.E. Grisak, W.F. Merritt, and B.A. Risto, 1978, A multilevel device for ground-water sampling and piezometric monitoring: Ground Water, v. 16, no. 5, pp. 322-327.

Robbins, G.A., and M.M. Gemmill, 1985, Factors requiring resolution in installing vadose zone monitoring systems: Ground Water Monitoring Review, v. 5, no. 3, pp. 75-80.

Scalf, M.R., J.F. McNabb, W.J. Dunlap, R.L. Cosby, and J. Fryberger, 1981, Manual of ground water quality sampling procedures: National Water Well Association, OH EPA-600/2-81-160..

- Schwarzenbach, R.P. and others, 1985, Ground-water contamination by volatile halogenated alkanes, abiotic formation of volatile sulfur compounds under anaerobic conditions: *Environmental Science and Technology*, v. 19, pp. 322-327.
- Sisk, S.W., 1981, NEIC manual for groundwater/subsurface investigations at hazardous waste sites: U.S. Environmental Protection Agency, Office of Enforcement, National Enforcement Investigations Center, Denver, CO.
- Skougstad, M.W., and G.F. Scarbo, Jr., 1968, Water sample filtration unit: *Environmental Science and Technology*, v. 2, no. 4, pp. 298-301.
- Stolzenburg, T.R., and D.G. Nichols, 1985, Preliminary results on chemical changes in ground water samples due to sampling devices: Report to Electric Power Research Institute, Palo Alto, California, EA-4118. Residuals Management Technology, Inc., Madison, WI.
- Tinlin, R.M., ed., 1976, Monitoring groundwater quality, illustrative examples: U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Las Vegas, NV, EPA-600/4-76-036.
- Todd, D.K., R.M. Tinlin, K.D. Schmidt, and L.G. Everett, 1976, Monitoring ground-water quality, monitoring methodology: U.S. Environmental Protection Agency, Las Vegas, NV, EPA-600/4-76-026.
- U.S. Geological Survey, 1977, National handbook of recommended methods for water-data acquisition: U.S. Geological Survey, Office of Water Data Coordination, Reston, VA.
- Villaume, J.R., 1985, Investigations at sites contaminated with dense, non-aqueous phase liquids (NAPLs): *Ground Water Monitoring Review*, v. 5, no. 2, pp. 60-74.
- Wehrmann, H.A., 1983, Monitoring well design and construction: *Ground Water Age*, v. 4, pp. 35-38.
- Wilson, J.T., and J. F. McNabb, 1983, Biological transformation of organic pollutants in ground water: *EOS*, v. 64, no. 33, pp. 505-506.
- Wilson, J.T. and others, 1983, Biotransformation of selected organic pollutants in ground water in Volume 24 *Developments in Industrial Microbiology*, Society for Industrial Microbiology.
- Wilson, L.G., 1983, Monitoring in the vadose zone, part III: *Ground Water Monitoring Review*, v. 3, no. 2, pp. 155-166.
- Wilson, L.G., 1982, Monitoring in the vadose zone, part II: *Ground Water Monitoring Review*, v. 2, no. 1, pp. 31-42.
- Wilson, L.G., 1981, Monitoring in the vadose zone, part I: *Ground Water Monitoring Review*, v. 1, no. 3, pp. 32-41.
- Winograd, I.J., and F.N. Robertson, 1982, Deep oxygenated ground water, anomaly or common occurrence?: *Science*, v. 216, pp. 1227-1230.
- Wood, W., and M.J. Petraitis, 1984, Origin and distribution of carbon dioxide in the unsaturated zone of the southern High Plains of Texas: *Water Resources Research*, v. 20, no. 9, pp. 1193-1208.
- Wood, W.W., 1976, Guidelines for collection and field analysis of groundwater samples for selected unstable constituents: *Techniques for Water Resources Investigations*, U.S. Geological Survey.
- Yare, B.S., 1975, The use of a specialized drilling and ground-water sampling technique for delineation of hexavalent chromium contamination in an unconfined aquifer, southern New Jersey Coastal Plain: *Ground Water*, v. 13, no. 2, pp. 151-154.

Chapter 3

TRANSPORT AND FATE OF CONTAMINANTS IN THE SUBSURFACE

Introduction

Protection and remediation of ground-water resources require an understanding of processes that affect fate and transport of contaminants in the subsurface environment. This understanding allows: (1) prediction of the time of arrival and concentration of contaminants at a receptor, such as a monitoring well, a water supply well, or a body of surface water; (2) design of cost-effective and safe waste management facilities; (3) installation of effective monitoring systems; and (4) development of efficient and cost-effective strategies for remediation of contaminated aquifers (Palmer and Johnson, 1989a).

Contaminants in ground water will move primarily in a horizontal direction that is determined by the hydraulic gradient. The contaminants will decrease in concentration because of such processes as dispersion (molecular and hydrodynamic), filtration, sorption, various chemical processes, microbial degradation, time rate release of contaminants, and distance of travel (U.S. Environmental Protection Agency, 1985). Processes such as hydrodynamic dispersion affect all contaminants equally, while sorption, chemical processes, and degradation may affect various contaminants at different rates. The complex factors that control the movement of contaminants in ground water and the resulting behavior of contaminant plumes are commonly difficult to assess because of the interaction of the many factors that affect the extent and rate of contaminant movement. Predictions of movement and behavior can be used only as estimates, and modeling is often a useful tool to integrate the various factors.

The U.S. Environmental Protection Agency (EPA) sponsored a series of technology transfer seminars between October 1987 and February 1988 that provided an overview of the physical, chemical, and biological processes that govern the transport and fate of contaminants in the subsurface. The following discussion is a summary of the workshops, and is based on the

seminar publication, *Transport and Fate of Contaminants in the Subsurface* (U.S. Environmental Protection Agency, 1989).

Physical Processes Controlling the Transport of Contaminants in the Aqueous Phase in the Subsurface

Advection-Dispersion Theory

The study of advection and dispersion processes is useful for predicting the time when an action limit, i.e., a concentration limit used in regulations such as drinking water standards, will be reached. Knowledge of advection-dispersion also can be used to select technically accurate and cost-effective remedial technologies for contaminated aquifers.

If concentrations of a contaminant were measured in a monitoring well that was located between a contaminant source and a receptor such as a water supply well, a graph of concentrations versus time would show a breakthrough curve, i.e., the concentrations do not increase in a step-function (i.e., plug flow), but rather in an S-shaped curve (Figure 3-1). In a one-dimensional, homogeneous system, the arrival of the center of the mass is due to advection, while the spread of the breakthrough curve is the result of dispersion (Palmer and Johnson, 1989a).

Advection

Advection is defined by the transport of a non-reactive, conservative tracer at an average ground-water velocity (Palmer and Johnson, 1989a). The average linear velocity is dependent on (1) the hydraulic conductivity of the subsurface geologic formation in the direction of ground-water flow, (2) the porosity of the formation and (3) the hydraulic gradient in the direction of ground-water flow. For waste contaminants that react through precipitation/dissolution, adsorption, and/or partitioning reactions within the subsurface formation, the velocity can be different from the average ground-water velocity.

BREAKTHROUGH CURVE

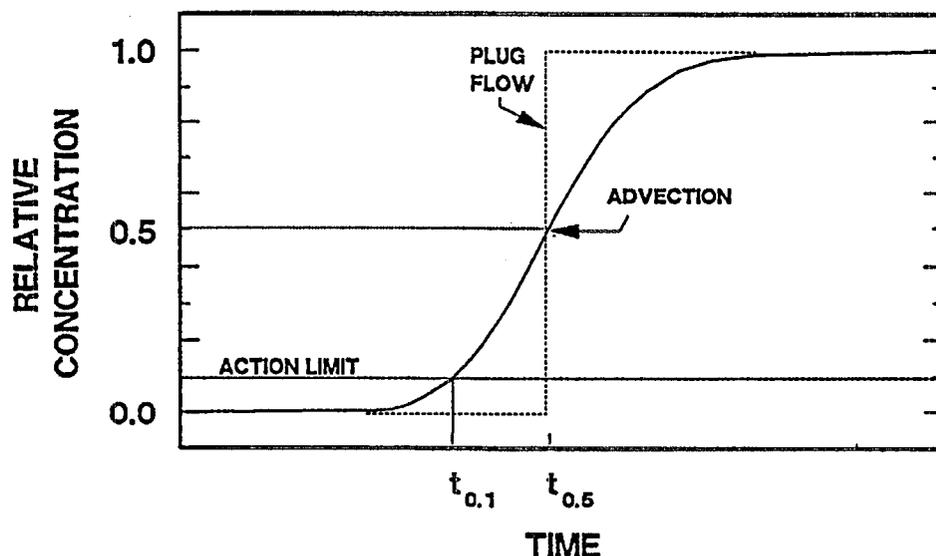


Figure 3-1. Breakthrough Curve for a Contaminant, as Measured in a Monitoring Well (Palmer and Johnson, 1989a)

Dispersion

Dispersion of waste contaminants in an aquifer causes the concentration of contaminants to decrease with increasing length of flow (U.S. Environmental Protection Agency, 1985). Dispersion is caused by: (1) molecular diffusion (important only at very low velocities) and (2) hydrodynamic mixing (occurring at higher velocities in laminar flow through porous media). Contaminants traveling through porous media have different velocities and flow paths with different lengths. Contaminants moving along a shorter flow path or at a higher velocity, therefore, arrive at a specific point sooner than contaminants following a longer path or traveling at a

lower velocity, resulting in hydrodynamic dispersion.

Figure 3-2 shows that dispersion can occur in both longitudinal (in the direction of ground-water flow) and transverse (perpendicular to ground-water flow) directions, resulting in the formation of a conic waste plume downstream from a continuous pollution source (U.S. Environmental Protection Agency, 1985). The concentration of waste contaminants is less at the margins of the plume and increases towards the source. A plume will increase in size with more rapid flow within a time period, because dispersion is directly related to ground-water velocity.

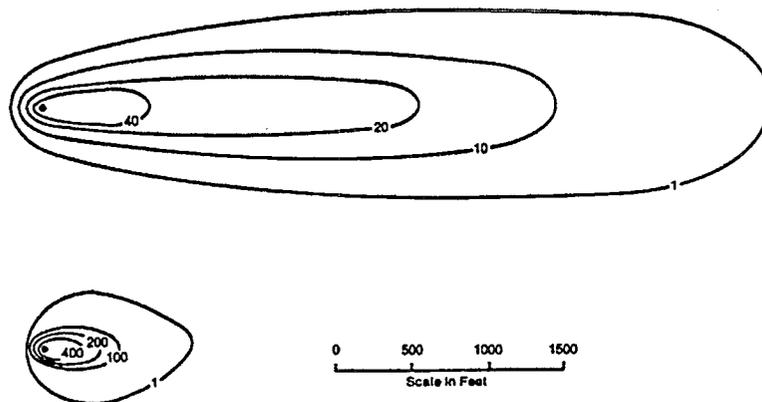


Figure 3-2. The Effects of Ground-Water Velocity on Plume Shape. Upper Plume Velocity: 1.5 ft/day and Lower Plume Velocity: 0.5 ft/day (U.S. Environmental Protection Agency, 1985).

The dispersion coefficient varies with ground-water velocity. At low velocity, the dispersion coefficient is relatively constant, but increases linearly with velocity as ground-water velocity increases. Based on these observations, investigators proposed that the dispersion coefficient can be expressed as a sum of an effective molecular diffusion coefficient and a mechanical dispersion coefficient (Palmer and Johnson, 1989a).

The effective molecular diffusion coefficient is a function of the solution diffusion coefficient and the tortuosity of the medium. Tortuosity accounts for the increased distance a diffusing ion must travel around sand grains. The mechanical dispersion coefficient is proportional to velocity. Specifically, mechanical dispersion is a result of: (1) velocity variations within a pore, (2) different pore geometries, and (3) divergence of flow lines around sand grains present in a porous medium (Gillham and Cherry, 1982).

The term dispersivity is often confused with dispersion. Dispersivity does not include velocity, so to convert dispersivity to dispersion requires multiplication by velocity. Since dispersion is dependent on site-specific velocity parameters and configuration of pore spaces within an aquifer, a dispersion coefficient should be determined experimentally or empirically for a specific aquifer. The selection of appropriate dispersion coefficients that adequately reflect existing aquifer conditions is critical to the success of chemical transport modeling (U.S. Environmental Protection Agency, 1985).

Advection-Dispersion Equation

An advection-dispersion equation is used to express the mass balance of a waste contaminant within an aquifer as a result of dispersion, advection, and change in storage. The mass balance is a function of the dispersion coefficient, the ground-water velocity, concentration of the contaminant, distance, and time (Palmer and Johnson, 1989a). An advection-dispersion equation can be applied to the description of three-dimensional transport of waste contaminants in an aquifer, using three dispersion coefficients (one longitudinal and two transverse). Mathematically detailed descriptions of the advection-dispersion equation are presented in Bear (1969, 1979).

Discrepancies between results generated from advection-dispersion equations and laboratory and field experiments have been found. These discrepancies have been attributed to: (1) immobile zones of water within the aquifer, (2) solution-solid interface processes, (3) anion exclusion, and (4) diffusion in and out of aggregates (Palmer and Johnson, 1989a).

Field observations using field tracer studies also have

shown that longitudinal dispersivity values are usually much larger than transverse dispersivity measurements (Palmer and Johnson, 1989a). Figure 3-3 shows three-dimensional field monitoring that has corroborated these observations by identifying long, thin contaminant plumes rather than plumes spread over the thickness of an aquifer. (Kimmel and Braids, 1980; MacFarlane and others, 1983). The large longitudinal dispersion coefficients are thought to result from aquifer heterogeneity. In an ideally stratified aquifer with layers of sediment of different hydraulic conductivities, contaminants move rapidly along layers with higher permeabilities and more slowly along the lower permeability layers (Figure 3-4) (Palmer and Johnson, 1989a). Sample concentration of a contaminant is an integration of the concentrations of each layer, if water is sampled from monitoring wells that are screened

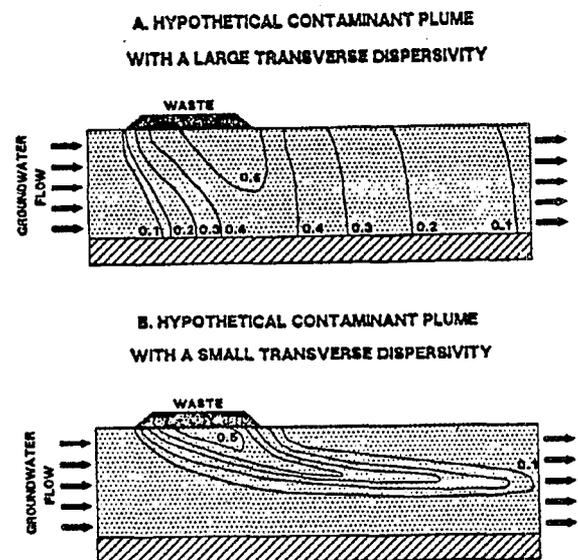


Figure 3-3. Hypothetical Contaminant Plumes for Large (A) and Small (B) Dispersivities (Palmer and Johnson, 1989a)

through the various layers. Results from plotting concentration versus distance show a curve with large differences in concentrations, even though only advection is considered. This dispersion is the result of aquifer heterogeneity and not pore-scale processes.

However, defining hydraulic conductivities in the subsurface is difficult, since not all geologic formations are perfectly stratified, but may contain cross-stratification or graded bedding (Palmer and Johnson, 1989a). To quantify heterogeneity in an aquifer, hydraulic conductivity is considered to be random, and statistical characteristics, such as mean, variance, and autocorrelation function, are determined.

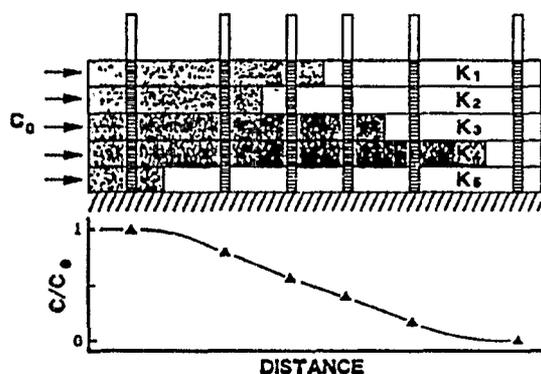


Figure 3-4. Contaminant Distributions and Concentrations in an Ideally Stratified Aquifer (after Gillham and Cherry, 1982, by Palmer and Johnson, 1989a)

In addition to aquifer heterogeneity, other processes contributing to the spread of contaminants include: (1) diverging flow lines resulting in the spread of contaminants by advection over a larger cross section of the aquifer, (2) temporal variations in the water table resulting in change of direction of ground-water flow and lateral spread of contamination, and (3) variations in concentration of contaminants at the source resulting in apparent dispersion in the longitudinal direction (Frind and Hokkanen, 1987; Palmer and Johnson, 1989a).

Ground-water sampling methods also may result in detection of apparent spreading of contaminant plumes (Palmer and Johnson, 1989a). An underestimation of contaminant concentrations at specific locations in an aquifer may be due to insufficient well-purging. Monitoring wells with different screen lengths that integrate ground water from different sections of the aquifer may yield dissimilar contaminant concentrations.

Diffusive Transport through Low Permeability Materials

In materials with low hydraulic conductivities (e.g., unfractured clays and rocks with conductivities less than 10^{-9} m/s), diffusive transport of waste contaminants is large compared to advective transport (Neuzil, 1986; Palmer and Johnson, 1989a). Contaminants can diffuse across natural aquitards or clay liners with low hydraulic conductivities, resulting in aquifer contamination. The extent of movement is dependent on diffusive flux, rate of ground-water flow in

the aquifer, and the length of the source area in the direction of ground-water flow.

Effects of Density on Transport of Contaminants

The density of a contaminant plume may contribute to the direction of solute transport if dissolved concentrations of contaminants are large enough (Palmer and Johnson, 1989a). For example, assume that the density of ground water within an aquifer is 1.00, the natural horizontal gradient is 0.005, and the natural vertical gradient is 0.000. If the density of the contaminant plume is equal to the density of the ground water, the plume moves horizontally with the naturally existing hydraulic gradient. If the density of the contaminated water is 1.005 (a concentration of approximately 7,000 mg/L total dissolved solids), then the driving force in the vertical direction is the same as the driving force in the horizontal direction. If the aquifer is isotropic, then the resulting vector of these two forces descends at 45 degrees into the aquifer. The contaminant plume moves deeply into the aquifer and may not be detected with shallow monitoring systems installed under the assumption of horizontal flow.

Retardation of Contaminants

If contaminants undergo chemical reactions while being transported through an aquifer, their movement rate may be less than the average ground-water flow rate (Palmer and Johnson, 1989a). Such chemical reactions that slow movement of contaminants in an aquifer include precipitation, adsorption, ion exchange, and partitioning into organic matter or organic solvents. Chemical reactions affect contaminant breakthrough, as shown in Figure 3-5. If the retardation factor, R (calculated from equations for contaminant transport that include retardation), is equal to 1.0, the solute is

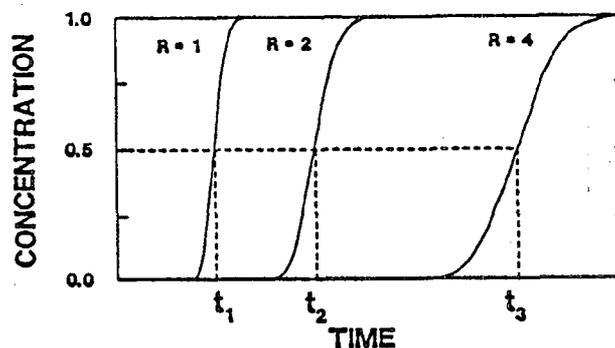


Figure 3-5. Time Required for Movement of Contaminants at Different Retardation Factors (Palmer and Johnson, 1989a)

nonreactive and moves with the ground water. If R is greater than 1.0, the average velocity of the solute is less than the velocity of the ground water, and the dispersion of the solute is reduced. If a monitoring well is located a distance from a contaminant source such that a nonreactive solute requires time, t_1 , to travel from the source to the well, a contaminant with a retardation factor of 2 will require $2t_1$ to reach the well, and $4t_1$ will be required for a contaminant with a retardation factor of 4.

Contaminants with lower retardation factors are transported greater distances over a given time than contaminants with larger retardation factors (Figure 3-6) (Palmer and Johnson, 1989a). A monitoring well network has a greater chance of detecting contaminants with lower retardation factors because they are found in a greater volume of the aquifer. Estimates of the total mass of a contaminant with a retardation factor of 1.0 in an aquifer may be more accurate than estimates for contaminants with greater amounts of retardation. Therefore, estimates of time required to remove nonreactive contaminants may be more accurate than time estimates for retarded contaminants. The slow movement of retarded contaminants may control the time and costs required to remediate a contaminated aquifer.

Transport through Fractured Media

Because fractured rock has both primary and secondary porosity, models used to describe solute transport in porous media, such as aquifers in recent alluvial deposits or glacial sediments, may not be appropriate for use at sites on fractured rock (Palmer and Johnson, 1989a). Primary porosity is the pore space formed at the time of deposition and formation of the rock mass, and secondary porosity is the pore space formed as the result of fracture of the rock.

Transport mechanisms in fractured media are advection and dispersion, the same as in porous media (Figure 3-7) (Palmer and Johnson, 1989a). In fractured media, however, contaminants are transported by advection only along fractures. Dispersion in fractured media is due to: (1) mixing at fracture intersections, (2) variations in opening widths across the width of the fracture, (3) variations in opening widths along stream lines, (4) molecular diffusion into microfractures penetrating the interfracture blocks and (5) molecular diffusion into interfracture porous matrix blocks (more important in fractured porous rock than in fractured crystalline rock).

Transport of contaminants through fractured media is described by one of four general models: continuum,

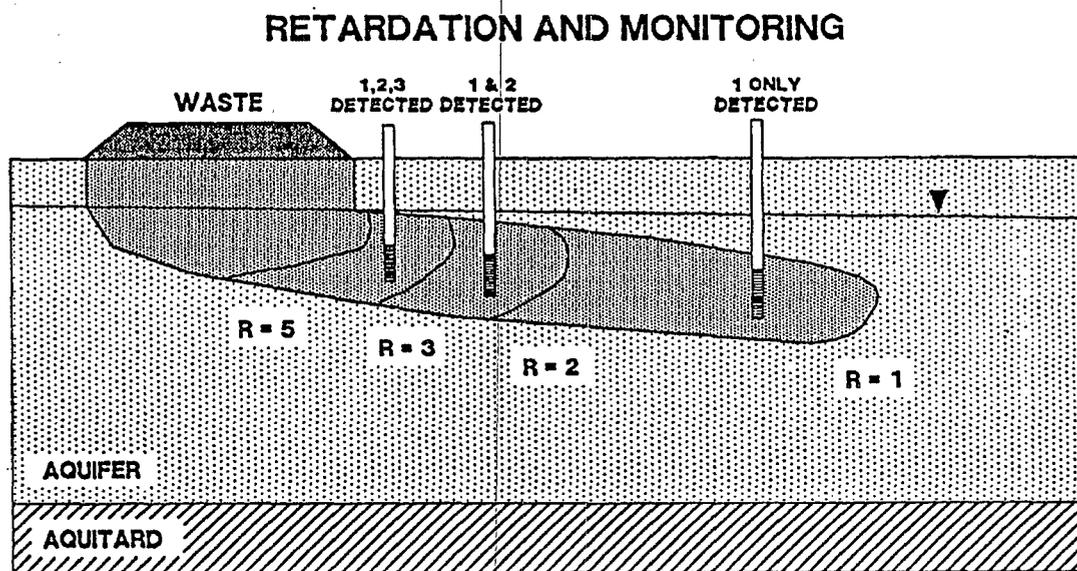


Figure 3-6. Transport of Contaminants with Varying Retardation Factors at a Waste Site (Palmer and Johnson, 1989a)

FRACTURED POROUS ROCK

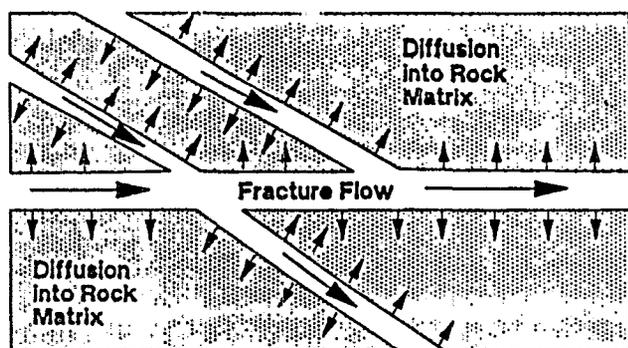


Figure 3-7. Transport in Fractured Porous Rock (Palmer and Johnson, 1989a)

discrete fracture, hybrid, and channel (Palmer and Johnson, 1989a).

In continuum models, individual fractures are ignored and the entire medium is considered to act as an equivalent porous medium. Single porosity continuum models are applicable where the only porosity of the rock mass is the fracture porosity, such as in fractured granite or basalt. Double porosity models are applicable to media in which there is both primary and secondary porosity such as sandstones and shales.

Discrete fracture models try to describe flow and transport in individual fractures. Because it can be difficult to obtain information about each fracture in the rock mass, stochastic models usually are required. These models use statistical information about distribution of fracture properties such as orientation and aperture widths to describe flow and transport.

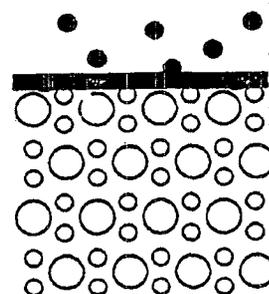
Hybrid models are combinations of discrete fracture and continuum models, while channel models describe solute transport as small fingers or channels rather than as a uniform front along the width of a fracture.

Particle Transport through Porous Media

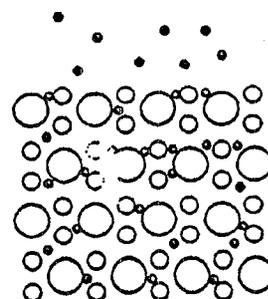
In addition to solute transport through porous media, the transport of particles (including bacteria, viruses, inorganic precipitates, natural organic matter, asbestos fibers, or clays) also may be important in investigations of contaminant transport. Particles can be removed from solution by surface filtration, straining, and physical-chemical processes (Figure 3-8) (Palmer and Johnson, 1989a).

The effectiveness of each process is dependent on the size of the specific particles present (Palmer and Johnson, 1989a). If particles are larger than the largest

SURFACE FILTRATION



STRAINING



PHYSICAL-CHEMICAL

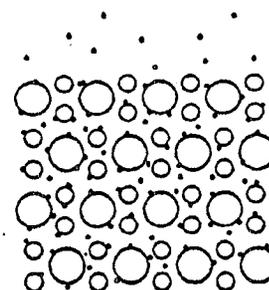


Figure 3-8. Mechanisms of Filtration (Palmer and Johnson, 1989a)

pore diameters, they cannot penetrate into the porous medium and are filtered at the surface of the medium. If particles are smaller than the largest pores but larger than the smallest, the particles are transported through the larger pore channels, but eventually encounter a pore channel with a smaller diameter and are removed by straining. If particles are smaller than the smallest pore openings, the particles can be transported long distances through the porous medium.

The rate at which particles move through the porous medium depends on several physical-chemical processes (Palmer and Johnson, 1989a). Particles may undergo random collisions with sand grains, and in a percentage of those collisions particles will adhere to the solid matrix by interception. Chemical conditions may affect particle transport; e.g., such processes as aggregation formation due to pH changes may change particle surface properties. These larger aggregates

can then be strained or filtered from the water.

Microorganism movement through geologic materials is limited by many processes (Palmer and Johnson, 1989a). Some bacteria are large enough to be strained from the water. Although viruses, which are smaller than bacteria, can pass through the pores, they may adsorb to geologic materials because their surfaces are charged. Microorganisms, like chemical constituents, can be transported by diffusion, or if they are motile, can move in response to changes in environmental conditions and chemical concentrations. Since microorganisms live and die, the rates of these processes should be included in the description of their transport in the subsurface.

Physical Processes Controlling the Transport of Non-Aqueous Phase Liquids (NAPLs) in the Subsurface

Transport and Dissolution of NAPLs

Non-aqueous phase liquids (NAPLs) are those liquids that do not readily dissolve in water and can exist as a separate fluid phase. (Palmer and Johnson, 1989b). NAPLs are divided into two classes: those that are lighter than water (LNAPLs) and those with a density greater than water (DNAPLs). LNAPLs include hydrocarbon fuels, such as gasoline, heating oil, kerosene, jet fuel, and aviation gas. DNAPLs include the chlorinated hydrocarbons, such as 1,1,1-trichloroethane, carbon tetrachloride, chlorophenols, chlorobenzenes, tetrachloroethylene, and polychlorinated biphenyls (PCBs).

As NAPLs move through geologic media, they displace water and air (Palmer and Johnson, 1989b). Water is the wetting phase relative to both air and NAPLs and tends to line edges of pores and cover sand grains. NAPLs are the non-wetting phase and tend to move through the center of pore spaces. Neither the water nor the NAPL phase occupies the entire pore, so the permeability of the medium with respect to these fluids is different than when the pore space is entirely occupied by a single phase. This reduction in permeability depends upon the specific medium and can be described in terms of relative permeability, i.e., permeability at a certain fraction of pore space occupied by the NAPL compared to the permeability of the medium at saturation with the NAPL. Relative permeability ranges from 1.0 at 100 percent saturation to 0.0 at 0 percent saturation.

Figure 3-9 shows permeability of a NAPL in a hypothetical medium during multiphase flow. (Palmer and Johnson, 1989b). At 100 percent water saturation, the relative permeabilities of the water and NAPL are 1.0 and 0.0, respectively. As the fraction of the pore space occupied by NAPL increases, a corresponding decrease occurs

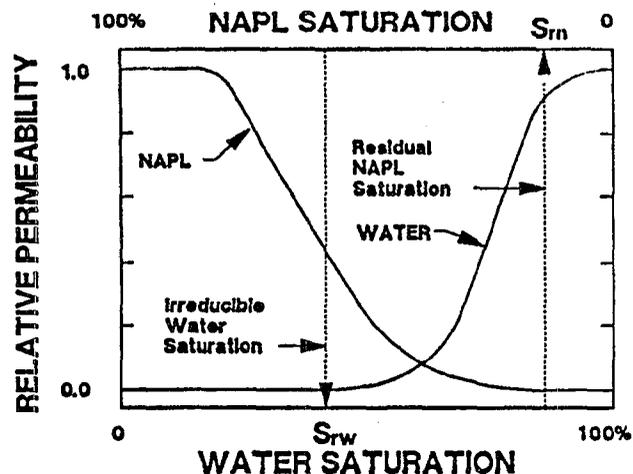


Figure 3-9. Relative Permeability as a Function of Saturation (Palmer and Johnson, 1989b)

in the fraction of water within the pore space. As the water fraction decreases, the relative permeability with respect to the water phase decreases to zero. Zero relative permeability is not obtained when the fraction of water within the pore space equals zero, but at the irreducible water saturation (S_{rw}), i.e., the level of water saturation at which the water phase is effectively immobile and there is no significant flow of water. The relative permeability of NAPL is similar. At 100 percent NAPL saturation, the relative permeability for the NAPL is equal to 1.0, but as the NAPL saturation decreases, the relative permeability of the NAPL decreases. At the residual NAPL saturation (S_{rn}), the relative permeability for the NAPL is effectively zero, and the NAPL is considered immobile. These immobile fractions of NAPL cannot be easily removed from pores except by dissolution by flowing water.

Transport of Light NAPLs

If small volumes of a spilled LNAPL enter the unsaturated zone (i.e., vadose zone), the LNAPL will flow through the central portion of the unsaturated pores until residual saturation is reached (Figure 3-10a) (Palmer and Johnson, 1989b). A three-phase system consisting of water, LNAPL, and air is formed within the vadose zone. Infiltrating water dissolves the components within the LNAPL (e.g., benzene, xylene, and toluene) and transports them to the water table. These dissolved contaminants form a contaminated plume radiating from the area of the residual product. Many components found in LNAPLs are volatile and can partition into soil air and be transported by molecular diffusion to other parts of the aquifer. As these vapors diffuse into adjoining soil areas, they may partition back into the water phase and transfer contamination over wider areas. If the soil

surface is relatively impermeable, vapors will not diffuse across the surface boundary and concentrations of contaminants in the soil atmosphere may build up to equilibrium conditions. However, if the surface is not covered with an impermeable material, vapors may diffuse into the atmosphere.

If large volumes of LNAPL are spilled (Figure 3-10b), the LNAPL flows through the pore space to the top of the capillary fringe of the water table. Dissolved components of the LNAPL precede the less soluble components and may change the wetting properties of the water, causing a reduction in the residual water content and a decrease in the height of the capillary fringe.

Since LNAPLs are lighter than water, they will float on top of the capillary fringe. As the head formed by the infiltrating LNAPLs increases, the water table is depressed and the LNAPLs accumulate in the depression. If the source of the spilled LNAPLs is removed or contained, LNAPLs within the vadose zone continue to flow under the force of gravity until reaching residual saturation. As the LNAPLs continue to enter the water table depression, they spread laterally on top of the capillary fringe (Figure 3-10c). The draining of the upper portions of the vadose zone reduces the total head at the interface between the LNAPLs and the ground water, causing the water table to rebound slightly. The rebounding water displaces only a portion of the LNAPLs because the LNAPLs remain at residual saturation. Ground water passing through the area of residual saturation dissolves constituents of the residual LNAPLs, forming a contaminant plume. Water infiltrating from the surface also can dissolve the residual LNAPLs and add to the contaminant load of the aquifer.

Decrease in the watertable level from seasonal variations or ground-water pumping also causes dropping of the pool of LNAPLs. If the watertable rises again, part of the LNAPLs may be pushed up, but a portion remains at residual saturation below the new watertable. Variations in the water table height, therefore, can spread LNAPLs over a greater thickness of the aquifer, causing larger volumes of aquifer materials to be contaminated. Selection of a remedial technology for LNAPLs in the ground water should not include techniques that move LNAPLs into uncontaminated areas where more LNAPLs can be held at residual saturation.

Transport of Dense NAPLs

DNAPLs are very mobile in the subsurface because of their relatively low solubility, high density, and low viscosity (Palmer and Johnson, 1989b). The low solubility means that DNAPLs do not readily mix with water and remain as separate phases. Their high density

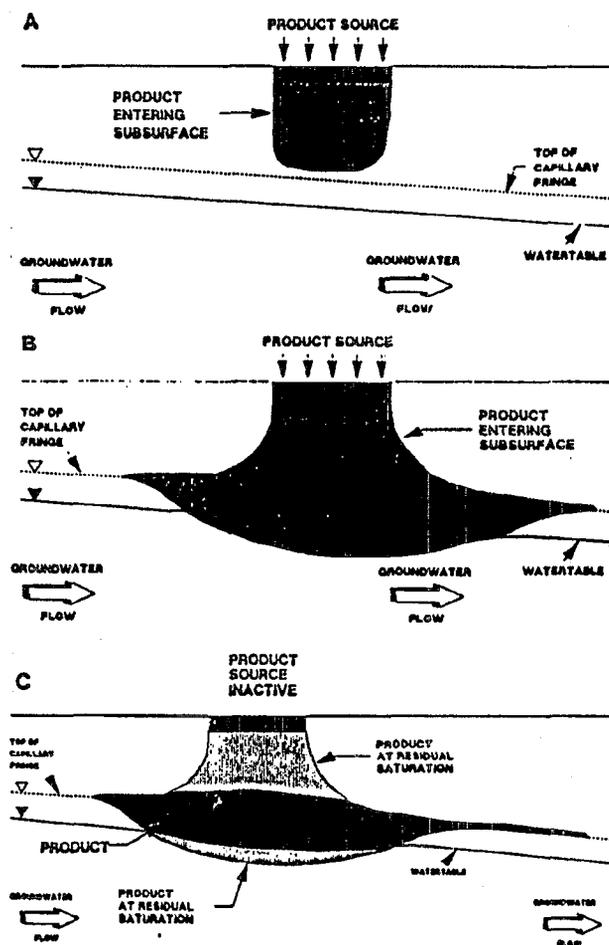


Figure 3-10. Movement of LNAPLs into the Subsurface: (A) Distribution of LNAPLs after Small Volume has Been Spilled; (B) Depression of the Capillary Fringe and Water Table; (C) Rebounding of the Water Table as LNAPLs Drain From Overlying Pore Space (Palmer and Johnson, 1989b)

provides a driving force that can carry them deep into aquifers. The combination of high density and low viscosity results in the displacement of the lower density, higher viscosity fluid, i.e., water, by DNAPLs, causing "unstable" flow and viscous fingering (Saffman and Taylor, 1958; Chouke and others, 1959; Homsy, 1987; Kueper and Frind, 1988).

If a small amount of DNAPL is spilled (Figure 3-11a), the DNAPL will flow through the unsaturated zone under the influence of gravity toward the water table, flowing until reaching residual saturation in the unsaturated zone (Palmer and Johnson, 1989b). If water is present in the vadose zone, viscous fingering

of the DNAPLs will be observed during infiltration. No viscous fingering will be exhibited if the unsaturated zone is dry. The DNAPLs can partition into the vapor phase, with the dense vapors sinking to the capillary fringe. Residual DNAPLs or vapors can be dissolved by infiltrating water and be transported to the water table, resulting in a contaminant plume within the aquifer.

If a greater amount of DNAPL is spilled (Figure 3-11b), the DNAPLs flow until they reach the capillary fringe and begin to penetrate the aquifer. To move through the capillary fringe, the DNAPLs must overcome the capillary forces between the water and the medium. A critical height of DNAPLs is required to overcome these forces. Larger critical heights are required for DNAPLs to move through unfractured, saturated clays and silts; thus these types of materials may be effective barriers to the movement of DNAPLs if the critical heights are not exceeded.

After penetrating the aquifer, DNAPLs continue to move through the saturated zone until they reach residual saturation. DNAPLs are then dissolved by ground water passing through the contaminated area, resulting in a contaminant plume that can extend over a large thickness of the aquifer. If finer-grained strata are contained within the aquifer, infiltrating DNAPLs accumulate on top of the strata, creating a pool. At the interface between the ground water and the DNAPL pool, the solvent dissolves into the water and spreads vertically by molecular diffusion. As water flows by the DNAPL pool, the concentration of the contaminants in the ground water increases until saturation is achieved or the downgradient edge of the pool is reached. DNAPLs, therefore, often exist in fingers or pools in the subsurface, rather than in continuous distributions. The density of pools and fingers of DNAPLs within an aquifer are important for controlling the concentrations of dissolved contaminants originating from DNAPLs.

If even larger amounts of DNAPLs are spilled (Figure 3-11c), DNAPLs can penetrate to the bottom of the aquifer, forming pools in depressions. If the impermeable lower boundary is sloping, DNAPLs flow down the dip of the boundary. This direction can be upgradient from the original spill area if the impermeable boundary slopes in that direction. DNAPLs also can flow along bedrock troughs, which may be oriented differently from the direction of ground-water flow. Flow along impermeable boundaries can spread contamination in directions that would not be predicted based on hydraulics.

Chemical Processes Controlling the Transport of Contaminants in the Subsurface

Introduction

Subsurface transport of contaminants often is controlled

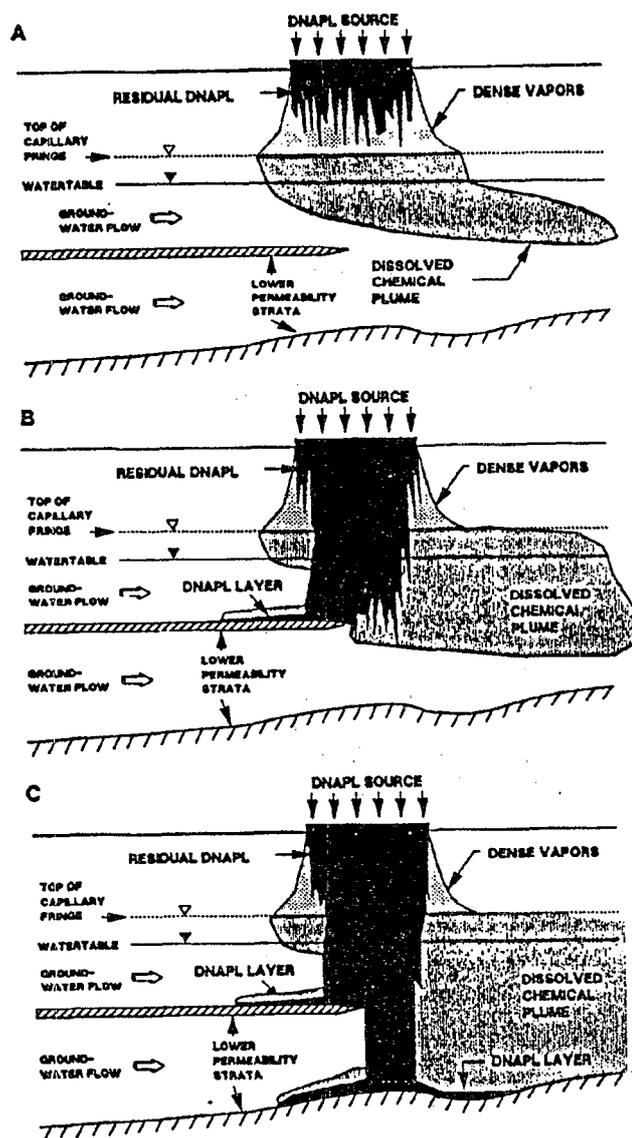


Figure 3-11. Movement of DNAPLs into the Subsurface (A) Distribution of DNAPLs after Small Volume has Been Spilled; (B) Distribution of DNAPLs after Moderate Volume has Been Spilled; (C) Distribution of DNAPLs after Large Volume has Been Spilled (after Feenstra and Cherry, 1988, by Palmer and Johnson, 1989b)

by complex interactions between physical, chemical, and biological processes. The advection-dispersion equation used to quantitatively describe and predict contaminant movement in the subsurface also must contain reaction terms added to the basic equation to account for chemical and biological processes important in controlling contaminant transport and fate (Johnson and others, 1989).

Chemical Reactions of Organic Compounds

Chemical reactions may transform one compound into another, change the state of the compound, or cause a compound to combine with other organic or inorganic chemicals (Johnson and others, 1989). For use in the advection-dispersion equation, these reactions represent changes in the distribution of mass within the specified volume through which the movement of the chemicals is modeled.

Chemical reactions in the subsurface often are characterized kinetically as equilibrium, zero, or first order, depending on how the rate is affected by the concentrations of the reactants. A zero-order reaction is one that proceeds at a rate independent of the concentration of the reactant(s). In a first-order process, the rate of the reactions is directly dependent on the concentration of one of the reactants. The use of zero or first-order rate expressions may oversimplify the description of a process, but higher order expressions, which may be more realistic, are often difficult to measure and/or model in complex environmental systems. Also first-order reactions are easy to incorporate into transport models (Johnson and others, 1989).

Sorption. Sorption is probably the most important chemical process affecting the transport of organic contaminants in the subsurface environment. Sorption of non-polar organics is usually considered an equilibrium-partitioning process between the aqueous phase and the porous medium (Chiou and others, 1979). When solute concentrations are low (i.e., either $\leq 10^{-5}$ Molar, or less than half the solubility, whichever is lower), partitioning often is described using a linear Freundlich isotherm, where the sorbed concentration is a function of the aqueous concentration and the partition coefficient (K_p) (Karickhoff and others, 1979; Karickhoff, 1984). K_p usually is measured in laboratory batch equilibrium tests, and the data are plotted as the concentration in the aqueous phase versus the amount sorbed onto the solid phase (Figure 3-12) (Chiou and others, 1979).

Under conditions of linear equilibrium partitioning, the sorption process is represented in the advection-dispersion equation as a "retardation factor," R (Johnson and others, 1989). The retardation factor is dependent on the partition coefficient K_p , bulk density of aquifer materials, and porosity.

The primary mechanism of organic sorption is the formation of hydrophobic bonding between a contaminant and the natural organic matter associated with aquifers (Tanford, 1973; Karickhoff and others, 1979; Karickhoff, 1984; Chiou and others, 1985; MacKay and Powers, 1987). Therefore, the extent of sorption of

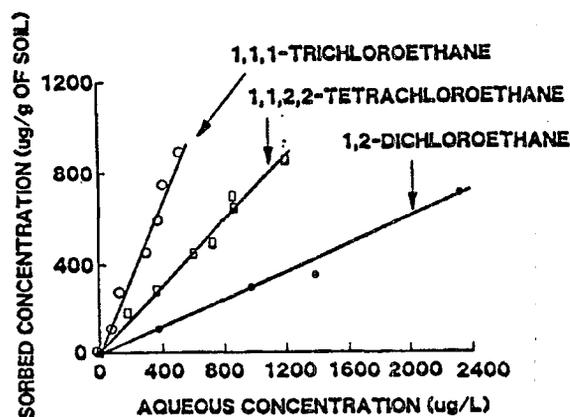


Figure 3-12. Batch Equilibrium Data for 1,1,1-TCA, 1,1,2,2,-TeCA and 1,2-DCA (adapted from Chiou and others, 1979, by Johnson and others, 1989)

a specific chemical can be estimated from the organic carbon content of the aquifer materials (f_{oc}) and a proportionality constant characteristic of the chemical (K_{oc}), if the organic content is sufficiently high (i.e., fraction organic carbon content (f_{oc}) > 0.001) (Karickhoff and others, 1979; Karickhoff, 1984). K_{oc} values for many compounds are not known, so correlation equations relating K_{oc} to more easily available chemical properties, such as solubility or octanol-water partition coefficients (Kenaga and Goring, 1980; Karickhoff, 1981; Schwarzenbach and Westall, 1981; Chiou and others, 1982, 1983), have been developed. Within a compound class, K_{oc} values derived from correlation expressions often can provide reasonable estimates of sorption. However, if correlations were developed covering a broad range of compounds, errors associated with the use of K_{oc} estimates can be large (Johnson and others, 1989).

This method of estimation of sorption, using K_{oc} and f_{oc} values, is less expensive than the use of batch equilibrium tests. However, in soils with lower carbon content, sorption of neutral organic compounds onto the mineral phase can cause significant errors in the estimate of the partition coefficient (Chiou and others, 1985).

Hydrolysis. Hydrolysis, an important abiotic degradation process in ground water for certain classes of compounds, is the direct reaction of dissolved compounds with water molecules (Mabey and Mill, 1978). Hydrolysis of chlorinated compounds, which are often resistant to biodegradation (Siegrist and McCarty, 1987), forms an alcohol or alkene (Figure 3-13).

Most information concerning rates hydrolysis is obtained from laboratory studies, since competing reactions and

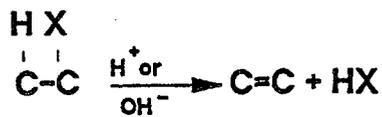


Figure 3-13. Schematic of Hydrolysis Reactions for Halogenated Organic Compounds (Johnson and others, 1989)

slow degradation rates make hydrolysis difficult to measure in the field. (Johnson and others, 1989). Often data for hydrolysis are fitted as a first-order reaction, and a hydrolysis rate constant, K , is obtained. The rate constant multiplied by the concentration of the contaminant is added to the advection-dispersion equation to account for hydrolysis of the contaminant.

Cosolvation and Ionization. Cosolvation and ionization are processes that may decrease sorption and thereby increase transport velocity (Johnson and others, 1989). The presence of cosolvents decreases entropic forces that favor sorption of hydrophobic organic contaminants by increasing interactions between the solute and the solvent (Nkedi-Kizza and others, 1985; Zachara and others, 1988). If biologically derived or anthropogenic solvent compounds are present at levels of 20 percent or more by volume, the solubility of hydrophobic organic contaminants can be increased by an order of magnitude or more (Nkedi-Kizza and others, 1985). In Figure 3-14, decrease in sorption of anthracene in three soils, as described by the sorption coefficient K_p , is illustrated, with methanol as the cosolvent. Since cosolvent concentration must be large for solute velocity to be increased substantially, cosolvation is important primarily near sources of ground-water contamination.

In the process of ionization, acidic compounds, such as phenols or organic acids, can lose a proton in solution to form anions that, because of their charge, tend to be water-soluble (Zachara and others, 1986). For example, the K_{oc} of 2,4,5-trichlorophenol can decrease from 2,330 for the phenol, to almost zero for the phenolate (Figures 3-15 and 3-16) (Johnson and others, 1989). Acidic compounds tend to ionize more as the pH increases. However, for many compounds, such as the chlorophenols, substantial ionization can occur at neutral pH values.

Volatilization and Dissolution. Two important pathways for the movement of volatile organic compounds in the subsurface are volatilization into the unsaturated zone and dissolution into the ground water

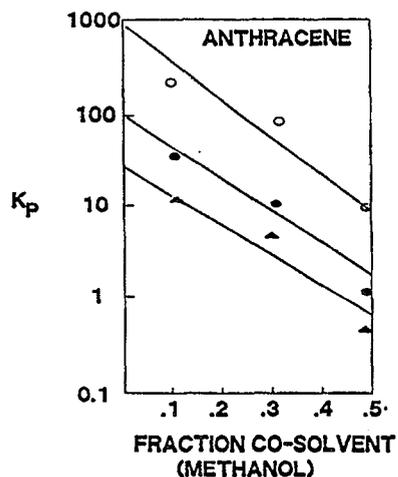


Figure 3-14. Effect of Methanol as a Cosolvent on Anthracene Sorption for Three Soils (Adapted from Nkedi-Kizza and others, 1985, by Johnson and others, 1989)

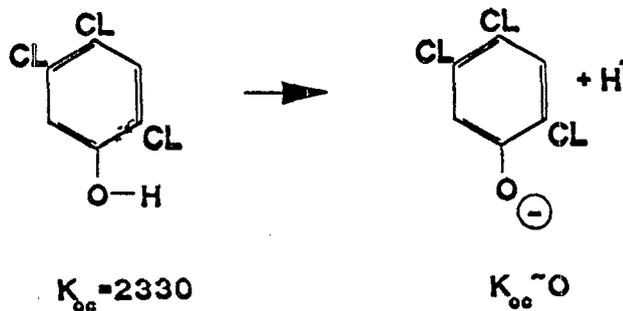


Figure 3-15. K_{oc} values for 2,4,5-trichlorophenol and 2,4,5-trichlorophenolate (Johnson and others, 1989)

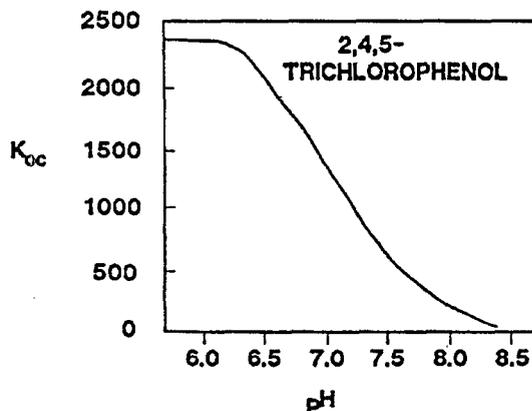


Figure 3-16. K_{oc} versus pH for 2,4,5-trichlorophenol (Johnson and others, 1989)

(Johnson and others, 1989). Contaminants in the aqueous and vapor phases are also more amenable to degradation.

The degree of volatilization of a contaminant is determined by: (1) the area of contact between the contaminated area and the unsaturated zone, which is affected by the nature of the medium (e.g., grain size, depth to water, water content) and the contaminant (e.g., surface tension and liquid density); (2) the vapor pressures of the contaminants; and (3) the rate at which the compound diffuses in the subsurface (Johnson and others, 1989).

The residual saturation remaining when immiscible liquids move downward through unsaturated porous media provides a large surface area for volatilization (Johnson and others, 1989). Vapor concentrations in the vicinity of the residual are often at saturation concentrations. Movement of vapor away from the residual saturation is usually controlled by molecular diffusion, which is affected by the tortuosity of the path through which the vapors move. Tortuosity also is affected by the air-filled porosity of the medium, so diffusion is reduced in porous media with a high water content.

Diffusion also is reduced by the partitioning of the vapors out of the gas phase and into the solid or aqueous phases (Johnson and others, 1989). The retardation factor developed for partitioning between the aqueous and solid phases can be modified with a term to describe partitioning between the vapor and aqueous phases.

When immiscible fluids reach the capillary fringe, their further movement is determined by the density of the fluids relative to water (Scheigg, 1984; Schwille, 1988). The LNAPLs pool on top of the water table while the DNAPLs penetrate into the ground water. Floating pools of LNAPL can provide substantial surface area for volatilization, with diffusion controlling the mass transfer of organic contaminants into the vapor phase.

The transport and fate of DNAPLs that penetrate into the ground water is controlled by dissolution. Experiments have shown that saturation concentration values can be maintained even with high ground-water velocities (e.g., 1 m/day) through a zone of contamination (Anderson and others, 1987). During remedial activities, such as pump-and-treat, ground-water velocities may be high, but the dissolution process should still be effective.

Chemical Reactions of Inorganic Compounds
In studies of organic contamination, the most important

characteristic is the total concentration of a contaminant in a certain phase (e.g., in water versus aquifer solid materials). However, studies of inorganic contamination are often more difficult because inorganic materials can occur in many chemical forms, and knowledge of these forms (i.e., species) is required to predict their behavior in ground water (Morel, 1983; Sposito, 1986).

In ground water, an inorganic contaminant may occur as: (1) "free ions" (i.e., surrounded only by water molecules); (2) insoluble species; (3) metal/ligand complexes; (4) adsorbed species; (5) species held on a surface by ion exchange; or (6) species differing by oxidation state (e.g., manganese (II) and (IV) or chromium (III) and (VI)) (Johnson and others, 1989).

The total concentration of an inorganic compound may not provide sufficient information to describe the fate and behavior of that compound in ground water. Mobility, reactivity, biological availability, and toxicity of metals and other inorganic compounds depend upon their speciation (Johnson and others, 1989). The primary reactions affecting the speciation of inorganic compounds are solubility and dissolution, complexation reactions, adsorption and surface chemistry, ion exchange, and redox chemistry.

Solubility, Dissolution, and Precipitation. Dissolution and weathering of minerals determine the natural composition of ground water (Johnson and others, 1989). Dissolution is the dissolving of all components within a mineral, while weathering is a partial dissolution process in which certain elements leach out of a mineral, leaving others behind.

Mineral dissolution is the source of most inorganic ions in ground water. In principle a mineral can dissolve up to the limits of its solubility, but in many cases, reactions occur at such a slow rate that true equilibrium is never attained (Morgan, 1967).

The contribution of ions from one mineral may affect the solubility of other minerals containing the same ion (i.e., the "common ion effect"). Computer programs such as MINTEQA2 (Felmly and others, 1984), MINEQL (Westall and others, 1976), and WATEQ2 (Ball and others, 1980) may be used to predict the equilibrium distribution of chemical species in ground water and indicate if the water is undersaturated, supersaturated, or at equilibrium with various mineral phases. Some of these programs also may be used to predict the ionic composition of ground water in equilibrium with assumed mineral phases (Jennings and others, 1982).

The weathering of silicate minerals contributes cations, such as calcium, magnesium, sodium, potassium, and

silica, to water and forms secondary weathering products such as kaolinite and montmorillonite clays (Johnson and others, 1989). This weathering increases the alkalinity of ground water to a level greater than its rainwater origins.

Weathering and dissolution also can be a source of contaminants. Leachates from mine tailings can yield arsenate, toxic metals, and strong mineral acids (Hem, 1970), while leachates from fly-ash piles can contribute selenium, arsenate, lithium, and toxic metals (Stumm and Morgan, 1981; Honeyman and others, 1982; Murarka and MacIntosh, 1987).

The opposite of dissolution reactions is precipitation of minerals or contaminants from an aqueous solution (Johnson and others, 1989). During precipitation, the least-soluble mineral at a given pH level is removed from solution. An element is removed by precipitation when its solution concentration saturates the solubility of one of its solid compounds. If the solution concentration later drops below the solubility limit, the solid will begin to dissolve until the solubility level is attained again. Contaminants may initially precipitate, then slowly dissolve later after a remedial effort has reduced the solution concentration; thus complete remediation of the aquifer may require years.

A contaminant initially may be soluble but later precipitate after mixing with other waters or after contact with other minerals (Drever, 1982; Williams, 1985; Palmer, 1989). For example, pumping water from an aquifer may mobilize lead until it converges and mixes with waters high in carbonates from a different formation and precipitates as a lead carbonate solid.

Complexation Reactions. In complexation reactions, a metal ion reacts with an anion that functions as a ligand (Johnson and others, 1989). The metal and the ligand bind together to form a new soluble species called a complex. Transition metals form the strongest complexes (Stumm and Morgan, 1981); alkaline earth metals form only weak complexes, while alkali metals do not form complexes (Dempsey and O'Melia, 1983). The approximate order of complexing strength of metals is:

Fe(III) > Hg > Cu > Pb > Ni > Zn > Cd > Fe(II) > Mn > Ca > Mg

Common inorganic ligands that bind with metals include: OH⁻, Cl⁻, SO₄⁼, CO₃⁼, S⁼, F⁻, NH₃, PO₄, CN⁻, and polyphosphates. Their binding strength depends primarily on the metal ion with which they are complexing (Johnson and others, 1989). Inorganic ligands are usually in excess compared to the "trace" metals with

which they bind, and, therefore, they affect the fate of the metals in the environmental system, rather than vice versa (Morel, 1983).

Organic ligands generally form stronger complexes with metals than inorganic ligands (Johnson and others, 1989). Organic ligands include: (1) synthetic compounds from wastes, such as amines, pyridines, phenols, and other organic bases and weak acids; and (2) natural organic materials, primarily humic materials (Schnitzer, 1969; Hayes and Swift, 1978; Stevenson, 1982, 1985; Johnson and others, 1989). Humic materials are complex structures, and their complexation behavior is difficult to predict (Perdue and Lytle, 1983; Sposito, 1984; Perdue, 1985; Dzombak and others, 1986; Fish and others, 1986). Generally, humic materials are found in significant concentrations only in shallow aquifers. In these aquifers, however, they may be the primary influence on the behavior of metals (Thurman, 1985).

Equilibrium among reactants and complexes for a given reaction is predicted by an equilibrium (or "stability") constant, K, which defines a mass-law relationship among the species (Johnson and others, 1989). For given total ion concentrations (measured analytically), stability constants can be used to predict the concentration of all possible species (Martell and Smith, 1974, 1977; Smith and Martell, 1975).

Because complexes decrease the amount of free ions in solution, less metal may sorb onto aquifer solid materials or participate in precipitation reactions (Johnson and others, 1989). The metal is more soluble because it is primarily bound up in the soluble complex. Research has demonstrated that a metal undergoing complexation may be less toxic to aquifer microorganisms (Reuter and others, 1979).

Sorption and Surface Chemistry. Surface sorption, in many cases, is the most important process affecting toxic metal transport in the subsurface (Johnson and others, 1989). Changes in metal concentration, as well as pH, can have a significant effect on the extent of sorption (Figure 3-17).

Approaches to predicting behavior of metal ions based on sorption processes include using isotherms (indicating that data were collected at a fixed temperature) to graphically and mathematically represent sorption data (Johnson and others, 1989). Two types of isotherms are commonly used: the Freundlich isotherm and the Langmuir isotherm (Figure 3-18). The Freundlich isotherm is empirical, and sorbed (S) and aqueous (C) concentration data are fitted by adjusting two parameters (K and a). The Langmuir

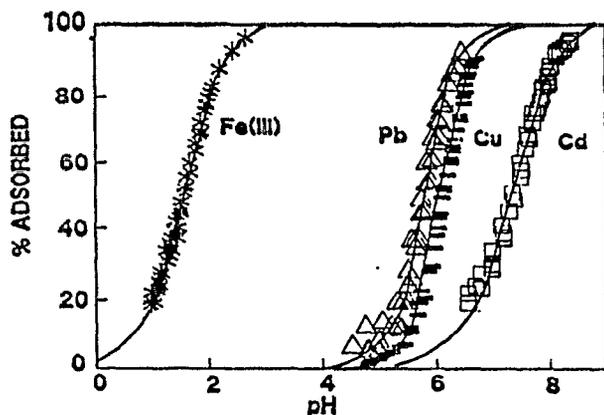


Figure 3-17. Adsorption of Metal Ions on Amorphous Silica as a Function of pH (adapted from Schindler and others, 1976, by Johnson and others, 1989)

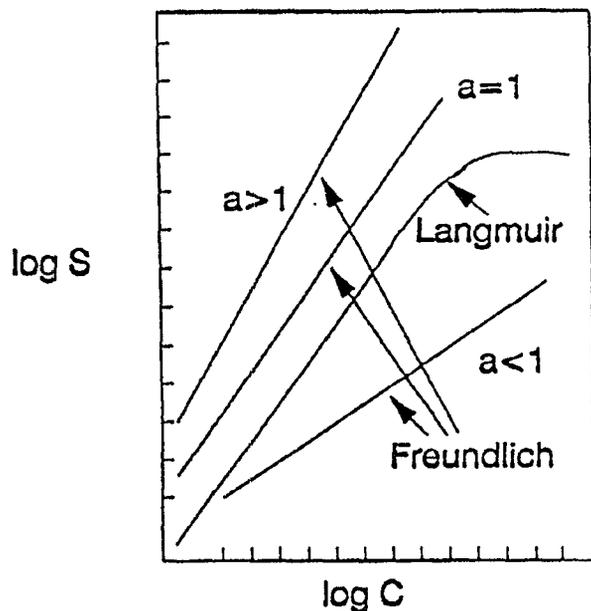


Figure 3-18. Schematic Representation of Freundlich and Langmuir Isotherm Shapes for Batch Equilibrium Tests (Johnson and others, 1989)

isotherm is based on the theory of surface complexation, using a parameter corresponding to the maximum amount that can be sorbed and the partition coefficient, K (Morel, 1983).

Another method to describe sorption is to use surface complexation models that represent sorption as ions binding to specific chemical functional groups on a reactive surface (Johnson and others, 1989). All surface

sites may be identical or may be grouped into different classes of sites (Benjamin and Leckie, 1981). Each type of site has a set of specific sorbing constants, one for each sorbing compound. Electrostatic forces at the surface also contribute to the overall sorption constant (Davis and others, 1978). Binding of ions to the surface is calculated from constants using mass-law equations similar to those used to calculate complex formation (Schindler and others, 1976; Stumm and others, 1976; Dzombak and Morel, 1986). However, the parameters used in surface complexation models are data-fitting parameters, which fit a specified set of data to a particular model, but have no thermodynamic meaning and no generality beyond the calibrating data set (Westall and others, 1980).

Ion-Exchange Reactions. Ion-exchange reactions are similar to sorption. However, sorption is coordination bonding of metals (or anions) to specific surface sites and is considered to be two-dimensional, while an ion-exchanger is a three-dimensional, porous matrix containing fixed charges (Helferich, 1962; Johnson and others, 1989). Ions are held by electrostatic forces rather than by coordination bonding. Ion-exchange "selectivity coefficients" are empirical and vary with the amount of ion present (Reichenburg, 1966). Ion exchange is used to describe the binding of alkali metals, alkaline earths, and some anions to clays and humic materials (Helferich, 1962; Sposito, 1984). Knowledge of ion exchange is used to understand the behavior of major natural ions in aquifers and also is useful for understanding behavior of contaminant ions at low levels. In addition, ion exchange models are used to represent competition among metals for surface binding (Sposito, 1984).

Redox Chemistry. Reduction-oxidation (redox) reactions involve a change in the oxidation state of elements (Johnson and others, 1989). The amount of change is determined by the number of electrons transferred during the reaction (Stumm and Morgan, 1981). The oxidation status of an element can be important in determining the potential for transport of that element. For example, in slightly acidic to alkaline environments, Fe(III) precipitates as a highly sorptive phase (ferric hydroxide), while Fe(II) is soluble and does not retain other metals. The reduction of Fe(III) to Fe(II) releases not only Fe^{+2} to the water, but also other contaminants sorbed to the ferric hydroxide surfaces (Evans and others, 1983; Sholkovitz, 1985).

Chromium (Cr) (VI) is a toxic, relatively mobile anion, while Cr(III) is immobile, relatively insoluble, and strongly sorbs to surfaces. Selenate (Se) (VI) is mobile but less toxic, while selenite Se(IV) is more toxic but less mobile (Johnson and others, 1989).

The redox state of an aquifer is usually closely related to microbial activity and the type of substrates available to the microorganisms (Johnson and others, 1989). As organic contaminants are oxidized in an aquifer, oxygen is depleted and chemically reducing (anaerobic) conditions form. The redox reactions that occur depend on the dominant electron potential, which is defined by the primary redox-active species. The combination of Fe(II)/Fe(III) defines a narrow range of electron potentials, while (S)(sulfur)(+IV)/S(-II) defines a broader range. Pairs of chemical species are called redox couples.

After oxygen is depleted from ground water, the most easily reduced materials begin to react and, along with the reduced product, determine the dominant potential. After that material is reduced, the next most easily reduced material begins to react. These series of reactions continue, usually catalyzed by microorganisms. An aquifer may be described as "mildly reducing" or "strongly reducing," depending on where it is in the chemical series (Stumm and Morgan, 1981).

The electron potential of water may be measured in volts, as Eh, or expressed by the "pe," which is the negative logarithm of the electron activity in the water (Johnson and others, 1989). A set of redox reactions is often summarized on a pH-pe (or pH-Eh) diagram, which shows the predominant redox species at any specified pH and pe (or Eh). In this theoretical approach, only one redox couple should define the redox potential of the system at equilibrium. However, in an aquifer, many redox couples not in equilibrium can be observed simultaneously (Lindberg and Runnels, 1984). Therefore, redox behavior of chemicals in aquifers is difficult to predict. However, the redox status of an aquifer is important because of its effects on the mobility of elements and the potential effects on biodegradation of organic contaminants. Anaerobic (reducing) conditions are not favorable for hydrocarbon degradation, but reducing conditions favor dehalogenation of chlorinated and other halogenated compounds (Johnson and others, 1989).

Biological Processes Controlling the Transport of Contaminants in the Subsurface

Introduction

Historically, ground water was thought to be a safe water source because it was protected by a metabolically diverse "living filter" of microorganisms in the soil root zone that converted organic contaminants to innocuous end-products (Sufliata, 1989a). Aquifers were considered to be abiotic environments, based on studies that showed that microbial numbers decreased with soil depth (Waksman, 1916) and that indicated that most

microorganisms were attached to soil particles (Balkwill and others, 1977). In addition, by estimating the time required for surface water to vertically penetrate subsurface formations, researchers felt that microorganisms travelling with water would utilize available nutrients and rapidly die off. Therefore, since aquifers were considered to be sterile, they could not be biologically remediated if contaminated with organic contaminants. However, microscopic, cultivation, metabolic, and biochemical investigations, using aseptically obtained aquifer materials, have shown that there are high numbers of metabolically diverse procaryotic and eucaryotic organisms present in the terrestrial subsurface environment (Sufliata, 1989a).

Evidence of Subsurface Microorganisms

Microbiological investigations have detected high numbers of microorganisms (up to 50×10^6 total cells/mL) in both contaminated and uncontaminated aquifers at various depths and geological composition (Sufliata, 1989a). Even deep geological formations may be suitable habitats for microorganisms (Kuznetsov and others, 1963; Updegraff, 1982). The microorganisms that have been detected in the subsurface are small, capable of response to addition of nutrients, and are primarily attached to solid surfaces. Eucaryotic organisms are present in the subsurface but are few in numbers and are probably of minor significance, existing as inert resting structures (Sufliata, 1989a).

Suitable sampling technology was developed to demonstrate the existence of subsurface microorganisms (Sufliata, 1989a). Samples must not be contaminated with nonindigenous microorganisms originating from drilling machinery, surface soil layers, drilling muds, and water used to make up drilling muds. Since most subsurface microorganisms are associated with aquifer solid materials, current sampling efforts use core recovery and dissection to remove microbiologically contaminated portions of the cores (McNabb and Mallard, 1984). This dissection is performed in the field, to prevent nonindigenous organisms from penetrating to the inner portions of the core, or in the laboratory if it is nearby. The outer few centimeters and the top and bottom portions of the aquifer cores are removed because of possible contamination by nonindigenous bacteria, and the center portions of the cores are used for microbiological analysis. An alcohol-sterilized paring device is used in the dissection process. The paring device has an inner diameter that is smaller than the diameter of the core itself. As the aquifer material is extruded out of the sampling core barrel and over the paring device, the potentially contaminated material is stripped away. For anaerobic aquifers, this field paring dissection is performed inside plastic anaerobic glove bags while the latter is purged with nitrogen to minimize

exposure of the microorganisms to oxygen (Beeman and Suflita, 1987). Samples obtained by this technique are considered to be aseptically acquired and are suitable for microbiological analyses.

Evidence of Activity of Subsurface Microorganisms

Although direct and conclusive evidence had been obtained about the existence of microorganisms in the subsurface, questions remained about their significance in ground water. Such questions included: (1) whether or not the indigenous microorganisms were metabolically active, (2) what was the diversity of the metabolic activities, (3) what factors served to limit and/or stimulate the growth and metabolism of these organisms, and (4) could the inherent metabolic versatility of aquifer microorganisms be utilized to remediate contaminated aquifers (Suflita, 1989a).

Microbial subsurface activity was studied, and the following metabolic processes were identified in the subsurface environment: (1) biodegradation of organic pollutants, including petroleum hydrocarbons, alkyipyridines, creosote chemicals, coal gasification products, sewage effluent, halogenated organic compounds, nitriloacetate (NTA), and pesticides; (2) nitrification; (3) denitrification; (4) sulfur oxidation and reduction; (5) iron oxidation and reduction; (6) manganese oxidation; and (7) methanogenesis (Suflita, 1989a). These metabolic processes include aerobic and anaerobic carbon transformations, many of which are important in aquifer contaminant biodegradation. The other processes are those required for the cycling of nitrogen, sulfur, iron, and manganese in microbial communities.

Biodegradation may refer to complete mineralization of organic contaminants (i.e., the parent compounds), to carbon dioxide, water, inorganic compounds, and cell protein (Sims and others, 1990). The ultimate products of aerobic metabolism are carbon dioxide and water, while under anaerobic conditions, metabolic activities also result in the formation of incompletely oxidized simple organic substances such as organic acids and other products such as methane or hydrogen gas.

Since contaminant biodegradation in the natural environment is frequently a stepwise process involving many enzymes and many species of organisms, a contaminant may not be completely degraded. Instead, it may be transformed to intermediate product(s) that may be less, equally, or more hazardous than the parent compound, and more or less mobile in the environment (Sims and others, 1990). The loss of a chemical, therefore, may or may not be a desirable consequence of the biodegradation process if biodegradation results in the production of undesirable

metabolites with their own environmental impact and persistence characteristics (Suflita, 1989b). For example, the reductive removal of tetrachloroethylene (TeCE) under anaerobic conditions results in a series of dehalogenated intermediates. TeCE's halogens are removed and replaced by protons in a series of sequential steps. However, the rate of reductive dehalogenation decreases as fewer and fewer halogens remain. Consequently, highly toxic vinyl chloride accumulates and, from a regulatory standpoint, causes greater concern than the parent contaminant. Bioremediation technologies should be selected with knowledge of metabolic processes of the specific contaminants at the site.

Biodegradation of most organic compounds in aquifer systems may be evaluated by monitoring their disappearance from the aquifer through time. Disappearance, or rate of degradation, is often expressed as a function of the concentration of one or more of the contaminants being degraded (Sims and others, 1990). Biodegradation in natural systems often can be modeled as a first-order chemical reaction (Johnson and others, 1989). Both laboratory and field data suggest that this is true when none of the reactants are in limited supply. A useful term to describe reaction kinetics is the half-life, $t_{1/2}$, which is the time required to transform 50 percent of the initial constituent.

As decomposable organic matter enters an oxygenated aquifer (Figure 3-19), microbial metabolism will likely begin to degrade the contaminating substrate; i.e., the indigenous microorganisms utilize the contaminant as an electron donor for heterotrophic microbial respiration (Suflita, 1989a). The aquifer microorganisms use oxygen as a co-substrate and as an electron acceptor to support their respiration. This oxygen demand may deplete oxygen and establish anaerobic conditions. When oxygen becomes limiting, aerobic respiration slows, and other microorganisms become active and continue to degrade the organic contaminants. Under conditions of anoxia, anaerobic bacteria use organic chemicals or certain inorganic anions as alternate electron acceptors.

Nitrate present in ground water is not rapidly depleted until oxygen is utilized. Organic matter is still metabolized, but, instead of oxygen, nitrate becomes the terminal electron acceptor during denitrification. Sulfate becomes a terminal electron acceptor when nitrate is limiting. When this occurs, hydrogen sulfide, an odorous gas, can often be detected in the ground water as a metabolic end-product. When very highly reducing conditions are present in an aquifer, carbon dioxide becomes an electron acceptor and methane is formed. Sometimes a spatial separation of dominant metabolic processes can occur in an aquifer, depending on the availability of

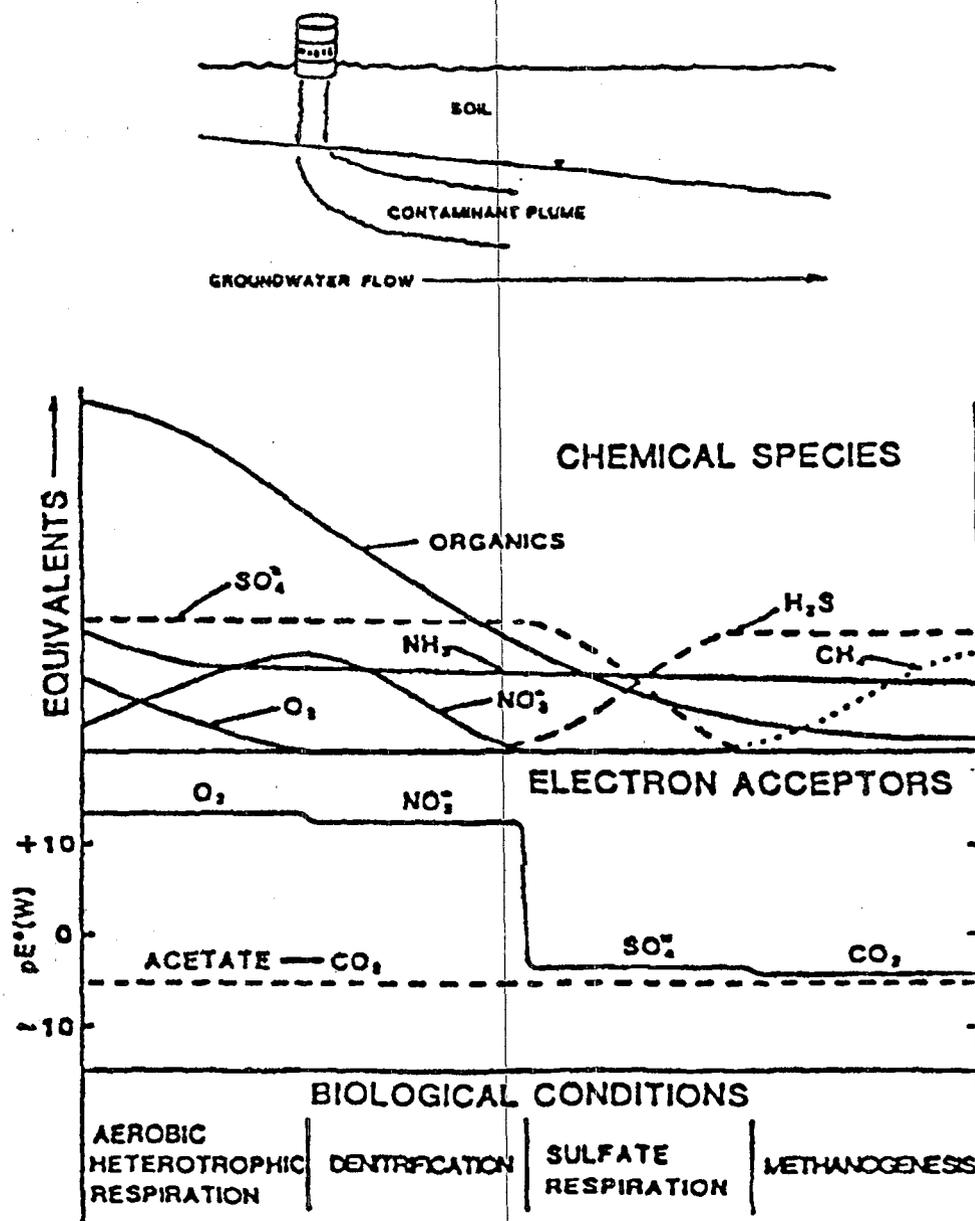


Figure 3-19. Microbially Mediated Changes in Chemical Species, Redox Conditions, and Spatial Regions Favoring Different Types of Metabolic Processes Along the Flow Path of a Contaminant Plume (adapted from Bower and McCarty, 1984, by Sufliita, 1989a)

electron acceptors, the presence of suitable microorganisms, and the energy benefit of the metabolic process to the specific microbial communities. As organic matter is transported in a contaminant plume, a series of redox zones can be established that range from highly oxidized to highly reduced conditions. The biodegradation potential and the expected rates of

metabolism will be different in each zone (Sufliita, 1989a). For many contaminants, aerobic decomposition is relatively fast, especially compared to methanogenic conditions. However, some contaminants, such as certain halogenated aliphatic compounds and 2,4,5-T, degrade faster when anaerobic conditions exist (Bower and others, 1981; Bower and McCarty, 1984; Gibson and Sufliita, 1986).

Environmental Factors Affecting Biodegradation
 Microorganisms need a suitable physical and chemical environment to grow and actively metabolize organic contaminants, (Sufflita, 1989a). Extremes of temperature, pH, salinity, osmotic or hydrostatic pressures, radiation, free water limitations, contaminant concentration, and/or the presence of toxic metals or other toxicant materials can limit the rate of microbial growth and/or substrate utilization. Often, two or more environmental factors interact to limit microbial decomposition processes. Selected critical environmental factors are presented in Table 3-1.

Limitations in the ability to alter environmental factors in the subsurface environment are important in selecting and implementing aquifer bioremediation technologies

(Sufflita, 1989a). For example, the temperature of aquifers probably cannot be significantly altered to stimulate in situ microbial growth and metabolism, but temperatures could be changed in a surface biological treatment reactor.

Physiological Factors Affecting Biodegradation
 In addition to environmental conditions, microbial physiological factors also influence organic contaminant biodegradation (Sufflita, 1989a). The supply of carbon and energy contained in organic contaminants must be sufficient for heterotrophic microbial growth. Too high a substrate concentration can limit microbial metabolism due to the toxicity of the substrate to microorganisms. If concentrations are too low, microbial response may be inhibited, or the substrates may not be suitable for

Environmental Factor	Optimum Levels
Available soil water	25-85% of water holding capacity; -0.01 MPa
Oxygen	Aerobic metabolism: Greater than 0.2 mg/l dissolved oxygen, minimum air-filled pore space of 10% by volume; Anaerobic metabolism: O ₂ concentrations less than 1% by volume
Redox potential	Aerobes & facultative anaerobes: greater than 50 millivolts; Anaerobes: less than 50 millivolts
pH	pH values of 5.5 - 8.5
Nutrients	Sufficient nitrogen, phosphorus, and other nutrients so as to not limit microbial growth (Suggested C:N:P ratio of 120:10:1)
Temperature	15 - 45° C (Mesophiles)

Table 3-1. Critical Environmental Factors for Microbial Activity (Sims and others, 1984; Huddleston and others, 1986; Paul and Clark, 1989)

growth. Growth and energy sources do not have to be supplied by the same carbon substrate. Growth and metabolism of microorganisms can be stimulated by providing a non-toxic primary carbon substrate so that the rate and extent of contaminant degradation can be increased (McCarty and others, 1981; McCarty, 1985; McCarty and others, 1984).

A contaminant also will be poorly metabolized if it is unable to enter microbial cells and gain access to intracellular metabolic enzymes, which may occur with larger molecular weight compounds (Sufliita, 1989a). A substrate also will persist if it fails to de-repress the enzymes required for its degradation. Appropriate enzymes sometimes can be induced by an alternate chemical compound. Sometimes initial biochemical reactions result in metabolites that tend to inhibit degradation of the parent molecule.

The absence of other necessary microorganisms can limit contaminant degradation, since often several microbial groups are required for complete degradation (Sufliita, 1989a). Microbial consortia are especially important in anaerobic mineralization of contaminants (McInerney and Bryant, 1981); if any individual members of a consortium are absent, biodegradation of the parent material effectively ceases.

Chemical Factors Affecting Biodegradation

One of the most important factors affecting contaminant biodegradation in aquifers is the structure of the contaminant, which determines its physical state (i.e., soluble, sorbed) and its tendency to biodegrade (Sufliita, 1989a). Aquifer contaminants may contain chemical linkages that tend to favor or hinder microbial degradation. The number, type, and position of substituents on a contaminant molecule should be considered when evaluating its metabolic fate in an aquifer.

Usually the closer a contaminant structurally resembles a naturally occurring compound, the better the possibility that the contaminant will be able to enter a microbial cell, de-repress the synthesis of metabolic enzymes, and be converted by those enzymes to metabolic intermediates (Sufliita, 1989a). Biodegradation is less likely (though not precluded) for those molecules having unusual structural features infrequently encountered in the natural environment. Therefore, xenobiotic compounds tend to persist in the natural environment because microorganisms have not evolved necessary metabolic pathways to degrade those compounds. However, microorganisms are nutritionally versatile, have the potential to grow rapidly, and possess only a single copy of DNA. Therefore, any genetic mutation or

recombination is immediately expressed. If the alteration is of adaptive significance, new species of microorganisms can be formed and grow. Contaminated environments supply selection pressure for the evolution of organisms with new metabolic potential that can grow utilizing the contaminating substance.

Aquifer Bioremediation

If an aquifer contaminant is determined to be susceptible to biodegradation, the goal of bioremediation is to utilize the metabolic capabilities of the indigenous microorganisms to eliminate that contaminant (Sufliita, 1989a). This practice generally does not include the inoculation of the aquifer with foreign bacteria.

Bioremediation technologies attempt to impose particular conditions in an aquifer to encourage microbial growth and the presence of desirable microorganisms. Bioremediation is based on knowledge of the chemical and physical needs of the microorganisms and the predominant metabolic pathways (Sufliita, 1989a). Most often, microbial activity is stimulated by supplying nutrients necessary for microbial growth. Bioremediation can take place either above ground or in situ. In situ systems are especially appropriate for contaminants that sorb to aquifer materials, since many decades of pumping may be required to reduce the contaminants to sufficiently low levels.

Successful implementation of aquifer bioremediation depends on determining site-specific hydrogeological variables, such as type and composition of an aquifer, permeability, thickness, interconnection to other aquifers, location of discharge areas, magnitude of water table fluctuations, and ground-water flow rates (Sufliita, 1989b). Generally, bioremediation is utilized in more permeable aquifer systems where movement of ground water can be more successfully controlled.

Removal of free product also is important for the success of bioremediation. Many substances that serve as suitable nutrients for microbial growth when present at low concentrations are inhibitory at high concentrations (Sufliita, 1989b).

Modeling Transport and Fate of Contaminants in an Aquifer

Introduction

Models are simplified representations of real-world processes and events, and their creation and use require many judgments based on observation of simulations of specific natural processes. Models may be used to simulate the response of specific problems to a variety of possible solutions (Keely, 1989b).

Physical models, including sand-filled tanks used to simulate aquifers and laboratory columns used to study contaminant flow through aquifer materials, often are used to obtain information on contaminant movement (Keely, 1989b). Analog models also are physically based, but are only similar to actual processes. An example is the electric analog model, where capacitors and resistors are used to replicate the effects of the rate of water release from storage in aquifers. The main disadvantage of physical models is the time and effort required to generate a meaningful amount of data.

Mathematical models are non-physical and rely on quantification of relationships between specific parameters and variables to simulate the effects of natural processes (Keely, 1989b, Weaver and others, 1989). Because mathematical models are abstract, they often do not provide an intuitive knowledge of real-world situations. However, mathematical models can provide insights into the functional dependencies between causes and effects in an actual aquifer. Large amounts of data can be generated quickly, and experimental modifications made easily, making possible for many situations to be studied in detail for a given problem.

Use and Categories of Mathematical Models

The application of mathematical models is subject to error in real-world situations when appropriate field determinations of natural process parameters are lacking. This source of error is not addressed adequately by sensitivity analyses or by the application of stochastic techniques for estimating uncertainty. The high degree of hydrogeological, chemical, and microbiological complexity typically present in field situations requires the use of site-specific characterization of the influences of various natural processes by detailed field and laboratory investigations (Keely, 1989b).

Mathematical models have been categorized by their technical bases and capabilities as: (1) parameter identification models; (2) prediction models; (3) resource management models; and (4) data manipulation codes. (Bachmat and others, 1978; van der Heidje and others, 1985).

Parameter identification models are used to estimate aquifer coefficients that determine fluid flow and contaminant transport characteristics (e.g., annual recharge, coefficients of permeability and storage, and dispersivity (Shelton, 1982; Guven and others, 1984; Puri, 1984; Khan, 1986a, b; Strecker and Chu, 1986)). Prediction models are the most numerous type because they are the primary tools used for testing hypotheses (Mercer and Faust, 1981; Anderson and others, 1984; Krabbenhoft and Anderson, 1986).

Resource management models are combinations of predictive models, constraining functions (e.g., total pumpage allowed), and optimization routines for objective functions (e.g., scheduling wellfield operations for minimum cost or minimum drawdown/pumping lift). Few of these types of models are developed well enough or supported to the degree that they are useful (van der Heidje, 1984a and b; van der Heidje and others, 1985).

Data manipulations codes are used to simplify data entry to other kinds of models and facilitate the productions of graphic displays of model outputs (van der Heidje and Srinivasan, 1983; Srinivasan, 1984; Moses and Herman, 1986).

Quality Control Measures

Quality control measures are required to assess the soundness and utility of a mathematical model and to evaluate its application to a specific problem. Huyakorn et al. (1984) and Keely (1989b) have suggested the following quality control measures:

1. Validation of the model's mathematical basis by comparing its output with known analytical solutions to specific problems.
2. Verification of the model's application to various problem categories by successful simulation of observed field data.
3. Benchmarking the problem-solving efficiency of a model by comparison with the performance of other models.
4. Critical review of the problem conceptualization to ensure that the modeling considers all physical, chemical, and biological processes that may affect the problem.
5. Evaluation of the specifics of the model's application, e.g., appropriateness of the boundary conditions, grid design, time steps.
6. Appraisal of the match between the mathematical sophistication of the model and the temporal and spatial resolution of the data.

Summary

Transport and fate assessments require interdisciplinary analyses and interpretations because processes are interdependent (Keely 1989a). Each transport process should be studied from interdisciplinary viewpoints, and interactions among processes identified and understood. In addition to a sound conceptual understanding of

transport processes, the integration of information on geologic, hydrologic, chemical, and biological processes into an effective contaminant transport evaluation requires data that are accurate, precise, and appropriate at the intended problem scale and that attempt to account for spatial and temporal variations.

References

- Anderson, M. A., J. F. Pankow, and R. L. Johnson, 1987, The dissolution of residual dense non-aqueous phase liquid (DNAPL) from a saturated porous medium: *in* Proceedings, Petroleum Hydrocarbons and Organic Chemicals in Ground Water. Nat. Water Well Assn and the American Petrol. Institute, Houston, TX, November, pp. 409-428.
- Anderson, P. F., C. R. Faust, and J. W. Mercer, 1984, Analysis of conceptual designs for remedial measures at Lipari Landfill, New Jersey: *Ground Water*, v. 22, pp. 176-190.
- Bachmat, Y., B. Andrews, D. Holtz, and S. Sebastian, 1978, Utilization of numerical groundwater models for Water Resource Management: EPA-600/8-78-012.
- Balkwill, D. L., T. E. Rucinski, and L. E. Casida, Jr., 1977, Release of microorganism from soil with respect to transmission electron microscopy viewing and plate counts: Antonie Van Leeuwenhoek ed., *Journal of Microbiology and Serology*, v. 43, pp. 73-87.
- Ball, J. W., D. K. Nordstrom, and E. A. Jenne, 1980, Additional and revised thermochemical data and computer code for WATEQ2: A Computerized Model for Trace and Major Element Speciation and Mineral Equilibria of Natural Waters. Water Resources Investigations U. S. Geological Survey, no. 78-116.
- Bear, J., 1969, Hydrodynamic dispersion: *in* Flow Through Porous Media, R.J.M. DeWiest, Editor: Academic Press, New York, pp. 109-199.
- Bear, J., 1979, *Hydraulics of groundwater*: McGraw-Hill, New York.
- Beeman, R. E. and J. M. Suflita, 1987, Microbial ecology of a shallow unconfined ground-water aquifer polluted by municipal landfill leachate: *Microbial Ecology*, v. 14, pp. 39-54.
- Benjamin, M. M. and J. O. Leckie, 1981, Multiple site adsorption of Cd, Cu, Zn, and Pb on amorphous iron oxyhydroxides: *Journal of Colloid and Interface Science*, v. 79, no. 2, pp. 209-221.
- Bouwer, E. J. and P. L. McCarty, 1984, Modeling of trace organics biotransformation in the subsurface: *Ground Water*, v. 22, pp. 433-440.
- Bouwer, E. J., B. E. Rittmann, and P. L. McCarty, 1981, Anaerobic degradation of halogenated 1- and 2-carbon organic compounds: *Environmental Science and Technology*, v.15, pp. 596-599.
- Chiou, C. T., D. W. Schmedding, and M. Manes, 1982, Partitioning of organic compounds on octanol-water systems: *Environmental Science and Technology*, v. 16, pp. 4-10.
- Chiou, C. T., L. J. Peters, and V. H. Freed, 1979, A physical concept of soil-water equilibria for nonionic compounds: *Science*, v. 206, pp. 831-832.
- Chiou, C. T., P. E. Porter, and D. W. Schmedding, 1983, Partition equilibria of nonionic organic compounds between soils organic matter and water: *Environmental Science and Technology*, v. 17, pp. 227-231.
- Chiou, C. T., T. D. Shoup, and P. E. Porter, 1985, Mechanistic roles of soil humus and minerals in the sorption of nonionic organic compounds from aqueous and organic solutions: *Organic Geochemistry*, v. 8, pp. 9-14.
- Chouke, R. L., P. van Meurs, and C. van der Poel, 1959, The instability of slow, immiscible, viscous liquid-liquid displacements in permeable media transactions: *American Institute of Mining Engineers*, v. 216, pp. 188-194.
- Davis, J. A., R. O. James, and J. O. Leckie, 1978, Surface ionization and complexation at the oxide/water interface: I. computation of electrical double layer properties in simple electrolytes: *Journal of Colloid and Interface Science*, v. 63, no. 3, pp. 480-499.
- Dempsey, B. A. and C. R. O'Melia, 1983, Proton and calcium complexation of four fulvic acid Fractions: *In*, Aquatic and Terrestrial Humic Materials, R. F. Christman and E. T. Gjessing, Editors. Ann Arbor Science, Ann Arbor, MI.
- Drever, J. I., 1982, *The geochemistry of natural waters*: Prentice-Hall, Englewood Cliffs, NJ.
- Dzombak, D. A. and F. M. M. Morel, 1986, Sorption of cadmium on hydrous ferric oxide at high sorbate/sorbent ratios: equilibrium, kinetics, and modelling: *Journal of Colloid and Interface Science*, v. 112, no. 2, pp. 588-598.

- Dzombak, D. A., W. Fish, and F. M. M. Morel, 1986, Metal-humate interactions. 1. discrete ligand and continuous distribution models: *Environmental Science and Technology*, v. 20, pp. 669-675.
- Evans, D. W., J. J. Alberts, and R. A. Clark, 1983, Reversible ion-exchange of cesium-137 leading to mobilization from reservoir sediments: *Geochimica et Cosmochimica Acta*, v. 47, no. 11, pp. 1041-1049.
- Felmy, A. R., D. C. Girvin, and E. A. Jenne. 1984. MINTEQA: A computer program for calculating aqueous geochemical equilibria: EPA/600/3-84-032, U. S. Environmental Protection Agency, Environmental Research Laboratory, Athens, GA.
- Feenstra, S. and J. A. Cherry, 1987, Dense organic solvents in ground water: an introduction: *in* Dense Chlorinated Solvents in Ground Water, Progress Report No. 083985, Institute for Ground Water Research, University of Waterloo, Ontario.
- Fish, W., D. A. Dzombak, and F. M. M. Morel, 1986, Metal-humate interactions. 2. application and comparison of models: *Environmental Science and Technology*, v. 20, pp. 676-683.
- Frind, E. O. and G. E. Hokkanen, 1987, Simulation of the borden plume using the alternating direction galerkin technique: *Water Resources Research*, v. 23, no. 5, pp. 918-930.
- Gibson, S. A. and J. M. Suflita, 1986, Extrapolation of biodegradative results to groundwater aquifers: reductive dehalogenation of aromatic compounds: *Applied and Environmental Microbiology*, v. 52:681-688.
- Gillham, R. W., and J. A. Cherry, 1982, Contaminant migration in saturated unconsolidated geologic deposits: *in* Recent Trends in Hydrogeology, T. N. Narasimhan, Editor. Geological Society of America, Paper 189, pp. 31-62, Boulder, CO.
- Guven, O., F. J. Molz, and J. G. Melville, 1984, An analysis of dispersion in a stratified aquifer: *Water Resources Research*, v. 20, pp. 1337-1354.
- Hayes, M. H. B. and R. S. Swift, 1978, The chemistry of soil organic colloids: *in* The Chemistry of Soil Constituents, D. J. Greenland and M. H. B. Hays, Editors. Wiley Interscience, New York, NY.
- Helferich, F., 1962, Ion exchange: McGraw-Hill, New York, NY.
- Hem, J. D., 1970, Study and interpretation of the chemical characteristics of natural water: Water Supply Paper 1473, U. S. Geological Survey, Reston, VA.
- Homsy, G. M., 1987, Viscous fingering in porous media: *Annual Review of Fluid Mechanics*, v. 19, pp. 271-311.
- Honeyman, B. D., K. F. Hayes, and J. O. Leckie, 1982, Aqueous chemistry of As, B, Cr, Se, and V with particular reference to fly-Ash transport water: Project Report EPRI-910-1, Electric Power Research Institute, Palo Alto, CA.
- Huddleston, R. L., C. A. Bleckmann, and J. R. Wolfe, 1986, Land treatment biological degradation processes: *in* Land Treatment: A Waste Management Alternative, R. C. Loehr and J. F. Malina, Jr., Editors. Water Resources Symposium, Center for Research in Water Resources, The University of Texas at Austin, Austin, TX, No. 13, pp. 41-61.
- Huyakorn, P. S., and others, 1984, Testing and validation of models for simulating solute transport in ground water: development and testing of benchmark techniques. IGWMC: Report No. GWMI 84-13. International Ground Water Modeling Center, Holcolm Research Institute, Butler University, Indianapolis, IN.
- Johnson, R. L., C. D. Palmer, and W. Fish. 1989. Subsurface chemical processes: *in* Transport and Fate of Contaminants in the Subsurface. U.S. Environmental Protection Agency, Center for Environmental Research Information, Cincinnati, OH, and Robert S. Kerr Environmental Research Laboratory, Ada, OK, EPA/625/4-89/019.
- Karickhoff, S. W., 1981, Semi-empirical estimation of sorption of hydrophobic pollutants on natural sediments and soils: *Chemosphere*, v. 10, pp. 833-846.
- Karickhoff, S. W., 1984, Organic pollutant sorption on aquatic systems: *Journal of Hydraulic Engineering*, v. 10, pp. 833-846.
- Karickhoff, S. W., D. S. Brown, and T. A. Scott, 1979, sorption of hydrophobic pollutants on natural sediments: *Water Research*, v. 13, pp. 241-248.
- Kenaga, E. E. and C. A. I. Goring, 1980, Relationship between water solubility, soil sorption, octanol-water partitioning, and concentrations of chemicals in Biota: *in* Aquatic Toxicology, Third Conference, J. G. Eaton, P. R. Parrish, and A. C. Hendricks, Editors. ASTM Special Publication 707. American Society for Testing Materials, Philadelphia, PA., pp. 78-115.
- Keely, J. F., 1989a, Introduction: *in* Transport and Fate

- of Contaminants in the Subsurface. U.S. Environmental Protection Agency, Center for Environmental Research Information, Cincinnati, OH, and Robert S. Kerr Environmental Research Laboratory, Ada, OK, EPA/625/4-89/019.
- Keely, J. F., 1989b, Modeling subsurface contaminant transport and fate: *in* Transport and Fate of Contaminants in the Subsurface. U.S. Environmental Protection Agency, Center for Environmental Research Information, Cincinnati, OH, and Robert S. Kerr Environmental Research Laboratory, Ada, OK, EPA/625/4-89/019.
- Khan, I. A., 1986a, Inverse problem in ground water: model development: *Ground Water*, v. 24, pp. 32-38.
- Khan, I. A., 1986b, Inverse problem in ground water: model application: *Ground Water*, v. 24, pp. 39-48.
- Kimmel, G. E. and O. C. Braids, 1980, Leachate plumes in groundwater from Babylon and Islip landfills, Long Island, New York: Professional Paper 1085, U. S. Geological Survey, Reston, VA.
- Krabbenhoft, D. P. and M. P. Anderson, 1986, Use of a numerical ground-water flow model for hypothesis testing: *Ground Water*, v. 24, pp. 49-55.
- Kueper, B. H. and E. O. Frind, 1988, An overview of immiscible fingering in porous media: *Journal of Contaminant Hydrology*, v. 2, pp. 95-110.
- Kuznetsov, S. I., N. V. Ivanov, and N. N. Lyalikova, 1963, The distribution of bacteria in groundwaters and sedimentary rocks: *in* Introduction to Geological Microbiology, C. Oppenheimer, Editor. McGraw-Hill Book Co., New York, NY.
- Lindberg, R. D. and D. D. Runnels, 1984, Ground water redox reactions: An analysis of equilibrium state applied to Eh measurements and geochemical modeling: *Science* v. 225, pp. 925-927.
- Mabey, W. R. and T. Mill, 1978, Critical review of hydrolysis of organic compounds in water under environmental conditions: *Journal of Physical and Chemical Reference Data*, v. 7, pp. 383-415.
- MacFarlane D. S., J. A. Cherry, R. W. Gillham, and E. A. Sudicky, 1983, Migration of contaminants in groundwater at a landfill: A case study; 1. groundwater flow and plume delineation: *Journal of Hydrology*, v. 63, pp. 1-29.
- MacKay, D. and B. Powers, 1987, Sorption of hydrophobic chemicals from water: A hypothesis for the mechanism of the particle concentration effect: *Chemosphere*, v. 16, pp. 745-757.
- Martell, A. E. and Smith, R. M., 1974, Critical stability constants: Amino Acids, v. 1, Plenum Press, New York, NY.
- Martell, A. E. and Smith, R. M., 1977., Critical stability constants: Other Organic Ligands, v. 3, Plenum Press, New York, NY.
- McCarty, P. L., 1985, Application of biological transformations in groundwater: *in* Proceedings, Second International Conference on Ground-Water Quality Research, N. N. Durham and A. E. Redelfs, Editors. National Center for Groundwater Research, Stillwater, OK.
- McCarty, P. L., B. E. Rittmann, and E. J. Bouwer, 1984, Microbiological processes affecting chemical transformations in ground water: *in* Groundwater Pollution Microbiology, G. Bitton and C. P. Gerba, Editors. John Wiley & Sons, New York, NY.
- McCarty, P. L., M. Reinhard, and B. E. Rittmann, 1981, Trace organics in ground water: *Environmental Science and Technology*, v. 15, pp. 47-51.
- McDowell-Boyer, L. M., J. R. Hunt, and N. Sitar, 1986, Particle transport through porous media: *Water Resources Research*, v. 22, no. 13, pp. 1901-1921.
- McInerney, M. J. and M. P. Bryant, 1981, Basic principles of bioconversion in anaerobic digestion and methanogenesis: *in* Biomass Conversion Processes for Energy and Fuels, S. S. Sofer and O. R. Zaborsky, Editors. Plenum Publishing Corporation, New York, NY, pp. 277-296.
- McNabb, J. F. and G. E. Mallard, 1984, Microbiological sampling in the assessment of groundwater pollution: *in* Groundwater Pollution Microbiology, G. Bitton and C. P. Gerba, Editors, John Wiley & Sons, New York, NY, pp. 235-260.
- Mercado, A., 1967, The spreading pattern of injected water in a permeability stratified aquifer: *in* Proceedings of the Symposium on Artificial Recharge and Management of Aquifers, Haifa, Israel, May 19-26. Publication No. 72, International Association of Scientific Hydrology, Gentbrugge, Belgium, pp. 23-36.
- Mercer, J. W. and C. R. Faust, 1981; Ground-water modeling: National Water Well Association, Worthington, OH.

- Morel, F. M. M., 1983, Principles of aquatic chemistry: Wiley Interscience, New York, NY.
- Morgan, J. J., 1967, Application and limitations of chemical thermodynamics in water systems: *in* Equilibrium Concepts in Natural Water Systems, Advances in Chemistry Series No. 67, American Chemical Society, Washington, DC.
- Moses, C. O. and J. S. Herman, 1986, Computer notes-WATIN-A computer program for generating input files for WATEQF: *Ground Water*, v. 24, pp. 83-89.
- Murarka, I. P. and D. A. McIntosh, 1987, Solid-waste environmental studies (SWES): description, status, and available results: EPRI EA-5322-SR, Electric Power Research Institute, Palo Alto, CA.
- Neuzil, C. E., 1986, Groundwater flow in low-permeability environments: *Water Resources Research*, v. 22, pp. 1163-1195.
- Nkedi-Kizza, P., P. S. C. Rao, and A. G. Hornsby, 1985, Influence of organic cosolvents on sorption of hydrophobic organic chemicals by soils: *Environmental Science and Technology*, v. 19, pp. 975-979.
- Palmer, C. D., 1990, Hydrogeochemistry of the subsurface: *in* Chemistry of Ground Water, C. Palmer, Editor, Lewis Publishers, Boca Raton, FL (In Review).
- Palmer, C. D., and R. L. Johnson, 1989a, Physical processes controlling the transport of contaminants in the aqueous phase: *in* Transport and Fate of Contaminants in the Subsurface, U.S. Environmental Protection Agency, Center for Environmental Research Information, Cincinnati, OH, and Robert S. Kerr Environmental Research Laboratory, Ada, OK, EPA/625/4-89/019.
- Palmer, C. D., and R. L. Johnson, 1989b, Physical processes controlling the transport of non-aqueous phase liquids in the subsurface: *in* Transport and Fate of Contaminants in the Subsurface, U.S. Environmental Protection Agency, Center for Environmental Research Information, Cincinnati, OH, and Robert S. Kerr Environmental Research Laboratory, Ada, OK, EPA/625/4-89/019.
- Paul, E. A. and F. E. Clark, 1989, Soil microbiology and biochemistry: Academic Press, Inc., San Diego, CA.
- Perdue, E. M., 1985, Acidic functional groups of humic substances: *in* Humic Substances in Soil, Sediment, and Water, G. R. Aiken, D. M. McKnight, R. L. Wershaw, and P. MacCarthy, Editors, Wiley Interscience, New York, NY.
- Perdue, E. M. and C. R. Lytle, 1983, A distribution model for binding of protons and metal ions by humic substances: *Environmental Science and Technology*, v. 17, pp. 654-660.
- Puri, S., 1984, Aquifer studies using flow simulation: *Ground Water*, v. 22, pp. 538-543.
- Reichenburg, D., 1966, Ion exchange selectivity: *in* Ion Exchange, Vol. 1, J. A. Marinsky, Editor, Marcel Dekker, New York, NY.
- Reuter, J. G., J. J. McCarthy, and E. J. Carpenter, 1979, The toxic effect of copper on ocellularia (*Trichodesmium*) *theibautii*: *Limnology and Oceanography*, v. 24, no. 3, pp. 558-561.
- Saffman, P. G. and G. Taylor, 1958, The penetration of a fluid into a porous medium or Hele-Shaw cell containing a more viscous liquid: *Proceeding of the Royal Society of London Series A*, v. 245, pp. 312-329.
- Scheigg, H. O., 1984, Considerations on water, oil, and air in porous media: *Water Science Technology*, v. 17, pp. 467-476.
- Schindler, P. W., B. Furst, R. Dick, and P. U. Wolf, 1976, Ligand properties of surface silanol groups. I. Surface complex formation with Fe³⁺, Cu²⁺, Cd²⁺, and Pb²⁺: *Journal of Colloid and Interface Science*, v. 55, no. 2, pp. 469-475.
- Schnitzer, M., 1969, Reactions between fulvic acid, a soil humic compound, and inorganic soil constituents: *Soil Science of America Proceedings*, v. 33, pp. 75-81.
- Schwarzenbach, R. and J. Westall, 1981, Transport of nonpolar organic compounds from surface water to ground water: laboratory sorption studies: *Environmental Science and Technology*, v. 15, pp. 1360-1367.
- Schwille, F., 1988, Dense chlorinated solvents in porous and fractured media: model experiments: J. F. Pankow, Translator. Lewis Publishers, Chelsea, MI.
- Shelton, M. L., 1982, Ground-water management in basalts: *Ground Water*, v. 20, pp. 86-93.
- Sholkovitz, E. R., 1985, Redox-related geochemistry in lakes: alkali metals, alkaline earth metals, and cesium-137: *in* Chemical Processes in Lakes, W. Stumm, Editor, Wiley-Interscience, New York, NY.
- Siegrist, H. and P. L. McCarty, 1987, Column methodologies for determining sorption and biotransformation potential for chlorinated aliphatic

- compounds in aquifers: *Journal of Contaminant Hydrology*, v. 2, pp. 31-50.
- Sims, J. L., R. C. Sims, and J. E. Matthews, 1990, Approach to bioremediation of contaminated soil: *Hazardous Waste & Hazardous Materials*, v. 7, pp. 117-149.
- Sims, R. C., D. L. Sorensen, J. L. Sims, J. E. McLean, R. Mahmood, and R. R. Dupont, 1984, Review of In-Place Treatment Techniques for Contaminated Surface Soils, Volume 2: Background Information for In Situ Treatment, U. S. Environmental Protection Agency, Hazardous Waste Engineering Research Laboratory, Cincinnati, OH, EPA/540/2-84-003a.
- Smith, R. M. and A. E. Martell, 1975, Critical stability constants, vol. 2: Amines, Plenum Press, New York, NY.
- Sposito, G., 1984, The surface chemistry of soils: Oxford University Press, New York, NY.
- Sposito, G., 1986, Sorption of trace metals by humic materials in soils and natural waters: *CRC Critical Reviews in Environmental Control*, v. 16, pp. 193-229.
- Stevenson, F. J., 1982, Humus chemistry: genesis, compositions, reactions: Wiley Interscience, New York, NY.
- Strecker, E. W. and W. Chu, 1986, Parameter identification of a ground-water contaminant transport model: *Ground Water*, v. 24, pp. 56-62.
- Stumm, W. and J. J. Morgan, 1981, Aquatic chemistry, second edition: Wiley Interscience, New York, NY.
- Stumm, W., H. Hohl, and F. Dalang, 1976, Interaction of metal ions with hydrous oxide surfaces: *Croatica Chemica Acta*, v. 48, no. 4, pp. 491-504.
- Suflita, J. M., 1989a, Microbial ecology and pollutant biodegradation in subsurface ecosystems: in *Transport and Fate of Contaminants in the Subsurface*, U.S. Environmental Protection Agency, Center for Environmental Research Information, Cincinnati, OH, and Robert S. Kerr Environmental Research Laboratory, Ada, OK, EPA/625/4-89/019.
- Suflita, J. M., 1989b, Microbiological principles influencing the bioremediation of aquifers: in *Transport and Fate of Contaminants in the Subsurface*, U.S. Environmental Protection Agency, Center for Environmental Research Information, Cincinnati, OH, and Robert S. Kerr Environmental Research Laboratory, Ada, OK, EPA/625/4-89/019.
- Tanford, C., 1973, The hydrophobic effect: formation of micelles and biological membranes: Wiley and Sons, New York, NY.
- Thurman, E. M., 1985, Humic substances in the ground water: in *Humic Substances in Soil, Sediment, and Water: Geochemistry, Isolation, and Characterization*, G. R. Aiken, D. M. McKnight, R. L. Wershaw, and P. MacCarthy, Editors, Wiley Interscience, New York, NY.
- Updegraff, D. M., 1982, Plugging and penetration of petroleum reservoir rock by microorganisms: Proceedings of 1982 International Conference on Microbial Enhancement of Oil Recovery, May 16-21, Shangri-La, Afton, OK.
- U. S. Environmental Protection Agency, 1985, Protection of public water supplies from ground-water contamination: U. S. Environmental Protection Agency, Center for Environmental Research Information, Cincinnati, OH.
- U. S. Environmental Protection Agency, 1989, Transport and fate of contaminants in the subsurface: EPA/625/4-89/019, U.S. Environmental Protection Agency, Center for Environmental Research Information, Cincinnati, OH, and Robert S. Kerr Environmental Research Laboratory, Ada, OK.
- van der Heidje, P. K. M., 1984a, Availability and applicability of numerical models for ground water resources management: IGWMC Report No. GWMI 84-19, International Ground Water Modeling Center, Holcolm Research Institute, Butler University, Indianapolis, IN.
- van der Heidje, P. K. M., 1984b, Utilization of models as analytic tools for groundwater management: IGWMC Report No. GWMI 84-18, International Ground Water Modeling Center, Holcolm Research Institute, Butler University, Indianapolis, IN.
- van der Heidje, P. K. M. and others, 1985, Groundwater management: the use of numerical models, second edition: AGU Water Resources Monograph No. 5, American Geophysical Union, Washington, DC.
- van der Heidje, P. K. M. and P. Srinivasan, 1983, Aspects of the use of graphic techniques in ground-water modeling. IGWMC Report No. GWMI 83-11, International Ground Water Modeling Center, Holcolm Research Institute, Butler University, Indianapolis, IN.

Waksman, S. A., 1916, Bacterial numbers in soil, at different depths, and in different seasons of the year: *Soil Science*, v. 1, pp. 363-380.

Weaver, J., C. G. Enfield, S. Yates, D. Kreamer, and D. White, 1989, Predicting subsurface contaminant transport and transformation: considerations for model selection and field validation: U. S. Environmental Protection Agency, Robert S. Kerr Environmental Research Laboratory, Ada, OK, EPA/600/2-89/045.

Westall, J. C., J. L. Zachary, and F. M. M. Morel, 1976, MINEQL: a computer program for the calculation of chemical equilibrium composition of aqueous systems: Technical Note No. 18, Massachusetts Institute of Technology, Boston, MA.

Williams, P. A., 1985, Secondary minerals: natural ion buffers: *in* *Environmental Inorganic Chemistry*, K. J. Irgolic and A. E. Martell, Editors, VCH Publishers, Deerfield Beach, FL.

Zachara, J. M., and others, 1988, Influence of cosolvents on quinoline sorption by subsurface materials and clays: *Journal of Contaminant Hydrology*, v. 2, pp. 343-364.

Chapter 4

GROUND-WATER TRACERS

In hydrogeology, "tracer" is a distinguishable matter or energy in ground water that carries information on the ground-water system. A tracer can be entirely natural, such as the heat carried by hot-spring waters; accidentally introduced, such as fuel oil from a ruptured storage tank; or intentionally introduced, such as dyes placed in water flowing within limestone caves.

Types and Uses of Tracer Tests

The variety of tracer tests is almost infinite, considering the various combinations of tracer types, local hydrologic conditions, injection methods, sampling methods, and geological settings. Tracer tests mainly are used (1) to measure one or more hydrogeologic parameters of an aquifer; and (2) to identify sources, velocity, and direction of movement of contaminants. Tracer tests also can be broadly classified according to whether they rely on natural gradient flow or an induced flow from pumping or some other means. Quinlan and others (1988) discuss how to recognize falsely negative or positive tracer results.

Measurement of Hydrogeologic Parameters

Tracers can be used to measure or estimate a wide variety of hydrogeologic parameters, most commonly direction and velocity of flow and dispersion. Depending on the type of test and the hydrogeologic conditions, other parameters such as hydraulic conductivity, porosity, chemical distribution coefficients, source of recharge, and age of ground water can be measured.

Figure 4-1 shows six examples of tracer measurement of hydrogeologic characteristics by natural gradient flow. Figure 4-1a shows flow velocity in a cave system, and Figure 4-1b shows subsurface flow patterns in a karst area with sinking and rising streams. Figure 4-1c shows the velocity of movement of dissolved material between two wells. Both velocity and direction of flow can be measured in a single well as shown in Figure 4-

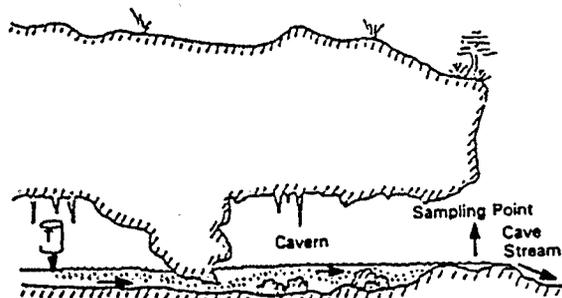
1d and by using multiple downgradient sampling wells as shown in Figure 4-1e. Finally, hydrodynamic dispersion can be measured by multiwell, multilevel sampling down gradient (Figure 4-1f).

Figure 4-2 shows four examples of tracer measurement of hydrogeologic parameters using induced flow. A tracer in surface water combined with pumping from a nearby well can verify a connection, as shown in Figure 4-2a. Interconnections between fractures can be mapped using tracers and inflatable packers in two uncased wells, as shown in Figure 4-2b. Figure 4-2c shows the measurement of a number of aquifer parameters using a pair of wells with forced circulation between wells. Figure 4-2d shows the evaluation of geochemical interactions between multiple tracers and aquifer material by alternating injection and pumping.

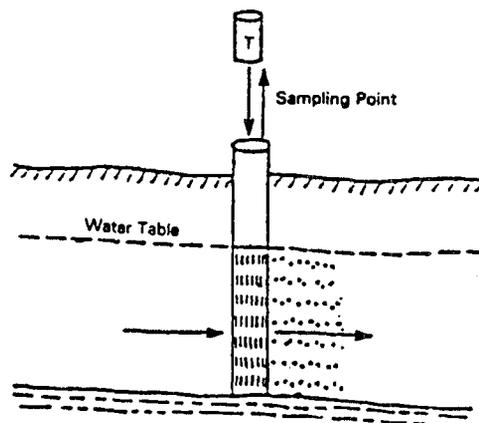
Tracers also can be used to determine ground-water recharge using environmental isotopes (Ferronsky and Polyakov, 1982; Moser and Rauert, 1985; Vogel and others, 1974), and to date ground water (Davis and Bentley, 1982).

Delineation of Contaminant Plumes

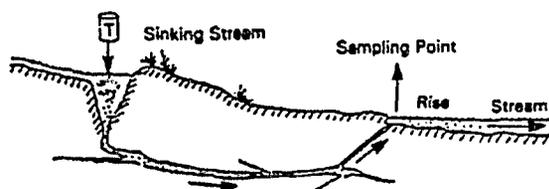
Any contaminant that moves in ground water acts as a tracer; thus the contaminant itself may be mapped, or other tracers may be added to map the velocity and direction of the flow. Contaminant plumes are not tracers in the sense used in this chapter and are not discussed further here. However, Figure 4-3 shows three examples of noncontaminant tracers used to identify contaminant sources and flow patterns. Figure 4-3a shows the use of a tracer in a sinkhole to determine if trash at a particular location is contributing to contamination of a spring. Similarly, Figure 4-3b shows that by flushing a dye tracer down a toilet one can determine whether septic seepage is causing contamination of a well or surface water. Figure 4-3c shows the use of multiple tracers at multiple sources of potential contamination to pinpoint the actual source.



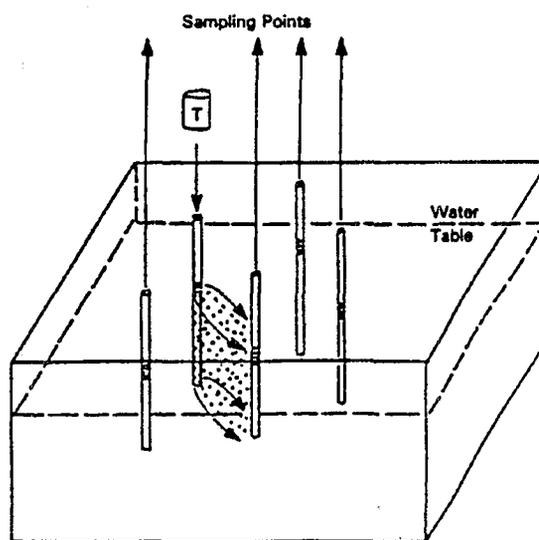
a. To measure velocity of water in cave stream.



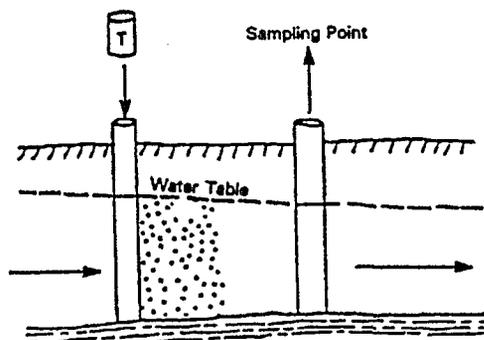
d. To determine velocity and direction of ground-water flow under natural conditions. Injection followed by sampling from same well.



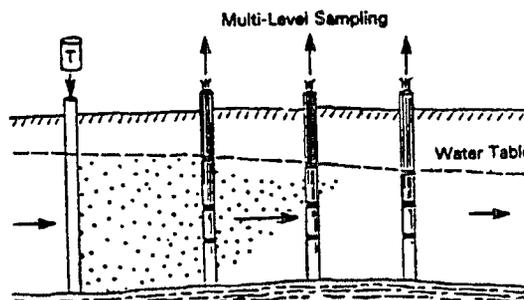
b. To check source of water at rise in stream bed.



e. To determine the direction and velocity of natural ground-water flow by drilling an array of sampling wells around a tracer injection well.

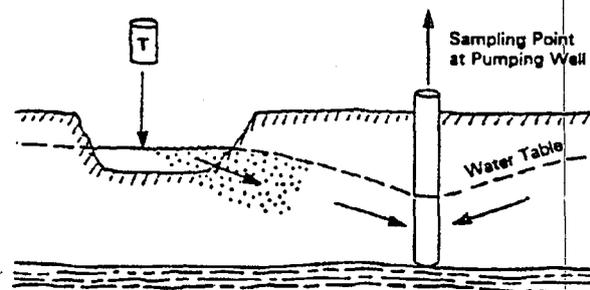


c. To test velocity of movement of dissolved material under natural ground-water gradients.

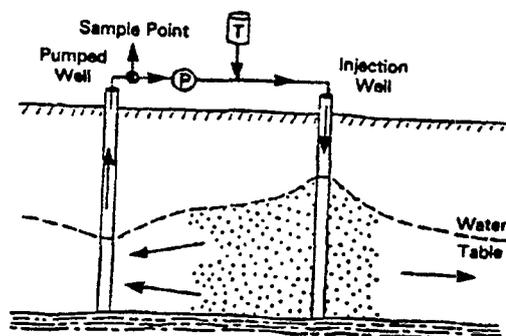


f. To test hydrodynamic dispersion in aquifer under natural ground-water gradients.

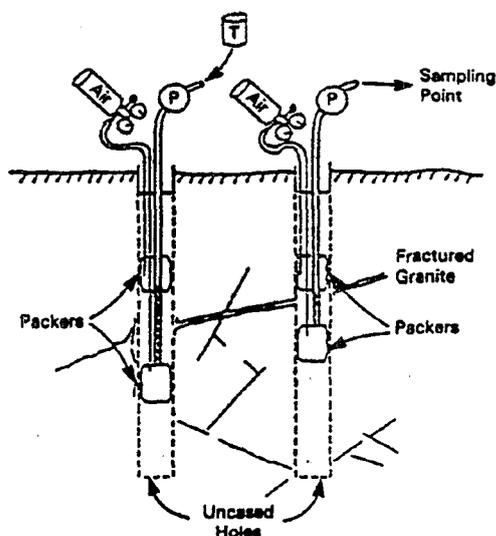
Figure 4-1. Common Configurations for Use of Tracer to Measure Hydrogeologic Parameters Using Natural Gradient Flow (from Davis and others, 1985)



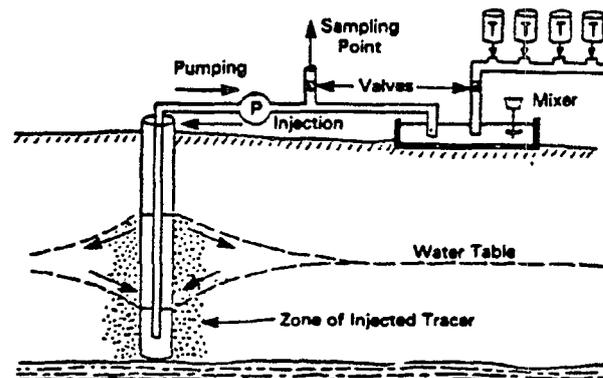
a. To verify connection between surface water and well.



c. To test a number of aquifer parameters using a pair of wells with forced circulation between wells.



b. To determine the interconnect fractures between two uncased holes. Packers are inflated with air and can be positioned as desired in the holes.



d. To test precipitation of selected constituents on the aquifer material by injecting multiple tracers into aquifer then pumping back the injected water.

Figure 4-2. Common Configurations for Use of Tracers to Measure Hydrogeologic Parameters Using Induced Flow (from Davis and others, 1985)

Tracer Selection

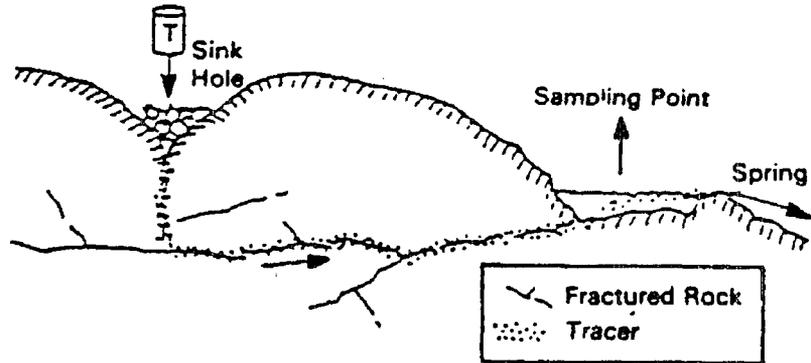
Overview of Types of Tracers

Ground-water tracers can be broadly classified as natural (environmental) tracers and injected tracers. Table 4-1 lists 14 natural tracers and 30 injected tracers. Table 4-2 lists review papers, reports, and bibliographies that are good sources for general information on ground-water tracing.

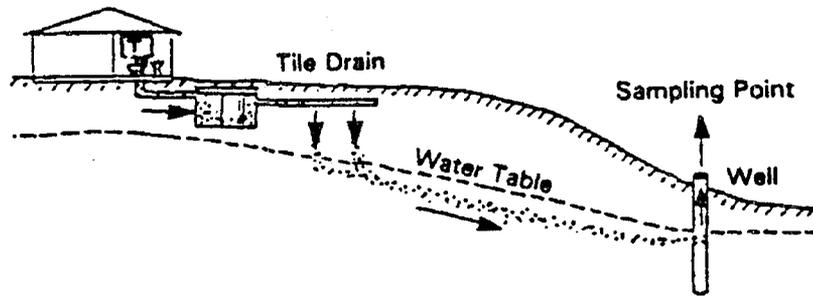
The potential chemical and physical behavior of the tracer in ground water is the most important selection criterion. Conservative tracers, used for most purposes, travel with the same velocity and direction as the water and do not interact with solid material. Nonconservative

tracers, which tend to be slowed by interactions with the solid matrix, are used to measure distribution coefficients and preferential flow zones in the vadose zone. For most uses, a tracer should be nontoxic, inexpensive, and easily detected to a low concentration with widely available and simple technology. If the tracer occurs naturally in ground water, it should be present in concentrations well above background concentrations. Finally, the tracer itself should not modify the hydraulic conductivity or other properties of the medium being studied.

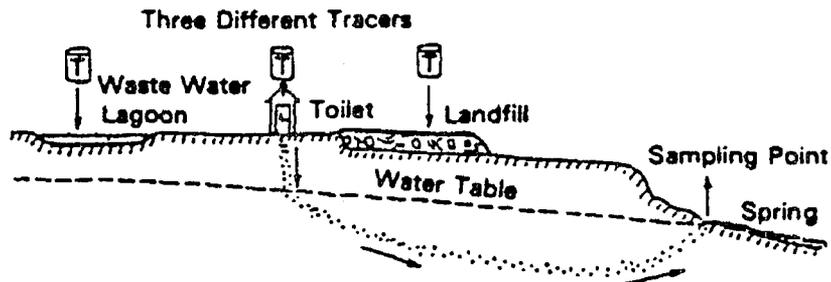
No one ideal tracer has been found. Because natural systems are so complex and the requirements for the tracers themselves are so numerous, the selection and



a. To determine if trash in sinkhole contributes to contamination of spring.



b. To determine if tile drain from septic tank contributes to contamination of well.



c. To determine source of pollution from three possibilities.

Figure 4-3. Common Configurations for Use of Tracers to Identify Contaminant Sources Using Natural Gradient Flow (from Davis and others, 1985)

NATURAL TRACERS				INJECTED TRACERS			
Stable Isotopes		Radioactive		Activatable		Inactive	
Deuterium	² H	Tritium	³ H	Bromine	³⁶ Br	Ionized Substances Drift Material	
Oxygen-18	¹⁸ O	Sodium-24	²⁴ Na	Indium	⁴⁹ In	Salts: Na ⁺ Cl	Lycopodium Spores
Carbon-13	¹³ C	Chromium-51	⁵¹ Cr	Manganese	²⁵ Mn	K ⁺ Cl ⁻	Bacteria
Nitrogen-15	¹⁵ N	Cobalt-58	⁵⁸ Co	Lanthanum	⁵⁷ La	Li ⁺ Cl ⁻	Viruses
Strontium-88	⁸⁸ Sr	Cobalt-60	⁶⁰ Co	Dysprosium	⁶³ Dy	Na ⁺ T ⁻	Fungi
						K ⁺ Br ⁻	Sawdust
Radioactive Isotopes							
Tritium-3	³ H	Gold-198	¹⁹⁸ Au			Fluorescent Dyes:	
Carbon-14	¹⁴ C	Iodine-131	¹³¹ I			Optical Brighteners	
Silicon-32	³² Si	Phosphorus-32	³² P			Tinopal 5Bm6x(FDA 22)	
Chlorine-36	³⁶ Cl					Direct Yellow 96	
Argon-37	³⁷ Ar					Fluorescein	
Argon-39	³⁹ Ar					Acid Yellow 7	
Krypton-81	⁸¹ Kr					Rhodamine WT	
Drypton-85	⁸⁵ Kr					Eosin (Acid Red 87)	
						Amidrhodamine 6 (Acid Red 50)	
						Physical Characteristics	
						Water Temperature	
						Flood Pulse	

Source: Modified from Jones, 1984.

Table 4-1. Survey of Ground-Water Tracers

Reference	Description
Atkinson and Smart (1981)	Review paper on uses of artificial tracers in hydrology.
Davis and others (1980)	Review paper on ground-water tracers.
Davis and others (1985)	Introductory EPA report on ground-water tracing. See also discussion by Quinlan (1986) and reply by Davis (1986)
Drew and Smith (1969)	Focuses on fluorescent dyes and lycopodium spores, but also contains annotated bibliography on other tracers.
Gaspar (1987)	Compilation of papers on modern trends in tracer hydrology.
Grisak and others (1983)	Report evaluating ground-water tracers for nuclear fuel waste management studies.
Kaufman and Orlob (1956)	Early review paper on use of radioactive and chemical tracers in porous media.
Keswick et al. (1982)	Review paper on use of microorganisms as ground-water tracers.
Knuttsen (1968)	Review paper on use of tracers for ground-water investigations.
McLaughlin (1982)	Review paper on use of dyes as soil water tracers.
Molz and others (1986)	Focuses on aquifer tracer tests in porous media and use in contaminant transport modeling.
Smart and Laidlaw (1977)	Classic paper on the use of fluorescent dyes for water tracers.
Taylor and Dey (1985)	Bibliography on borehole geophysics as applied to ground-water hydrology containing 42 references on tracers.
Turner Design's Ground Water Tracing Series	A series of annotated bibliographies concerning solute movement in aquifers and use of dyes as tracers. Smart et al. (1988) review 57 papers that compare dyes with other tracers. See also Edwards and Smart (1988a, b).
van der Leeden (1987)	The section in this bibliography on tracers and ground-water dating contains 69 references.

Table 4-2. Sources of Information on General Ground-Water Tracing

use of tracers is almost as much an art as a science. The following sections discuss factors that should be considered when selecting a tracer.

Hydrogeologic Considerations

The initial step in determining the physical feasibility of a tracer test is to collect as much hydrogeologic information about the field area as possible. The logs of the wells at the site to be tested, or logs of the wells closest to the proposed site, will give some idea of the homogeneity of the aquifer, layers present, fracture patterns, porosity, and boundaries of the flow system. Local or regional piezometric maps, or any published reports on the hydrology of the area (including results of aquifer tests), are valuable, as they may give an indication of the hydraulic gradient and hydraulic conductivity.

Major hydrogeologic factors that should be considered when selecting a tracer include:

Lithology. Fine-grained materials, particularly clays, have higher sorptive capacities than coarse-grained material. The sorptive capacity must be considered when evaluating the potential mobility of a tracer.

Flow Regime. Whether flow is predominantly through porous media (alluvium, sandstone, soil), solution features (karst limestone), or fractures will influence the choice of tracer. For example, fluorescent dyes work well in karst settings, but because of sorption effects are less effective than ground-water tracers in porous media.

Direction of Flow. For tracer studies using two or more wells, the general direction of ground-water movement must be known.

Travel Time. The equation for estimating travel time was discussed previously. In two-well tracer tests, travel time must be known to estimate spacing for wells.

Dispersion. Tracer tests often are used to measure dispersion. In two-well tests, some preliminary estimates may be required to estimate the quantity of tracer to inject so that concentrations will be high enough to detect.

Tracer Characteristics

Tracers have a wide range of physical, chemical, and biological characteristics. These properties, as they relate to hydrogeologic and other factors will determine the most suitable tracer for the purposes desired.

Detectability. Injected tracers should have no, or very low, natural background levels. Lower

detection limit is for instruments (ppm, ppb, ppt), are better. The degree of dilution is a function of type of injection, distance, dispersion, porosity, and hydraulic conductivity. Too much dilution may result in failure to observe the tracer when it reaches a sampling point because concentrations are below the detection limit. Possible interferences from other tracers and natural water chemistry may have the same effect.

Mobility. Conservative tracers used to measure aquifer parameters such as flow direction and velocity should be (1) stable (i.e., not subject to transformation by biodegradation or nonbiological processes during the length of the test and analysis); (2) soluble in water; (3) of a similar density and viscosity; and (4) not subject to adsorption or precipitation. Nonconservative, nontoxic tracers used to simulate transport of contaminants should have adsorptive and other chemical properties similar to the contaminant of concern.

Toxicity. Nontoxic tracers should be used if at all possible. If a tracer may be toxic at certain concentrations, maximum permissible levels as determined by federal, state, or county agencies must be considered in relation to expected dilution and proximity to drinking water sources. Most agencies have set no limits, partly because the commonly used tracers are nontoxic in concentrations usually employed, and partly because they never considered tracers to be a problem demanding regulation.

Other Considerations

A tracer may be suitable for the test's purpose and the hydrogeologic setting, yet still not be suitable for reasons of economics, technological availability or sophistication, or public health.

Economics. The tracer or the instrumentation to analyze samples may be expensive. In this situation, another less-expensive tracer with somewhat less favorable characteristics may suffice.

Technology. Some tracers may be difficult to obtain, or may require more complicated sampling methods. Gases, for example, will escape easily from poorly sealed containers. Similarly, instrumentation for gas or isotope analyses may not be available; e.g., only one or two laboratories in the world can perform analyses of ^{36}Cl .

Public Health. Tracer injections must involve a careful consideration of possible health implications. Some local or state health agencies insist on review

authority prior to use of artificially introduced tracers, but most do not. Local citizens must be informed of the tracer injections, and usually the results should be made available to the public. Under some circumstances, analytical work for tracer studies must be performed in appropriately certified laboratories. These are job-specific decisions.

Tracing in Karst vs. Porous Media

Ground-water flow in karst terranes is characterized by conduit flow and diffuse flow through often complex subsurface channel systems. Ground-water contaminants tend to move rapidly in karst and resurge at the surface in locations that cannot be readily predicted from the morphology of surface drainage patterns. In contrast, ground-water flow in porous media is characterized by slow travel times and more generally predictable flow directions. These differences require substantially different approaches to conducting tracer tests, as discussed in karst and porous media sections in this document.

Types of Tracers

Considering the full range of organic ground-water contaminants, hundreds, and possibly thousands, of substances have been used as tracers in ground water. The most commonly used tracers can be grouped into six categories: (1) water temperature, (2) particulates (called drift material in Table 4-1), (3) ions, (4) dyes, (5) gases, and (6) isotopes. These categories are not mutually exclusive (i.e., isotopes may take the form of ions or gases). Selected tracers in each category in relation to applicability in different hydrologic settings, field methods, and type of detection used, are discussed in the following sections.

Water Temperature

The temperature of water changes slowly as it migrates through the subsurface, because water has a high specific heat capacity compared to most natural materials. For example, temperature anomalies associated with the spreading of warm wastewater in the Hanford Reservation in south central Washington have been detected more than 8 km (5 mi) from the source.

Water-temperature tracing is potentially useful, although it has not been used frequently. The method may be applicable in granular media, fractured rock, or karst regions. Keys and Brown (1978) traced thermal pulses from the artificial recharge of playa lake water into the Ogallala formation in Texas. They described the use of temperature logs (temperature measurements at intervals in cased holes) to detect hydraulic conductivity

differences in an aquifer. Temperature logs also have been used to determine vertical movement of water in a borehole (Keys and MacCary, 1971; Sorey, 1971).

Changes in water temperature are accompanied by changes in water density and viscosity, which in turn alter the velocity and direction of flow. For example, injected ground water with a temperature of 40°C will travel more than twice as fast in the same aquifer under the same hydraulic gradient as water at 5°C. Because the warm water has a slightly lower density than cold water, buoyant forces give rise to flow that "floats" on top of the cold water. To minimize temperature-induced-convection problems, accurately measured small temperature differences should be used if hot or cold water is in the introduced tracer.

Davis and others (1985) used temperature as a tracer for small-scale field tests, in shallow drive-point wells 2 feet apart in an alluvial aquifer. The transit time of the peak temperature was about 107 min, while the resistivity data indicated a travel time of about 120 min (Figure 4-4). The injected water had a temperature of 38°C, while the ground-water temperature was 20°C; the peak temperature obtained in the observation well was 27°C. In these tests, temperature indicated breakthrough of

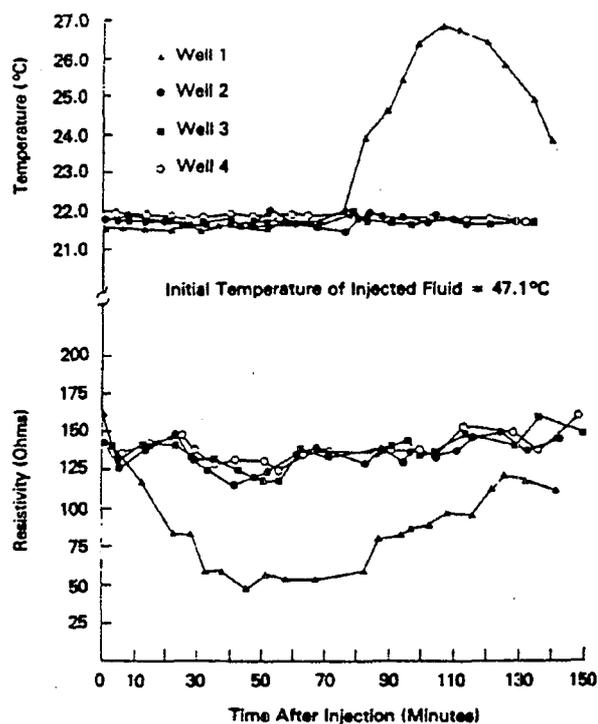


Figure 4-4. Results of Field Test Using a Hot Water Tracer (from Davis and others, 1985)

the chemical tracers, aiding in the timing of sampling. It also was useful as a simple, inexpensive tracer for determining the correct placement of sampling wells.

Water-temperature tracing also can be used to detect river recharge in an aquifer. Most rivers have large seasonal water temperature fluctuations. If the river is recharging an aquifer, the seasonal fluctuations can be detected in the ground water relative to the river (Rorabaugh, 1956).

Particulates

Solid material in suspension, such as spores, can be a useful tracer in areas where water flows in large conduits such as in some basalt, limestone, or dolomite aquifers. Seismic methods at the surface have been used to detect the location of time-delayed explosives floating through a cave system (Arandjelovic, 1969). Small particulate tracers, such as bacteria, can travel through any porous media such as soils and fractured bedrock where the pore size is larger than the size of the microorganism. Microorganisms are probably the most commonly used particulate tracers. Table 4-3 compares characteristics of microbial tracers.

Yeast. Wood and Ehrlich (1978) reported the use of

baker's yeast (*Saccharomyces cerevisiae*) as a ground-water tracer in a sand and gravel aquifer. Yeast is a single-celled fungus that is ovoid in shape. The diameter of a yeast cell is 2 to 3 μm , which closely approximates the size of pathogenic bacterial cells. This tracer probably provides most information about the potential movement of bacteria.

Wood and Ehrlich (1978) found that the yeast penetrated more than 7 m into a sand and gravel aquifer in less than 48 hours after injection. This tracer is very inexpensive, as is analysis. Another advantage is the lack of environmental concerns.

Bacteria. Bacteria are the most commonly used microbial tracers, because they grow well and are easily detected. Keswick and others (1982) reviewed over 20 case studies of bacteria tracers. Some bacteria that have been used successfully are *Escherichia coli* (*E. coli*), *Streptococcus faecalis*, *Bacillus stearothermophilus*, *Serratia marcescens*, and *Serratia indica*. These bacteria range in size from 1 to 10 μm and have been used in a variety of applications.

A fecal coliform, *E. coli*, has been used to indicate fecal pollution at pit latrines, septic fields, and sewage disposal

Tracer	Size (μm)	Time Required for Assay (days)	Essential Equipment Required
Bacteria	1-10	1-2	Incubator*
Spores	25-33	1/2	Microscope Plankton nets
Yeast	2-3	1-2	Incubator*
Viruses: Animal (enteric)	0.2-0.8	3-5	Incubator Tissue Culture Laboratory
Bacterial	0.2-1.0	1/2-1	Incubator*

*Many may be assayed at room temperature

Source: Keswick and others (1982)

Table 4-3. Comparison of Microbial Tracers

sites. A "marker" such as antibiotic resistance or H₂S production is used to distinguish the tracer from background organisms.

The greatest health concern in using these tracers is that the bacteria must be nonpathogenic to humans. Even *E. coli* has strains that can be pathogenic. Davis and others (1970) and Wilkowske and others (1970) have reported that *Serratia marcescens* may be life-threatening to patients who are hospitalized with other illnesses. Antibiotic-resistant strains are another concern, as the antibiotic resistance can be transferred to potential human pathogens. This problem can be avoided by using bacteria that cannot transfer this genetic information. As is true with most other injected tracers, permission to use bacterial tracers should be obtained from the proper federal, state, and local health authorities.

Viruses. Animal, plant, and bacterial viruses also have been used as ground-water tracers. Viruses are generally much smaller than bacteria, ranging from 0.2 to 1.0 μm (see Table 4-1). In general, human enteric viruses cannot be used because of disease potential. Certain vaccine strains, however, such as a type of polio virus, have been used but are considered risky. Most animal enteric viruses are considered safer as they are not known to infect humans (Keswick and others, 1982). Neither human nor most animal viruses, however, are generally considered suitable tracers for field work because of their potential to infect humans.

Spores. Lycopodium spores have been widely used as tracers in karst hydrogeologic systems in Europe since the early 1950s, and less frequently used in the United States since the 1970s. Much of the literature on the use of spores, however, is in obscure European and American speleological journals. More readily accessible references on the use of spores include Atkinson and others (1973), Gardner and Gray (1976), and Smart and Smith (1976).

Lycopodium is a clubmoss that has spores nearly spherical in shape, with a mean diameter of 33 μm . It is composed of cellulose and is slightly denser than water, so that some turbulence is required to keep the material in suspension. Some advantages of using lycopodium spores as a tracer are:

- * The spores are relatively small.
- * They are not affected by water chemistry or adsorbed by clay or silt.
- * They travel at approximately the same velocity as the surrounding water.

- * The injection concentration can be very high (e.g., 8×10^6 spores per cm^3).
- * They pose no health threat.
- * The spores are easily detectable under the microscope.
- * At least five dye colors may be used, allowing five tracings to be conducted simultaneously in a karst system.

Some disadvantages associated with lycopodium spores include the large amount of time required for their preparation and analysis, and the filtration of spores by sand or gravel if flow is not sufficiently turbulent.

The basic procedure involves adding a few kilograms of dyed spores to a cave or sinking stream. The movement of the tracer is monitored by sampling downstream in the cave or with plankton nets installed in the stream bed at a spring. The sediment caught in the net is concentrated and treated to remove organic matter. The spores are then examined under the microscope.

Tracing by lycopodium spores is most useful in open joints or solution channels (karst terrane) where there is minimal suspended sediment. It is not useful in wells or boreholes unless the water is pumped continuously to the surface and filtered. The spores survive well in polluted water, but do not perform well in slow flow or in water with a high sediment concentration. A velocity of a few miles per hour has been found sufficient to keep the spores in suspension. According to Smart and Smith (1976), lycopodium is preferable to dyes for use in large-scale water resource reconnaissance studies in karst areas. Skilled personnel should be available to sample and analyze the spores and a relatively small number of sampling sites should be used.

Ions

Inorganic ionic compounds such as common salts have been used extensively as ground-water tracers. This category of tracers includes those compounds that undergo ionization in water, resulting in their separation into charged species possessing a positive charge (cations) or a negative charge (anions). The charge on an ion affects its movement through aquifers by numerous mechanisms.

Ionic tracers have been used as tools to determine flow paths and residence times and measure aquifer properties. Slichter (1902, 1905) was probably the first to use ionic tracers to study ground water in the United States. Specific characteristics of individual ions or

ionic groups may approach those of an ideal tracer, particularly dilute concentrations of certain anions.

In most situations, anions (negatively charged ions) are not affected by the aquifer medium. Mattson (1929), however, showed that the capacity of clay minerals for holding anions increases with decreasing pH. Under conditions of low pH, anions in the presence of clay, other minerals, or organic detritus may undergo anion exchange. Other possible effects include anion exclusion and precipitation/dissolution reactions. Cations (positively charged ions) react much more frequently with clay minerals through the process of cation exchange, which displaces other cations such as sodium and calcium into solution. Because of their interaction with the aquifer media, little work has been done with cations. Natural variations in Ca and Mg concentrations, however, have been used to separate baseflow and stormflow components in a karst aquifer (Dreiss, 1989).

One advantage of simple ionic tracers is that they do not decompose and, therefore, are not lost from the system. However, a large number of ions (including Cl⁻ and NO₃⁻) have high natural background concentrations; thus requiring the injection of a highly concentrated tracer. More importantly, several hundred pounds of chloride or nitrate may have an adverse effect on water quality and biota, thus becoming a pollutant. This also may result in density separation and gravity segregation during the tracer test (Grisak and Pickens, 1980b). Density differences will alter flow patterns, the degree of ion exchange, and secondary chemical precipitation, all of which may change the aquifer permeability. Comparisons of tracer mobilities under laboratory and field conditions by Everts and others (1989) found bromide (Br⁻) to be only slightly less mobile than nitrate. The generally low background concentrations of bromide often make it the ion of choice when a conservative tracer is desired.

Various applications of ionic tracers have been described in the literature. Murray and others (1981) used lithium bromide (LiBr) in carbonate terrane to establish hydraulic connection between a landfill and a freshwater spring, where use of Rhodamine WT dye tracer proved inappropriate. Mather and others (1969) used sodium chloride (NaCl) to investigate the influence of mining subsidence on the pattern of ground-water flow. Tennyson and Settergren (1980) used bromide (Br⁻) to evaluate pathways and transit time of recharge through soil at a proposed sewage effluent irrigation site. Schmotzer and others (1973) used post-sampling neutron activation to detect a Br⁻ tracer. Chloride (Cl⁻) and calcium (Ca⁺) were used by Grisak and Pickens (1980b) to study solute transport mechanisms in fractures. Potassium (K⁺) was used to determine

leachate migration and the extent of dilution by receiving waters located by a waste disposal site (Ellis, 1980).

Non-ionic organic compounds that are not dyes (see below) have received little attention as injected tracers. The ubiquitousness of trace levels of organic contaminants such as methylene chloride creates some problems in evaluating the integrity of clay liners at waste disposal sites. Ilgenfritz and others (1988) have suggested using fluorobenzene as a field monitoring tracer because it would not be likely to occur in normal industrial and commercial activities.

Dyes

Dyes are relatively inexpensive, simple to use, and effective. Either fluorescent or nonfluorescent dyes may be useful in studies of water movement in soil if the soil material that has absorbed the dye is excavated and visually inspected. Fluorescent dyes are preferable to nonfluorescent varieties in ground-water tracer studies because they are easier to detect. Dole (1906) was the first recommended use of dyes to study ground water in the United States by reporting the results of fluorescein and other dyes used in France beginning around 1882. Stiles and others (1927) conducted early experiments using uranine (fluorescein) to demonstrate pollution of wells in a sandy aquifer, and Meinzer (1932) described use of fluorescein as a ground-water tracer. However, extensive use of fluorescent dyes for ground-water tracing did not begin until after 1960. Quinlan (1986) provides a concise, but comprehensive, guide to the literature on dye tracing.

The advantages of using fluorescent dyes include very high detectability, rapid field analysis, and relatively low cost and low toxicity. Smart and Laidlaw (1977) classified commonly used fluorescent dyes by color: orange (Rhodamine B, Rhodamine WT, and Sulforhodamine B); green (fluorescein, Lissamine FF, and pyranine); and blue—also called optical brighteners. Aley and others (in press) classify dyes according to the detector (also called bug) used to recover them: dyes recovered on cotton include optical brighteners (such as Tinopal 5BM GX, and Phorwhite BBH) and Direct Yellow 96; and dyes recovered on activated charcoal (fluorescein and Rhodamine WT).

The literature on fluorescent dye use is plagued by a lack of consistency in dye nomenclature (Quinlan, 1986). The standard reference to dyes is the Colour Index (CI) (SDC & AATCC, 1971-1982). Most dyes are classified according to the CI generic name (related to method of dyeing) and chemical structure (the CI constitution number). Abrahart (1968, pp. 15-43) provides a concise guide to dye nomenclature. Dyes also are classified according to their use in foods, drugs and cosmetics

(Marmion, 1984). There are numerous commercial names for most dyes. Consequently reported results of dye tracing experiments should always specify (1) the CI generic name or CI constitution number, and (2) the manufacturer and the manufacturer's commercial name. The full name of the dye should be mentioned at least once to distinguish it from other dyes with the same or similar names. For example, in 1985, four structurally different kinds of Rhodamine were sold in the United States under 11 different names by five manufacturers, and there are more than 180 kinds of Direct Yellow dye (Quinlan, 1986).

The first part of the commercial name of a dye should not be confused with the dye itself. For example, Tinopal and Phorwhite are trade names used for whole series of chemically unrelated dyes made by a single company and should be capitalized. Seven chemically different Tinopals and 20 different Phorwhites are currently sold in the United States as optical brighteners (Aley and others, in press).

A particularly confusing point of dye nomenclature is that there are two fluorescein dyes with the same CI name and number, although they do have different (Drug and Cosmetic) D&C designations: fluorescein (C20H12O5)—D&C Yellow 7—and fluorescein sodium (C20H12O5Na2)—D&C Yellow 8. Only D&C Yellow 8 is soluble in water and, therefore, suitable for groundwater tracing. In the American and British literature this is referred to as fluorescein, whereas in the European literature it is called uranine (Quinlan, 1986).

Although fluorescent dyes exhibit many of the properties of an ideal tracer, a number of factors interfere with concentration measurement. Fluorescence is used to measure dye concentration, but the amount of fluorescence may vary with suspended sediment load, temperature, pH, CaCO₃ content, salinity, etc. Other variables that affect tracer test results are "quenching" (some emitted fluorescent light is reabsorbed by other molecules), adsorption, and photochemical and biological decay. A disadvantage of fluorescent dyes in tropical climates is poor performance because of chemical reactions with dissolved carbon dioxide (Smart and Smith, 1976).

Fluorescence intensity is inversely proportional to temperature. Smart and Laidlaw (1977) described the numerical relationship and provided temperature correction curves. Low pH tends to reduce fluorescence. Figure 4-5 shows that the fluorescence of Rhodamine WT decreases rapidly at increasingly acidic pHs below about 6.0. An increase in the suspended sediment concentration also generally causes a decrease in fluorescence.

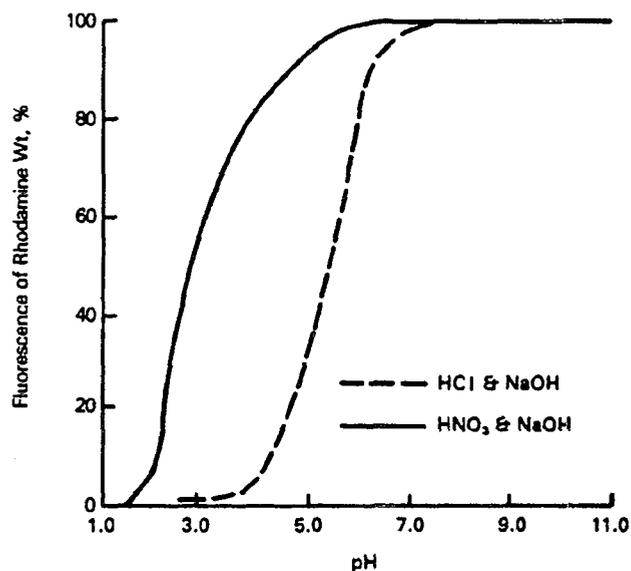


Figure 4-5. The Effect of pH on Rhodamine WT (adapted from Smart and Laidlaw, 1977)

Dyes travel slower than water due to adsorption, and are generally not as conservative as radioactive tracers or some of the ionic tracers. Adsorption can occur on organic matter, clays (bentonite, kaolinite, etc.), sandstone, limestone, plants, plankton, and even glass sample bottles. However, the detected fluorescence may decrease or actually increase due to adsorption. Adsorption on kaolinite caused a decrease in the measured fluorescence of several dyes, as measured by Smart and Laidlaw (1977). If dye is adsorbed onto suspended solids, and the fluorescence measurements are taken without separating the water samples from the sediment, the dye concentration is a measure of sediment content rather than water flow.

These possible adsorption effects are a strong incentive to choose a dye that is nonsorptive for the type of medium tested. Different dyes vary greatly in amount of sorption on specific materials. For example, Repogle and others (1966) measured sorption of three orange dyes on bentonite clay with the following results: Rhodamine WT, 28%; Rhodamine B, 65%; and Sulforhodamine B, 96%.

In a review of the toxicity of 12 fluorescent dyes Smart (1984) identified only three tracers (Tinopal CBS-X, Fluorescein, and Rhodamine WT) with no demonstrated carcinogenic or mutagenic hazard. Use of Rhodamine B was not recommended because it is a known

carcinogen. Use of the other dyes was considered acceptable provided normal precautions are observed during dye handling. Aulenbach and others (1978) concluded that Rhodamine B should not be used as a ground-water tracer simply on the basis of sorption losses.

Currently, the U.S. Geological Survey has a policy of limiting the maximum concentration of fluorescent dyes at water-user withdrawal points to 0.01 ppm (Hubbard and others, 1982). This is a conservative, non-obligatory limit, and Field and others (1990) recommend that tracer concentrations not exceed 1 ppm for a period in excess of 24 hours in ground water. Dyes should probably not be used where water supplies are chlorinated because dye molecules may react with chlorine to form chlorophenols (Smart and Laidlaw, 1977). Field and others (1990) recommend careful evaluation of a tracer before use in a sensitive or unique ecosystem.

General references on fluorescent dye use are three U.S. Geological Survey publications (Hubbard and others, 1982; Kilpatrick and Cobb, 1985; Wilson and others, 1986), reviews by Smart and Laidlaw (1977) and Jones (1984), and two reports prepared for EPA (Mull, 1988; Quinlan, 1989). Aley and Fletcher (1976) remains a classic but outdated text on practical aspects of dye tracing; it will be replaced by *The Joy of Dyeing* (Aley and others, in press) when that compendium is published.

Fluorescein, also known as uranine, sodium fluorescein, and other names, has been one of the most widely used green dyes. Like all green dyes, its use is commonly complicated by high natural background fluorescence, which lowers sensitivity of analyses and makes interpretation of results more difficult. Feuerstein and Selleck (1963) recommend that fluorescein be restricted to short-term studies of only the highest quality water.

Lewis and others (1966) used fluorescein in a fractured rock study. Mather and others (1969) recorded its use in a mining subsidence investigation in South Wales. Tester and others (1982) used fluorescein to determine fracture volumes and diagnose flow behavior in a fractured granitic geothermal reservoir. They found no measurable adsorption or decomposition of the dye during the 24-hr exposures to rocks at 392°F. At the other extreme, Rahe and others (1978) did not recover any injected dye in their hillslope studies, even at a distance of 2.5 m downslope from the injection point. The same experiment used bacterial tracers successfully.

Another green fluorescent dye, pyranine, has a stronger

fluorescent signal than does fluorescein, but is much more expensive. It has been used in several soil studies. Reynolds (1966) found pyranine to be the most stable dye for use in an acidic, sandy soil. Drew and Smith (1969) stated that pyranine is not as easily detectable as fluorescein, but is more resistant to decoloration and adsorption. Pyranine has a very high photochemical decay rate, and is strongly affected by pH in the range found in most natural waters (McLaughlin, 1982).

Rhodamine WT has been considered one of the most useful tracers for quantitative studies, based on minimum detectability, photochemical and biological decay rates, and adsorption (Knuttsen, 1968; Smart and Laidlaw, 1977; Wilson and others, 1986). Rhodamine WT is the most conservative dye available for stream tracing (Hubbard and others, 1982). Fluorescein is the most common dye used for tracing ground water in karst.

Aulenbach and others (1978) compared Rhodamine B, Rhodamine WT, and tritium as tracers in effluent from a sewage treatment plant that was applied to natural delta sand beds. The Rhodamine B was highly adsorbed, while the Rhodamine WT and tritium yielded similar breakthrough curves. Aulenbach and Clesceri (1980) found Rhodamine WT very successful in a sandy medium. Gann and Harvey (1975) used Rhodamine WT for karst tracing in a limestone and dolomite system in Missouri.

Rhodamine B and Sulforhodamine B are poor tracers for use in ground water and most surface waters; it could be said the "B" stands for "bad." Amidorhodamine G is a significantly better tracer; similarly, it can be said that the "G" stands for "good" (personal communication, James Quinlan, ATEC Environmental Consultants, Nashville, TN, July, 1990).

Blue fluorescent dyes, or optical brighteners, have been used in increasing amounts in the past decade in textiles, paper, and other materials to enhance their white appearance. Water that has been contaminated by domestic waste entering septic tank soil absorption fields can be used as a "natural" tracer if it contains detectable amounts of the brighteners. Glover (1972) was the first to describe the use of optical brighteners as tracers in karst environments. Since then, they have been extensively used in the United States (Quinlan, 1986). The tracer Amino G acid is a dye intermediate used in the manufacture of dyes that is sometimes mistakenly classified as an optical brightener (Quinlan, 1986). Amino G acid is now recognized as a carcinogenic and should not be used in water that might be used for drinking (personal communication, James Quinlan, ATEC Environmental Consultants, Nashville, TN, July,

1990). Smart and Laidlaw (1977) provide detailed information on the characteristics of the optical brightener Photine CU and Amino G acid.

Gases

Numerous natural and artificially produced gases have been found in ground water. Some of the naturally produced gases can be used as tracers, and gas also can be injected into ground water where it dissolves and can be used as a tracer. Only a few examples of gases being used as ground-water tracers are found in the literature, however. Table 4-4 lists possible gases to use in hydrogeologic studies. Gases are useful tracers in the saturated zone. They are less reliable in the unsaturated zone because bleeding into the atmosphere can give falsely negative results.

Inert Natural Gases. Because of their nonreactive and nontoxic nature, noble gases are potentially useful tracers. Helium is used widely as a tracer in industrial processes. Carter and others (1959) studied the feasibility of using helium as a tracer in ground water and found that it traveled at a slightly lower velocity than chloride. Advantages of using helium as a tracer are its (1) safety, (2) low cost, (3) relative ease of analysis, (4) low concentrations required, and (5) chemical inertness. Disadvantages identified by Carter and others (1959) include (1) relatively large errors in analysis, (2) difficulties in maintaining a constant recharge rate, (3) time required to develop equilibrium in unconfined aquifers, and (4) possible loss to the atmosphere in unconfined aquifers.

Neon, krypton, and xenon are other possible candidates for injected tracers because their natural concentrations are very low (Table 4-4). Although the gases do not undergo chemical reactions and do not participate in ion exchange, the heavier noble gases (krypton and xenon) do sorb to some extent on clay and organic material. The solubility of the noble gases decreases with increases in temperature. Therefore, the natural concentrations of these gases in ground water are an indication of surface temperatures at the time of water infiltration. This property has been used to reconstruct palaeoclimatic trends in a sandstone aquifer in England using argon and krypton for age estimates (Andrews and Lee, 1979). Sugisaki (1969) and Mazor (1972) also have used natural inert gases in this way.

Anthropogenic Gases. Numerous artificial gases have been manufactured during the past decade, and several of them have been released in sufficient volumes to produce measurable concentrations in the atmosphere on a worldwide scale. One of the most interesting groups of these gases is the fluorocarbons. These gases generally pose a very low biological hazard, are generally stable for periods measured in years, do not react chemically with other materials, can be detected in very low concentrations, and sorb only slightly on most minerals. They do sorb strongly, however, on organic matter.

Fluorocarbons have two primary applications. First, because large amounts of fluorocarbons were not

	Approximate Natural Background Assuming Equilibrium with Atmosphere at 20°C (mg gas/L water)	Maximum Amount in Solution Assuming 100% Gas at Pressure of 1 atm at 20°C (mg gas/L water)
Argon	0.57	60.6
Neon	1.7×10^{-4}	9.5
Helium	8.2×10^{-6}	1.5
Krypton	2.7×10^{-4}	234
Xenon	5.7×10^{-5}	658
Carbon monoxide	6.0×10^{-6}	28
Nitrous oxide	3.3×10^{-4}	1,100

Source: Davis and others (1985)

Table 4-4. Gases of Potential Use as Tracers

released into the atmosphere until the later 1940s and early 1950s, the presence of fluorocarbons in ground water indicates that the water was in contact with the atmosphere within the past 30 to 40 years (Thompson and Hayes, 1979). The second application of fluorocarbon compounds is as injected tracers (Thompson and others, 1974). Because detection limits are so low, large volumes of water can be labeled with the tracers at a rather modest cost. Despite the problem of sorption on natural material and especially on organics, initial tests have been quite encouraging.

Isotopes

An isotope is any of two or more forms of the same element having the same atomic number and nearly the same chemical properties but with different atomic

weights and different numbers of neutrons in the nuclei. Isotopes may be stable (they do not emit radiation) or radioactive (they emit alpha, beta, and/or gamma rays). There are over 280 isotopic forms of stable elements and 40 or so radioactive isotopes (Glasstone, 1967). A wide variety of stable and radioactive isotopes have been used in ground-water tracer studies. There is an extensive literature on the use of isotopes in ground-water investigations; Table 4-5 lists 15 general sources of information. Isotopes have been used mainly in porous media to study regional ground-water flow regimes and measure aquifer parameters. Back and Zoetl (1975) and LaMoreaux and others (1984) review use of isotopes in karst hydrologic systems. Lack of familiarity with techniques to analyze environmental isotopes has limited their use by practicing field

Reference	Description
Back and Cherry (1976)	Contains a brief review of use of environmental isotopes in ground-water studies.
Csallany (1966)	Early review paper on use of radioisotopes in water resources research.
Davis and Bentley (1982)	Review paper on ground-water dating techniques.
Ferronsky and Polyakov (1982)	Text on use of environmental isotopes in the study of water.
Fritz and Fontes (1980, 1986)	Handbook on environmental isotope geochemistry (two volumes).
Gaspar and Oncescu (1972)	Text on use of radioactive tracers in hydrology (14 chapters).
IAEA (1963)	Symposium on radioisotopes in hydrology.
IAEA (1966)	Symposium on isotopes in hydrology with 21 papers on subsurface hydrology.
IAEA (1967)	Symposium on radioisotope tracers in industry and geophysics contains a number of papers related to ground-water applications.
IAEA (1970)	Symposium on isotopes in hydrology with 25 papers on subsurface hydrology.
IAEA (1974)	Symposium on isotopes in ground-water hydrology with 51 papers.
IAEA (1978)	Symposium on isotopes in hydrology with 41 papers on subsurface hydrology.
Moser and Rauert (1985)	Review paper on use of environmental isotopes for determining ground-water movement.
Wiebenga and others (1967)	Review paper on use of radioisotopes in ground-water tracing.

Table 4-5. Sources of Information on Uses of Isotopes in Ground-Water Tracing

hydrogeologists ground-water contamination studies. Hendry (1988) recommends the use of hydrogen and oxygen isotopes as a relatively inexpensive way to estimate the age of near-surface ground-water samples.

Stable Isotopes. Stable isotopes are rarely used for artificially injected tracer studies in the field because (1) it is difficult to detect small artificial variations of most isotopes against the natural background, (2) their analysis is costly, and (3) preparing isotopically enriched tracers is expensive. The average stable isotope composition of deuterium (^2H) and ^{18}O in precipitation changes with elevation, latitude, distance from the coast, and temperature. Consequently, measurement of these isotopes in ground water can be used to trace the large-scale movement of ground water and to locate areas of recharge (Gat, 1971; Ferronsky and Polyakov, 1982).

The two abundant isotopes of nitrogen (^{14}N and ^{15}N) can vary significantly in nature. Ammonia (NH_3) escaping as vapor from decomposing animal wastes, for example, will tend to remove the lighter (^{14}N) nitrogen and will leave behind a residue rich in heavy nitrogen. In contrast, many fertilizers with an ammonia base will be isotopically light. Natural soil nitrate will be somewhat between these two extremes. As a consequence, nitrogen isotopes have been used to determine the origin of unusually high amounts of nitrate in ground water. Also, the presence of more than about 5 mg/L of nitrate is commonly an indirect indication of contamination from chemical fertilizers and sewage.

The stable sulfur isotopes (^{32}S , ^{34}S , and ^{36}S) have been used to distinguish between sulfate originating

from natural dissolution of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and sulfate originating from an industrial spill of sulfuric acid (H_2SO_4).

Two stable isotopes of carbon (^{12}C and ^{13}C) and one radioisotope (^{14}C) are used in hydrogeologic studies. Although not as commonly studied as ^{14}C , the ratio of the stable isotopes, $^{13}\text{C}/^{12}\text{C}$, is potentially useful in sorting out the origins of certain contaminants found in water. For example, methane (CH_4) originating from some deep geologic deposits is isotopically heavier than methane originating from near-surface sources. This contrast forms the basis for identifying aquifers contaminated with methane from pipelines and from subsurface storage tanks.

Isotopes of other elements such as chlorine, strontium, and boron are used to determine regional directions of ground-water flow rather than to identify sources of contamination.

Radionuclides. Radioactive isotopes of various elements are collectively referred to as radionuclides. In the early 1950s there was great enthusiasm for using radionuclides both as natural "environmental" tracers and as injected artificial tracers. The use of artificially injected radionuclides has all but ceased in many countries, including the United States, however, because of concerns about possible adverse health effects (Davis and others, 1985). Artificially introduced radioactive tracing mostly is confined to carefully controlled laboratory experiments or to deep petroleum production zones that are devoid of potable water. Table 4-6 lists eight radionuclides commonly used as injected tracers, their half-lives, and the chemical form in which they are typically used.

Radionuclide	Half-Life y = year d = day h = hour	Chemical Compound
^2H	12.3y	H_2O
^{32}P	14.3d	H_2HPO_4
^{51}Cr	27.8d	EDTA-Cr and CrCl_3
^{60}Co	.25y	EDTA-Co and $\text{K}_3\text{Co}(\text{CN})_6$
^{82}Br	33.4h	NH_4Br , NaBr, LiBr
^{85}Kr	10.7y	Kr (gas)
^{131}I	8.1d	I and KI
^{98}Au	2.7d	AuCl_3

Source: Davis and others (1985)

Table 4-6. Commonly Used Radioactive Tracers for Ground-Water Studies

The use of natural environmental tracers has expanded so that they are now a major component of many hydrochemical studies. A number of radionuclides are present in the atmosphere from natural and artificial sources, and many of these are carried into the subsurface by rain water. The most common hydrogeologic use of these radionuclides is to estimate the average length of time ground water has been isolated from the atmosphere. This measurement is complicated by dispersion in the aquifer and mixing in wells that sample several hydrologic zones. Nevertheless, the age of water in an aquifer usually can be established as being older than some given limiting value. For example, detection of atmospheric radionuclides might indicate that ground water was recharged more than 1,000 years ago or that, in another region, all the ground water in a given shallow aquifer is younger than 30 years.

Since the 1950s, atmospheric tritium, the radioactive isotope of hydrogen (^3H) with a half life of 12.3 years, has been dominated by tritium from the detonation of thermonuclear devices. Thermonuclear explosions increased the concentration of tritium in local rainfall to more than 1,000 tritium units (TU) in the northern hemisphere by the early 1960s (Figure 4-6). As a result, ground water in the northern hemisphere with more than about 5 TU is generally less than 30 years old. Very small amounts of tritium, 0.05 to 0.5 TU, can be produced by natural subsurface processes, so the presence of these low levels does not necessarily indicate a recent age.

The radioactive isotope of carbon, ^{14}C (with a half-life of 5,730 years), is also widely studied in ground water. In practice, the use of ^{14}C is rarely simple. Sources of old carbon, primarily from limestone and dolomite, will dilute the sample, and a number of processes, such as the formation of CH_4 gas or the precipitation of carbonate minerals, will fractionate the isotopes and alter the apparent age. Interpreting ^{14}C "ages" of water is so complex that it should be attempted only by hydrochemists specializing in isotope hydrology. Despite the complicated nature of ^{14}C studies, they are highly useful in determining the approximate residence time of old water (500 to 30,000 years) in aquifers. In certain circumstances, this information cannot be obtained in any other way.

Inert Radioactive Gases. Chemically inert but radioactive ^{133}Xe and ^{85}Kr appear to be suitable for many injected tracer applications (Robertson, 1969; Wagner, 1977), provided legal restrictions can be overcome. ^{222}Rn , one of the daughter products from the spontaneous fission of ^{238}U , is the most abundant of the natural inert radioactive gases. Radon is present

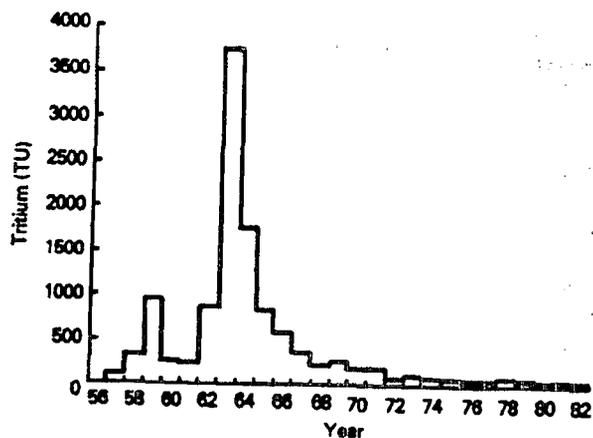


Figure 4-6. Average Annual Tritium Concentration of Rainfall and Snow for Arizona, Colorado, New Mexico, and Utah (from Davis and others, 1985, after Vuataz and others, 1984)

in the subsurface, but owing to the short half-life (3.8 d) of ^{222}Rn , and the absence of parent uranium nuclides in the atmosphere, radon is virtually absent in surface water that has reached equilibrium with the atmosphere. Surveys of radon in surface streams and lakes have, therefore, been useful in detecting locations where ground water enters surface waters (Rogers, 1958). Hoehn and von Gunten (1989) measured dilution of radon in ground water to assess infiltration from surface waters to an aquifer.

Tracer Tests in Karst

Probably no hydrogeologic system has been more extensively studied by a more diverse group of people with such a plethora of tracing techniques as karst limestone terranes. Geese (Aley and Fletcher, 1976), tagged eels (Bögli, 1980), computer punch-card confetti (Davis and others, 1985), and time bombs (Arandjelovich, 1969) are among the more exotic tracers that have been used in karst.

There is an extensive international literature on karst tracing. Table 4-7 describes 18 major sources of general information on this topic. There is a substantial English-language literature in American caving journals, such as Cave Notes/Caves and Karst (which ceased publication in 1973), Missouri Speleology, and the National Speleological Society Bulletin, and similar British periodicals, such as Transactions of the Cave Research Group (now Cave Science), and the Proceedings of the University of Bristol Speleological Society. The international symposia on underground

water tracing (SUWT— see Table 4-7) provide the best systematic compilations of international research on this topic. Probably the easiest way to monitor the international literature on dye-tracing in karst terranes and other karst and speleological literature is the annual Speleological Abstracts published by the Union Internationale de Spèléologie in Switzerland.

Table 4-8 summarizes information on the most commonly used water tracers in North American karst studies. Dyes are almost ideal tracers because the adsorption is usually not a problem in karst hydrogeologic systems. Smart (1985) lists four applications of

fluorescent dye tracers in evaluating existing or potential contamination in carbonate rocks: (1) confirmation of leachate contamination, (2) determination of on site hydrology, (3) determination of hydraulic properties of landfill materials, and (4) prediction of leachate contamination and dilution.

Fluorescein, Rhodamine WT, optical brighteners (Tinopal 5BM GX), and Direct Yellow 96 are the most commonly used dyes. The amount of dye injected depends on whether qualitative or quantitative analysis is planned. Qualitative tests involve simple visual detection of dye in flowing water or captured by a

Reference	Description
Aley and Fletcher (1976)	Classic guide to use of tracers in karst. Should be replaced by Aley et al. (in press) when it is published.
Aley and others (in press)	Compendium of techniques for ground-water tracing focusing on karst terranes.
Back and Zoetl (1975)	Review of the use of geochemical, isotopic, dye, spore, and artificial radioisotopes as tracers in karst systems.
Bögli (1980)	Pages 138-143 review use of tracers in karst hydrology.
Brown (1972)	Chapter III reviews tracer methods in karst hydrologic systems.
Gospodaric and Habic (1976)	Pages 217-230 contain reviews of the applicability of dyes, salts, radionuclides, drifting materials, and other tracers in karst.
Gunn (1982)	Review paper on karst water tracing in Ireland.
Jones (1984)	Review paper on use of dye tracers in karst.
LaMoreaux and others	Pages 196-210 of the 1984 annotated bibliography focus (1984, 1989) on isotope techniques for water tracing in carbonate rocks. The 1989 annotated bibliography contains a section reviewing pollution assessment in carbonate terranes.
Milanovia (1981)	Pages 263-309 focus on karst water tracing.
Mull and others (1988)	EPA report on dye-tracing techniques in karst terranes.
Quinlan (1989)	EPA report with recommended dye-tracing protocols for ground-water tracing in karst terranes.
Sweeting (1973)	Pages 218-251 focus on karst water and karst water tracing.
SUWT (1966, 1970, 1976, 1981, and 1986)	Publications related to the various international symposia on underground water tracing (SUWT) contain numerous papers on ground-water tracing techniques, mostly focusing on karst.
Thrailkill and others (1983)	Report focusing on karst dye-tracing techniques.

Table 4-7. Sources of Information on Ground-Water Tracing in Karst Systems

Tracer & Color	Passive Detector	Test (elutriant)	Maximum Excitation & Emission nm	Detectable Conc.	Advantages	Disadvantages	Remarks
Fluorescein Sodium $C_{20}H_{12}Na_2O_5$ Yellow-Green Xanthone	Activated coconut charcoal 6-14 mesh	Ethyl alcohol and 5% KOH. Visual test or fluorometer & 2A-47B; 2A-12, 65A filters	485 515	0.1 µg/l Dependent on background levels. "Controls" must be used to determine background	1) Does not require constant monitoring or any special equipment. 2) Inexpensive.	1) Dye is photochemically unstable. 2) Moderate sorption on clay. 3) pH sensitive.	This is the most popular method used in the USA. Carbon detectors first suggested by Dunn, 1957.
Rhodamine WT $C_{28}H_{30}N_2O_6Cl$ Red-Purple Xanthone	Activated coconut charcoal 6-14 mesh	Ethyl alcohol or 1-Propanol + NH ₄ OH. Solution tested using fluorometer and 546-590 filters.	550 580	.01 µg/l. Dependent on background levels and fluctuation.	1) Dye is photochemically stable. 2) Dye may be used in low pH waters.	1) Requires the use of a fluorometer. 2) Moderate clay sorption.	Rhodamine has been used extensively in Canada & USA. This is not a suitable method for amateurs without access to a fluorometer.
<i>Lycopodium</i> Spores <i>Lycopodium Calvitum</i>	Plankton netting nylon-25 micron	Spores & sediment are washed from the nets. Microscopic examination is used to identify spores.	N/A	Dependent on background levels. Several kilograms of spores are usually used.	1) Several simultaneous tests may be conducted using different colored spores 2) No coloring of water occurs.	1) Spores may be prematurely filtered out. 2) Field collection system elaborate. 3) System is generally more expensive.	1) Spores have not been used in North America.
Optical Brighteners Colorless normal light	Unbleached cotton	Visual examination of detectors under UV light or 7-37; 2A + 47B Filters.	360 435	Dependent on background levels, but generally at least .1 µg/l.	1) Inexpensive. 2) No coloring of water occurs	1) Background readings may be excessively high. 2) Adsorbed onto organics.	May be used simultaneously with a green & red dye using fluorometric separation.
Direct Yellow (DY 96) Low Visibility Stilbene derivative	Unbleached cotton	Visual examination of detectors under UV light or 7-37; 2A + 47B Filters	N/A	1.0 µg/l on cotton, and with fluorometric analysis.	1) Little natural background. 2) Good stability and low sorption. 3) No coloring of water.	1) Moderate cost. 2) Sensitive to pH.	Has been used extensively in Kentucky.
Salt NaCl Colorless	Recording specific conductance meter or regular sampling	Either a direct test for an increase in chloride, or a substantial increase in specific conductance	N/A	Dependent on background levels. Several hundred kilograms may be needed for larger tests.	1) Generally considered safe for use on public water systems. 2) Useful where fluorescent background conditions exclude other methods	1) Large quantities usually needed. 2) Background specific conductance is often high.	Salt is occasionally used by the US Geological Survey for tests dealing with public water supplies.

¹ G.K. Turner Filters for Turner 111 Filter Fluorometer.

² Dye is usually most visible in clear water, deep pools, and in bright sunlight. These figures are not exact.

³ Very dilute dye solutions may be concentrated upon the detector over a period of time.

Source: Jones, 1984.

Table 4-8. Evaluation of Principal Water Tracers Used in North American Karst Studies

detector (see discussion below). Semi-quantitative results can be obtained by using a fluorometer or spectrofluorometer to detect amounts of dye captured by detectors such as activated charcoal that may not be discernible to the eye. Interpretation of values from such measurements is limited due to lack of precise information on the variation in ground water flow and dye concentration between collection of detectors. Quantitative tests involve precise measurement of dye concentrations in grab samples of water. If the exact

amount of injected dye is known, and flow measurements are taken along with each sample, a mass-balance analysis allows estimation of how much dye has been distributed through different parts of the subsurface flow system.

In qualitative tests, enough dye must be injected for visual detection; quantitative tests using a fluorometer or spectrofluorometer generally require one-tenth to one hundredth as much dye. Determination of the

correct quantity to inject is as much an art as a science, and this should be determined by, or with the assistance of, someone with experience in karst tracer tests.

Dye is recovered with detectors called bugs (cotton or activated charcoal, depending on the tracer), that are typically suspended in streams and springs on hydrodynamically stable stands called gumdrops. Detectors are placed at springs or in streams where flow from the point of injection is suspected of reaching the surface. At chosen time intervals related to the distance from the source of injection, detectors are collected and replaced with fresh detectors. Detectors are usually collected frequently during the first few days after injection to pinpoint the most rapid dye arrival time, and then typically on a daily basis for several weeks. Background tests always must be run before injection, especially with optical brighteners because sewage effluent from individual septic tank absorption fields may increase background levels substantially.

Qualitative tracer tests in which two dyes are injected into two different locations are readily done by combining a fluorescent dye and an optical brightener, which use different detectors. Quantitative techniques are available (developed originally in Europe) for separating mixtures of fluorescent dyes (Quinlan, 1986). A 5-dye tracer test has recently been conducted using these techniques (personal communication, James Quinlan, January 1990). Perhaps the most comprehensive karst tracing experiments in a single location were carried out in Slovenia, Yugoslavia, in the early 1970s where five dyes, lycopodium spores, lithium chloride, potassium chloride, chromium-51, and detergents all were used (Gospodaric and Habic, 1976).

Reports prepared for EPA by Mull and others (1988) and Quinlan (1989) are the most comprehensive references currently available on procedures for dye-tracing in karst terranes. Aley and others (in press) should be obtained when it becomes available. Smoot and others (1987), and Smart (1988a) describe quantitative dye-tracing techniques in karst, and Smart (1988b) describes an approach to the structural interpretation of ground-water tracers in karst terrane.

Tracer Tests in Porous Media

Tracer tests in porous media are used primarily to characterize aquifer parameters such as regional velocity (Leap, 1985), hydraulic conductivity distributions (Molz and others, 1988), anisotropy (Kenoyer, 1988), dispersivity (Bumb and others, 1985), and distribution coefficient or retardation (Pickens and others, 1981; Rainwater and others, 1987). Smart and others (1988) have prepared an annotated bibliography on ground-

water tracing that focuses on use of tracers in porous media.

The purpose and practical constraints of a tracer test must be clearly understood prior to actual planning. Following are a few of the questions that need to be addressed:

- * Is only the direction of water flow to be determined?
- * Are other parameters such as travel time, porosity, and hydraulic conductivity of interest?
- * How much time is available for the test?
- * How much money is available for the test?

If results must be obtained within a few weeks, then certain kinds of tracer tests would normally be out of the question. Those using only the natural hydraulic gradient between two wells that are more than about 20 m apart typically require long time periods for the tracer to flow between the wells. Another primary consideration is budget. Costs for tests that involve drilling several deep holes, setting packers to control sampling or injection, and analyzing hundreds of samples in an EPA-certified laboratory could easily exceed \$1 million. In contrast, some short-term tracer tests may cost less than \$1,000.

Choice of a tracer will depend partially on which analytical techniques are easily available and which background constituents might interfere with these analyses. The chemist or technician who will analyze the samples can advise whether background constituents might interfere with the analytical techniques to be used. Bacteria, isotopes, and ions are the most frequently used types of tracers in porous media. Fluorescent dyes are less commonly used as tracers because they tend to adsorb. A more common use of dyes in porous media is to locate zones of preferential flow in the vadose zone. In this application, adsorption on soil particles is desirable because it allows visual inspection of flow patterns when the soil is excavated.

Estimating the Amount of Tracer to Inject

The amount of tracer to inject is based on the natural background concentrations, the detection limit for the tracer, the dilution expected, and experience. Adsorption, ion exchange, and dispersion will decrease the amount of tracer arriving at the observation well, but recovery of the injected mass is usually not less than 20 percent for two-hole tests using a forced recirculation system and conservative tracers. The concentration should not be increased so much that density effects become a problem. Lenda and Zuber (1970) presented graphs that can be used to estimate the approximate

quantity of tracer needed. These values are based on estimates of the porosity and dispersion coefficient of the aquifer.

Single-Well Techniques

Two techniques, injection/withdrawal and borehole dilution, produce parameter values from a single well that are valid at a local scale. Advantages of single-well techniques are:

- * Less tracer is required than for two-well tests.
- * The assumption of radial flow is generally valid, so natural aquifer velocity can be ignored, making solutions easier.
- * Knowledge of the exact direction of flow is not necessary.

Molz and others (1985) describe design and performance of single-well tracer tests conducted at the Mobile site.

Injection/Withdrawal. The single-well injection/withdrawal (or pulse) technique can be used to obtain a pore velocity value and a longitudinal dispersion coefficient. The method assumes that porosity is known or can be estimated with reasonable accuracy. In this procedure, a given quantity of tracer is instantaneously added to the borehole, the tracer is mixed, and then two to three borehole volumes of freshwater are pumped in to force the tracer to penetrate the aquifer. Only a small quantity is injected so as not to disturb natural flow.

After a certain time, the borehole is pumped out at a constant rate large enough to overcome the natural ground-water flow. Tracer concentration is measured with time or pumped volume. If the concentration is measured at various depths with point samplers, the relative permeability of layers can be determined. The dispersion coefficient is obtained by matching experimental breakthrough curves with theoretical curves based on the general dispersion equation. A finite difference method is used to simulate the theoretical curves (Fried, 1975).

Fried concluded that this method is useful for local information (2-to 4-m radius) and for detecting the most permeable strata. A possible advantage of this test is that nearly all of the tracer is removed from the aquifer at the end of the test.

Borehole Dilution. This technique, also called point dilution, can be used to measure the magnitude and direction of horizontal tracer velocity and vertical flow

(Fried, 1975; Gaspar and Oncescu, 1972; Klotz and others, 1978).

The procedure introduces a known quantity of tracer instantaneously into the borehole, mixes it well, and then measures the concentration decrease with time. The tracer is generally introduced into an isolated volume of the borehole using packers. Radioactive tracers have been most commonly used for borehole dilution tests, but other tracers can be used.

Factors to consider when conducting a point dilution test include the homogeneity of the aquifer, effects of drilling (mudcake, etc.), homogeneity of the mixture of tracer and well water, degree of tracer diffusion, and density effects.

Ideally, the test should be conducted using a borehole with no screen or gravel pack. If a screen is used, it should be next to the borehole because dead space alters the results. Samples should be very small in volume so that flow is not disturbed by their removal.

A variant of the point dilution method allows measurement of the direction of ground-water flow. In this procedure, a section of the borehole is usually isolated by packers, and a tracer (often radioactive) is introduced slowly and without mixing. Then, after some time, a compartmental sampler (four to eight compartments) within the borehole is opened. The direction of minimum concentration corresponds to the flow direction. A similar method is to introduce a radioactive tracer and subsequently measure its adsorption on the borehole or well screen walls by means of a counting device in the hole. Gaspar and Oncescu (1972) describe the method in more detail.

Another common strategy is to inject and subsequently remove the water containing a conservative tracer from a single well. If injection is rapid and immediately followed by pumping to remove the tracer, then almost all of the injected conservative tracer can be recovered. If the pumping is delayed, the injected tracer will drift downgradient with the general flow of the ground water and the percentage of tracer recovery will decrease with time. Successive tests with increasingly longer delay times between injection and pumping can be used to estimate ground-water velocities in permeable aquifers with moderately large hydraulic gradients.

Two-Well Techniques

There are two basic approaches to using tracers with multiple wells: one measures tracer movement in uniform (natural) flow and the other measures movement

by radial (induced) flow. The parameters measured (dispersion coefficient and porosity) are assumed to be the same for both types of flow.

Uniform Flow. This approach involves placing a tracer in one well without disturbing the flow field, and sampling periodically to detect the tracer in observation wells. This test can be used at a local (2 to 5 m) or intermediate (5 to 100 m) scale, but it requires much more time than radial tests. If the direction and magnitude of the velocity are not known, a large number of observation wells are needed. Furthermore, local flow directions may diverge widely from directions predicted on the basis of widely spaced water wells. Failure to intercept a tracer in a well just a few meters away from the injection well is not uncommon under natural-gradient flow conditions.

The quantity of tracer needed to cover a large distance can be expensive. On a regional scale, environmental tracers, including seawater intrusion, radionuclides, or stable isotopes of hydrogen and oxygen, are used. Manmade pollution also has been used. For regional problems, a mathematical model is calibrated with concentration versus time curves from field data, and is used to predict future concentration distributions.

Local- or intermediate-scale uniform flow problems can be solved analytically, semianalytically, or by curve-matching. Layers of different permeability can cause distorted breakthrough curves, which can usually be analyzed using one- or two-dimensional models (Gaspar and Oncescu, 1972). Fried (1975) and Lenda and Zuber (1970) present analytical solutions.

Radial Flow. Radial flow techniques work by altering the flow field of an aquifer through pumping. Solutions are generally easier if radial flow velocity greatly exceeds uniform flow. This method yields values for porosity and the dispersion coefficient, but not natural ground-water velocity. Types of radial flow tests include diverging, converging, and recirculating tests.

A diverging test involves constant injection of water into an aquifer. The tracer is introduced into the injected water as a slug or continuous flow and the tracer is detected at an observation well that is not pumping. Point or integrated samples of small volume are carefully taken at the observation well so that flow is not disturbed. Packers can be used in the injection well to isolate an interval.

In a converging test, the tracer is introduced at an observation well, while another well is pumped. Concentrations are monitored at the pumped well. The

tracer often is injected between two packers or below one packer; then two to three well-bore volumes are injected to push the tracer out into the aquifer. At the pumping well, intervals of interest are isolated (particularly in fractured rock), or an integrated sample is obtained.

A recirculating test is similar to a converging test, but the pumped water is injected back into the injection well. This tests a significantly greater part of the formation because the wells inject to and pump from 360 degrees. The flow lines are longer, however, partially canceling out the advantage of a higher gradient. Sauty (1980) provides theoretical curves for recirculating tests.

Design and Construction of Test Wells

In many tracer tests, construction of the test wells is the single greatest expense. Procedures for the proper design and construction of monitoring wells for sampling ground-water quality (discussed in Chapter 3) apply equally to wells used for tracer tests.

Special considerations for designing and constructing test wells for tracer tests include:

- * Drilling muds and mud additives tend to have a high capacity for the sorption of most types of tracers and, therefore, should be avoided.
- * Drilling methods that alter the hydrologic characteristics of the aquifer being tested (such as clogging of pores) should be avoided.
- * Use of packers to isolate the zones being sampled from the rest of the water in the well (see Figure 4-2b) allows the most precise measurements of vertical variations in hydrologic parameters. This approach tends to be more expensive, takes longer, and requires more technical training than whole-well tests.
- * If packers are not used, the diameter of the sampling well should be as small as possible so that the amount of "dead" water in the well during sampling is minimized.
- * Well casing material should not be reactive with the tracer used.
- * Well-screen slot size and gravel pack must be selected and installed with special care when using single-well tests with alternating cycles of injection and pumping large volumes of water into and out of loose fine-grained sand. On the other hand, if the aquifer being tested contains a very permeable coarse gravel and the casing

diameter is small, then numerous holes drilled in the solid casing may be adequate.

- * As with any monitoring well, tracer test wells should be properly developed to remove silt, clay, drilling mud, and other materials that would prevent free movement of water in and out of the well.

Injection and Sample Collection

Choice of injection equipment depends on the depth of the borehole and the funds available. In very shallow holes, the tracer can be lowered through a tube, placed in an ampule that is lowered into the hole, and broken, or just poured in. Mixing of the tracer with the aquifer water is desirable and important for most types of tests and is simple for very shallow holes. For example, a plunger can be surged up and down in the hole or the tracer can be released through a pipe with many perforations. Flanges on the outer part of the pipe will mix the tracer as the pipe is raised and lowered. For deeper holes, tracers must be injected under pressure and equipment can be quite sophisticated.

Sample collection also can be simple or sophisticated. For tracing thermal pulses, only a thermistor needs to be lowered into the ground water. For chemical tracers, a variety of sampling methods may be used. Some special sampling considerations for tracer tests include:

- * Bailers should not be used if mixing of the tracer in the borehole is to be avoided.
- * Where purging is required, removal of more than the minimum required to obtain fresh aquifer water may create a gradient towards the well and distort the natural movement of the tracer.
- * Use of existing water wells that tap multiple aquifers should be generally avoided in tracer tests except to establish whether a hydrologic connection with the point of injection exists.

Interpretation of Results

This section provides a brief qualitative introduction to the interpretation of tracer test results. More extensive and quantitative treatments are found in the works of Halevy and Nir (1962), Theis (1963), Fried (1975), Saaty (1978), and Grisak and Pickens (1980a,b). Some more recent papers on analysis of tracer tests include Güven and others (1985, 1986), Molz and others (1986, 1987), and Bullivant and O'Sullivan (1989).

The basic plot of the concentration of a tracer as a function of time or water volume passed through the

system is called a breakthrough curve. The concentration either is plotted as the actual concentration (Figure 4-7) or, quite commonly, as the ratio of the measured tracer concentration at the sampling point, C , to the input tracer concentration, C_0 (Figure 4-8).

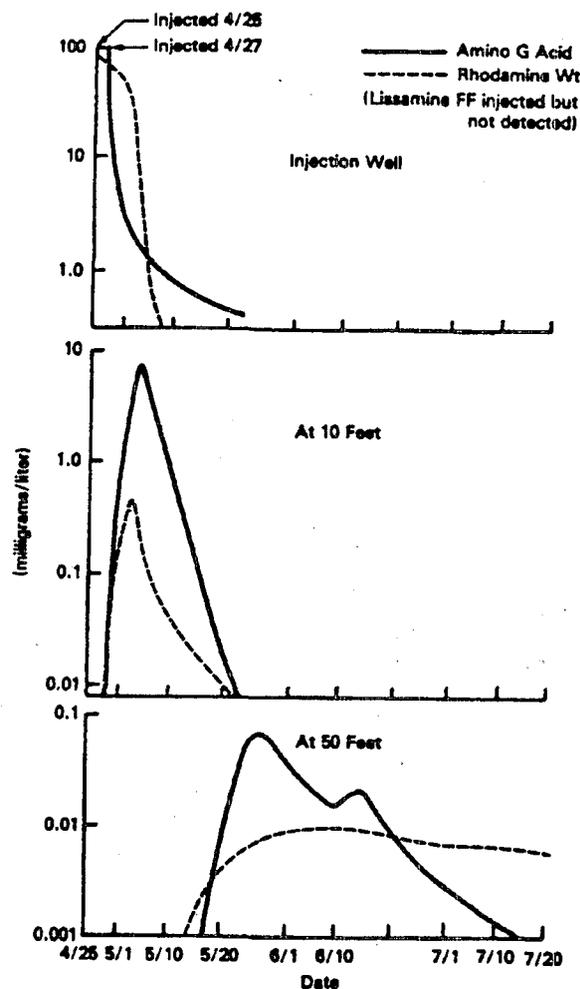
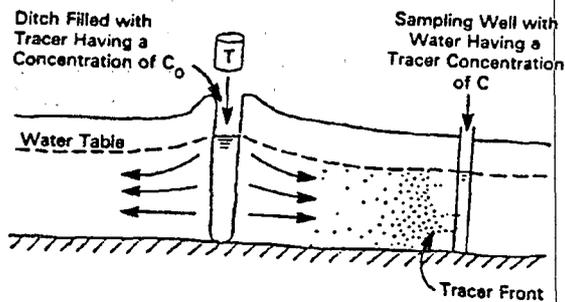
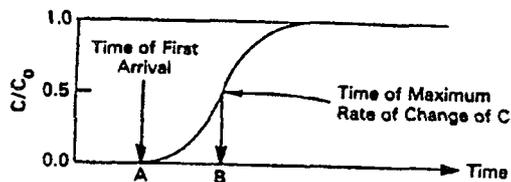


Figure 4-7. Results of Tracer Tests at the Sand Ridge State Forest, Illinois (from Naymik and Sievers, 1983)

The measured quantity that is fundamental for most tracer tests is the first arrival time of the tracer as it goes from an injection point to a sampling point. The first arrival time conveys at least two bits of information. First, it indicates that a connection for ground-water flow actually exists between the two points. For many tracer tests, particularly in karst regions, this is all the information that is desired. Second, if the tracer is conservative, the maximum velocity of ground-water flow between the two points may be estimated.



A. Tracer movement from injection ditch to sampling well.



B. Breakthrough Curve.

Figure 4-8. Tracer Concentration at Sampling Well, C , Measured Against Tracer Concentration at Input, C_0 (from Davis and others, 1985)

Interpretations more elaborate than the two mentioned above depend very much on the type of aquifer being tested, the velocity of ground-water flow, the configuration of the tracer injection and sampling systems, and the type of tracer or mixture of tracers used in the test.

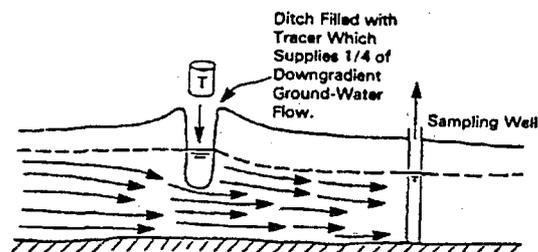
The value of greatest interest after the first arrival time is the arrival time of the peak concentration for a slug injection; or, for a continuous feed of tracers, the time since injection when the concentration of the tracer changes most rapidly as a function of time (Figure 4-8). In general, if conservative tracers are used, this time is close to the theoretical travel time of an average molecule of ground water traveling between the two points.

If a tracer is being introduced continuously into a ditch penetrating an aquifer, as shown in Figure 4-8, then the ratio C/C_0 will approach 1.0 after the tracer starts to pass the sampling point. The ratio of 1.0 is rarely approached in most tracer tests in the field, however, because waters are mixed by dispersion and diffusion in the aquifer and because wells used for sampling will commonly intercept far more ground water than has been tagged by tracers (Figure 4-9). Ratios of C/C_0 ranging between 10^{-5} and 2×10^{-1} often are reported from field tests.

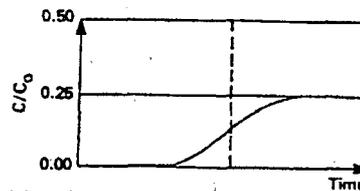
If a tracer is introduced passively into an aquifer but it is recovered by pumping a separate sampling well, then various mixtures of the tracer and the native ground

water will be recovered depending on the amount of water pumped, the transmissivity of the aquifer, the slope of the water table, and the shape of the tracer plume. Keely (1984) has presented this problem graphically with regard to the removal of contaminated water from an aquifer.

With the introduction of a mixture of tracers, possible interactions between the tracers and the solid part of the aquifer may be studied. If interactions take place, they can be detected by comparing breakthrough curves of a conservative tracer with the curves of the other tracers being tested (Figure 4-10). Quantitative analyses of tracer breakthrough curves are generally conducted by curve-matching computer-generated type curves, or by applying analytical methods.



A. Tracer does not fully saturate aquifer.



B. Breakthrough curve.

Figure 4-9. Incomplete Saturation of Aquifer with Tracer (from Davis and others, 1985)

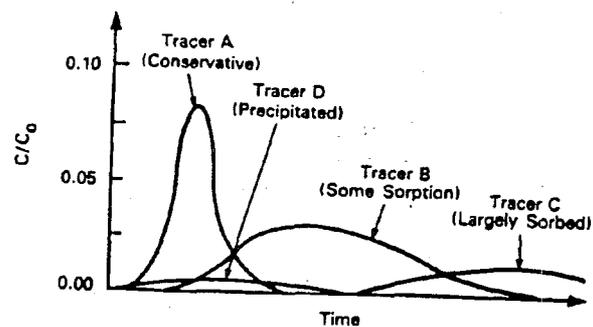


Figure 4-10. Breakthrough Curves for Conservative and Nonconservative Tracers (from Davis and others, 1985)

References

- Abrahart, E.N., 1968, Dyes and their intermediates: Pergamon Press, Oxford.
- Aley, T. and M.W. Fletcher, 1976, The water tracer's cookbook: Missouri Speleology, v. 16, no. 3, pp. 1-32.
- Aley, T, J.F. Quinlan, E.C. Alexander, and H. Behrens, In press, The joy of dyeing, a compendium of practical techniques for tracing groundwater, especially in karst terranes: National Water Well Association, Dublin, OH.
- Andrews, J.H. and D.J. Lee, 1979, Inert gases in groundwater from the Bunter Sandstone of England as indicators of age and palaeoclimatic trends: J. Hydrology, v. 41, pp. 233-252.
- Arandjelovic, D., 1969, A possible way of tracing groundwater flows in karst: Geophysical Prospecting, v. 17, no. 4, pp. 404-418.
- Atkinson, T.C. and P.L. Smart, 1981, Artificial tracers in hydrology: in A survey of British hydrology: The Royal Society, London, pp.173-190.
- Atkinson, T.C., D.I. Smith, J.J. Lavis, and R.J. Whitaker, 1973, Experiments in tracing underground waters in limestones: J. Hydrology, v. 19, pp. 323-349.
- Aulenbach, D.B., J.H. Bull, and B.C. Middlesworth, 1978, Use of tracers to confirm ground-water flow: Ground Water, v. 61, no. 3, pp. 149-157.
- Aulenbach, D.B. and N.L. Clesceri, 1980, Monitoring for land application of wastewater: Water, Air, and Soil Pollution, v. 14, pp. 81-94.
- Back, W. and J. Zoetl, 1975, Application of geochemical principles, isotopic methodology, and artificial tracers to karst hydrology: in Hydrogeology of karstic terrains; A. Burger and L. Dubertret (eds.): Int. Ass. Hydrogeologists, Paris, pp. 105-121.
- Back, W. and J.A. Cherry, 1976, Chemical aspects of present and future hydrogeologic problems: Advances in Groundwater Hydrology, September, pp. 153-172.
- Bögli, A., 1980, Karst hydrology and physical speleology: Springer-Verlag, New York.
- Bullivant, D.P. and M.J. O'Sullivan, 1989, Matching field tracer test with some simple models: Water Resources Research, v. 25, no. 8, pp. 1879-1891.
- Bumb, A.C., J.I. Drever, and C.R. McKee, 1985, In situ determination of dispersion coefficients and adsorption parameters for contaminations using a pull-push test: in Proc. 2nd Int. Conf. on Ground Water Quality Research(Oklahoma), N.N. Durham and A.E. Redelfs (eds.): Oklahoma State University Printing, pp. 186-190.
- Brown, M.C., 1972, Karst hydrology of the lower Maligne basin, Jasper, Alberta: Cave Studies No. 13: Cave Research Associates, Castro Valley, CA.
- Brown, M.C. and D.C. Ford, 1971, Quantitative tracer methods for investigation of karst hydrology systems, with reference to the Maligne basin area: Cave Research Group (Great Britain), v. 13, no. 1, pp. 37-51.
- Carter, R.C., W.J. Kaufman, G.T. Orlob, and D.K. Todd, 1959, Helium as a ground-water tracer: J. Geophysical Research, v. 64, pp. 2433-2439.
- Csallany, S.C., 1966, Application of radioisotopes in water resources research: in Proc. 2nd Annual American Water Resource Conference, American Water Resource Association, Champaign, IL, pp. 365-373.
- Davis, J.T., E. Flotz, and W.S. Blakemore, 1970, Serratia marcescens, a pathogen of increasing clinical importance: J. American Medical Association, v. 214, no. 12, pp. 2190-2192.
- Davis, S.N., 1986, Reply to the discussion by James F. Quinlan of ground water tracers: Ground Water, v. 24, no. 3, pp. 398-399.
- Davis, S.N. and H.W. Bentley, 1982, Dating groundwater, a short review: in Nuclear and chemical dating techniques, L. Currie (ed.): ACS Symposium Series 176, pp. 187-222.
- Davis, S.N., D.J. Campbell, H.W. Bentley, and T.J. Flynn, 1985, Introduction to ground-water tracers: (NTIS PB86-100591). Also published under the title Ground Water Tracers in NWWA/EPA Series, National Water Well Association, Dublin, OH, EPA 600/2-85/022.
- Davis, S.N., G.M. Thompson, H.W. Bentley, and G. Stiles, 1980, Ground water tracers—a short review: Ground Water, v. 18, pp. 14-23.
- Dole, R.B., 1906, Use of fluorescein in the study of underground waters: U.S. Geological Survey Water Supply and Irrigation Paper 160, pp. 73-85.
- Dreiss, S.J., 1989, Regional scale transport in a karst aquifer 1. component separation of spring flow hydrographs: Water Resources Research, v. 25, no. 1, pp. 117-125.

- Drew, D.P. and D.I. Smith, 1969, Techniques for the tracing of subterranean drainage: British Geomorphological Research Group Tech. Bulletin, v. 2, pp. 1-36.
- Dunn, J.R., 1957, Streamtracing: National Speleological Society Mid-Appalachian Region, v. 2, pp. 1-7.
- Edwards, A.J. and P.L. Smart, 1988a, Solute interaction processes: an annotated bibliography: Turner Designs, Sunnyvale, CA (61 references).
- Edwards, A.J. and P.L. Smart, 1988b, Contaminant transport modeling: an annotated bibliography: Turner Designs, Sunnyvale, CA (58 references).
- Ellis, J., 1980, A convenient parameter for tracing leachate from sanitary landfills: Water Research, v. 14, no. 9, pp. 1283-1287.
- Everts, C.J., R.S. Kanwar, E.C. Alexander, Jr., and S.C. Alexander, 1989, Comparison of tracer mobilities under laboratory and field conditions: J. Environ. Quality, v. 18, pp. 491-498.
- Ferronsky, V.I. and V.A. Polyakov, 1982, Environmental isotopes in the hydrosphere: Wiley-Interscience, New York.
- Feuerstein, D.L. and R.E. Selleck, 1963, Fluorescent tracers for dispersion measurements: J. ASCE August, pp. 1-21.
- Field, M.S., R.G. Wilhelm, and J.F. Quinlan, 1990, Use and toxicity of dyes for tracing ground water (Abstract): Ground Water, v. 28, no. 1, pp. 154-155 [The complete paper is available from Malcolm S. Field, Exposure Research Group, Office of Research and Development, U.S. Environmental Protection Agency (RO-689), Washington, DC 20460].
- Fried, J.J., 1975, Groundwater pollution: theory, methodology modeling, and practical rules: Elsevier, New York.
- Fritz, P. and J.C. Fontes (eds.), 1980, Handbook of environmental isotope geochemistry, vol. 1, the terrestrial environment: Elsevier, New York.
- Fritz, P. and J.C. Fontes (eds.), 1986, Handbook of environmental isotope geochemistry, vol. 2, the terrestrial environment, Part B: Elsevier, New York.
- Gann, E.E. and E.J. Harvey, 1975, Norman Creek: a source of recharge to Maramec Spring, Phelps County, Missouri: J. Res. U. S. Geological Survey, v. 3, no. 1, pp. 99-102.
- Gardner, G.D. and R.E. Gray, 1976, Tracing subsurface flow in karst regions using artificially colored spores: Association of Engineering Geologists Bulletin, v. 13, pp. 177-197.
- Gaspar, E. (ed.), 1987, Modern trends in tracer hydrology: CRC Press, Boca Raton, FL.
- Gaspar, E. and M. Oncescu, 1972, Radioactive tracers in hydrology: Elsevier Scientific Publishing Co., New York.
- Gat, J.R., 1971, Comments on the stable isotope method in regional ground water investigations: Water Resources Research, v. 7, pp. 980-993.
- Glasstone, S., 1967, Sourcebook on atomic energy: D. Van Nostrand Company, Inc., Princeton, NJ.
- Glover, R.R., 1972, Optical brighteners—a new water tracing reagent: Trans. Cave Research Group (Great Britain), v. 14, no. 2, pp. 84-88.
- Gospodaric, R. and P. Habic (eds.), 1976, Underground water tracing: investigations in Slovenia 1972-1975: Institute Karst Research, Ljubljana, Yugoslavia.
- Grisak, G.E. and J.F. Pickens, 1980a, Solute transport through fractured media 1. the effect of matrix diffusion: Water Resources Research, v. 16, no. 4, pp. 719-730.
- Grisak, G.E. and J.F. Pickens, 1980b, Solute transport through fractured media 2. column study of fractured till: Water Resources Research, v. 16, no. 4, pp. 731-739.
- Grisak, G.E., J.F. Pickens, F.J. Pearson, and J.M. Bahr, 1983, Evaluation of ground water tracers for nuclear fuel waste management studies: Report Prepared by Geologic Testing Consultants, Ltd. for Atomic Energy of Canada, Ltd., Whiteshell Nuclear Research Establishment, Pinawa, Manitoba.
- Güven, O., R.W. Falta, F.J. Molz, and J.G. Melville, 1985, Analysis and interpretation of single-well tracer tests in stratified aquifers: Water Resources Research, v. 21, pp. 676-684.
- Güven, O., R.W. Falta, F.J. Molz, and J.G. Melville, 1986, A simplified analysis of two-well tracer tests in stratified aquifers: Ground Water, v. 24, pp. 63-71.
- Gunn, J., 1982, Water tracing in Ireland: a review with

special references to the Cuillcagh karst: *Irish Geography*, v. 15, pp. 94-106.

Halevy, E. and A. Nir, 1962, The determination of aquifer parameters with the aid of radioactive tracers: *J. Geophysical Research*, v. 61, pp. 2403-2409.

Hendry, M.J., 1988, Do isotopes have a place in ground-water studies?: *Ground Water*, v. 26, no. 4, pp. 410-415.

Hoehn, E. and H.J.R. von Gunten, 1989, Radon in groundwater: a tool to assess infiltration from surface waters to aquifers: *Water Resources Research*, v. 25, no. 8, pp. 1795-1803.

Hubbard, E.F., F.A. Kilpatrick, L.A. Martens, and J.F. Wilson, Jr., 1982, Measurement of time of travel and dispersion in streams by dye tracing: U.S. Geological Survey TWI 3-A9.

Ilgenfritz, E.M., F.A. Blanchard, R.L. Masselink, and B.K. Panigrahi, 1988, Mobility and effects in liner clay of fluorobenzene tracer and leachate: *Ground Water*, v. 26, no. 1, pp. 22-30.

International Atomic Energy Agency (IAEA), 1963, Proceedings of the symposium on radioisotopes in hydrology (Tokyo): International Atomic Energy Agency, Vienna.

International Atomic Energy Agency (IAEA), 1967, Radioisotopes in industry and geophysics—a symposium (Prague): International Atomic Energy Agency, Vienna.

International Atomic Energy Agency (IAEA), 1966, Isotopes in hydrology: Proc. of the Symposium on Isotopes in Hydrology (Vienna), International Atomic Energy Agency, Vienna.

International Atomic Energy Agency (IAEA), 1970, Isotope hydrology (1970): Proc. of the Symposium on Use of Isotopes in Hydrology (Vienna). International Atomic Energy Agency, Vienna.

International Atomic Energy Agency (IAEA), 1974, Isotope techniques in groundwater hydrology (1970): Proc. Vienna Symposium, International Atomic Energy Agency, Vienna.

International Atomic Energy Agency (IAEA), 1978, Isotope hydrology (1978): Proc. International Symposium on Isotope Hydrology (Neuherberg). International Atomic Energy Agency, Vienna.

Jones, W.K., 1984, Dye tracers in karst areas: *National Speleological Society Bulletin*, v. 36, pp. 3-9.

Kaufman, W.J., and G.T. Orlob, 1956, Measuring ground-water movements with radioactive and chemical tracers: *Am. Waterworks Ass. J.*, v. 48, pp. 559-572.

Keely, J.F., 1984, Optimizing pumping strategies for contaminant studies and remedial actions: *Ground Water Monitoring Review*, v. 4, no. 3, pp. 63-74.

Kenoyer, G.J., 1988, Tracer test analysis of anisotropy in hydraulic conductivity of granular aquifers: *Ground Water Monitoring Review*, v. 8, no. 3, pp. 67-70.

Keswick, B.H., D. Wang, and C.P. Gerba, 1982, The use of microorganisms as ground-water tracers: a review: *Ground Water*, v. 20, no. 2, pp. 142-149.

Keys, W.S. and R.F. Brown, 1978, The use of temperature logs to trace the movement of injected water: *Ground Water*, v. 16, no. 1, pp. 32-48.

Keys, W.S. and L.M. MacCary, 1971, Application of borehole geophysics to water-resources investigations: U.S. Geological Survey TWI 2-E1.

Kilpatrick, F.A. and E.D. Cobb, 1985, Measurement of discharge using tracers: U.S. Geological Survey TWI 3-A16.

Klotz, D., H. Moser, and P. Trimborn, 1978, Single-borehole techniques, present status and examples of recent applications: in Proc. IAEA Symp. Isotope Hydrology, Part 1, International Atomic Energy Agency, Vienna, pp. 159-179.

Knuttson, G., 1968, Tracers for ground-water investigations: in *Ground Water Problems*, E. Eriksson, Y. Gustafsson, and K. Nilsson (eds.), Pergamon Press, London.

LaMoreaux, P.E., B.M. Wilson, and B.A. Mermon (eds.), 1984, Guide to the hydrology of carbonate rocks: UNESCO Studies and Reports in Hydrology, No. 41.

LaMoreaux, P.E., E. Prohic, J. Zoetl, J.M. Tanner, and B.N. Roche (eds.), 1989, Hydrology of limestone terranes: annotated bibliography of carbonate rocks, volume 4: International Association of Hydrogeologists Int. Cont. to Hydrogeology Volume 10. Verlag Heinz Heise GmbH., Hannover, West Germany.

Leap, D.I., 1985, A simple, two-pulse tracer method for estimating steady-state ground water parameters: *Hydrological Science and Technology: Short Papers*, v.1, no. 1, pp. 37-43.

Lenda, A. and A. Zuber. 1970. Tracer dispersion in

- groundwater experiments: *in* Proc. IAEA Symp. Isotope Hydrology, International Atomic Energy Agency, Vienna, pp. 619-641.
- Lewis, D.C., G.J. Kriz, and R.H. Burgy, 1966, Tracer dilution sampling technique to determine hydraulic conductivity of fractured rock: *Water Resources Research*, v. 2, pp. 533-542.
- Marmion, D.M., 1984, Handbook of U.S. colorants for foods, drugs, and cosmetics, 2nd ed.: Wiley-Interscience, New York.
- Mather, J.D., D.A. Gray, and D.G. Jenkins, 1969, The Use of Tracers to Investigate the Relationship between Mining Subsidence and Groundwater Occurrence of Aberdare, South Wales: *J. Hydrology*, v. 9, pp. 136-154.
- Mattson, W., 1929, The laws of soil colloidal behavior I: *Soil Science*, pp. 27-28 and pp. 71-87.
- Mazor, E., 1972, Paleotemperatures and other hydrological parameters deduced from noble gases dissolved in ground waters, Jordan Rift Valley, Israel: *Geochimica et Cosmochimica Acta*, v. 36, pp. 1321-1336.
- McLaughlin, M.J., 1982, A review of the use of dyes as soil water tracers. water S.A.: Water Research Commission, Pretoria, South Africa, v. 8, no. 4, pp. 196-201.
- Meinzer, O.E., 1932, Outline of methods for estimating ground water supplies: U.S. Geological Survey Water-Supply Paper 638-C, pp. 126-131.
- Milanovia, P.T., 1981, Karst Hydrogeology: Water Resource Publications, Littleton, CO.
- Molz, F.J., J.G. Melville, O. Güven, R.D. Crocker and K.T. Matteson, 1985, Design and performance of single-well tracer tests at the Mobile site: *Water Resources Research*, v. 21, pp. 1497-1502.
- Molz, F.J., O. Güven, J.G. Melville, and J.F. Keely, 1986, Performance and analysis of aquifer tracer tests with implications for contaminant transport modeling: (NTIS PB86-219086) EPA 600/2-86/062.
- Molz, F.J., O. Güven, J.G. Melville, and J.F. Keely, 1987, Performance and analysis of aquifer tracer tests with implications for contaminant transport modeling—a project summary: *Ground Water*, v. 25, pp. 337-341.
- Molz, F.J., O. Güven, J.G. Melville, J.S. Nohrstedt, and J.K. Overholtzer, 1988, Forced-gradient tracer tests and inferred hydraulic conductivity distributions at the Mobile site: *Ground Water*, v. 26, no. 5, pp. 570-579.
- Moser, H. and W. Rauert, 1985, Determination of groundwater movement by means of environmental isotopes: State of the Art: *in* Relation of Groundwater Quantity and Quality, F.X. Dunin, G. Matthes, and R.A. Gras (eds.), Int. Ass. Hydrological Sciences no. 146, pp. 241-257.
- Mull, D.S., T.D. Lieberman, J.L. Smoot, and L.H. Woosely, Jr., 1988, Application of dye-tracing techniques for determining solute-transport characteristics of ground water in karst terranes: Region 4, Atlanta, GA, EPA 904/6-88-001.
- Murray, J.P., J.V. Rouse, and A.B. Carpenter, 1981, Groundwater contamination by sanitary landfill leachate and domestic wastewater in carbonate terrain: principle source diagnosis, chemical transport characteristics and design implications: *Water Research*, v. 15, no. 6, pp. 745-757.
- Naymik, T.G. and M.E. Sievers, 1983, Ground-water tracer experiment (II) at Sand Ridge State Forest, Illinois: ISWS Contract Report 334, Illinois State Water Survey, Champaign, IL.
- Pickens, J.F., R.E. Jackson, K.J. Inch, and W.F. Merritt, 1981, Measurement of distribution coefficients using radial injection dual-tracer tests: *Water Resource Research*, v. 17, pp. 529-544.
- Quinlan, J.F., 1986, Discussion of "Groundwater tracers" by Davis and others (1985) with emphasis on dye tracing, especially in karst terranes: *Ground Water*, v. 24, no. 2, pp. 253-259 and v. 24, no. 3, pp. 396-397 (References).
- Quinlan, J.F., 1989, Ground-water monitoring in karst terranes: Recommended Protocols and Implicit Assumptions: EMSL, Las Vegas, NV, EPA 600/X-89/050.
- Quinlan, J.F., R.O. Ewars, and M.S. Fiel, 1988, How to use ground-water tracing to "prove" that leakage of harmful materials from a site in karst terrane will not occur: *in* Proc. Second Conf. on Environmental Problems in Karst Terranes and Their Solutions (Nashville, TN), National Water Well Association, Dublin, OH, pp. 265-288.
- Rahe, T.M., C. Hagedorn, E.L. McCoy, and G.G. Kling, 1978, Transport of antibiotic-resistant *Escherichia Coli* through western Oregon hill slope soils under conditions of saturated flow: *J. Environ. Quality*, v. 7, pp. 487-494.

- Rainwater, K.A., W.R. Wise, and R.J. Charbeneau, 1987, Parameter estimation through groundwater tracer tests: *Water Resources Research*, v. 23, pp. 1901-1910.
- Repogle, J.A., L.E. Myers, and K.J. Brus, 1966, Flow measurements with fluorescent tracers: *J. Hydraulics Division ASCE*, v. 92, pp. 1-15.
- Reynolds, E.R.C., 1966, The percolation of rainwater through soil demonstrated by fluorescent dyes: *J. Soil Science*, v. 17, no. 1, pp. 127-132.
- Robertson, J.B., 1969, Behavior of Xenon-133 gas after injection underground: U.S. Geological Survey Open File Report ID022051.
- Rogers, A.S., 1958, Physical behavior and geologic control of radon in mountain streams: *U.S. Geological Survey Bulletin 1052E*, pp. 187-211.
- Rorabaugh, M.I., 1956, Ground water in Northeastern Louisville, Kentucky: U.S. Geological Survey Water-Supply Paper 1360-B, pp. 101-169.
- Sauty, J.P., 1978, Identification of hydrodispersive mass transfer parameters in aquifers by interpretation of tracer experiments in radial converging or diverging flow (in French): *J. Hydrology*, v. 39, pp. 69-103.
- Sauty, J.P., 1980, An analysis of hydrodispersive transfer in aquifers: *Water Resources Research*, v. 16, no. 1, pp. 145-158.
- Slichter, C.S., 1902, The motions of underground waters: U.S. Geological Survey Water-Supply and Irrigation Paper 67.
- Slichter, C.S., 1905, Field measurement of the rate of movement of underground waters: U.S. Geological Survey Water-Supply and Irrigation Paper 140, pp. 9-34.
- Schmolzer, J.K., W.A. Jester, and R.R. Parizek, 1973, Groundwater tracing with post sampling activation analysis: *J. Hydrology*, v. 20, pp. 217-236.
- SDC & AATC (Society of Dyers & Colorists and American Association of Textile Chemists), 1971-1982, *Color Index*, 3rd ed.
- Smart, C.C., 1988a, Quantitative tracing of the Maligne Karst System, Alberta, Canada: *J. Hydrology*, v. 98, pp. 185-204.
- Smart, C.C., 1988b, Artificial tracer techniques for the determination of the structure of conduit aquifers: *Ground Water*, v. 26, no. 4, pp. 445-453.
- Smart, P.L., 1976, Catchment delimitation in karst areas by the use of qualitative tracer methods: *in Proc. 3rd Int. Symp. of Underground Water Tracing*, Bled, Yugoslavia, pp. 291-298.
- Smart, P.L., 1984, A review of the toxicity of twelve fluorescent dyes used for water tracing: *National Speleological Society Bulletin* 46, pp. 21-33.
- Smart, P.L., 1985, Applications of fluorescent dye tracers in the planning and hydrological appraisal of sanitary landfills: *Q. J. Eng. Geol. (London)* v. 18, pp. 275-286.
- Smart, P.L. and I.M.S. Laidlaw, 1977, An evaluation of some fluorescent dyes for water tracing: *Water Resources Research*, v. 13, no. 1, pp. 15-33.
- Smart, P.L. and D.I. Smith, 1976, Water tracing in tropical regions; the use of fluorometric techniques in Jamaica: *J. Hydrology*, v. 30, pp. 179-195.
- Smart, P.L., F. Whitaker, and J.F. Quinlan, 1988, *Ground water tracing: An annotated bibliography*: Turner Designs, Sunnyvale, CA.
- Smoot, J.L., D.S. Mull, and T.D. Liebermann, 1987, Quantitative dye tracing techniques for describing the solute transport characteristics of ground-water flow in karst terrain: *in 2nd Multidisciplinary Conf. Sinkholes and the Environmental Impacts of Karst* (Orlando), Beck, B.F. and W.L. Wilson (eds.), Balkema, Accord, MA, pp. 29-35.
- Sorey, M.L., 1971, Measurement of vertical ground-water velocity from temperature profiles in wells: *Water Resources Research*, v. 7, no. 4, pp. 963-970.
- Stiles, C.W., H.R. Crohurst, and G.E. Thomson, 1927, Uranin test to demonstrate pollution of wells: *in Experimental Bacterial and Chemical Pollution of Wells via Ground Water and the Factors Involved*, U.S. Public Health Service Hygienic Laboratory Bulletin No. 147, pp. 84-87.
- Sugisaki, R., 1969, Measurement of effective flow velocity of groundwater by means of dissolved gases: *American Jour. Science*, v. 259, pp. 144-153.
- Sweeting, M.M., 1973, *Karst landforms*: Columbia University Press, New York.
- Symposium on Underground Water Tracing (SUWT), 1966, 1st SUWT (Graz, Austria): *in Steirisches Beitrage zur Hydrogeologie Jg. 1966/67*.

Symposium on Underground Water Tracing (SUWT), 1970, 2nd SUWT (Freiburg/Br., West Germany): Published in *Steirisches Beitrage zur Hydrogeologie* 22(1970):5-165, and *Geologisches Jahrbuch, Reihe C*. 2(1972):1-382.

Symposium on Underground Water Tracing (SUWT), 1976, 3rd SUWT (Ljubljana-Bled, Yugoslavia), published by Ljubljana Institute for Karst Research: Volume 1 (1976), 213 pp., Volume 2 (1977) 182 pp. See also Gospodaric and Habic (1976).

Symposium on Underground Water Tracing (SUWT), 1981, 4th SUWT (Bern, Switzerland): in *Steirisches Beitrage zur Hydrogeologie* 32(1980):5-100; 33(1981):1-264; and *Beitrage zur Geologie der Schweiz—Hydrologie* 28 pt.1(1982):1-236; 28 pt.2(1982):1-213.

Symposium on Underground Water Tracing (SUWT), 1986, 5th SUWT (Athens, Greece), published by Institute of Geology and Mineral Exploration, Athens.

Taylor, T.A. and J.A. Dey, 1985, Bibliography of borehole geophysics as applied to ground-water hydrology, U.S. Geological Survey Circular 926.

Tennyson, L.C. and C.D. Settergren, 1980, Percolate water and bromide movement in the root zone of effluent irrigation sites: *Water Resources Bulletin*, v. 16, no. 3, pp. 433-437.

Tester, J.W., R.L. Bivens, and R.M. Potter, 1982, Interwell tracer analysis of a hydraulically fractured granitic geothermal reservoir: *Soc. Petroleum Engineers Jour.* v. 8, pp. 537-554.

Theis, C.V., 1963, Hydrologic phenomena affecting the use of tracers in timing ground-water flow: in *Proc. IAEA Tokyo Symp. Radioisotopes in Hydrology*, International Atomic Energy Agency, Vienna, Austria (as cited by Davis and others, 1985).

Thompson, G.M. and J.M. Hayes, 1979, Trichlorofluoromethane in ground water, a possible tracer and indicator of ground-water age: *Water Resources Research*, v. 15, no. 3, pp. 546-554.

Thompson, G.M., J.M. Hayes, and S.N. Davis, 1974, Fluorocarbon tracers in hydrology: *Geophysical Research Letters*, v. 1, pp. 177-180.

Thraillkill, J., and others, 1983, Studies in dye-tracing techniques and karst hydrogeology: Univ. of Kentucky, Water Resources Research Center Research Report No. 140.

van der Leeden, F., 1987, Geraghty & Miller's groundwater bibliography, 4th ed: Water Information Center, Plainview, New York.

Vogel, J.C., L. Thilo, and M. Van Dijken, 1974, Determination of groundwater recharge with tritium: *Jour. Hydrology*, v. 23, pp. 131-140.

Vuataz, F.D., J. Stix, F. Goff, and C.F. Pearson, 1984, Low-temperature geothermal potential of the Ojo Caliente warm spring area in Northern New Mexico: Los Alamos National Laboratory Publication LA-10105-OBES/VC-666.

Wagner, O.R., 1977, The use of tracers in diagnosing interwell reservoir heterogeneities: *J. Petroleum Technology*, v. 11, pp. 1410-1416.

Wiebenga, W.A., W.R. Ellis, B.W. Seatonberry, and J.T.G. Andrew, 1967, Radioisotopes as ground-water tracers: *Jour. Geophysical Research*, v. 72, pp. 4081-4091.

Wilkowske, C.J., J.A. Washington II, W.J. Martin, and R.E. Ritts, Jr., 1970, *Serratia marcescens*: Biochemical characteristics, antibiotic susceptibility and clinical significance: *Jour. American Medical Association*, v. 214, no. 12, pp. 2157-2162.

Wilson, Jr. J.F., E.D. Cobb, and F.A. Kilpatrick, 1986, Fluorometric procedures for dye tracing (Revised): U.S. Geological Survey TWI 3-A12. (updates report with the same title by J.F. Wilson, Jr. published in 1968).

Wood, W.W. and G.G. Ehrlich, 1978, Use of baker's yeast to trace microbial movement in ground water: *Ground Water*, v. 16, no. 6, pp. 398-403.

INTRODUCTION TO AQUIFER TEST ANALYSIS

Cone of Depression

Both wells and springs can be ground-water supply sources. However, most springs with yields large enough to meet municipal, industrial, and large commercial and agricultural needs are located only in areas underlain by cavernous limestones and lava flows. Most ground-water needs, therefore, are met by withdrawals from wells.

An understanding of the response of aquifers to withdrawals from wells is important to an understanding of ground-water hydrology. When withdrawals start and water is removed from storage in the well, the water level in the well begins to decline. The head in the well falls below the level in the surrounding aquifer, and water begins to move from the aquifer into the well. As pumping continues, the water level in the well continues to decline, and the rate of flow into the well from the aquifer continues to increase until the rate of inflow equals the rate of withdrawal.

When water moves from an aquifer into a well, a cone

of depression is formed (Figure 5-1). Because water must converge on the well from all directions and because the area through which the flow occurs decreases toward the well, the hydraulic gradient must get steeper toward the well.

There are several important differences between cones of depression in confined and unconfined aquifers. Withdrawals from an unconfined aquifer cause drainage of water from the rocks, and the water table declines as the cone of depression forms (Figure 5-1a). Because the storage coefficient of an unconfined aquifer equals the specific yield of the aquifer material, the cone of depression expands very slowly. On the other hand, dewatering of the aquifer results in a decrease in transmissivity, which causes, in turn, an increase in drawdown both in the well and in the aquifer.

Withdrawals from a confined aquifer cause a drawdown in artesian pressure but normally do not cause a dewatering of the aquifer (Figure 5-1b). The water withdrawn from a confined aquifer is derived from expansion of the water and compression of the rock

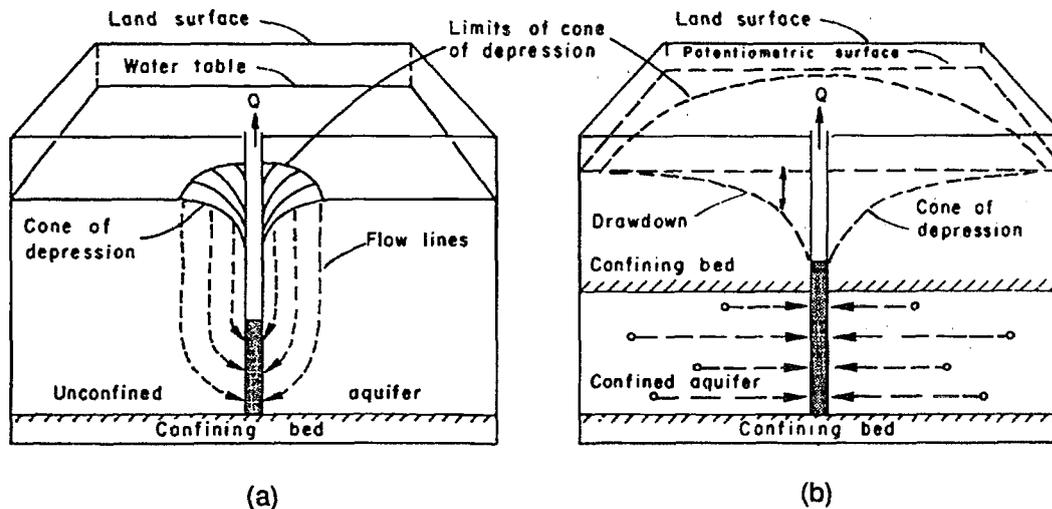


Figure 5-1. Cone of Depression in an Unconfined and a Confined Aquifer

skeleton of the aquifer. The small storage coefficient of confined aquifers results in a rapid expansion of the cone of depression. Consequently, the mutual interference of expanding cones around adjacent wells occurs more rapidly in confined aquifers than it does in unconfined aquifers.

SOURCE OF WATER DERIVED FROM WELLS

Both the economic development and the effective management of any ground-water system require an understanding of the system's response to withdrawals from wells. The first concise description of the hydrologic principles involved in this response was presented by Theis (1940).

Theis pointed out that the aquifer's response to withdrawals from wells depends on:

1. The rate of expansion of the cone of depression caused by the withdrawals, which depends on the transmissivity and the storage coefficient of the aquifer.
2. The distance to areas in which the rate of water discharging from the aquifer can be reduced.
3. The distance to recharge areas in which the rate of recharge can be increased.

Over a sufficiently long period of time and under natural conditions—that is, before the start of withdrawals—the discharge from every ground-water system equals the recharge to it (Figure 5-2a). This property is expressed by the equation:

$$\text{natural discharge (D)} = \text{natural recharge (R)}$$

In the eastern United States and in the more humid areas in the West, the amount and distribution of precipitation are such that the period of time over which discharge and recharge balance may be less than a year or, at most, a few years. In the drier parts of the country—that is, in the areas that generally receive less than about 500 mm of precipitation annually—the period over which discharge and recharge balance may be several years or even centuries. Over shorter periods of time, differences between discharge and recharge involve changes in ground-water storage. When discharge exceeds recharge, ground-water storage (S) is reduced by an amount (ΔS) equal to the difference between discharge and recharge:

$$D = R + \Delta S \quad (1)$$

Conversely, when recharge exceeds discharge, ground-water storage is increased:

$$D = R - \Delta S \quad (2)$$

When withdrawal through a well begins, water is removed from storage in the well's vicinity as the cone of depression develops (Figure 5-2b). Thus, the withdrawal (Q) is balanced by a reduction in ground-water storage:

$$Q = \Delta S \quad (3)$$

As the cone of depression expands outward from the pumping well, it may reach an area where water is discharging from the aquifer. The hydraulic gradient will be reduced toward the discharge area, and the rate of natural discharge will decrease (Figure 5-2c). To the extent that the decrease in natural discharge compensates for the pumpage, the rate at which water is being removed from storage also will decrease, and the rate of expansion of the cone of depression will decline. If and when the reduction in natural discharge (ΔD) equals the rate of withdrawal (Q), a new balance will be established in the aquifer. This balance is represented as:

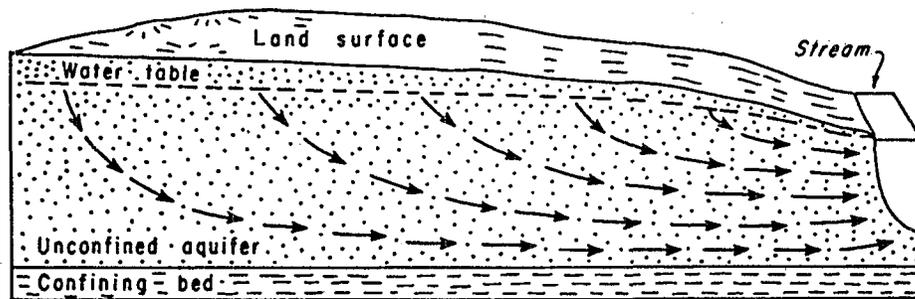
$$(D - \Delta D) + Q = R \quad (4)$$

Conversely, if the cone of depression expands into a recharge area rather than into a natural discharge area, the hydraulic gradient between the recharge area and the pumping well will increase. If, under natural conditions, more water was available in the recharge area than the aquifer could accept (the condition that Theis referred to as rejected recharge), the increase in the gradient away from the recharge area will permit more recharge to occur, and the rate of growth of the cone of depression will decrease. If the increase in recharge (ΔR) equals the rate of withdrawal (Q), a new balance will be established in the aquifer, and expansion of the cone of depression will cease. The new balance is represented as:

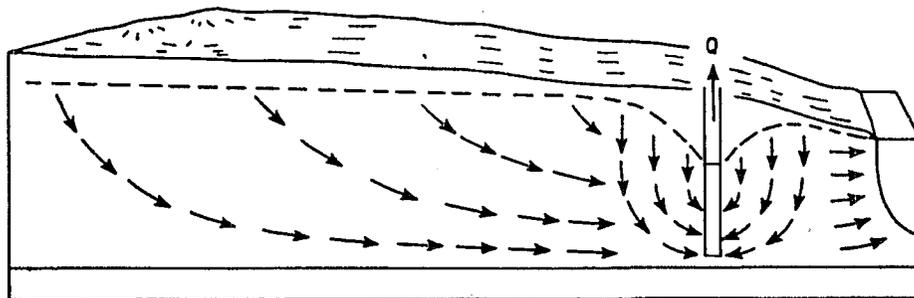
$$D + Q = R + \Delta R \quad (5)$$

In the eastern United States, gaining streams are relatively closely spaced, and areas in which rejected recharge occurs are relatively unimportant. In this region, the growth of cones of depression first commonly causes a reduction in natural discharge. If the pumping wells are near a stream or if the withdrawals are continued long enough, ground-water discharge to a stream may be stopped entirely in the vicinity of the wells, and water may be induced to move from the stream into the aquifer (Figure 5-2d). The tendency in this region is for withdrawals to change discharge areas into recharge areas. This consideration is important where the streams contain brackish or polluted water or where the streamflow is committed or required for other purposes.

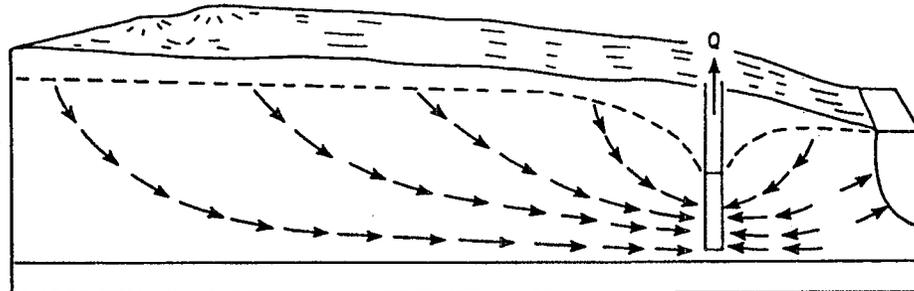
In summary, withdrawal of ground water through a well reduces the water in storage in the source aquifer



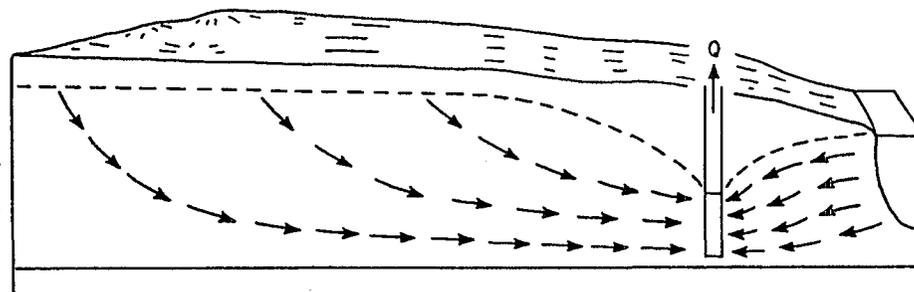
$$\text{Discharge (D)} = \text{Recharge (R)}$$



$$\text{Withdrawal (Q)} = \text{Reduction in storage } (\Delta s)$$



$$\text{Withdrawal (Q)} = \text{Reduction in storage } (\Delta s) + \text{Reduction in discharge } (\Delta D)$$



$$\text{Withdrawal (Q)} = \text{Reduction in discharge } (\Delta D) + \text{Increase in recharge } (\Delta R)$$

Figure 5-2. Source of Water Derived From Wells

during the growth of the cone of depression. If the cone of depression ceases to expand, the rate of withdrawal is being balanced by a reduction in the rate of natural discharge and (or) by an increase in the rate of recharge. Under this condition,

$$Q = \Delta D + \Delta R \quad (6)$$

AQUIFER TESTS

Determining the yield of ground-water systems and evaluating the movement and fate of ground-water pollutants require, among other information, knowledge of:

1. The position and thickness of aquifers and confining beds.
2. The transmissivity and storage coefficient of the aquifers.
3. The hydraulic characteristics of the confining beds.
4. The position and nature of the aquifer boundaries.
5. The location and amounts of ground-water withdrawals.
6. The locations, kinds, and amounts of pollutants and pollutant practices.

Acquiring knowledge of these factors requires both geologic and hydrologic investigations. One of the most important hydrologic studies involves analyzing the change, with time, in water levels (or total heads) in an aquifer caused by withdrawals through wells. This type of study is referred to as an aquifer test and, in most cases, includes pumping a well at a constant rate for a period ranging from several hours to several days and measuring the change in water level in observation

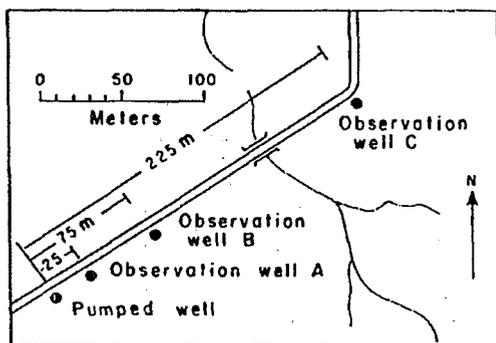


Figure 5-3. Map of Aquifer Test Site

wells located at different distances from the pumped well (Figure 5-3).

Successful aquifer tests require, among other things:

1. Determination of the prepumping water-level trend (that is, the regional trend).
2. A carefully controlled constant pumping rate.
3. Accurate water-level measurements made at precise times during both the drawdown and the recovery periods.

Drawdown is the difference between the water level at any time during the test and the position at which the water level would have been if withdrawals had not started. Drawdown is very rapid at first. As pumping continues and the cone of depression expands, the rate of drawdown decreases (Figure 5-4).

The recovery of the water level under ideal conditions is a mirror image of the drawdown. The change in water level during the recovery period is the same as if withdrawals had continued at the same rate from the pumped well but, at the moment of pump cutoff, a recharge well had begun recharging water at the same point and at the same rate. Therefore, the recovery of the water level is the difference between the actual measured level and the projected pumping level (Figure 5-4).

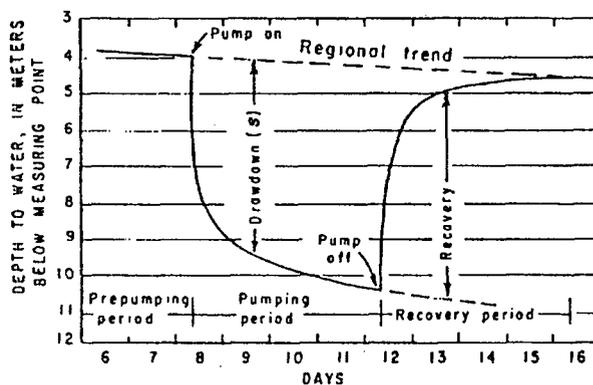


Figure 5-4. Change of Water Level in Well B

In addition to the constant-rate aquifer test mentioned above, analytical methods also have been developed for several other types of aquifer tests. These methods include tests in which the rate of withdrawal is variable and tests that involve leakage of water across confining beds into confined aquifers. The analytical methods available also permit analysis of tests conducted on both vertical wells and horizontal wells or drains.

The most commonly used method of aquifer-test-data

analysis—that for a vertical well pumped at a constant rate from an aquifer not affected by vertical leakage and lateral boundaries—is discussed below. The method of analysis requires the use of a type curve based on the values of $W(u)$ and $1/u$ listed in Table 5-1. Preparation and use of the type curve are covered in the following discussion.

3. The discharging well penetrates the entire thickness of the aquifer, and its diameter is small in comparison with the pumping rate, so that storage in the well is negligible.

These assumptions are most nearly met by confined aquifers at sites remote from their boundaries. However,

$1/u$	10	7.69	5.88	5.00	4.00	3.33	2.86	2.5	2.22	2.00	1.67	1.43	1.25	1.11
10^{-1}	0.219	0.135	0.075	0.049	0.025	0.013	0.007	0.004	0.002	0.001	0.000	0.000	0.000	0.000
1	1.82	1.59	1.36	1.22	1.04	.91	.79	.70	.63	.56	.45	.37	.31	.26
10	4.04	3.78	3.51	3.35	3.14	2.96	2.81	2.68	2.57	2.47	2.30	2.15	2.03	1.92
10^2	6.33	6.07	5.80	5.64	5.42	5.23	5.08	4.95	4.83	4.73	4.54	4.39	4.26	4.14
10^3	8.63	8.37	8.10	7.94	7.72	7.53	7.38	7.25	7.13	7.02	6.84	6.69	6.55	6.44
10^4	10.94	10.67	10.41	10.24	10.02	9.84	9.68	9.55	9.43	9.33	9.14	8.99	8.86	8.74
10^5	13.24	12.98	12.71	12.55	12.32	12.14	11.99	11.85	11.73	11.63	11.45	11.29	11.16	11.04
10^6	15.54	15.28	15.01	14.85	14.62	14.44	14.29	14.15	14.04	13.93	13.75	13.60	13.46	13.34
10^7	17.84	17.58	17.31	17.15	16.93	16.74	16.59	16.46	16.34	16.23	16.05	15.90	15.76	15.65
10^8	20.15	19.88	19.62	19.45	19.23	19.05	18.89	18.76	18.64	18.54	18.35	18.20	18.07	17.95
10^9	22.45	22.19	21.92	21.76	21.53	21.35	21.20	21.06	20.94	20.84	20.66	20.50	20.37	20.25
10^{10}	24.75	24.49	24.22	24.06	23.83	23.65	23.50	23.36	23.25	23.14	22.96	22.81	22.67	22.55
10^{11}	27.05	26.79	26.52	26.36	26.14	25.96	25.80	25.67	25.55	25.44	25.26	25.11	24.97	24.86
10^{12}	29.36	29.09	28.83	28.66	28.44	28.26	28.10	27.97	27.85	27.75	27.56	27.41	27.28	27.16
10^{13}	31.66	31.40	31.13	30.97	30.74	30.56	30.41	30.27	30.15	30.05	29.87	29.71	29.58	29.46
10^{14}	33.96	33.70	33.43	33.27	33.05	32.86	32.71	32.58	32.46	32.35	32.17	32.02	31.88	31.76

Examples: When $1/u = 10 \times 10^{-1}$, $W(u) = 0.219$; when $1/u = 3.33 \times 10^2$, $W(u) = 5.23$.

Table 5-1. Selected Values of $W(u)$ for values of $1/u$

Analysis of Aquifer-Test Data

In 1935, C. V. Theis of the New Mexico Water Resources District of the U.S. Geological Survey developed the first equation to include time of pumping as a factor that could be used to analyze the effect of withdrawals from a well. The Theis equation permitted, for the first time, determination of the hydraulic characteristics of an aquifer before the development of new steady-state conditions resulting from pumping. This capacity is important because, under most conditions, a new steady state cannot be developed or, if it can, many months or years may be required.

In the development of the equation, Theis assumed that:

1. The transmissivity of the aquifer tapped by the pumping well is constant during the test to the limits of the cone of depression.
2. The water withdrawn from the aquifer is derived entirely from storage and is discharged instantaneously with the decline in head.

if certain precautions are observed, the equation also can be used to analyze tests of unconfined aquifers. The forms of the Theis equation used to determine the transmissivity and storage coefficient are

$$T = (Q \times W(u)) / (4 \times \pi \times s) \quad (7)$$

$$S = (4 \times T \times t \times u) / r^2 \quad (8)$$

where T is transmissivity, S is the storage coefficient, Q is the pumping rate, s is drawdown, t is time, r is the distance from the pumping well to the observation well, $W(u)$ is the well function of u , which equals

$$-.577216 - \log_e u + u - u^2/(2 \times 2!) + u^3/(3 \times 3!) - u^4/(4 \times 4!) + \dots$$

$$\text{and } u = (r^2 S) / (4 T t). \quad (9)$$

The Theis equation is in a form that cannot be solved directly. To overcome this problem, Theis devised a convenient graphic method of solution that uses a type curve (Figure 5-5). To apply this method, a data plot of drawdown versus time (or drawdown versus t/r^2) is

matched to the type curve of $W(u)$ versus $1/u$ (Figure 5-6). At some convenient point on the overlapping part of the sheets containing the data plot and type curve, values of s , t (or t/r^2), $W(u)$, and $1/u$ are noted (Figure 5-6). These values are then substituted in the equations, which are solved for T and S , respectively.

A Theis type curve of $W(u)$ versus $1/u$ can be prepared

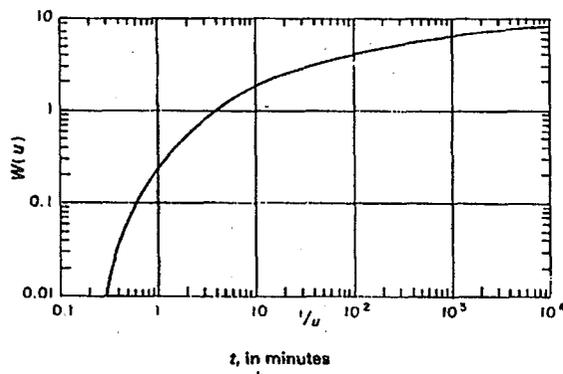


Figure 5-5. Theis Type Curve

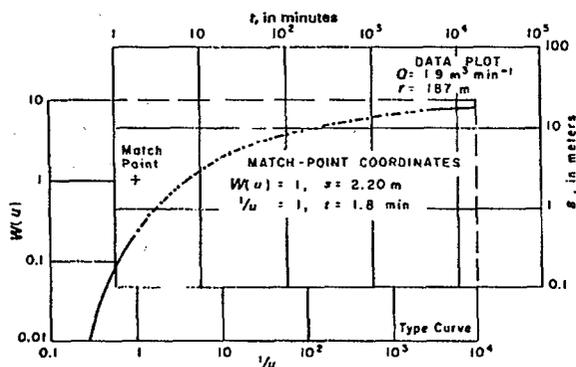


Figure 5-6. Data Plot of Drawdown Versus Time Matched to Theis Type Curve

from the values given in Table 5-1. The data points are plotted on logarithmic graph paper—that is, graph paper having logarithmic divisions in both the x and y directions.

The dimensional units of transmissivity (T) are L^2/t , where L is length and t is time in days. Thus, if Q is in cubic

meters per day and s is in meters, T will be in square meters per day. Similarly, if T is in square meters per day, t is in days, and r is in meters, S will be dimensionless.

Traditionally, in the United States, T has been expressed in units of gallons per day per foot. The common practice now is to report transmissivity in units of square meters per day or square feet per day. If Q is measured in gallons per minute, as is still normally the case, and drawdown is measured in feet, as is also normally the case, the equation is modified to obtain T in square feet per day as follows:

$$T = (Q \times W(u)) / (4\pi s) = (\text{gal/min}) \times (1.440 \text{ min/d}) \times (\text{ft}^3 / 7.48 \text{ gal}) \times 1/\text{ft} \times W(u) / (4\pi r) \quad (10)$$

or

$$T (\text{in ft}^2 \text{ d}^{-1}) = (15.3 \times Q \times W(u)) / s \quad (11)$$

(when Q is in gallons per minute and s is in feet). To convert square feet per day to square meters per day, divide by 10.76.

The storage coefficient is dimensionless. Therefore, if T is in square feet per day, t is in minutes, and r is in feet, then,

$$S = (4Tt) / r^2 = (4/1) \times \text{ft}^2/\text{d} \times \text{min}/\text{ft}^2 \times \text{d}/1440 \text{ min} \quad (12)$$

or

$$S = (Tt) / 360r^2 \quad (13)$$

(when T is in square feet per day, t is in minutes, and r is in feet).

Analysis of aquifer-test data using the Theis equation involves plotting both the type curve and the test data on logarithmic graph paper. If the aquifer and the conditions of the test satisfy Theis' assumptions, the type curve has the same shape as the cone of depression along any line radiating away from the pumping well and the drawdown graph at any point in the cone of depression.

There are two considerations for using the Theis equation for unconfined aquifers. First, if the aquifer is relatively fine grained, water is released slowly over a period of hours or days, not instantaneously with the decline in head. Therefore, the value of S determined from a short-period test may be too small.

Second, if the pumping rate is large and the observation well is near the pumping well, dewatering of the aquifer may be significant, and the assumption that the

transmissivity of the aquifer is constant is not satisfied. The effect of dewatering of the aquifer can be eliminated with the following equation:

$$s' = s - s^2 / (2b) \quad (14)$$

where s is the observed drawdown in the unconfined aquifer, b is the aquifer thickness, and s' is the drawdown that would have occurred if the aquifer had been confined (that is, if no dewatering had occurred).

To determine the transmissivity and storage coefficient of an unconfined aquifer, a data plot consisting of s versus t (or tr^2) is matched with the Theis type curve of $W(u)$ versus $1/u$. Both s and b must be in the same units, either feet or meters.

As noted above, Theis assumed in the development of his equation that the discharging well penetrates the entire thickness of the aquifer. However, because it is not always possible, or necessarily desirable, to design a well that fully penetrates the aquifer under development, most discharging wells are open to only a part of the aquifer that they draw from. Such partial penetration creates vertical flow in the vicinity of the discharging well that may affect drawdowns in observation wells located relatively close to the discharging well. Drawdowns in observation wells that are open to the same zone as the discharging well will be larger than the drawdowns in wells at the same distance from the discharging well but open to other zones. The possible effect of partial penetration on drawdowns must be considered in the analysis of aquifer-test data. If aquifer-boundary and other conditions permit, the problem can be avoided by locating observation wells beyond the zone in which vertical flow exists.

Time-Drawdown Analysis

The Theis equation is only one of several methods that have been developed for the analysis of aquifer-test data. Another somewhat more convenient method, was developed from the Theis equation by C. E. Jacob. The greater convenience of the Jacob method derives partly from its use of semilogarithmic graph paper instead of the logarithmic paper used in the Theis method, and from the fact that, under ideal conditions, the data plot along a straight line rather than along a curve.

However, it is essential to note that, whereas the Theis equation applies at all times and places (if the assumptions are met), Jacob's method applies only under certain additional conditions. These conditions

also must be satisfied in order to obtain reliable answers. To understand the limitations of Jacob's method, the changes that occur in the cone of depression during an aquifer test must be considered. The changes that are of concern involve both the shape of the cone and the rate of drawdown. As the cone of depression migrates outward from a pumping well, its shape (and, therefore, the hydraulic gradient at different points in the cone) changes. We can refer to this condition as unsteady shape. At the start of withdrawals, the entire cone of depression has an unsteady shape (Figure 5-7a). After a test has been underway for some time, the cone of depression begins to assume a relatively steady shape, first at the pumping well and then gradually to greater and greater distances (Figure 5-7b). If withdrawals continue long enough for increases in recharge and/or reductions in discharge to balance the rate of withdrawal, drawdowns cease, and the cone of depression is said to be in a steady state (Figure 5-7c).

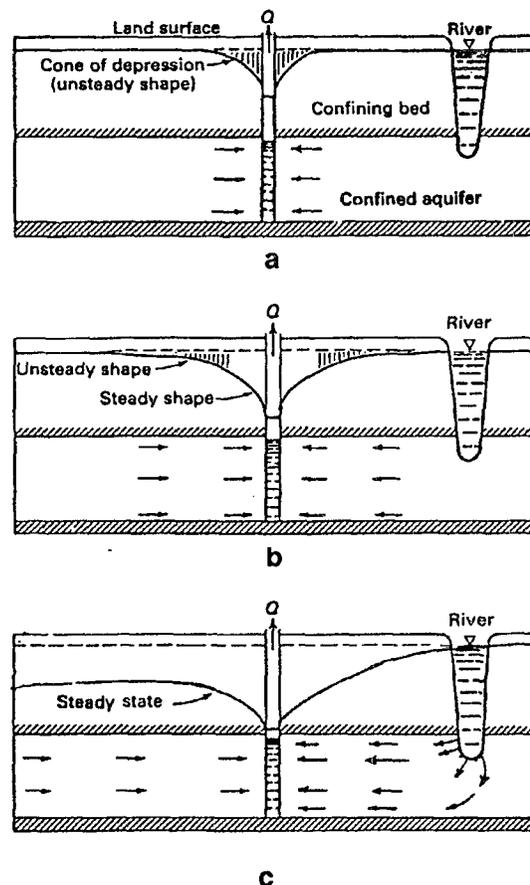


Figure 5-7. Development of Cone of Depression from Start of Pumping to Steady-State

The Jacob method is applicable only to the zone in which steady-shape conditions prevail or to the entire cone only after steady-state conditions have developed. For practical purposes, this condition is met when $u = (r^2 S) / (4Tt)$ is equal to or less than about 0.05.

Substituting this value in the equation for u and solving for t , we can determine the time at which steady-shape conditions develop at the outermost observation well. Thus,

$$t_c = (7,200 r^2 S) / T \quad (15)$$

where t_c is the time, in minutes, at which steady-shape conditions develop, r is the distance from the pumping well, in feet (or meters), S is the estimated storage coefficient (dimensionless), and T is the estimated transmissivity, in square feet per day (or square meters per day).

After steady-shape conditions have developed, the drawdowns at an observation well begin to fall along a straight line on semilogarithmic graph paper, as Figure 5-8 shows. Before that time, the drawdowns plot below the extension of the straight line. When a time-drawdown graph is prepared, drawdowns are plotted on the vertical (arithmetic) axis versus time on the horizontal (logarithmic) axis.

one log cycle, t_0 is the time at the point where the straight line intersects the zero-drawdown line, and r is the distance from the pumping well to the observation well.

These equations are in consistent units. Thus, if Q is in cubic meters per day and s is in meters, T is in square meters per day. S is dimensionless, so that if r is in square meters per day, then r must be in meters and t_0 must be in days.

It is still common practice in the United States to express Q in gallons per minute, s in feet, t in minutes, T in feet, and T in square feet per day. The equations can be modified for direct substitution of these units as follows:

$$T = (2.3Q) / (4\pi\Delta s) = (2.3/4\pi) \times (\text{gal}/\text{min}) \times (1,440 \text{ min}/\text{d}) \times (\text{ft}^3/74.8 \text{ gal}) \times (1/\text{ft}) \quad (18)$$

$$T = (35Q) / s \quad (19)$$

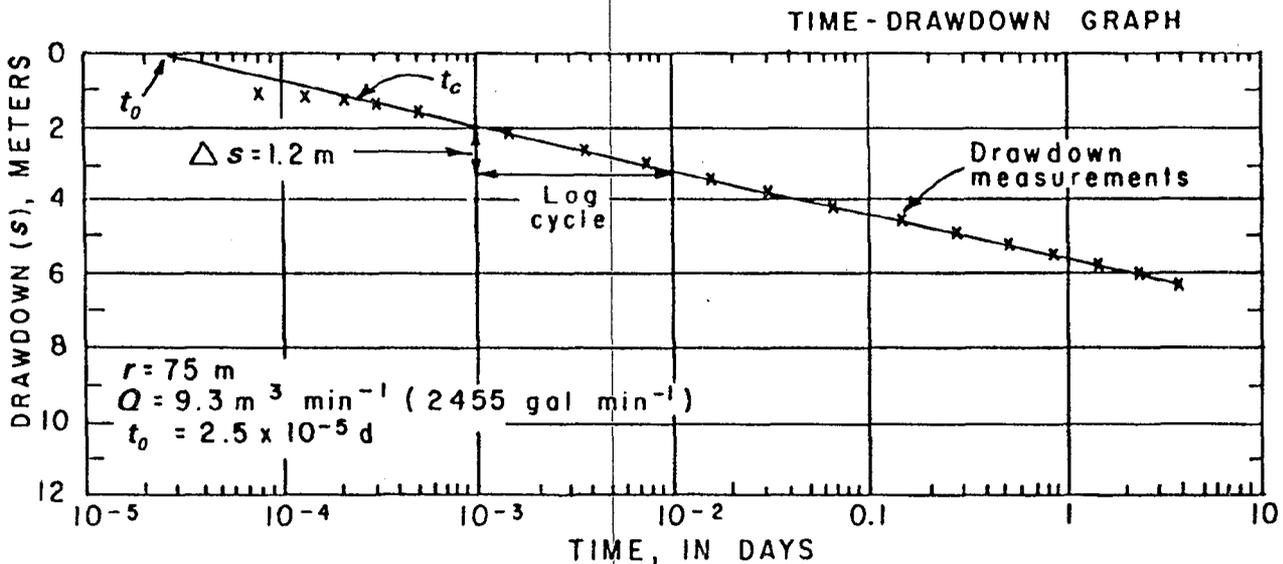


Figure 5-8. Time-Drawdown Graph

The slope of the straight line is proportional to the pumping rate and to the transmissivity. Jacob derived the following equations for determination of transmissivity and storage coefficient from the time-drawdown graphs:

$$T = (2.3Q) / (4\pi\Delta s) \quad (16)$$

$$S = (2.25Tt_0) / r^2 \quad (17)$$

where Q is the pumping rate, Δs is the drawdown across

where T is in square feet per day, Q is in gallons per minute and s is in feet, and

$$S = (2.25Tt_0 / r^2) = (2.25/1) \times (\text{ft}^2/\text{d}) \times (\text{min}/\text{ft}^2) \times (\text{d}/1,440 \text{ min}) \quad (20)$$

$$S = (Tt_0) / (640r^2) \quad (21)$$

where T is in square feet per day, t_0 is in minutes, and r is in feet.

Distance-Drawdown Analysis

Aquifer tests should have at least three observation wells located at different distances from the pumping well (Figure 5-9). Drawdowns measured at the same time in these wells can be analyzed with the Theis equation and type curve to determine the aquifer transmissivity and storage coefficient.

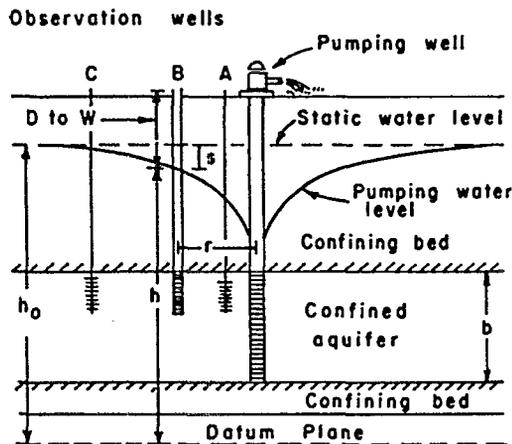


Figure 5-9. Desirable Location for Observation Wells in Aquifer Tests

After the test has been underway long enough, drawdowns in the wells also can be analyzed by the Jacob method, either through the use of a time-drawdown graph using data from individual wells or through the use of a distance-drawdown graph using simultaneous measurements in all of the wells. To determine when sufficient time has elapsed, see the discussion of time-drawdown analysis earlier in this chapter.

In the Jacob distance-drawdown method, drawdowns are plotted on the vertical axis versus distance on the horizontal axis (Figure 5-10). If the aquifer and test conditions satisfy the Theis assumptions and the limitation of the Jacob method, the drawdowns measured at the same time in different wells should plot along a straight line (Figure 5-10).

The slope of the straight line is proportional to the pumping rate and to the transmissivity. Jacob derived the following equations for determination of the transmissivity and storage coefficient from distance-drawdown graphs:

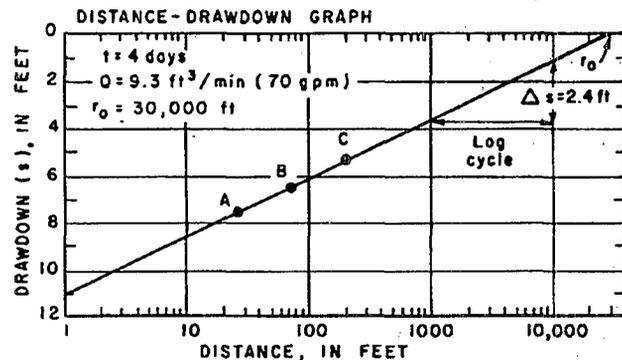


Figure 5-10. Distance-Drawdown Graph

$$T = (2.3Q)/(2\pi\Delta s) \quad (22)$$

$$S = (2.25Tt)/r_0^2 \quad (23)$$

where Q is the pumping rate, Δs is the drawdown across one log cycle, t is the time at which the drawdowns were measured, and r_0 is the distance from the pumping well to the point where the straight line intersects the zero-drawdown line.

These equations are in consistent units. For the inconsistent units still in relatively common use in the United States, the equations should be used in the following forms:

$$T = (70Q)/\Delta s \quad (24)$$

where T is in square feet per day, Q is in gallons per minute, and s is in feet and

$$S = (Tt)/(640r_0^2) \quad (25)$$

where T is in square feet per day, t is in minutes, and r_0 is in feet.

The distance r_0 does not indicate the outer limit of the cone of depression. Because nonsteady-state conditions exist in the outer part of the cone, before the development of steady-state conditions, the Jacob method does not apply to that part. If the Theis equation were used to calculate drawdowns in the outer part of the cone, it would be found that they would plot below the straight line. In other words, the measurable limit of the cone of depression is beyond the distance r_0 .

If the straight line of the distance-drawdown graph is

extended inward to the radius of the pumping well, the drawdown indicated at that point is the drawdown in the aquifer outside of the well. If the drawdown inside the well is found to be greater than the drawdown outside, the difference is attributable to well loss. (See Single-Well Tests.)

The hydraulic conductivities and, therefore, the transmissivities of aquifers may be different in different directions. These differences may cause differences in drawdowns measured at the same time in observation wells located at the same distances but in different directions from the discharging well. Where this condition exists, the distance-drawdown method may yield satisfactory results only where three or more observation wells are located in the same direction but at different distances from the discharging well.

Single-Well Tests

The most useful aquifer tests are multiple-well tests, which are those that include water-level measurements in observation wells. It also is possible to obtain useful data from production wells, even where observation wells are not available. These single-well tests may consist of pumping a well at a single constant rate, or at two or more different but constant rates or, if the well is not equipped with a pump, by instantaneously introducing a known volume of water into the well. The following discussion is limited to tests involving a single constant rate.

In order to analyze the data, the nature of the drawdown in a pumping well must be understood. The total drawdown (s_t) in most, if not all, pumping wells consists of two components (Figure 5-11). One is the drawdown (s_a) in the aquifer, and the other is the drawdown (s_w) that occurs as water moves from the aquifer into the well and up the well bore to the pump intake. Thus, the drawdown in most pumping wells is greater than the drawdown in the aquifer at the radius of the pumping well.

The total drawdown (s_t) in a pumping well can be expressed in the form of the following equations:

$$s_t = s_a + s_w$$

$$s_t = BQ + CQ^2 \quad (26)$$

where s_a is the drawdown in the aquifer at the effective radius of the pumping well, s_w is well loss, Q is the pumping rate, B is a factor related to the hydraulic characteristics of the aquifer and the length of the pumping period, and C is a factor related to the characteristics of the well.

The factor C is normally considered to be constant, so that, in a constant rate test, CQ^2 is also constant. As a result, the well loss (s_w) increases the total drawdown in the pumping well but does not affect the rate of change in the drawdown with time. It is, therefore, possible to analyze drawdowns in the pumping well with

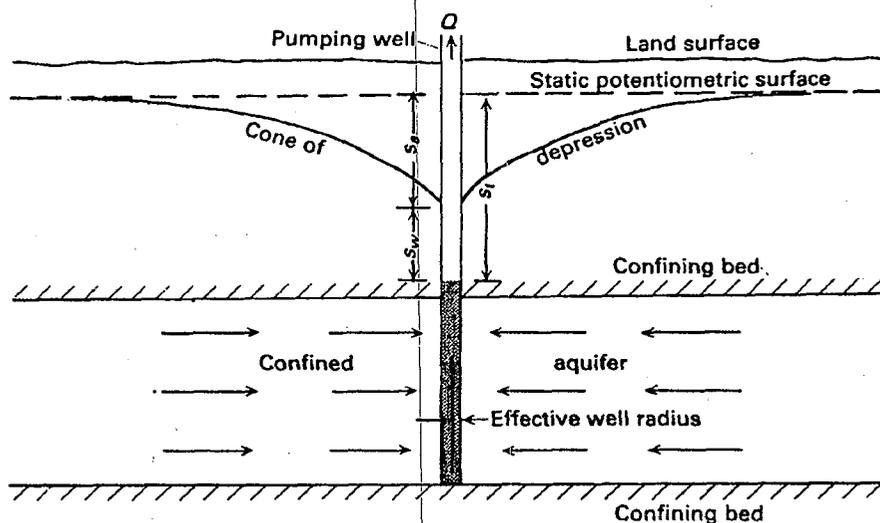


Figure 5-11. Two Components of Total Drawdown in a Pumping Well

the Jacob time-drawdown method using semilogarithmic graph paper. (See "Time-Drawdown Analysis" earlier in this section.) Drawdowns are plotted on the arithmetic scale versus time on the logarithmic scale (Figure 5-12), and transmissivity is determined from the slope of the straight line by using the following equation:

$$T = (2.3Q)/(4\pi\Delta s) \quad (27)$$

Where well loss is present in the pumping well, the storage coefficient cannot be determined by extending the straight line to the line of zero drawdown. Even where well loss is not present, the determination of the storage coefficient from drawdowns in a pumping well likely will be subject to large error because the effective radius of the well may differ significantly from the nominal radius.

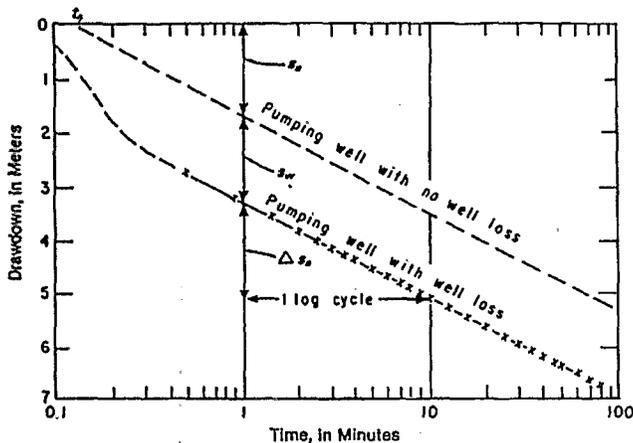


Figure 5-12. Time-Drawdown Plot With and Without Well Loss

In this equation, drawdown in the pumping well is proportional to the pumping rate. The factor B in the aquifer-loss term (BQ) increases with time of pumping as long as water is being derived from storage in the aquifer. The factor C in the well-loss term (CQ^2) is a constant if the characteristics of the well remain unchanged, but, because the pumping rate in the well-loss term is squared, drawdown due to well loss increases rapidly as the pumping rate is increased. The relation between pumping rates and drawdown in a pumping well, if the well was pumped for the same length of time at each rate, is shown in Figure 5-13. The effect of well loss on drawdown in the pumping well is important both for pumping wells data analysis, and supply well design.

Well Interference

Pumping a well causes a drawdown in the ground-water

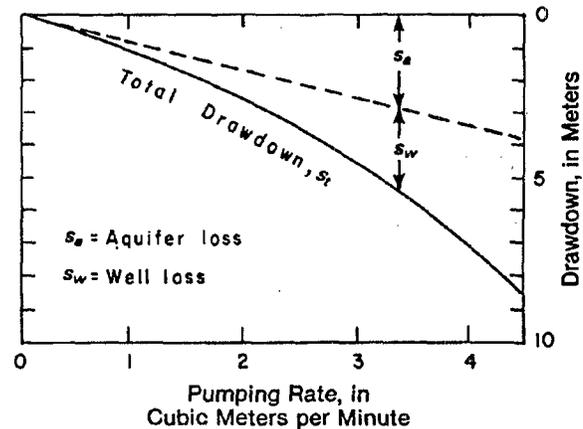


Figure 5-13. Relation of Pumping Rate and Drawdown

level in the surrounding area. The drawdown in water level forms a conical-shaped depression in the water table or potentiometric surface which is referred to as a cone of depression. (See "Cone of Depression" at the beginning of this section.) Similarly a well through which water is injected into an aquifer (that is a recharge or injection well) causes a buildup in ground-water level in the form of a conical-shaped mound.

The drawdown (s) in an aquifer caused by pumping at any point in the aquifer is directly proportional to the pumping rate (Q) and the length of time (t) that pumping has been in progress and is inversely proportional to the transmissivity (T), the storage coefficient (S), and the square of the distance (r^2) between the pumping well and the point. This is represented by the equation:

$$s = (Q,t)/T,S,r^2 \quad (28)$$

Where pumping wells are spaced relatively close together, pumping of one will cause a drawdown in the others. Because drawdowns are additive, the total drawdown in a pumping well is equal to its own drawdown plus the drawdowns caused at its location by other pumping wells (Figures 5-14 and 5-15). The drawdowns in pumping wells caused by withdrawals from other pumping wells are referred to as well interference. As Figure 5-15 shows, a divide forms in the potentiometric surface (or the water table in the case of an unconfined aquifer) between pumping wells.

At any point in an aquifer affected by both a discharging well and a recharging well, the change in water level is

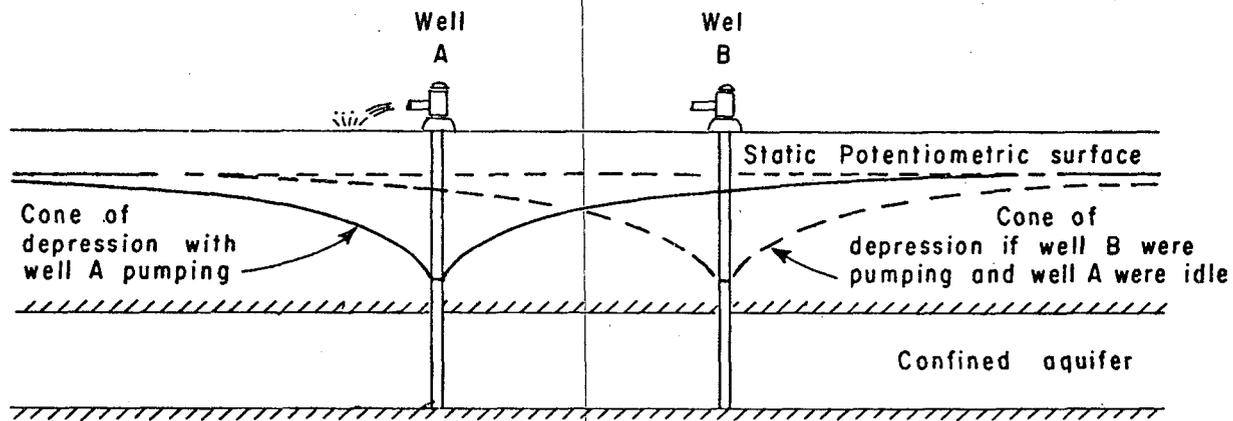


Figure 5-14. Cone of Depression When Well A or B is Pumped

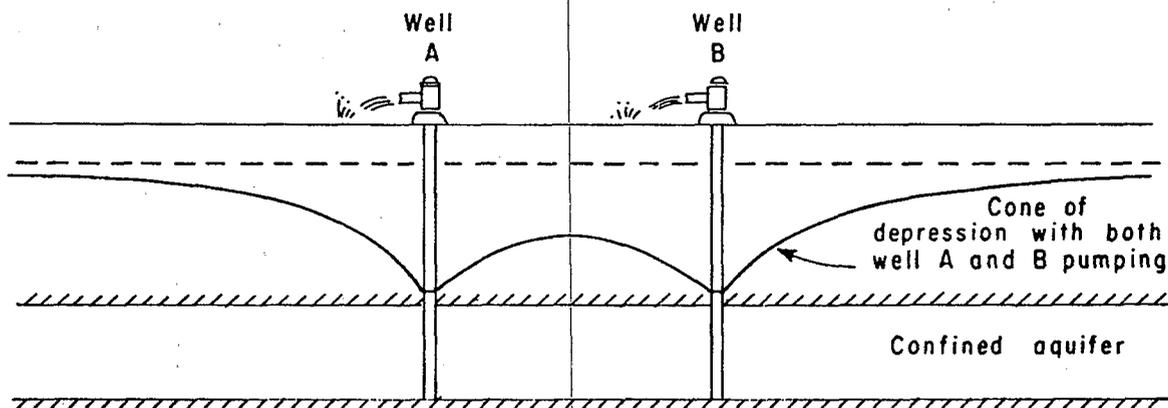


Figure 5-15. Total Drawdown Caused by Overlapping Cones of Depression

equal to the difference between the drawdown and the buildup. If the rates of discharge and recharge are the same and if the wells are operated on the same schedule, the drawdown and the buildup will cancel midway between the wells and the water level at that point will remain unchanged from the static level (Figure 5-16). (See "Aquifer Boundaries" below.)

From the functional equation above, it can be seen that, in the absence of well interference, drawdown in an aquifer at the effective radius of a pumping well is directly proportional to the pumping rate. Conversely,

the maximum pumping rate is directly proportional to the available drawdown. For confined aquifers, available drawdown is normally considered to be the distance between the prepumping water level and the top of the aquifer. For unconfined aquifers, available drawdown is normally considered to be about 60 percent of the saturated aquifer thickness.

Where the pumping rate of a well is such that only a part of the available drawdown is utilized, the only effect of well interference is to lower the pumping level and, thereby, increase pumping costs. In the design of a well

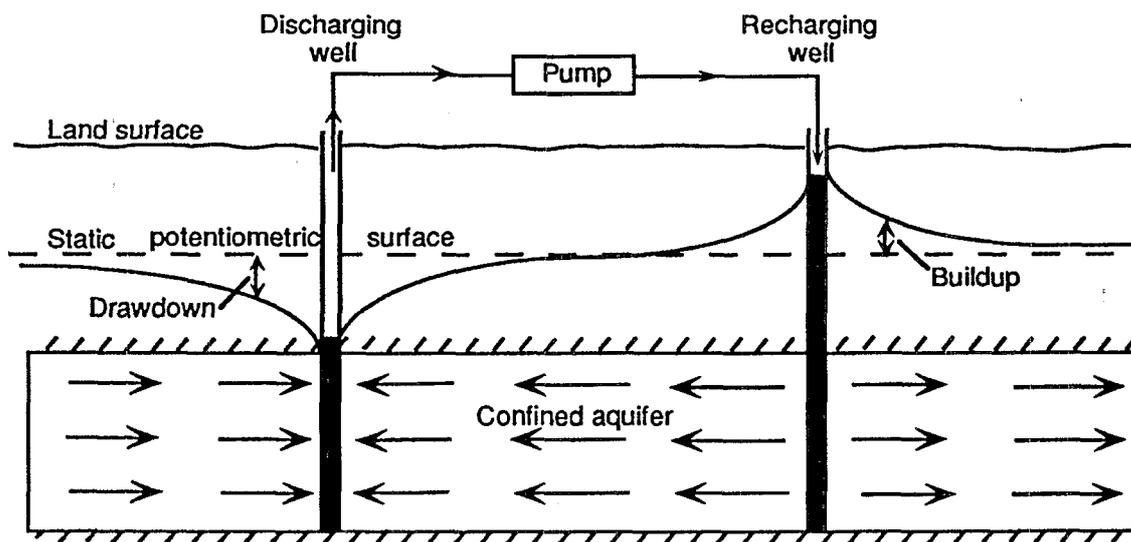


Figure 5-16. Cones of Depression and Buildup Surrounding Discharging and Recharging Wells

field, the increase in pumping cost must be evaluated along with the cost of the additional waterlines and powerlines that must be installed if the spacing of wells is increased to reduce well interference.

Because well interference reduces the available drawdown, it also reduces the maximum yield of a well. Well interference is, therefore, an important matter in the design of well fields where it is desirable for each well to be pumped at the largest possible rate. For a group of wells pumped at the same rate and on the same schedule, the well interference caused by any well on another well in the group is inversely proportional to the square of the distance between the two wells (r^2). Therefore, excessive well interference is avoided by increasing the spacing between wells and by locating the wells along a line rather than in a circle or in a grid pattern.

Aquifer Boundaries

One of the assumptions inherent in the Theis equation (and in most other fundamental ground-water flow equations) is that the aquifer to which it is being applied is infinite in extent. Obviously, no such aquifer exists on Earth. However, many aquifers are areally extensive, and, because pumping will not affect recharge or discharge significantly for many years, most water pumped is from ground-water storage; as a consequence water levels must decline for many years. An excellent example of such an aquifer is that underlying the High Plains from Texas to South Dakota.

All aquifers are vertically and horizontally bounded. Vertical boundaries may include the water table, the plane of contact between each aquifer and each confining bed, and the plane marking the lower limit of the zone of interconnected openings—in other words, the base of the ground-water system.

Hydraulically, aquifer boundaries are of two types: recharge boundaries and impermeable boundaries. A recharge boundary is a boundary along which flow lines originate. Under certain hydraulic conditions, this boundary will serve as a source of recharge to the aquifer. Examples of recharge boundaries include the zones of contact between an aquifer and a perennial stream that completely penetrates the aquifer or the ocean.

An impermeable boundary is a boundary that flow lines do not cross. Such boundaries exist where aquifers terminate against impermeable material. Examples include the contact between an aquifer composed of sand and a laterally adjacent bed composed of clay.

The position and nature of aquifer boundaries are critical to many ground-water problems, including those involved in the movement and fate of pollutants and the response of aquifers to withdrawals. Depending on the direction of the hydraulic gradient, a stream, for example, may be either the source or the destination of a pollutant.

Lateral boundaries within the cone of depression have a profound effect on the response of an aquifer to

withdrawals. To analyze or predict the effect of a lateral boundary, it is necessary to "make" the aquifer appear to be of infinite extent by using imaginary wells and the theory of images. Figures 5-17 and 5-18 show, in both plan view and profile, how image wells are used to compensate hydraulically for the effects of both recharging and impermeable boundaries. (See "Well Interference" earlier in this section.)

The key feature of a recharge boundary is that withdrawals from the aquifer do not produce drawdowns across the boundary. A perennial stream in intimate contact with an aquifer represents a recharge boundary because pumping from the aquifer will induce recharge from the stream. The hydraulic effect of a recharge boundary can be duplicated by assuming that a recharging image well is present on the side of the boundary opposite the real discharging well. Water is injected into the image well at the same rate and on the same schedule that water is withdrawn from the real well. In the plan view in Figure 5-17, flow lines originate at the boundary and equipotential lines parallel the boundary at the closest point to the pumping (real) well.

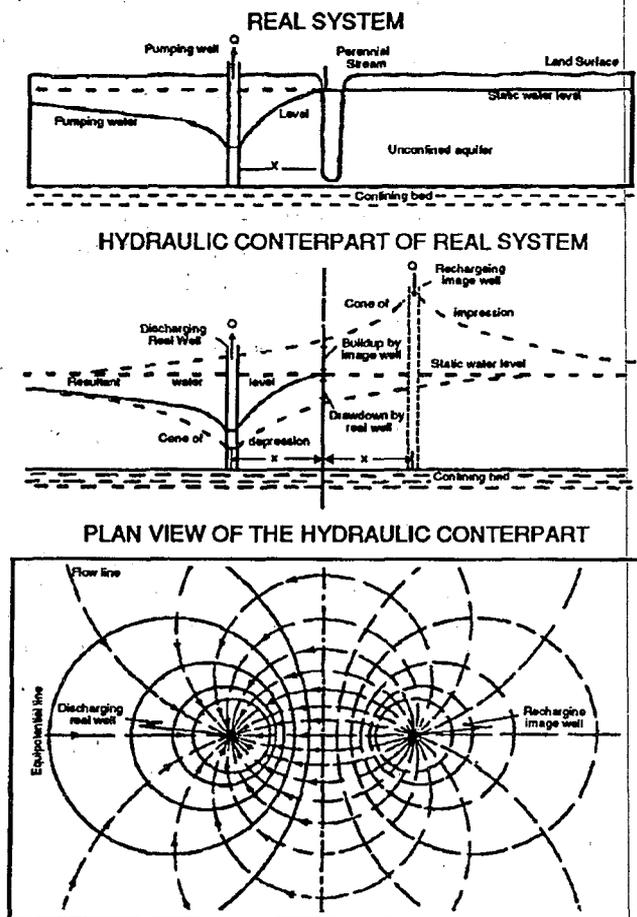


Figure 5-17. Recharge or Positive Boundary

The key feature of an impermeable boundary is that no water can cross it. Such a boundary, sometimes termed a "no-flow boundary," resembles a divide in the water table or the potentiometric surface of a confined aquifer. The effect of an impermeable boundary can be duplicated by assuming that a discharging image well is present on the side of the boundary opposite the real discharging well. The image well withdraws water at the same rate and on the same schedule as the real well. Flow lines tend to parallel an impermeable boundary and equipotential lines intersect it at a right angle.

The image-well theory is an essential tool in the design of well fields near aquifer boundaries. To minimize lowering water levels, apply the following conditions:

1. Pumping wells should be located parallel to and as close as possible to recharging boundaries.
2. Pumping wells should be located perpendicular to and as far as possible from impermeable boundaries.

Figures 5-17 and 5-18 illustrate the effect of single

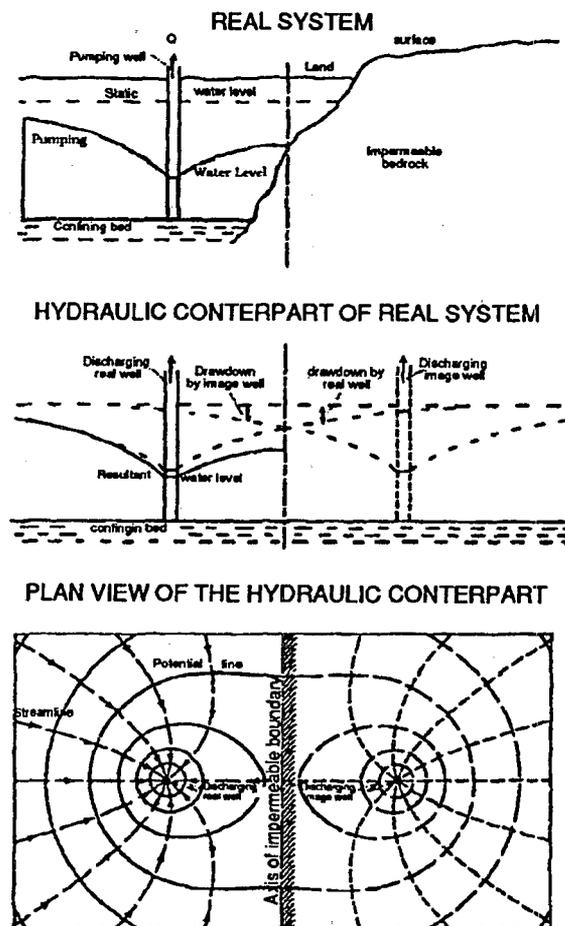


Figure 5-18. Discharge or Negative Boundary

boundaries and show how their hydraulic effect is compensated for through the use of single image wells. It is assumed in these figures that other boundaries are so remote that they have a negligible effect on the areas depicted. At many places, however, pumping wells are affected by two or more boundaries. One example is an alluvial aquifer composed of sand and gravel bordered on one side by a perennial stream (a recharge boundary) and on the other by impermeable bedrock (an impermeable boundary).

Contrary to first impression, these boundary conditions cannot be satisfied with only a recharging image well and a discharging image well. Additional image wells are required, as Figure 5-19 shows, to compensate for the effect of the image wells on the opposite boundaries. Because each additional image well affects the opposite boundary, it is necessary to continue adding image wells until their distances from the boundaries are so great that their effect becomes negligible.

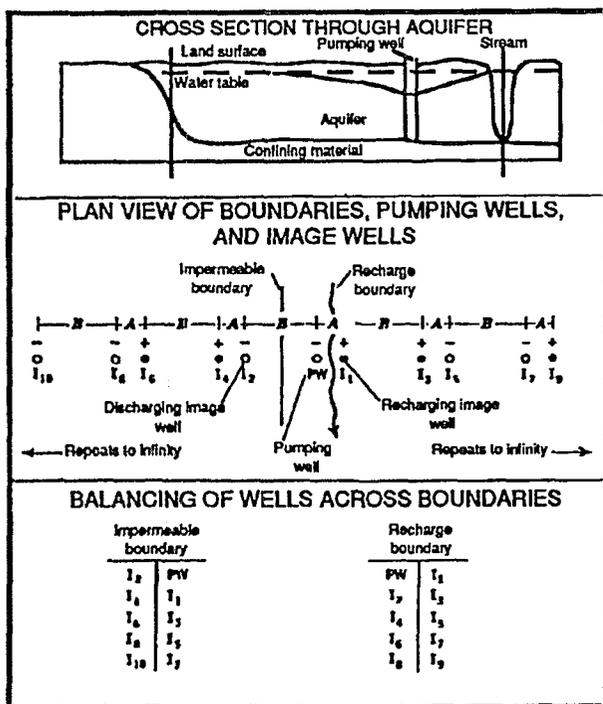


Figure 5-19. A Sequence of Image Wells

Tests Affected By Lateral Boundaries

When an aquifer test is conducted near one of the lateral boundaries of an aquifer, the drawdown data depart from the Theis type curve and from the initial straight line produced by the Jacob method. The hydraulic effect of lateral boundaries is assumed, for analytical convenience, to be due to the presence of other wells. (See "Aquifer Boundaries" earlier in this

section.) Thus, a recharge boundary has the same effect on drawdowns as a recharging image well located across the boundary and at the same distance from the boundary as the real well. The image well is assumed to operate on the same schedule and at the same rate as the real well. Similarly, an impermeable boundary has the same effect on drawdowns as a discharging image well.

To analyze aquifer-test data affected by either a recharge boundary or an impermeable boundary, the early drawdown data in the observation wells nearest the pumping well must not be affected by the boundary. These data, then, show only the effect of the real well and can be used to determine the transmissivity (T) and the storage coefficient (S) of the aquifer. (See "Analysis of Aquifer-Test Data" and "Time-Drawdown Analysis" earlier in this section.) In the Theis method, the type curve is matched to the early data and a "match point" is selected to calculate the values of T and S. The position of the type curve in the region where the drawdowns depart from the type curve is traced onto the data plot (Figures 5-20 and 5-21). The trace of the type curve shows where the drawdowns would have plotted if there had been no boundary effect. The differences in drawdown between the data plot and the trace of the type curve show the effect of an aquifer boundary. The direction in which the drawdowns depart from the type curve—that is in the direction of either greater drawdowns or lesser drawdowns—shows the type of boundary.

Drawdowns greater than those defined by the trace of the type curve indicate the presence of an impermeable boundary because, as noted above, the effect of such boundaries can be duplicated with an imaginary discharging well. Conversely, a recharge boundary causes drawdowns to be less than those defined by the trace of the type curve.

In the Jacob method, drawdowns begin to plot along a straight line after the test has been underway for some time (Figures 5-22 and 5-23). The time at which the straight-line plot begins depends on the values of T and S of the aquifer and on the square of the distance between the observation well and the pumping well. (See "Time-Drawdown Analysis" earlier in this section.) Values of T and S are determined from the first straight-line segment defined by the drawdowns after the start of the aquifer test. The slope of this straight line depends on the transmissivity (T) and on the pumping rate (Q). If a boundary is present, the drawdowns will depart from the first straight-line segment and begin to fall along another straight line.

According to image-well theory, the effect of a recharge boundary can be duplicated by assuming that water is

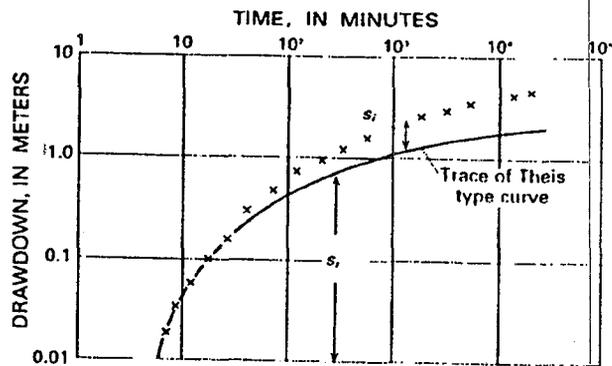


Figure 5-20. Theis Time-Drawdown Plot Showing a Negative Boundary

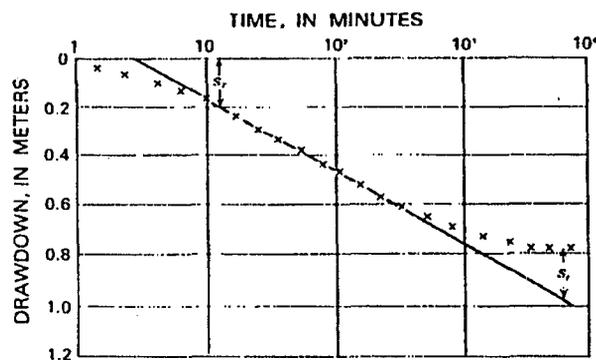


Figure 5-23. Jacob Time-Drawdown Plot Showing a Positive Boundary

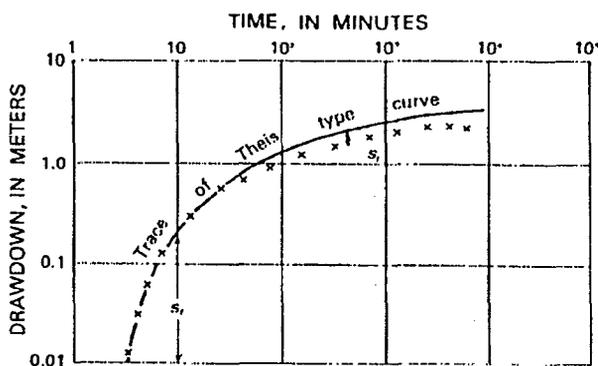


Figure 5-21. Theis Time-Drawdown Plot Showing a Positive Boundary

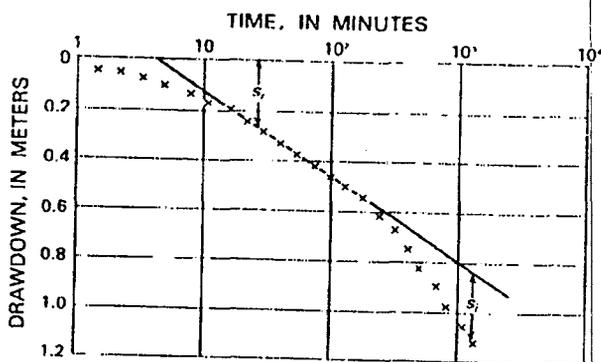


Figure 5-22. Jacob Time-Drawdown Plot Showing a Negative Boundary

injected into the aquifer through a recharging image well at the same rate that water is being withdrawn from the real well. It follows, therefore, that, when the full effect of a recharge boundary is felt at an observation well, there will be no further increase in drawdown and the water level in the well will stabilize. At this point in both the Theis and the Jacob methods, drawdowns plot along a straight line having a constant drawdown. Conversely, an impermeable boundary causes the rate of drawdown to increase. In the Jacob method, as a result, the drawdowns plot along a new straight line having twice the slope as the line drawn through the drawdowns that occurred before the boundary effect was felt.

The Jacob method should be used carefully when it is suspected that an aquifer test may be affected by boundary conditions. In many cases, the boundary begins to affect drawdowns before the method is applicable, the result being that T and S values determined from the data are erroneous and the effect of the boundary is not identified. When it is suspected that an aquifer test may be affected by boundary conditions, the data should, at least initially, be analyzed with the Theis method.

The position and the nature of many boundaries are obvious. For example, the most common recharge boundaries are streams and lakes; possibly, the most common impermeable boundaries are the bedrock walls of alluvial valleys. The hydraulic distance to these boundaries, however, may not be obvious. A stream or lake may penetrate only a short distance into an aquifer and their bottoms may be underlain by fine-grained material that hampers movement of water into the aquifer. Hydraulically, the boundaries formed by these surface-water bodies will appear to be farther from the

pumping well than the near shore. Similarly, if a small amount of water moves across the bedrock wall of a valley, the hydraulic distance to the impermeable boundary will be greater than the distance to the valley wall.

Fortunately, the hydraulic distance to boundaries can be determined from aquifer-test data analysis. According to the Theis equation, for equal drawdowns caused by the real well and the image well (in other words, if $s_r = s_i$), then

$$r_r^2/t_r = r_i^2/t_i \quad (29)$$

where r_r is the distance from the observation well to the real well, r_i is the distance from the observation well to the image well, t is the time at which a drawdown of s is caused by the real well at the observation well, and t_i is the time at which a drawdown of s_i is caused by the image well at the observation well.

Solving this equation for the distance to the image well from the observation well, results in

$$r_i = r_r(t_i/t_r)^{1/2} \quad (30)$$

The image well is located at some point on a circle having a radius of r_i centered on the observation well (Figure 5-24). Because the image well is the same distance from the boundary as the real well, the boundary must be located halfway between the image well and the pumping well (Figure 5-24).

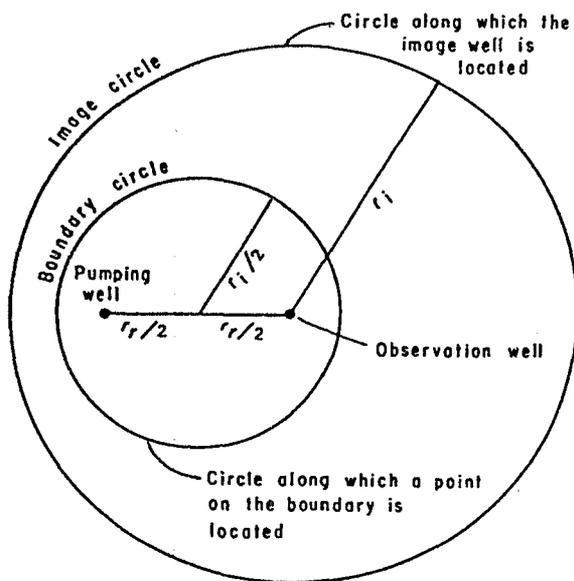


Figure 5-24. Method for Determining Location of Boundary

If the boundary is a stream or valley wall or some other feature whose physical position is obvious, its "hydraulic position" may be determined by using data from a single observation well. If, on the other hand, the boundary is the wall of a buried valley or some other feature not obvious from the land surface, distances to the image well from three observation wells may be needed to identify the position of the boundary.

Tests Affected By Leaky Confining Beds

In the development of the Theis equation for aquifer-test data analysis, it was assumed that all water discharged from the pumping well was derived instantaneously from storage in the aquifer. (See "Analysis of Aquifer-Test Data" earlier in this section.) Therefore, in the case of a confined aquifer, at least during the period of the test, the movement of water into the aquifer across its overlying and underlying confining beds is negligible. This assumption is satisfied by many confined aquifers. Many other aquifers, however, are bounded by leaky confining beds that transmit water into the aquifer in response to the withdrawals and cause drawdowns to differ from those that would be predicted by the Theis equation. The analysis of aquifer tests conducted on these aquifers requires the use of the methods that have been developed for semiconfined aquifers (also referred to in ground-water literature as "leaky aquifers").

Figures 5-25, 5-26, and 5-27 illustrate three different conditions commonly encountered in the field. Figure 5-25 shows a confined aquifer bounded by thick, impermeable confining beds. Water initially pumped from such an aquifer is from storage, and aquifer-test data can be analyzed by using the Theis equation. Figure 5-26 shows an aquifer overlain by a thick, leaky confining bed that, during an aquifer test, yields significant water from storage. The aquifer in this case may properly be referred to as a semiconfined aquifer, and the release of water from storage in the confining bed affects the analysis of aquifer-test data. Figure 5-27 shows an aquifer overlain by a thin confining bed that does not yield significant water from storage but that is sufficiently permeable to transmit water from the overlying unconfined aquifer into the semiconfined aquifer. Methods have been devised largely by Madhi Hantush and C. E. Jacob, 1955, for use in analyzing the leaky conditions illustrated in Figures 5-26 and 5-27.

These methods use matching data plots with type curves, as the Theis method does. The major difference is that, whereas the Theis method uses a single type curve, the methods applicable to semiconfined aquifers involve "families" of type curves, each curve of which reflects different combinations of the hydraulic characteristics of the aquifer and the confining beds.

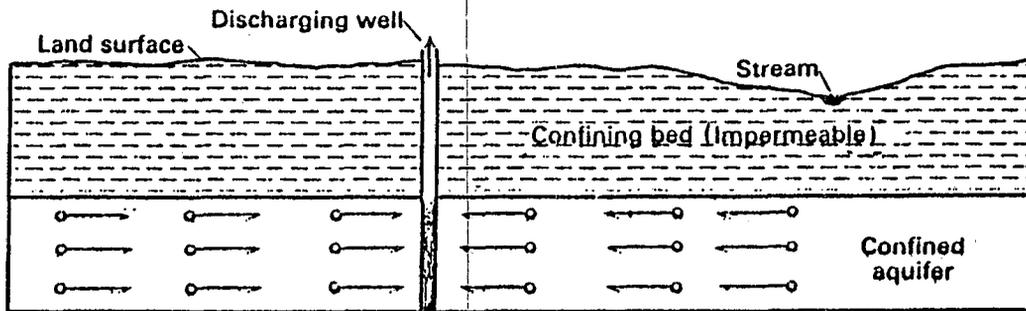


Figure 5-25. Nonleaky Artesian Conditions

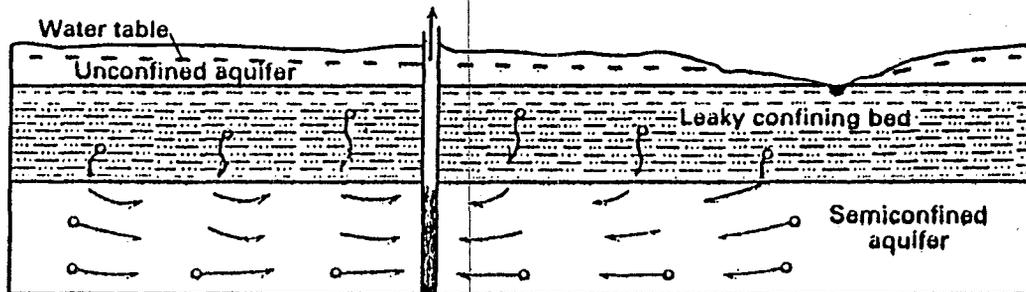


Figure 5-26. Semiconfined Aquifer with Leakage From Confining Bed

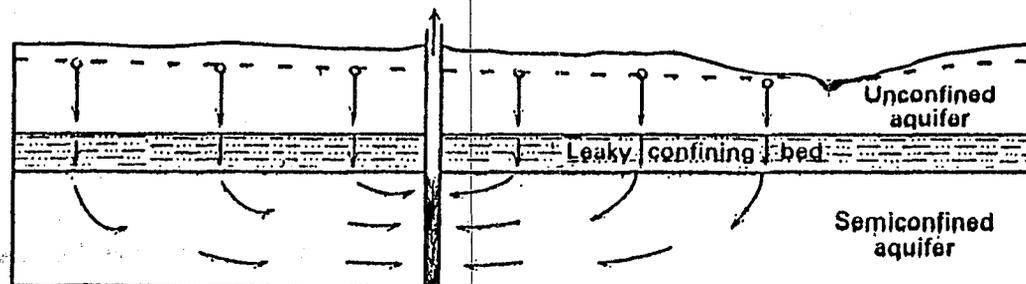


Figure 5-27. Semiconfined Aquifer with Leakage Through a Confining Bed

Data plots of s versus t on logarithmic graph paper for aquifer tests affected by release of water from storage in the confining beds are matched to the family of type curves illustrated in Figure 5-28. For convenience, these curves are referred to as Hantush type. Four match-point coordinates are selected and substituted into the following equations to determine values of T and S :

$$T = (QH(u, \beta)) / (4\pi s) \quad (31)$$

$$S = (4Ttu) / r^2 \quad (32)$$

aquifer tests affected by leakage of water across confining beds are matched to the family of type curves shown in Figure 5-29. These type curves are based on equations developed by Hantush and Jacob and, for convenience, will be referred to as the Hantush-Jacob curves. The four coordinates of the match point are substituted into the following equations to determine T and S :

$$T = QW(u, r/B) / (4\pi s) \quad (33)$$

$$S = 4Ttu / r^2 \quad (34)$$

Data plots of s versus t on logarithmic graph paper for In planning and conducting aquifer tests, hydrologists

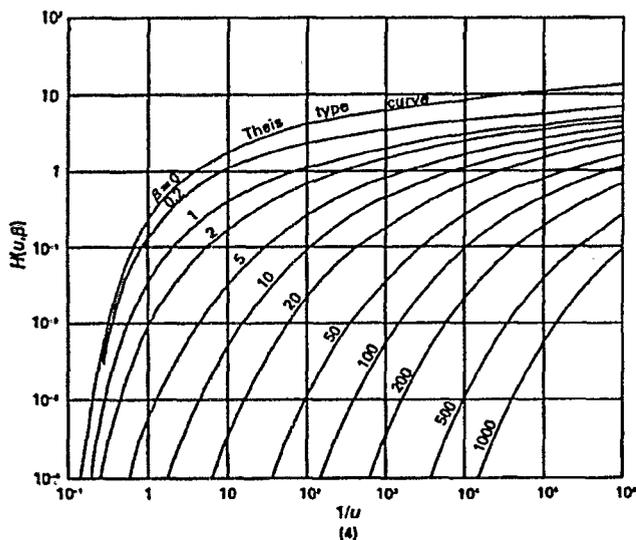


Figure 5-28. Hantush Type Curves for Semiconfined Aquifers that Receive Water From Storage in Confining Beds

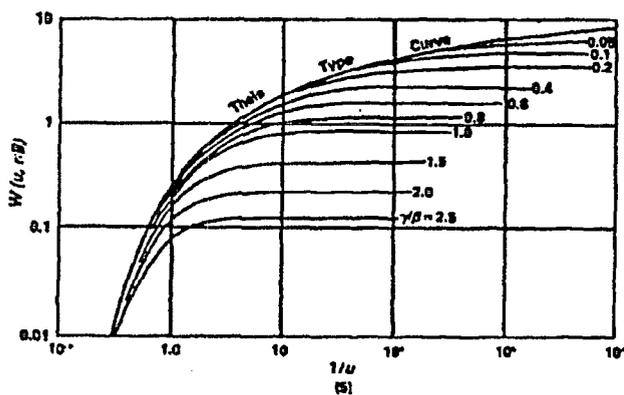


Figure 5-29. Hantush-Jacob Curves for Aquifers Receiving Leakage Across Confining Beds

must give careful consideration to the hydraulic characteristics of the aquifer and to the type of boundary conditions (either recharge or impermeable) that are likely to exist in the vicinity of the test site. Following completion of the test, the next problem is to select the method of analysis that most closely represents the geologic and hydrologic conditions in the area affected by the test. When these conditions are not well known, the common practice is to prepare a data plot of s versus t on logarithmic paper and match it with the Theis type curve. If the data closely match the type curve, the values of T and S determined by using the Theis

equation should be reliable. Significant departures of the data from the type curve generally reflect the presence of lateral boundaries or leaky confining beds. Both the geology of the area and the shape of the data plot may provide clues as to which of these conditions most likely exist. It is important to note however that some data plots for tests affected by impermeable boundaries are similar in shape to the Hantush curves.

SPECIFIC CAPACITY AND TRANSMISSIVITY

The specific capacity of a well depends both on the hydraulic characteristics of the aquifer and on the construction and other features of the well. Values of specific capacity available for many supply wells for which aquifer-test data are not available are widely used by hydrologists to estimate transmissivity. Such estimates are used to evaluate regional differences in transmissivity and to prepare transmissivity maps for use in models of ground-water systems.

The factors that affect specific capacity include:

1. The transmissivity of the zone supplying water to the well which, depending on the length of the screen or open hole, may be considerably less than the transmissivity of the aquifer.
2. The storage coefficient of the aquifer.
3. The length of the pumping period.
4. The effective radius of the well, which may be significantly greater than the "nominal" radius.
5. The pumping rate.

The Theis equation can be used to evaluate the effect of the first four factors on specific capacity. The last factor, pumping rate, affects the well loss and can be determined only from a stepped-rate test or an aquifer test in which drawdowns are measured in both the pumping well and observation wells.

The Theis equation modified for the determination of transmissivity from specific capacity is

$$T = W(u)/4\pi \times Q/s \quad (35)$$

where T is transmissivity, Q/s is specific capacity, Q is the pumping rate, s is the drawdown, and $W(u)$ is the well function of u where

$$u = (r^2 S)/(4Tt) \quad (36)$$

where r is the effective radius of the well, S is the storage coefficient, and t is the length of the pumping period preceding the determination of specific capacity.

For convenience in using this equation it is desirable to

express $W(u)/4\pi$ as a constant. To do so it is first necessary to determine values for u and, using a table of values of u (or $1/u$) and $W(u)$, determine the corresponding values for $W(u)$.

Values of u are determined by substituting in the equation values of T , S , r , and t that are representative of conditions in the area. For example, assume that in an area under investigation and for which a large number of values of specific capacity are available, that:

1. The principal aquifer is confined and aquifer tests indicate that it has a storage coefficient of about 2×10^{-4} and a transmissivity of about $11,000 \text{ ft}^2 \text{ d}^{-1}$.
2. Most supply wells are 8 in. (20 cm) in diameter (radius 0.33 ft).
3. Most values of specific capacity are based on 12-hour well acceptance tests ($t = 0.5 \text{ d}$).

Substituting these values, results in

$$u = (r^2 S)/(4Tt) = (0.33 \text{ ft})^2 \times (2 \times 10^{-4}) / (4 \times (11,000 \text{ ft}^2 \text{ d}^{-1}) \times 0.5 \text{ d}) \quad (37)$$

$$u = (2.22 \times 10^{-5} \text{ ft}^2) / (2.2 \times 10^4 \text{ ft}^2) = 1.01 \times 10^{-9} \quad (38)$$

A table of values of $W(u)$ for values of $1/u$ is contained in Table 5-1. Therefore the value of u determined above must be converted to $1/u$ which is 9.91×10^8 and this value is used to determine the value of $W(u)$. Values of $W(u)$ are given for values of $1/u$ of 7.69×10^8 and 10×10^8 but not for 9.91×10^8 . However the value of 10 is close enough to 9.91 for the purpose of estimating transmissivity from specific capacity. From Table 5-1 we determine that, for a value of $1/u$ of 10×10^8 , the value of $W(u)$ is 20.15. Substituting this value we find the constant $W(u)/4\pi$ to be 1.60.

In using the equation, modified as necessary to fit the conditions in an area, it is important to recognize its limitations. Among the most important factors that affect its use are the accuracy with which the thickness of the zone supplying water to the well can be estimated, the magnitude of the well loss in comparison with drawdown in the aquifer, and the difference between the "nominal" radius of the well and its effective radius.

Relative to these factors the common practice is to assume that the value of transmissivity estimated from specific capacity applies only to the screened zone or to the open hole. To apply this value to the entire aquifer, the transmissivity is divided by the length of the screen or open hole (to determine the hydraulic conductivity per unit of length) and the result is multiplied by the entire thickness of the aquifer. The value of transmissivity

determined by this method is too large if the zone supplying water to the well is thicker than the length of the screen or the open hole. Similarly, if the effective radius of the well is larger than the "nominal" radius (assuming that the "nominal" radius is used in the equation), the transmissivity based on specific capacity again will be too large.

On the other hand, if a significant part of the drawdown in the pumping well is due to well loss, the transmissivity based on specific capacity will be too small. Whether the effects of all three of these factors cancel out depends on the characteristics of both the aquifer and the well.

REFERENCES

Bouwer, Herman, 1978, *Groundwater hydrology*: New York, McGraw-Hill, 480p.

Ferris, J. G., D.B. Knowles, R.H. Brown, and R.W. Stallman, 1962, *Theory of aquifer tests*: U.S. Geol. Survey Water-Supply Paper 1536-E, pp. E69-E174.

Fetter, C. W., Jr., 1980, *Applied hydrogeology*: Columbus, Charles E. Merrill, 488p.

Freeze, R. A., and J.A. Cherry, 1979, *Groundwater*: Englewood Cliffs, N.J., Prentice Hall, 604p.

Hantush, M. S., and C.E. Jacob, 1955, Non-steady radial flow in an infinite leaky aquifer: *Trans. of the Amer. Geophysical Union*, v. 36, no. 1, pp. 95-100.

Hantush, M. S., 1960, Modification of the theory of leaky aquifers: *Jour. of Geophysical Research*, v. 65, no. 11, pp. 3713-3725.

Heath, R. C., and F.W. Trainer, 1981, *Introduction to ground-water hydrology*: Worthington, Ohio, Water-Well Journal Publishing Co., 285p.

Jacob, C. E., 1946, Radial flow in a leaky artesian aquifer: *Trans. of the Amer. Geophysical Union*, v. 27, no. 2, pp. 198-205.

Jacob, C. E., 1950, *Flow of ground water in Rouse, Hunter, Engineering hydraulics*: New York, John Wiley, chapter 5, pp. 321-386.

Jacob, C. E., 1963, Determining the permeability of water-table aquifers: U.S. Geol. Survey Water-Supply Paper 1536-1, pp. 1245-1271.

Lohman, S. W., 1972, *Ground-water hydraulics*: U.S. Geol. Survey Professional Paper 708, 70p.

McClymonds, N. E., and O.L. Franke, 1972, Water-transmitting properties of aquifers on Long Island, New York: U.S. Geol. Survey Professional Paper 627-E, 24p.

Meinzer, O. E., 1923, The occurrence of ground water in the United States, with a discussion of principles: U.S. Geol. Survey Water-Supply Paper 489, 321p.

Moulder, E. A., 1963, Locus circles as an aid in the location of a hydrogeologic boundary in Bentall, Ray, comp., Shortcuts and special problems in aquifer tests: U.S. Geol. Survey Water-Supply Paper 1545-C, pp. C110-C115.

Stallman, R. W., 1971, Aquifer-test design, observations, and data analysis: U.S. Geol. Survey Techniques of Water-Resources Investigations, Book 3, Chapter B1, 26p.

Theis, C. V., 1935, The relation between the lowering of the piezometric surface and the rate and duration of discharge of a well using ground-water storage: Trans. of the Amer. Geophysical Union, v. 16, pp. 519-524.

Theis, C. V., 1940, The source of water derived from wells, essential factors controlling the response of an aquifer to development: Civil Engineering, v. 10, no. 5, pp. 277-280.

Todd, D. K., 1980, Groundwater hydrology, 2d ed.: New York, John Wiley, 535p.

Walton, W. C., 1970, Groundwater resource evaluation: New York, McGraw-Hill, 664p.

MODELS AND COMPUTERS IN GROUND-WATER INVESTIGATIONS

Models, in the broadest sense, are simplified descriptions of an existing physical system. Any ground-water investigation that does more than simply collect and tabulate data involves modeling. A preliminary model, or hypothesis, describing the ground-water system is tested by collecting data. If the data fit the hypothesis, the model is accepted; otherwise, the model must be revised. Models can be (1) qualitative descriptions of how processes operate in a system; (2) simplified physical representations of the system such as "sand tank" physical aquifer models and laboratory batch experiments to measure adsorption isotherms; and (3) mathematical representations of the physical system.

This chapter focuses on models that can be expressed in mathematical form and adapted for use in computer codes. The American Society for Testing and Materials (ASTM) defines model and computer code as follows (ASTM, 1984):

A model is an assembly of concepts in the form of a mathematical equation that portrays understanding of a natural phenomenon.

A computer code is the assembly of numerical techniques, bookkeeping, and control languages that represents the model from acceptance of input data and instruction to delivery of output.

Modeling with computers is a specialized field that requires considerable training and experience. In the last few decades, literally hundreds of computer codes for simulating various aspects of ground-water systems have been developed. Refinements to existing codes and development of new codes proceed at a rapid pace. This chapter provides a basic understanding of modeling and data analysis with computers, including (1) their uses; (2) basic hydrogeologic parameters that define their type and capabilities; (3) classification according to mathematical approach and major types of hydrogeologic parameters simulated; (4) special

management considerations in their use; and (5) their limitations.

Uses of Models and Computers

The great advantage of the computer is that large amounts of data can be manipulated quickly, and experimental modifications can be made with minimal effort, so that many possible situations for a given problem can be studied in great detail. The danger is that without proper selection, data collection and input, and quality control procedures, the computer's usefulness can be quickly undermined, bringing to bear the adage "garbage in, garbage out."

Computer codes involving ground water can be broadly categorized as (1) predictive, (2) resource optimizing, or (3) manipulative. Predictive codes simulate physical and chemical processes in the subsurface to provide estimates of how far, how fast, and in what directions a contaminant may travel. These are the most widely used codes and are the focus of most of this chapter.

Resource-optimizing codes combine constraining functions (e.g., total pumpage allowed) and optimization routines for objective functions (e.g., optimization of well field operations for minimum cost or minimum drawdown/pumping lift) with predictive codes. The U.S. Forest Service's multiple-objective planning process for management of national forests makes extensive use of resource-optimizing codes (Iverson and Alston, 1986). The availability of such codes for ground-water management is limited and is not a very active area of research and development (van der Heijde and others, 1985).

Manipulative codes primarily process and format data for easier interpretation or to assist in data input into predictive and resource-optimizing codes. A specific computer code may couple one or more of these types

of codes. For example, codes that facilitate data entry (preprocessors) and data output (postprocessors) are becoming an increasingly common feature of predictive codes.

Government Decision-Making

Computers can assist government decisions concerning ground-water evaluation/protection in the areas of (1) policy formulation, (2) rule-making, and (3) regulatory action.

A study by the Holcomb Research Institute (1976) of environmental modeling and decision-making in the United States provides a good overview of modeling for policy formulation, although most of the case studies involve surface water and resources other than ground water. The Office of Technology Assessment (1982) more specifically addresses the use of water resource models for policy formulation.

The U.S. EPA's Underground Injection Control Program regulations on restrictions and requirements for Class I wells exemplify the use of modeling to assist in rule-making (Proposed Rules: 52 Federal Register 32446-32476, August 27, 1987; Final Rules: 53 Federal Register 28118-28157, July 26, 1988). The 10,000-year no-migration standard in 40 CFR 128.20(a)(1) for injected wastes is based, in part, on numerical modeling of contaminant transport in four major hydrogeologic settings by Ward and others (1987). Furthermore, worst-case modeling of typical injection sites by EPA formed the basis for the decision not to require routine modeling of dispersion in no-migration petitions.

Ground-water flow and, possibly, solute transport modeling are required to obtain a permit to inject hazardous wastes into Class I wells. Permitting decisions involving activities that may pose a threat to ground-water quality, such as landfills and surface storage of industrial wastes, commonly require ground-water simulations to demonstrate that no hazard exists. U.S. EPA (1987) provides a good overview of the use of models in managing ground-water protection programs.

Site Assessment and Remediation

Use of modeling and computer codes can be valuable in three phases of site-specific ground-water investigations: (1) site characterization, (2) exposure assessment, and (3) remediation assessment.

Site Characterization. Relatively simple models (such as analytic solutions) may be useful at the early stage for roughly defining the possible magnitude of a

contaminant problem. Solute transport models that account for dispersion but not retardation may be useful in providing a worst-case analysis of the situation. They may help in defining the size of the area to be studied and in siting of monitoring wells. If more sophisticated computer modeling is planned, the specific code to be used will, to a certain extent, guide site characterization efforts by the aquifer parameters required as inputs to the model. Site characterization, particularly where water-quality samples are tested for possible organic contaminants, can generate large amounts of data. Computers are invaluable in compiling and processing these data.

Exposure Assessment. There is growing use of exposure assessments across EPA's regulatory programs (U.S. EPA, 1987). In the case of ground-water contamination, the results of an exposure assessment will often determine whether remediation will be required.

Remediation. Predictive models can be particularly valuable in estimating the possible effectiveness of alternative approaches to remediating ground-water contamination (Boutwell and others, 1985). Table 6-1 summarizes the types of modeling required for various remediation design features.

Hydrogeologic Model Parameters

All modeling involves simplifying assumptions concerning parameters of the physical system that is being simulated. Furthermore, these parameters will influence the type and complexity of the equations that are used to represent the model mathematically. There are six major parameters of ground-water systems that must be considered when developing or selecting a computer code for simulating ground-water flow and six additional parameters for contaminant transport.

Ground-Water Flow Parameters

Type of Aquifer. Confined aquifers of uniform thickness are easier to model than unconfined aquifers because the transmissivity remains constant. The thickness of unconfined aquifers varies with fluctuations in the water table, thus complicating calculations. Similarly, simulation of variable-thickness confined aquifers is complicated by the fact that velocities will generally increase in response to reductions and decrease in response to increases in aquifer thickness.

Matrix Characteristics. Flow in porous media is much easier to model than in rocks with fractures or solution porosity. This is because (1) equations governing laminar flow are simpler than those for turbulent flow,

Table 6-1. Modeling Designed-System Alterations and Corrective Action

Design Feature	Effects on Ground Water	Type of Model Required	Typical Modeling Problems
Capping, grading and revegetation	Reduction of infiltration Reduction of successive leachate generation	Unsaturated zone model, vertical layered	Parameters related to leaching characteristics of reworked soil
Ground-water pumping (and optional reinjection of treated water)	Changes in heads, direction of flow, and contaminant migration Controlled plume removal	Saturated zone model, two-dimensional areal, axisymmetric or three-dimensional; well or series of wells assigned to individual node	Representing partial penetration
Wastewater injection	Changes in heads and direction of flow Plume generation	Saturated zone model, two-dimensional areal, axisymmetric or three-dimensional; density-dependent flow; temperature difference effects	Representing density-dependent effects
Interceptor trenches	Changes in heads, direction of flow, and contaminant migration Plume removal	Saturated zone model, two-dimensional areal or cross-sectional, or three dimensional; trenches are represented by line of nodes with assigned heads	Representing partial penetration, resolution near trenches

Table 6-1. Continued

Design Feature	Effects on Ground Water	Type of Model Required	Typical Modeling Problems
Impermeable barrier (optional drainage system to prevent mounding)	Containment of polluted water	Saturated zone model, two-dimensional areal or cross-sectional, or three-dimensional; possibly two-dimensional cross-sectional unsaturated zone for liners	Representing partial penetration, flow and transport around end of barrier(s)
	Routing unpolluted ground water around site		Conductivity liner or barrier material
	Changes in heads and direction of flow		Large changes in conductivity between neighboring elements Differences in required grid resolution
Subsurface drains	Removal of leachate	Saturated or combined unsaturated-saturated zone model, two-dimensional cross-sectional or three-dimensional	Resolution near drain
	Changes in heads, direction of flow, and contaminant migration		
Solution mining	Removal of contaminants after induced mobilization	Saturated or combined unsaturated-saturated zone model, two-dimensional areal, cross-sectional or three-dimensional Lines of Sources (injection) and sinks (removal)	Parameters related to mobilization (sorption coefficient, retardation coefficient)
Excavation	Removal of waste material and pollutes soil	Unsaturated, saturated, or combined unsaturated-saturated zone model; for unsaturated some models minimal one-dimensional vertical, for other types minimal two-dimensional, cross-sectional.	Parameters of backfill material
	changes in hydraulic characteristics and boundary conditions		
	changes in heads and direction of flow		

Source: Adapted by van der Heijde et al. (1988) from Boutwell et al. (1985).

which may occur in fracture; and (2) effective porosity and hydraulic conductivity can be more easily estimated for porous media.

Homogeneity and Isotropy. Homogeneous and isotropic aquifers are easiest to model because their properties do not vary in any direction. If hydraulic properties and concentrations are uniform vertically, and in one of two horizontal dimensions, a one-dimensional simulation is possible. Horizontal variations in properties combined with uniform vertical characteristics can be modeled two-dimensionally. Most aquifers, however, show variation in all directions and, consequently, require three-dimensional simulation, which also necessitates more extensive site characterization data. The spatial uniformity or variability of aquifer parameters such as recharge, hydraulic conductivity, effective porosity, transmissivity, and storativity will determine the number of dimensions to be modeled.

Phases. Flow of ground water and contaminated ground water in which the dissolved constituents do not create a plume that differs greatly from the unpolluted aquifer in density or viscosity are fairly easy to simulate. Multiple phases, such as water and air in the vadose zone and NAPLs in ground water, are more difficult to simulate.

Number of Aquifers. A single aquifer is easier to simulate than multiple aquifers.

Flow Conditions. Steady-state flow, where the magnitude and direction of flow velocity are constant with time at any point in the flow field, is much easier to simulate than transient flow. Transient, or unsteady flow, occurs when the flow varies in the unsaturated zone in response to variations in precipitation, and in the saturated zone when the water table fluctuates.

Contaminant Transport Parameters

Type of Source. For simulation purposes, sources can be characterized as point, line, area, or volume. A point source enters the ground water at a single point, such as a pipe outflow or injection well, and can be simulated with either a one-, two-, or three-dimensional model. An example of a line source would be contaminants leaching from the bottom of a trench. An area source enters the ground water through a horizontal or vertical plane. The actual contaminant source may occupy three dimensions outside of the aquifer, but contaminant entry into the aquifer can be represented as a plane for modeling purposes. Leachate from a waste lagoon or an agricultural field are examples of area sources. A volume source occupies three dimensions within an aquifer. A DNAPL that has sunk to the bottom of an aquifer would be a volume source. Line and area sources may be simulated by either two- or three-

dimensional models, whereas a volume source would require a three-dimensional model. Figure 6-1 illustrates the type of contaminant plume that results from a landfill in the following cases: (1) area source on top of the aquifer, (2) area source within the aquifer and perpendicular to the direction of flow, (3) vertical line source in the aquifer, and (4) point source on top of the aquifer.

Type of Source Release. Release of an instantaneous pulse, or slug, of contaminant is easier to model than a continuous release. A continuous release may be either constant or variable.

Dispersion. Accurate contaminant modeling requires incorporation of transport by dispersion. Unfortunately, the conventional convective-dispersion equation often does not accurately predict field-scale dispersion (U.S. EPA, 1988).

Adsorption. It is easiest to simulate adsorption with a single distribution or partition coefficient. Nonlinear adsorption and temporal and spatial variation in adsorption are more difficult to model.

Degradation. As with adsorption, simulation of degradation is easiest when using a simple first-order degradation coefficient. Second-order degradation coefficients, which result from variations in various parameters, such as pH, substrate concentration, and microbial population, are much more difficult to model. Simulation of radioactive decay is complicated but easier to simulate with precision because decay chains are well known.

Density/Viscosity Effects. If temperature or salinity of the contaminant plume is much different than that of the pristine aquifer, simulations must include the effects of density and viscosity variations.

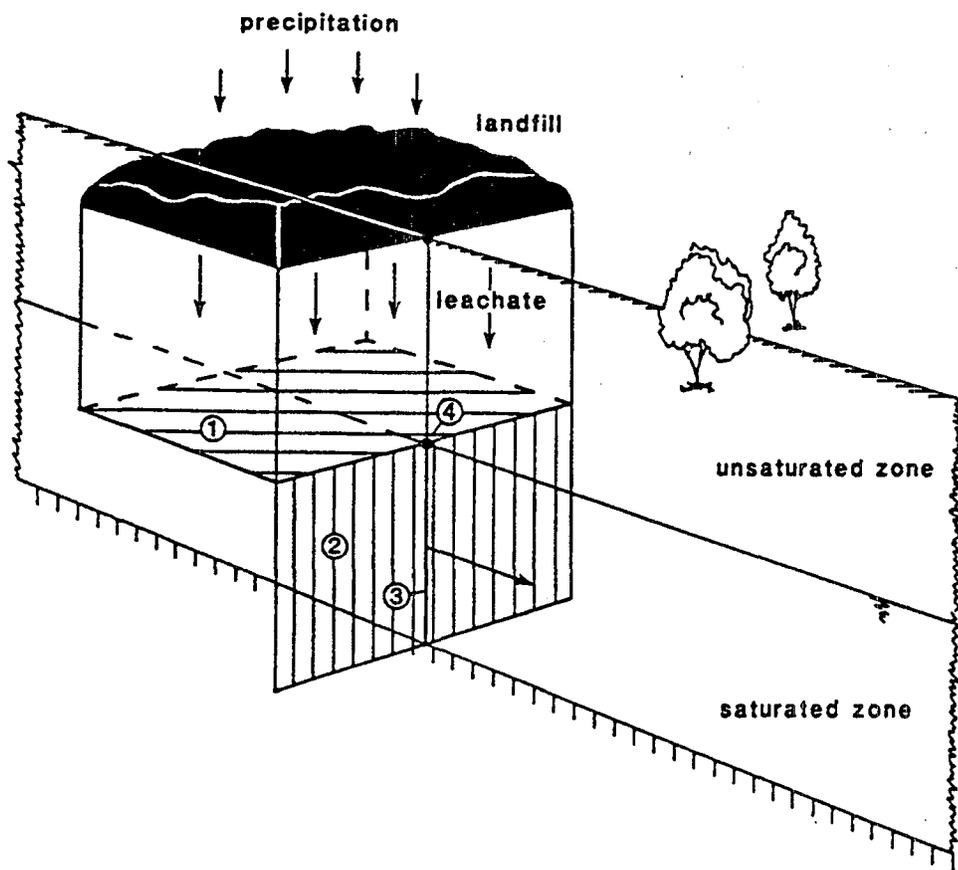
Types of Models and Codes

Ground-water models and codes can be classified in many different ways, including the mathematical approaches used to develop computer codes, as computer prediction codes, and as manipulative codes.

Mathematical Approaches

Models and codes are usually described by the number of dimensions simulated and the mathematical approaches used. At the core of any model or computer code are governing equations that represent the system being modeled. Many different approaches to formulating and solving the governing equations are possible. The specific numerical technique embodied in a computer code is called an algorithm. The following

a. various ways to represent source.



b. horizontal spreading resulting from various source assumptions.

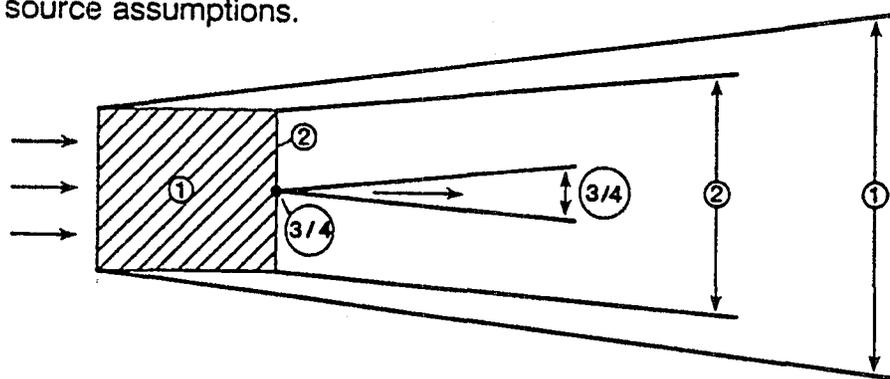
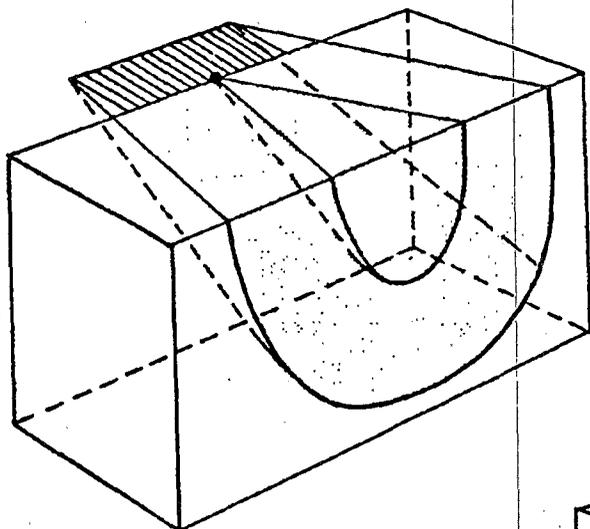


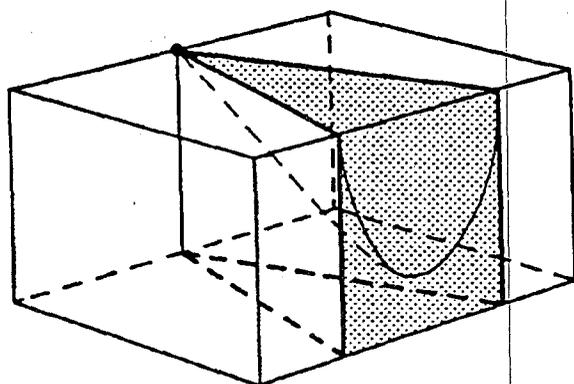
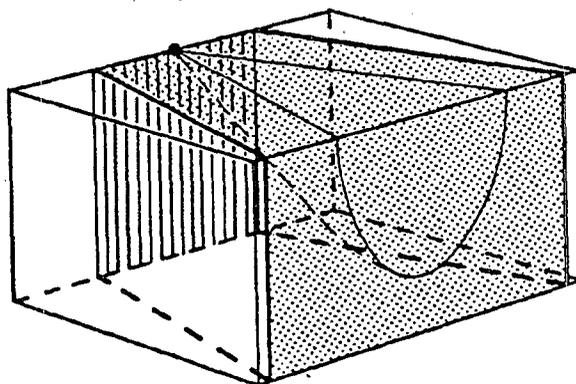
Figure 6-1. Definition of the Source Boundary Condition Under a Leaking Landfill (numbers 1 to 4 refer to cases 1 to 4) (from van der Heijde and others, 1988)

c. detailed view of 3D spreading for various ways to represent source boundary.



Case 1:
horizontal 2D-areal source at top
of aquifer (for 3D modeling)

Case 2: vertical 2D-source in aquifer
(for 2D horizontal, vertically
averaged, or 3D modeling)



Case 3:
1D vertical line source in aquifer
(for 2D horizontal, vertically
averaged, 2D cross-sectional, or
3D modeling)

Case 4: point source at top of aquifer
(for 2D or 3D modeling)

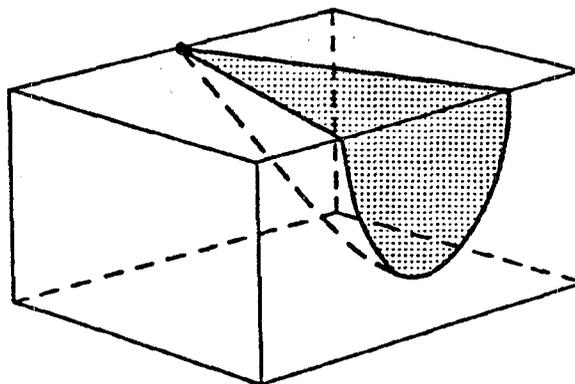


Figure 6-1. Continued

discussion compares and contrasts some of the most important choices that must be made in mathematical modeling.

Deterministic vs. Stochastic Models. A deterministic model presumes that a system or process operates so that a given set of events leads to a uniquely definable outcome. The governing equations define precise cause-and-effect or input-response relationships. In contrast, a stochastic model presumes that a system or process operates so that a given set of events leads to an uncertain outcome. Such models calculate the probability, within a desired level of confidence, of a specific value occurring at any point.

Most available models are deterministic. However, the heterogeneity of hydrogeologic environments, particularly the variability of parameters, such as effective porosity and hydraulic conductivity, plays a key role in influencing the reliability of predictive ground-water modeling (Smith, 1987; Freeze and others, 1989). Stochastic approaches to characterizing variability with the use of geostatistical methods, such as kriging, are being used with increasing frequency to characterize soil and hydrogeologic data (Hoeksma and Kitandis, 1985; Warrick and others, 1986). The governing equations for both deterministic and stochastic models can be solved either analytically or numerically.

Analytical vs. Numerical Models. A model's governing equation can be solved either analytically or numerically. Analytical models use exact closed-form solutions of the appropriate differential equations. The solution is continuous in space and time. In contrast, numerical models apply approximate solutions to the same equations.

Analytical models provide exact solutions, but employ many simplifying assumptions in order to produce tractable solutions; thus placing a burden on the user to test and justify the underlying assumptions and simplifications (Javandel and others, 1984).

Numerical models are much less burdened by these assumptions and, therefore, are inherently capable of addressing more complicated problems, but they require significantly more data, and their solutions are inexact (numerical approximations). For example, the assumptions of homogeneity and isotropy are unnecessary because the model can assign point (nodal) values of transmissivity and storativity. Likewise, the capacity to incorporate complex boundary conditions provides greater flexibility. The user, however, faces difficult choices regarding time steps, spatial grid designs, and ways to avoid truncation errors and numerical oscillations (Remson and others, 1971; Javandel and

others, 1984). Improper choices may result in errors unlikely to occur with analytical approaches (e.g., mass imbalances, incorrect velocity distributions, and grid-orientation effects).

Grid Design. A fundamental requirement of the numerical approach is the creation of a grid that represents the aquifer being simulated (see Figures 6-2 and 6-3). This grid of interconnected nodes, at which process input parameters must be specified, forms the basis for a matrix of equations to be solved. A new grid must be designed for each site-specific simulation based on data collected during site characterization. Good grid design is one of the most critical elements for ensuring accurate computational results.

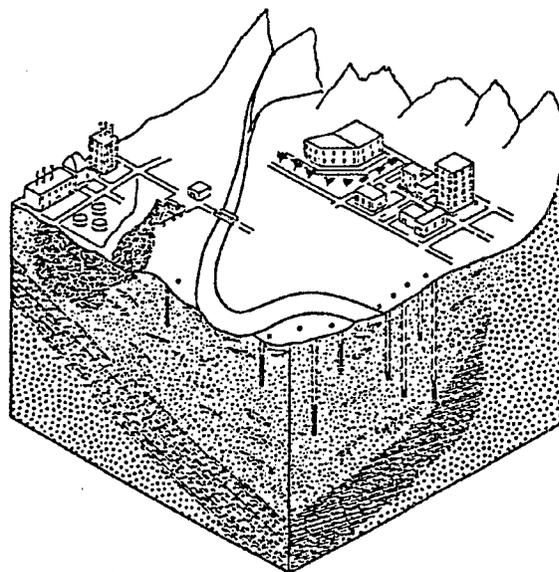
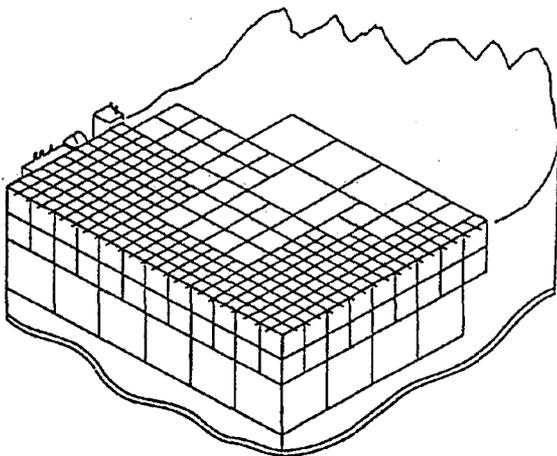


Figure 6-2. Typical Ground-Water Contamination Scenario. Several Water-Supply Production Wells are Located Downgradient of a Contaminant Source and the Geology is Complex.

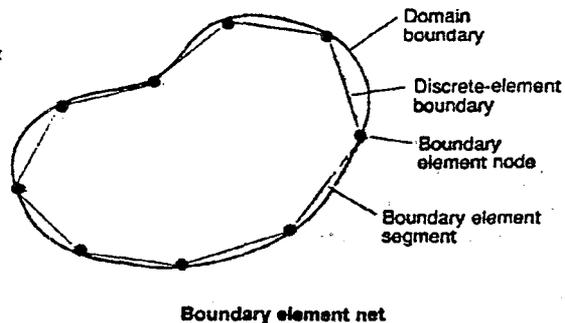
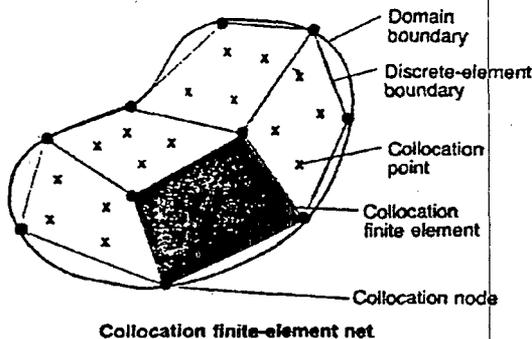
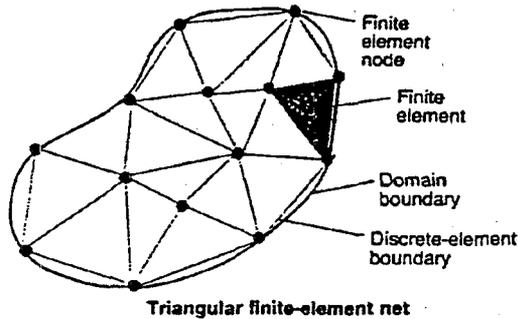
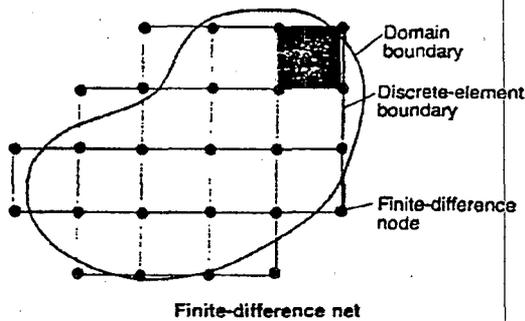
The grid design is influenced by the choice of numerical solution technique. Numerical solution techniques include (1) finite-difference methods (FD); (2) integral finite-difference methods (IFDM); (3) Galerkin and variational finite element methods (FE); (4) collocation methods; (5) boundary (integral) element methods (BIEM or BEM); (6) particle mass tracking methods, such as the RANDOM WALK (RW) model; and (7) the method of characteristics (MOC) (Huyakorn and Pinder, 1983; Kinzelbach, 1986). Figure 6-4 illustrates grid designs involving FD, FE, collocation, and boundary methods. Finite-difference and finite-element methods are the most frequently used and are discussed further below.



Values for natural process parameters would be specified at each node of the grid in performing simulations. The grid density is greatest at the source and at potential impact locations.

Figure 6-3. Possible Contaminant Transport Model Grid Design for the Situations Shown in Figure 6-2

Defining discrete elements



Note: Each node represents one equation per independent variable, except in the case of collocation, in which each collocation point represents one equation. The boundary element, collocation, and finite-element methods offer flexibility in geometric representation.

Figure 6-4. Influence of Numerical Solution Technique on Grid Design (from Pinder, 1984)

Finite Difference vs. Finite Element. The finite-element method approximates the solution of partial differential equations by using finite-difference equivalents, whereas the finite-difference method approximates differential equations by an integral approach. Figure 6-5 illustrates the mathematical and computational differences in the two approaches. Table 6-2 compares the relative advantages and disadvantages of the two methods. In general, finite-difference methods are best suited for relatively simple hydrogeologic settings, whereas finite-element methods are required where hydrogeology is complex.

Ground-Water Computer Prediction Codes

Terminology for classifying computer codes according to the kind of ground-water system they simulate is not uniformly established. There are so many different ways that such models can be classified (i.e., porous vs. fractured-rock flow, saturated vs. unsaturated flow, mass flow vs. chemical transport, single phase vs. multiphase, isothermal vs. variable temperature) that a systematic classification cannot be developed that would not require placement of single codes in multiple categories.

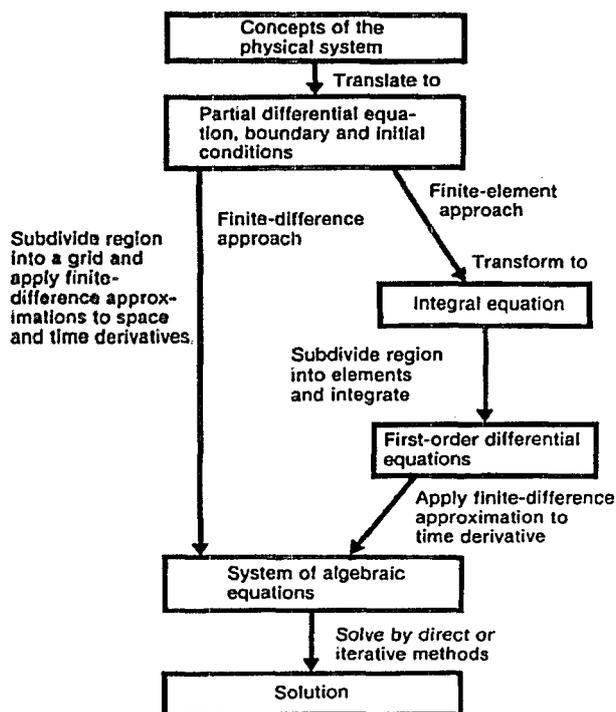


Figure 6-5. Generalized Model Development by Finite-Difference and Finite-Element Methods (from Mercer and Faust, 1981)

Table 6-3 identifies four major categories of codes and 11 major subdivisions, which are discussed below. This classification scheme differs from others (see, for example, Mangold and Tsang, 1987; van der Heijde and others, 1988), by distinguishing among solute transport models that simulate (1) only dispersion, (2) chemical reactions with a simple retardation or degradation factor, and (3) complex chemical reactions.

The literature on ground-water codes often is further confused by conflicting terminology. For example, the term "hydrochemical" has been applied to completely different types of codes. Van der Heijde and others (1988) used the term hydrochemical for codes listed in the geochemical category in Table 6-3, whereas Mangold and Tsang (1987) used the same term to describe coupled geochemical and flow models (chemical-reaction transport codes in Table 6-3).

Porous Media Flow Codes. Modeling of saturated flow in porous media is relatively straightforward; consequently, by far the largest number of codes are available in this category. Van der Heijde and others (1988) summarize 97 such models. These models are not suitable for modeling contaminant transport if dispersion is a significant factor, but they may be required for evaluating hydrodynamic containment of contaminants and pump-and-treat remediation efforts. Modeling variably saturated flow in porous media (most

Advantages	Disadvantages
<u>Finite-Difference Method</u>	
<ul style="list-style-type: none"> Intuitive basis Easy data entry Efficient matrix techniques Programming changes easy 	<ul style="list-style-type: none"> Low accuracy for some problems Regular grids required
<u>Finite-Element Method</u>	
<ul style="list-style-type: none"> Flexible grid geometry High accuracy possible Evaluates cross-product terms better 	<ul style="list-style-type: none"> Complex mathematical basis Difficult data input Difficult programming

Source: Adapted from Mercer and Faust (1981).

Table 6-2. Advantages and Disadvantages of FDM and FEM Numerical Methods

typically soils and unconsolidated geologic material) is more difficult because hydraulic conductivity varies with changes in water content in unsaturated materials. Such codes typically must model processes, such as capillarity, evapotranspiration, diffusion, and plant water uptake. Van der Heijde and others (1988) summarized 29 models in this category.

Solute Transport Codes. The most important types of codes in the study of ground-water contamination simulate the transport of contaminants in porous media. This is the second largest category (73 codes) identified by van der Heijde and others (1988) as being readily available. Solute transport codes fall into three major categories (see Table 6-3 for descriptions): (1) dispersion codes, (2) retardation/degradation codes, and (3) chemical-reaction transport codes.

Dispersion codes differ from saturated flow codes only in having a dispersion factor, and they have limited utility except perhaps for worst-case analyses, since few contaminants act as conservative tracers. Retardation/degradation codes are slightly more sophisticated because they add a retardation or degradation factor to the mass transport and diffusion equations. Chemical reaction-transport codes are the most complex (but not necessarily the most accurate) because they couple geochemical codes with flow codes. Chemical reaction-transport codes may be classified as integrated or two-step codes.

Geochemical Codes. Geochemical codes simulate chemical reactions in ground-water systems without considering transport processes. These fall into three major categories (see Table 6-3): (1) thermodynamic

Type of Code	Description/Uses
Flow (Porous Media)	
Saturated	Simulates movement of water in saturated porous media. Used primarily for analyzing ground-water availability.
Variable saturated	Simulates unsaturated flow of water in the vadose (unsaturated) zone. Used in study of soil-plant relationships, hydrologic cycle budget analysis.
Solute Transport (Porous Media)	
Dispersion	Simulates transport of conservative contaminants (not subject to retardation) by adding a dispersion factor into flow calculations. Used for nonreactive contaminants such as chloride and for worst-case analysis of contaminant flow.
Retardation/ Degradation	Simulates transport contaminants that are subject to partitioning of transformation by the addition of relatively simple retardation or degradation factors to algorithms for advection-dispersion flow. Used where retardation and degradation are linear with respect to time and do not vary with respect to concentration.
Chemical-reaction	Combines an advection-dispersion code with a transport geochemical code (see below) to simulate chemical speciation and transport. Integrated codes solve all mass momentum, energy-transfer, and chemical reaction equations simultaneously for each time interval. Two-step codes first solve mass momentum and energy balances for each time step and then equilibrate the chemistry using a distribution-of-species code. Used primarily for modeling behavior of inorganic contaminants.

Table 6-3. Classification of Types of Computer Codes

Type of Code	Description/Uses
Geochemical Codes	
Thermodynamic	Processes empirical data so that thermodynamic data at a standard reference state can be obtained for individual species. Used to calculate reference state values for input into geochemical speciation calculations.
Distribution-of-species (equilibrium)	Solves a simultaneous set of equations that describe equilibrium reactions and mass balances of the dissolved elements.
Reaction progress (mass-transfer)	Calculates both the equilibrium distribution of species (as with equilibrium codes) and the new composition of the water, as selected minerals are precipitated or dissolved.
Specialized Codes	
Fracture rock	Simulates flow of water in fractured rock. Available codes cover the spectrum of advective flow, advection-dispersion, heat, and chemical transport.
Heat transport	Simulates flow where density-induced and other flow variations resulting from fluid temperature differences invalidate conventional flow and chemical transport modeling. Used primarily in modeling of radioactive waste and deep-well injection.
Multiphase flow	Simulates movement of immiscible fluids (water and nonaqueous phase liquids) in either the vadose or saturated zones. Used primarily where contamination involves liquid hydrocarbons or solvents.

Source: Adapted from van der Heijde and others (1988) and U.S. EPA (1989).

Table 6-3. Continued

codes, (2) distribution-of-species codes, and (3) reaction progress codes. Thermodynamic codes perhaps would be classified more properly as manipulative codes, but are included here because of their special association with geochemical codes. Such codes are especially important for geochemical modeling of deep-well injection where temperatures and pressures are higher than near-surface conditions for which most geochemical codes were developed. Apps (1989) reviews the availability and use of thermodynamic codes

By themselves, geochemical codes can provide qualitative insights into the behavior of contaminants in the subsurface. They also may assist in identifying possible precipitation reactions that might adversely affect the performance of injection wells in pump-and-

treat remediation efforts. Chemical transport modeling of any sophistication requires coupling geochemical codes with flow codes. Over 50 geochemical codes have been described in the literature (Nordstrom and Ball, 1984), but only 15 are cited by van der Heijde and others (1988) as passing their screening criteria for reliability and usability.

Specialized Codes. This category contains special cases of flow codes and solute transport codes (see Table 6-3), including (1) fractured rock, (2) heat transport, and (3) multiphase flow. Fractured rock creates special problems in the modeling of contaminant transport for several reasons. First, mathematical representation is more complex due to the possibility of turbulent flow and the need to consider roughness effects. Furthermore,

precise field characterization of fracture properties that influence flow, such as orientation, length, and degree of connection between individual fractures, is extremely difficult. In spite of these difficulties, much work is being done in this area (Schmelling and Ross, 1989). Van der Heijde and others (1988) identified 27 fractured rock models.

Heat transport models have been developed primarily in connection with enhanced oil-recovery operations (Kayser and Collins, 1986) and programs assessing disposal of radioactive wastes. Van der Heijde and others (1988) summarized 36 codes of this type. Early work in multiphase flow centered in the petroleum industry focusing on oil-water-gas phases. In the last decade, multiphase behavior of nonaqueous phase liquids in near-surface ground-water systems has received increasing attention. However, the number of codes capable of simulating multiphase flow is still limited.

Manipulative Codes

Manipulative codes that may be of value in ground-water investigations include (1) parameter identification codes, (2) data processing codes, and (3) geographic information systems.

Parameter Identification Codes. Parameter identification codes most often are used to estimate the aquifer parameters that determine fluid flow and contaminant transport characteristics. Examples of such codes include annual recharge (Pettyjohn and Henning, 1979; Puri, 1984), coefficients of permeability and storage (Shelton, 1982; Khan, 1986a and 1986b), and dispersivity (Guvén and others, 1984; Strecker and Chu, 1986).

Data Processing Codes. Data manipulation codes specifically designed to facilitate ground-water modeling efforts have received little attention until recently. They are becoming increasingly popular, because they simplify data entry (preprocessors) to other kinds of models and facilitate the production of graphic displays (postprocessors) of the data outputs of other models (van der Heijde and Srinivasan, 1983; Srinivasan, 1984; Moses and Herman, 1986). Other software packages are available for routine and advanced statistics, specialized graphics, and database management needs (Brown, 1986).

Geo-EAS (Geostatistical Environmental Assessment Software) is a collection of interactive software tools for performing two-dimensional geostatistical analyses of spatially distributed data. It includes programs for data file management, data transformations, univariate

statistics, variogram analysis, cross validation, kriging, contour mapping, post plots, and line/scatter graphs in a user-friendly format. This package can be obtained from the Arizona Computer Oriented Geological Society (ACOGS), P.O. Box 44247, Tucson, AZ, 85733-4247.

Geographic Information Systems. Geographic information systems (GIS) provide data entry, storage, manipulation, analysis, and display capabilities for geographic, environmental, cultural, statistical, and political data in a common spatial framework. EPA's Environmental Monitoring System Laboratory in Las Vegas (EMSL-LV) has been piloting use of GIS technology at hazardous waste sites that fall under RCRA and CERCLA guidance. The American Society for Photogrammetry and Remote Sensing is a primary source of information on GIS.

Management Considerations for Code Use

The effective use of ground-water models is often inhibited by a communication gap between managers who make policy and regulatory decisions and technical personnel who develop and apply the models (van der Heijde and others, 1988). This section focuses on the following management considerations for using models and codes: personnel and communication requirements, cost of hardware and software options, selection criteria, and quality assurance.

Personnel/Communication

The successful use of mathematical models depends on the training and experience of the technical support staff applying the model to a problem, and on the degree of communication between these technical persons and management. Managers should be aware that a fair degree of specialized training and experience are necessary to develop and apply mathematical models, and relatively few technical support staff can be expected currently to have such skills (van der Heijde and others, 1985). Technical personnel need to be familiar with a number of scientific disciplines, so that they can structure models to faithfully simulate real-world problems.

A broad, multidisciplinary team is mandatory for adequate modeling of complex problems, such as contaminant transport in ground water. No individual can master the numerous disciplines involved in such an effort; however, staff should have a working knowledge of many sciences so that they can address appropriate questions to specialists, and achieve some integration of the various disciplines involved in the project. In practice, ground-water modelers should become involved in continuing education efforts, which managers should expect and encourage. The benefits

of such efforts are likely to be large, and the costs of not engaging in them may be equally large.

Technical staff also must be able to communicate effectively with management. As with statistical analyses, an ill-posed problem yields answers to the wrong questions. Tables 6-3 through 6-5 list some useful questions managers and technical support staff should ask each other to ensure that the solution being developed is appropriate to the problems. Table 6-3 consists of "screening level" questions, Table 6-4 addresses correct conceptualizations, and Table 6-5 contains questions of sociopolitical concern.

Cost of Hardware and Software Options

The nominal costs of the support staff, computing facilities, and specialized graphics' production equipment associated with numerical modeling efforts can be high. In addition, quality control activities can result in substantial costs, depending on the degree to which a manager must be certain of the model's characteristics and accuracy of output.

As a general rule, costs are greatest for personnel, moderate for hardware, and minimal for software. An optimally outfitted business computer (e.g., VAX 11/785 or IBM 3031) costs about \$100,000, but it can rapidly pay for itself in terms of dramatically increased speed and computational power. In contrast, a well-complemented personal computer (e.g., IBM-PC/AT or DEC Rainbow) may cost \$10,000, but the significantly slower speed and limited computational power may incur hidden costs in terms of its inability to perform specific tasks. For example, highly desirable statistical packages like SAS and SPSS are unavailable or available only with reduced capabilities for personal computers. Many of the most sophisticated mathematical models are available in their fully capable form only on business computers.

Figure 6-6 compares typical software costs for different levels of computing power. Obviously, the software for less capable computers is less expensive, but the programs are not equivalent; managers need to seriously consider which level is appropriate. If the modeling

Assumptions and Limitations

What are the assumptions made, and do they cast doubt on the model's projections for this problem?

What are the model's limitations regarding the natural processes controlling the problem? Can the full spectrum of probable conditions be addressed?

How far in space and time can the results of the model simulations be extrapolated?

Where are the weak spots in the application, and can these be further minimized or eliminated?

Input Parameters and Boundary Conditions

How reliable are the estimates of the input parameters? Are they quantified within accepted statistical bounds?

What are the boundary conditions, and why are they appropriate to this problem?

Have the initial conditions with which the model is calibrated been checked for accuracy and internal consistency?

Are the spatial grid design(s) and time-steps of the model optimized for this problem?

Quality Control and Error Estimation

Have these models been mathematically validated against other solutions to this kind of problem?

Has anyone field verified these models before, by direct applications or simulation of controlled experiments?

How do these models compare with others in terms of computational efficiency, and ease of use or modification?

What special measures are being taken to estimate the overall errors of the simulations?

Source: Keely (1987).

Table 6-4. Conceptualization Questions for Mathematical Modeling Efforts

Demographic Considerations

- Is there a larger population endangered by the problem than we are able to provide sufficient responses to?
- Is it possible to present the model's results in both nontechnical and technical formats, to reach all audiences?
- What role can modeling play in public information efforts?
- How prepared are we to respond to criticism of the model(s)?

Political Constraints

- Are there nontechnical barriers to using this model, such as "tainted by association" with a controversy elsewhere?
- Do we have the cooperation of all involved parties in obtaining the necessary data and implementing the solution?
- Are similar technical efforts for this problem being undertaken by friend or foe?
- Can the results of the model simulations be turned against us? Are the results ambiguous or equivocal?

Legal Concerns

- Will the present schedule allow all regulatory requirements to be met in a timely manner?
 - If we are dependent on others for key inputs to the model(s), how do we recoup losses stemming from their nonperformance?
 - What liabilities are incurred for projections that later turn out to be misinterpretations originating in the model?
 - Do any of the issues relying on the applications of the model(s) require the advice of attorneys?
-

Source: Keely (1987).

Table 6-5. Sociopolitical Questions for Mathematical Modeling Efforts

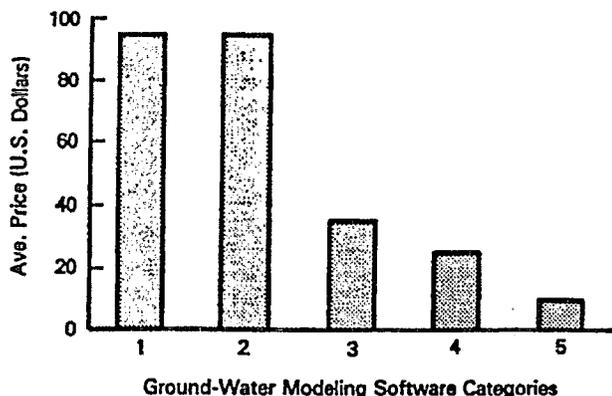
decisions will be based on very little data, it may not make sense to insist on the most elegant software and hardware. If the intended use involves substantial amounts of data, however, and sophisticated analyses are desired, it would be unwise to opt for the least expensive combination.

There is an increasing trend away from both ends of the hardware and software spectrum and toward the middle; that is, the use of powerful personal computers is increasing rapidly, whereas the use of small programmable calculators and large business computers alike is declining. In part, this trend stems from significant improvements in the computing power and quality of printed outputs obtainable from personal computers. It also is due to the improved telecommunications capabilities of personal computers, which are now able to emulate the interactive terminals of large business computers so that vast computational power can be

accessed and the results retrieved with no more than a phone call. Most importantly for ground-water managers, many of the mathematical models and data packages have been "down-sized" from mainframe computers to personal computers; many more are now being written directly for this market. Figure 6-7 provides some idea of the costs of available software and hardware for personal computers.

Code Selection Criteria

Technical criteria for selecting ground-water modeling codes have been formulated by U.S. EPA (1988) in the form of a decision tree (Figure 6-8). These technical criteria correspond roughly to the hydrogeologic model parameters discussed earlier. Table 6-6 summarizes information with respect to these technical criteria for 49 analytical and numerical ground-water codes. More detailed information about these codes can be found in U.S. EPA (1988).



- Categories
- 1 Mainframe/business computer models
 - 2 Personal computer versions of mainframe models
 - 3 Original IBM-PC and compatibles' models
 - 4 Handheld microcomputer models (e.g., Sharp PC1500)
 - 5 Programmable calculator models (e.g., HP41-CV)
- Prices include software and all available documentation, reports, etc.

A code might meet all of the above technical criteria and still not be suitable for use due to deficiencies in the code itself. An ongoing program at the International Ground Water Modeling Center evaluates codes using performance standards and acceptance criteria (van der Heijde, 1987). The Center has rated 296 codes in seven major categories using a variety of usability and reliability criteria (van der Heijde and others, 1988). Favorable ratings for the usability criteria include:

Pre- and Postprocessors. Code incorporates one or more of this type of code.

Documentation. Code has an adequate description of user's instructions and example data sets.

Support. Code is supported and maintained by the developers or marketers.

Hardware Dependency. Code is designed to function on a variety of hardware configurations.

Figure 6-6. Average Price per Category for Ground-Water Models from the International Ground Water Modeling Center

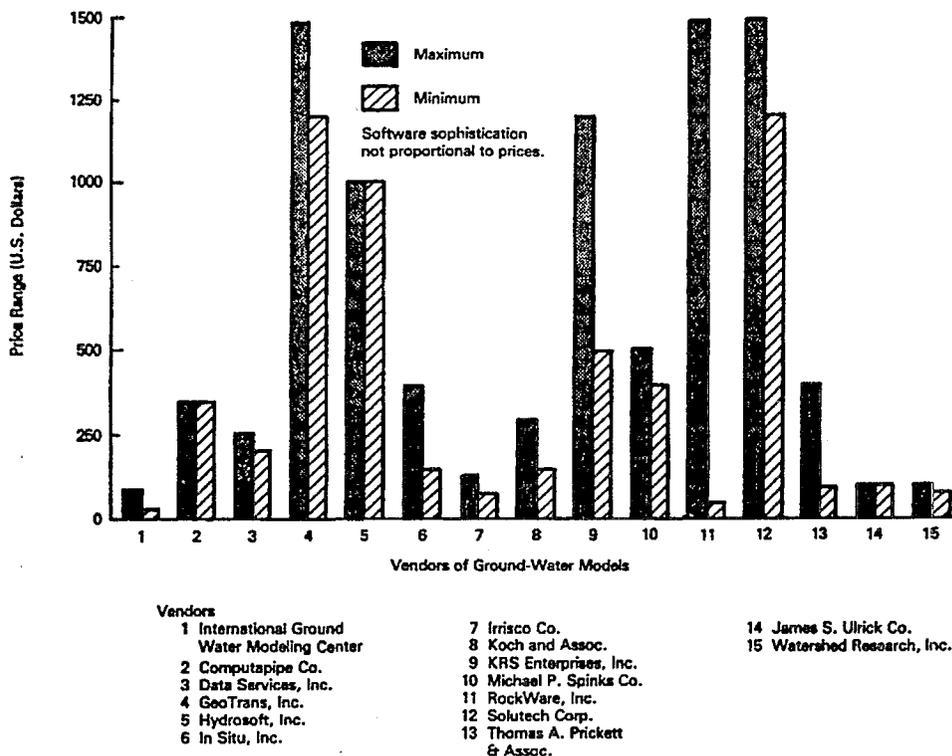
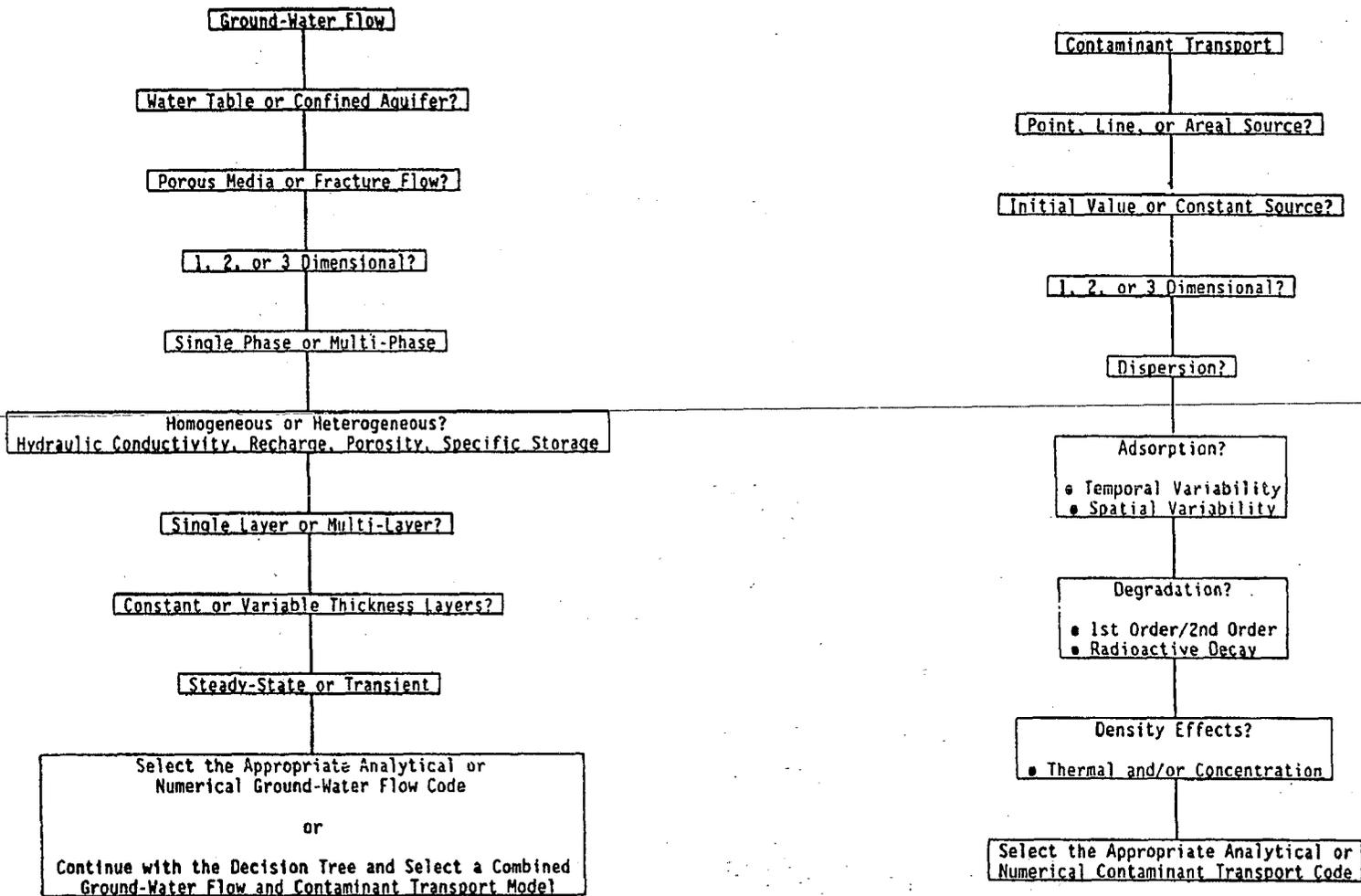


Figure 6-7. Price Ranges for IBM-PC Ground-Water Models Available from Various Sources (from Graves, 1986)

Figure 6-8. Ground-Water Computer Code Selection Decision Tree (from U.S. EPA, 1988)



Model Names	Water Table Aquifer	Confined Aquifer	Porous Media	Fracture Flow	Dimension Flow	Single-Phase	Multi-Phase	Homogeneous Hydraulic Parameters	Heterogeneous Hydraulic Parameters	Single-Layer	Multi-Layer	Constant Thickness	Variable Thickness	Steady State	Transient	Point, Line, or Areal Source	Initial Value Source	Constant Source	Dimension Transport	Dispersion	Absorption	Degradation 0,1,2 - order radio active	Density Effects	Solution Technique
Analytical Flow																								
PATHS	X	X			2	X		X		X	X	X	X	X	X	A	X	X	2		X			AN
Analytical Transport																								
AT123D		X			1,2,3	X		X		X	X	X	X			A	X	X	1,2,3	X		1		AN
CHAM		X			1	X		X		X	X	X	X			P	X	X	1	X	X	1,R		AN
CETOUT		X			1	X		X		X	X	X	X			P	X	X	1	X	X	1,R		AN
GWMTM1&2		X			1,2	X		X		X	X	X	X			P,L	X	X	1,2	X	X	1		AN
MUTRAN		X			1,2,3	X		X		X	X	X	X			P,L,A	X	X	1,2,3	X	X	R		AN
NWFT/GVM		X			1	X		X		X	X	X	X				X		1	X	X	R		SALT AN
Numerical Flow (Saturated/Unsaturated)																								
UNSAT1		X			1	X		X		X	X	X	X											FE
FEMWATER1		X			2	X		X		X	X	X	X											FE
UNSAT 2		X			2	X		X		X	X	X	X											FE
FREEZE	X	X	X		3	X		X		X	X	X	X											FD
Numerical Flow (Saturated Only)																								
BEWTA	X	X			2	X		X		X	X	X	X											FD
COOLEY	X	X	X		2	X		X		X	X	X	X											FE
FEBGGW	X	X	X		2	X		X		X	X	X	X											FE
FLUMP	X	X	X		2	X		X		X	X	X	X											FE
FRESURF 1 & 2	X	X			2	X		X		X	R-2	X	R-2											FE
TEMAGI	X	X			1	X		X		X	X	X	X											FD
USGS2D	X	X	X		2	X		X		X	X	X	X											FD
V7T	X	X	X		2	X		X		X	X	X	X											FD
V3	X	X	X		2	X		X		X	X	X	X											FD
USGS3D - MODULAR	X	X	X		3	X		X		X	X	X	X											FD
USGS3D - TRESMOTT	X	X	X		3	X		X		X	X	X	X											FD
Numerical Transport (Saturated/Unsaturated)																								
FEMWASTE 1	X	X			2	X		X		X	X	X	X			A	X	X	2	X	X	1		FE
PERCOL	X	X			1	X		X		X	X	X	X			P	X	X	1	X	X	R		NR
SATURN	X	X			2	X		X		X	X	X	X			A	X	X	2	X	X	1,R		FE
SEGOL	X	X			3	X		X		X	X	X	X			A	X	X	3	X	X			FE
SUMATRA - 1	X	X			1	X		X		X	X	X	X			P	X	X	1	X	X	0,1	X	FE
SUTRA	X	X			2	X		X		X	X	X	X			A	X	X	2	X	X	1		FE
TRANSAT	X	X			1,2	X		X		X	X	X	X						1,2	X	X	1		IFD
TRUST	X	X			1,2,3	X		X		X	X	X	X			P,L,A	X	X	1,2,3	X	X			FD
Numerical Transport (Saturated Only)																								
CHAMT	X	X			X			X		X	X	X	X			A	X	X	2	X	X	R,CH		FE
DUGUID-REEVES	X	X			X			X		X	X	X	X			A	X	X	2	X	X	R		FE
GROVEGALERKN	X	X			3	X		X		X	X	X	X			A	X	X	3	X	X	1		FE
ISOQUAD,ISOQUAD2	X	X			X			X		X	X	X	X			A	X	X	2	X	X			FE
COMBRED					1,2			X		X	X	X	X			A	X	X	1,2	X	X	1		FD,
USGS2D - MOC								X		X	X	X	X			A	X	X	2	X	X	R		NR
DPCT	X	X			2	X		X		X	X	X	X			A	X	X	2	X	X	R		FE,
MMT		X			X			X		X	X	X	X			P	X	X	1	X		1,R,		RW
PINDER	X	X			X			X		X	X	X	X			A	X	X	3	X	X			FE
ROBERTSON1	X	X			X			X		X	X	X	X			P	X	X	2	X		R		FD
ROBERTSON2	X	X			2	X		X		X	X	X	X			A	X	X	2	X	X	R		FD,
SWENT	X	X			1,2,3	X		X		X	X	X	X			A	X	X	1,2,3	X	X	1,R,	X	MOC
TRANS (Prickett-Lonnquist)	X	X	X		2	X		X		X	X	X	X			A	X	X	2	X		CH		RW
TRANSAT 2	X	X			3	X		X		X	X	X	X						3	X	X	1		FE
Numerical Coupled Solute and Heat Transport																								
CFEST	X	X			1,2,3	X		X		X	X	X	X			A	X	X	1,2,3	X	X	1	X	FE
QWITHERM	X	X			2	X		X		X	X	X	X			A	X	X	2	X	X	X		FD
OCRE	X	X			1,2	X		X		X	X	X	X			A	X	X	1,2	X	X	R		FE
SHALT	X	X			2	X		X		X	X	X	X			A	X	X	2	X	X	1	X	FE
SWFT	X	X	X		3	X		X		X	X	X	X			A	X	X	3	X	X	R,CH	X	FD
SWP2	X	X	X		3	X		X		X	X	X	X			A	X	X	3	X	X	1	X	FD

LEGEND

AN - Analytical

Degradation

- 0 - Zero Order Decay
- 1 - First Order Decay
- 2 - Second Order Decay
- R - Radioactive Decay
- CH - Radioactive chain Decay

Dimensionality

- 1 - One Dimensional
- 2 - Two Dimensional
- 3 - Three Dimensional

FD - Finite Difference

FE - Finite Element

IFD - Integrated Finite Difference

MOC - Method of Characteristics

NR - Newton Raphson

Source Type

- A - Areal Source
- L - Line Source
- P - Point Source

Source: U.S. EPA, 1988

Table 6-6. Analytical and Numerical Models Worksheet

Favorable ratings for the reliability criteria include:

Review. Both theory behind the coding and the coding itself are peer reviewed.

Verification. Code has been verified.

Field Testing. Code has been extensively field tested for site-specific conditions for which extensive datasets are available.

Extent of Use. Code has been used extensively by other modelers.

Quality Assurance/Quality Control

The increasing use of modeling and computer codes in regulatory settings where decisions may be contested in court requires careful attention to quality assurance and quality control in both model development and application. The American Society for Testing and Materials (ASTM) defines several important terms that relate to QA/QC procedures for computer code modeling (ASTM, 1984):

Verification involves examination of the numerical technique in the computer code to ascertain that it truly represents the conceptual model and that there are no inherent numerical problems associated with obtaining a solution.

Validation involves comparison of model results with numerical data independently derived from experiments or observations of the environment.

Calibration is a test of a model with known input and output information that is used to adjust or estimate factors for which data are not available.

Sensitivity is the degree to which the model result is affected by changes in a selected input parameter.

Huyakorn and others (1984) identified three major levels of quality control in the development of ground-water models:

1. Verification of the model's mathematics by comparison of its output with known analytical solutions to specific problems.
2. Validation of the general framework of the model by successful simulation of observed field data.
3. Benchmarking of the model's efficiency in solving problems by comparison with other models.

These levels of quality control address the soundness

and utility of the model alone, but do not treat questions of its application to a specific problem. Hence, at least two additional levels of quality control appear justified:

1. Critical review of the problem's conceptualization to ensure that the modeling effort considers all physical and chemical aspects that may affect the problem.
2. Evaluation of the specifics of the application, e.g., appropriateness of the boundary conditions, grid design, time steps, etc. Calibration and sensitivity analysis to determine if the model outputs vary greatly with changes in input parameters are important aspects of this process.

Verification of the mathematical framework of a numerical model and of a code for internal consistency is relatively straightforward. Field validation of a numerical model consists of first calibrating the model using one set of historical records (e.g., pumping rates and water levels from a certain year), and then attempting to predict the next set of historical records. In the calibration phase, the aquifer coefficients and other model parameters are adjusted to achieve the best match between model outputs and known data; in the predictive phase, no adjustments are made (excepting actual changes in pumping rates, etc.). Presuming that the aquifer coefficients and other parameters were known with sufficient accuracy, a mismatch means that either the model is not correctly formulated or that it does not treat all of the important phenomena affecting the situation being simulated (e.g., does not allow for leakage between two aquifers when this is actually occurring).

Field validation exercises usually lead to additional data gathering efforts, because existing data for the calibration procedure commonly are insufficient to provide unique estimates of key parameters. Such efforts may produce a "black box" solution that is so site-specific that the model cannot be readily applied to another site. For this reason, the blind prediction phase is an essential check on the uniqueness of the parameter values used. Field verification is easiest if the model can be calibrated to data sets from controlled research experiments.

Benchmarking routines to compare the efficiency of different models in solving the same problem have only recently become available (Ross and others, 1982; Huyakorn and others, 1984). Van der Heijde and others (1988) discuss, in some detail, procedures for developing QA plans for code development/maintenance and code application.

Limitations of Computer Codes

Mathematical models are useful only within the context of the assumptions and simplifications on which they

are based and according to their ability to approximate the field conditions being simulated. Faust and others (1981) rated the predictive capabilities of available models with respect to 10 issues involving quantity and quality of ground water (Table 6-7). A four-tiered classification scheme for models is shown in Table 6-7: (1) geographic scope (site, local, regional); (2) pollutant movement (flow only, transport without reactions, and transport with reactions); (3) type of flow (saturated or unsaturated); and (4) type of media (porous or fractured). The rating scale by Faust and others (1981) in Table 6-7 also can be viewed as stages of model development:

- 0 = No model exists.
- 1 = Models are still in the research stage.
- 2 = Models can serve as useful conceptual tools for synthesizing complicated hydrologic and quality data.
- 3 = Models can make short-term predictions (a few years) with a moderate level of credibility, given sufficient data.

4 = Models can make predictions with a high degree of reliability and credibility, given sufficient data.

The most advanced model is only able to simulate available supplies and conjunctive use at the local level. Contaminant transport modeling is generally at stage 3 for transport without reactions in saturated porous flow at the site and local level. Models at the stage 2 level of development generally include transport without reactions (saturated fractured, unsaturated porous), and transport with reactions (saturated porous) at the site and local level. Models at the earliest stage of development involve transport with reactions in saturated, fractured media.

Advances have been made in all areas of modeling since the ratings in Table 6-7 were made, but the basic relationships are essentially unchanged. This is illustrated in Table 6-8, which shows the percentage of computer codes in seven categories that received favorable usability and reliability ratings by van der Heijde and others (1988). The heat transport and geochemical model categories do not have direct

Spatial considerations: Pollutant movement, if any:	Model Types																			
	Site										Local						Regional			
	Flow only				Transport w/o reactions			Transport w/ reactions			Flow only		Transport w/o reactions		Transport w/ reactions		Flow only		Transport w/o reactions	
Flow conditions:	sat P	sat F	unsat P	multi fluid	sat P	sat F	unsat P	sat P	sat F	unsat P	sat P	sat F	sat P	sat F	sat P	sat F	sat P	sat F	sat P	sat F
Issues																				
Quantity Available supplies	3	2									4	3					3	3		
Quantity Conjunctive use	3	1									4	3					3	3		
Quality Accidental Petroleum products				1	3	2	1							2	1					
Quality Accidental Road salt					3	2	2													
Quality Accidental Industrial chemicals					3	2	2	2	1	0			3	2	2	0				
Quality Agriculture Pesticides & herbicides					3	2	2	2	1	0			3	2	2	0				
Quality Agriculture Salt buildup					3	2	2						3	2						
Quality Waste disposal Landfills					3	2	2	2	1	0			3	2	2	0				
Quality Waste disposal Injection					3	2	2	2	1	0			3	2	2	0				
Quality Sea-water intrusion				3	3	2	2						3	2					2	2

Table 6-7. Matrix Summarizing Reliability and Credibility of Models Used In Ground-Water Resource Evaluation

Key to Matrix

<i>Rows</i>	issue and subissue areas.
<i>Columns</i>	model types and scale of applications; for example, sixth column applies to a site-scale problem in which pollutant movement is described by a transport model without reactions and with saturated flow in fractured media.
<i>Application scale</i>	
Site	area modeled less than a few square miles.
Local	area modeled greater than a few square miles but less than a few thousand square miles.
Regional	area modeled greater than a few thousand square miles.
<i>Abbreviations</i>	
w/	with.
w/o	without.
sat	saturated ground-water flow conditions.
unsat	unsaturated flow conditions.
P	porous media.
F	fractured, fissured, or solution cavity media.
<i>Entries</i>	
4	a useable predictive tool having a high degree of reliability and credibility given sufficient data.
3	a reliable conceptual tool capable of short-term (a few years) prediction with a moderate level of credibility given sufficient data.
2	a useful conceptual tool for helping the hydrologist synthesize complicated hydrologic and quality data.
1	a model that is still in the research stage.
0	no model exists.
blank	model type not applicable to issue area.

Table 6-7. Continued

counterparts in Table 6-7. The multiphase flow category is closest to the accidental petroleum products quality category in Table 6-8.

Not surprisingly, the largest number of codes are in the saturated flow category (97), followed by the saturated solute-transport category (73). The more limited availability of models for unsaturated flow, fractured rock, multiphase flow, and geochemistry primarily reflects the difficulties in mathematical formulation due to complexity of processes, process interactions, and field heterogeneities.

Table 6-8 also provides an overview of the status of ground-water modeling from a quality assurance perspective. In general, a high percentage of codes have been peer reviewed in terms of the basic theory. The exceptions are fractured-rock (44%) and multiphase flow models (21%). In contrast, relatively few models have been reviewed in terms of actual coding. Only the geochemical model category has more than half its models (60%) meeting this criterion. As was noted earlier, model verification is a relatively straightforward procedure, which is demonstrated in Table 6-8 where high percentages of all categories have been verified. In contrast, very few codes have had any significant amount of field testing. Less than a third of the codes in the saturated flow category have been extensively field tested, and field testing of codes in the other

categories ranges from none for fractured rock and geochemical to 21% for variable saturated flow. The percentages in Table 6-8 should be viewed with the following caveats: (1) many codes received an "unknown" rating, which means that the percentages may underestimate the number of codes with actual favorable ratings; and (2) many of the codes have been subjected to limited field testing.

A number of possible pitfalls will doom a ground-water modeling effort to failure (OTA, 1982; van der Heijde and others, 1985):

1. Inadequate conceptualization of the physical system, such as flow in fractured bedrock
2. Use of insufficient or incorrect data
3. Incorrect use of available data
4. Use of invalid boundary conditions
5. Selection of an inadequate computer code
6. Incorrect interpretation of the computational results
7. Imprecise or wrongly posed management problems

Type of code	Total	Support	Theory Rev.	Code Rev.	Verification	Field Tested
Saturated flow	97	65%	74%	12%	90%	32%
Solute transport	73	67%	68%	29%	96%	14%
Heat transport	36	78%	78%	42%	97%	6%
Variable saturated flow	29	48%	72%	21%	83%	21%
Fractured rock models	27	7%	44%	33%	100%	0%
Multiphase flow	19	5%	21%	11%	89%	11%
Geochemical	15	33%	60%	60%	100%	0%

Source: Adapted from van der Heijde and others (1988).

Table 6-8. Percentage of Computer Codes with Favorable Usability and Reliability Ratings

REFERENCES

American Society for Photogrammetry and Remote Sensing (ASPRS), 1989, *Fundamental of GIS: a compendium*, ASPRS, Falls Church, VA.

American Society for Testing and Materials (ASTM), 1984, *Standard practices for evaluating environmental fate models of chemicals: Annual Book of ASTM Standards*, E 978-84, ASTM, Philadelphia, PA.

Anderson, M.P., 1979, Using models to simulate the movement of contaminants through groundwater flow systems: *CRC Critical Reviews on Environmental Control* v. 9, no. 2, pp. 97-156.

Appel, C.A. and J.D. Bredehoeft, 1976, Status of groundwater modeling in the U.S. Geological Survey: *U.S. Geological Survey Circular* 737.

Apps, J.A., 1989, Current geochemical models to predict the fate of hazardous waste in the injection zones of deep disposal wells: *in Assessing the Geochemical Fate of Deep-Well-Injected Hazardous Waste: Summaries of Recent Research*, Chapter 6, EPA 625/6-89/025b.

Bachmat, Y., B. Andrews, D. Holtz, and S. Sebastian,

1978, Utilization of numerical groundwater models for water resource management: EPA 600/8-78/012.

Bear, J., 1979, *Hydraulics of groundwater*: McGraw-Hill Book Company, New York.

Boutwell, S.H., S.M. Brown, B.R. Roberts, and D.F. Atwood, 1985, *Modeling remedial actions at uncontrolled hazardous waste sites*: EPA 540/2-85/001.

Brown, J., 1986, 1986 Environmental software review: *Pollution Engineering*, v. 18, no. 1, pp. 18-28.

Cherry and others, 1989.

Donigan, A.S., Jr. and P.S.C. Rao, 1986, Overview of terrestrial processes and modeling: *in* Hern and Melancon (eds.) pp. 3-35.

Faust, C.R., L.R. Silka, and J.W. Mercer, 1981, Computer modeling and ground-water protection: *Ground Water*, v. 19, no. 4, pp. 362-365.

Freeze, R.A., G. DeMarsily, L. Smith, and J. Massmann, 1989, Some uncertainties about uncertainty: *in Proceedings of the Conference Geostatistical, Sensitivity, and Uncertainty Methods for Ground-Water Flow and Radionuclide Transport Modeling*, San

Francisco, CA, September 15-17, 1987. CONF-870971. Battelle Press, Columbus, OH.

Graves, B., 1986, Ground water software-trimming the confusio: *Ground Water Monitoring Review*, v. 6, no. 1, pp. 44-53.

Guven, O., F.J. Molz, and J.G. Melville, 1984, An analysis of dispersion in a stratified aquifer: *Water Resources Research* v. 20, no. 10, pp. 1337-1354.

Hoeksma, R.J. and P.K. Kitandis, 1985, Analysis of the spatial structure of properties of selected aquifers: *Water Resources Research*, v. 21, no. 4, pp. 563-572.

Holcomb Research Institute, 1976, *Environmental modeling and decision-making*: Praeger Publishers, New York.

Huyakorn, P.S. and G.F. Pinder, 1983, *Computational methods in subsurface flow*: Academic Press, New York.

Huyakorn, P.S., A.G. Kretschek, R.W. Broome, J.W. Mercer, and B.H. Lester, 1984, Testing and validation of models for simulating solute transport in ground water: development, evaluation, and comparison of benchmark techniques: GWMI 84-13. International Ground Water Modeling Center, Butler University, Indianapolis, IN.

Iverson, D.C. and R.M. Alston, 1986, The genesis of FORPLAN: A historical and analytical review of forest service planning models: GTR-INT-214. U.S. Forest Service Intermountain Research Station, Ogden, UT.

Javandel, I., C. Doughty, and C.F. Tsang, 1984, *Groundwater transport: Handbook of mathematical models*: AGU Water Resources Monograph No. 10. American Geophysical Union, Washington, DC.

Kayser, M.B. and A.G. Collins, 1986, Computer simulation models relevant to ground water contamination from EOR or other fluids—State-of-the-Art. NIPER-102: National Institute for Petroleum and Energy Research, Bartlesville, OK.

Khan, I.A., 1986a, Inverse problem in ground water: model development: *Ground Water* v. 24, no. 1, pp. 32-38.

Khan, I.A., 1986b, Inverse problem in ground water: model application: *Ground Water* v. 24, no. 1, pp. 39-48.

Kincaid, C.T., J.R. Morrey, and J.E. Rogers, 1984, *Geohydrochemical models for solute migration. Volume 1: process description and computer code selection*:

EPRI EA-3417-1. Electric Power Research Institute, Palo Alto, CA.

Kincaid, C.T. and J.R. Morrey, 1984, *Geohydrochemical models for solute migration. Volume 2: preliminary evaluation of selected computer codes*: EPRI EA-3417-2. Electric Power Research Institute, Palo Alto, CA.

Kinzelbach, W., 1986, *Groundwater modeling: an introduction with simple programs in BASIC*: Elsevier Scientific Publishers, Amsterdam, The Netherlands

Mangold, D.C. and C.-F. Tsang, 1987, Summary of hydrologic and hydrochemical models with potential application to deep underground injection performance: LBL-23497. Lawrence Berkeley Laboratory, Berkeley, CA.

Mercer, J.W. and C.R. Faust, 1981, *Ground-water modeling*: National Water Well Association, Dublin, OH.

Mills, W.B. and others, 1985, *Water quality assessment: a screening procedure for Toxic and Conventional Pollutants (Revised 1985)*: EPA/600/6-85/002a&b.

Morrey, J.R., C.T. Kincaid, and C.J. Hostetler, 1986, *Geohydrochemical models for solute migration. Volume 3: evaluation of selected computer codes*: EPRI EA-3417-3. Electric Power Research Institute, Palo Alto, CA.

Moses, C.O. and J.S. Herman, 1986, Computer notes - WATIN - a computer program for generating input files for WATEQF: *Ground Water*, v. 24, no. 1, pp. 83-89.

National Water Well Association/International Ground Water Modeling Center, 1984, *Proceedings of conference on practical applications of ground water models*: NWWA, Dublin, OH. [44 papers]

National Water Well Association/International Ground Water Modeling Center, 1985, *Proceedings of conference on practical applications of ground water models*: NWWA, Dublin, OH. [27 papers]

National Water Well Association/International Ground Water Modeling Center, 1987, *Proceedings of conference on solving ground Water Problems with Models*. NWWA, Dublin, OH. [45+ papers]

National Water Well Association/International Ground Water Modeling Center, 1989, *Fourth international conference on solving ground water problems with models*. NWWA, Dublin, OH. [44+ papers]

- Nordstrom, D.K. and others, (19 total authors), 1979, A comparison of computerized chemical models for equilibrium calculations in aqueous systems: in *Chemical Modeling in Aqueous Systems: Speciation, Sorption, Solubility and Kinetics*, E.A. Jenne, (ed.), ACS Symp. Series 93, American Chemical Society, Washington DC, pp. 857-892.
- Nordstrom, D.K. and J.W. Ball, 1984, Chemical models, computer programs and metal complexation in natural waters: in *Complexation of Trace Metals in Natural Waters*, C.J.M. Kramer and J.C. Duinker (eds.), Martinus Nijhoff/Dr. W. Junk Publishers, The Hague, pp. 149-164.
- Office of Technology Assessment (OTA), 1982, Use of models for water resources management, planning, and policy. OTA, Washington, DC.
- Oster, C.A., 1982, Review of groundwater flow and transport models in the unsaturated zone. NUREG/CR-2917, PNL-4427. Pacific Northwest Laboratory, Richland, WA.
- Pettyjohn, Wayne A. and R. J. Henning, 1979, Preliminary estimate of ground-water recharge rates in Ohio: Water Resources Center, Ohio State Univ., 323p.
- Pinder, G.F., 1984, Groundwater contaminant transport modeling. *Environ. Sci. Technol.* v. 18, no. 4, pp. 108A-114A.
- Puri, S., 1984, Aquifer studies using flow simulations. *Ground Water* v. 22, no. 5, pp. 538-543.
- Remson, I., G.M. Hornberger, and F.J. Molz, 1971, Numerical methods in subsurface hydrology. John Wiley & Sons, New York.
- Ross, B., J.W. Mercer, S.D. Thomas, and B.H. Lester, 1982, Benchmark problems for repository siting models. NUREG/CR-3097. U.S. Nuclear Regulatory Commission, Washington, DC.
- Schechter, R.S., L.W. Lake, and M.P. Walsh, 1985, Development of environmental attractive leachants. Vol. III. U.S. Bureau of Mines Mining Research Contract Report, Washington, DC.
- Schmelling, S.G. and R.R. Ross, 1989, Contaminant transport in fractured media: models for decision makers. Superfund Ground Water Issue Paper. EPA 540/4-89/004.
- Shelton, M.L., 1982, Ground-water management in basalts. *Ground Water*, v. 20, no. 1, pp. 86-93.
- Smith, L., 1987, The role of stochastic modeling in the analysis of groundwater problems. *Ground Water Modeling Newsletter*, v. 6, no. 1.
- Sposito, G., 1985, Chemical models of inorganic pollutants in soils. *CRC Critical Reviews in Environmental Control*, v. 15, no. 1, pp. 1-24.
- Srinivasan, P., 1984, PIG - A graphic interactive preprocessor for ground-water models. GWMI 84-15. International Ground Water Modeling Center, Butler University, Indianapolis, IN.
- Strecker, E.W. and W. Chu, 1986, Parameter Identification of a Ground-Water Contaminant Transport Model. *Ground Water*, v. 2, no. 1, pp. 56-62.
- U.S. Environmental Protection Agency (EPA), 1987, The use of models in managing ground-water protection programs, EPA 600/8-87/003.
- U.S. Environmental Protection Agency (EPA), 1988, Selection criteria for mathematical models used in exposure assessments: Ground-Water Models, EPA 600/8-88/075.
- U.S. Environmental Protection Agency (EPA), 1989, Assessing the geochemical fate of deep-well-injected hazardous waste: A Reference Guide, EPA 625/6-89/025a.
- van der Heijde, P.K.M., 1984a, Availability and applicability of numerical models for ground water resources management. GWMI 84-14. International Ground Water Modeling Center, Butler University, Indianapolis, IN.
- van der Heijde, P.K.M., 1984b, Utilization of models as analytic tools for groundwater management. GWMI 84-19. International Ground Water Modeling Center, Butler University, Indianapolis, IN.
- van der Heijde, P.K.M., 1985, The role of modeling in development of ground-water protection policies. *Ground Water Modeling Newslette*, v. 4, no. 2.
- van der Heijde, P.K.M., 1987, Performance standards and acceptance criteria in groundwater modeling. *Ground Water Modeling Newsletter*, v. , no. 2.
- vander Heijde, P.K.M. and P. Srinivasan, 1983, Aspects of the use of graphic techniques in ground water modeling. GWMI 83-11. International Ground Water Modeling Center, Butler University, Indianapolis, IN.
- van der Heijde, P.K.M., Y. Bachmat, J. Bredehoeft, B. Andrews, D. Holtz, and S. Sebastian, 1985, Groundwater

management: The use of numerical models. 2nd ed. AGU Water Resources Monograph No. 5, American Geophysical Union, Washington, DC.

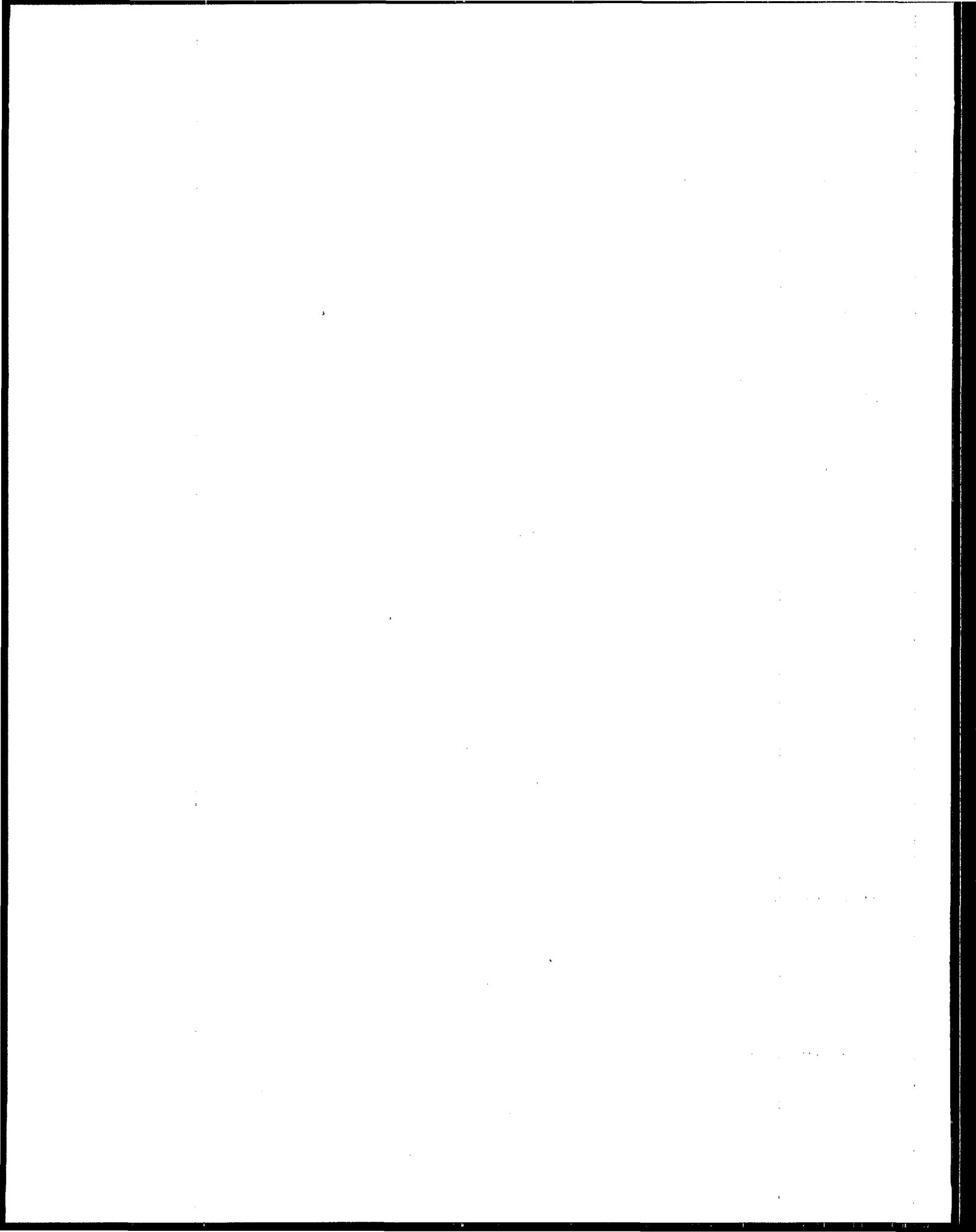
van der Heijde, P.K.M., A.I. El-Kadi, and S.A. Williams, 1988, Groundwater modeling: An overview and status report. International Ground Water Modeling Center, Butler University, Indianapolis, IN.

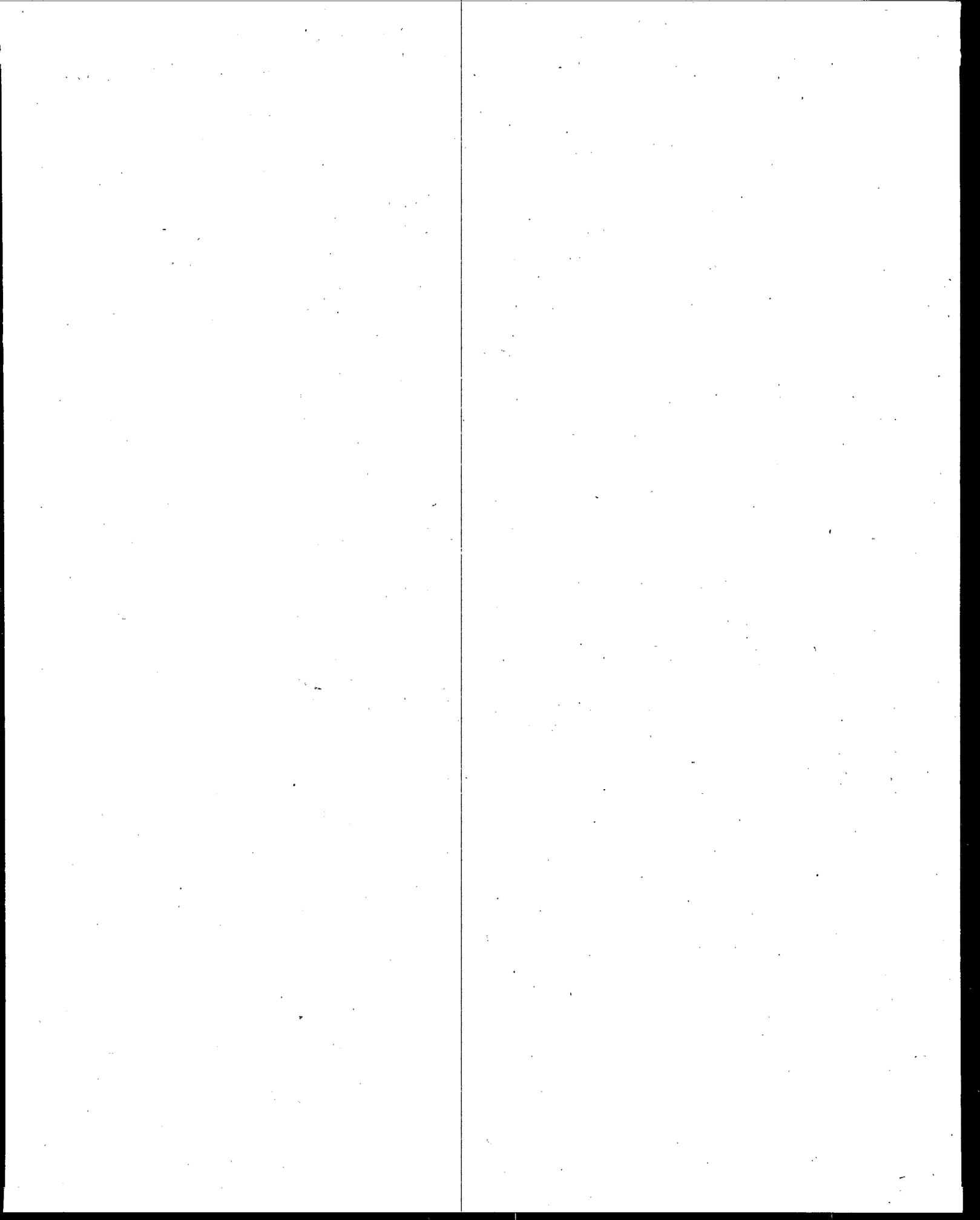
Walton, W.C., 1984, Practical aspects of groundwater modeling: Analytical and computer models for flow, mass and heat transport, and subsidence. National Water Well Association, Dublin, OH.

Wang, H.F. and M.P. Anderson, 1982, Introduction to groundwater modeling: Finite difference and finite element methods. W.H. Freeman and Company, San Francisco, CA.

Ward, D.S., D.R. Buss, and J.W. Mercer, 1987, A numerical evaluation of class I injection wells for waste confinement performance, Final Report. Prepared for U.S. EPA by GeoTrans, Herndon, VA.

Warrick, A.W., D.E. Myers, and D.R. Nielsen, 1986, Geostatistical methods applied to soil science: in Methods of Soil Analysis, Part I—Physical and Mineralogical Methods, 2nd ed., A. Klute (ed.), ASA Monograph No. 9, American Society of Agronomy, Madison, WI, pp. 53-82.





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